X-Y_1 and X-Y_2 correlation data according to the following equation (29), and correlating X with Y_1 and Y_2 using only thermodynamically consistent data:

[0100]

[Formula 42]

$$H = \left| \frac{\beta_{exp} - \beta_{cal}}{\beta_{cal}} \right| \quad (29)$$

wherein β_{exp} represents a value of β that is calculated according to F / |B - A| using F, A, and B determined from actually measured values; and β_{cal} represents a value of β that is calculated from the right side in the following equation (14) using values of a and b obtained by correlation of actually measured values:

[0101] [Formula 43]

$$\beta = \frac{F}{|B - A|} = aP^b \quad (14)$$

wherein A and B represent binary parameters; F represents deviation from A = B in the one-parameter Margules equation; P represents a pressure or an average vapor pressure; and a and b represent constants specific for the binary system.

[7] The method for designing or controlling a component separator or refiner according to [4] above, wherein the infinite dilution activity coefficients γ_1^∞ and γ_2^∞ or the binary parameters A and B are data from a plurality of systems of homologous series, and infinite dilution activity coefficients γ_1^∞ and γ_2^∞ or binary parameters A and B in other systems of homologous series are predicted from the data from a plurality of systems of homologous series.

[0102] [8] The method for designing or controlling a component separator or refiner according to [4] above, further comprising calculating infinite dilution activity coefficients or binary parameters for atomic groups from the calculated infinite dilution activity coefficients γ_1^∞ and γ_2^∞ or binary parameters A and B, and predicting new binary phase equilibrium data based on the calculated infinite dilution activity coefficients or binary parameters for atomic groups.

[0103] [9] A program for designing or controlling a component separator or a refiner, the program allowing a computer having an arithmetic processing unit and a data storage unit or a networked computer having an arithmetic processing unit and a data storage unit to function to implement the method for designing or controlling a component separator or refiner according to [4] above, the method comprising the steps of:

storing existing binary phase equilibrium data on the data storage unit;

outputting the binary phase equilibrium data from the data storage unit to the arithmetic processing unit and a predetermined arithmetic expression stored on the data storage unit in advance, substituting the binary phase equilibrium data into the arithmetic expression by means of the arithmetic processing unit to calculate an index X of proximity ratio to critical points and infinite dilution pressure gradients Y_1 and Y_2, correlating the obtained index X of proximity ratio to critical points with the infinite dilution pressure gradients Y_1 and Y_2, and calculating infinite dilution activity coefficients γ_1^{∞} and γ_2^{∞} or binary parameters A and B from the X-Y_1 correlation and the X-Y_2 correlation, respectively;

processing the infinite dilution activity coefficients γ_1^{∞} and γ_2^{∞} or the binary parameters A and B to predict new binary phase equilibrium data; and

calculating information for designing or controlling the component separator or the refiner from the new binary phase equilibrium data.

[0104] [10] An apparatus for designing or controlling a component separator or a refiner, comprising:

a phase equilibrium information recording unit which receives existing binary phase equilibrium data input to a computer through an information input unit;

a phase equilibrium correlation unit which calculates an index X of proximity ratio to critical points and infinite dilution pressure gradients Y_1 and Y_2 on the basis of the binary phase equilibrium data output from the phase equilibrium information recording unit, and correlates the obtained index X of proximity ratio to critical points with the infinite dilution pressure gradients Y_1 and Y_2 to calculate infinite dilution activity coefficients γ_1^{∞} and γ_2^{∞} or binary parameters A and B from the X-Y_1 correlation and the X-Y_2 correlation, respectively;

a phase equilibrium prediction unit which receives the input of the infinite dilution activity coefficients γ_1^{∞} and γ_2^{∞} or binary parameters A and B output from the phase equilibrium correlation unit to predict new binary phase equilibrium data;

a component separator/refiner design/control information calculation unit which receives the input of the new binary phase equilibrium data output from the phase equilibrium prediction unit to calculate component separator/refiner design/control information; and

a component separator/refiner design/control unit which designs or controls the component separator or the refiner on the basis of the information calculated through the component separator/refiner design/control information calculation unit.

[0105] [11] The apparatus for designing or controlling a component separator or refiner according to [10] above, wherein the index X of proximity ratio to critical points is calculated according to the equation (22):

[0106] [Formula 44]

$$X = \frac{p_{1s} + p_{2s}}{P_{c1} + p_{2s}} \qquad (22)$$

wherein P_{c1} represents the critical pressure of a lighter component in the binary system; and p_{1s} and p_{2s} represent the vapor pressures of components 1 and 2, respectively, at a temperature T, and

the infinite dilution pressure gradients Y_1 and Y_2 are calculated according to the equation (24):

[0107] [Formula 45]

$$Y_1 = \frac{\gamma_1^{\infty} p_{1s} - p_{2s}}{P_{c1} - p_{2s}} \qquad (24)$$

and the equation (25):

[0108]

[Formula 46]

$$Y_2 = \frac{p_{1s} - \gamma_2^{\infty} p_{2s}}{P_{c1} - p_{2s}} \quad (25)$$

wherein γ_i^{∞} represents the infinite dilution activity coefficient of component i in the liquid phase; and P_{c1}, p_{1s}, and p_{2s} are as defined in the equation (22).

[0109] [12] The apparatus for designing or controlling a component separator or refiner according to [10] above, further comprising evaluating the thermodynamic consistency of the $X\text{-}Y_1$ and $X\text{-}Y_2$ correlation data according to the following equation (29), and correlating X with Y_1 and Y_2 using only thermodynamically consistent data:

[0110] [Formula 47]

$$H = \left| \frac{\beta_{\exp} - \beta_{cal}}{\beta_{cal}} \right| \quad (29)$$

wherein β_{exp} represents a value of β that is calculated according to F / |B - A| using F, A, and B determined from actually measured values; and β_{cal} represents a value of β that is calculated from the right side in the following equation (14) using values of a and b obtained by correlation of actually measured values:

[0111] [Formula 48]

$$\beta = \frac{F}{|B - A|} = aP^b \quad (14)$$

wherein A and B represent binary parameters; F represents deviation from A = B in the one-parameter Margules equation; P represents a pressure or an average vapor pressure; and a and b represent constants specific for the binary system.

[13] The apparatus for designing or controlling a component separator or refiner according to [10] above, wherein the infinite dilution activity coefficients γ_1^{∞} and γ_2^{∞} or binary parameters A and B calculated through the phase equilibrium correlation unit are data

from a plurality of systems of homologous series, and infinite dilution activity coefficients γ_1^∞ and γ_2^∞ or binary parameters A and B in other systems of homologous series are predicted from the data from a plurality of systems of homologous series.

[0112] [14] The apparatus for designing or controlling a component separator or refiner according to [10] above, wherein the phase equilibrium correlation unit calculates infinite dilution activity coefficients or binary parameters for atomic groups from the calculated infinite dilution activity coefficients γ_1^∞ and γ_2^∞ or binary parameters A and B, and the phase equilibrium prediction unit receives the input of the calculated infinite dilution activity coefficients or binary parameters for atomic groups.

ADVANTAGEOUS EFFECTS OF INVENTION

[0113] The present invention has achieved the highly accurate correlation of phase equilibrium data by use of relationships between infinite dilution pressure gradients and vapor pressures in the binary system and thereby enabled one set of infinite dilution activity coefficients (or binary parameters A and B) to be precisely calculated. As a result, phase equilibrium relationship can be predicted in a highly accurate manner that has not been achieved by conventional methods. Thus, binary phase equilibrium relationship can be determined precisely from existing data and can be used to precisely design or control a component separator or refiner such as a distillation column, an extraction column, or a crystallizer. This apparatus design neither requires further experimentally obtaining or validating binary phase equilibrium data nor has to be performed in expectation of safety factors larger than necessary. Thus, an apparatus that can be operated inexpensively in a simple process can be designed, i.e., an economically excellent apparatus can be designed. In addition, an existing apparatus can be controlled on the basis of phase equilibrium data more precise than that at the time of its design. As a result, component separation or refining for chemicals, petroleum, or natural gases can be carried out more precisely under inexpensive operational conditions by, for example, the correction of existing data. Also, the present invention produces precise phase equilibrium data and thus has the advantage that apparatus design procedures can be simplified more than ever before. The precise phase

equilibrium data thus obtained can contribute to the improvement of solution models representing non-ideality in the liquid phase, such as activity coefficient equations or group contribution methods. Thus, the present invention can make a significant contribution to industry.

BRIEF DESCRIPTION OF DRAWINGS

[0114] FIG. 1 is a diagram showing P-x and P-y relationships for the methanol (1)-water (2) system at a temperature of 323.15 K;

FIG. 2 is a diagram showing relationships between mutual solubility and temperature for the 1-butanol (1)-water (2) system (FIG. 2(a)) and a diagram showing relationships between mutual solubility and temperature for the 2-butanone (1)-water (2) system (FIG. 2(b));

FIG. 3 is a diagram showing the temperature dependence of infinite dilution activity coefficients γ_1^{∞} (FIG. 3(a)) and γ_2^{∞} (FIG. 3(b)) for the methanol (1)-water (2) system;

FIG. 4 is a diagram for illustrating the highly accurate method for correlation of phase equilibrium data of the present invention using relationships between infinite dilution pressure gradients and vapor pressures for the methanol (1)-water (2) system, wherein FIG. 4(a) is a diagram showing a thermodynamic consistency line for the methanol (1)-water (2) system, FIG. 4(b) is a diagram showing X vs. Y_1 relationships for the methanol (1)-water (2) system, FIG. 4(c) is a diagram showing X vs. Y_2 relationships, FIG. 4(d) is a diagram showing X vs. γ_1^{∞} relationships for the methanol (1)-water (2) system, and FIG. 4(e) is a diagram showing X vs. γ_2^{∞} relationships;

FIG. 5 is a diagram showing constant-temperature or constant-pressure P-x and P-y relationships for the methanol (1)-water (2) system derived from the results of FIGS. 4(b) to 4(e), wherein FIG. 5(a) is a diagram showing P-x and P-y relationships for the methanol (1)-water (2) system at a temperature of 298.15 K, and FIG. 5(b) is a diagram showing T-x and T-y relationships for the methanol (1)-water (2) system at 101.3 kPa;

FIG. 6 is a diagram showing X vs. Y relationships for the heptane (1)-octane (2) system, wherein FIG. 6(a) is a diagram showing X vs. Y_1 relationships, and FIG. 6(b) is a

diagram showing X vs. Y_2 relationships;

FIG. 7 is a diagram for illustrating the highly accurate method for correlation of phase equilibrium data of the present invention using relationships between infinite dilution pressure gradients and vapor pressures for the 1-propanol (1)-water (2) system, wherein FIG. 7(a) is a diagram showing a thermodynamic consistency line for the 1-propanol (1)-water (2) system, FIG. 7(b) is a diagram showing X vs. Y_1 and X vs. Y_2 relationships for the 1-propanol (1)-water (2) system, FIG. 7(c) is a diagram showing P-x and P-y relationships for the 1-propanol (1)-water (2) system at a temperature of 333.15 K, and FIG. 7(d) is a diagram showing x_1 vs. y_1 relationships for the 1-propanol (1)-water (2) system at 101.3 kPa;

FIG. 8 is a diagram for illustrating the highly accurate method for correlation of phase equilibrium data of the present invention using relationships between infinite dilution pressure gradients and vapor pressures for the acetone (1)-chloroform (2) system, wherein FIG. 8(a) is a diagram showing a thermodynamic consistency line for the acetone (1)-chloroform (2) system, FIG. 8(b) is a diagram showing X vs. Y_1 relationships for the acetone (1)-chloroform (2) system, and FIG. 8(c) is a diagram showing X vs. Y_2 relationships for the acetone (1)-chloroform (2) system;

FIG. 9 is a diagram for illustrating the highly accurate method for correlation of phase equilibrium data of the present invention using relationships between infinite dilution pressure gradients and vapor pressures for the 1-butanol (1)-water (2) system, wherein FIG. 9(a) is a diagram showing a thermodynamic consistency line for the 1-butanol (1)-water (2) system, FIG. 9(b) is a diagram showing X vs. Y_1 relationships for the 1-butanol (1)-water (2) system, and FIG. 9(c) is a diagram showing X vs. Y_2 relationships for the 1-butanol (1)-water (2) system;

FIG. 10 is a diagram showing X vs. Y_1 and X vs. Y_2 relationships for the 2-butanone (1)-water (2) system;

FIG. 11 is a diagram showing X vs. Y_1 and X vs. Y_2 relationships for the carbon dioxide (1)-ethane (2) system;

FIG. 12 is a diagram showing results of comparing mutual solubility data for the 1-

butanol (1)-water (2) system (FIG. 12(a)) and the 2-butanone (1)-water (2) system (FIG. 12(b)) between actually measured values and predicted values obtained by the method of the present invention;

FIG. 13 is a diagram showing results of comparing X vs. Y_1 relationships for the methanol (1)-water (2) system and the 1-butanol (1)-water (2) system between actually measured values of infinite dilution activity coefficients and predicted values obtained by the method of the present invention on the basis of actually measured values of VLE;

FIG. 14 is a diagram showing relationships between the composition of an azeotrope and temperature, wherein FIGS. 14(a) to 14(d) are diagrams for the 1-propanol (1)-water (2) system, the 1-butanol (1)-water (2) system, the benzene (1)-methanol (2) system, and the acetone (1)-chloroform (2) system, respectively;

FIG. 15 is a diagram showing that Y_1 and Y_2 can be predicted by the homologous series method, wherein FIG. 15(a) is a diagram showing relationships between the number of carbon atoms in hydrocarbon and Y_1 or Y_2 for the carbon dioxide (1)-alkane (2) system and the carbon dioxide (1)-alkene (2) system, and FIG. 15(b) is a diagram showing relationships between the number of carbon atoms in hydrocarbon and Y_1 or Y_2 for the hydrogen sulfide (1)-alkane (2) system;

FIG. 16 is a diagram showing the calculation of the number of equilibrium stages in a distillation column using x-y relationships determined by the method for prediction of phase equilibrium data of the present invention;

FIG. 17 is a table showing 60 constant-temperature or constant-pressure data sets for the methanol (1)-water (2) system (the data is cited from Non-patent Document 1);

FIG. 18 is a table showing VLE data for the heptane (1)-octane (2) system (the data is cited from Non-patent Document 1);

FIG. 19 is a table showing VLE data for the 1-propanol (1)-water (2) system (the data is cited from Non-patent Document 1);

FIG. 20 is a table showing VLE data for the acetone (1)-chloroform (2) system (the data is cited from Non-patent Document 1);

FIG. 21 is a table showing LLE data for the 1-butanol (1)-water (2) system (the data is cited from Non-patent Document 2);

FIG. 22 is a table showing LLE data for the 2-butanone (1)-water (2) system (the data is cited from Non-patent Document 2); and

FIG. 23 is a table showing constant-temperature VLE data for the carbon dioxide (1)-ethane (2) system (the data is cited from Non-patent Document 6).

FIG. 24 is a diagram showing the value of A determined from a carbon number N_{c1} and the high accurate correlation according to the present invention, for the n-alkanol (1)+water (2) system, the 2-alkanol (1)+water (2) system, the 1,2-propanediol (1)+water (2) system, and the ethanolamine (1)+water (2) system at 40°C.

FIG. 25 is a diagram showing the value of B determined from a carbon number N_{c1} and the high accurate correlation according to the present invention, for the n-alkanol (1)+water (2) system, the 2-alkanol (1)+water (2) system, the 1,2-propanediol (1)+water (2) system, and the ethanolamine (1)+water (2) system at 40°C.

DESCRIPTION OF EMBODIMENTS

[0115] Hereinafter, the method for correlation of binary phase equilibrium data, the method for prediction of binary phase equilibrium data, and the method and apparatus for designing or controlling a component separator or refiner according to the present invention will be described more specifically.

[0116] First, the highly accurate method for correlation of phase equilibrium data of the present invention using relationships between infinite dilution pressure gradients and vapor pressures, and the method for prediction of binary phase equilibrium data based on the correlation results will be described specifically.

[Correlation of low-pressure VLE data]

(i) Methanol (1)-water (2) system

FIG. 4(a) shows a thermodynamic consistency line for the methanol (1)-water (2) system as a typical nonazeotropic system. The binary VLE data is cited from Non-patent Document 1. The values of vapor pressures in the analyses shown below are cited from

Non-patent Document 1. In the drawing, the open circle (○) denotes constant-temperature data, and the filled circle (●) denotes constant-pressure data. The values of the critical pressure P_{c1} of the lighter component (methanol) are cited from Non-patent Document 3. FIG. 4(a) shows that: (i) data converges to the line; (ii) data convergence is high; and (iii) constant-temperature data and constant-pressure data converge to the same line. The tolerance of data reliability was set to 1%, and data deviated by 1% or more from the correlation line was excluded. As a result, 54 out of 60 data sets fell in the error range of 1%. A thermodynamic consistency line determined from these 54 reliable data sets is shown in a linear form in FIG. 4(a). The 60 constant-temperature or constant-pressure data sets are shown in the table of FIG. 17.

[0117] FIG. 4(b) shows X vs. Y_1 relationships for the 60 data sets. The calculation depended on the equations (22), (24), and (25). In the drawing, the open circle (○) denotes constant-temperature data, and the filled circle (●) denotes constant-pressure data. Also, the solid line denotes a correlation line optimized using the equation (30). FIG. 4(b) shows that: (i) the correlation according to the present invention is highly accurate; (ii) constant-temperature data and constant-pressure data converge to the same correlation line; and (iii) this correlation line is slightly inferior in convergence to the thermodynamic consistency line.

[0118] In this context, the correlation line optimized using the equation (30) was calculated as follows: first, a thermodynamic consistency line was determined from the 60 data sets shown in FIG. 17, and data deviated by 1% or more therefrom was excluded to select 54 data sets. Next, for these 54 sets, the values of X were calculated according to the equation (22) while the values of Y_1 were determined according to the equation (24). In this case, for constant-pressure data, vapor pressures were calculated using the temperature given by the equation (23). The values of infinite dilution activity coefficients were calculated according to $\gamma_1^{\infty} = \exp(A)$ and $\gamma_2^{\infty} = \exp(B)$ from A and B given in FIG. 17. Next, correlation constants were determined by the method of least squares using the equations (30) and (32) as X vs. Y_1 correlation equations. In the case of FIG. 4B, the equation (30) was superior in correlation accuracy. Specifically, the correlation was achieved according to the equation

(34) with 7.6% errors.

[0119] [Formula 49]

$$Y_1 = -0.00070 - 0.2573X + 0.63004X^2 + 1.75319\ln(1+X) \quad (34)$$

In FIG. 4(b), a representative line of the above equation is indicated by the solid line.

[0120] FIG. 4(c) shows X vs. Y_2 relationships for the 60 data sets. In the drawing, the open circle (○) denotes constant-temperature data, and the filled circle (●) denotes constant-pressure data. Also, the thin solid line denotes a correlation line optimized using the equation (31). The calculation of FIG. 4(c) was also performed in the same way as in FIG. 4(b) using the 60 data sets. In this case, the following correlation equation was obtained:

[0121] [Formula 50]

$$Y_2 = 0.2985X^{0.882} \quad (35)$$

FIG. 4(c) shows that: (i) the correlation according to the present invention is highly accurate; (ii) constant-temperature data and constant-pressure data converge to the same correlation line; and (iii) this correlation line is slightly inferior in convergence to the thermodynamic consistency line. In FIG. 4(c), $X = Y_2$ relationships were also indicated by the thick solid line. This demonstrates that the methanol-water system, for which $Y_2 > 0$ holds, does not form azeotropes, but is not a complete asymmetric system (for which $p_{1s} >> p_{2s}$ holds). As is evident from FIGS. 4(b) and 4(c), the X vs. Y_1 and X vs. Y_2 correlations proposed by the present invention are much more highly accurate than the conventional correlation of VLE data shown in FIG. 3. FIGS. 4(b) and 4(c) demonstrate the effectiveness of the present invention for the nonazeotropic system.

[0122] FIGS. 4(d) and 4(e) show X vs. γ_1^∞ and X vs. γ_2^∞ relationships, respectively, for the methanol (1)-water (2) system. X is plotted as a single function of temperature on the abscissa. These data sets are significantly variable, as in FIG. 3. Thus, FIGS. 4(d) and 4(e) show that the conversion of a reciprocal of temperature to X on the abscissa is not enough to converge data sets to the line. Since vapor-liquid equilibrium relationship is

proportional to activity coefficients as shown in the equations (2) and (3), variations appearing in FIGS. 3, 4(d) and 4(e) are directly reflected in the VLE relationship. In FIGS. 4(d) and 4(e), the values of γ_1^∞ and γ_2^∞ determined from the representative lines of FIGS. 4(b) and 4(c) are indicated by the solid line. The calculation was performed as follows: first, X was determined according to the equation (22) from a system temperature, and Y_1 and Y_2 were calculated according to the equations (34) and (35). Next, γ_1^∞ and γ_2^∞ were calculated according to the equations (24) and (25). FIGS. 4(d) and 4(e) show that one-to-one relationships of temperature with γ_1^∞ and γ_2^∞ can be determined by the present invention in an accurate manner that has not been achieved by conventional methods.

