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(54) Title: AQUEOUS SOLUTIONS CONTAINING A COMPLEXING AGENT IN HIGH CONCENTRATION

(57) Abstract: Aqueous solution comprising (A) in the range of from 30 to 60% by weight of a complexing agent, selected from the alkali metal salts of methylglycine diacetic acid and the alkali metal salts of glutamic acid diacetic acid, (B) in the range of from 1 to 25 % by weight of at least one salt of a sulfonic acid or of an organic acid, percentages referring to the total respective aqueous solution.

## Aqueous Solutions containing a complexing agent in high concentration

The present invention is directed towards an aqueous solution comprising

(A) in the range of from 30 to 60% by weight of a complexing agent, selected from the alkali metal salts of methylglycine diacetic acid and the alkali metal salts of glutamic acid diacetic acid,

(B) in the range of from 1 to 25 % by weight of at least one salt of a sulfonic acid or of an organic acid,

percentages referring to the total respective aqueous solution,

said aqueous solution being free from surfactants.

Complexing agents such as methyl glycine diacetic acid (MGDA) and glutamic acid diacetic acid (GLDA) and their respective alkali metal salts are useful sequestrants for alkaline earth metal ions such as  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ . For that reason, they are recommended and used for various purposes such as laundry detergents and for automatic dishwashing (ADW) formulations, in particular for so-called phosphate-free laundry detergents and phosphate-free ADW formulations. For shipping such complexing agents, in most cases either solids such as granules are being applied or aqueous solutions.

Granules and powders are useful because the amount of water shipped can be neglected but for most mixing and formulation processes an extra dissolution step is required.

Many industrial users wish to obtain complexing agents in aqueous solutions that are as highly concentrated as possible. The lower the concentration of the requested complexing agent the more water is being shipped. Said water adds to the costs of transportation, and it has to be removed later. Although about 40% by weight solutions of MGDA and even 45% by weight solutions of GLDA can be made and stored at room temperature, local or temporarily colder solutions may lead to precipitation of the respective complexing agent, as well as nucleating by impurities. Said precipitations may lead to incrustations in pipes and containers, and/or to impurities or inhomogeneity during formulation.

It can be tried to increase the solubility of complexing agents by adding a solubilizing agent, for example a solubility enhancing polymer or a surfactant. However, many users wish to be flexible with their own detergent formulation, and they wish to avoid polymeric or surface-active additives in the complexing agent.

Additives that may enhance the solubility of the respective complexing agents may be considered but such additives should not negatively affect the properties of the respective complexing agent.

It was therefore the objective of the present invention to provide highly concentrated aqueous solutions of complexing agents such as MGDA or GLDA that are stable at temperatures in the range from zero to 50°C, without the addition of surfactants or polymers. It was further an objec-

tive of the present invention to provide a method for manufacture of highly concentrated aqueous solutions of complexing agents such as MGDA or GLDA that are stable at temperatures in the range from zero to 50°C. Neither such method nor such aqueous solution should require the use of additives that negatively affect the properties of the respective complexing agent.

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Accordingly, the aqueous solutions defined at the outset have been found, hereinafter also being referred to as aqueous solutions according to the invention.

Aqueous solutions according to the invention contain

10 (A) in the range of from 30 to 60% by weight of a complexing agent, hereinafter also being referred as "complexing agent (A)", selected from the alkali metal salts of methylglycine diacetic acid and the alkali metal salts of glutamic acid diacetic acid,

(B) in the range of from 1 to 25 % by weight of least one salt of a sulfonic acid or of an organic acid, said salt hereinafter also being referred to as "salt (B)",

15 said aqueous solution being free from surfactants,  
percentages referring to the total respective aqueous solution according to the invention.

Complexing agent (A) is selected from alkali metal salts of methylglycine diacetic acid and the alkali metal salts of glutamic acid diacetic acid.

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In the context of the present invention, alkali metal salts of methylglycine diacetic acid are selected from lithium salts, potassium salts and preferably sodium salts of methylglycine diacetic acid. Methylglycine diacetic acid can be partially or preferably fully neutralized with the respective alkali. In a preferred embodiment, an average of from 2.7 to 3 COOH groups of MGDA is  
25 neutralized with alkali metal, preferably with sodium. In a particularly preferred embodiment, complexing agent (A) is the trisodium salt of MGDA.

