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PROCESS FOR THE PURIFICATION OF VIRTUALLY ANHYDROUS ORGANIC

LIQUIDS ✓

5 The present invention relates to the purification
of virtually anhydrous liquids consisting of one or more
organic compounds and its subject-matter is more particularly
a process for removing the metallic impurities present in
such liquids.

10 The majority of commercial organic liquids are
available on the market in a purity which is already very
high, generally higher than 99 %. However, as the data in
Table 1 show, metals in trace form are still found in these
liquids, which require an additional purification to permit
15 their use in industries such as electronics or pharmacy. In
general, organic liquids containing less than 10 ppb of each
alkali and alkaline-earth metal and metal contaminant would
be necessary for most of the uses in these two technical
fields (1 ppb = 1 part by weight per thousand million, that
20 is 1 μ g per kg).

TABLE 1

Compound		1-methyl- 2-pyrrol- idone	isopropyl alcohol	N,N- dimethyl- acetamide	mono- ethanol- amine	benzyl alcohol
Supplier		S.G.S.	S.D.S.	Aldrich	Hüls	Elf Atochem
Grade		ultra- pure	purex for analysis	H.P.L.C.	ultra- pure	photo- graphic grade
Purity (%)		99.95	99.7	99.9	99.90	99.90
Water (%)		0.02	0.1	< 0.03	0.06	< 0.1
Metal	Detec- tion limit (ppb)	Content as metal (ppb)				
Na	2	30	30	150	20	240
Fe	1	15	6	85	5	5

It therefore appears desirable to have available a
 5 process for the purification of commercial liquids containing
 one or more organic compounds, which are already of a good
 purity, but nevertheless insufficient for some applications,
 this process being aimed especially at reducing their content
 of traces of metals.

10 Ion exchange resins are very commonly employed
 nowadays for deionizing water. On the other hand, their use
 in an organic medium appears to be markedly less widespread
 or investigated. This absence of development owes its origins

to the special properties of water, which ionizes salts and separates the anions completely from the cations. On the other hand, depending on the dielectric constant of the organic medium, the ions formed by ionization are found to be
5 more or less dissociated and more or less free to exchange with the functional groups of the resin.

Nevertheless some published research is found (C.A. Fleming and A.J. Monhemus, Hydrometallurgy, 4, pp. 159-167, 1979), the objective of which is to improve by a solvent
10 effect the selectivity of exchange of some metals with cationic resins, the final aim being to determine the conditions which permit the separation of the metals in preparative ion chromatography. These studies describe exchange isotherms, that is to say the laws which govern the
15 equilibrium between the metal ion in solution and the metal ion bound to the resin. The usual conditions of such work consequently remain very far from a method of deionization of an organic medium.

US Patent 4 795 565 describes the purification of
20 an aqueous solution of ethanolamine on an ion exchange resin. The objective of this patent is the removal of some salts produced during the ethanolamine extraction of carbon dioxide and hydrogen sulphide present in refinery gases. The spent ethanolamine solution containing between 80 and 50 % water by
25 weight is passed successively over a stationary bed of strong anionic resin and then over a stationary bed of strong cationic resin. US Patent 5 162 084 relates to the same type of application, but improves the purification efficiency by employing a combination of two anionic resins and by

judiciously controlling the operation of the unit with the aid of conductimetric sensors. These patents do not describe the purification of ethanolamine with a low water content on ion exchange resins.

- 5 Patent GB 2 088 850 describes the purification of 1-methyl-2-pyrrolidone (NMP) by passing over an anionic resin binding the chloride and carboxylic ions. This treatment is inserted into a process of selective extraction with NMP of the aromatic hydrocarbons present in a mixture of paraffins.
- 10 No purification with cationic resins is described in this patent. Furthermore, 10 % of water by weight is advantageously added to the NMP to improve the selectivity of extraction.

- Patent RU 2 032 655 relates to the deionization of
- 15 aliphatic alcohols or of diols with the aim of reducing their electric conductivity. For this purpose the authors employ a stationary bed of anionic resin and of cationic resin in equal proportions, these resins being saturated with water beforehand. In a subsequent publication (Vysokochist.
- 20 Veshchestva, 2, pp. 71-75, 1992), A. G. Myakon'kii et al. have indicated that a minimum water content of 2.5 % in the medium is necessary to obtain deionization with the aid of the pair of dry resins.

- In an article intituled "Novel resin-based
- 25 ultrapurification system for reprocessing IPA in the semiconductor industry" (Ind. Eng. Chem. Res. 1996, 35, 3149-3154), P.V. Buragohain et al. propose using cation exchange resins (Amberlite® IR 120, Dowex® M31 and Ionac® CFP 110) to purify isopropyl alcohol (IPA). In these cationic resins,

the divinylbenzene content in the copolymer does not exceed 20%.

