Solubilization of Water in Non-polar Solvents by Detergent Mixtures.

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It was expected, on the basis of Winsor's theory, that a combination in suitable proportions of a hydrophilic and a lipophilic detergent would show considerably increased solubilizing power. This is experimentally confirmed by studying the solubilization of water in non-polar solvents by means of binary mixtures of dodecylammonium chloride, formate, acetate, laurate, or oleate; the detergent mixtures considerably increase the solubility although the separate constituents alone have but little effect. This effect is observed only for mixtures of a hydrophilic (*e.g.*, dodecylammonium chloride, formate, and acetate) and a lipophilic (*e.g.*, the laurate and oleate) detergent, but not where both the " amphiphiles " are either hydrophilic or lipophilic. These results constitute strong support to Winsor's theory of solubilization and demonstrate the utility of the conception of the ratio, R, introduced by him, in understanding the various phenomena.

Freezing-point data obtained with mixtures of detergents show that there is little change on mixing in the average degree of association of the two individual detergents. Thus increased solubility does not necessarily mean the existence of more micelles, and it is suggested that micelle formation and solubilization are parallel phenomena originating from the same cause, *viz.*, the inherent tendency of soap molecules to associate either with themselves or with other molecules.

WINSOR (*Trans. Faraday Soc.*, 1948, **44**, 376, 382, 387, 390) and Palit (*J. Colloid Sci.*, 1949, **4**, 523) observed that solubilization by amphiphiles is greatly increased in mixed solvents even though the amphiphiles have little solubilizing power in the individual solvents. An

explanation of this phenomenon has been advanced by Winsor in terms of his general theory of solubilization on the basis of the lipophilic–hydrophilic affinity ratio R, where $R = A_{C\bar{O}}/A_{C\bar{W}}$, in which C represents the detergent, $\bar{O}$ the oily phase, and $\bar{W}$ water, and the A terms represent the affinities denoted by their subscripts. Winsor further resolves each of these affinities into two parts, one due to hydrophilic attraction, A_H, originating from hydrogen bonding, and another due to lipophilic attraction, A_L, originating from van der Waals forces, and his final formulation for R is

$$R = A_{C\bar{O}}/A_{C\bar{W}} = (A_{L,C\bar{O}} + A_{H,C\bar{O}})/(A_{L,C\bar{W}} + A_{H,CW}) \quad . \quad . \quad . \quad . \quad (1)$$

According to Winsor, maximum solubilization occurs where R is near unity, and any system with $R < 1$ gives a predominantly hydrophilic system (called Type I system by Winsor) whereas with $R > 1$ the system becomes predominantly lipophilic (Type II system). It is evident that, for a mixture of two solvents to show enhanced solubilization, one should form a Type I system ($R < 1$) and the other a Type II system ($R > 1$), and this is found to be the case.

If Winsor's theory is correct, similar considerations must hold as regards solubilization by mixtures of detergents. Our earlier work (*Proc. Roy. Soc.*, 1951, **208**, *A*, 542) on solubilization by dodecylamine soaps of fatty acids (C_1 to C_{18}) has shown the significance of the ratio R in governing the extent of solubilization. It has been found that dodecylammonium butyrate exhibits maximum solubilizing power when R is presumably closest to unity, and the dodecylamine salts of lower and higher fatty acids solubilize but little and form systems of respectively Type I and Type II.

Evidently, the condition that R should approximate to unity can also be achieved by suitably mixing the two extreme types of detergent, and it might be expected that a poorly solubilizing Type I-forming detergent and a poorly solubilizing Type II-forming system would show greatly enhanced solubilization when mixed in appropriate proportions. Winsor (*loc. cit.*) himself observed this feature qualitatively with mixtures of aerosol OT and sodium undecanoate. The present paper reports the results of a systematic study of solubilization by mixtures of detergents where the individual detergents are known to form either Type I or Type II systems. These observations also open up the possibility of putting the micellar theory of solubilization to a critical test by simple physicochemical measurements, and the results of such a test are also reported.