Likewise, alkali metal salts of glutamic acid diacetic acid are selected from lithium salts, potassium salts and preferably sodium salts of glutamic acid diacetic acid. Glutamic acid diacetic acid  
30 can be partially or preferably fully neutralized with the respective alkali. In a preferred embodiment, an average of from 3.5 to 4 COOH groups of GLDA is neutralized with alkali metal, preferably with sodium. In a particularly preferred embodiment, complexing agent (A) is the tetrasodium salt of GLDA.

35 In one embodiment of the present invention, aqueous solutions according to the invention contain in the range of from 30 to 60% by weight alkali metal salt of MGDA as complexing agent (A), preferably 35 to 50% by weight and even more preferably 37 to 45% by weight.

In one embodiment of the present invention, aqueous solutions according to the invention contain  
40 in the range of from 30 to 60% by weight alkali metal salt of GDA as complexing agent (A), preferably 45 to 58% by weight and even more preferably 46 to 53 % by weight.

Complexing agent (A) can be selected from racemic mixtures of alkali metal salts of MGDA or GLDA, and of the pure enantiomers such as alkali metal salts of L-MGDA, alkali metal salts of L-GLDA, alkali metal salts of D-MGDA and alkali metal salts of D-GLDA, and of mixtures of enantiomerically enriched isomers.

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In any way, minor amounts of complexing agent (A) may bear a cation other than alkali metal. It is thus possible that minor amounts, such as 0.01 to 5 mol-% of total complexing agent (A) bear alkali earth metal cations such as  $Mg^{2+}$  or  $Ca^{2+}$ , or  $Fe^{+2}$  or  $Fe^{3+}$  cations.

10 Aqueous solutions according to the invention further comprise

(B) in the range of from 1 to 25 % by weight, preferably 3 to 15 % by weight of salt (B).

In the context of the present invention, salt (B) is selected from the salts of mono- and dicarboxylic acids. Furthermore, salt (B) is thus different from complexing agent (A).

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In a preferred embodiment of the present invention, salt (B) is selected from alkali metal salts of acetic acid, tartaric acid, lactic acid, maleic acid, fumaric acid, and malic acid.

Preferred examples of salt (B) are potassium acetate and sodium acetate.

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In one embodiment of the present invention, salt (B) is the potassium salt of methyl sulfonic acid and preferably the sodium salt of methyl sulfonic acid.

25 Aqueous solutions according the invention furthermore contain water. In one embodiment of the present invention, in aqueous solutions according to the invention, the balance of complexing agent (A) and salt (B), and, optionally, inorganic base, is water. In other embodiments, aqueous solutions according to the invention may contain one or more liquids or solids other than complexing agent (A) and salt (B) and water.

30 The aqueous according to the present invention is free from surfactants. Free from surfactants shall mean, in the context of the present invention, that the total contents of surfactants is 0.1 % by weight or less, referring to the amount of complexing agent (A). In a preferred embodiment, the term "free from surfactants" shall encompass a concentration in the range of from 50 ppm to 0.05 %, both ppm and % referring to ppm by weight or % by weight, respectively, and referring  
35 to the total respective aqueous solution.

In one embodiment of the present invention, aqueous solutions according the invention have a pH value in the range of from 9 to 14, preferably from 10.5 to 13. The pH value is determined at ambient temperature.

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The aqueous according to the present invention is preferably free from polymers. Free from polymers shall mean, in the context of the present invention, that the total contents of surfac-

tants is 0.1 % by weight or less, referring to the amount of complexing agent (A). However, polyethylene glycol (C) is not being considered a polymer in the context of the present invention.

5 In one embodiment of the present invention, aqueous solutions according to the present invention may contain at least one inorganic base, for example potassium hydroxide or preferably sodium hydroxide. Preferred is an amount of 0.1 to 20 mol-% of inorganic base, referring to the total of COOH groups in complexing agent.

10 In one embodiment of the present invention, aqueous solutions according to the invention further comprise

(C) at least one polyethylene glycol with an average molecular weight  $M_n$  in the range of from 400 to 10,000 g/mol, hereinafter also being referred to as "polyethylene glycol (C)", preferably 600 to 6,000 g/mol.

15 In one embodiment of the present invention, polyethylene glycol (C) may be capped, that is converted to a polyether, for example with one methyl group per molecule. In another embodiment, polyethylene glycol (C) bears two hydroxyl groups per molecule.

