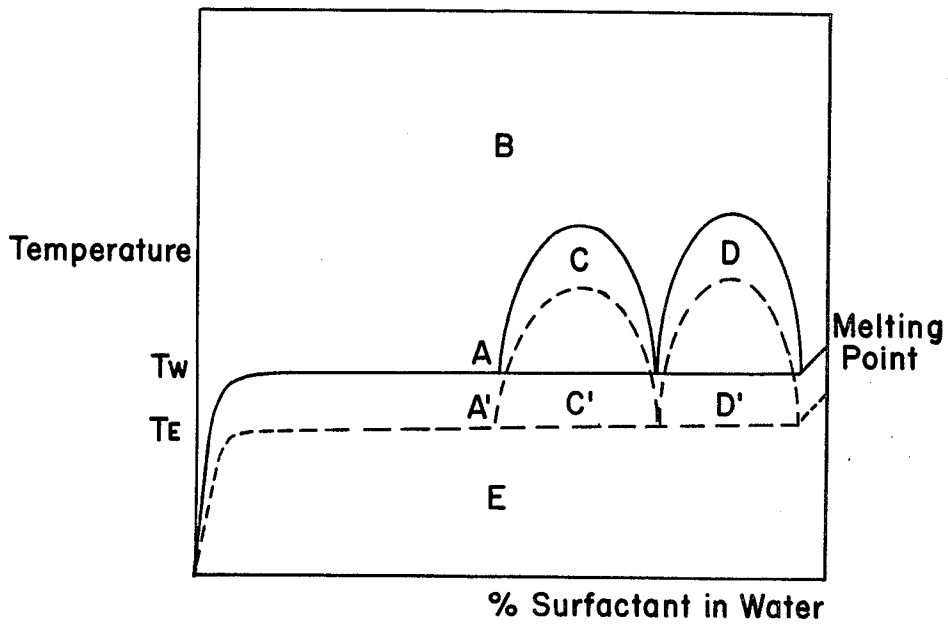


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LIQUID DETERGENT COMPOSITION CONTAINING
SOLUBILIZING ELECTROLYTES
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LIQUID DETERGENT COMPOSITION CONTAINING SOLUBILIZING ELECTROLYTES

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This application is a continuation-in-part of copending application Ser. No. 421,142, filed Dec. 14, 1964, now abandoned which is a continuation-in-part of copending application Ser. No. 291,528, filed June 28, 1963, now abandoned, and application Ser. No. 216,119 filed Aug. 10, 1962, now abandoned.

This invention relates to liquid detergent compositions. Specifically, this invention relates to liquid detergent compositions containing certain detergent surfactants and certain solubilizing electrolytes.

The formulation of liquid detergent compositions is very complex. Ordinarily, it is desirable to keep inert ingredients at a minimum and yet it often becomes necessary to add some compound to the formula which has no active detergent effect or detergency builder effect merely to make the active ingredients compatible with each other and thereby create a homogeneous composition (i.e., a composition in which there is no bulk separation of a phase). It would therefore be desirable to provide, in liquid detergent compositions, effective, low cost solubilizing agents to replace all or part of the usual organic solubilizing agents and solvents.

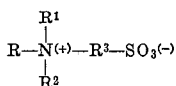
Accordingly, it is an object of this invention to provide homogeneous liquid detergent compositions.

It is a further and more specific object of this invention to provide such compositions containing solubilizing electrolytes and certain specific detergents.

The aqueous homogeneous liquid detergent compositions of this invention which achieve these objects comprise:

(I) From about 1% to about 40% by weight of the composition of a detergent selected from the group consisting of

(A) A detergent having the formula



(sultaine detergent) wherein R^1 and R^2 are each selected from the group consisting of hydrogen, methyl, and ethyl groups, R^3 is a straight chain alkylene group containing from two to four carbon atoms, and having from 0 to one hydroxyl group substituted on a secondary carbon, and R is an alkyl chain of from about 10 to about 20 carbon atoms;

(B) A detergent having the formula $R^7R^8R^9P \rightarrow O$ (phosphine oxide detergent) wherein R^7 is selected from the groups consisting of alkyl, and alkyl monohydroxy radicals containing from about 8 to about 16 carbon atoms and R^8 and R^9 are each selected from the group consisting of alkyl radicals and alkanol radicals containing from one to about three carbon atoms; and

(C) Mixtures thereof;

(II) From 0% to about 40% by weight of the composition of a polyvalent electrolyte salt selected from the group consisting of sulfates; carbonates; pyrophosphates; phosphates; hexametaphosphates; ethylenediaminetetraacetates; N - (2-hydroxyethyl)-ethylenediaminetriacetates; nitrilotriacetates; N - (2 - hydroxyethyl)-nitrilodiacetates; phytates; ethane-1-hydroxy-1,1-diphosphonates; methylene diphosphonates; ethylidene, isopropylidene, benzylmethylidene and chloromethylidene diphosphonates; salts of polymers of itaconic acid, aconitic acid, maleic acid, mesaconic acid, fumaric acid, methylene malonic acid and citraconic acid and copolymers with themselves and ethylene; and mixtures thereof, the cations of the above polyvalent electrolytes being selected from the group consisting of sodium, potassium, ammonium, triethanol ammonium, diethanol ammonium and monoethanol ammonium cations and mixtures thereof;