Experimental

The detergents used were dodecylammonium formate, acetate, laurate, oleate, and chloride, prepared in the usual manner by mixing equivalent quantities of the amine and acid in light petroleum. The solvent was evaporated off and the detergents were dried in a vacuum. In preparing the hydrochloride, the amine and acid were allowed to react in a small quantity of freshly distilled absolute alcohol and, when the reaction was complete, the detergent was precipitated by acetone, washed with small amounts of light petroleum, and dried in a vacuum. All the detergents are white crystalline compounds at room temperature except the oleate which is an orange-brown liquid. Dodecylamine (supplied by Armour & Co., of U.S.A.) and the fatty acids (White Label, Eastman Kodak Co.) were used after purification by conventional methods.

Solubilization measurements were carried out in the usual manner (Palit and Venkateswarlu, *loc. cit.*; Palit and McBain, *J. Soc. Chem. Ind.*, 1947, **66**, 3), 5 c.c. of the solution containing 0·5 g. of the detergent (sometimes 10 c.c. containing 1 g.) being used, and solubilizing power is expressed as the weight of water solubilized per g. of detergent (pure or mixture). After the limit of solubilization has been attained, the type formed, *i.e.*, whether I or II, is determined in each case. In Winsor's terminology, these types respectively indicate whether the system is predominantly aqueous or non-aqueous. This was ascertained by adding a drop of oleic acid to the turbid detergent solution saturated with water and observing whether the system clears or further clouds, this indicating Type I and II, respectively. This test is also supplemented by electrical conductivity and miscibility (in water and organic solvent) tests. The types formed are indicated in the curves (Figs. 1—4) by the corresponding Roman numeral near each experimental point.

Results and Discussion

Mixtures of Detergents of Opposite Types.—Figs. 1—4 represent the data of solubilization of water in solvents such as toluene and carbon tetrachloride by detergent mixtures. All the measurements were at 40° unless otherwise stated. For economy of space actual data are omitted but the values are ascertainable from the graphs.

Fig. 1. *Solubilization of water in toluene at 40° by dodecylammonium formate–laurate (A) and acetate–laurate (B) mixtures.*

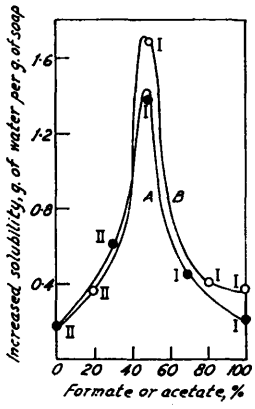

Fig. 2. *Solubilization of water at 40° by dodecylamine soaps; A, formate–oleate in toluene; B, acetate–oleate in toluene; C, acetate–laurate in carbon tetrachloride.*

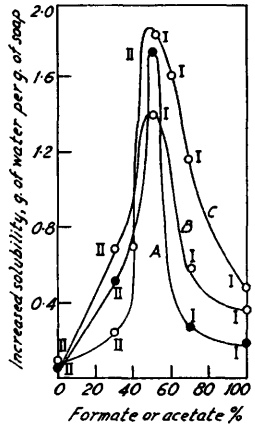

Fig. 3. *Solubilization of water at 35° by dodecylammonium chloride–oleate mixture in chloroform.*

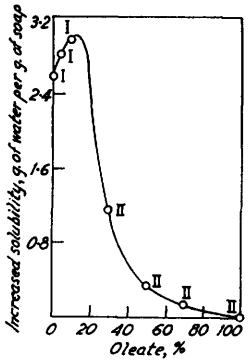

Fig. 4. *Solubilization of water at 40° by dodecylamine soaps: A, formate–acetate; B, chloride–acetate, in chloroform (ordinates for B, right-hand scale); C, formate–acetate in toluene. (All systems are of Type I.)*