20 In one embodiment of the present invention, aqueous solutions according to the invention may contain in the range of from 1 to 20 % by weight, preferably 5 to 15% by weight of polyethylene glycol (C).

The average molecular weight  $M_n$  of polyethylene glycol (C) can be determined, for example, by determining the hydroxyl number, preferably according to DIN 53240-1:2012-07.

25 In other embodiments of the present invention, aqueous solutions according to the invention do not contain any polyethylene glycol (C).

30 In one embodiment of the present invention, complexing agent (A) may contain minor amounts of impurities stemming from its synthesis, such as lactic acid, alanine, propionic acid or the like. "Minor amounts" in this context refers to a total of 0.1 to 1% by weight, referring to complexing agent (A).

35 In one embodiment of the present invention, aqueous solutions according to the invention may have a dynamic viscosity in the range of from 80 to 500 mPa·s, preferably up to 100 mPa·s, determined according to DIN 53018-1:2008-09 at 25°C.

40 In one embodiment of the present invention, aqueous solutions according to the invention may have a color number according to Hazen in the range of from 15 to 400, preferably to 360, determined according to DIN EN 1557:1997-03 at 25°C.

In one embodiment of the present invention, aqueous solutions according to the present invention have a total solids content in the range of from 31 to 65% by weight, preferably at least 38 % by weight.

- 5 Aqueous solutions according to the invention exhibit extremely low a tendency of having solid precipitates of complexing agent (A) or other solids. Therefore, they can be stored and transported in pipes and/or containers without any residue, even at temperatures close to the freezing point of the respective aqueous solution according to the invention.
- 10 Another aspect of the present invention is thus the use of of aqueous solutions according to the invention for transportation in a pipe or a container. Transportation in a pipe or a container in the context of the present invention preferably does not refer to parts of the plant in which complexing agent (A) is being manufactured, nor does it refer to storage buildings that form part of the respective production plant in which complexing agent (A) has being manufactured. Containers
- 15 can, for example, be selected from tanks, bottles, carts, road container, and tank wagons. Pipes can have any diameter, for example in the range of from 5 cm to 1 m, and they can be made of any material which is stable to the alkaline solution of complexing agent (A). Transportation in pipes can also include pumps that form part of the overall transportation system.
- 20 Another aspect of the present invention is a process for making aqueous solutions according to the invention, said process also being referred to as inventive process. The inventive process comprises the step of combining an aqueous solution of complexing agent (A) with salt (B), said salt (B) being applied as solid or in aqueous solution.
- 25 In one embodiment, said combination step may be followed by removal of excess water. Water will be removed as measure in the inventive process in particular in such embodiments when aqueous solution of complexing agent (A) has a concentration of less than 40% by weight, in particular less than 35% by weight.
- 30 In one embodiment of the present invention, the combination of aqueous solution of complexing agent (A) with salt (B) may be performed at a temperature in the range of from 30 to 75°C, preferably 25 to 50°C. In another embodiment of the present invention, aqueous solution of complexing agent (A) can be combined with salt (B) at ambient temperature or slightly elevated temperature, for example in the range of from 21 to 29°C.
- 35 The inventive process can be performed at any pressure, for example at a pressure in the range of from 500 mbar to 25 bar. Normal pressure is preferred.
- The inventive process can be performed in any type of vessel, for example in a stirred tank reactor or in a pipe with means for dosage of salt (B) or in a beaker, flask or bottle.
- 40

Removal of water can be achieved, for example, with the help of membranes or by evaporation. Evaporation of water can be performed by distilling off water, with or without stirring, at temperature in the range of from 20 to 65°C.

- 5 Another aspect of the present invention is the use of aqueous solutions according to the invention for the manufacture of a laundry care or dish wash formulation, said aspect also being referred to as inventive use or inventive application. Another aspect of the present invention is a process for making a laundry care or dish wash formulation by using at least one aqueous solution according to the invention. The inventive use and the respective process comprise the step
- 10 of mixing at least one aqueous solution according to the invention with at least one ingredient for a laundry care or dish wash formulation, for example at least one surfactant, optionally followed by at least partially removing the water.

The invention is further illustrated by the following working examples.

15 Working examples

Percentages refer to % by weight unless expressly noted otherwise.