(III) From about 0.5% to about 20% by weight of the composition and sufficient to keep the composition homogeneous, of inorganic solubilizing electrolytes having a monovalent anion with a volume greater than 25^3 \AA^3 , said volume being calculated using Pauling's ionic radius for monoatomic anions and a radius equal to the sum of the largest interatomic bond distance and the radius of the outer atom for polyatomic anions; and

(IV) The balance substantially water, the composition being substantially non-homogeneous when only Components I, II, and IV are present, the amount of Component II being no more than can be dissolved in the composition.

The solubilizing electrolyte, Component III, makes homogeneous those aqueous mixtures of Component I, surfactant, and any polyvalent electrolyte, e.g., builder, present which otherwise would be nonhomogeneous due to the presence of a bulk, separated phase, e.g., a crystalline phase, or a second immiscible isotropic liquid phase as hereinafter more fully described.

FIGURE 1 is a representative phase diagram for the sultaine detergents utilized in the compositions of this invention as hereinafter more fully discussed.

The first group (A) of the specific detergents, as hereinbefore described, will be referred to hereinafter as sultaines or sultaine detergents. These sultaines are solubilized, according to the instant invention, in an aqueous solution by the solubilizing inorganic electrolytes hereinbefore named. Sultaines of particular interest are those in which the long alkyl chain (R) is a mixture of alkyl chains derived from naturally occurring substances, whether hydrogenated or not, and the short alkyl chains are methyl groups. For instance, where R is derived from tallow or coconut oil, R^3 contains three carbon atoms with a hydroxyl group substituted on the middle carbon atom, and R^1 and R^2 are methyl groups, the sultaines are of particular interest since they are readily prepared.

Specific examples of the above sultaines include 3-(N,N-dimethyl-N-hexadecyl ammonio)-propane-1-sulfonate, 3-(N-hexadecylammonio)-propane-1-sulfonate, and 3-(N,N-dimethyl-N-hexadecyl ammonio)-2-hydroxypropane-1-sulfonate. Other specific examples include the corresponding decyl, dodecyl, tetradecyl, and octadecyl homologs of the above compounds.

Of special interest as regards the solubilizing electrolytes of this invention are relatively water-insoluble sultaines wherein R is an alkyl chain of (1) from about 12 to about 18 carbon atoms when R^1 and R^2 are hydrogens, (2) from about 16 to about 20 carbon atoms when R^1 , R^2 , and R^3 contain no substituents, and (3) from about 14 to about 18 carbon atoms when R^1 and R^2 are alkyl chains, and R^3 is a three carbon atom alkylene group with a hydroxyl group substituted on the middle carbon atom. The solubilizing electrolytes of this invention "solubilize" the crystalline phase of these sultaines as hereinbefore described.

Specific examples of the phosphine oxide detergents include:

65 dimethyldodecylphosphine oxide
dimethyltetradecylphosphine oxide
ethylmethyltetradecylphosphine oxide
cetyldimethylphosphine oxide
70 dimethylstearylphosphine oxide
cetyethylpropylphosphine oxide
diethyldodecylphosphine oxide

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diethyltetradecylphosphine oxide
 dipropyldodecylphosphine oxide
 bis-(hydroxymethyl)dodecylphosphine oxide
 bis-(2-hydroxyethyl)dodecylphosphine oxide
 (2-hydroxypropyl)methyltetradecylphosphine oxide
 dimethyloleyphosphine oxide, and
 dimethyl-(2-hydroxydodecyl)phosphine oxide

and the corresponding decyl, hexadecyl, and octadecyl homologs of the above compounds. These phosphine oxide detergents are solubilized, according to the instant invention, in an aqueous solution by the solubilizing inorganic electrolytes hereinbefore named.

All the detergents of this invention normally contain mixtures of long alkyl chains (R and R'). These can be derived from naturally occurring substances such as tallow and coconut oil, and can also be derived from petroleum fractions, e.g., by polymerizing propylene or cracking waxes to form the proper chain length, e.g., in the form of olefin. The method of deriving the alkyl chain is immaterial. The alkyl chains can be unsaturated.

The liquid detergent compositions of this invention contain from about 1% to about 40% by weight of the composition of the detergents hereinbefore described. The minimum amount is set by practical product considerations of detergency benefits derived per unit volume. The upper limit, on the other hand, is set by several considerations including viscosity, crystalline solubility, and the possibility of forming liquid mesomorphic phases or an insolubilizable, immiscible second isotropic phase.