[0123] FIG. 5(a) shows P-x and P-y relationship data for the methanol (1)-water (2) system at a temperature of 298.15 K. In the drawing, the open circle (○) denotes Px(1,42), the filled circle (●) denotes Py(1,42), the open triangle (Δ) denotes Px(1,44), the open square (□) denotes Px(1a,49), the filled square (■) denotes Py(1a,49), the open inverted triangle (▽) denotes Px(1b,29), and the filled inverted triangle (▼) denotes Py(1b,29). m of the numeric values in the parentheses (m,n) denotes part number in Non-patent Document 1, and n thereof denotes page number therein. In the drawing, values predicted from the X vs. Y_1 relationships (FIG. 4(b)) and X vs. Y_2 relationships (FIG. 4(c)) determined by the present invention were indicated by the solid line (P-x calculated value) and the broken line (P-y calculated value), respectively. This prediction was calculated as follows: first, the vapor pressures of methanol and water were determined at 298.15 K based on Non-patent Document 1 (p_{1s} = 16.93 kPa, p_{2s} = 3.16 kPa, P_{c1} = 8090 kPa), and the values were substituted into the equation (22) to determine an index X of proximity ratio to critical points (X = 0.00248). Then, Y_1 and Y_2 were calculated according to the equations (34) and (35) (Y_1 = 0.00301, Y_2 = 0.00150). Next, infinite dilution activity coefficients γ_1^∞ and γ_2^∞ were determined according to the equations (24) and (25) (γ_1^∞ = 1.439, γ_2^∞ = 1.511). Next, binary parameters A and B were determined according to the equations (6) and (7) (A = 0.3639, B = 0.4130), and activity coefficients γ_1 and γ_2 were determined according to the equations (4) and (5) for arbitrary x_1 (for example, when x_1 = 0.5, γ_1 = 1.109 and γ_2 = 1.095). These

values were substituted into the equation (8) to determine a pressure P (P = 11.11 kPa). y_1 was determined according to the equation (9) (y_1 = 0.844). An activity coefficient was calculated for a liquid composition different from x_1 = 0.5, a pressure P was determined, the procedure to determine y_1 was repeated, and plots were prepared to obtain the curves of the calculated P-x values and calculated P-y values as shown in FIG. 5(a). As is evident from FIG. 5(a), the calculated values are in exceedingly good agreement with the measurement values shown in the document.

[0124] FIG. 5(b) shows T-x and T-y relationships for the methanol (1)-water (2) system at 101.3 kPa. In FIG. 5(b), × denotes the relationship of x_1 and T-273.15 for actually measured values, and + denotes the relationship of y_1 and T-273.15 for actually measured values. P-x and P-y values predicted from the X vs. Y_1 and X vs. Y_2 relationships determined by the present invention are indicated by the solid line and the broken line, respectively. This prediction was performed as follows: first, the boiling points of methanol and water were determined at 101.3 kPa (t_{b1} = 64.55°C, t_{b2} = 100.00°C), and an average boiling point was determined according to the equation (23) ($t_{b,ave}$ = 82.27°C). Vapor pressures were determined at the average boiling point (p_{1s} = 195.82 kPa, p_{2s} = 51.78 kPa). The value of an index X of proximity ratio to critical points was determined using the average boiling point (X = 0.0304). Then, Y_1 and Y_2 were calculated according to the equations (34) and (35) (Y_1 = 0.0446, Y_2 = 0.01371). Next, infinite dilution activity coefficients γ_1^∞ and γ_2^∞ were determined according to the equations (24) and (25) (γ_1^∞ = 1.842, γ_2^∞ = 1.654). Next, binary parameters A and B were determined according to the equations (6) and (7) (A = 0.6107, B = 0.5029), and activity coefficients were determined according to the equations (4) and (5) for arbitrary x_1 (for example, when x_1 = 0.5, γ_1 = 1.134 and γ_2 = 1.165). These values were substituted into the equation (8) (P = 101.3 kPa) to determine a system temperature T that satisfied the equation (8) based on the calculated boiling points (T = 73.3°C). y_1 was determined according to the equation (9). FIG. 5(b) shows that the predicted values according to the present invention agree with the average values of actually measured values, whereas FIG. 5(b) also shows that the actually measured

values are significantly variable, indicating the risk of conventional design methods based only on actually measured values. By contrast, FIGS. 4(b), 4(c), 5(a) and 5(b) show that use of the present invention allows precise prediction of VLE relationship at an arbitrary temperature and pressure. Thus, the present invention represents a landmark because it can put an end to the long absence of prediction methods.

(ii) Heptane (1)-octane (2) system

In order to examine the applicability of the present invention to the ideal system ($\gamma_i = 1$), FIG. 6(a) shows X vs. Y_1 relationships for the heptane (1)-octane (2) system. The binary VLE data is cited from Non-patent Document 1 (see FIG. 18). According to the equation (29), the tolerance of data reliability was set to 1%, and data deviated by 1% or more from the thermodynamic consistency line was removed. As a result, 10 out of 13 data sets fell in the error range of 1%. FIG. 6(a) also shows an X vs. Y_1 correlation line. The calculation of this correlation line depended on the same method as in the methanol (1)-water (2) system. FIG. 6(a) shows that: data convergence is high; and constant-temperature data and constant-pressure data converge to the same correlation line. FIG. 6(b) shows X vs. Y_2 relationships for the same data sets as above. In the drawing, the open circle (○) denotes constant-temperature data, and the filled circle (●) denotes constant-pressure data. In FIG. 6(b), a correlation line is also indicated. FIG. 6(b) shows that data convergence is high. FIGS. 6(a) and 6(b) demonstrate the effectiveness of the present invention for the ideal system.

(iii) 1-propanol (1)-water (2) system (minimum boiling azeotrope)

FIG. 7(a) shows a thermodynamic consistency line for the 1-propanol (1)-water (2) system. The binary VLE data is cited from Non-patent Document 1 (see FIG. 19). In the drawing, the open circle (○) denotes constant-temperature data, and × denotes constant-pressure data. Since this system forms minimum boiling azeotropes, the accuracy of VLE data convergence is lower than that in the methanol-water system. Also, FIG. 7(a) shows that: data converges to the line; and constant-temperature data and constant-pressure data converge to the same line. The tolerance of data reliability was set to 0.6%, and data

deviated by 0.6% or more from the correlation line was excluded. As a result, 7 out of 31 data sets fell in the error range of 0.6%. Therefore, a thermodynamic consistency line determined from these 7 reliable data sets is shown in FIG. 7(a).

[0125] FIG. 7(b) shows X vs. Y_1 relationships determined according to the Wilson equation for the 1-propanol (1)-water (2) system. In the drawing, the open circle (○) denotes X vs. Y_1 constant-temperature data, the filled circle (●) denotes X vs. Y_1 constant-pressure data, the open square (□) denotes X vs. Y_2 constant-temperature data, and the filled square (■) denotes X vs. Y_2 constant-pressure data. For this system, vapor-liquid equilibrium relationships can be more represented by the Wilson equation than by the Margules equation. The Wilson binary parameters representing vapor-liquid equilibrium relationships are listed in Non-patent Document 1. The calculation was performed in the same way as in FIG. 4 except that the Wilson equation was used instead of the Margules equation.

[0126] The Wilson equation was as follows:

[0127] [Formula 51]

$$\ln\gamma_1 = -\ln(x_1 + \Lambda_{12}x_2) + x_2\left(\frac{\Lambda_{12}}{x_1 + \Lambda_{12}x_2} - \frac{\Lambda_{21}}{\Lambda_{21}x_1 + x_2}\right) \tag{36}$$

[0128] [Formula 52]

$$\ln\gamma_2 = -\ln(x_2 + \Lambda_{21}x_1) - x_1\left(\frac{\Lambda_{12}}{x_1 + \Lambda_{12}x_2} - \frac{\Lambda_{21}}{\Lambda_{21}x_1 + x_2}\right) \tag{37}$$

wherein γ_1 and γ_2 represent the activity coefficients of components 1 and 2, respectively; x_1 and x_2 represent the mole fractions of components 1 and 2, respectively, in the liquid phase; and Λ_{12} and Λ_{21} represent binary parameters. The infinite dilution activity coefficients can be associated with Λ_{12} and Λ_{21} by considering $x_1 = 0$ in the equation (36) and $x_2 = 0$ in the equation (37).

[0129] FIG. 7(b) shows both X vs. Y_1 and X vs. Y_2 relationships. $Y_2 < 0$ holds true for this system that forms minimum boiling azeotropes. Thus, in order to examine detailed data convergence, negative signs of X vs. Y_2 relationships are shown therein. FIG. 7(b) shows

that data convergence is high even when azeotropes are formed. It also shows that constant-temperature data and constant-pressure data converge to the same correlation line. Thus, in FIG. 7(b), the representative lines of data were indicated by the solid line for the X vs. Y_1 correlation line and the broken line for the X vs. Y_2 correlation line. FIG. 7(b) demonstrates the effectiveness of the present invention for the azeotropes. In addition, the values of γ_1^{∞} and γ_2^{∞} were determined at a temperature of 333.15 K from the representative lines shown in FIG. 7(b), and P-x and P-y relationships predicted according to the Wilson equation using the values are indicated in FIG. 7(c). In the drawing, the open circle (○) denotes P-x data, the filled circle (●) denotes P-y data, the solid line denotes P-x predicted values according to the present invention, and the broken line denotes P-y predicted values according to the present invention. FIG. 7(c) shows that P-x relationships can be predicted properly. It also shows that the P-y data is less reliable. FIG. 7(d) shows x-y relationships at 101.3 kPa. FIG. 7(d) shows a diagonal representing $x_1 = y_1$ by a thin solid line. Usually, it is not easy to correlate P-x data and allow x-y relationships to agree with the data (Non-patent Document 1). In spite of this fact, FIG. 7(d) shows that the predicted values according to the present invention (thick line) are in surprisingly good agreement with actually measured values (plot), indicating exceedingly good prediction, though the present invention provides pure prediction, which determines data only from the values of binary parameters and pressures. The precise determination of x-y relationships leads to the prediction of azeotropic points that give operating limits, and is thus practically important. FIGS. 7(a) to 7(d) clearly demonstrate that the correlation of X vs. Y_1 and X vs. Y_2 relationships according to the present invention is effective for the minimum boiling azeotropes.

(iv) Acetone-chloroform system (maximum boiling azeotrope)

FIG. 8(a) shows a thermodynamic consistency line for the acetone (1)-chloroform (2) system. The binary VLE data is cited from Non-patent Document 1 (see FIG. 20). In the drawing, the open circle (○) denotes constant-temperature data, and the filled circle (●) denotes constant-pressure data. $Y_1 < 0$ holds true for this system that forms maximum boiling azeotropes. The Margules equation was used in analysis. FIG. 8(a) shows that:

data converges to the line; and constant-temperature data and constant-pressure data converge to the same line. According to the equation (29), the tolerance of data reliability was set to 2%, and data deviated by 2% or more from the correlation line was excluded. As a result, 25 out of 59 data sets fell in the error range of 2%. A thermodynamic consistency line determined from these 25 reliable data sets is shown in FIG. 8(a).

[0130] FIG. 8(b) shows X vs. Y_1 relationships determined according to the Margules equation for the acetone (1)-chloroform (2) system. $Y_1 < 0$ holds true for this system that forms maximum boiling azeotropes. Thus, in order to examine detailed data convergence, negative signs of X vs. Y_1 relationships are shown therein. In FIG. 8(b), an X vs. Y_1 correlation line was also indicated. FIG. 8(b) shows that data convergence is high even when azeotropes are formed. It also shows that constant-temperature data and constant-pressure data converge to the same correlation line.

[0131] FIG. 8(c) shows X vs. Y_2 relationships for the same data set as above. In FIG. 8(c), a correlation line was also indicated. FIG. 8(c) shows that data convergence is high even for the system that forms maximum boiling azeotropes. FIGS. 8(b) and 8(c) demonstrate the effectiveness of the present invention for the azeotropes.

[Correlation of LLE data]

Next, the correlation of LLE data will be described in detail with reference to specific examples.

(i) 1-butanol (1)-water (2) system

Infinite dilution activity coefficients γ_1^{∞} and γ_2^{∞} can be defined from binary liquid-liquid equilibrium (mutual solubility) to determine Y_1 and Y_2. Preferably, the following UNIQUAC equation, which calculationally provides the highest convergence, is used for determining γ_1^{∞} and γ_2^{∞} from mutual solubility:

[0132]

[Formula 53]

$$\ln\gamma_i = \ln\frac{\Phi_i}{x_i} + \frac{z}{2}q_i\ln\frac{\theta_i}{\Phi_i} + \Phi_i\left(l_i - \frac{r_i}{r_j}l_j\right) - q_i\ln\left(\theta_i + \theta_j\tau_{ji}\right) + \theta_j q_i\left(\frac{\tau_{ij}}{\theta_i + \theta_j\tau_{ji}} - \frac{\tau_{ij}}{\theta_j + \theta_i\tau_{ij}}\right) \quad (38)$$

[0133] [Formula 54]

$$\Phi_i = \frac{x_i r_i}{x_1 r_1 + x_2 r_2} \quad (39)$$

[0134] [Formula 55]

$$\theta_i = \frac{x_i q_i}{x_1 q_1 + x_2 q_2} \quad (40)$$

[0135] [Formula 56]

$$l_i = \frac{z}{2}(r_i - q_i) - (r_i - 1) \quad (41)$$

In the above equations, r_i represents a molecular volume index, and q_i represents a molecular surface area index. These values are provided by Non-patent Document 2. Also, x_i represents the mole fraction of component i; z is equal to 10 and fixed; τ_{ij} and τ_{ji} represent binary parameters; and Φ_i, θ_i, and l_i represent variables defined by the equations (39), (40), and (41), respectively. $x_i = 0$ is substituted into the equation (38) to obtain the following equation for an infinite dilution activity coefficient:

[0136] [Formula 57]

$$\ln\gamma_i^{\infty} = \ln\frac{r_i}{r_j} + \frac{z}{2}q_i\ln\frac{r_j q_i}{r_i q_j} + \frac{z}{2}(r_i - q_i) - (r_i - 1) - \frac{r_i}{r_j}\left[\frac{z}{2}(r_j - q_j) - (r_j - 1)\right] - q_i\ln(\tau_{ji}) + q_i\left(1 - \tau_{ij}\right) \quad (42)$$

Thus, τ_{ij} and τ_{ji} are determined according to the equations (10) and (38) from mutual

solubility data at a certain temperature. Infinite dilution activity coefficients are determined according to the equation (42). Then, A and B can be determined according to the equations (6) and (7). After A and B are determined, β, X, Y_1, and Y_2 can be calculated according to the equations (14), (22), (24) and (25), respectively.

[0137] FIG. 9(a) shows a thermodynamic consistency line for the 1-butanol (1)-water (2) system. In the drawing, the open circle (○) denotes LLE data (the data is cited from Non-patent Document 2; see FIG. 21), and the filled circle (●) denotes VLE data (the data is cited from Non-patent Document 1). From the mutual solubility data (Non-patent Document 2) shown in FIG. 2(a), the values of A and B were determined according to the UNIQUAC equation, and β was determined from the equation (14) according to the UNIQUAC equation. Since the vapor-liquid equilibrium data for the 1-butanol (1)-water (2) system has also been reported in Non-patent Document 1, the value of β for the VLE data determined from the equation (14) according to the UNIQUAC equation as an activity coefficient is also indicated in FIG. 9(a). FIG. 9(a) shows that: (i) liquid-liquid equilibrium data and vapor-liquid equilibrium data give the same thermodynamic consistency line (Non-patent Document 4); and (ii) liquid-liquid equilibrium data gives a more converged thermodynamic consistency line than vapor-liquid equilibrium data (Non-patent Document 5). FIG. 9(b) shows X vs. Y_1 relationships determined according to the UNIQUAC equation for the 1-butanol (1)-water (2) system. In the drawing, the open circle (○) denotes LLE data, the filled circle (●) denotes constant-temperature VLE data, × denotes constant-pressure VLE data, and the solid line (-) denotes a correlation line for the LLE data. FIG. 9(b) shows that LLE data and VLE data give the same X vs. Y_1 relationships. Specifically, FIG. 9(b) demonstrates that the present invention is effective commonly for liquid-liquid equilibrium data and vapor-liquid equilibrium data. FIG. 9(c) shows X vs. Y_2 relationships for the 1-butanol (1)-water (2) system. The 1-butanol (1)-water (2) system forms minimum boiling azeotropes and was thus indicated by negative signs. In the drawing, the open circle (○) denotes LLE data, the filled circle (●) denotes constant-temperature VLE data, × denotes constant-pressure VLE data, and the solid line (-) denotes a correlation line for the LLE data. In FIG. 9(c), the

convergence of LLE data and VLE data was high, demonstrating the effectiveness of the present invention which determines binary parameters A and B and uses a proximity ratio to critical points determined according to the equation (22) and infinite dilution pressure gradients determined according to the equations (24) and (25), on the basis of only highly reliable data.

(ii) 2-butanone (1)-water (2) system

FIG. 10 shows both X vs. Y_1 relationships (solid line with open circles (○)) and X vs. Y_2 relationships (broken line with filled circles (●)) determined according to the UNIQUAC equation for the 2-butanone (1)-water (2) system. The LLE data is cited from Non-patent Document 2 (see FIG. 22). FIG. 10 shows that by use of the index of proximity ratio to critical points infinite dilution pressure gradients can converge even to LLE data with high accuracy. Specifically, it demonstrates the effectiveness of the present invention for LLE.

[Correlation of high-pressure VLE data]

(i) Lumped non-ideality correlation

A method involving lumping parameters for non-ideality in the liquid phase and non-ideality in the vapor phase and representing non-ideality according to the equation (28) was examined for its effectiveness. Non-patent Document 1 has reported more than 12500 low-pressure data sets, to which the lumped non-ideality correlation was applied. Correlation errors have also been reported therein. Table 1 shows relative values of correlation errors in constant-temperature P-x data according to the Margules equation reported in Non-patent Document 1.

[0138]

[Table 1]

Table 1 P-x correlation errors in constant-temperature VLE data

Binary system	Number of data sets	Average correlation error [1] %
(Low-pressure VLE data)		
Aqueous solutions	508	4.20
Organic compounds with OH groups	1900	2.70
Compounds with aldehydes, ketones, ethers	1399	1.20
Compounds with carboxylic acids, esters	234	2.30
Aliphatic hydrocarbons	1583	1.20
Aromatic hydrocarbons	1007	1.00
Compounds with halogen, nitrogen, sulfur, and others	630	1.60
(High-pressure VLE data)		
Compounds with carbon dioxide	112	1.00
Whole binary system	265	0.90

[1]: $(100/n)\sum\Delta P_i/P_{s,ave}$

n: The number of data sets

ΔP_i: Correlation error of pressure for i-th data set

$P_{s,ave}$: Average pressure of i-th data set

Table 1 shows the increasing tendency of correlation errors in polar mixtures compared with errors on the order of 1% in non-polar mixtures. Table 1 also reveals the

degree of correlation errors derived from the lumped non-ideality correlation previously applied to low-pressure data. A large number of binary high-pressure VLE data sets are listed in Non-patent Document 6. Thus, P-x relationships for constant-temperature VLE data that satisfied $T < T_{c1}$ (T_{c1} represents the critical temperature of a light component, i.e., a component having a high vapor pressure) were subjected to the lumped non-ideality correlation according to the Margules equation to determine correlation errors of pressure in each data set. The average relative errors thereof were indicated in Table 1. Table 1 shows that correlation errors even in the high-pressure P-x data are equal to or lower than the level of hydrocarbon mixtures in low-pressure vapor-liquid equilibrium. This means that the lumped non-ideality correlation of P-x data is effective even for high-pressure data, as in low-pressure data. The conventional correlation using mixing rules for high-pressure data has the disadvantage that it cannot be applied to the prediction of VLE relationship. By contrast, particularly notable is the accomplishment of the present invention, which has found that the lumped non-ideality correlation is effective even for high-pressure data. This is because the method of the present invention can determine X vs. Y_1 and X vs. Y_2 relationships even for high-pressure VLE data at totally the same level as in low-pressure data and can be used with its effectiveness easily proved.

(ii) Correlation of constant-temperature/high-pressure VLE data for carbon dioxide (1)-ethane (2) system

Binary high-pressure VLE data is compiled in Non-patent Document 6. Thus, P-x relationships for the constant-temperature VLE data of the carbon dioxide (1)-water (2) system (see FIG. 23) that satisfied $T < T_{c1}$ were subjected to the lumped non-ideality correlation according to the Margules equation. Y_1 and Y_2 were calculated from the determined values of γ_1^{∞} and γ_2^{∞}. FIG. 11 shows X vs. Y_1 and X vs. Y_2 relationships. In the drawing, the open circle (○) denotes X vs. Y_1 relationships, and the filled inverted triangle (▼) denotes X vs. Y_2 relationships. Since the carbon dioxide-ethane system forms minimum boiling azeotropes, negative signs of Y_2 are shown therein. FIG. 11 demonstrates that: both the X vs. Y_1 and X vs. Y_2 relationships give converged relationships; and the

correlation method according to the present invention can also be used effectively for high-pressure vapor-liquid equilibrium data.

[0139] The most important application of the highly accurate method for correlation of phase equilibrium data of the present invention using relationships between infinite dilution pressure gradients and vapor pressures is the precise pure prediction of vapor-liquid equilibrium (VLE) relationship. Specifically, X vs. Y_1 and X vs. Y_2 relationships are individually determined by correlation from existing data, and the values of γ_1^{∞} and γ_2^{∞} are determined for the binary system on the basis of these correlations. As a result, phase equilibrium relationship can be predicted purely without the use of individual data. The effectiveness of the present invention for the pure prediction of binary VLE is expressed in terms of an example of the constant-temperature methanol (1)-water (2) system in FIG. 5(a) and an example of the constant-pressure methanol (1)-water (2) system in FIG. 5(b) as to the nonazeotropic system. Also, it is expressed in terms of an example of the constant-temperature 1-propanol (1)-water (2) system in FIG. 7(c) and an example of the constant-pressure 1-propanol (1)-water (2) system in FIG. 7(d) as to the minimum boiling azeotropes. The conventional group contribution method is known as a pure prediction method without the use of individual actually measure data, albeit with disadvantageously significantly low prediction accuracy. The pure prediction of VLE based on the correlation method according to the present invention is advantageously reliable with significantly high prediction accuracy.