The use of an ion exchange resin of sulphonic type which has its active groups in SO_3H acidic form for the
5 purification of dimethyl sulphoxide (DMSO) forms the subject matter of the Patent Application W097/19057 published on May 29, 1997.

It has now been found that the use of a cationic resin of sulphonic type based on a polystyrene-divinylbenzene
10 copolymer having a high content of divinylbenzene allows, in a virtually anhydrous organic liquid, to retain and exchange any cation M^{n+} (n having values from 1 to 4) with n H^+ protons or with n NH_4^+ ions of such a resin in protonic or ammonium form.

15 According to the present invention, there is provided a process for the purification of a virtually anhydrous organic liquid other than DMSO alone, to decrease its content of alkali metal, alkaline-earth metal and/or other metal cations, which process comprises placing the organic
20 liquid to be purified in contact with one or more cation exchange resins and then separating from the resin(s) the purified organic liquid, the resin or at least one of the resins being a sulphonic resin in $-\text{SO}_3\text{H}$ or $-\text{SO}_3\text{NH}_4$ form based on a polystyrene-divinylbenzene copolymer having a
25 divinylbenzene content of from 50 to 60% by weight, without taking the sulphonic groups into account.

A virtually anhydrous organic liquid is here intended to mean suitably an organic liquid which has a water content lower than or equal to 1% by weight, preferably lower than

or equal to 0.15 % by weight.

The process according to the invention can suitably be applied to purify any liquid organic compound which exhibits a dielectric constant ϵ ranging from 5 to 50 and a pKa higher than 2. Nonlimiting examples of such compounds which may be mentioned more particularly are 1-methyl-2-pyrrolidone (NMP), isopropyl alcohol (IPA), benzyl alcohol (BYA), dimethylacetamide (DMAC), monoethanolamine (MEA), ethyl acetate, butyl acetate, ethyl lactate, butyl lactate, tetrahydrothiophene 1,1-dioxide (sulfolane), glycerol, acetic acid, acetone and propylene glycol monomethyl ether acetate (PGMEA). The process is also suitable for the purification of mixtures of these compounds with each other or with DMSO in very variable proportions. Nonlimiting examples of such mixtures which may be mentioned are more particularly DMSO/MEA, NMP/MEA, DMSO/BYA and DMSO/BYA/MEA mixtures.

Cation resins which can be used for implementing the process according to the invention are well-known products and are commercially available, especially under the names Amberlyst[®] and XN 1010 (marketed by Rohm & Haas), Hypersol Macronet[®] (marketed by Purolite) and Relite[®] (marketed by Mitsubishi).

At least one of the resins used in accordance with the invention is a sulphonic resin based on a polystyrene-divinylbenzene copolymer wherein the divinylbenzene represents from 50 to 60 % by weight and the polystyrene from 50 to 40 % by weight relative to the total weight of the copolymer, without taking the sulphonic groups into account. This ratio of divinylbenzene ensures a good kinetic activity

of the exchange of the M^{n+} cations with the $n H^+$ protons or the $n NH_4^+$ cations.

When several resins are employed, at least one of these resins is such as defined above, it being possible for the other(s) to be of chelating type. The organic liquid to be purified may be placed in contact with a mixture of the various resins or successively with each of the various resins.

The contact of the organic liquid to be purified with the resin(s), preferably in the H^+ form, is brought about at a temperature ranging from the melting point of the liquid to be purified to $120^\circ C$ (thermal stability limit temperature of the resins). This temperature is advantageously between 19 and $80^\circ C$, preferably between 20 and $50^\circ C$.

The operation may be carried out noncontinuously (batchwise) or continuously, in conditions and equipment which are well known to a person skilled in the art. The separation of the purified liquid from the resin(s) can be done by any appropriate known means, especially by filtration, percolation or centrifuging.

The invention is further illustrated with reference to the following experimental part describing examples of implementation of the present invention.

Experimental part

I. Methodology

The trace metals are in M^{n+} form. On contact of the liquid to be purified with the cation exchange resin or resins, themselves in H^+ or NH_4^+ form, the M^{n+} ions in

solution are replaced with H^+ protons or with NH_4^+ ions.

In a first step, batchwise tests were carried out to treat various organic compounds, which were pure or mixed.

In a second step, some media were purified continuously, by passing the liquid over a stationary bed of ion exchange resin. This technique is actually more satisfactory and representative of a real production of purified liquid.

II. Method of analysis

10 The method of analysis of trace metals in organic media is I.C.P. (plasma torch - atomic emission spectrometry): the sample is introduced into a plasma torch, where the various elements are excited and emit photons whose energy is characteristic of the element, since it is defined
15 by the electron structure of the element in question. A Perkin Elmer instrument (Optima 3000 DV model) was employed routinely.