Although it is not desired to be bound by theory, it is believed that certain inorganic electrolytes having an anion with relatively low charge density (ratio of number of charges in the anion to volume of the anion) are most effective in preventing phase separation in the compositions of this invention. The effective anions are singly charged. Therefore, the anions with large volumes are effective. For these solubilizing inorganic anions the volume of the anion should be at least about 25^3 A. This volume is calculated using Pauling's ionic radius for monoatomic atoms and a radius equal to the sum of the longest interatomic bond distance plus the radius of the outer atom for polyatomic anions. These interatomic distances and atomic radii can be obtained by consulting "The Nature of the Chemical Bond," Linus Pauling, Cornell University Press (1939).

The following are illustrative of the calculations. The radius of the iodide anion is 2.16 A. (op cit., p. 346). This corresponds to a volume of $\frac{4}{3} \pi (2.16)^3$ or approximately 42^3 A. The volume of a nitrate anion is determined by first adding the radii of the nitrogen and the oxygen to determine the interatomic [0.70 A. (radius of nitrogen)+0.66 A. (radius of oxygen)=1.36 A.] distance between nitrogen and oxygen. Then the radius of the oxygen (0.66 A.) is added to the interatomic distance. (1.36 A.+0.66 A.=2.02 A.) The volume of the nitrate anion is then $\frac{4}{3} \pi (2.02)^3$ or approximately 35^3 A. These inorganic solubilizing electrolytes include the alkali metal, ammonium, and substituted ammonium chlorides, bromides, and iodides such as sodium chloride, potassium chloride, sodium bromide, potassium bromide, ammonium chloride and triethanolammonium chloride and the corresponding iodides; and alkali metal, ammonium and substituted ammonium chlorates, nitrites, bromates, iodates, perchlorates, thiocyanates, periodates, bicarbonates, borates, and nitrates such as sodium, ammonium and potassium chlorates, and sodium, ammonium, monoethanolammonium, diethanolammonium, and potassium nitrates.

Variation in degree of effectiveness is found in solubilizing the various detergents with the various solubilizing electrolytes. Inorganic solubilizing electrolytes with smaller inorganic anions such as the chloride anion have a generally much lower degree of effectiveness, however, sodium chloride is desirable for solubilizing the rela-

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tively insoluble sultaine surfactants as hereinafter described since it is inexpensive.

The solubilizing electrolytes of this invention are used in an amount from about 0.5% to about 20% by weight of the liquid detergent composition and sufficient to provide a homogeneous composition. Preferably only sufficient solubilizing electrolyte is used to create a single phase in the temperature range desired. This temperature range is usually from about 40° F. to about 120° F.

It will be understood that where the sole separating phase is one which is not affected by the action of the solubilizing electrolyte, e.g., where the sole separating phase is crystalline inorganic builder, there is no benefit from using a solubilizing electrolyte. These solubilizing electrolytes can be used in combination with other solubilizing agents and solvents which solubilize other separating phases.

With respect to the separating phases solubilized by the inorganic solubilizing electrolytes hereinbefore described, the presence of a second immiscible isotropic liquid phase can be a function of temperature. As the temperature of the composition is raised, a second liquid phase separates. For some detergents this separation occurs only when a polyvalent electrolyte, e.g., builder, is present. The solubilizing electrolytes of this invention raise the temperature at which this separation occurs, whereas other electrolytes having anions with relatively high charge densities have generally the opposite effect, i.e., promote separation at lower temperatures. Examples of electrolytes which tend to cause a separation of a second isotropic liquid phase include many of the common ingredients found in detergent compositions such as the polyvalent electrolytes hereinbefore mentioned, e.g., potassium and sodium pyrophosphates, sodium and potassium tripolyphosphates, potassium and sodium silicates, potassium and sodium sulfates, potassium and sodium ethylenediamine tetraacetates, and sodium and potassium nitrito triacetates.

The presence of a temperature-dependent second liquid phase which exists without a polyvalent electrolyte being present is a function of detergent molecular structure and cannot readily be predicted. In general, with respect to the hydrophobic group, the longer chain lengths are less soluble and more prone to exhibit this phenomenon. With respect to the hydrophilic group, phosphine oxide detergents are more likely to exhibit this phenomenon, whereas anionic detergents generally do not. A primary benefit from the use of solubilizing electrolytes in a liquid composition of this invention is derived whenever a second liquid phase, as hereinbefore described, is the separating phase.

When used with the relatively water-insoluble sultaine detergents hereinbefore described, the electrolyte solubilizing agents of this invention are present in the liquid detergent composition in an amount from about 0.5% to about 20% by weight of the liquid detergent composition and sufficient to lower the Krafft temperature of the sultaine detergent in the liquid detergent composition below about 70° F. (room temperature), preferably below 40° F., to prevent the crystalline detergent from separating out of solution during normal use and storage.

These particularly relatively water-insoluble sultaine detergents are unique in that the addition of the electrolytes of this invention to their aqueous solution lowers their Krafft temperature as hereinafter more fully described. This Krafft temperature is really a narrow range of temperature for a given compound within which a small increase in temperature gives a very large increase in solubility of the crystalline surfactant. Lowering of the Krafft temperature for a given sultaine-electrolyte-water system has the practical effect of raising the solubility of the surfactant in water for any temperature which is above the temperature to which the Krafft temperature is lowered and which is below the Krafft temperature of the surfactant in water (without solubilizing elec-

trolyte). Normally, the addition of an electrolyte to an aqueous anionic surfactant solution will raise this Krafft temperature (lowering practical solubility), but the addition of the electrolytes of this invention to the sultaine detergents utilized in the compositions of this invention lowers their Krafft temperature (increases practical solubility).