The following substances were used:

- 20 Complexing agent (A.1): trisodium salt of MGDA, provided as 40% by weight aqueous solution, pH value: 13  
Salt (B.1): sodium acetate, solid  
Salt (B.2): potassium acetate, solid

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I. Manufacture of concentrated aqueous solutions according to the invention

I.1 Manufacture of Aqueous Solutions containing (A.1) and (B.1)

- 30 A 25 ml glass bottle with plastic stopper was charged with 22.5 g of the above 40% by weight aqueous solution of (A.1). It was warmed to 75°C. To said solution, 2.5 g of (B.1) were added under repeated shaking. The resulting aqueous solution had a total solids content of 46% by weight. It was a clear solution and did not show any sign of crystallization or precipitation of MGDA even after 30 days at 23°C.

35 I.2 Manufacture of Aqueous Solutions containing (A.1) and (B.1)

- A 25 ml glass bottle with plastic stopper was charged with 20 g of the above 40% by weight aqueous solution of (A.1). It was warmed to 75°C. To said solution, 5 g of (B.1) were added under repeated shaking. The resulting aqueous solution had a total solids content of 52% by
- 40 weight. It was a clear solution and did not show any sign of crystallization or precipitation of MGDA even after 30 days at 23°C.

## I.3 Manufacture of Aqueous Solutions containing (A.1) and (B.2)

5 A 25 ml glass bottle with plastic stopper was charged with 22.5 g of the above 40% by weight aqueous solution of (A.1). It was warmed to 75°C. To said solution, 2.5 g of (B.2) were added under repeated shaking. The resulting aqueous solution had a total solids content of 46% by weight. It was a clear solution and did not show any sign of crystallization or precipitation of MGDA even after 30 days at 23°C.

## I.4 Manufacture of Aqueous Solutions containing (A.1) and (B.2)

10

A 25 ml glass bottle with plastic stopper was charged with 20 g of the above 40% by weight aqueous solution of (A.1). It was warmed to 75°C. To said solution, 5 g of (B.2) were added under repeated shaking. The resulting aqueous solution had a total solids content of 52% by weight. It was a clear solution and did not show any sign of crystallization or precipitation of MGDA even after 30 days at 23°C.

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## Patent claims

1. Aqueous solution comprising  
5 (A) in the range of from 30 to 60% by weight of a complexing agent, selected from the alkali metal salts of methylglycine diacetic acid and the alkali metal salts of glutamic acid diacetic acid,  
(B) in the range of from 1 to 25 % by weight of at least one salt of a sulfonic acid or of an organic acid,  
10 percentages referring to the total respective aqueous solution, said aqueous solution being free from surfactants.
2. Aqueous solution according to claim 1, having a pH value in the range of from 9 to 13.
3. Aqueous solution according to claim 1 or 2, wherein (B) is selected from selected from  
15 alkali metal salts of acetic acid, tartaric acid, lactic acid, maleic acid, fumaric acid, and malic acid.
4. Aqueous solution according to any of the preceding claims wherein salt (B) is being selected from the alkali metal salts of methyl sulfonic acid.  
20
5. Aqueous solution according to any of the preceding claims, further comprising  
(C) at least one polyethylene glycol with an average molecular weight  $M_n$  in the range of  
from 400 to 10,000 g/mol.
- 25 6. Process for making an aqueous solution according to at least one of the preceding claims, comprising the step of combining an aqueous solution of complexing agent (A) with salt (B).
- 30 7. Use of aqueous solutions according to at least one of claims 1 to 6 for manufacture of a laundry care or dish wash formulation.

## INTERNATIONAL SEARCH REPORT

International application No

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A. CLASSIFICATION OF SUBJECT MATTER  
 INV. C11D7/26 C11D7/32 C11D7/34  
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According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C11D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, WPI Data

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2012/028203 A1 (ECOLAB INC [US]) 8 March 2012 (2012-03-08)	1-3,5-7
A	page 21, lines 9-24 page 30, lines 1-9 claims; examples	4
A	----- WO 2012/025160 A1 (ECOLAB INC [US]) 1 March 2012 (2012-03-01)	1-7
A	----- WO 2012/142396 A1 (BASF SE [DE]) 18 October 2012 (2012-10-18)	1-7
	paragraphs [0017] - [0029], [0039], [0040]; claims; examples -----	



Further documents are listed in the continuation of Box C.



