

Blending Soaps With Organic Solvents in Industrial Products*

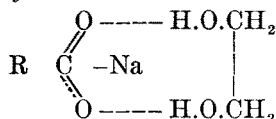
SANTI R. PALIT **

Department of Chemistry, Stanford University, California

IT has been observed by the author (2) that soaps, the alkali metal salts of long chain fatty acids, are highly soluble in a mixture of solvents, termed G-II mixtures. Here G stands for any glycol or any dihydroxylic solvent, particularly with the two hydroxyl groups in contiguous position, and II stands for any hydrocarbon or a solvent which can dissolve hydrocarbon, for example, chlorinated hydrocarbons, alcohols, ketones, etc. The mixed solvent has a high solvent power for soap even when the separate solvents do not dissolve it. We shall call this enhanced dissolving power of a mixture "co-solvency" and the individual solvents co-solvents. In cases where one of the co-solvents is a fairly good solvent and the other is practically a non-solvent in the pure state we might call the latter a latent solvent or an activator, particularly if it is required in a comparatively small proportion to produce a large effect.

The purpose of the present paper is to indicate how co-solvency opens possibilities of soap blending in various technical products which employ soap in conjunction with organic solvents.

As a preliminary it is well briefly to review the theory of soap solubility. The insolubility of a soap, such as sodium stearate in the usual organic solvents, is due to the fact that a molecule of it is composed of two very different groups, a hydrocarbon chain and a $-\text{COONa}$ group, and hence it is unlikely that the same type of solvent molecule is capable of simultaneous solvency of both these groups. In a mixture of glycol and alcohol, the two hydroxyl groups of the glycol solvate the $-\text{COONa}$ group as shown below, both the oxygen atoms in the $-\text{COONa}$ group being equivalent due to resonance. The solvency is brought about by hydrogen bonding, i.e., a type of bond where a hydrogen atom attached to a negative atom can unite with another negative atom, by a weak type of valency.



The insolubility of soap in common organic solvents is mainly attributable to the $-\text{COONa}$ group, but after hydrogen bonding to the glycol this group goes readily into solution. At the same time the hydrocarbon chain is dissolved by the alcohol, or hydrocarbon if present, producing the enhanced solvency of the G-II mixtures. Any solvent containing at least two hydroxyl groups (e.g., glycol, glycerol, etc.) in mixture with another solvent that has some dissolving power for hydrocarbons is a good solvent for soap. The solvent power increases for the same glycol with the increasing hydrocarbon nature of the co-solvent. The more any molecule combines a gly-

colic nature with a hydrocarbon type, the better it is as a solvent for soap. The relation between hydrogen bonding and solubility has already been pointed out for single solvents (1) whereas the present paper emphasizes the results which can be obtained by suitable mixtures of solvents.

The following are some of the chief uses of soaps in organic solvents: a) emulsification, as for example, in the manufacture of soluble oils, to be used as cutting oils, textile oils, agricultural sprays, etc.; b) lubricating greases and oils; c) specialty soaps, e.g., mechanics' washing soap, pine oil soap, trichloroethylene soap (Westropol soap), liquid soap, transparent soap, metal polish, leather polish, shampoo, shaving paste, etc.; d) dry cleaning; e) defoaming, and so on. It will be indicated how the solvent power of G-II mixtures can be advantageously employed to produce these types of industrial products.

In most of the above industrial products the main problem is to incorporate soap in a hydrocarbon-type solvent, usually a petroleum fraction. For example, soluble oil is a clear solution of a soap type of emulsifier, usually in a mineral oil and occasionally in a vegetable oil; lubricating grease is often a heterogeneous mixture of minute soap crystals and thick mineral oil; in dry cleaning the cleansing power of solvent naphtha is much improved by dissolving in it a small quantity of soap; trichloroethylene soap of the Westropol type is a thick soap paste in a mixture of alcohol, water, and trichloroethylene. The last is added to increase the grease-removing power of soap.

THE chief difficulty in the manufacture of all these products arises from the fact that the usual alkali metal soaps are practically insoluble in hydrocarbon solvents. To obviate this difficulty one of the methods is to use a large excess of a fatty acid, sometimes in the presence of alcohols. Another process, which is widely used, substitutes for sodium soap specialty soaps such as triethanolamine oleate, glycol laurate, etc.

From the author's work it follows that ordinary soaps can be dissolved in hydrocarbons by the use of glycol type compounds as co-solvents. Unfortunately, however, ordinary glycols are immiscible with hydrocarbons, and hence higher glycols or other derivatives which are fairly miscible with hydrocarbons must often be sought. In compounding such mixtures, the now well-known property of soap of bringing about a pronounced increase in the mutual solubility of liquids will be of help. This is particularly true as the author has observed that soaps profoundly increase the mutual solubility of a glycol and a hydrocarbon. For example, an addition of 15% sodium oleate will make benzene and propylene glycol completely miscible at room temperature, forming a clear mobile fluid, although the critical solution temperature of the system without soap is near 80°C . If a few of the paraffinic hydrogen atoms in glycol could be replaced by big alkyl or aryl radicals, the resulting