The effect of this lowering of the Krafft temperature is such that homogeneous liquid detergent formulations can be prepared containing a considerable amount of sultaine detergent by the use of solubilizing electrolytes. To explain, the mechanism by which these particular electrolytes solubilize these sultaine detergents, reference is made to a phase diagram typical of the liquid systems of this invention, FIG. 1, in which the crystalline solubility (to left of point A) of a representative sultaine detergent of this invention in water is plotted as a function of temperature with a solid line (T_w is the Krafft temperature of the sultaine detergent in water) and the crystalline solubility (to the left of point A¹) of the same representative sultaine detergent in an aqueous solubilizing-electrolyte solution of constant concentration is plotted as a function of temperature with a broken line (T_E is the Krafft temperature of the sultaine detergent in electrolyte solution). It will be understood that the position of this broken line varies with the concentration of solubilizing-electrolyte in water and that there is a series of these broken line curves for different electrolyte concentrations. Up to a certain limit, the more electrolyte that is present the lower the broken line curve is on the diagram.

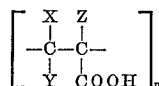
The lines on the diagram represent the boundaries for homogeneous solutions. Region B is homogeneous and is commonly referred to as nigré; regions C and C¹ are characterized by the presence of liquid mesomorphic phase; regions D and D¹ are characterized by the presence of another liquid mesomorphic phase; and region E is characterized by the presence of crystals of detergent plus detergent solution.

When the addition of the solubilizing-electrolytes of this invention lowers the Krafft temperature of the sultaine detergent, as hereinbefore described, below the temperature of the liquid detergent composition, the crystalline solubility of the sultaine detergent in water is substantially increased. The practical result is that a greater amount of the sultaine detergent can be used in the detergent composition while maintaining homogeneity. In general, the liquid compositions of this invention containing the relatively water-insoluble sultaines will be to the left of A and A¹ on the accompanying sultaine-water phase diagram (FIG. 1). (A and A¹ are the crystalline solubility points hereinbefore described.) The amount of lowering of the Krafft temperature is dependent upon the amount and, particularly, the type of electrolyte present as well as the molecular structure of the sultaine.

In addition to the detergents and solubilizing agents hereinbefore described, the detergent compositions can also contain from 0% to about 40% by weight of the composition of polyvalent electrolytes, but no more than can be dissolved in the compositions. These polyvalent electrolytes can be inert salts, which are associated with the detergent materials, such as sodium sulfate or can be desirable detergent builder electrolytes. Examples of water soluble inorganic alkaline detergency builder salts are alkali metal carbonates, phosphates, polyphosphates, and silicates. Specific examples of such salts are sodium and potassium tripolyphosphates, carbonates, pyrophosphates, phosphates, and hexametaphosphates. Examples of organic alkaline sequestrant builder salts are (1) alkali metal amino polycarboxylates [e.g., sodium and potassium ethylene diaminetetraacetates, N-(2-hydroxyethyl)-ethylene diamine triacetates, nitrilo triacetates, and N-(2-hydroxyethyl)-nitrilo diacetates]; (2) alkali metal salts of phytic acid (e.g., sodium and potassium phy-

tates—see U.S. Patent 2,739,942); (3) water soluble ethane-1-hydroxy-1,1-diphosphonates (e.g., the trisodium and tripotassium salts); (4) water soluble salts of methylene diphosphonic acid (e.g., trisodium and tripotassium methylene diphosphonate and the other salts described in the copending application of Francis L. Diehl, Ser. No. 266,025, filed Mar. 18, 1963, now Patent No. 3,213,030); (5) water soluble salts of substituted methylene diphosphonic acids (e.g., trisodium and tripotassium ethylidene, isopropylidene, benzylmethylidene, and halomethylidene diphosphonates and the other substituted methylene diphosphonates disclosed in the copending application of Clarence H. Roy, Ser. No. 266,055, filed Mar. 18, 1963); (6) water soluble salts of polycarboxylic polymers and copolymers as described in the copending application of Francis L. Diehl, Ser. No. 269,359, filed Apr. 1, 1963, now Patent No. 3,308,067, i.e., a polyelectrolyte builder material consisting of water-soluble salts of a polymeric aliphatic polycarboxylic acid selected from the group consisting of

(a) water-soluble salt of a homopolymer of an aliphatic polycarboxylic acid having the following empirical formula:



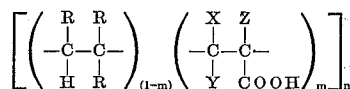
wherein X, Y, and Z are each selected from the group consisting of

hydrogen,
methyl,
carboxyl, and
carboxymethyl,

at least one of X, Y, and Z being selected from the group consisting of carboxyl and carboxymethyl, provided that X and Y can be carboxymethyl only when Z is selected from carboxyl and carboxymethyl, wherein n is a whole integer having a value within a range, the lower limit of which is three and the upper limit of which is determined by the solubility characteristics in an aqueous system;

(b) a water-soluble salt of a copolymer of at least two of the monomeric species having the empirical formula described in (a) and,

(c) a water-soluble salt of a copolymer of a member selected from the group of alkylenes and monocarboxylic acids with the aliphatic polycarboxylic compounds described in (a), said copolymers having the general formula:



wherein R is selected from the group consisting of

hydrogen,
methyl,
carboxyl,
carboxymethyl, and
carboxyethyl;

wherein only one R can be methyl; wherein m is at least 45 mole percent of the copolymer; wherein X, Y, and Z are each selected from the group consisting of

hydrogen,
methyl,
carboxyl, and
carboxymethyl;

at least one of X, Y, and Z being selected from the group of carboxyl and carboxymethyl provided that X and Y can be carboxymethyl only when Z is selected from the group of carboxyl and carboxymethyl, wherein

only one of X, Y, and Z can be methyl and wherein n is a whole integer within a range, the lower limit of which is three and the upper limit of which is determined primarily by the solubility characteristics in an aqueous system; said polyelectrolyte builder material having a minimum molecular weight of 350 calculated as the acid form and an equivalent weight of about 50 to about 80, calculated as the acid form, (e.g., polymers of itaconic acid, aconitic acid; maleic acid; mesaconic acid; fumaric acid; methylene malonic acid; and citraconic acid and copolymers with themselves and other compatible monomers such as ethylene); and (7) mixtures thereof.

Mixtures of any and all of the organic and/or inorganic builders can be used and are generally desirable. Especially preferred are the mixtures of builders disclosed in the copending application of Burton H. Gedge, Ser. No. 398,705, filed Sept. 23, 1964, e.g., ternary mixtures of sodium tripolyphosphate, sodium nitrilotriacetate, and sodium ethane-1-hydroxy-1,1, diphosphonate.

Other ingredients can also be present in the liquid detergent compositions of this invention without detracting from the advantageous properties of the invention.

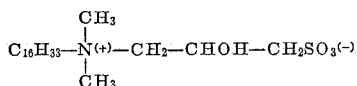
Anti-redeposition agents such as carboxymethylcellulose and anionic, cationic or nonionic detergents can also be added. Typical minor additives which can be present include suds boosters and suppressants, dyes, opacifiers, perfume, corrosion inhibitors and anti-microbial agents.

All percentages, ratios and parts herein are by weight unless otherwise specified.

The practice of this invention is demonstrated in the following examples.

Example I

Aqueous mixtures were prepared with 1% by weight of the mixture of a sultaine detergent with the formula



and 1% of the following electrolytes. Since 1% of this sultaine detergent is not normally soluble in water, observations were made as to the temperature at which the mixture clouded on cooling and cleared upon heating after 15 minute equilibration. The temperature was changed in 5° increments. These observations are indicative of crystalline detergent solubility and solubilization. The different results obtained on heating and cooling are explainable due to the non-equilibrium conditions employed. Where there are large differences, supersaturation on cooling undoubtedly occurred.

Inorganic Solubilizing Electrolyte	Anion Volume, A ³	Clouds on Cooling (° C.)	Clears on Heating (° C.)
NaI.....	42	1	1
NaClO ₄	42	15	15
NaCl.....	25	1	35
Na ₃ PO ₄	(*)	45	45
Na ₂ SO ₄	(*)	60	60
K ₄ P ₂ O ₇	(*)	70	70
Potassium ethylene diamine tetraacetate.....	(*)	75	75
None.....	(*)	90	90

*Multivalent.

The first three electrolytes are examples of the solubilizers of the invention and the rest show the relative ineffectiveness of conventional electrolytes in increasing the solubility of crystalline sultaine.

Similar aqueous mixtures of 1% by weight of the mixture, of the same sultaine detergent were prepared with varying concentrations of the same electrolytes

(same anions) to determine how much electrolyte was necessary to clear the mixture at room temperature (approximately 27° C.).

Inorganic solubilizing electrolyte:	Percent by weight of inorganic solubilizing electrolyte
NaI.....	0.8
NaCl.....	1.0
NaClO ₄	0.5
NaSO ₄	Saturated solutions of these electrolytes failed to solubilize the 1% sultaine detergent.
Na ₂ SO ₄	
K ₄ P ₂ O ₇	
Tetrasodium ethylene diamine tetraacetate.....	

15 More aqueous mixtures were prepared with the same sultaine detergent to determine how much of the crystalline surfactant was soluble at room temperature when 1% of some preferred electrolyte solubilizing agents was present.