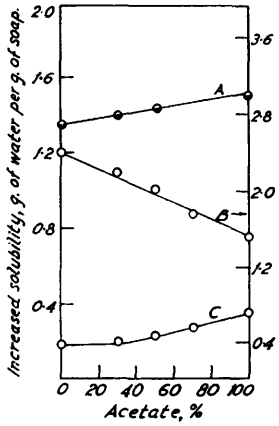

Fig. 1 shows the results obtained by using formate–laurate and acetate–laurate mixtures in toluene, and Fig. 2 those for formate–oleate and acetate–oleate mixtures in toluene and for acetate–laurate mixtures in carbon tetrachloride. Figs. 1 and 2 show that the foregoing four detergents have only a slight effect individually but show pronounced solubilization when suitably admixed. For instance, the acetate and laurate separately solubilize 0·364 and 0·179 g. of water respectively per g. of soap, but a 1 : 1 (wt.) mixture solubilizes 1·68 g., which is about 6 times greater than the mean of these values. Similar behaviour is found for the other three combinations mentioned above. From the graphs it is seen that all these curves show peak solubilization when the constituent detergents are present in

approximately equal weight, the peak solubilities for such formate–laurate, acetate–oleate, and formate–oleate mixtures being respectively 1·38, 1·392, and 1·728 g. of water per g. of soap, *i.e.*, about 7, 4, and 7 times the amounts to be expected from the means.

It is also seen from the graphs that acetate and formate invariably form Type I systems ($R < 1$), and laurate and oleate Type II ($R > 1$) systems. Admixture of these two classes of detergents would produce, at some suitable proportion, a system having the ratio, R, close to unity, and hence, according to Winsor's theory, would give rise to a maximum in the solubilization curve for the mixture. The fact that the solubilization-increase curve is more or less symmetrical indicates that the detergents formate and acetate are roughly as strongly hydrophilic as laurate and oleate are lipophilic. These results are just what would be expected qualitatively from Winsor's theory and constitute strong evidence in its favour and show the utility of his concept of the ratio R.

It may be pointed out that the mixed detergent effect is not only analogous to that of mixed solvent effect observed by Palit (*loc. cit.*), but is fundamentally the same. In the former R is brought towards unity by suitably mixing the detergents, and in the latter the same result is accomplished by mixing solvents.

Effect of Solvent.—This mixed detergent phenomenon, though demonstrated above in only toluene and carbon tetrachloride, should also happen in other solvents, in fact, in any solvent wherever one of the detergents forms a Type I system and the other a Type II system. This has been shown to be the case with a large number of solvents by studying only three systems, *viz.*, the individual detergents and a 1 : 1 mixture by weight of the two. The results are given in Table 1, and, except in chloroform (see next paragraph), the

TABLE 1. *Solubilization of water by detergents and their* 1 : 1 *mixtures.**

Solvents	G. of H_2O solubilized per g. of detergent					
	Acetate	Laurate	1 : 1 Mixture	Formate	Oleate	1 : 1 Mixture
n-Hexane	0·149 (I)	0·239 (II)	1·62 (*a*)	0·062 (I)	<0·1 in all cases	2·576 (II)
n-Heptane	0·222 (I)	0·249 (II)	0·90 (I)	—		—
*cyclo*Hexane	0·904 (I)	0·270 (II)	1·37 (I)	0·125 (I)		1·65 (II)
Methyl*cyclo*hexane	0·906 (I)	0·176 (II)	0·90 (I)	—	All Type II systems	—
Benzene	—	—	—	0·228 (I)		1·7 (II)
Toluene	0·364 (I)	0·179 (II)	1·68 (I)	0·196 (I)		1·728 (II)
Xylene	0·320 (I)	0·189 (II)	1·43 (I)	—		1·808 (II)
Ethylbenzene	—	—	—	0·143 (I)		1·844 (II)
Chlorobenzene	—	—	—	0·23 (I)		1·78 (II)
Carbon tetrachloride	0·48 (I)	0·093 (II)	1·82 (I)	0·525 (I)		1·596 (II)
Chloroform	1·50 (I)	0·233 (II)	0·18 (II)	1·35 (I)		1·356 (II)
Tetrachloroethylene	—	—	—	—		1·5 (II)