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** Bristol-Myers Company post-doctorate fellow in chemistry.

compounds might be expected to serve our purpose. In the absence of commercial availability of such compounds dibutyl tartrate and diamyl tartrate, sold as nitrocellulose plasticisers, bid fair to satisfy the needs, since besides the two contiguous hydroxyl groups as in a glycol, they are miscible with hydrocarbons like benzene, cyclohexane, hexane, etc., due evidently to the presence of the COOR groups. Besides acting as expected from our theory as a powerful solvent and co-solvent for soap these compounds have one very desirable property which makes them almost ideal for our purpose. These solvents have very little tendency to gel soaps so that if a solution of a soap in a hydrocarbon-dibutyl tartrate mixture is cooled, jellies are not formed, but the dissolved soap precipitates, usually in the crystalline state.

The solubility of soap in dibutyl tartrate is very high, and it is greatly increased by the presence of small proportions of hydrocarbons or chlorinated hydrocarbons. Thus, 100 g. of dibutyl tartrate dissolves 41.3 g. of sodium oleate at 25°C. and an addition of about 20% of chloroform, benzene, amyl alcohol or any H-solvent increases the solubility by 10 to 30%. A very useful property of such solutions is that they can be diluted with light petroleum fractions without precipitation of the soap. Hence, to prepare soluble oil, commercial soap, particularly castile soap, is dissolved in dibutyl tartrate containing 20% benzene or trichloroethylene. In this way, a 30% solution of soap is easily prepared, and this soap solution is then diluted with oil, vegetable or mineral, to make a final concentration of soap of about 3 to 5%. The oil thus prepared can be thinned to a creamy emulsion with water. The emulsion thus formed is found to be very stable. By changing the type of oil, cutting oil, textile oil, agricultural spray, etc., can be made.

The same stock solution of soap can be used for dry cleaning since this stock solution can be diluted by dry cleaning fluids, like Stoddard solvent, without precipitation of soap. Such solutions have been found to have good detergent power.

WITH the help of the above principle the preparation of the specialty soaps as listed above offers no difficulty. It is necessary only to use a suitable compound having the glycolic group which is soluble in the solvent medium used. When aqueous systems are concerned, any of the usual glycols can be used as each of them increases the solubility of the soap to a remarkable extent. Monoglycerides or monoethers of glycerol can also be profitably used. In non-aqueous systems in addition to dibutyl tartrate any higher glycol or monoglyceride can be profitably used if its solubility permits.

The application of this principle to the preparation of lubricating grease is a little more complicated because of the fact that the high viscosity oils used for making lubricating grease have poor mutual solubility with all glycolic compounds, even including dibutyl tartrate. This can, however, be overcome by using a non-volatile common solvent like pine oil which enhances their mutual solubility. Since a combination of high soap solubility and gelling power is wanted, alkyl or aryl derivatives of glycol or diethylene glycol may be tried as the basic com-

pounds have fairly high solubility combined with gelling power.

One unexpected feature of soap solutions in G-H mixtures is their complete freedom from foaming though containing as high as 20 or 30% soap. This property might have some application in defoaming. If a glycolic compound is added to an aqueous soap solution, the foaming power is considerably checked and with a higher proportion, say 30 or 40%, is practically destroyed. For some reason ethylene glycol is not as effective as the other glycols. Propylene glycol, particularly in mixture with an alcohol or a ketone, can be used for such purposes. Catechol, an unusual compound with a glycolic group, has very strong foam-depressing power, but it is rather liable to oxidation and cannot be used extensively. Some of its higher homologues might prove to be more suitable compounds. Salts of tartaric acid mixed with a small amount of water-soluble alcohols also have defoaming power, as expected.

We may now discuss a few compounds which, from theoretical considerations, appear to be of great potentiality in the soap-organic solvent field. According to our theory the more a solvent combines the nature of a glycol and a hydrocarbon-dissolving solvent, the better it is. Two starting materials due to their cheapness and easy availability seem to have great technical possibilities in synthesizing such compounds. They are tartaric acid and monochlorohydrin, both of which are ordinary commercial products. From tartaric acid the esters of various aliphatic and aromatic alcohols can be prepared; and from α -monochlorohydrin, by the Friedel Crafts reaction or similar reaction, various aryl substituted compounds can be produced which reasonably can be expected to be very powerful soap solvents.

IT should be finally pointed out, however, that what is needed is not necessarily a glycolic compound but any compound containing hydrogen atoms which are sufficiently electropositive to be capable of forming hydrogen bonds with the carboxylate oxygen atom. The activity of glycol is not due to simultaneous presence of two hydroxyl groups but is owing to the fact that one hydroxyl group by virtue of its electron attractive power mutually reacts inductively on the other to make the hydroxylic hydrogen much more electropositive than usual. Even when only one hydroxyl group is present in a compound, and this hydroxylic hydrogen atom owing to inductive effect of the negative groups present in the molecule or to mesomeric shift of electron pairs becomes sufficiently positive, such a compound will show soap-dissolving power since two such molecules will bring about adequate solvency of the $-\text{COO}-$ group. Even in the case of glycol it is more likely that in the solvency process which is certainly a dynamic one, two separate glycol molecules will more often dissolve one $-\text{COO}-$ group than both the hydroxyl groups being simultaneously operative on the same end to form a closed, many-membered ring, though it is well established that in hydrogen bonding such as dimerisation of acetic acid, eight-membered rings occur extensively. In fact, terpineol, cholesterol, phenol, etc., have been found to have appreciable soap solubility in conjunction with hydrocarbon solvents, which might be ascribed to such internal activation. More extensive

discussion of the theoretical aspect of this question will, however, be made elsewhere.