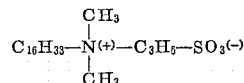
Electrolyte:	Sultaine detergent gms./100 gms. of water
NaClO ₄ *.....	24.3
NaI.....	4.1
NaCl.....	2.8
None, Na ₃ PO ₄ , Na ₂ SO ₄ , and K ₄ P ₂ O ₇	<0.1

25 *The mixture became very viscous at 4.2 gms. and formed a gel at 7.8 gms., but remained homogeneous.

It is apparent from the above data that the particular electrolyte solubilizing agents of the present invention are surprisingly effective in solubilizing crystalline sultaine detergents in water to form homogeneous liquid detergent compositions.

Example II

Mixtures of 5% by weight of the mixture of a sultaine surfactant with the formula



40 and 1% by weight of the mixture of various inorganic electrolytes were prepared and observations were made of the temperature at which the crystalline surfactant became soluble on heating and cooling as evidenced by the cloudiness or clarity of the mixture.

Electrolyte	Clouds on Cooling (° C.)	Clears on Heating (° C.)
None.....	10-15	25-30
NaI.....	0 to -4	
NaNO ₃	0 to -4	
NaClO ₄	5-10	5-10
K ₄ P ₂ O ₇	5-10	25-30
Na ₃ PO ₄	10-15	10-15

55 The mixtures containing water, the above sultaine detergent and the NaI, NaNO₃ and NaClO₄ solubilizing inorganic electrolytes were homogeneous detergent compositions which maintained their homogeneity over a broad temperature range.

Example III

Mixtures containing 1% by weight of the sultaine detergent of Example I, 10% K₄P₂O₇, and 1% by weight of various electrolyte solubilizing agents of this invention were prepared and the temperature at which the mixture became homogeneous was determined by observing the point at which the mixture became cloudy or clear upon heating and cooling.

Electrolyte	Clouds on Cooling (° C.)	Clears on Heating (° C.)
KI.....	0-5	10-15
KClO ₄	35	45
KNO ₃	10	30

When in the above example, any of the following detergent compounds, or mixtures of the following compounds, are substituted for the specific sultaine detergent, either wholly or in part, substantially equivalent results are obtained in that significantly more of the sultaine detergents and/or builder can be added to form a homogeneous solution than can be added without the solubilizing electrolytes being present:

- 3-(N,N-dimethyl-N-hexadecylammonio)-propane-1-sulfonate,
 2-(N,N-dihydrogen-N-dodecylammonio)-ethane-1-sulfonate,
 4-(N,N-diethyl-N-tetradecylammonio)-2-hydroxybutane-1-sulfonate,
 4-(N,N-diethyl-N-icosylammonio)-butane-1-sulfonate,
 3-(N-methyl-N-ethyl-N-octadecylammonio)-2-hydroxypropane-1-sulfonate,
 4-(N-hydrogen-N-methyl-N-decylammonio)-3-hydroxybutane-1-sulfonate,
 2-(N-hydrogen-N-ethyl-N-oleylammonio)-ethane-1-sulfonate;

the corresponding compounds wherein N-methyl groups are substituted for N-hydrogens and/or N-ethyl groups; N-ethyl groups are substituted for N-hydrogens and/or N-methyl groups; N-hydrogens are substituted for N-methyl and/or N-ethyl groups; the corresponding compounds wherein decyl, dodecyl, tetradecyl, hexadecyl, octadecyl, eicosyl, oleyl, linoleyl, linolenyl, 4-propyldodecyl, tetrapropyl, tetrabutyl, pentadecyl, and heptadecyl groups are substituted for the long alkyl chains in the above compounds.

Example IIIa

Aqueous mixtures containing 1% by weight of dimethyldodecyl phosphine oxide and the indicated percentages by weight of the indicated inorganic solubilizing electrolytes (these percentages are equivalent on a molar basis—0.2 molar) and builder electrolyte were prepared and the lowest temperatures above which the mixtures were two phase were determined.

Electrolytes	Percent By Weight of Electrolyte	Boundary of Two-phase Region, ° C.
None		39
NaClO ₄ (Solubilizer)	2.5	42
NaI (Solubilizer)	3.0	47
K ₄ P ₂ O ₇ (Builder)	6.6	20

This shows the greater temperature stability achieved with the solubilized phosphine oxide detergents of this invention.

When any of the following compounds, or mixtures thereof, are substituted, either wholly or in part for the specifically named detergent in the above example, substantially equivalent results are obtained in that more detergents and builders are solubilized with the solubilizing electrolytes than without:

- dimethyltetradecylphosphine oxide;
 diethyldecylphosphine oxide;
 bis-(2-hydroxyethyl)hexadecylphosphine oxide;
 dihydroxymethylpentadecyl phosphine oxide;
 dipropyldodecylphosphine oxide;
 bis-(2-hydroxypropyl)tetrapropylene phosphine oxide;
 bis-(3-hydroxypropyl)oleylphosphine oxide;

the corresponding compounds in which methyl, ethyl, 2-hydroxyethyl, hydroxy methyl, propyl, 2-hydroxypropyl and 3-hydroxy propyl groups are substituted for one of the short chain groups in the above compounds; the corresponding compounds in which decyl, undecyl, dodecyl, tetradecyl, pentadecyl, tridecyl, hexadecyl, heptadecyl, octadecyl, eicosyl, tetrapropylene, diheptene, oleyl, linoleyl, and linolenyl groups are substituted for the long chain group in each of the above compounds.