 This technique allows the content of several metals to be analysed simultaneously. For the sake of clarity of the
20 results, it was chosen to indicate only the content of iron and of sodium, which are tracers representing all the metallic impurities present. Sodium reflects an atmospheric and accidental contamination (dust) and iron is characteristic of a contamination originating from the
25 process of manufacture or from packaging (contact of the liquid with steel).

 The detection limits of this technique of analysis depend on the metal in question. In the case of sodium the detection limit is 2 ppb and in the case of iron 1 ppb.

III. Batchwise tests

III.1. Experimental preparation

Between 100 and 1000 ppb of sodium and iron were added to 100 g of organic liquid and this solution was then placed in contact with a known quantity of resin (between 2 and 10 g) in H^+ form. Samples of liquid were taken in the course of time in order to follow the change in the iron and sodium concentrations.

The resin employed (Hypersol Macronet[®] MN 500 supplied in H^+ form by Purolite) is a sulphonic resin with a styrene/ divinylbenzene structure. It was dried beforehand by suspension in methanol and evaporation under vacuum in the rotary evaporator (90°C, 2000 Pa) until a constant weight was observed.

III.2. Reduction in the cation content (other than H^+) of NMP: Example 1

The effectiveness of the MN 500 resin was tested in the purification of NMP by employing 10 g of resin per 100 g of NMP. The change in the iron and sodium contents in the course of time are collated in Table 2.

TABLE 2

Example 1

Time (hr)	0	4	8	24
[Na] (ppb)	110	< 2	< 2	< 2
[Fe] (ppb)	100	3	< 1	< 1

III.3. Reduction in the cation content (other than H^+) of various pure or mixed organic media: Examples 2 to 12.

The efficiency of the ion exchange between a resin and an organic medium depends on the nature of the resin and also on the medium in question. In Examples 2 to 9 the activity of Purolite MN 500 sulphonic resin was tested with regard to the cations present in various pure organic media or mixtures of organic compounds. Table 3 (Example 2) shows the change in the iron and sodium concentration as a function of time in benzyl alcohol treated with 2 % by weight of MN 500 resin.

TABLE 3

Example 2

Time (min)	0	5	10	20	25	30	45	60	90	120
[Na] (ppb)	450	200	80	40	20	18	10	10	8	8
[Fe] (ppb)	530	440	340	280	150	130	110	60	12	10

15

Collated in Table 4 (Examples 3 to 7) are the results relating to the kinetics of exchange of iron and sodium in five other organic compounds: isopropyl alcohol (IPA), N,N-dimethylacetamide (DMAC), monoethanolamine (MEA), propylene glycol monomethyl ether acetate (PGMEA) and acetic acid (AcOH).

20

TABLE 4

Examples 3 to 7

Example No.	3		4		5		6		7	
Organic liquid	IPA		DMAC		MEA		PGMEA		AcOH	
Amount of resin (% w/w)	5		5		5		10		10	
Time (hours)	[Na] (ppb)	[Fe] (ppb)	[Na] (ppb)	[Fe] (ppb)	[Na] (ppb)	[Fe] (ppb)	[Na] (ppb)	[Fe] (ppb)	[Na] (ppb)	[Fe] (ppb)
0	250	240	530	570	100	100	30	40	420	100
1	5	36	5	70	20	3	22	20	30	6
2	3	6	2	30	12	2	20	12	19	3
4	2	5	<2	15	10	<2	19	9	15	2
6	3	6	2	13	8	2	-	-	-	-
8	2	7	<2	10	3	2	10	7	10	3
24	-	-	-	-	-	-	9	6	7	2

5

The exchange kinetics of sodium and of iron in binary mixtures of organic compounds are collated in Table 5. The same resin as previously (MN 500) was employed.



12

TABLE 5

Examples 8 to 12

Example No.	8	9	10	11	12
Mixture	DMSO/MEA 70/30 (w/w)	DMSO/MEA 30/70 (w/w)	NMP/MEA 70/30 (w/w)	NMP/MEA 30/70 (w/w)	DMSO/BYA 50/50 (w/w)
Quantity of resin (% w/w)	5	5	5	5	5
Time (hours)	[Na] [Fe] (ppb) (ppb)	[Na] [Fe] (ppb) (ppb)	[Na] [Fe] (ppb) (ppb)	[Na] [Fe] (ppb) (ppb)	[Na] [Fe] (ppb) (ppb)
0	160 270	150 210	155 170	125 170	500 600
8	<2 9	10 13	2 6	< 2 9	< 2 7
24	2 5	8 9	2 3	< 2 4	< 2 9

5 IV. Continuous tests

IV.1. Experimental preparation

Starting from the batchwise results, several continuous tests were undertaken according to the rules commonly followed by a person skilled in the art with regard to the column diameter/particle size and column height/column diameter ratios and to the linear velocity, in order not to have a limitation related to diffusion.