See patent family annex.

## \* Special categories of cited documents :

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"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&amp;" document member of the same patent family

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# INTERNATIONAL SEARCH REPORT

Information on patent family members

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Patent document cited in search report			Publication date		Patent family member(s)			Publication date	
WO 2012028203	A1	08-03-2012	EP	2611896	A1		10-07-2013		
			WO	2012028203	A1		08-03-2012		
-----									
WO 2012025160	A1	01-03-2012	EP	2609185	A1		03-07-2013		
			WO	2012025160	A1		01-03-2012		
-----									
WO 2012142396	A1	18-10-2012	AU	2012242671	A1		14-11-2013		
			CA	2833150	A1		18-10-2012		
			CN	103562144	A		05-02-2014		
			EP	2697171	A1		19-02-2014		
			KR	20140022068	A		21-02-2014		
			TW	201323604	A		16-06-2013		
			US	2012260938	A1		18-10-2012		
			WO	2012142396	A1		18-10-2012		
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权利要求书1页 说明书4页

(54) 发明名称

以高浓度含有配位剂的水溶液

(57) 摘要

水溶液, 包含 (A) 30-60 重量% 配位剂, 其选自甲基甘氨酸二乙酸的碱金属盐和谷氨酸二乙酸的碱金属盐, (B) 1-25 重量% 至少一种磺酸盐或有机酸盐, 百分数涉及整个相应水溶液。

1. 水溶液, 包含:
  - (A) 30-60 重量%配位剂, 其选自甲基甘氨酸二乙酸的碱金属盐和谷氨酸二乙酸的碱金属盐,
  - (B) 1-25 重量%至少一种磺酸盐或有机酸盐,百分数涉及整个相应水溶液,  
所述水溶液不含表面活性剂。
2. 根据权利要求 1 的水溶液, 具有的 pH 值为 9-13。
3. 根据权利要求 1 或 2 的水溶液, 其中 (B) 选自乙酸、酒石酸、乳酸、马来酸、富马酸和苹果酸的碱金属盐。
4. 根据前述权利要求中任一项的水溶液, 其中盐 (B) 选自甲基磺酸的碱金属盐。
5. 根据前述权利要求中任一项的水溶液, 进一步包含 (C) 至少一种平均分子量  $M_n$  为 400-10,000g/mol 的聚乙二醇。
6. 制备根据前述权利要求中任一项的水溶液的方法, 包括将配位剂 (A) 的水溶液与盐 (B) 合并的步骤。
7. 根据权利要求 1-6 中任一项的水溶液在制备洗衣护理或洗碟配制剂中的用途。

## 以高浓度含有配位剂的水溶液

[0001] 本发明涉及一种水溶液, 包含:

[0002] (A) 30-60 重量%配位剂, 其选自甲基甘氨酸二乙酸的碱金属盐和谷氨酸二乙酸的碱金属盐,

[0003] (B) 1-25 重量%至少一种磺酸盐或有机酸盐,

[0004] 百分数涉及整个相应水溶液,

[0005] 所述水溶液不含表面活性剂。

[0006] 配位剂如甲基甘氨酸二乙酸 (MGDA) 和谷氨酸二乙酸 (GLDA) 及其相应碱金属盐是碱土金属离子如  $\text{Ca}^{2+}$  和  $\text{Mg}^{2+}$  的有用螯合剂。为此, 它们被推荐用于各种目的如衣用洗涤剂和自动洗碟 (ADW) 配制剂, 尤其是所谓的无磷酸盐衣用洗涤剂和无磷酸盐 ADW 配制剂。为了装运该类配位剂, 在大多数情况下使用固体如颗粒或水溶液。

[0007] 颗粒和粉末是有用的, 因为装运的水量可以忽略不计, 但对于大多数混合和配制方法需要额外的溶解步骤。

[0008] 许多工业用户希望以尽可能高度浓缩的水溶液获得配位剂。所要求的配位剂浓度越低, 则装运的水越多。所述水增添了运输成本并且必须随后除去。尽管 MGDA 的约 40 重量%和甚至 GLDA 的 45 重量%溶液可以在室温下制备并储存, 但局部或临时更冷溶液可能导致相应配位剂沉淀以及因杂质而成核。所述沉淀可能导致在管道和容器中结壳和/或在配制过程中产生杂质或不均匀。

