Application WO 2018/080869 A1 describes the synthesis of 10-aminodecanoic acid from 9-decenoic acid obtained from a palm oil composition. In particular, the hydrobromination of 9-decenoic acid is carried out by bubbling gaseous hydrogen bromide through a solution of 9-decenoic acid in toluene in the presence of benzoyl peroxide at a temperature of from 5°C to 15°C. After washing, drying and purification in hexane, the yield of 10-bromodecanoic acid is 64%. The 10-bromodecanoic acid can react with 28% ammonium hydroxide at ambient temperature then at 45°C to form 10-aminodecanoic acid, which is recovered by crystallization at ambient temperature then filtration, washing and drying.

It is known to those skilled in the art that 11-dodecenoic acid, manufactured from 10-undecenoic acid, can react with hydrogen bromide in the presence of benzoyl hydroperoxide to give 12-bromododecanoic acid with a yield of 88% (see Chemistry & Industry (London) 1954, 190-191).

All of these processes have the drawback of requiring substantial amounts of hydrogen bromide, generally produced on-site by expensive reaction of bromine with hydrogen, and of producing large amounts of salt-laden effluents.

It is known to convert the ammonium bromide obtained in the ammonolysis step to hydrogen bromide, via a conversion to sodium bromide then to bromine, which is then reacted with hydrogen (see Kunststoff Handbuch, Polyamide, 3/4, published by L. Bottenbruch and R. Binsack, Hanser Fachbuchverlag 1998, pp. 646-648).

Despite the progress, there still remains a need to improve this process. In particular, low yields are observed for the conversion of sodium bromide to bromine and fouling is observed during the conversion of the bromine thus obtained to hydrogen bromide.

[Summary of the disclosure]

The objective of the disclosure is therefore to propose a process for manufacturing aminocarboxylic acids, in particular 12-aminododecanoic acid, 11-aminoundecanoic acid and 10-aminodecanoic acid, which is more economical and makes it possible to reduce the amount of effluents.

Specifically, the present disclosure is based on the observation that it is possible to reduce the amount of bromine required for the process and also the amount of bromides discharged into the environment by replacing a portion of the bromine with chlorine.

Furthermore, it has been discovered that a step of purifying the sodium bromide before the conversion to bromine made it possible to substantially reduce the fouling of the reactor during the conversion to hydrogen bromide.

Therefore, according to a first aspect, one subject of the disclosure is a process for producing aminocarboxylic acid of formula (I) below:

NH_3-CH_2-$(CH_2)_n$-COOH (I)

in which n is an integer from 7 to 12, preferably from 8 to 10, comprising the following steps:

(i) reacting the unsaturated carboxylic acid of formula (II) below:

$CH=CH-(CH_2)_{n-1}-COOH$ (II)

with hydrogen bromide (HBr) to form the ω-bromoalkanoic acid of formula (III) below:

$Br-CH_2-(CH_2)_n-COOH$ (III);

(ii) reacting the ω-bromoalkanoic acid of formula (III) obtained with ammonia in aqueous solution to form a reaction mixture comprising the aminocarboxylic acid of formula (I) and ammonium bromide;

(iii) separating the reaction mixture of the aminocarboxylic acid of formula (I) and an aqueous solution rich in ammonium bromide;

(iv) bringing the aqueous solution rich in ammonium bromide obtained into contact with sodium hydroxide to form ammonia and an aqueous solution rich in sodium bromide;

(v) purifying the aqueous solution rich in sodium bromide obtained in order to eliminate the organic impurities;

(vi) bringing the purified aqueous solution rich in sodium bromide obtained into contact with chlorine to form bromine and an aqueous solution rich in sodium chloride;

(vii) reacting the bromine obtained with hydrogen to form hydrogen bromide; and

(viii) recycling the hydrogen bromide obtained to step (i).

According to one example, bromides originating from another process are added to the solution rich in ammonium bromide or sodium bromide of step (iv). According to another example, bromine originating from another process is added to the bromine obtained in step (vi).

According to one example, step (v) of purifying the aqueous solution of bromides makes it possible to reduce the TOC (total organic carbon) by a factor of more than 5. According to another embodiment, step (vi) is performed with a bromide solution having less than 2%, and preferably less than 1% of TOC and more preferentially less than 0.5% of TOC.

According to a first example of the process that is the subject of the disclosure, step (v) is carried out by acidification of the aqueous solution rich in sodium bromide resulting from step (iv) followed by a decantation of the oily phase formed. Preferably, the aqueous solution rich in sodium bromide resulting from step (iv) is acidified by addition of acid to a pH of between 3 and 5. Advantageously, step (v) comprises a subsequent step (va) in which the oily phase formed in step (v) is subjected to an extraction operation to obtain an aqueous solution enriched in sodium bromide, which is sent back to step (iv) or (vi). Advantageously, the operation that makes it possible to extract an aqueous solution enriched in sodium bromide in step (va) is a liquid/liquid extraction.

According to a second example of the process that is the subject of the disclosure, step (v) is carried out by neutralization of the aqueous solution rich in sodium bromide followed by a liquid/liquid extraction. Preferably, the aqueous solution rich in sodium bromide is neutralized in

step (v) to a pH of between 3 and 10. Advantageously, the neutralization in step (v) is carried out by addition of an aqueous solution of hydrochloric acid, of hydrobromic acid, of sulfuric acid or of a mixture thereof.

According to a third example of the process that is the subject of the disclosure, step (v) is carried out by adsorption on an adsorbent material. Preferably, the adsorption material is chosen from mineral materials such as activated carbon; a silica or an alumina or a mixture thereof; organic materials such as adsorbent macrocrosslinked resins or ion-exchange resins.

According to a fourth example of the process that is the subject of the disclosure, step (v) is carried out by membrane separation to form a permeate enriched in sodium bromide and depleted in organic impurities and a concentrate depleted in sodium bromide and enriched in organic impurities. Step (v) may be carried out notably by means of one or more nanofiltration membranes. Advantageously, step (v) comprises a subsequent step (va') in which the concentrate depleted in sodium bromide and enriched in organic impurities which is obtained in step (v) is subjected to a step of diafiltration in order to recover an aqueous solution enriched in sodium bromide and depleted in organic impurities, which solution will be able to be mixed with the permeate resulting from step (v). Furthermore, step (v) may comprise a subsequent step (vb) in which the permeate enriched in sodium bromide and depleted in organic impurities which is obtained in step (v) and also, where appropriate, the aqueous solution enriched in sodium bromide and depleted in organic impurities resulting from step (va') are subjected to a second step of membrane separation.

According to another aspect, there is provided a process for producing a polyamide or copolyamide, from the aminocarboxylic acid of formula (I) obtained by the process as defined above.

According to another example, the disclosure also relates to a process for producing polyamide or copolyamide from said aminocarboxylic acid.

[**Description of the embodiments**]

Definition of the terms

The term “**bromide**” is understood to denote generally a compound comprising a bromine atom in the (-I) oxidation state devoid of a carbon-hydrogen bond, such as a bromide salt, notably an alkali metal bromide such as sodium bromide or potassium bromide, ammonium bromide or else hydrogen bromide or hydrobromic acid.

As mentioned above, the object of the present invention is to improve the economics of the process for producing aminocarboxylic acids such as 12-aminododecanoic acid, 11-aminoundecanoic acid or 10-aminodecanoic acid by reducing, or even preventing the provision of bromine and the fouling during the conversion of the bromine thus obtained to hydrogen bromide.

According to the invention, the process for producing an aminocarboxylic acid of formula (I) below:

NH_3-CH_2-$(CH_2)_n$-COOH (I)