[0140] Another important application of the correlation method according to the present invention is the pure prediction of mutual solubility. None of the previously proposed methods are capable of highly accurately correlating relationships between mutual solubility and temperature. The application of the correlation method according to the present invention to binary LLE is expressed in terms of the 1-butanol (1)-water (2) system in FIG. 12(a). The mutual solubility data is the same as in FIG. 2(a). In the drawing, the open circle (○) denotes actually measured values of $(x_1)_2$ (cited from Non-patent Document 2), the filled circle (●) denotes actually measured values of $(x_1)_1$ (cited from Non-patent Document 2), the solid line (-) denotes predicted values of $(x_1)_2$ according to the present

invention, and the broken line (...) denotes predicted values of $(x_1)_I$ according to the present invention. FIG. 12(a) demonstrates that mutual solubility can be predicted favorably using the present invention. Also, FIG. 12(b) shows an example of mutual solubility prediction for the 2-butanone (1)-water (2) system. The mutual solubility data is the same as in FIG. 2(b). In the drawing, the open circle (○) denotes actually measured values of $(x_1)_2$ (cited from Non-patent Document 2), the filled circle (●) denotes actually measured values of $(x_1)_I$ (cited from Non-patent Document 2), the solid line (-) denotes predicted values of $(x_1)_2$ according to the present invention, and the broken line (...) denotes predicted values of $(x_1)_I$ according to the present invention. FIG. 12(b) shows the slight difference of the data from the predicted values for $(x_1)_I$. This is because correlation functions are not properly selected for X vs. Y_2 relationships, as shown in FIG. 10. FIG. 12(b) demonstrates that infinite dilution activity coefficients must be correlated with significantly high accuracy for the mutual solubility prediction. This is the reason for the conventional unfavorable correlation of temperature for LLE. The method of the present invention can converge X vs. Y_2 relationships for LLE data with high accuracy, as shown in FIG. 10, and thus has the advantage that correlation functions can be selected strictly. FIG. 10 and FIG. 12(b) show that the correlation of LLE requires significantly high accuracy and the effectiveness of the present invention.

[0141] The phase equilibrium relationship can be predicted precisely if the values of infinite dilution activity coefficients are correctly determined. The correlation method according to the present invention has the great advantage that it can easily give the values of infinite dilution activity coefficients. FIG. 13 shows X vs. Y_1 relationships (indicated by the open circle (○)) calculated for the methanol (1)-water (2) system from the actually measured values of γ_1^∞ cited from Non-patent Document 7. In FIG. 13, X vs. Y_1 relationships determined from the VLE data shown in FIG. 4(b) are also indicated by the solid line (-). These results are in good agreement with each other. FIG. 13 further shows results of similar comparison for the 1-butanol (1)-water (2) system. In the drawing, the filled circle (●) denotes γ_1^∞ data for the 1-butanol (1)-water (2) system, and the broken line (- -) denotes a

representative line of VLE data for the 1-butanol (1)-water (2) system. FIG. 13 demonstrates that the values of infinite dilution activity coefficients determined from VLE data using the converged correlations obtained by the present invention agree with the actually measured values of infinite dilution activity coefficients. As shown in FIGS. 4(d) and 4(e), it has been considered that reliable infinite dilution activity coefficients cannot be determined from VLE data. The correlation method developed by the present invention produces high convergence, breaks through this common knowledge and serves as a novel reliable approach capable of providing infinite dilution activity coefficients. Particularly, a method for measuring infinite dilution activity coefficients has not yet been found for heavy components, such as water in alcohol. The method of the present invention can correlate more accurately X vs. Y_2 relationships for heavy components than X vs. Y_1 relationships for the same. Specifically, as is evident from these results, the method of the present invention can determine infinite dilution activity coefficients, which are basic determinants necessary for phase equilibrium relationship, from abundant VLE data and as such, is exceedingly useful.

[Prediction of azeotrope]

Mixtures cannot be enriched by a distillation method at a temperature exceeding the azeotropic point. The definition of relationships between the composition of azeotropes and temperature is exceedingly important for determining the operational conditions of distillation. The method of the present invention can purely predict precise vapor-liquid equilibrium relationship and consequently has the great advantage that it can highly accurately predict azeotropes whose highly accurate prediction has been difficult for conventional methods. FIG. 14(a) shows relationships between the composition of an azeotrope and temperature for the 1-propanol (1)-water (2) system. Since binary parameters A and B determined from the Margules equation are provided by Non-patent Document 1, the relationships are obtained for VLE data using these parameters. X vs. Y_1 and X vs. Y_2 relationships are obtained using the Margules equation, and relationships between composition $x_{1,azeo}$ of an azeotrope and a temperature T_{azeo} calculated from these correlations

are indicated by the solid line in FIG. 14(a). In addition, similar relationships are indicated for the 1-butanol (1)-water (2) system, the benzene (1)-methanol (2) system, and the acetone (1)-chloroform (2) system in FIGS. 14(b), 14(c), and 14(d), respectively. In FIGS. 14(a) to 14(c), the data and the predicted values are in good agreement with each other, demonstrating that the correlation method according to the present invention is effective for the prediction of azeotropic points.

[Assessment of phase equilibrium data consistency]

Aside from thermodynamic consistency lines, data consistency can be assessed using the data convergence of X vs. Y_1 and X vs. Y_2 relationships. Particularly, data consistency can be assessed easily if relationships between an index X of proximity ratio to critical points and infinite dilution pressure gradients converge to a line. This assessable data consistency means that the correlation method according to the present invention produces high data convergence.

[Prediction of ternary VLE]

Three sets of binary parameters for basic binary systems constituting a ternary system can be determined from ternary VLE data by use of activity coefficient equations such as Margules, UNIQUAC, Wilson, and NRTL equations. Thus, when X vs. Y_1 and X vs. Y_2 relationships determined from ternary VLE data agree with X vs. Y_1 and X vs. Y_2 relationships determined from binary VLE data, the ternary data can be assessed as being consistent. On the other hand, three sets of binary parameters for basic binary systems can be determined on the basis of X vs. Y_1 and X vs. Y_2 relationships determined from binary VLE data, and used in the prediction of ternary VLE relationship. An example of the ternary system using the Margules equation is shown below. The activity coefficient equation of component i in the multicomponent system is obtained by differentiating an excess function g^E by the number of moles n_i of component i as follows:

[0142] [Formula 58]

$$\ln \gamma_i = \frac{\partial g^E \sum_{k=1}^{n} n_k}{\partial n_i} \qquad (43)$$

For the ternary system, g^E is represented by the following Margules equation (see Non-patent Document 8):

[0143] [Formula 59]

$$g^E = x_1x_2(x_1B_{12} + x_2A_{12}) + x_1x_3(x_1B_{13} + x_3A_{13}) + x_2x_3(x_2B_{23} + x_3A_{23}) + x_1x_2x_3(B_{12} + A_{13} + B_{23}) \qquad (44)$$

wherein g^E represents an excess function; x_i represents the mole fraction of component i in the liquid phase; and A_{ij} and B_{ij} represent binary parameters consisting of i and j in the binary system. Specific equations for extending the UNIQUAC, NRTL, or Wilson equation to the multicomponent system is shown in Non-patent Document 3. Since three sets of binary parameters constituting the ternary system, i.e., a total of 6 binary parameters, can be determined using the present invention, the excess function and the activity coefficient can be determined according to the equations (44) and (43), respectively. For the multicomponent system, the activity coefficient can be easily determined directly by numerical differentiation of the equation (43). Also, the pressure can be determined according to the following equation:

[0144] [Formula 60]

$$P = \sum_{k=1}^{n} \gamma_k x_k p_{ks} \qquad (45)$$

wherein P represents a system pressure; γ_k represents the activity coefficient of component k; x_k represents the mole fraction of component k in the liquid phase; and p_{ks} represents the vapor pressure of component k. In order to demonstrate that the present invention can be applied to the prediction of multicomponent vapor-liquid equilibrium, Table 2 compares predicted values (calculated values) of pressure according to the present invention with actually measured values (the data is cited from Part 1a, p. 494 of Non-patent Document 1)

for the water (1)-methanol (2)-ethanol (3) ternary system at 298.15 K. A_{ij}, B_{ij}, etc., in the equation (44) are calculated from the correlation equation according to the present invention using actually measured values of three binary vapor-liquid equilibria consisting of the water (1)-methanol (2) system, the water (1)-ethanol (3) system, and the methanol (2)-ethanol (3) system. Table 2 shows that: the measured and predicted values of pressure agree with each other with a difference of 0.5% when mole fractions x_1 and x_2 of water and methanol in the liquid phase have various values; and average errors of mole fractions y_1 and y_2 in the vapor phase are merely 0.8%. Thus, the values are in surprisingly good agreement. These results demonstrate that multicomponent vapor-liquid equilibrium can be predicted with exceedingly high accuracy using the present invention.

[0145] [Table 2]

Table 2 Comparison between actually measured VLE data and predicted values of ternary VLE according to the present invention for water (1)-methanol (2)-ethanol (3) system

Actually measured value				
x_1	x_2	y_1	y_2	P
0.0955	0.0992	0.077	0.183	64.59
0.103	0.1974	0.072	0.335	70.87
0.094	0.7047	0.035	0.847	103.98
0.0966	0.8067	0.032	0.915	110.71
0.1513	0.2243	0.1	0.37	72.18
0.2989	0.1525	0.191	0.267	64.98
Calculated value				
x_1	x_2	y_1	y_2	P
0.0955	0.0992	0.0789	0.1829	64.98
0.103	0.1974	0.0738	0.3347	70.92

0.094	0.7047	0.0353	0.8476	104.24
0.0966	0.8067	0.0317	0.9155	111.39
0.1513	0.2243	0.0996	0.3712	71.94
0.2989	0.1525	0.186	0.2688	65.61

[0146] [Prediction of phase equilibrium using homologous series]

The method according to the present invention has the high correlation accuracy of X vs. Y_1 and X vs. Y_2 relationships and thus permits phase equilibrium prediction using homologous series, which has been difficult to conventional methods for prediction of phase equilibrium. FIG. 15(a) shows relationships between the number of carbon atoms and Y_1 and Y_2 determined at X = 0.5 for the carbon dioxide (1)-alkane (2) system and the carbon dioxide (1)-alkene (2) system from high-pressure VLE data (cited from Non-patent Document 6). In FIG. 15(a), the X vs. Y_1 and X vs. Y_2 relationships are indicated by the open circle (○) and the open triangle (△), respectively, for the carbon dioxide (1)-alkane (2) system. Also, the X vs. Y_1 and X vs. Y_2 relationships are indicated by the filled circle (●) and the filled triangle (▲), respectively, for the carbon dioxide (1)-alkene (2) system. The tendency in which the values of Y_1 and Y_2 increase with increase in the number of carbon atoms is clearly shown for all the homologous series. FIG. 15(a) also shows that the value of Y_2 is substantially the same between alkane and alkene having the same number of carbon atoms. It further shows that these systems form minimum boiling azeotropes at $Y_2 < 0$ for ethane or ethylene and can be handled easily as asymmetric systems when the number of carbon atoms becomes larger than that of butane (i.e., $X = Y_2 = 0.5$ is satisfied). It should be understood that such uniform relationships of high-pressure VLE data can be established for homologous series because the present invention successfully provides highly accurate correlation.

[0147] FIG. 15(b) shows relationships between the number of carbon atoms and Y_1 and Y_2 determined at X = 0.4 for the hydrogen sulfide (1)-alkane (2) system from high-pressure VLE data (cited from Non-patent Document 6). In this context, the X vs. Y_1 and X vs. Y_2

relationships are indicated by the open circle (○) and the open triangle (Δ), respectively. Again, the tendency in which the values of Y_1 and Y_2 increase with increase in the number of carbon atoms is clearly shown in FIG. 15(b). FIG. 15(b) also shows that this system forms minimum boiling azeotropes at $Y_2 < 0$ for hydrogen sulfide (1)-ethane (2) system and can be handled as an asymmetric system when the number of carbon atoms in alkane is close to 5 (i.e., $Y_1 = Y_2 = 0.4$ holds)). Constant-temperature data for defining binary parameters A and B is absent for propane, a principal component of natural gases. FIG. 15(b) demonstrates that the values of Y_1 and Y_2 and, by extension, γ_1^∞ and γ_2^∞ can be predicted even for undocumented hydrogen sulfide (1)-alkane (2) systems by use of the representative line representing homologous series relationship. In addition, phase equilibrium relationship can be predicted accurately by use of homologous series relationship for binary systems that are less reliable due to the limited number of data sets. Hydrogen sulfide, which is an extremely poisonous substance, is limited in measurement data. The absence of phase equilibrium data containing hydrogen sulfide has been a difficult-to-solve problem in, for example, the design of natural gas processing. In such a case, the present invention, which has achieved phase equilibrium prediction using homologous series, is of great significance.

[0148] [Prediction of vapor-liquid equilibrium using atomic group contribution method]

Conventional atomic group contribution methods, such as the UNIFAC method, are characterized in that they are significantly low in prediction accuracy since they determine the values of groups vs. parameters by using all existing phase equilibrium data and the values are used as constant values. By contrast, the atomic group contribution method based on the present invention selects only binary systems including atomic groups required, determines the logarithmic values of infinite dilution activity coefficients from the X vs. Y_1 and X vs. Y_2 relationships at a temperature or pressure of interest, and determines the group contribution to nondimensional infinite dilution excess partial molar free energy, i.e., $\ln\gamma_i^\infty$. Thus, the method based on the present invention is characterized by high prediction accuracy. An example in which the vapor-liquid equilibrium for a system of 1-propanol (1) + water (2)

is predicted by the atomic group contribution method will be explained.

(a) Determination of atomic group: In this step, a methyl group (CH_3) and a methylene group (CH_2) are indicated by Me, identically, and the system of 1-propanol (1) + water (2) consists of three atomic groups: Me, OH and H_2O.

(b) Selection of reference binary systems including atomic groups: A system of methanol (1) + water (2) and a system of ethanol (1) + water (2) are selected as binary systems including Me, OH and H_2O.

(c) The values of Y_1 and Y_2 are determined for the reference binary systems at a temperature or pressure at which vapor-liquid equilibrium is to be determined. For example, for the system of methanol (1) + water (2), Y_1 and Y_2 are determined according to the equations (34) and (35), respectively. From these values, the values of $\ln\gamma_1^{\infty}$ and $\ln\gamma_2^{\infty}$ are determined for the respective reference binary systems.

(d) The group contribution to $\ln\gamma_1^{\infty}$ and $\ln\gamma_2^{\infty}$ is formulated. Specifically, since methanol consists of an Me group and an OH group and ethanol consists of two Me groups and an OH group, the following equation holds for methanol (MeOH):

[0149] [Formula 61]

$$(\ln\gamma_1^{\infty})_{MeOH} = \ln\gamma_{Me/H2O}^{\infty} + \ln\gamma_{OH/H2O}^{\infty}$$

The following equation holds for ethanol (EtOH):

[0150] [Formula 62]

$$(\ln\gamma_1^{\infty})_{EtOH} = 2\ln\gamma_{Me/H2O}^{\infty} + \ln\gamma_{OH/H2O}^{\infty}$$

wherein $(\ln\gamma_1^{\infty})_{MeOH}$ represents the $\ln\gamma_1^{\infty}$ of the system of methanol (1) + water (2); $(\ln\gamma_1^{\infty})_{EtOH}$ represents the $\ln\gamma_1^{\infty}$ of the system of ethanol (1) + water (2); $\ln\gamma_{1/H2O}^{\infty}$ represents a logarithmic value of an infinite dilution activity coefficient in water for an atomic group i, wherein the logarithmic value is regarded as justifying the additivity of atomic groups. The contribution to the two atomic groups, i.e., $\ln\gamma_{Me/H2O}^{\infty}$ and $\ln\gamma_{OH/H2O}^{\infty}$, can be determined according to those two equations. $\ln\gamma_2^{\infty}$ is represented in the same manner as above. Specifically, the following equation holds for methanol (MeOH):

[0151] [Formula 63]

$$(\ln\gamma_2^{\infty})_{MeOH} = \ln\gamma_{H2O/Me}^{\infty} + \ln\gamma_{H2O/OH}^{\infty}$$

The following equation holds for ethanol (EtOH):

[0152] [Formula 64]

$$(\ln\gamma_2^{\infty})_{EtOH} = 2\ln\gamma_{H2O/Me}^{\infty} + \ln\gamma_{H2O/OH}^{\infty}$$

wherein $(\ln\gamma_2^{\infty})_{MeOH}$ represents the $\ln\gamma_2^{\infty}$ of the system of methanol (1) + water (2); $(\ln\gamma_2^{\infty})_{EtOH}$ represents the $\ln\gamma_2^{\infty}$ of the system of ethanol (1) + water (2); $\ln\gamma_{H2O/i}^{\infty}$ represents a logarithmic value of an infinite dilution activity coefficient in a pure atomic group i for water.

[0153] The contribution to the two atomic groups, i.e., $\ln\gamma_{H2O/Me}^{\infty}$ and $\ln\gamma_{H2O/OH}^{\infty}$, can be determined according to those two equations. Since the free energy contribution to the atomic groups has been determined, Margules binary parameters A and B can be determined for the system of 1-propanol (1) + water (2).

[0154] [Formula 65]

$$A = \ln\gamma_1^{\infty} = 3\ln\gamma_{Me/H2O}^{\infty} + \ln\gamma_{OH/H2O}^{\infty}$$

$$B = \ln\gamma_2^{\infty} = 3\ln\gamma_{H2O/Me}^{\infty} + \ln\gamma_{H2O/OH}^{\infty}$$

As a method for prediction of a vapor-liquid equilibrium relationship from the values of A and B, for example, the method described for FIGS. 5(a) and 5(b) may be used. Alternatively, much more binary system of alcohol (1) + water (2) may be added as a reference binary system of FIG. 5(b) to determine the group contribution as an average value.

[0155] The method for prediction of phase equilibrium according to the present invention can be used in the apparatus or operational design of a distillation column, an absorption column, an extraction column, or a crystallizer, which inevitably requires phase equilibrium relationship. For such use, the method of the present invention can be incorporated, as described above, in software for phase equilibrium calculation and applied thereto. Also, such use encompasses the determination of the sizes of individual apparatuses as well as the design and control of a separation process using a plurality of apparatuses in combination. In Example 1, an example of design calculation for determining the number of equilibrium stages in a stage contact-type distillation column is compared between use of the present invention and use of a conventional method dependent on measurement data.

EXAMPLE 1

[0156] (Calculation of equilibrium stages in distillation column according to McCabe-Thiele method)

The case is assumed where a 50 mol% methanol (1)-water (2) mixed solution is supplied as a boiling solution to a plate column at 101.3 kPa, and 95% concentrates are obtained from the top of the column while 5% bottoms are obtained from the bottom of the column. The reflux ratio is set to 3. The vapor-liquid equilibrium of the methanol (1)-water (2) system at 101.3 kPa is determined according to the present invention, and x-y relationships are given by the solid line of FIG. 16. The x-y relationships are determined from two representative lines drawn in FIG. 5(b). The specific calculation method thereof is as follows: first, the boiling points of methanol and water at 101.3 kPa are calculated to determine an average boiling point. X at this average boiling point is calculated according to the equation (22). Next, the values of Y_1 and Y_2 are determined from the value of X according to the equations (34) and (35), respectively. Subsequently, γ_1^{∞} and γ_2^{∞} are calculated from the equations (24) and (25), respectively, and A and B are determined according to the equations (6) and (7), respectively. Subsequently, a temperature that satisfies the equation (8) is determined by boiling point calculation. Since vapor pressures can be calculated from the thus-determined boiling point, the value of y_1 for x_1 is determined according to the equation (9). In this way, x-y relationships are calculated. The number of equilibrium stages appropriate for the design conditions is determined using the McCabe-Thiele method. An enriching section operating line and a stripping section operating line are drawn, and stepwise graphics are created with mole fractions of methanol from 0.95 to 0.05 between the operating line and the equilibrium line to determine 5 stages. As a result of subtracting the equilibrium stage of the distillation still therefrom, it is determined that 4 equilibrium stages are necessary. A raw material supply stage corresponds to the third stage from the top.

COMPARATIVE EXAMPLE 1

[0157] A large number of vapor-liquid equilibrium data sets at 101.3 kPa have been

reported. Using the data sets listed in Part 1 of page 43 of Non-patent Document 1, x-y relationships are given by the dotted line of FIG. 16. As a result of creating similar stepwise graphics using these data sets, 5.6 stages are determined. This means that a difference of 10% or more appears. In this case, a raw material supply stage corresponds to the fourth stage from the top, which largely differs from the correct value (third stage). Apparatus design based on such data is risky.

EXAMPLE 2

[0158] [Application of atomic group contribution method]

Existing group contribution methods such as the UNIFAC or ASOG method determine group parameters without excluding errors from measurement data, whereas the atomic group contribution method according to the present invention is characterized by exceedingly high accuracy in application because the method uses a highly accurate method for correlation of infinite dilution activity coefficients to exclude measurement errors. In the application of the contribution method, data correlated with high accuracy by excluding measurement errors may also be analyzed in the same manner as a conventional method such as the UNIFAC or ASOG method to determine group parameters. Alternatively, a method of determining the atomic group contribution to nondimensional infinite dilution excess partial molar free energies, $\ln\gamma_1^{\infty}$ and $\ln\gamma_2^{\infty}$, may be used. Based on the system of alkanol (1) + water (2), an example of the application of the atomic group contribution method will be shown below.

[0159] Vapor-liquid equilibrium measurement values for the binary system of n-alkanol (1) + water (2) comprising an alkanol selected from alkanols ranging from methanol to hexanol as a first component and water as a second component are correlated according to the Margules equation to determine Margules binary parameters, which are given by Non-patent Document 1. First, these parameters are used for the highly accurate correlation according to the present invention to determine correlation equations for X vs. Y_1 and X vs. Y_2 relationships. Since only one data set has been found for the system of 2-hexanol (1) + water (2), the X vs. Y_1 relationship is approximated by a straight line connecting (X, Y_1) and

the origin. The X vs. Y_2 relationship is approximated in the same manner as the X vs. Y_1 relationship. From these correlation equations, the values of Margules parameters A and B (i.e., nondimensional infinite dilution excess partial molar free energies, $\ln\gamma_1^{\infty}$ and $\ln\gamma_2^{\infty}$) at 40°C are calculated and shown in Table 3. FIG. 24 shows the relationship between the values of a carbon number N_{c1} of alkanol and A for the of n-alkanol (1) + water (2) at 40°C. FIG. 25 shows the relationship between the values of a carbon number N_{c1} of alkanol and B for the system of n-alkanol (1) + water (2) at 40°C. In FIG. 24, when the point of methanol is extended to that of 1-propanol through that of ethanol, the relationship (N_{c1}, A) = (3, 2.381) is obtained. This value is close to the value of n-propanol which is shown in Table 3 (A = 2.281). Likewise, the relationship B = 1.37 is obtained as B of n-propanol and is close to (N_{c1}, B) = (3, 1.234) in Table 3. This reveals that the linear sum rule can be applied effectively to the atomic group contribution method.