[0009] 可以尝试通过加入加溶剂, 例如溶解度提高性聚合物或表面活性剂来提高配位剂的溶解度。然而, 许多用户希望灵活使用其自己的洗涤剂配制剂并且它们希望在配位剂中避免聚合添加剂或表面活性添加剂。

[0010] 可以考虑可以提高相应配位剂的溶解度的添加剂, 但该类添加剂不应不利地影响相应配位剂的性能。

[0011] 因此, 本发明的目的是要提供配位剂如 MGDA 或 GLDA 的在 0-50°C 的温度下在不加入表面活性剂或聚合物下稳定的高度浓缩水溶液。此外, 本发明的目的是要提供一种制造配位剂如 MGDA 或 GLDA 的在 0-50°C 的温度下稳定的高度浓缩水溶液的方法。该方法或该水溶液均不要求使用不利地影响相应配位剂的性能的添加剂。

[0012] 因此, 发现了开头所定义的水溶液, 下文也称为本发明水溶液。

[0013] 本发明水溶液含有

[0014] (A) 30-60 重量%配位剂, 下文也称为“配位剂 (A)”, 其选自甲基甘氨酸二乙酸的碱金属盐和谷氨酸二乙酸的碱金属盐,

[0015] (B) 1-25 重量%至少一种磺酸盐或有机酸盐, 所述盐下文也称为“盐 (B)”, 所述水溶液不含表面活性剂,

[0016] 百分数涉及整个本发明相应水溶液。

[0017] 配位剂 (A) 选自甲基甘氨酸二乙酸的碱金属盐和谷氨酸二乙酸的碱金属盐。

[0018] 在本发明上下文中, 甲基甘氨酸二乙酸的碱金属盐选自甲基甘氨酸二乙酸自的锂盐、钾盐和优选钠盐。甲基甘氨酸二乙酸可以部分或优选完全被相应碱金属中和。在优选

实施方案中, MGDA 的平均 2.7-3 个 COOH 基团用碱金属, 优选钠中和。在特别优选的实施方案中, 配位剂 (A) 为 MGDA 的三钠盐。

[0019] 同样, 谷氨酸二乙酸的碱金属盐选自谷氨酸二乙酸的锂盐、钾盐和优选钠盐。谷氨酸二乙酸可以部分或优选完全被相应碱金属中和。在优选实施方案中, GLDA 的平均 3.5-4 个 COOH 基团用碱金属, 优选钠中和。在特别优选的实施方案中, 配位剂 (A) 为 GLDA 的四钠盐。

[0020] 在本发明的一个实施方案中, 本发明水溶液含有 30-60 重量%, 优选 35-50 重量%, 甚至更优选 37-45 重量% MGDA 的碱金属盐作为配位剂 (A)。

[0021] 在本发明的一个实施方案中, 本发明水溶液含有 30-60 重量%, 优选 45-58 重量%, 甚至更优选 46-53 重量% GDA 的碱金属盐作为配位剂 (A)。

[0022] 配位剂 (A) 可以选自 MGDA 或 GLDA 的碱金属盐的外消旋混合物, 纯对映体如 L-MGDA 的碱金属盐、L-GLDA 的碱金属盐、D-MGDA 的碱金属盐和 D-GLDA 的碱金属盐, 以及对映体富集异构体的混合物。

[0023] 无论怎样, 少量配位剂 (A) 可以带有碱金属以外的阳离子。因此, 可能的是全部配位剂 (A) 中少量, 如 0.01-5mol% 带有碱土金属阳离子如  $Mg^{2+}$  或  $Ca^{2+}$ , 或  $Fe^{+2}$  或  $Fe^{+3}$  阳离子。

[0024] 本发明水溶液进一步包含 (B) 1-25 重量%, 优选 3-15 重量% 盐 (B)。

[0025] 在本发明上下文中, 盐 (B) 选自单羧酸和二羧酸的盐。此外, 盐 (B) 因此不同于配位剂 (A)。

[0026] 在本发明的优选实施方案中, 盐 (B) 选自乙酸、酒石酸、乳酸、马来酸、富马酸和苹果酸的碱金属盐。

[0027] 盐 (B) 的优选实例是乙酸钾和乙酸钠。

[0028] 在本发明的一个实施方案中, 盐 (B) 为甲基磺酸的钾盐以及优选甲基磺酸的钠盐。

[0029] 此外, 本发明水溶液含有水。在本发明的一个实施方案中, 在本发明水溶液中配位剂 (A) 和盐 (B) 以及任选无机碱的余量为水。在其他实施方案中, 本发明水溶液可以含有配位剂 (A) 和盐 (B) 以及水以外的一种或多种液体或固体。