Example IV

When in the previous examples any of the following solubilizer compounds, or mixtures thereof, are substituted, either wholly or in part, for the specifically named solubilizing electrolytes, substantially equivalent results are obtained in that more of the detergents and builders can be formed into homogeneous solutions with the solubilizing electrolytes than without: chlorides, bromides, iodides, chlorates, nitrites, bromates, iodates, perchlorates, thiocyanates, periodates, bicarbonates, borates, and nitrates in the form of their sodium, potassium, monoethanolammonium, diethanolammonium, and triethanolammonium salts.

Example V

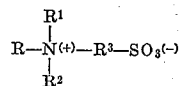
When in the previous examples any of the following polyvalent electrolytes, or mixtures thereof are substituted, either wholly or in part, for the specifically named polyvalent electrolytes, substantially equivalent results are obtained in that more of the detergents and builders can be formed into homogeneous solutions with the solubilizing electrolytes than without: tripolyphosphates; sulfates; carbonates; pyrophosphates; phosphates; hexametaphosphates; ethylenediamine tetraacetates; N-(2-hydroxyethyl)-ethylenediaminetriacetates; nitrilotriacetates; N-(2-hydroxyethyl)-nitrilodiacetates; phytates; ethane-1-hydroxy-1,1-diphosphonates; methylene diphosphonates; and ethylidene, isopropylidene, benzylmethylidene and chloromethylidene diphosphonates; salts of polymers of itaconic acid, aconitic acid, maleic acid, mesaconic acid, fumaric acid, methylene malonic acid and citraconic acid and copolymers with themselves and/or ethylene and/or acrylic acid in e.g. 1:1 molar ratios and having molecular weights of 75,000; 100,000; and 125,000 (the copolymers with ethylene and/or acrylic acid having equivalent weights, based on the acid form of 65, 70 and 75); in the form of their sodium, potassium, triethanolammonium, diethanolammonium, and monoethanolammonium salts.

What is claimed is:

1. An aqueous homogeneous liquid detergent composition consisting essentially of:

(I) from about 1% to about 40% by weight of the composition of a detergent selected from the group consisting of

(A) a detergent having the formula



wherein R¹ and R² are each selected from the group consisting of hydrogen, methyl, and ethyl groups, R³ is a straight chain alkylene group containing two to four carbon atoms, and having from 0 to 1 hydroxyl group substituted on a secondary carbon atoms, and R is an alkyl chain of from about 10 to about 20 carbon atoms;

(B) a detergent having the formula R⁷R⁸R⁹P→O wherein R⁷ is selected from the group consisting of alkyl and monohydroxy alkyl radicals containing from about 8 to about 16 carbon atoms and R⁸ and R⁹ are each selected from the group consisting of alkyl radicals and alkanol radicals containing from one to about three carbon atoms; and

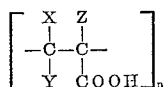
(C) mixtures thereof;

(II) from 0% to about 40% by weight of the composition of a polyvalent electrolyte salt selected from the group consisting of (1) sulfates; (2) carbonates; (3) tripolyphosphates; (4) pyrophosphates; (5) orthophosphates; (6) hexametaphosphates; (7) ethylenediaminetetraacetates; (8) N-(2-hydroxyethyl)-ethylenediaminetriacetates; (9) nitrilotriacetates; (10) N-(2-hydroxyethyl)-nitrilodiacetates; (11) phytates; (12) ethane-1-hydroxy-1,1-diphosphonates; (13) methylene diphosphonates; (14) eth-

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ylidene diphosphonates; (15) isopropylidene diphosphonates; (16) benzylmethylenediphosphonates; (17) chloromethylidene diphosphonates; (18) a polyelectrolyte builder material consisting of water-soluble salts of a polymeric aliphatic polycarboxylic acid selected from the group consisting of

- (a) water-soluble salt of a homopolymer of an aliphatic polymer of an aliphatic polycarboxylic acid having the following empirical formula:



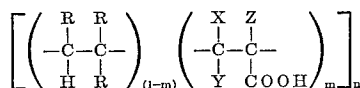
wherein X, Y, and Z are each selected from the group consisting of

hydrogen,
methyl,
carboxyl, and
carboxymethyl,

at least one of X, Y, and Z being selected from the group consisting of carboxyl and carboxymethyl, provided that X and Y can be carboxymethyl, only when Z is selected from carboxyl and carboxymethyl, wherein only one of X, Y, and Z can be methyl, and wherein n is a whole integer having a value within a range, the lower limit of which is three and the upper limit of which is determined by the solubility characteristics in an aqueous system;

- (b) a water-soluble salt of a copolymer of at least two of the monomeric species having the empirical formula described in (a); and