[0160] On the other hand, the filled circle (●) in FIGS. 24 and 25 indicates that the linearity for the system of n-alkanol (1) + water (2) holds only in $N_{c1} \leq 3$. The values of A and B for 2-alkanol are indicated by symbol (×) in FIGS. 24 and 25. These figures show that the values of A and B for n-alkanol and 2-alkanol are different. Conventional group contribution methods cannot identify the difference in binding sites of groups in a molecule, whereas FIGS. 24 and 25 show that the present invention can identify the difference in binding sites.

[0161] In FIGS. 24 and 25, the filled inverted triangle (▼) denotes the values of A and B for the system of 1,2-propanediol (1) + water (2) and the filled triangle (▲) denotes the values for the system of ethanolamine (1) + water (2). FIGS. 24 and 25 show that those values are significantly different from those for the system of n-alkanol (1) + water (2).

[0162] In conventional group contribution methods, the contribution of diol is incorporated by the doubling of the contribution of -OH groups. The value of A for the system of 1,2-propanediol (1) + water (2) is determined as follows according to a conventional method: first, in FIG. 24, a straight line is drawn from the point of ethanol to that of methanol to determine the Y-intercept (A = -0.22). This value represents the value of A in $N_{c1} = 0$, i.e.,

$\ln\gamma_{OH/H2O}^{\infty}$, and the contribution of OH groups in water. The value is close to zero and this reflects that the characteristics of OH groups and water are similar to each other. The value of A for 1,2-propanediol is A = 2.281 + (-0.22) = 2.061, assuming that the -H group of n-propanol has been replaced by an -OH group.

[0163] However, as shown in Table 3, the actual value of A is A = 0.096, indicating that the value of $\ln\gamma_1^{\infty}$ becomes closer to zero due to hydrophilicity enhanced by the binding of two OH groups to adjacent carbon atoms. When each -OH group is replaced by an $-NH_2$ group, the synergism effect obtained by this group is further increased as indicated by the value of ethanolamine in Table 3 (A = -0.891). This synergism effect changes in intensity when a solvent other than water is used. Thus, FIGS. 24 and 25 show that assigning common synergism effects among groups, regardless of solvents and systems, as in conventional methods, is one cause of the significant reduction of the accuracy in prediction of excess partial molar free energies, i.e., a vapor-liquid equilibrium relationship.

[0164] The atomic group contribution method according to the present invention is characterized by the reliability obtained by the determination of the values of nondimensional infinite dilution excess partial molar free energies (A and B) from a highly accurate correlation line and the exclusion of measurement errors therefrom. Specifically, to determine the value of A for the system of 1,2-diol (1) + water (2), the line indicating the relationship between A and N_{c1} for n-alkanol (i.e., the relationship indicated by a solid polygonal line) is parallelly shifted downward to that for 1,2-propanediol to determine the N_{c1} dependency of A on the basis of the already known value of the system of 1,2-propanediol (1) + water (2). By this procedure, the synergism effect of diol can be properly incorporated. Likewise, to determine the value of A for the system of alkanolamine (1) + water (2), the line indicating the relationship between A and N_{c1} for n-alkanol is parallelly shifted downward to that for ethanolamine to determine the relationship between A and N_{c1}. Also, the synergism effect can be incorporated by parallel shifting of the line indicating the relationship between B and N_{c1} for n-alkanol in the same manner as above. Since there are abundant reports on vapor-liquid equilibrium measurement values for n-alkanol which are

obtained using solvents other than water, the respective relationships between A or B and N_{c1} can be easily determined. Thus, compared with existing methods using all existing vapor-liquid equilibrium measurement values to determine group contribution on a large scale, the present atomic group contribution method is characterized in that it can determine group contribution individually and easily. Users of the atomic group contribution method specify binary systems and temperature or pressure to prepare the relationship indicated by the solid line in FIGS. 24 and 25, i.e., the relationship between A or B and the carbon number N_{c1} of alkane for homologous series including the groups at the end of the alkane. Next, the relationship between A or B and a carbon number N_{c1} (reference relationship) for a binary system including synergism effect is determined from measurement values. Finally, the line indicating the carbon number dependency of the already determined values of A and B is parallelly shifted to the reference value to determine the values of A and B for the binary system. As shown by FIGS. 24 and 25, abundant measurement values of the system of 2-alkanol (1) + water (2) are found and thus the measurement values are preferably used without parallel shifting. Also, an interpolation or extrapolation method may be used for carbon number data that is missing.

[0165] [Simple application of atomic group contribution method]

The atomic group contribution method can also be simply applied. FIGS. 24 and 25 show one example of the application. The relationship between nondimensional infinite dilution excess partial molar free energies (A and B) and a carbon number N_{c1} may be approximated by a straight broken line. In this case, straight-line approximation is possible taking advantage of data abundance. A straight line (broken line) has been determined from two points for methanol and ethanol for the system of n-alkanol (1) + water (2) which is shown in FIGS. 24 and 25. Further, as shown by the dotted line in FIG. 24 or 25, the broken line may be parallelly shifted and the relationship for 1,2-diol or alkanolamine in which synergism effect is expected may be approximated by a straight line including the point for the component. Alternatively, in a simple method, an average value may be used as the slope of straight-line approximation or the slope may be made approximate to zero.

[0166]

[Table 3]

Values of A and B determined from carbon number N_{c1} and highly accurate correlation according to the present invention for the system of n-alkanol (1) + water (2), the system of 2-alkanol (1) + water (2), the system of 1,2-propanediol (1) + water (2) and the system of ethanolamine (1) + water (2) at 40°C

Carbon number	n-Alkanol		Number of data sets	2-Alkanol		Number of data sets
N_{c1}	A	B		A	B	
1	0.649	0.412	60	0.649	0.412	60
2	1.515	0.891	104	1.515	0.891	104
3	2.281	1.234	31	2.129	1.085	42
4	3.454	1.038	25	3.066	0.641	13
5				3.043	1.42	3
6	3.13	1.936	6	3.204	1.656	1
	1,2-Propanediol			Ethanolamine		
	A	B		A	B	
3	0.096	−0.246	13	−0.891	−0.907	5

CLAIMS

1. A method for correlating or predicting binary phase equilibrium data, comprising:

calculating an index X of proximity ratio to critical points and infinite dilution pressure gradients Y_1 and Y_2 using binary phase equilibrium measurement data;

correlating the obtained index X of proximity ratio to critical points with the infinite dilution pressure gradients Y_1 and Y_2 and calculating infinite dilution activity coefficients γ_1^∞ and γ_2^∞ or binary parameters A and B from the X-Y_1 correlation and the X-Y_2 correlation, respectively; and

predicting new binary phase equilibrium data using the calculated values of the infinite dilution activity coefficients γ_1^∞ and γ_2^∞ or binary parameters A and B.

2. The method for correlating or predicting binary phase equilibrium data according to claim 1, wherein the index X of proximity ratio to critical points is calculated according to the equation (22):

[Formula 1]

$$X = \frac{p_{1s} + p_{2s}}{P_{c1} + p_{2s}} \qquad (22)$$

wherein P_{c1} represents the critical pressure of a lighter component in the binary system; and p_{1s} and p_{2s} represent the vapor pressures of components 1 and 2, respectively, at a temperature T, and

the infinite dilution pressure gradients Y_1 and Y_2 are calculated according to the equation (24):

[Formula 2]

$$Y_1 = \frac{\gamma_1^\infty p_{1s} - p_{2s}}{P_{c1} - p_{2s}} \qquad (24)$$

and the equation (25):

[Formula 3]

$$Y_2 = \frac{p_{1s} - \gamma_2^{\infty} p_{2s}}{P_{c1} - p_{2s}} \qquad (25)$$

wherein γ_i^{∞} represents the infinite dilution activity coefficient of component i in the liquid phase; and P_{c1}, p_{1s}, and p_{2s} are as defined in the equation (22).

3. The method for correlating or predicting binary phase equilibrium data according to claim 1, further comprising evaluating the thermodynamic consistency of the X-Y_1 and X-Y_2 correlation data according to the following equation (29), and correlating X with Y_1 and Y_2 using only thermodynamically consistent data:

[Formula 4]

$$H = \left| \frac{\beta_{\exp} - \beta_{cal}}{\beta_{cal}} \right| \qquad (29)$$

wherein β_{exp} represents a value of β that is calculated according to F / |B - A| using F, A, and B determined from actually measured values; and β_{cal} represents a value of β that is calculated from the right side in the following equation (14) using values of a and b obtained by correlation of actually measured values:

[Formula 5]

$$\beta = \frac{F}{|B - A|} = aP^b \qquad (14)$$

wherein A and B represent binary parameters; F represents deviation from A = B in the one-parameter Margules equation; P represents a pressure or an average vapor pressure; and a and b represent constants specific for the binary system.

4. A method for designing or controlling a component separator or a refiner, comprising the steps of:

recording existing binary phase equilibrium data;

implementing the method for correlating or predicting binary phase equilibrium data

according to claim 1; and

inputting the calculated new binary phase equilibrium data to a component separator/refiner design/control unit to design or control the component separator or the refiner.

5. The method for designing or controlling a component separator or refiner according to claim 4, wherein the index X of proximity ratio to critical points is calculated according to the equation (22):

[Formula 6]

$$X = \frac{p_{1s} + p_{2s}}{P_{c1} + p_{2s}} \qquad (22)$$

wherein P_{c1} represents the critical pressure of a lighter component in the binary system; and p_{1s} and p_{2s} represent the vapor pressures of components 1 and 2, respectively, at a temperature T, and

the infinite dilution pressure gradients Y_1 and Y_2 are calculated according to the equation (24):

[Formula 7]

$$Y_1 = \frac{\gamma_1^{\infty} p_{1s} - p_{2s}}{P_{c1} - p_{2s}} \qquad (24)$$

and the equation (25):

[Formula 8]

$$Y_2 = \frac{p_{1s} - \gamma_2^{\infty} p_{2s}}{P_{c1} - p_{2s}} \qquad (25)$$

wherein γ_i^{∞} represents the infinite dilution activity coefficient of component i in the liquid phase; and P_{c1}, p_{1s}, and p_{2s} are as defined in the equation (22).

6. The method for designing or controlling a component separator or refiner according to claim 4, further comprising evaluating the thermodynamic consistency of the X-Y_1 and X-

Y_2 correlation data according to the following equation (29), and correlating X with Y_1 and Y_2 using only thermodynamically consistent data:

[Formula 9]

$$H = \left| \frac{\beta_{\exp} - \beta_{cal}}{\beta_{cal}} \right| \tag{29}$$

wherein β_{exp} represents a value of β that is calculated according to F / |B - A| using F, A, and B determined from actually measured values; and β_{cal} represents a value of β that is calculated from the right side in the following equation (14) using values of a and b obtained by correlation of actually measured values:

[Formula 10]

$$\beta = \frac{F}{|B - A|} = aP^b \tag{14}$$

wherein A and B represent binary parameters, F represents deviation from A = B in the one-parameter Margules equation; P represents a pressure or an average vapor pressure; and a and b represent constants specific for the binary system.

7. The method for designing or controlling a component separator or refiner according to claim 4, wherein the infinite dilution activity coefficients γ_1^∞ and γ_2^∞ or the binary parameters A and B are data from a plurality of systems of homologous series, and infinite dilution activity coefficients γ_1^∞ and γ_2^∞ or binary parameters A and B in other systems of homologous series are predicted from the data from a plurality of systems of homologous series.

8. The method for designing or controlling a component separator or refiner according to claim 4, further comprising calculating infinite dilution activity coefficients or binary parameters for atomic groups from the calculated infinite dilution activity coefficients γ_1^∞ and γ_2^∞ or binary parameters A and B, and predicting new binary phase equilibrium data based on the calculated infinite dilution activity coefficients or binary parameters for atomic groups.

9. A program for designing or controlling a component separator or a refiner, the program allowing a computer having an arithmetic processing unit and a data storage unit or a networked computer having an arithmetic processing unit and a data storage unit to function to implement the method for designing or controlling a component separator or refiner according to claim 4, the method comprising the steps of:

storing existing binary phase equilibrium data on the data storage unit;

outputting the binary phase equilibrium data from the data storage unit to the arithmetic processing unit and a predetermined arithmetic expression stored on the data storage unit in advance, substituting the binary phase equilibrium data into the arithmetic expression by means of the arithmetic processing unit to calculate an index X of proximity ratio to critical points and infinite dilution pressure gradients Y_1 and Y_2, correlating the obtained index X of proximity ratio to critical points with the infinite dilution pressure gradients Y_1 and Y_2, and calculating infinite dilution activity coefficients γ_1^{∞} and γ_2^{∞} or binary parameters A and B from the X-Y_1 correlation and the X-Y_2 correlation, respectively;

processing the infinite dilution activity coefficients γ_1^{∞} and γ_2^{∞} or the binary parameters A and B to predict new binary phase equilibrium data; and

calculating information for designing or controlling the component separator or the refiner from the new binary phase equilibrium data.

10. An apparatus for designing or controlling a component separator or a refiner, comprising:

a phase equilibrium information recording unit which receives existing binary phase equilibrium data input to a computer through an information input unit;

a phase equilibrium correlation unit which calculates an index X of proximity ratio to critical points and infinite dilution pressure gradients Y_1 and Y_2 on the basis of the binary phase equilibrium data output from the phase equilibrium information recording unit, and correlates the obtained index X of proximity ratio to critical points with the infinite dilution pressure gradients Y_1 and Y_2 to calculate infinite dilution activity coefficients γ_1^{∞} and γ_2^{∞} or binary parameters A and B from the X-Y_1 correlation and the X-Y_2 correlation, respectively;

a phase equilibrium prediction unit which receives the input of the infinite dilution activity coefficients γ_1^{∞} and γ_2^{∞} or binary parameters A and B output from the phase equilibrium correlation unit to predict new binary phase equilibrium data;

a component separator/refiner design/control information calculation unit which receives the input of the new binary phase equilibrium data output from the phase equilibrium prediction unit to calculate component separator/refiner design/control information; and

a component separator/refiner design/control unit which designs or controls the component separator or the refiner on the basis of the information calculated through the component separator/refiner design/control information calculation unit.

11. The apparatus for designing or controlling a component separator or refiner according to claim 10, wherein the index X of proximity ratio to critical points is calculated according to the equation (22):

[Formula 11]

$$X = \frac{p_{1s} + p_{2s}}{P_{c1} + p_{2s}} \qquad (22)$$

wherein P_{c1} represents the critical pressure of a lighter component in the binary system; and p_{1s} and p_{2s} represent the vapor pressures of components 1 and 2, respectively, at a temperature T, and

the infinite dilution pressure gradients Y_1 and Y_2 are calculated according to the equation (24):

[Formula 12]

$$Y_1 = \frac{\gamma_1^{\infty} p_{1s} - p_{2s}}{P_{c1} - p_{2s}} \qquad (24)$$

and the equation (25):

[Formula 13]

$$Y_2 = \frac{p_{1s} - \gamma_2^{\infty} p_{2s}}{P_{c1} - p_{2s}} \quad (25)$$

wherein γ_i^{∞} represents the infinite dilution activity coefficient of component i in the liquid phase; and P_{c1}, p_{1s}, and p_{2s} are as defined in the equation (22).

12. The apparatus for designing or controlling a component separator or refiner according to claim 10, further comprising evaluating the thermodynamic consistency of the $X\text{-}Y_1$ and $X\text{-}Y_2$ correlation data according to the following equation (29), and correlating X with Y_1 and Y_2 using only thermodynamically consistent data:

[Formula 14]

$$H = \left| \frac{\beta_{\exp} - \beta_{cal}}{\beta_{cal}} \right| \quad (29)$$

wherein β_{exp} represents a value of β that is calculated according to F / |B - A| using F, A, and B determined from actually measured values; and β_{cal} represents a value of β that is calculated from the right side in the following equation (14) using values of a and b obtained by correlation of actually measured values:

[Formula 15]

$$\beta = \frac{F}{|B - A|} = aP^b \quad (14)$$

wherein A and B represent binary parameters; F represents deviation from A = B in the one-parameter Margules equation; P represents a pressure or an average vapor pressure; and a and b represent constants specific for the binary system.

13. The apparatus for designing or controlling a component separator or refiner according to claim 10, wherein the infinite dilution activity coefficients γ_1^{∞} and γ_2^{∞} or binary parameters A and B calculated through the phase equilibrium correlation unit are data from a

plurality of systems of homologous series, and infinite dilution activity coefficients γ_1^{∞} and γ_2^{∞} or binary parameters A and B in other systems of homologous series are predicted from the data from a plurality of systems of homologous series.

14. The apparatus for designing or controlling a component separator or refiner according to claim 10, wherein the phase equilibrium correlation unit calculates infinite dilution activity coefficients or binary parameters for atomic groups from the calculated infinite dilution activity coefficients γ_1^{∞} and γ_2^{∞} or binary parameters A and B, and the phase equilibrium prediction unit receives the input of the calculated infinite dilution activity coefficients or binary parameters for atomic groups.

$X\text{-}Y_1$ and $X\text{-}Y_2$ correlation data according to the following equation (29), and correlating X with Y_1 and Y_2 using only thermodynamically consistent data:

[0100] [Formula 42]

$$H = \left| \frac{\beta_{\exp} - \beta_{cal}}{\beta_{cal}} \right| \tag{29}$$

wherein β_{exp} represents a value of β that is calculated according to $F / |B - A|$ using F, A, and B determined from actually measured values; and β_{cal} represents a value of β that is calculated from the right side in the following equation (14) using values of a and b obtained by correlation of actually measured values:

[0101] [Formula 43]

$$\beta = \frac{F}{|B - A|} = aP^b \tag{14}$$

wherein A and B represent binary parameters; F represents deviation from A = B in the one-parameter Margules equation; P represents a pressure or an average vapor pressure; and a and b represent constants specific for the binary system.

[7] The method for designing or controlling a component separator or refiner according to [4] above, wherein the infinite dilution activity coefficients γ_1^∞ and γ_2^∞ or the binary parameters A and B are data from a plurality of systems of homologous series, and infinite dilution activity coefficients γ_1^∞ and γ_2^∞ or binary parameters A and B in other systems of homologous series are predicted from the data from a plurality of systems of homologous series.

[0102] [8] The method for designing or controlling a component separator or refiner according to [4] above, further comprising calculating infinite dilution activity coefficients or binary parameters for atomic groups from the calculated infinite dilution activity coefficients γ_1^∞ and γ_2^∞ or binary parameters A and B, and predicting new binary phase equilibrium data based on the calculated infinite dilution activity coefficients or binary parameters for atomic

groups.

[0103] [9] A program for designing or controlling a component separator or a refiner, the program allowing a computer having an arithmetic processing unit and a data storage unit or a networked computer having an arithmetic processing unit and a data storage unit to function to implement the method for designing or controlling a component separator or refiner according to [4] above, the method comprising the steps of:

storing existing binary phase equilibrium data on the data storage unit;

outputting the binary phase equilibrium data from the data storage unit to the arithmetic processing unit and a predetermined arithmetic expression stored on the data storage unit in advance, substituting the binary phase equilibrium data into the arithmetic expression by means of the arithmetic processing unit to calculate an index X of proximity ratio to critical points and infinite dilution pressure gradients Y_1 and Y_2, correlating the obtained index X of proximity ratio to critical points with the infinite dilution pressure gradients Y_1 and Y_2, and calculating infinite dilution activity coefficients γ_1^{∞} and γ_2^{∞} or binary parameters A and B from the X-Y_1 correlation and the X-Y_2 correlation, respectively;

processing the infinite dilution activity coefficients γ_1^{∞} and γ_2^{∞} or the binary parameters A and B to predict new binary phase equilibrium data; and

calculating information for designing or controlling the component separator or the refiner from the new binary phase equilibrium data.

[0104] [10] An apparatus for designing or controlling a component separator or a refiner, comprising:

a phase equilibrium information recording unit which receives existing binary phase equilibrium data input to a computer through an information input unit;

a phase equilibrium correlation unit which calculates an index X of proximity ratio to critical points and infinite dilution pressure gradients Y_1 and Y_2 on the basis of the binary phase equilibrium data output from the phase equilibrium information recording unit, and correlates the obtained index X of proximity ratio to critical points with the infinite dilution pressure gradients Y_1 and Y_2 to calculate infinite dilution activity coefficients γ_1^{∞} and γ_2^{∞} or

binary parameters A and B from the X-Y_1 correlation and the X-Y_2 correlation, respectively;

a phase equilibrium prediction unit which receives the input of the infinite dilution activity coefficients γ_1^{∞} and γ_2^{∞} or binary parameters A and B output from the phase equilibrium correlation unit to predict new binary phase equilibrium data;

a component separator/refiner design/control information calculation unit which receives the input of the new binary phase equilibrium data output from the phase equilibrium prediction unit to calculate component separator/refiner design/control information; and

a component separator/refiner design/control unit which designs or controls the component separator or the refiner on the basis of the information calculated through the component separator/refiner design/control information calculation unit.

[0105] [11] The apparatus for designing or controlling a component separator or refiner according to [10] above, wherein the index X of proximity ratio to critical points is calculated according to the equation (22):

[0106] [Formula 44]

$$X = \frac{p_{1s} + p_{2s}}{P_{c1} + p_{2s}} \qquad (22)$$

wherein P_{c1} represents the critical pressure of a lighter component in the binary system; and p_{1s} and p_{2s} represent the vapor pressures of components 1 and 2, respectively, at a temperature T, and

the infinite dilution pressure gradients Y_1 and Y_2 are calculated according to the equation (24):

[0107] [Formula 45]

$$Y_1 = \frac{\gamma_1^{\infty} p_{1s} - p_{2s}}{P_{c1} - p_{2s}} \qquad (24)$$

and the equation (25):

[0108] [Formula 46]

$$Y_2 = \frac{p_{1s} - \gamma_2^{\infty} p_{2s}}{P_{c1} - p_{2s}} \tag{25}$$

wherein γ_i^{∞} represents the infinite dilution activity coefficient of component i in the liquid phase; and P_{c1}, p_{1s}, and p_{2s} are as defined in the equation (22).