* The type of system is indicated by Roman numerals; *a* denotes that the behaviour is ambiguous, the system responding to some tests of Type I and others of Type II systems—presumably R is very near to unity.

increase in solubilizing power is evident in all cases. Sometimes it is very marked; *e.g.*, in *n*-hexane the formate–oleate mixture gives a solubility at least 30 times greater than the mean value for the individual detergents.

Unsymmetrical Increase of Solubilization.—The behaviour in chloroform is exceptional in that the individual detergent, say the acetate, is a better solubilizer than a 1 : 1 mixture of acetate and laurate, the values being 1·5 g. and 0·18 g., respectively. The explanation is simple. Dodecylammonium acetate has higher affinity for chloroform than for the other solvents, as also shown by the high solubility of the long-chain amine salts in chloroform. In other words $A_{\bar{O}\bar{O}}$ (eqn. 1) is higher, and so R has a higher value which makes it approach unity more closely though remaining at a value less than unity. Hence, a small addition of laurate ($R \gg 1$) produces peak solubilization and any further addition of laurate brings down the solubilization sharply. This results in a highly unsymmetrical solubilization curve. A 1 : 1 mixture lies on the falling branch of the solubilization curve and so it is not necessarily more powerful than any of the other detergent mixtures but may have all intermediate values.

Experimental support to the views expressed above is obtained by a study of a similar system, *viz.*, dodecylammonium chloride and oleate in chloroform (at 35°), the results of

which are shown in Fig. 3. Here the chloride forms a Type I system of appreciable solubilizing power, *i.e.*, R is very near to but less than unity. On the other hand, oleate forms a Type II system with very little solubilization, *i.e.*, R is greater than and far removed from unity. It may be expected on the basis of Winsor's theory and the above reasonings that only a small amount of oleate is required to increase to a maximum the solvent power of the system, and further quantities would only reverse the type and decrease solubilization; for instance, it is seen from Fig. 3 that a peak solubilization of 2·94 g. of water per g. of soap is attained at a proportion of 90 : 10 of the chloride and oleate respectively.

Mixtures of Detergents of the Same Type.—The detergent mixtures studied so far are those where one of the components forms a Type I system and the other a Type II system. If detergents which form the same type of system are combined, then only intermediate quantities are expected to be solubilized and no pronounced maximum should occur. Accordingly, detergent mixtures of dodecylammonium chloride, formate, and acetate were studied which are invariably found to form Type I systems. Results are shown in Fig. 4. It is seen that the amount of water solubilized varies almost linearly with the proportions of the individual detergents and increases as the proportion of the more solubilizing detergent increases. This constitutes another confirmation of Winsor's theory.

A Critical Test of the Micellar Concept of Solubilization.—The foregoing work suggests a critical experimental test of the micellar theory. It is generally conceded that micelle formation is the cause of solubilization. If that is so, we should expect that this profound increase in solubilization on mixing detergents would reveal highly increased micelle formation if examined by any of the cryoscopic methods. We have attempted to verify the foregoing deduction by freezing-point measurements and the results are described below. The electrical conductivity of quaternary salts in weakly polar organic solvents is extremely small (Strong and Kraus, *J. Amer. Chem. Soc.*, 1950, **72**, 166; Winsor, *Trans. Faraday Soc.*, 1950, **46**, 762) and so the results are free from any complication due to dissociation. The effect of the very small solubility of water in the solvents on freezing point was found to be small (0·03° for benzene and less than 0·01° for the other solvents) and was neglected.