[0030] 本发明水溶液不含表面活性剂。在本发明上下文中, “不含表面活性剂” 应指表面活性剂的总含量参考配位剂 (A) 的量为 0.1 重量% 或更低。在优选实施方案中, 术语 “不含表面活性剂” 应包括浓度为 50ppm 至 0.05%, 其中 ppm 和 % 二者分别是指重量 ppm 或重量% 且参考整个相应水溶液。

[0031] 在本发明的一个实施方案中, 本发明水溶液具有 9-14, 优选 10.5-13 的 pH 值。pH 值在环境温度下测定。

[0032] 本发明水溶液优选不含聚合物。不含聚合物在本发明上下文中应指表面活性剂的总含量参考配位剂 (A) 的量为 0.1 重量% 或更低。然而, 聚乙二醇 (C) 在本发明上下文中不被认为是聚合物。

[0033] 在本发明的一个实施方案中, 本发明水溶液可以含有至少一种无机碱, 例如氢氧化钾或优选氢氧化钠。优选无机碱的量为 0.1-20mol%, 这涉及配位剂中 COOH 基团的总和。

[0034] 在本发明的一个实施方案中, 本发明水溶液进一步包含 (C) 至少一种平均分子量  $M_n$  为 400-10,000g/mol, 优选 600-6,000g/mol 的聚乙二醇, 下文也称为 “聚乙二醇 (C)”。

[0035] 在本发明的一个实施方案中,聚乙二醇(C)可以例如每分子被一个甲基封端,即转化成聚醚。在另一实施方案中,聚乙二醇(C)每分子带有两个羟基。

[0036] 在本发明的一个实施方案中,本发明水溶液可以含有1-20重量%,优选5-15重量%聚乙二醇(C)。

[0037] 聚乙二醇(C)的平均分子量 $M_n$ 例如可以通过测定羟值而测定,优选根据DIN 53240-1:2012-07测定羟值。

[0038] 在本发明的其他实施方案中,本发明水溶液不含任何聚乙二醇(C)。

[0039] 在本发明的一个实施方案中,配位剂(A)可以含有少量源自其合成的杂质,如乳酸、丙氨酸、丙酸等。“少量”就此而言是指参考配位剂(A)总共为0.1-1重量%。

[0040] 在本发明的一个实施方案中,本发明水溶液可以具有80-500mPa·s,优选至多100mPa·s的运动粘度,根据DIN 53018-1:2008-09在25℃下测定。

[0041] 在本发明的一个实施方案中,本发明水溶液可以具有的色数根据Hazen为15-400,优选15-360,根据DIN EN 1557:1997-03在25℃下测定。

[0042] 在本发明的一个实施方案中,本发明水溶液具有31-65重量%,优选至少38重量%的总固体含量。

[0043] 本发明水溶液呈现极低的具有配位剂(A)或其他固体的固体沉淀物的倾向。因此,它们可以在管道和/或容器中没有任何残留地储存和运输,甚至在接近相应本发明水溶液的凝固点的温度下。

[0044] 因此,本发明的另一方面是本发明水溶液在管道或容器中运输的用途。在管道或容器中运输在本发明上下文中优选不涉及在其中制造配位剂(A)的装置的各部分,也不涉及构成在其中制造配位剂(A)的相应生产装置的部分的仓储建筑。容器例如可以选自罐、瓶、手推车、集装箱和拖罐车。管道可以具有任何直径,例如5cm-1m,并且它们可以由任何对配位剂(A)的碱性溶液稳定的材料制成。在管道中运输也可以包括构成整个运输系统的一部分的泵。

[0045] 本发明的另一方面是一种制造本发明水溶液的方法,所述方法也称为本发明方法。本发明方法包括将配位剂(A)的水溶液与盐(B)合并的步骤,所述盐(B)作为固体或以水溶液使用。