[0109] [12] The apparatus for designing or controlling a component separator or refiner according to [10] above, further comprising evaluating the thermodynamic consistency of the $X\text{-}Y_1$ and $X\text{-}Y_2$ correlation data according to the following equation (29), and correlating X with Y_1 and Y_2 using only thermodynamically consistent data:

[0110] [Formula 47]

$$H = \left| \frac{\beta_{\exp} - \beta_{cal}}{\beta_{cal}} \right| \tag{29}$$

wherein β_{exp} represents a value of β that is calculated according to F / |B - A| using F, A, and B determined from actually measured values; and β_{cal} represents a value of β that is calculated from the right side in the following equation (14) using values of a and b obtained by correlation of actually measured values:

[0111] [Formula 48]

$$\beta = \frac{F}{|B - A|} = aP^b \tag{14}$$

wherein A and B represent binary parameters; F represents deviation from A = B in the one-parameter Margules equation; P represents a pressure or an average vapor pressure; and a and b represent constants specific for the binary system.

[13] The apparatus for designing or controlling a component separator or refiner according to [10] above, wherein the infinite dilution activity coefficients γ_1^{∞} and γ_2^{∞} or binary parameters A and B calculated through the phase equilibrium correlation unit are data from a plurality of systems of homologous series, and infinite dilution activity coefficients

γ_1^{∞} and γ_2^{∞} or binary parameters A and B in other systems of homologous series are predicted from the data from a plurality of systems of homologous series.

[0112] [14] The apparatus for designing or controlling a component separator or refiner according to [10] above, wherein the phase equilibrium correlation unit calculates infinite dilution activity coefficients or binary parameters for atomic groups from the calculated infinite dilution activity coefficients γ_1^{∞} and γ_2^{∞} or binary parameters A and B, and the phase equilibrium prediction unit receives the input of the calculated infinite dilution activity coefficients or binary parameters for atomic groups.

ADVANTAGEOUS EFFECTS OF INVENTION

[0113] The present invention has achieved the highly accurate correlation of phase equilibrium data by use of relationships between infinite dilution pressure gradients and vapor pressures in the binary system and thereby enabled one set of infinite dilution activity coefficients (or binary parameters A and B) to be precisely calculated. As a result, phase equilibrium relationship can be predicted in a highly accurate manner that has not been achieved by conventional methods. Thus, binary phase equilibrium relationship can be determined precisely from existing data and can be used to precisely design or control a component separator or refiner such as a distillation column, an extraction column, or a crystallizer. This apparatus design neither requires further experimentally obtaining or validating binary phase equilibrium data nor has to be performed in expectation of safety factors larger than necessary. Thus, an apparatus that can be operated inexpensively in a simple process can be designed, i.e., an economically excellent apparatus can be designed. In addition, an existing apparatus can be controlled on the basis of phase equilibrium data more precise than that at the time of its design. As a result, component separation or refining for chemicals, petroleum, or natural gases can be carried out more precisely under inexpensive operational conditions by, for example, the correction of existing data. Also, the present invention produces precise phase equilibrium data and thus has the advantage that apparatus design procedures can be simplified more than ever before. The precise phase equilibrium data thus obtained can contribute to the improvement of solution models

representing non-ideality in the liquid phase, such as activity coefficient equations or group contribution methods. Thus, the present invention can make a significant contribution to industry.

BRIEF DESCRIPTION OF DRAWINGS

[0114] FIG. 1 is a diagram showing P-x and P-y relationships for the methanol (1)-water (2) system at a temperature of 323.15 K;

FIG. 2 is a diagram showing relationships between mutual solubility and temperature for the 1-butanol (1)-water (2) system (FIG. 2(a)) and a diagram showing relationships between mutual solubility and temperature for the 2-butanone (1)-water (2) system (FIG. 2(b));

FIG. 3 is a diagram showing the temperature dependence of infinite dilution activity coefficients γ_1^{∞} (FIG. 3(a)) and γ_2^{∞} (FIG. 3(b)) for the methanol (1)-water (2) system;

FIG. 4 is a diagram for illustrating the highly accurate method for correlation of phase equilibrium data of the present invention using relationships between infinite dilution pressure gradients and vapor pressures for the methanol (1)-water (2) system, wherein FIG. 4(a) is a diagram showing a thermodynamic consistency line for the methanol (1)-water (2) system, FIG. 4(b) is a diagram showing X vs. Y_1 relationships for the methanol (1)-water (2) system, FIG. 4(c) is a diagram showing X vs. Y_2 relationships, FIG. 4(d) is a diagram showing X vs. γ_1^{∞} relationships for the methanol (1)-water (2) system, and FIG. 4(e) is a diagram showing X vs. γ_2^{∞} relationships;

FIG. 5 is a diagram showing constant-temperature or constant-pressure P-x and P-y relationships for the methanol (1)-water (2) system derived from the results of FIGS. 4(b) to 4(e), wherein FIG. 5(a) is a diagram showing P-x and P-y relationships for the methanol (1)-water (2) system at a temperature of 298.15 K, and FIG. 5(b) is a diagram showing T-x and T-y relationships for the methanol (1)-water (2) system at 101.3 kPa;

FIG. 6 is a diagram showing X vs. Y relationships for the heptane (1)-octane (2) system, wherein FIG. 6(a) is a diagram showing X vs. Y_1 relationships, and FIG. 6(b) is a diagram showing X vs. Y_2 relationships;

FIG. 7 is a diagram for illustrating the highly accurate method for correlation of phase equilibrium data of the present invention using relationships between infinite dilution pressure gradients and vapor pressures for the 1-propanol (1)-water (2) system, wherein FIG. 7(a) is a diagram showing a thermodynamic consistency line for the 1-propanol (1)-water (2) system, FIG. 7(b) is a diagram showing X vs. Y_1 and X vs. Y_2 relationships for the 1-propanol (1)-water (2) system, FIG. 7(c) is a diagram showing P-x and P-y relationships for the 1-propanol (1)-water (2) system at a temperature of 333.15 K, and FIG. 7(d) is a diagram showing x_1 vs. y_1 relationships for the 1-propanol (1)-water (2) system at 101.3 kPa;

FIG. 8 is a diagram for illustrating the highly accurate method for correlation of phase equilibrium data of the present invention using relationships between infinite dilution pressure gradients and vapor pressures for the acetone (1)-chloroform (2) system, wherein FIG. 8(a) is a diagram showing a thermodynamic consistency line for the acetone (1)-chloroform (2) system, FIG. 8(b) is a diagram showing X vs. Y_1 relationships for the acetone (1)-chloroform (2) system, and FIG. 8(c) is a diagram showing X vs. Y_2 relationships for the acetone (1)-chloroform (2) system;

FIG. 9 is a diagram for illustrating the highly accurate method for correlation of phase equilibrium data of the present invention using relationships between infinite dilution pressure gradients and vapor pressures for the 1-butanol (1)-water (2) system, wherein FIG. 9(a) is a diagram showing a thermodynamic consistency line for the 1-butanol (1)-water (2) system, FIG. 9(b) is a diagram showing X vs. Y_1 relationships for the 1-butanol (1)-water (2) system, and FIG. 9(c) is a diagram showing X vs. Y_2 relationships for the 1-butanol (1)-water (2) system;

FIG. 10 is a diagram showing X vs. Y_1 and X vs. Y_2 relationships for the 2-butanone (1)-water (2) system;

FIG. 11 is a diagram showing X vs. Y_1 and X vs. Y_2 relationships for the carbon dioxide (1)-ethane (2) system;

FIG. 12 is a diagram showing results of comparing mutual solubility data for the 1-butanol (1)-water (2) system (FIG. 12(a)) and the 2-butanone (1)-water (2) system (FIG.

12(b)) between actually measured values and predicted values obtained by the method of the present invention;

FIG. 13 is a diagram showing results of comparing X vs. Y_1 relationships for the methanol (1)-water (2) system and the 1-butanol (1)-water (2) system between actually measured values of infinite dilution activity coefficients and predicted values obtained by the method of the present invention on the basis of actually measured values of VLE;

FIG. 14 is a diagram showing relationships between the composition of an azeotrope and temperature, wherein FIGS. 14(a) to 14(d) are diagrams for the 1-propanol (1)-water (2) system, the 1-butanol (1)-water (2) system, the benzene (1)-methanol (2) system, and the acetone (1)-chloroform (2) system, respectively;

FIG. 15 is a diagram showing that Y_1 and Y_2 can be predicted by the homologous series method, wherein FIG. 15(a) is a diagram showing relationships between the number of carbon atoms in hydrocarbon and Y_1 or Y_2 for the carbon dioxide (1)-alkane (2) system and the carbon dioxide (1)-alkene (2) system, and FIG. 15(b) is a diagram showing relationships between the number of carbon atoms in hydrocarbon and Y_1 or Y_2 for the hydrogen sulfide (1)-alkane (2) system;

FIG. 16 is a diagram showing the calculation of the number of equilibrium stages in a distillation column using x-y relationships determined by the method for prediction of phase equilibrium data of the present invention;

FIG. 17 is a table showing 60 constant-temperature or constant-pressure data sets for the methanol (1)-water (2) system (the data is cited from Non-patent Document 1);

FIG. 18 is a table showing VLE data for the heptane (1)-octane (2) system (the data is cited from Non-patent Document 1);

FIG. 19 is a table showing VLE data for the 1-propanol (1)-water (2) system (the data is cited from Non-patent Document 1);

FIG. 20 is a table showing VLE data for the acetone (1)-chloroform (2) system (the data is cited from Non-patent Document 1);

FIG. 21 is a table showing LLE data for the 1-butanol (1)-water (2) system (the data

is cited from Non-patent Document 2);

FIG. 22 is a table showing LLE data for the 2-butanone (1)-water (2) system (the data is cited from Non-patent Document 2); and

FIG. 23 is a table showing constant-temperature VLE data for the carbon dioxide (1)-ethane (2) system (the data is cited from Non-patent Document 6).

FIG. 24 is a diagram showing the value of A determined from a carbon number N_{cl} and the high accurate correlation according to the present invention, for the n-alkanol (1)+water (2) system, the 2-alkanol (1)+water (2) system, the 1,2-propanediol (1)+water (2) system, and the ethanolamine (1)+water (2) system at 40°C.

FIG. 25 is a diagram showing the value of B determined from a carbon number N_{cl} and the high accurate correlation according to the present invention, for the n-alkanol (1)+water (2) system, the 2-alkanol (1)+water (2) system, the 1,2-propanediol (1)+water (2) system, and the ethanolamine (1)+water (2) system at 40°C.

DESCRIPTION OF EMBODIMENTS

[0115] Hereinafter, the method for correlation of binary phase equilibrium data, the method for prediction of binary phase equilibrium data, and the method and apparatus for designing or controlling a component separator or refiner according to the present invention will be described more specifically.

[0116] First, the highly accurate method for correlation of phase equilibrium data of the present invention using relationships between infinite dilution pressure gradients and vapor pressures, and the method for prediction of binary phase equilibrium data based on the correlation results will be described specifically.

[Correlation of low-pressure VLE data]

(i) Methanol (1)-water (2) system

FIG. 4(a) shows a thermodynamic consistency line for the methanol (1)-water (2) system as a typical nonazeotropic system. The binary VLE data is cited from Non-patent Document 1. The values of vapor pressures in the analyses shown below are cited from Non-patent Document 1. In the drawing, the open circle (○) denotes constant-temperature

data, and the filled circle (●) denotes constant-pressure data. The values of the critical pressure P_{c1} of the lighter component (methanol) are cited from Non-patent Document 3. FIG. 4(a) shows that: (i) data converges to the line; (ii) data convergence is high; and (iii) constant-temperature data and constant-pressure data converge to the same line. The tolerance of data reliability was set to 1%, and data deviated by 1% or more from the correlation line was excluded. As a result, 54 out of 60 data sets fell in the error range of 1%. A thermodynamic consistency line determined from these 54 reliable data sets is shown in a linear form in FIG. 4(a). The 60 constant-temperature or constant-pressure data sets are shown in the table of FIG. 17.

[0117] FIG. 4(b) shows X vs. Y_1 relationships for the 60 data sets. The calculation depended on the equations (22), (24), and (25). In the drawing, the open circle (○) denotes constant-temperature data, and the filled circle (●) denotes constant-pressure data. Also, the solid line denotes a correlation line optimized using the equation (30). FIG. 4(b) shows that: (i) the correlation according to the present invention is highly accurate; (ii) constant-temperature data and constant-pressure data converge to the same correlation line; and (iii) this correlation line is slightly inferior in convergence to the thermodynamic consistency line.

[0118] In this context, the correlation line optimized using the equation (30) was calculated as follows: first, a thermodynamic consistency line was determined from the 60 data sets shown in FIG. 17, and data deviated by 1% or more therefrom was excluded to select 54 data sets. Next, for these 54 sets, the values of X were calculated according to the equation (22) while the values of Y_1 were determined according to the equation (24). In this case, for constant-pressure data, vapor pressures were calculated using the temperature given by the equation (23). The values of infinite dilution activity coefficients were calculated according to $\gamma_1^{\infty} = \exp(A)$ and $\gamma_2^{\infty} = \exp(B)$ from A and B given in FIG. 17. Next, correlation constants were determined by the method of least squares using the equations (30) and (32) as X vs. Y_1 correlation equations. In the case of FIG. 4B, the equation (30) was superior in correlation accuracy. Specifically, the correlation was achieved according to the equation (34) with 7.6% errors.

[0119] [Formula 49]

$$Y_1 = -0.00070 - 0.2573X + 0.63004X^2 + 1.75319\ln(1+X) \qquad (34)$$

In FIG. 4(b), a representative line of the above equation is indicated by the solid line.

[0120] FIG. 4(c) shows X vs. Y_2 relationships for the 60 data sets. In the drawing, the open circle (○) denotes constant-temperature data, and the filled circle (●) denotes constant-pressure data. Also, the thin solid line denotes a correlation line optimized using the equation (31). The calculation of FIG. 4(c) was also performed in the same way as in FIG. 4(b) using the 60 data sets. In this case, the following correlation equation was obtained:

[0121] [Formula 50]

$$Y_2 = 0.2985X^{0.882} \qquad (35)$$

FIG. 4(c) shows that: (i) the correlation according to the present invention is highly accurate; (ii) constant-temperature data and constant-pressure data converge to the same correlation line; and (iii) this correlation line is slightly inferior in convergence to the thermodynamic consistency line. In FIG. 4(c), $X = Y_2$ relationships were also indicated by the thick solid line. This demonstrates that the methanol-water system, for which $Y_2 > 0$ holds, does not form azeotropes, but is not a complete asymmetric system (for which $p_{1s} >> p_{2s}$ holds). As is evident from FIGS. 4(b) and 4(c), the X vs. Y_1 and X vs. Y_2 correlations proposed by the present invention are much more highly accurate than the conventional correlation of VLE data shown in FIG. 3. FIGS. 4(b) and 4(c) demonstrate the effectiveness of the present invention for the nonazeotropic system.

[0122] FIGS. 4(d) and 4(e) show X vs. γ_1^∞ and X vs. γ_2^∞ relationships, respectively, for the methanol (1)-water (2) system. X is plotted as a single function of temperature on the abscissa. These data sets are significantly variable, as in FIG. 3. Thus, FIGS. 4(d) and 4(e) show that the conversion of a reciprocal of temperature to X on the abscissa is not enough to converge data sets to the line. Since vapor-liquid equilibrium relationship is proportional to activity coefficients as shown in the equations (2) and (3), variations

appearing in FIGS. 3, 4(d) and 4(e) are directly reflected in the VLE relationship. In FIGS. 4(d) and 4(e), the values of γ_1^∞ and γ_2^∞ determined from the representative lines of FIGS. 4(b) and 4(c) are indicated by the solid line. The calculation was performed as follows: first, X was determined according to the equation (22) from a system temperature, and Y_1 and Y_2 were calculated according to the equations (34) and (35). Next, γ_1^∞ and γ_2^∞ were calculated according to the equations (24) and (25). FIGS. 4(d) and 4(e) show that one-to-one relationships of temperature with γ_1^∞ and γ_2^∞ can be determined by the present invention in an accurate manner that has not been achieved by conventional methods.

[0123] FIG. 5(a) shows P-x and P-y relationship data for the methanol (1)-water (2) system at a temperature of 298.15 K. In the drawing, the open circle (○) denotes Px(1,42), the filled circle (●) denotes Py(1,42), the open triangle (Δ) denotes Px(1,44), the open square (□) denotes Px(1a,49), the filled square (■) denotes Py(1a,49), the open inverted triangle (▽) denotes Px(1b,29), and the filled inverted triangle (▼) denotes Py(1b,29). m of the numeric values in the parentheses (m,n) denotes part number in Non-patent Document 1, and n thereof denotes page number therein. In the drawing, values predicted from the X vs. Y_1 relationships (FIG. 4(b)) and X vs. Y_2 relationships (FIG. 4(c)) determined by the present invention were indicated by the solid line (P-x calculated value) and the broken line (P-y calculated value), respectively. This prediction was calculated as follows: first, the vapor pressures of methanol and water were determined at 298.15 K based on Non-patent Document 1 (p_{1s} = 16.93 kPa, p_{2s} = 3.16 kPa, P_{c1} = 8090 kPa), and the values were substituted into the equation (22) to determine an index X of proximity ratio to critical points (X = 0.00248). Then, Y_1 and Y_2 were calculated according to the equations (34) and (35) (Y_1 = 0.00301, Y_2 = 0.00150). Next, infinite dilution activity coefficients γ_1^∞ and γ_2^∞ were determined according to the equations (24) and (25) (γ_1^∞ = 1.439, γ_2^∞ = 1.511). Next, binary parameters A and B were determined according to the equations (6) and (7) (A = 0.3639, B = 0.4130), and activity coefficients γ_1 and γ_2 were determined according to the equations (4) and (5) for arbitrary x_1 (for example, when x_1 = 0.5, γ_1 = 1.109 and γ_2 = 1.095). These values were substituted into the equation (8) to determine a pressure P (P = 11.11 kPa). y_1

was determined according to the equation (9) ($y_1 = 0.844$). An activity coefficient was calculated for a liquid composition different from $x_1 = 0.5$, a pressure P was determined, the procedure to determine y_1 was repeated, and plots were prepared to obtain the curves of the calculated P-x values and calculated P-y values as shown in FIG. 5(a). As is evident from FIG. 5(a), the calculated values are in exceedingly good agreement with the measurement values shown in the document.

[0124] FIG. 5(b) shows T-x and T-y relationships for the methanol (1)-water (2) system at 101.3 kPa. In FIG. 5(b), × denotes the relationship of x_1 and T-273.15 for actually measured values, and + denotes the relationship of y_1 and T-273.15 for actually measured values. P-x and P-y values predicted from the X vs. Y_1 and X vs. Y_2 relationships determined by the present invention are indicated by the solid line and the broken line, respectively. This prediction was performed as follows: first, the boiling points of methanol and water were determined at 101.3 kPa ($t_{b1} = 64.55°C$, $t_{b2} = 100.00°C$), and an average boiling point was determined according to the equation (23) ($t_{b,ave} = 82.27°C$). Vapor pressures were determined at the average boiling point ($p_{1s} = 195.82$ kPa, $p_{2s} = 51.78$ kPa). The value of an index X of proximity ratio to critical points was determined using the average boiling point ($X = 0.0304$). Then, Y_1 and Y_2 were calculated according to the equations (34) and (35) ($Y_1 = 0.0446$, $Y_2 = 0.01371$). Next, infinite dilution activity coefficients γ_1^{∞} and γ_2^{∞} were determined according to the equations (24) and (25) ($\gamma_1^{\infty} = 1.842$, $\gamma_2^{\infty} = 1.654$). Next, binary parameters A and B were determined according to the equations (6) and (7) ($A = 0.6107$, $B = 0.5029$), and activity coefficients were determined according to the equations (4) and (5) for arbitrary x_1 (for example, when $x_1 = 0.5$, $\gamma_1 = 1.134$ and $\gamma_2 = 1.165$). These values were substituted into the equation (8) ($P = 101.3$ kPa) to determine a system temperature T that satisfied the equation (8) based on the calculated boiling points ($T = 73.3°C$). y_1 was determined according to the equation (9). FIG. 5(b) shows that the predicted values according to the present invention agree with the average values of actually measured values, whereas FIG. 5(b) also shows that the actually measured values are significantly variable, indicating the risk of conventional design methods based

only on actually measured values. By contrast, FIGS. 4(b), 4(c), 5(a) and 5(b) show that use of the present invention allows precise prediction of VLE relationship at an arbitrary temperature and pressure. Thus, the present invention represents a landmark because it can put an end to the long absence of prediction methods.

(ii) Heptane (1)-octane (2) system

In order to examine the applicability of the present invention to the ideal system ($\gamma_i = 1$), FIG. 6(a) shows X vs. Y_1 relationships for the heptane (1)-octane (2) system. The binary VLE data is cited from Non-patent Document 1 (see FIG. 18). According to the equation (29), the tolerance of data reliability was set to 1%, and data deviated by 1% or more from the thermodynamic consistency line was removed. As a result, 10 out of 13 data sets fell in the error range of 1%. FIG. 6(a) also shows an X vs. Y_1 correlation line. The calculation of this correlation line depended on the same method as in the methanol (1)-water (2) system. FIG. 6(a) shows that: data convergence is high; and constant-temperature data and constant-pressure data converge to the same correlation line. FIG. 6(b) shows X vs. Y_2 relationships for the same data sets as above. In the drawing, the open circle (○) denotes constant-temperature data, and the filled circle (●) denotes constant-pressure data. In FIG. 6(b), a correlation line is also indicated. FIG. 6(b) shows that data convergence is high. FIGS. 6(a) and 6(b) demonstrate the effectiveness of the present invention for the ideal system.