TABLE 2. *Freezing-point depression and solubilization by detergent mixtures.*

Detergent: dodecylammonium salt	Solvent	G. of H_2O solubilized per 15 c.c. of soln.	F.p. depression, ΔT	α *	Solubilizing power
Propionate (A)	Benzene (5% soln.)	nil	0·205°	5·57	0·92 (10% soln.)
Oleate (B)	,,	,,	0·21	3·02	≃0
70% of (A) and 30% of (B)	,,	,,	0·23	4·81	1·76
50% of (A) and 50% of (B)	,,	,,	0·27	4·29	1·54
	,,	0·11	0·22	5·27	—
	,,	0·22	0·215	5·39	—
	,,	0·33	0·21	5·52	—
	,,	1·01	0·195	5·94	—
A	*cyclo*Hexane (1% soln.)	nil	0·10	10·1	1·5 (1% soln.)
B	,,	,,	0·11	5·1	nil
70% of (A) and 30% of (B)	,,	,,	0·10	8·6	2·0
	,,	0·10	0·10	8·6	—
Acetate (C)	Bromoform (1% soln.)	nil	0·04	5·1	1·0 (1% soln.)
Oleate (B)	,,	,,	0·06	1·8	nil
80% of (C) and 20 % of (B)	,,	,,	0·048	4·4	1·6
	,,	0·05	0·05	4·3	—

* α = Degree of association.

Freezing-point measurements were carried out first in benzene with dodecylammonium propionate and oleate and 7 : 3 and 1 : 1 (wt.) mixtures of the two, the former mixture being known to give a solubilization about twice the mean value. The results are presented in Table 2. Acetate or formate could not be used in this investigation owing to solubility limitations. It will be seen from the Table that the pure soaps are not highly associated, the average degree of association being about 4·2, a value close to previous

observations in similar systems (Palit and McBain, *loc. cit.*; Gonick, *J. Colloid Sci.*, **1946**, **1**, 393; Gilmour, Nelson, and Pink, *Nature*, **1953**, **171**, 1075). The most unexpected thing, however, is that the mixture gives a freezing-point depression which is practically the mean of the values for the two soaps. This definitely discounts the idea that a higher solubilizing power is necessarily associated with more micelle formation.

We next investigated by the same technique what happens when these systems solubilize water, and the results are also included in Table 2. It is seen that the first small portion of solubilized water increases the average degree of association, whereafter later additions of water cause no further change : the average degree of association of the mixture in a 5% solution is 4·3, and 0·11 c.c. of water solubilized in 15 c.c. of this solution increases the degree of association to 5·3 but this is not appreciably altered by further solubilization up to near saturation point, *i.e.*, 1·01 c.c. of water. Hence, we conclude that (*a*) solubilization does not run parallel with pre-existing micelles and (*b*) more solubilization does not necessarily mean more micelle formation.

We also studied two other solvents, *viz.*, *cyclo*hexane and bromoform, by the cryoscopic method. In these the solubility of the more polar detergent is much less than that in benzene. (Ethylene dibromide, a solvent of similar type, did not give solutions of suitable concentration.) The results are given in Table 2. *cyclo*Hexane behaves very similarly to benzene and so the conclusions for benzene solutions are confirmed. Bromoform also qualitatively shows the same behaviour as does benzene : the mixture effect is found here also, and the mixture does not show any perceptibly higher micelle formation, and thus the general conclusions are confirmed.

A radical departure from the existing micellar theory is needed to understand the varied aspects of solubilization : it is quite likely that these are not ascribable to a common mechanism, but it seems that the associating tendency of some molecules with molecules containing complementary groups lies at the root of all types of solubilization phenomena. The strong micelle-forming and solubilizing power of soap molecules is ascribable to the inherent tendency of soap molecules to associate either with themselves or with other types of molecule, and it is more logical to regard micelle formation and solubilization as parallel phenomena arising out of a common origin rather than to regard the latter as being caused by the former, as has been done by almost all workers in this field.

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