The resin pretreated as indicated above is suspended in 90 ml of liquid in a beaker and gently stirred (to remove air bubbles). This suspension is introduced into a column made of Teflon, in vertical position, and the lower part of which is equipped with a polyethylene sinter of 70 μm

porosity. The beaker is rinsed with 10 ml liquid. Under the sinter the column is equipped with a Teflon stopcock. This stopcock is closed during the filling operation. Once the resin has been deposited and packed down in the column, the
 5 stopcock is opened and the column is fed continuously with medium to be purified by virtue of a pump equipped with a Teflon head. Samples are taken at regular intervals. All the pipes and couplings are made of Teflon. The bottles are made of high density polyethylene.

10 IV.2. Reduction in the cation content (other than H^+) of various media consisting of one or more organic products: Examples 13 to 16

MN 500 resin

Volume of dry resin: 35 cm^3

15 (except Example 16: 88 cm^3)

Particle size: 0.3 to 1.2 mm

The results appear in Table 6, which follows. The equivalent volume, which expresses the change in the test is the ratio of the volume of liquid (in litres) to the volume
 20 of resin (in ml).

TABLE 6**Examples 13 to 16**

Example 13 DMSO/MEA 70/30 (w/w)	Equivalent volume	0	0.49	2.8	3.6	5.6	6.5	7.2
	[Na] (ppb)	26	4	5	4	5	4	3
	[Fe] (ppb)	9	7	8	7	7	7	7
Example 14 DMSO/MEA 30/70 (w/w)	Equivalent volume	0	0.31	2.3	3.13	5.2	7.4	8.14
	[Na] (ppb)	40	< 2	< 2	< 2	< 2	< 2	< 2
	[Fe] (ppb)	33	20	12	7	< 1	< 1	< 1
Example 15 NMP/MEA 70/30 (w/w)	Equivalent volume	0	0.45	2.7	3.4	5.8	6.1	6.9
	[Na] (ppb)	27	5	5	5	5	5	5
	[Fe] (ppb)	5	3	2.5	1	1	1	1
Example 16 n-Butyl acetate	Equivalent volume	0	0.07	0.12				
	[Na] (ppb)	140	3	2				
	[Fe] (ppb)	9	2	2				

CLAIMS

1. Process for purification of a virtually anhydrous organic liquid other than dimethyl sulphoxide alone, to decrease its content of alkali metal, alkaline-
5 earth metal and/or other metal cations, which process comprises placing the organic liquid to be purified in contact with one or more cation exchange resin(s) in acidic or ammonium form and then separating from the resin(s) the purified organic liquid, the resin or at least one of the
10 resins being a sulphonic resin in $-SO_3H$ or $-SONH_4$ form based on a polystyrene-divinylbenzene copolymer having a divinylbenzene content of from 50 to 60% by weight, without taking the sulphonic groups into account.
2. Process according to Claim 1, in which the
15 water content of the organic liquid is lower than or equal to 1% by weight.
3. Process according to claim 2 in which the water content of the organic liquid is lower than or equal to 0.15% by weight.
- 20 4. Process according to any one of Claims 1 to 3, in which the liquid to be purified is an organic compound exhibiting a dielectric constant ϵ ranging from 5 to 50 and a pK_a higher than 2, or a mixture of such compounds with each other and/or with dimethyl sulphoxide (DMSO).
- 25 5. Process according to any one of Claims 1 to 3, in which the liquid to be purified is chosen from 1-methyl-2-pyrrolidone (NMP), isopropyl alcohol, benzyl alcohol



(BYA), dimethylacetamide, monoethanolamine (MEA), ethyl acetate, butyl acetate, ethyl lactate, butyl lactate, sulfolane, glycerol, acetic acid, acetone, propylene glycol monomethyl ether acetate and DMSO/MEA, NMP/MEA, DMSO/BYA
5 and DMSO/BYA/MEA mixtures.

6. Process according to any one of Claims 1 to 5, in which at least two resins are used, at least one of which is a sulphonic resin as defined in claim 1 and the other(s) may be of chelating type.

10 7. Process according to any one of Claims 1 to 6, in which the resin or resins are in the H⁺ form.

8. Process according to any one of Claims 1 to 7, in which the contact of the liquid to be purified with the exchange resin(s) takes place at a temperature ranging from
15 19 to 80°C.

9. Process according to Claim 8, in which the temperature is between 20 and 50°C.

10. Purified virtually anhydrous organic liquid obtained by the process according to any one of claims 1 to
20 9.