(iii) 1-propanol (1)-water (2) system (minimum boiling azeotrope)

FIG. 7(a) shows a thermodynamic consistency line for the 1-propanol (1)-water (2) system. The binary VLE data is cited from Non-patent Document 1 (see FIG. 19). In the drawing, the open circle (○) denotes constant-temperature data, and × denotes constant-pressure data. Since this system forms minimum boiling azeotropes, the accuracy of VLE data convergence is lower than that in the methanol-water system. Also, FIG. 7(a) shows that: data converges to the line; and constant-temperature data and constant-pressure data converge to the same line. The tolerance of data reliability was set to 0.6%, and data deviated by 0.6% or more from the correlation line was excluded. As a result, 7 out of 31

data sets fell in the error range of 0.6%. Therefore, a thermodynamic consistency line determined from these 7 reliable data sets is shown in FIG. 7(a).

[0125] FIG. 7(b) shows X vs. Y_1 relationships determined according to the Wilson equation for the 1-propanol (1)-water (2) system. In the drawing, the open circle (○) denotes X vs. Y_1 constant-temperature data, the filled circle (●) denotes X vs. Y_1 constant-pressure data, the open square (□) denotes X vs. Y_2 constant-temperature data, and the filled square (■) denotes X vs. Y_2 constant-pressure data. For this system, vapor-liquid equilibrium relationships can be more represented by the Wilson equation than by the Margules equation. The Wilson binary parameters representing vapor-liquid equilibrium relationships are listed in Non-patent Document 1. The calculation was performed in the same way as in FIG. 4 except that the Wilson equation was used instead of the Margules equation.

[0126] The Wilson equation was as follows:

[0127] [Formula 51]

$$\ln\gamma_1 = -\ln(x_1 + \Lambda_{12}x_2) + x_2\left(\frac{\Lambda_{12}}{x_1 + \Lambda_{12}x_2} - \frac{\Lambda_{21}}{\Lambda_{21}x_1 + x_2}\right) \tag{36}$$

[0128] [Formula 52]

$$\ln\gamma_2 = -\ln(x_2 + \Lambda_{21}x_1) - x_1\left(\frac{\Lambda_{12}}{x_1 + \Lambda_{12}x_2} - \frac{\Lambda_{21}}{\Lambda_{21}x_1 + x_2}\right) \tag{37}$$

wherein γ_1 and γ_2 represent the activity coefficients of components 1 and 2, respectively; x_1 and x_2 represent the mole fractions of components 1 and 2, respectively, in the liquid phase; and Λ_{12} and Λ_{21} represent binary parameters. The infinite dilution activity coefficients can be associated with Λ_{12} and Λ_{21} by considering $x_1 = 0$ in the equation (36) and $x_2 = 0$ in the equation (37).

[0129] FIG. 7(b) shows both X vs. Y_1 and X vs. Y_2 relationships. $Y_2 < 0$ holds true for this system that forms minimum boiling azeotropes. Thus, in order to examine detailed data convergence, negative signs of X vs. Y_2 relationships are shown therein. FIG. 7(b) shows that data convergence is high even when azeotropes are formed. It also shows that constant-

temperature data and constant-pressure data converge to the same correlation line. Thus, in FIG. 7(b), the representative lines of data were indicated by the solid line for the X vs. Y_1 correlation line and the broken line for the X vs. Y_2 correlation line. FIG. 7(b) demonstrates the effectiveness of the present invention for the azeotropes. In addition, the values of γ_1^{∞} and γ_2^{∞} were determined at a temperature of 333.15 K from the representative lines shown in FIG. 7(b), and P-x and P-y relationships predicted according to the Wilson equation using the values are indicated in FIG. 7(c). In the drawing, the open circle (○) denotes P-x data, the filled circle (●) denotes P-y data, the solid line denotes P-x predicted values according to the present invention, and the broken line denotes P-y predicted values according to the present invention. FIG. 7(c) shows that P-x relationships can be predicted properly. It also shows that the P-y data is less reliable. FIG. 7(d) shows x-y relationships at 101.3 kPa. FIG. 7(d) shows a diagonal representing $x_1 = y_1$ by a thin solid line. Usually, it is not easy to correlate P-x data and allow x-y relationships to agree with the data (Non-patent Document 1). In spite of this fact, FIG. 7(d) shows that the predicted values according to the present invention (thick line) are in surprisingly good agreement with actually measured values (plot), indicating exceedingly good prediction, though the present invention provides pure prediction, which determines data only from the values of binary parameters and pressures. The precise determination of x-y relationships leads to the prediction of azeotropic points that give operating limits, and is thus practically important. FIGS. 7(a) to 7(d) clearly demonstrate that the correlation of X vs. Y_1 and X vs. Y_2 relationships according to the present invention is effective for the minimum boiling azeotropes.

(iv) Acetone-chloroform system (maximum boiling azeotrope)

FIG. 8(a) shows a thermodynamic consistency line for the acetone (1)-chloroform (2) system. The binary VLE data is cited from Non-patent Document 1 (see FIG. 20). In the drawing, the open circle (○) denotes constant-temperature data, and the filled circle (●) denotes constant-pressure data. $Y_1 < 0$ holds true for this system that forms maximum boiling azeotropes. The Margules equation was used in analysis. FIG. 8(a) shows that: data converges to the line; and constant-temperature data and constant-pressure data

converge to the same line. According to the equation (29), the tolerance of data reliability was set to 2%, and data deviated by 2% or more from the correlation line was excluded. As a result, 25 out of 59 data sets fell in the error range of 2%. A thermodynamic consistency line determined from these 25 reliable data sets is shown in FIG. 8(a).

[0130] FIG. 8(b) shows X vs. Y_1 relationships determined according to the Margules equation for the acetone (1)-chloroform (2) system. $Y_1 < 0$ holds true for this system that forms maximum boiling azeotropes. Thus, in order to examine detailed data convergence, negative signs of X vs. Y_1 relationships are shown therein. In FIG. 8(b), an X vs. Y_1 correlation line was also indicated. FIG. 8(b) shows that data convergence is high even when azeotropes are formed. It also shows that constant-temperature data and constant-pressure data converge to the same correlation line.

[0131] FIG. 8(c) shows X vs. Y_2 relationships for the same data set as above. In FIG. 8(c), a correlation line was also indicated. FIG. 8(c) shows that data convergence is high even for the system that forms maximum boiling azeotropes. FIGS. 8(b) and 8(c) demonstrate the effectiveness of the present invention for the azeotropes.

[Correlation of LLE data]

Next, the correlation of LLE data will be described in detail with reference to specific examples.

(i) 1-butanol (1)-water (2) system

Infinite dilution activity coefficients γ_1^{∞} and γ_2^{∞} can be defined from binary liquid-liquid equilibrium (mutual solubility) to determine Y_1 and Y_2. Preferably, the following UNIQUAC equation, which calculationally provides the highest convergence, is used for determining γ_1^{∞} and γ_2^{∞} from mutual solubility:

[0132]

[Formula 53]

$$\ln\gamma_i = \ln\frac{\Phi_i}{x_i} + \frac{z}{2}q_i\ln\frac{\theta_i}{\Phi_i} + \Phi_i\left(l_i - \frac{r_i}{r_j}l_j\right) - q_i\ln\left(\theta_i + \theta_j\tau_{ji}\right) + \theta_j q_i\left(\frac{\tau_{ij}}{\theta_i + \theta_j\tau_{ji}} - \frac{\tau_{ij}}{\theta_j + \theta_i\tau_{ij}}\right) \quad (38)$$

[0133] [Formula 54]

$$\Phi_i = \frac{x_i r_i}{x_1 r_1 + x_2 r_2} \quad (39)$$

[0134] [Formula 55]

$$\theta_i = \frac{x_i q_i}{x_1 q_1 + x_2 q_2} \quad (40)$$

[0135] [Formula 56]

$$l_i = \frac{z}{2}\left(r_i - q_i\right) - \left(r_i - 1\right) \quad (41)$$

In the above equations, r_i represents a molecular volume index, and q_i represents a molecular surface area index. These values are provided by Non-patent Document 2. Also, x_i represents the mole fraction of component i; z is equal to 10 and fixed; τ_{ij} and τ_{ji} represent binary parameters; and Φ_i, θ_i, and l_i represent variables defined by the equations (39), (40), and (41), respectively. $x_i = 0$ is substituted into the equation (38) to obtain the following equation for an infinite dilution activity coefficient:

[0136] [Formula 57]

$$\ln\gamma_i^{\infty} = \ln\frac{r_i}{r_j} + \frac{z}{2}q_i\ln\frac{r_j q_i}{r_i q_j} + \frac{z}{2}(r_i - q_i) - (r_i - 1) - \frac{r_i}{r_j}\left[\frac{z}{2}(r_j - q_j) - (r_j - 1)\right] - q_i\ln(\tau_{ji}) + q_i\left(1 - \tau_{ij}\right) \quad (42)$$

Thus, τ_{ij} and τ_{ji} are determined according to the equations (10) and (38) from mutual

solubility data at a certain temperature. Infinite dilution activity coefficients are determined according to the equation (42). Then, A and B can be determined according to the equations (6) and (7). After A and B are determined, β, X, Y_1, and Y_2 can be calculated according to the equations (14), (22), (24) and (25), respectively.

[0137] FIG. 9(a) shows a thermodynamic consistency line for the 1-butanol (1)-water (2) system. In the drawing, the open circle (○) denotes LLE data (the data is cited from Non-patent Document 2; see FIG. 21), and the filled circle (●) denotes VLE data (the data is cited from Non-patent Document 1). From the mutual solubility data (Non-patent Document 2) shown in FIG. 2(a), the values of A and B were determined according to the UNIQUAC equation, and β was determined from the equation (14) according to the UNIQUAC equation. Since the vapor-liquid equilibrium data for the 1-butanol (1)-water (2) system has also been reported in Non-patent Document 1, the value of β for the VLE data determined from the equation (14) according to the UNIQUAC equation as an activity coefficient is also indicated in FIG. 9(a). FIG. 9(a) shows that: (i) liquid-liquid equilibrium data and vapor-liquid equilibrium data give the same thermodynamic consistency line (Non-patent Document 4); and (ii) liquid-liquid equilibrium data gives a more converged thermodynamic consistency line than vapor-liquid equilibrium data (Non-patent Document 5). FIG. 9(b) shows X vs. Y_1 relationships determined according to the UNIQUAC equation for the 1-butanol (1)-water (2) system. In the drawing, the open circle (○) denotes LLE data, the filled circle (●) denotes constant-temperature VLE data, × denotes constant-pressure VLE data, and the solid line (-) denotes a correlation line for the LLE data. FIG. 9(b) shows that LLE data and VLE data give the same X vs. Y_1 relationships. Specifically, FIG. 9(b) demonstrates that the present invention is effective commonly for liquid-liquid equilibrium data and vapor-liquid equilibrium data. FIG. 9(c) shows X vs. Y_2 relationships for the 1-butanol (1)-water (2) system. The 1-butanol (1)-water (2) system forms minimum boiling azeotropes and was thus indicated by negative signs. In the drawing, the open circle (○) denotes LLE data, the filled circle (●) denotes constant-temperature VLE data, × denotes constant-pressure VLE data, and the solid line (-) denotes a correlation line for the LLE data. In FIG. 9(c), the

convergence of LLE data and VLE data was high, demonstrating the effectiveness of the present invention which determines binary parameters A and B and uses a proximity ratio to critical points determined according to the equation (22) and infinite dilution pressure gradients determined according to the equations (24) and (25), on the basis of only highly reliable data.

(ii) 2-butanone (1)-water (2) system

FIG. 10 shows both X vs. Y_1 relationships (solid line with open circles (○)) and X vs. Y_2 relationships (broken line with filled circles (●)) determined according to the UNIQUAC equation for the 2-butanone (1)-water (2) system. The LLE data is cited from Non-patent Document 2 (see FIG. 22). FIG. 10 shows that by use of the index of proximity ratio to critical points infinite dilution pressure gradients can converge even to LLE data with high accuracy. Specifically, it demonstrates the effectiveness of the present invention for LLE.

[Correlation of high-pressure VLE data]

(i) Lumped non-ideality correlation

A method involving lumping parameters for non-ideality in the liquid phase and non-ideality in the vapor phase and representing non-ideality according to the equation (28) was examined for its effectiveness. Non-patent Document 1 has reported more than 12500 low-pressure data sets, to which the lumped non-ideality correlation was applied. Correlation errors have also been reported therein. Table 1 shows relative values of correlation errors in constant-temperature P-x data according to the Margules equation reported in Non-patent Document 1.

[0138] [Table 1]

Table 1 P-x correlation errors in constant-temperature VLE data

Binary system	Number of data sets	Average correlation error [1] %
(Low-pressure VLE data)		
Aqueous solutions	508	4.20

Organic compounds with OH groups	1900	2.70
Compounds with aldehydes, ketones, ethers	1399	1.20
Compounds with carboxylic acids, esters	234	2.30
Aliphatic hydrocarbons	1583	1.20
Aromatic hydrocarbons	1007	1.00
Compounds with halogen, nitrogen, sulfur, and others	630	1.60
(High-pressure VLE data)		
Compounds with carbon dioxide	112	1.00
Whole binary system	265	0.90

[1]: $(100/n)\sum\Delta P_i/P_{s,ave}$

n: The number of data sets

ΔP_i: Correlation error of pressure for i-th data set

$P_{s,ave}$: Average pressure of i-th data set

Table 1 shows the increasing tendency of correlation errors in polar mixtures compared with errors on the order of 1% in non-polar mixtures. Table 1 also reveals the degree of correlation errors derived from the lumped non-ideality correlation previously applied to low-pressure data. A large number of binary high-pressure VLE data sets are listed in Non-patent Document 6. Thus, P-x relationships for constant-temperature VLE data that satisfied $T < T_{c1}$ (T_{c1} represents the critical temperature of a light component, i.e., a component having a high vapor pressure) were subjected to the lumped non-ideality correlation according to the Margules equation to determine correlation errors of pressure in each data set. The average relative errors thereof were indicated in Table 1. Table 1 shows that correlation errors even in the high-pressure P-x data are equal to or lower than the

level of hydrocarbon mixtures in low-pressure vapor-liquid equilibrium. This means that the lumped non-ideality correlation of P-x data is effective even for high-pressure data, as in low-pressure data. The conventional correlation using mixing rules for high-pressure data has the disadvantage that it cannot be applied to the prediction of VLE relationship. By contrast, particularly notable is the accomplishment of the present invention, which has found that the lumped non-ideality correlation is effective even for high-pressure data. This is because the method of the present invention can determine X vs. Y_1 and X vs. Y_2 relationships even for high-pressure VLE data at totally the same level as in low-pressure data and can be used with its effectiveness easily proved.

(ii) Correlation of constant-temperature/high-pressure VLE data for carbon dioxide (1)-ethane (2) system

Binary high-pressure VLE data is compiled in Non-patent Document 6. Thus, P-x relationships for the constant-temperature VLE data of the carbon dioxide (1)-water (2) system (see FIG. 23) that satisfied $T < T_{c1}$ were subjected to the lumped non-ideality correlation according to the Margules equation. Y_1 and Y_2 were calculated from the determined values of γ_1^{∞} and γ_2^{∞}. FIG. 11 shows X vs. Y_1 and X vs. Y_2 relationships. In the drawing, the open circle (○) denotes X vs. Y_1 relationships, and the filled inverted triangle (▼) denotes X vs. Y_2 relationships. Since the carbon dioxide-ethane system forms minimum boiling azeotropes, negative signs of Y_2 are shown therein. FIG. 11 demonstrates that: both the X vs. Y_1 and X vs. Y_2 relationships give converged relationships; and the correlation method according to the present invention can also be used effectively for high-pressure vapor-liquid equilibrium data.

[0139] The most important application of the highly accurate method for correlation of phase equilibrium data of the present invention using relationships between infinite dilution pressure gradients and vapor pressures is the precise pure prediction of vapor-liquid equilibrium (VLE) relationship. Specifically, X vs. Y_1 and X vs. Y_2 relationships are individually determined by correlation from existing data, and the values of γ_1^{∞} and γ_2^{∞} are determined for the binary system on the basis of these correlations. As a result, phase

equilibrium relationship can be predicted purely without the use of individual data. The effectiveness of the present invention for the pure prediction of binary VLE is expressed in terms of an example of the constant-temperature methanol (1)-water (2) system in FIG. 5(a) and an example of the constant-pressure methanol (1)-water (2) system in FIG. 5(b) as to the nonazeotropic system. Also, it is expressed in terms of an example of the constant-temperature 1-propanol (1)-water (2) system in FIG. 7(c) and an example of the constant-pressure 1-propanol (1)-water (2) system in FIG. 7(d) as to the minimum boiling azeotropes. The conventional group contribution method is known as a pure prediction method without the use of individual actually measure data, albeit with disadvantageously significantly low prediction accuracy. The pure prediction of VLE based on the correlation method according to the present invention is advantageously reliable with significantly high prediction accuracy.

[0140] Another important application of the correlation method according to the present invention is the pure prediction of mutual solubility. None of the previously proposed methods are capable of highly accurately correlating relationships between mutual solubility and temperature. The application of the correlation method according to the present invention to binary LLE is expressed in terms of the 1-butanol (1)-water (2) system in FIG. 12(a). The mutual solubility data is the same as in FIG. 2(a). In the drawing, the open circle (○) denotes actually measured values of $(x_1)_2$ (cited from Non-patent Document 2), the filled circle (●) denotes actually measured values of $(x_1)_1$ (cited from Non-patent Document 2), the solid line (-) denotes predicted values of $(x_1)_2$ according to the present invention, and the broken line (...) denotes predicted values of $(x_1)_1$ according to the present invention. FIG. 12(a) demonstrates that mutual solubility can be predicted favorably using the present invention. Also, FIG. 12(b) shows an example of mutual solubility prediction for the 2-butanone (1)-water (2) system. The mutual solubility data is the same as in FIG. 2(b). In the drawing, the open circle (○) denotes actually measured values of $(x_1)_2$ (cited from Non-patent Document 2), the filled circle (●) denotes actually measured values of $(x_1)_1$ (cited from Non-patent Document 2), the solid line (-) denotes predicted values of $(x_1)_2$ according to the present invention, and the broken line (...) denotes predicted values of $(x_1)_1$

according to the present invention. FIG. 12(b) shows the slight difference of the data from the predicted values for $(x_1)_1$. This is because correlation functions are not properly selected for X vs. Y_2 relationships, as shown in FIG. 10. FIG. 12(b) demonstrates that infinite dilution activity coefficients must be correlated with significantly high accuracy for the mutual solubility prediction. This is the reason for the conventional unfavorable correlation of temperature for LLE. The method of the present invention can converge X vs. Y_2 relationships for LLE data with high accuracy, as shown in FIG. 10, and thus has the advantage that correlation functions can be selected strictly. FIG. 10 and FIG. 12(b) show that the correlation of LLE requires significantly high accuracy and the effectiveness of the present invention.

[0141] The phase equilibrium relationship can be predicted precisely if the values of infinite dilution activity coefficients are correctly determined. The correlation method according to the present invention has the great advantage that it can easily give the values of infinite dilution activity coefficients. FIG. 13 shows X vs. Y_1 relationships (indicated by the open circle (○)) calculated for the methanol (1)-water (2) system from the actually measured values of γ_1^∞ cited from Non-patent Document 7. In FIG. 13, X vs. Y_1 relationships determined from the VLE data shown in FIG. 4(b) are also indicated by the solid line (-). These results are in good agreement with each other. FIG. 13 further shows results of similar comparison for the 1-butanol (1)-water (2) system. In the drawing, the filled circle (●) denotes γ_1^∞ data for the 1-butanol (1)-water (2) system, and the broken line (- -) denotes a representative line of VLE data for the 1-butanol (1)-water (2) system. FIG. 13 demonstrates that the values of infinite dilution activity coefficients determined from VLE data using the converged correlations obtained by the present invention agree with the actually measured values of infinite dilution activity coefficients. As shown in FIGS. 4(d) and 4(e), it has been considered that reliable infinite dilution activity coefficients cannot be determined from VLE data. The correlation method developed by the present invention produces high convergence, breaks through this common knowledge and serves as a novel reliable approach capable of providing infinite dilution activity coefficients. Particularly, a

method for measuring infinite dilution activity coefficients has not yet been found for heavy components, such as water in alcohol. The method of the present invention can correlate more accurately X vs. Y_2 relationships for heavy components than X vs. Y_1 relationships for the same. Specifically, as is evident from these results, the method of the present invention can determine infinite dilution activity coefficients, which are basic determinants necessary for phase equilibrium relationship, from abundant VLE data and as such, is exceedingly useful.

[Prediction of azeotrope]

Mixtures cannot be enriched by a distillation method at a temperature exceeding the azeotropic point. The definition of relationships between the composition of azeotropes and temperature is exceedingly important for determining the operational conditions of distillation. The method of the present invention can purely predict precise vapor-liquid equilibrium relationship and consequently has the great advantage that it can highly accurately predict azeotropes whose highly accurate prediction has been difficult for conventional methods. FIG. 14(a) shows relationships between the composition of an azeotrope and temperature for the 1-propanol (1)-water (2) system. Since binary parameters A and B determined from the Margules equation are provided by Non-patent Document 1, the relationships are obtained for VLE data using these parameters. X vs. Y_1 and X vs. Y_2 relationships are obtained using the Margules equation, and relationships between composition $x_{1,azeo}$ of an azeotrope and a temperature T_{azeo} calculated from these correlations are indicated by the solid line in FIG. 14(a). In addition, similar relationships are indicated for the 1-butanol (1)-water (2) system, the benzene (1)-methanol (2) system, and the acetone (1)-chloroform (2) system in FIGS. 14(b), 14(c), and 14(d), respectively. In FIGS. 14(a) to 14(c), the data and the predicted values are in good agreement with each other, demonstrating that the correlation method according to the present invention is effective for the prediction of azeotropic points.

[Assessment of phase equilibrium data consistency]

Aside from thermodynamic consistency lines, data consistency can be assessed

using the data convergence of X vs. Y_1 and X vs. Y_2 relationships. Particularly, data consistency can be assessed easily if relationships between an index X of proximity ratio to critical points and infinite dilution pressure gradients converge to a line. This assessable data consistency means that the correlation method according to the present invention produces high data convergence.