[0046] 在一个实施方案中,所述合并步骤之后可以除去过量水。当配位剂(A)的水溶液具有的浓度小于40重量%,尤其小于35重量%时,尤其在该类实施方案中将除去水作为本发明方法中的措施。

[0047] 在本发明的一个实施方案中,配位剂(A)的水溶液与盐(B)的合并可以在30-75℃,优选25-50℃的温度下进行。在本发明的另一实施方案中,配位剂(A)的水溶液可以与盐(B)在环境温度或稍微升高的温度,例如21-29℃下合并。

[0048] 本发明方法可以在任何压力下,例如在500毫巴至25巴的压力下进行。优选常压。

[0049] 本发明方法可以在任何类型容器中,例如在搅拌釜反应器或具有用于投料盐(B)的装置的管道中或者在烧杯、烧瓶或瓶中进行。

[0050] 水的除去例如可以借助膜或通过蒸发实现。水的蒸发可以通过在有或无搅拌下在20-65℃的温度下蒸除水而进行。

[0051] 本发明的另一方面是本发明水溶液在制造洗衣护理或洗碟配制剂中的用途,所述



方面也称为本发明用途或本发明应用。本发明的另一方面是一种通过使用至少一种本发明水溶液制造洗衣护理或洗碟配制剂的方法。本发明用途和相应方法包括将至少一种本发明水溶液与用于洗衣护理或洗碟配制剂的至少一种活性成分,例如至少一种表面活性剂混合的步骤并任选随后至少部分除去水。

[0052] 本发明由下列工作实施例进一步说明。

[0053] 工作实施例

[0054] 百分数涉及重量%,除非另有明确指明。

[0055] 使用下列物质:

[0056] 配位剂 (A. 1):MGDA 的三钠盐,作为 40 重量%水溶液提供, pH 值:13 盐 (B. 1):乙酸钠,固体

[0057] 盐 (B. 2):乙酸钾,固体

[0058] I. 制造本发明的浓缩水溶液

[0059] I. 1 制造含有 (A. 1) 和 (B. 1) 的水溶液

[0060] 向具有塑料瓶塞的 25ml 玻璃瓶中加入 22.5g (A. 1) 的上述 40 重量%水溶液。将其温热至 75℃。在反复振摇下向所述溶液中加入 2.5g (B. 1)。所得水溶液具有的总固体含量为 46 重量%。它为清澈溶液且甚至在 23℃ 下 30 天之后也不显示 MGDA 的任何结晶或沉淀迹象。

[0061] I. 2 制造含有 (A. 1) 和 (B. 1) 的水溶液

[0062] 向具有塑料瓶塞的 25ml 玻璃瓶中加入 20g (A. 1) 的上述 40 重量%水溶液。将其温热至 75℃。在反复振摇下向所述溶液中加入 5g (B. 1)。所得水溶液具有的总固体含量为 52 重量%。它为清澈溶液且甚至在 23℃ 下 30 天之后也不显示 MGDA 的任何结晶或沉淀迹象。

[0063] I. 3 制造含有 (A. 1) 和 (B. 2) 的水溶液

[0064] 向具有塑料瓶塞的 25ml 玻璃瓶中加入 22.5g (A. 1) 的上述 40 重量%水溶液。将其温热至 75℃。在反复振摇下向所述溶液中加入 2.5g (B. 2)。所得水溶液具有的总固体含量为 46 重量%。它为清澈溶液且甚至在 23℃ 下 30 天之后也不显示 MGDA 的任何结晶或沉淀迹象。

[0065] I. 4 制造含有 (A. 1) 和 (B. 2) 的水溶液

[0066] 向具有塑料瓶塞的 25ml 玻璃瓶中加入 20g (A. 1) 的上述 40 重量%水溶液。将其温热至 75℃。在反复振摇下向所述溶液中加入 5g (B. 2)。所得水溶液具有的总固体含量为 52 重量%。它为清澈溶液且甚至在 23℃ 下 30 天之后也不显示 MGDA 的任何结晶或沉淀迹象。

## Abstract

Aqueous solution comprising (A) in the range of from 30 to 60% by weight of a complexing agent, selected from the alkali metal salts of methylglycine diacetic acid and the alkali metal salts of glutamic acid diacetic acid, (B) in the range of from 1 to 25 % by weight of at least one salt of a sulfonic acid or of an organic acid, percentages referring to the total respective aqueous solution.