- (c) a water-soluble salt of a copolymer of a member selected from the group of alkenes and monocarboxylic acids with the aliphatic polycarboxylic compounds described in (a), said copolymers having the general formula:



wherein R is selected from the group consisting of

hydrogen,
methyl,
carboxyl,
carboxymethyl, and
carboxyethyl;

wherein only one R can be methyl; wherein m is at least 45 mole percent of the copolymer; wherein X, Y, and Z are each selected from the group consisting of

hydrogen,
methyl,
carboxyl, and
carboxymethyl,

at least one of X, Y and Z being selected from the group of carboxyl and carboxymethyl provided that X and Y can be carboxymethyl only when Z is selected from carboxyl and carboxymethyl, wherein only one of X, Y, and Z can be methyl, and wherein n is a whole integer within a range, the lower limit of which is three and the upper limit of which is determined primarily by the solubility characteristics in an aqueous system; said polyelectrolyte builder material having a minimum molecular weight of 350 calculated as the acid form and an equivalent weight of about 50 to about 80, calculated as the acid form; and (19) mixtures thereof, the cations of the above polyvalent electrolytes being selected from the group consisting of sodium, potassium, ammonium, triethanol ammonium, diethanol ammonium and monoethanol ammonium cations and mixtures thereof;

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(III) from about 0.5% to about 20% by weight of the composition, and sufficient to keep the composition homogeneous, of inorganic solubilizing electrolytes selected from the group consisting of sodium, potassium, ammonium, monoethanol ammonium, diethanol ammonium and triethanol ammonium chlorides, bromides, iodides, nitrites, bromates, iodates, chlorates, thiocyanates, perchlorates, nitrates and mixtures thereof; and

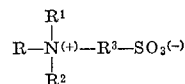
(IV) the balance substantially water.

2. The composition of claim 1 wherein the detergent comprises a surface active agent having the formula $\text{R}^7\text{R}^8\text{R}^9\text{P}\rightarrow\text{O}$ wherein R^7 is selected from the group consisting of alkyl and alkyl monohydroxy radicals containing from about 8 to about 16 carbon atoms and R^8 and R^9 are each selected from the group consisting of alkyl radicals and alkanol radicals containing from one to about three carbon atoms.

3. The liquid detergent composition of claim 1 wherein the R^3 of the detergent is an alkylene chain of three carbon atoms with a hydroxyl group substituted on the middle carbon atom, R^1 and R^2 are methyl groups, and R is a mixture of alkyl groups derived from tallow; and the solubilizing agent is NaCl.

4. A homogeneous liquid detergent composition consisting essentially of:

- (1) from about 1% to about 40% by weight of the composition of a detergent having the formula

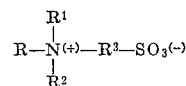


wherein R^1 and R^2 are selected from the group consisting of hydrogen, methyl and ethyl groups, R^3 is an alkylene group containing from two to four carbon atoms, and having from 0 to 1 hydroxyl group substituted on a secondary carbon atom, and R is an alkyl chain of (A) from about 12 to about 18 carbon atoms when R^1 and R^2 are hydrogens, (B) from about 16 to about 20 carbon atoms when R^1 and R^2 are alkyl chains and R^3 is an alkylene chain, and (C) from about 14 to about 18 carbon atoms when R^1 and R^2 are alkyl chains and R^3 is a three-carbon atom alkylene chain with a hydroxyl group substituted on the middle carbon atom;

- (2) from about 0.5% to about 20% by weight of the composition of an inorganic electrolyte solubilizing agent selected from the group consisting of sodium, potassium, ammonium, monoethanol ammonium, diethanol ammonium, and triethanol ammonium chlorides, bromides, iodides, nitrites, bromates, iodates, chlorates, thiocyanates, perchlorates, nitrates and mixtures thereof; and

- (3) balance water.

5. The composition of claim 1 wherein the detergent has the formula



and wherein R^1 and R^2 are each selected from the group consisting of hydrogen, methyl and ethyl groups, R^3 is selected from the group consisting of an unsubstituted alkylene group containing from two to four carbon atoms and an alkylene group of three carbon atoms with a hydroxyl group substituted on the middle carbon atom, and R is an alkyl chain of (A) from about 12 to about 18 carbon atoms when R^1 and R^2 are hydrogens, (B) from about 16 to about 20 carbon atoms when R^1 and R^2 are each selected from the group consisting of methyl and ethyl groups and R^3 is an unsubstituted alkylene group containing from 2 to 4 carbon atoms as hereinbefore described, and (C) from about 14 to about 18 carbon atoms when R^1 and R^2 are selected from the group con-

sisting of methyl and ethyl groups and R³ is a three carbon atom alkylene group with a hydroxyl group substituted on the middle carbon atom, as hereinbefore described.

6. The composition of claim 1 wherein the inorganic solubilizing electrolyte is selected from the group consisting of sodium, potassium, ammonium, monoethanolammonium, diethanolammonium and triethanolammonium nitrites, bromates, iodates, chlorates, thiocyanates, perchlorates and nitrates and mixtures thereof.

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