[Prediction of ternary VLE]

Three sets of binary parameters for basic binary systems constituting a ternary system can be determined from ternary VLE data by use of activity coefficient equations such as Margules, UNIQUAC, Wilson, and NRTL equations. Thus, when X vs. Y_1 and X vs. Y_2 relationships determined from ternary VLE data agree with X vs. Y_1 and X vs. Y_2 relationships determined from binary VLE data, the ternary data can be assessed as being consistent. On the other hand, three sets of binary parameters for basic binary systems can be determined on the basis of X vs. Y_1 and X vs. Y_2 relationships determined from binary VLE data, and used in the prediction of ternary VLE relationship. An example of the ternary system using the Margules equation is shown below. The activity coefficient equation of component i in the multicomponent system is obtained by differentiating an excess function g^E by the number of moles n_i of component i as follows:

[0142] [Formula 58]

$$\ln \gamma_i = \frac{\partial g^E \sum_{k=1}^{n} n_k}{\partial n_i} \qquad (43)$$

For the ternary system, g^E is represented by the following Margules equation (see Non-patent Document 8):

[0143] [Formula 59]

$$g^E = x_1x_2(x_1B_{12} + x_2A_{12}) + x_1x_3(x_1B_{13} + x_3A_{13}) + x_2x_3(x_2B_{23} + x_3A_{23}) + x_1x_2x_3(B_{12} + A_{13} + B_{23}) \qquad (44)$$

wherein g^E represents an excess function; x_i represents the mole fraction of component i in the liquid phase; and A_{ij} and B_{ij} represent binary parameters consisting of i and j in the binary

system. Specific equations for extending the UNIQUAC, NRTL, or Wilson equation to the multicomponent system is shown in Non-patent Document 3. Since three sets of binary parameters constituting the ternary system, i.e., a total of 6 binary parameters, can be determined using the present invention, the excess function and the activity coefficient can be determined according to the equations (44) and (43), respectively. For the multicomponent system, the activity coefficient can be easily determined directly by numerical differentiation of the equation (43). Also, the pressure can be determined according to the following equation:

[0144] [Formula 60]

$$P = \sum_{k=1}^{n} \gamma_k x_k p_{ks} \qquad (45)$$

wherein P represents a system pressure; γ_k represents the activity coefficient of component k; x_k represents the mole fraction of component k in the liquid phase; and p_{ks} represents the vapor pressure of component k. In order to demonstrate that the present invention can be applied to the prediction of multicomponent vapor-liquid equilibrium, Table 2 compares predicted values (calculated values) of pressure according to the present invention with actually measured values (the data is cited from Part 1a, p. 494 of Non-patent Document 1) for the water (1)-methanol (2)-ethanol (3) ternary system at 298.15 K. A_{ij}, B_{ij}, etc., in the equation (44) are calculated from the correlation equation according to the present invention using actually measured values of three binary vapor-liquid equilibria consisting of the water (1)-methanol (2) system, the water (1)-ethanol (3) system, and the methanol (2)-ethanol (3) system. Table 2 shows that: the measured and predicted values of pressure agree with each other with a difference of 0.5% when mole fractions x_1 and x_2 of water and methanol in the liquid phase have various values; and average errors of mole fractions y_1 and y_2 in the vapor phase are merely 0.8%. Thus, the values are in surprisingly good agreement. These results demonstrate that multicomponent vapor-liquid equilibrium can be predicted with exceedingly high accuracy using the present invention.

[0145] [Table 2]

Table 2 Comparison between actually measured VLE data and predicted values of ternary VLE according to the present invention for water (1)-methanol (2)-ethanol (3) system

Actually measured value

x_1	x_2	y_1	y_2	P
0.0955	0.0992	0.077	0.183	64.59
0.103	0.1974	0.072	0.335	70.87
0.094	0.7047	0.035	0.847	103.98
0.0966	0.8067	0.032	0.915	110.71
0.1513	0.2243	0.1	0.37	72.18
0.2989	0.1525	0.191	0.267	64.98

Calculated value

x_1	x_2	y_1	y_2	P
0.0955	0.0992	0.0789	0.1829	64.98
0.103	0.1974	0.0738	0.3347	70.92
0.094	0.7047	0.0353	0.8476	104.24
0.0966	0.8067	0.0317	0.9155	111.39
0.1513	0.2243	0.0996	0.3712	71.94
0.2989	0.1525	0.186	0.2688	65.61

[0146] [Prediction of phase equilibrium using homologous series]

The method according to the present invention has the high correlation accuracy of X vs. Y_1 and X vs. Y_2 relationships and thus permits phase equilibrium prediction using homologous series, which has been difficult to conventional methods for prediction of phase equilibrium. FIG. 15(a) shows relationships between the number of carbon atoms and Y_1 and Y_2 determined at X = 0.5 for the carbon dioxide (1)-alkane (2) system and the carbon

dioxide (1)-alkene (2) system from high-pressure VLE data (cited from Non-patent Document 6). In FIG. 15(a), the X vs. Y_1 and X vs. Y_2 relationships are indicated by the open circle (○) and the open triangle (Δ), respectively, for the carbon dioxide (1)-alkane (2) system. Also, the X vs. Y_1 and X vs. Y_2 relationships are indicated by the filled circle (●) and the filled triangle (▲), respectively, for the carbon dioxide (1)-alkene (2) system. The tendency in which the values of Y_1 and Y_2 increase with increase in the number of carbon atoms is clearly shown for all the homologous series. FIG. 15(a) also shows that the value of Y_2 is substantially the same between alkane and alkene having the same number of carbon atoms. It further shows that these systems form minimum boiling azeotropes at $Y_2 < 0$ for ethane or ethylene and can be handled easily as asymmetric systems when the number of carbon atoms becomes larger than that of butane (i.e., $X = Y_2 = 0.5$ is satisfied). It should be understood that such uniform relationships of high-pressure VLE data can be established for homologous series because the present invention successfully provides highly accurate correlation.

[0147] FIG. 15(b) shows relationships between the number of carbon atoms and Y_1 and Y_2 determined at $X = 0.4$ for the hydrogen sulfide (1)-alkane (2) system from high-pressure VLE data (cited from Non-patent Document 6). In this context, the X vs. Y_1 and X vs. Y_2 relationships are indicated by the open circle (○) and the open triangle (Δ), respectively. Again, the tendency in which the values of Y_1 and Y_2 increase with increase in the number of carbon atoms is clearly shown in FIG. 15(b). FIG. 15(b) also shows that this system forms minimum boiling azeotropes at $Y_2 < 0$ for hydrogen sulfide (1)-ethane (2) system and can be handled as an asymmetric system when the number of carbon atoms in alkane is close to 5 (i.e., $Y_1 = Y_2 = 0.4$ holds)). Constant-temperature data for defining binary parameters A and B is absent for propane, a principal component of natural gases. FIG. 15(b) demonstrates that the values of Y_1 and Y_2 and, by extension, γ_1^{∞} and γ_2^{∞} can be predicted even for undocumented hydrogen sulfide (1)-alkane (2) systems by use of the representative line representing homologous series relationship. In addition, phase equilibrium relationship can be predicted accurately by use of homologous series relationship for binary

systems that are less reliable due to the limited number of data sets. Hydrogen sulfide, which is an extremely poisonous substance, is limited in measurement data. The absence of phase equilibrium data containing hydrogen sulfide has been a difficult-to-solve problem in, for example, the design of natural gas processing. In such a case, the present invention, which has achieved phase equilibrium prediction using homologous series, is of great significance.

[0148] [Prediction of vapor-liquid equilibrium using atomic group contribution method]

Conventional atomic group contribution methods, such as the UNIFAC method, are characterized in that they are significantly low in prediction accuracy since they determine the values of groups vs. parameters by using all existing phase equilibrium data and the values are used as constant values. By contrast, the atomic group contribution method based on the present invention selects only binary systems including atomic groups required, determines the logarithmic values of infinite dilution activity coefficients from the X vs. Y_1 and X vs. Y_2 relationships at a temperature or pressure of interest, and determines the group contribution to nondimensional infinite dilution excess partial molar free energy, i.e., $\ln\gamma_i^{\infty}$. Thus, the method based on the present invention is characterized by high prediction accuracy. An example in which the vapor-liquid equilibrium for a system of 1-propanol (1) + water (2) is predicted by the atomic group contribution method will be explained.

(a) Determination of atomic group: In this step, a methyl group (CH_3) and a methylene group (CH_2) are indicated by Me, identically, and the system of 1-propanol (1) + water (2) consists of three atomic groups: Me, OH and H_2O.

(b) Selection of reference binary systems including atomic groups: A system of methanol (1) + water (2) and a system of ethanol (1) + water (2) are selected as binary systems including Me, OH and H_2O.

(c) The values of Y_1 and Y_2 are determined for the reference binary systems at a temperature or pressure at which vapor-liquid equilibrium is to be determined. For example, for the system of methanol (1) + water (2), Y_1 and Y_2 are determined according to the equations (34) and (35), respectively. From these values, the values of $\ln\gamma_1^{\infty}$ and $\ln\gamma_2^{\infty}$ are determined for

the respective reference binary systems.

(d) The group contribution to $\ln\gamma_1^{\infty}$ and $\ln\gamma_2^{\infty}$ is formulated. Specifically, since methanol consists of an Me group and an OH group and ethanol consists of two Me groups and an OH group, the following equation holds for methanol (MeOH):

[0149] [Formula 61]

$$(\ln\gamma_1^{\infty})_{MeOH} = \ln\gamma_{Me/H2O}^{\infty} + \ln\gamma_{OH/H2O}^{\infty}$$

The following equation holds for ethanol (EtOH):

[0150] [Formula 62]

$$(\ln\gamma_1^{\infty})_{EtOH} = 2\ln\gamma_{Me/H2O}^{\infty} + \ln\gamma_{OH/H2O}^{\infty}$$

wherein $(\ln\gamma_1^{\infty})_{MeOH}$ represents the $\ln\gamma_1^{\infty}$ of the system of methanol (1) + water (2); $(\ln\gamma_1^{\infty})_{EtOH}$ represents the $\ln\gamma_1^{\infty}$ of the system of ethanol (1) + water (2); $\ln\gamma_{1/H2O}^{\infty}$ represents a logarithmic value of an infinite dilution activity coefficient in water for an atomic group i, wherein the logarithmic value is regarded as justifying the additivity of atomic groups. The contribution to the two atomic groups, i.e., $\ln\gamma_{Me/H2O}^{\infty}$ and $\ln\gamma_{OH/H2O}^{\infty}$, can be determined according to those two equations. $\ln\gamma_2^{\infty}$ is represented in the same manner as above. Specifically, the following equation holds for methanol (MeOH):

[0151] [Formula 63]

$$(\ln\gamma_2^{\infty})_{MeOH} = \ln\gamma_{H2O/Me}^{\infty} + \ln\gamma_{H2O/OH}^{\infty}$$

The following equation holds for ethanol (EtOH):

[0152] [Formula 64]

$$(\ln\gamma_2^{\infty})_{EtOH} = 2\ln\gamma_{H2O/Me}^{\infty} + \ln\gamma_{H2O/OH}^{\infty}$$

wherein $(\ln\gamma_2^{\infty})_{MeOH}$ represents the $\ln\gamma_2^{\infty}$ of the system of methanol (1) + water (2); $(\ln\gamma_2^{\infty})_{EtOH}$ represents the $\ln\gamma_2^{\infty}$ of the system of ethanol (1) + water (2); $\ln\gamma_{H2O/i}^{\infty}$ represents a logarithmic value of an infinite dilution activity coefficient in a pure atomic group i for water.

[0153] The contribution to the two atomic groups, i.e., $\ln\gamma_{H2O/Me}^{\infty}$ and $\ln\gamma_{H2O/OH}^{\infty}$, can be determined according to those two equations. Since the free energy contribution to the atomic groups has been determined, Margules binary parameters A and B can be determined for the system of 1-propanol (1) + water (2).

[0154] [Formula 65]

$$A = \ln\gamma_1^{\infty} = 3 \ln\gamma_{Me/H2O}^{\infty} + \ln\gamma_{OH/H2O}^{\infty}$$

$$B = \ln\gamma_2^{\infty} = 3 \ln\gamma_{H2O/Me}^{\infty} + \ln\gamma_{H2O/OH}^{\infty}$$

As a method for prediction of a vapor-liquid equilibrium relationship from the values of A and B, for example, the method described for FIGS. 5(a) and 5(b) may be used. Alternatively, much more binary system of alcohol (1) + water (2) may be added as a reference binary system of FIG. 5(b) to determine the group contribution as an average value.

[0155] The method for prediction of phase equilibrium according to the present invention can be used in the apparatus or operational design of a distillation column, an absorption column, an extraction column, or a crystallizer, which inevitably requires phase equilibrium relationship. For such use, the method of the present invention can be incorporated, as described above, in software for phase equilibrium calculation and applied thereto. Also, such use encompasses the determination of the sizes of individual apparatuses as well as the design and control of a separation process using a plurality of apparatuses in combination. In Example 1, an example of design calculation for determining the number of equilibrium stages in a stage contact-type distillation column is compared between use of the present invention and use of a conventional method dependent on measurement data.

EXAMPLE 1

[0156] (Calculation of equilibrium stages in distillation column according to McCabe-Thiele method)

The case is assumed where a 50 mol% methanol (1)-water (2) mixed solution is supplied as a boiling solution to a plate column at 101.3 kPa, and 95% concentrates are obtained from the top of the column while 5% bottoms are obtained from the bottom of the column. The reflux ratio is set to 3. The vapor-liquid equilibrium of the methanol (1)-water (2) system at 101.3 kPa is determined according to the present invention, and x-y relationships are given by the solid line of FIG. 16. The x-y relationships are determined from two representative lines drawn in FIG. 5(b). The specific calculation method thereof is as follows: first, the boiling points of methanol and water at 101.3 kPa are

calculated to determine an average boiling point. X at this average boiling point is calculated according to the equation (22). Next, the values of Y_1 and Y_2 are determined from the value of X according to the equations (34) and (35), respectively. Subsequently, γ_1^{∞} and γ_2^{∞} are calculated from the equations (24) and (25), respectively, and A and B are determined according to the equations (6) and (7), respectively. Subsequently, a temperature that satisfies the equation (8) is determined by boiling point calculation. Since vapor pressures can be calculated from the thus-determined boiling point, the value of y_1 for x_1 is determined according to the equation (9). In this way, x-y relationships are calculated. The number of equilibrium stages appropriate for the design conditions is determined using the McCabe-Thiele method. An enriching section operating line and a stripping section operating line are drawn, and stepwise graphics are created with mole fractions of methanol from 0.95 to 0.05 between the operating line and the equilibrium line to determine 5 stages. As a result of subtracting the equilibrium stage of the distillation still therefrom, it is determined that 4 equilibrium stages are necessary. A raw material supply stage corresponds to the third stage from the top.

COMPARATIVE EXAMPLE 1

[0157] A large number of vapor-liquid equilibrium data sets at 101.3 kPa have been reported. Using the data sets listed in Part 1 of page 43 of Non-patent Document 1, x-y relationships are given by the dotted line of FIG. 16. As a result of creating similar stepwise graphics using these data sets, 5.6 stages are determined. This means that a difference of 10% or more appears. In this case, a raw material supply stage corresponds to the fourth stage from the top, which largely differs from the correct value (third stage). Apparatus design based on such data is risky.

EXAMPLE 2

[0158] [Application of atomic group contribution method]

Existing group contribution methods such as the UNIFAC or ASOG method determine group parameters without excluding errors from measurement data, whereas the atomic group contribution method according to the present invention is

characterized by exceedingly high accuracy in application because the method uses a highly accurate method for correlation of infinite dilution activity coefficients to exclude measurement errors. In the application of the contribution method, data correlated with high accuracy by excluding measurement errors may also be analyzed in the same manner as a conventional method such as the UNIFAC or ASOG method to determine group parameters. Alternatively, a method of determining the atomic group contribution to nondimensional infinite dilution excess partial molar free energies, $\ln\gamma_1^{\infty}$ and $\ln\gamma_2^{\infty}$, may be used. Based on the system of alkanol (1) + water (2), an example of the application of the atomic group contribution method will be shown below.

[0159] Vapor-liquid equilibrium measurement values for the binary system of n-alkanol (1) + water (2) comprising an alkanol selected from alkanols ranging from methanol to hexanol as a first component and water as a second component are correlated according to the Margules equation to determine Margules binary parameters, which are given by Non-patent Document 1. First, these parameters are used for the highly accurate correlation according to the present invention to determine correlation equations for X vs. Y_1 and X vs. Y_2 relationships. Since only one data set has been found for the system of 2-hexanol (1) + water (2), the X vs. Y_1 relationship is approximated by a straight line connecting (X, Y_1) and the origin. The X vs. Y_2 relationship is approximated in the same manner as the X vs. Y_1 relationship. From these correlation equations, the values of Margules parameters A and B (i.e., nondimensional infinite dilution excess partial molar free energies, $\ln\gamma_1^{\infty}$ and $\ln\gamma_2^{\infty}$) at 40°C are calculated and shown in Table 3. FIG. 24 shows the relationship between the values of a carbon number N_{c1} of alkanol and A for the of n-alkanol (1) + water (2) at 40°C. FIG. 25 shows the relationship between the values of a carbon number N_{c1} of alkanol and B for the system of n-alkanol (1) + water (2) at 40°C. In FIG. 24, when the point of methanol is extended to that of 1-propanol through that of ethanol, the relationship (N_{c1}, A) = (3, 2.381) is obtained. This value is close to the value of n-propanol which is shown in Table 3 (A = 2.281). Likewise, the relationship B = 1.37 is obtained as B of n-propanol and is close to (N_{c1}, B) = (3, 1.234) in Table 3. This reveals that the linear sum rule can be applied

effectively to the atomic group contribution method.

[0160] On the other hand, the filled circle (●) in FIGS. 24 and 25 indicates that the linearity for the system of n-alkanol (1) + water (2) holds only in $N_{c1} \leq 3$. The values of A and B for 2-alkanol are indicated by symbol (×) in FIGS. 24 and 25. These figures show that the values of A and B for n-alkanol and 2-alkanol are different. Conventional group contribution methods cannot identify the difference in binding sites of groups in a molecule, whereas FIGS. 24 and 25 show that the present invention can identify the difference in binding sites.

[0161] In FIGS. 24 and 25, the filled inverted triangle (▼) denotes the values of A and B for the system of 1,2-propanediol (1) + water (2) and the filled triangle (▲) denotes the values for the system of ethanolamine (1) + water (2). FIGS. 24 and 25 show that those values are significantly different from those for the system of n-alkanol (1) + water (2).

[0162] In conventional group contribution methods, the contribution of diol is incorporated by the doubling of the contribution of -OH groups. The value of A for the system of 1,2-propanediol (1) + water (2) is determined as follows according to a conventional method: first, in FIG. 24, a straight line is drawn from the point of ethanol to that of methanol to determine the Y-intercept (A = -0.22). This value represents the value of A in $N_{c1} = 0$, i.e., $\ln\gamma_{OH/H2O}^{\infty}$, and the contribution of OH groups in water. The value is close to zero and this reflects that the characteristics of OH groups and water are similar to each other. The value of A for 1,2-propanediol is A = 2.281 + (-0.22) = 2.061, assuming that the -H group of n-propanol has been replaced by an -OH group.

[0163] However, as shown in Table 3, the actual value of A is A = 0.096, indicating that the value of $\ln\gamma_1^{\infty}$ becomes closer to zero due to hydrophilicity enhanced by the binding of two OH groups to adjacent carbon atoms. When each -OH group is replaced by an $-NH_2$ group, the synergism effect obtained by this group is further increased as indicated by the value of ethanolamine in Table 3 (A = -0.891). This synergism effect changes in intensity when a solvent other than water is used. Thus, FIGS. 24 and 25 show that assigning common synergism effects among groups, regardless of solvents and systems, as in conventional

methods, is one cause of the significant reduction of the accuracy in prediction of excess partial molar free energies, i.e., a vapor-liquid equilibrium relationship.

[0164] The atomic group contribution method according to the present invention is characterized by the reliability obtained by the determination of the values of nondimensional infinite dilution excess partial molar free energies (A and B) from a highly accurate correlation line and the exclusion of measurement errors therefrom. Specifically, to determine the value of A for the system of 1,2-diol (1) + water (2), the line indicating the relationship between A and N_{c1} for n-alkanol (i.e., the relationship indicated by a solid polygonal line) is parallelly shifted downward to that for 1,2-propanediol to determine the N_{c1} dependency of A on the basis of the already known value of the system of 1,2-propanediol (1) + water (2). By this procedure, the synergism effect of diol can be properly incorporated. Likewise, to determine the value of A for the system of alkanolamine (1) + water (2), the line indicating the relationship between A and N_{c1} for n-alkanol is parallelly shifted downward to that for ethanolamine to determine the relationship between A and N_{c1}. Also, the synergism effect can be incorporated by parallel shifting of the line indicating the relationship between B and N_{c1} for n-alkanol in the same manner as above. Since there are abundant reports on vapor-liquid equilibrium measurement values for n-alkanol which are obtained using solvents other than water, the respective relationships between A or B and N_{c1} can be easily determined. Thus, compared with existing methods using all existing vapor-liquid equilibrium measurement values to determine group contribution on a large scale, the present atomic group contribution method is characterized in that it can determine group contribution individually and easily. Users of the atomic group contribution method specify binary systems and temperature or pressure to prepare the relationship indicated by the solid line in FIGS. 24 and 25, i.e., the relationship between A or B and the carbon number N_{c1} of alkane for homologous series including the groups at the end of the alkane. Next, the relationship between A or B and a carbon number N_{c1} (reference relationship) for a binary system including synergism effect is determined from measurement values. Finally, the line indicating the carbon number dependency of the already determined values of A and B is

parallelly shifted to the reference value to determine the values of A and B for the binary system. As shown by FIGS. 24 and 25, abundant measurement values of the system of 2-alkanol (1) + water (2) are found and thus the measurement values are preferably used without parallel shifting. Also, an interpolation or extrapolation method may be used for carbon number data that is missing.