Acknowledgment

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terms co-solvency and co-solvents in the sense used in the paper.

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Uptake of Hydrochloric Acid by Cottonseed and Cotton Fiber During "Fuming" of Analytical Samples

ALVA F. FAUST and FRANCES A. HENSON

Southern Regional Research Laboratory¹
New Orleans, Louisiana

IN collaborative work on the determination of residual lint on cottonseed by the official method of the American Oil Chemists' Society some workers obtained negative values ranging from -0.1 to -0.4% on bald seed with practically no lint. On the supposition that this was because of increase of weight of the fumed sample due to combination of the hydrochloric acid with the seed, some experiments were made to determine the amount of hydrochloric acid taken up by cottonseed during fuming.

Various cottonseed samples were fumed according to the official method using 1.5 ml. of concentrated hydrochloric acid to each fuming pot which contained about 60 g. of seed. In one experiment the cottonseed was ground and analyzed whole; in another, the fumed cottonseed was separated by hand into lint, hulls, and meats, each of which was analyzed separately. In order to see whether all parts of the seed were capable of taking up hydrochloric acid, hand-separated hulls, meats, and raw cotton fiber were fumed. For comparison with the raw fiber a sample of cotton fiber that had been purified by the method used for production of "chemical cotton" was included. Samples of raw cotton fiber that had been extracted with water, as well as with alcohol in Soxhlet extractors were also fumed. Prior to analysis, all samples were heated for two hours at 101° C. in order to drive off any hydrochloric acid that would be removed in the official moisture determination. Samples of 10 g. each were burned in 2-g. portions in a Parr oxygen bomb and chlorine determined gravimetrically as silver chloride. The results are shown in Table I. It will be noted that cottonseed takes up 0.4 to 0.5% total chlorine when fumed with hydrochloric acid. This is not driven off in the moisture determination. All parts of the seed are capable of taking up hydrochloric acid although when whole seed is fumed, the hydrochloric acid may not reach the meats. The calculated effect of the uptake of hydrochloric acid by cottonseed is a lowering of the

percentage of oil by about 0.1% and of the total nitrogen by about 0.02%. This is probably of little significance in view of the usual errors of oil and nitrogen determinations. In the case of lint determinations the calculated error due to the uptake of hydrochloric acid is -0.3 to -0.4% . This is probably compensated for to a large extent in the official lint method by errors in the other direction such as the somewhat longer heating time of the fumed samples and the fact that small hull particles may be broken from the seed when the lint is removed by brushing.

In the case of raw cotton fiber one or more of the noncellulosic constituents appears to be largely responsible for the uptake of hydrochloric acid since cotton fiber purified to remove these constituents takes up and retains very little hydrochloric acid although it is made brittle by the treatment. Since extraction with hot water removes about 80% of the ash constituents of raw cotton fiber and extraction with alcohol removes the wax, the results indicate that neither the ash constituents nor the wax are responsible for the major part of the uptake of hydrochloric acid. However, since neither water nor alcohol extracts much protein from the fiber, it seems likely that protein is the constituent of raw cotton fiber that takes up hydrochloric acid.

TABLE I.
Uptake of Hydrochloric Acid by Cottonseed and Cotton Fiber
When Fumed as Shown by Analysis for Total Chlorine.

Material Fumed	Material Analyzed	Total Chlorine	
		Fumed	Control Not Fumed
		%	%
Cottonseed, 12.8% linters.....	Whole seed	0.41	0.03
Cottonseed, 2.0% linters.....	Whole seed	0.49	0.05
Cottonseed, 12.8% linters.....	Linters	0.58	0.05
Cottonseed, 0.04% linters.....	Hulls	0.57	0.07
Cottonseed, 0.04% linters, No. 1.....	Meats	0.04	0.03
Cottonseed, 0.04% linters, No. 2.....	Meats	0.05	0.03
Cottonseed hulls.....	Hulls	0.62	0.05
Cottonseed meats, No. 1.....	Meats	0.58	0.05
Cottonseed meats, No. 2.....	Meats	0.81	0.05
Cotton fiber, raw.....	Fiber	0.53	0.05
Cotton fiber, purified.....	Fiber	0.13	0.02
Cotton fiber, water-extracted.....	Fiber	0.37	0.01
Cotton fiber, alcohol-extracted.....	Fiber	0.45	0.01
Cotton linters, purified.....	Linters	0.06	0.01

¹One of the laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, U. S. Department of Agriculture.