[0165] [Simple application of atomic group contribution method]

The atomic group contribution method can also be simply applied. FIGS. 24 and 25 show one example of the application. The relationship between nondimensional infinite dilution excess partial molar free energies (A and B) and a carbon number N_{c1} may be approximated by a straight broken line. In this case, straight-line approximation is possible taking advantage of data abundance. A straight line (broken line) has been determined from two points for methanol and ethanol for the system of n-alkanol (1) + water (2) which is shown in FIGS. 24 and 25. Further, as shown by the dotted line in FIG. 24 or 25, the broken line may be parallelly shifted and the relationship for 1,2-diol or alkanolamine in which synergism effect is expected may be approximated by a straight line including the point for the component. Alternatively, in a simple method, an average value may be used as the slope of straight-line approximation or the slope may be made approximate to zero.

[0166] [Table 3]

Values of A and B determined from carbon number N_{c1} and highly accurate correlation according to the present invention for the system of n-alkanol (1) + water (2), the system of 2-alkanol (1) + water (2), the system of 1,2-propanediol (1) + water (2) and the system of ethanolamine (1) + water (2) at 40°C

Carbon number	n-Alkanol		Number of data sets	2-Alkanol		Number of data sets
N_{c1}	A	B		A	B	
1	0.649	0.412	60	0.649	0.412	60
2	1.515	0.891	104	1.515	0.891	104
3	2.281	1.234	31	2.129	1.085	42
4	3.454	1.038	25	3.066	0.641	13
5				3.043	1.42	3
6	3.13	1.936	6	3.204	1.656	1
	1,2-Propanediol			Ethanolamine		
	A	B		A	B	
3	0.096	−0.246	13	−0.891	−0.907	5

Claims

1. A method of designing a separator or a refiner,

wherein the method is implemented by a computer having an arithmetic processing unit and a data storage unit or a networked computer having an arithmetic processing unit and a data storage unit,

wherein the method comprises:

(1) identifying a binary system for obtaining phase equilibrium relationship from components in a compound that is subject to separation or refining and recording existing binary phase equilibrium data regarding the identified binary system on a phase equilibrium information recording unit in the computer;

(2) on the basis of the binary phase equilibrium data output from the phase equilibrium information recording unit, by means of a phase equilibrium correlation unit in the computer, (a) determining binary parameters A and B using an activity coefficient equation most representing the phase equilibrium data, (b) identifying data for which a relative difference H converges within a predetermined error range as a highly reliable data using a polarity exclusion factor β_{exp} calculated using the value of the determined binary parameter A and B and a polarity exclusion factor β_{cal} determined from actually measured values, (c) calculating an index X of proximity ratio to critical points and infinite dilution pressure gradients Y_1 and Y_2 and correlating the obtained index X of proximity ratio to critical points with the infinite dilution pressure gradients Y_1 and Y_2 to determine correlation coefficient, and (d) calculating new set of infinite dilution activity coefficients γ_1^{∞} and γ_2^{∞} or binary parameters A and B from the obtained $X\text{-}Y_1$ correlation and the obtained $X\text{-}Y_2$ correlation;

(3) inputting the thus-obtained new set of infinite dilution activity coefficients γ_1^{∞} and γ_2^{∞} or binary parameters A and B to a phase equilibrium prediction unit in the computer to newly predict binary phase equilibrium data; and

(4) inputting the calculated new binary phase equilibrium data to a separator design unit or a refiner design unit to design the separator or the refiner;

wherein the index X of proximity ratio to critical points, the infinite dilution pressure gradients Y_1 and Y_2, the infinite dilution activity coefficients γ_1^{∞} and γ_2^{∞} or the binary parameters A and B and the relative difference H in the step (2) are calculated according to the equations below:

the index X of proximity ratio to critical points:

[Formula 1]

$$X = \frac{p_{1s} + p_{2s}}{P_{c1} + p_{2s}} \tag{22}$$

(wherein P_{c1} represents the critical pressure of a lighter component in the binary system; and p_{1s} and p_{2s} represent the vapor pressures of components 1 and 2, respectively, at a temperature T)

the infinite dilution pressure gradients Y_1 and Y_2:

$$Y_1 = \frac{\gamma_1^{\infty} p_{1s} - p_{2s}}{P_{c1} - p_{2s}} \tag{24}$$

$$Y_2 = \frac{p_{1s} - \gamma_2^{\infty} p_{2s}}{P_{c1} - p_{2s}} \tag{25}$$

(wherein γ_1^{∞} and γ_2^{∞} represent the infinite dilution activity coefficients of components 1 and 2 in the liquid phase; and P_{c1}, p_{1s}, and p_{2s} are as defined in the equation (22))

the infinite dilution activity coefficients γ_1^{∞} and γ_2^{∞} or the binary parameters A and B:

[Formula 2]

$$A = \ln \gamma_1^{\infty} \tag{6}$$

$$B = \ln \gamma_2^{\infty} \tag{7}$$

the relative difference H:

[Formula 3]

$$H = \left| \frac{\beta_{\exp} - \beta_{cal}}{\beta_{cal}} \right| \tag{29}$$

(wherein β_{exp} represents a value of β that is calculated according to F / |B - A| using F, A, and B determined from actually measured values; and β_{cal} represents a value of β that is calculated from the right side in the following equation (14) using values of a and b obtained by correlation of actually measured values)

$$\beta = \frac{F}{|B - A|} = aP^b \qquad (14)$$

(wherein P represents a pressure or an average vapor pressure; and a and b represent constants specific for the binary system; and F represents deviation from A = B in the one-parameter Margules equation); and

the X-Y_1 correlation and the X-Y_2 correlation are calculated according to the equations below:

[Formula 4]

$$Y_1 = s_{10} + s_{11}X + s_{12}X^2 + s_{13}\ln(1 + X) \qquad (30)$$

$$Y_2 = s_{20} + s_{21}X + s_{22}X^2 + s_{23}\ln(1 + X) \qquad (31)$$

or

$$Y_1 = s_{11}X^{s_{12}} \qquad (32)$$

$$Y_2 = s_{21}X^{s_{22}} \qquad (33)$$

(wherein s_{10} to s_{23} represent correlation coefficients).

2. A method of controlling a separator or a refiner,

wherein the method is implemented by a computer having an arithmetic processing unit and a data storage unit or a networked computer having an arithmetic processing unit and a data storage unit,

wherein the method comprises:

(1) identifying a binary system for obtaining phase equilibrium relationship from components in a compound that is subject to separation or refining and recording existing binary phase equilibrium data regarding the identified binary system on a phase equilibrium information recording unit in the computer;

(2) on the basis of the binary phase equilibrium data output from the phase equilibrium information recording unit, by means of a phase equilibrium correlation unit in the computer, (a) determining binary parameters A and B using an activity coefficient equation most representing the phase equilibrium data, (b) identifying data for which a relative difference H converges within a predetermined error range as a highly reliable data using a polarity exclusion factor β_{exp} calculated using the value of

the determined binary parameter A and B and a polarity exclusion factor β_{cal} determined from actually measured values, (c) calculating an index X of proximity ratio to critical points and infinite dilution pressure gradients Y_1 and Y_2 and correlating the obtained index X of proximity ratio to critical points with the infinite dilution pressure gradients Y_1 and Y_2 to determine correlation coefficient, and (d) calculating new set of infinite dilution activity coefficients γ_1^∞ and γ_2^∞ or binary parameters A and B from the obtained X-Y_1 correlation and the obtained X-Y_2 correlation;

(3) inputting the thus-obtained new set of infinite dilution activity coefficients γ_1^∞ and γ_2^∞ or binary parameters A and B to a phase equilibrium prediction unit in the computer to newly predict binary phase equilibrium data; and

(4) inputting the calculated new binary phase equilibrium data to a separator control unit or a refiner control unit to control the separator or the refiner;

wherein the index X of proximity ratio to critical points, the infinite dilution pressure gradients Y_1 and Y_2, the infinite dilution activity coefficients γ_1^∞ and γ_2^∞ or the binary parameters A and B and the relative difference H in the step (2) are calculated according to the equations below:

the index X of proximity ratio to critical points:

[Formula 5]

$$X = \frac{p_{1s} + p_{2s}}{P_{c1} + p_{2s}} \tag{22}$$

(wherein P_{c1} represents the critical pressure of a lighter component in the binary system; and p_{1s} and p_{2s} represent the vapor pressures of components 1 and 2, respectively, at a temperature T)

the infinite dilution pressure gradients Y_1 and Y_2:

[Formula 6]

$$Y_1 = \frac{\gamma_1^\infty p_{1s} - p_{2s}}{P_{c1} - p_{2s}} \tag{24}$$

$$Y_2 = \frac{p_{1s} - \gamma_2^\infty p_{2s}}{P_{c1} - p_{2s}} \tag{25}$$

(wherein γ_1^∞ and γ_2^∞ represent the infinite dilution activity coefficients of components 1

and 2 in the liquid phase; and P_{c1}, p_{1s}, and p_{2s} are as defined in the equation (22))
the infinite dilution activity coefficients γ_1^{∞} and γ_2^{∞} or the binary parameters A and B:
[Formula 7]

$$A = \ln \gamma_1^{\infty} \tag{6}$$

$$B = \ln \gamma_2^{\infty} \tag{7}$$

the relative difference H:
[Formula 8]

$$H = \left| \frac{\beta_{\exp} - \beta_{cal}}{\beta_{cal}} \right| \tag{29}$$

(wherein β_{exp} represents a value of β that is calculated according to F / |B - A| using F, A, and B determined from actually measured values; and β_{cal} represents a value of β that is calculated from the right side in the following equation (14) using values of a and b obtained by correlation of actually measured values)

$$\beta = \frac{F}{|B - A|} = aP^b \tag{14}$$

(wherein P represents a pressure or an average vapor pressure; and a and b represent constants specific for the binary system; and F represents deviation from A = B in the one-parameter Margules equation); and

the $X\text{-}Y_1$ correlation and the $X\text{-}Y_2$ correlation are calculated according to the equations below:
[Formula 9]

$$Y_1 = s_{10} + s_{11}X + s_{12}X^2 + s_{13}\ln(1 + X) \tag{30}$$

$$Y_2 = s_{20} + s_{21}X + s_{22}X^2 + s_{23}\ln(1 + X) \tag{31}$$

or

$$Y_1 = s_{11}X^{s_{12}} \tag{32}$$

$$Y_2 = s_{21}X^{s_{22}} \qquad (33)$$

(wherein s_{10} to s_{23} represent correlation coefficients).

3. An apparatus for designing a separator or a refiner, comprising:

a phase equilibrium information recording unit which receives existing binary phase equilibrium data input to a computer through an information input unit;

a phase equilibrium correlation unit which implements, on the basis of the binary phase equilibrium data output from the phase equilibrium information recording unit, (a) determining binary parameters A and B using an activity coefficient equation most representing the phase equilibrium data, (b) identifying data for which a relative difference H converges within a predetermined error range as a highly reliable data using a polarity exclusion factor β_{exp} calculated using the value of the determined binary parameter A and B and a polarity exclusion factor β_{cal} determined from actually measured values, (c) calculating an index X of proximity ratio to critical points and infinite dilution pressure gradients Y_1 and Y_2 and correlating the obtained index X of proximity ratio to critical points with the infinite dilution pressure gradients Y_1 and Y_2 to determine correlation coefficient, and (d) calculating new set of infinite dilution activity coefficients γ_1^{∞} and γ_2^{∞} or binary parameters A and B from the obtained X-Y_1 correlation and the obtained X-Y_2 correlation;

a phase equilibrium prediction unit which receives the new set of infinite dilution activity coefficients γ_1^{∞} and γ_2^{∞} or binary parameters A and B output from the phase equilibrium correlation unit to predict new binary phase equilibrium data;

a design information calculation unit which receives the input of the new binary phase equilibrium data output from the phase equilibrium prediction unit to calculate design information for the separator or the refiner; and

a design unit which designs the separator or the refiner on the basis of the design information calculated through the design information calculation unit,

wherein the phase equilibrium correlation unit (a) determines binary parameters A and B using an activity coefficient equation most representing the phase equilibrium data, (b) identifies data for which a relative difference H converges within a predetermined error range as a highly reliable data using a polarity exclusion factor β_{exp} calculated using the value of the determined binary parameter A and B and a polarity exclusion factor β_{cal} determined from actually measured values, (c) calculates an index X of proximity ratio to critical points and infinite dilution pressure gradients Y_1 and Y_2 and correlating the obtained index X of proximity ratio to critical points with the infinite

dilution pressure gradients Y_1 and Y_2 to determine correlation coefficient, and (d) calculates new set of infinite dilution activity coefficients γ_1^{∞} and γ_2^{∞} or binary parameters A and B from the obtained X-Y_1 correlation and the obtained X-Y_2 correlation,

wherein the index X of proximity ratio to critical points, the infinite dilution pressure gradients Y_1 and Y_2, the infinite dilution activity coefficients γ_1^{∞} and γ_2^{∞} or the binary parameters A and B and the relative difference H in the step (2) are calculated according to the equations below:

the index X of proximity ratio to critical points:

[Formula 10]

$$X = \frac{p_{1s} + p_{2s}}{P_{c1} + p_{2s}} \tag{22}$$

(wherein P_{c1} represents the critical pressure of a lighter component in the binary system; and p_{1s} and p_{2s} represent the vapor pressures of components 1 and 2, respectively, at a temperature T)

the infinite dilution pressure gradients Y_1 and Y_2:

[Formula 11]

$$Y_1 = \frac{\gamma_1^{\infty} p_{1s} - p_{2s}}{P_{c1} - p_{2s}} \tag{24}$$

$$Y_2 = \frac{p_{1s} - \gamma_2^{\infty} p_{2s}}{P_{c1} - p_{2s}} \tag{25}$$

(wherein γ_1^{∞} and γ_2^{∞} represent the infinite dilution activity coefficients of components 1 and 2 in the liquid phase; and P_{c1}, p_{1s}, and p_{2s} are as defined in the equation (22))

the infinite dilution activity coefficients γ_1^{∞} and γ_2^{∞} or the binary parameters A and B:

[Formula 12]

$$A = \ln \gamma_1^{\infty} \tag{6}$$

$$B = \ln \gamma_2^{\infty} \tag{7}$$

the relative difference H:

[Formula 13]

$$H = \left| \frac{\beta_{\exp} - \beta_{cal}}{\beta_{cal}} \right| \quad (29)$$

(wherein β_{exp} represents a value of β that is calculated according to F / |B - A| using F, A, and B determined from actually measured values; and β_{cal} represents a value of β that is calculated from the right side in the following equation (14) using values of a and b obtained by correlation of actually measured values)

$$\beta = \frac{F}{|B - A|} = aP^b \quad (14)$$

(wherein P represents a pressure or an average vapor pressure; and a and b represent constants specific for the binary system; and F represents deviation from A = B in the one-parameter Margules equation); and

the $X\text{-}Y_1$ correlation and the $X\text{-}Y_2$ correlation are calculated according to the equations below:

[Formula 14]

$$Y_1 = s_{10} + s_{11}X + s_{12}X^2 + s_{13}\ln(1+X) \quad (30)$$

$$Y_2 = s_{20} + s_{21}X + s_{22}X^2 + s_{23}\ln(1+X) \quad (31)$$

or

$$Y_1 = s_{11}X^{s_{12}} \quad (32)$$

$$Y_2 = s_{21}X^{s_{22}} \quad (33)$$

(wherein s_{10} to s_{23} represent correlation coefficients).

4. An apparatus for controlling a separator or a refiner, comprising:

a phase equilibrium information recording unit which receives existing binary phase equilibrium data input to a computer through an information input unit;

a phase equilibrium correlation unit which implements, on the basis of the binary phase equilibrium data output from the phase equilibrium information recording

unit, (a) determining binary parameters A and B using an activity coefficient equation most representing the phase equilibrium data, (b) identifying data for which a relative difference H converges within a predetermined error range as a highly reliable data using a polarity exclusion factor β_{exp} calculated using the value of the determined binary parameter A and B and a polarity exclusion factor β_{cal} determined from actually measured values, (c) calculating an index X of proximity ratio to critical points and infinite dilution pressure gradients Y_1 and Y_2 and correlating the obtained index X of proximity ratio to critical points with the infinite dilution pressure gradients Y_1 and Y_2 to determine correlation coefficient, and (d) calculating new set of infinite dilution activity coefficients γ_1^∞ and γ_2^∞ or binary parameters A and B from the obtained X-Y_1 correlation and the obtained X-Y_2 correlation;

a phase equilibrium prediction unit which receives the new set of infinite dilution activity coefficients γ_1^∞ and γ_2^∞ or binary parameters A and B output from the phase equilibrium correlation unit to predict new binary phase equilibrium data;

a control information calculation unit which receives the input of the new binary phase equilibrium data output from the phase equilibrium prediction unit to calculate control information for the separator or the refiner; and

a control unit which controls the separator or the refiner on the basis of the control information calculated through the control information calculation unit,

wherein the phase equilibrium correlation unit (a) determines binary parameters A and B using an activity coefficient equation most representing the phase equilibrium data, (b) identifies data for which a relative difference H converges within a predetermined error range as a highly reliable data using a polarity exclusion factor β_{exp} calculated using the value of the determined binary parameter A and B and a polarity exclusion factor β_{cal} determined from actually measured values, (c) calculates an index X of proximity ratio to critical points and infinite dilution pressure gradients Y_1 and Y_2 and correlating the obtained index X of proximity ratio to critical points with the infinite dilution pressure gradients Y_1 and Y_2 to determine correlation coefficient, and (d) calculates new set of infinite dilution activity coefficients γ_1^∞ and γ_2^∞ or binary parameters A and B from the obtained X-Y_1 correlation and the obtained X-Y_2 correlation,

wherein the index X of proximity ratio to critical points, the infinite dilution pressure gradients Y_1 and Y_2, the infinite dilution activity coefficients γ_1^∞ and γ_2^∞ or the binary parameters A and B and the relative difference H in the step (2) are calculated according to the equations below:

the index X of proximity ratio to critical points:

[Formula 10]

$$X = \frac{p_{1s} + p_{2s}}{P_{c1} + p_{2s}} \tag{22}$$

(wherein P_{c1} represents the critical pressure of a lighter component in the binary system; and p_{1s} and p_{2s} represent the vapor pressures of components 1 and 2, respectively, at a temperature T)

the infinite dilution pressure gradients Y_1 and Y_2:

[Formula 11]

$$Y_1 = \frac{\gamma_1^{\infty} p_{1s} - p_{2s}}{P_{c1} - p_{2s}} \tag{24}$$

$$Y_2 = \frac{p_{1s} - \gamma_2^{\infty} p_{2s}}{P_{c1} - p_{2s}} \tag{25}$$

(wherein γ_1^{∞} and γ_2^{∞} represent the infinite dilution activity coefficients of components 1 and 2 in the liquid phase; and P_{c1}, p_{1s}, and p_{2s} are as defined in the equation (22))

the infinite dilution activity coefficients γ_1^{∞} and γ_2^{∞} or the binary parameters A and B:

[Formula 12]

$$A = \ln \gamma_1^{\infty} \tag{6}$$

$$B = \ln \gamma_2^{\infty} \tag{7}$$

the relative difference H:

[Formula 13]

$$H = \left| \frac{\beta_{\exp} - \beta_{cal}}{\beta_{cal}} \right| \tag{29}$$

(wherein β_{exp} represents a value of β that is calculated according to F / |B - A| using F, A, and B determined from actually measured values; and β_{cal} represents a value of β that is calculated from the right side in the following equation (14) using values of a and b

obtained by correlation of actually measured values)

$$\beta = \frac{F}{|B - A|} = aP^b \qquad (14)$$

(wherein P represents a pressure or an average vapor pressure; and a and b represent constants specific for the binary system; and F represents deviation from A = B in the one-parameter Margules equation); and

the X-Y_1 correlation and the X-Y_2 correlation are calculated according to the equations below:

[Formula 14]

$$Y_1 = s_{10} + s_{11}X + s_{12}X^2 + s_{13}\ln(1+X) \qquad (30)$$

$$Y_2 = s_{20} + s_{21}X + s_{22}X^2 + s_{23}\ln(1+X) \qquad (31)$$

or

$$Y_1 = s_{11}X^{s_{12}} \qquad (32)$$

$$Y_2 = s_{21}X^{s_{22}} \qquad (33)$$

(wherein s_{10} to s_{23} represent correlation coefficients).

5. The apparatus for designing a separator or a refiner according to claim 3, wherein the new set of infinite dilution activity coefficients γ_1^∞ and γ_2^∞ or binary parameters A and B calculated through the phase equilibrium correlation unit are data from a plurality of systems of homologous series, and new set of infinite dilution activity coefficients γ_1^∞ and γ_2^∞ or binary parameters A and B in other systems of homologous series are predicted from the data from a plurality of systems of homologous series.

6. The apparatus for controlling a separator or a refiner according to claim 4, wherein the new set of infinite dilution activity coefficients γ_1^∞ and γ_2^∞ or binary parameters A and B calculated through the phase equilibrium correlation unit are data from a plurality of systems of homologous series, and new set of infinite dilution activity coefficients γ_1^∞ and γ_2^∞ or binary parameters A and B in other systems of homologous series are predicted from the data from a plurality of systems of

homologous series.

7. The apparatus for designing a separator or a refiner according to claim 3, wherein the phase equilibrium correlation unit selects a specified binary system comprising required atomic group i; and determines infinite dilution activity coefficients γ_1^{∞} and γ_2^{∞} or binary parameters A and B on the basis of an atomic group contribution of the atomic group i calculated from the X-Y_1 correlation and the X-Y_2 correlation at a temperature or pressure of interest; and wherein new set of infinite dilution activity coefficients γ_1^{∞} and γ_2^{∞} or binary parameters A and B for atomic groups are input to the phase equilibrium prediction unit.

8. The apparatus for controlling a separator or a refiner according to claim 4, wherein the phase equilibrium correlation unit selects a specified binary system comprising required atomic group i; and determines infinite dilution activity coefficients γ_1^{∞} and γ_2^{∞} or binary parameters A and B on the basis of an atomic group contribution of the atomic group i calculated from the X-Y_1 correlation and the X-Y_2 correlation at a temperature or pressure of interest, and wherein new set of infinite dilution activity coefficients γ_1^{∞} and γ_2^{∞} or binary parameters A and B for atomic groups are input to the phase equilibrium prediction unit.