

Solubilization of Polar Species by Micelle-Forming Soaps in a Nonpolar Solvent

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ABSTRACT

The solubilization of diethyl ether, acetone, n-propylamine, and methyl acetate by sodium and magnesium dinonylnaphthalene sulfonates in toluene solution was studied by gas-liquid chromatography. Results are compared with data for the solubilization of methanol and acetic acid. Of the solubilizates studied, all were less extensively solubilized than methanol. Within the scope of the data, n-propylamine and acetic acid were solubilized approximately equally by the magnesium soap, but the sodium soap solubilized the acid more vigorously than the amine. The ether and ketone were only faintly solubilized and the ester occupied an intermediate position. The data are consistent with conclusions derived from earlier studies of micelle formation and solubilization by the same soaps. At very dilute concentrations of solubilizate, the cation of the soap controls the interaction, but with increasing concentrations, after the coordinating tendency of the cation is satisfied, the anion is the effective moiety.

Solubilization imposes no restrictions upon the nature of the micelle or upon changes the micelle may undergo as solubilization commences and proceeds. The criterion of solubilization is the reduction of solubilizate activity.

PROBLEM STATUS

This is an interim report; work on this problem is continuing.

AUTHORIZATION

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SOLUBILIZATION OF POLAR SPECIES BY MICELLE-FORMING SOAPS IN A NONPOLAR SOLVENT

INTRODUCTION

Solubilization is frequently considered a process wherein successive solubilize molecules enter into and accumulate within persistent micelles, as in the solubilization of hydrocarbons by aqueous soap micelles (1). Not all cases of solubilization conform to this pattern. The solubilization of methanol by both sulfonate and carboxylate soaps in toluene leads to the degeneration or disappearance of micelles (2,3); water is known to expand zinc dinonylnaphthalene sulfonate micelles in benzene (4); and no substantial difference is observed in the size or general nature of barium dinonylnaphthalene sulfonate micelles in benzene whether solubilized Rhodamine B is present (4) or absent (5). A useful concept of solubilization imposes no restrictions upon the nature of the micelle or upon any changes it may undergo as solubilization commences and proceeds. Although this investigation did not include measurements of micelle size, the possibility of change in this and other properties of micelles with solubilization must be recognized. The term solubilization need not be restricted to species which are insoluble in the absence of the solubilizing agent; a soluble or insoluble species may be considered solubilized if it interacts with the solubilizing agent and both remain soluble thereafter. According to this concept, for any given stoichiometric concentration of solubilize, its activity must be less in the presence of the solubilizing agent than in its absence, and the change in activity reflects the extent of solubilization.

The purpose of this investigation was to study the extent to which various classes of organic compounds are solubilized by micelle-forming soaps in a nonpolar solvent. Dinonylnaphthalene sulfonates in toluene solutions were used as solubilizing agents for diethyl ether, acetone, n-propylamine, and methyl acetate. By a gas-liquid chromatographic technique previously described (2,3), saturated vapors over toluene solutions of the solubilize with and without soap were analyzed. Quantitative inferences concerning solubilization were drawn from the observed changes in composition of the vapors caused by addition of soap to the solutions.

MATERIALS

The sodium and magnesium dinonylnaphthalene sulfonates (NaDNNS and $\text{Mg}(\text{DNNS})_2$) were repetitively lyophilized and dried *in vacuo*. Details of their preparations have been described earlier (2,3). Anhydrous ACS grade diethyl ether was percolated immediately before use through Linde Molecular Sieve 5A and activated alumina to remove traces of moisture and peroxides, respectively. Iodometric analysis of the percolate revealed no detectable quantity of peroxides and gas chromatographic tests showed water to be absent. The toluene has been described earlier (2,3). The acetone was a spectrographic grade and was percolated immediately before use through Linde Molecular Sieve 5A and activated alumina to remove possible traces of water and acidic impurities. No moisture was found in the percolate by gas chromatography. The most suitable of several lots of Eastman 1216 n-propylamine was selected on the basis of its gas chromatogram, which was free of extraneous peaks except for water, estimated at 1 part in 1000. Because of the satisfactory purity of this amine, and because of its tendency to develop impurities on attempts at further purification, it was used as received.

The methyl acetate was Fisher Scientific Co. reagent grade M-203. This ester was percolated immediately before use through Linde Molecular Sieve 13X and activated alumina. The gas chromatogram of the percolate indicated no water, but about 4 parts methanol in 10,000 by volume. Any acidity present was assumed to be acetic acid. The pH of a dilute solution of the ester in boiled distilled water was determined. All the hydrogen ions present were assumed to be those derived from the acid, and the contribution from the water was neglected. This assumption exaggerates any acid present. The following simultaneous equations were used to solve for the concentration of acetic acid in the solution:

$$\frac{C^2 \alpha^2}{(1 - \alpha) C} = K$$

$$\frac{[H^+]^2}{(1 - \alpha) C} = K$$

where

C = the stoichiometric concentration of acid,

α = the degree of dissociation of the acid,

$[H^+]$ = the hydrogen-ion concentration of the solution, and

K = the dissociation constant of the acid.

By this method it was estimated that the ester to acid molar ratio was greater than 10^6 to 5. The method was validated by comparing results of titrations with those derived from pH measurements on untreated samples of the ester. Gas chromatographic determinations of moisture in the various liquids were made on a column packed with 0.2% tetrahydroxyethyl ethylene diamine (THEED) on 40-60 mesh Columpak T (Teflon).

EXPERIMENTAL DETAILS

Compositions of the vapors were studied with a Perkin-Elmer 154B fractometer. Details of method, procedure, and apparatus have been described (2,3). Experimental modifications and features pertinent to the present measurements are reported here. To improve the baseline stability of chromatograms, the carrier-gas stream was split to provide independent channels for the reference and sample detectors. A capillary was interposed between the helium supply and the reference detector to moderate the flow of carrier gas in the reference channel. The flow meter monitoring the carrier-gas velocity was stabilized by moving it to the exit of the sample channel. Occasional trouble shooting was simplified by this change. The velocity of the carrier gas in the reference channel was not monitored, but was controlled by the inlet pressure and geometry of the channel so that it bore a fixed relationship to the velocity in the sample channel. The potential applied to the thermal conductivity bridge was 8.0 v and the exit pressure was atmospheric. The modified experimental arrangement is shown in Fig. 1. Operating conditions are tabulated in Table 1.

Samples of saturated vapor (25°C) over a series of toluene solutions of a given solubilize were analyzed. The results were compared with those of a similar series of solutions containing known concentrations of soap. Differences between total solubilize concentrations in the liquid at equal vapor compositions reflect the loss of activity of the solubilize due to interaction with soap. The extent of this interaction, or solubilization, can therefore be calculated from the chromatographic data.

Table 1
Chromatography Operating Conditions

	Column* Packings	Temp (°C)	Inlet Pressure (psig)	Carrier-Gas Flow Rate (cc/min)
Diethyl ether	Apiezon L, 20% by weight on 60-80 mesh Gas Chrom P	70	13.0	260
Acetone†	Carbowax 400 (polyethylene glycol), 29% by weight on 35-80 mesh Chromosorb Regular and Apiezon L, 20% by weight on 60-80 mesh Gas Chrom P	74	12.0	260
n-Propylamine	Armeen SD, 20% by weight on 60-80 mesh Gas Chrom P	64	12.0	160
Methyl acetate	Apiezon L, 20% by weight on 60-80 mesh Gas Chrom P	54	12.2	110

*Columns were all six-foot long and 1/4 inch O. D.

†Composite column - 2-three-foot sections in series.

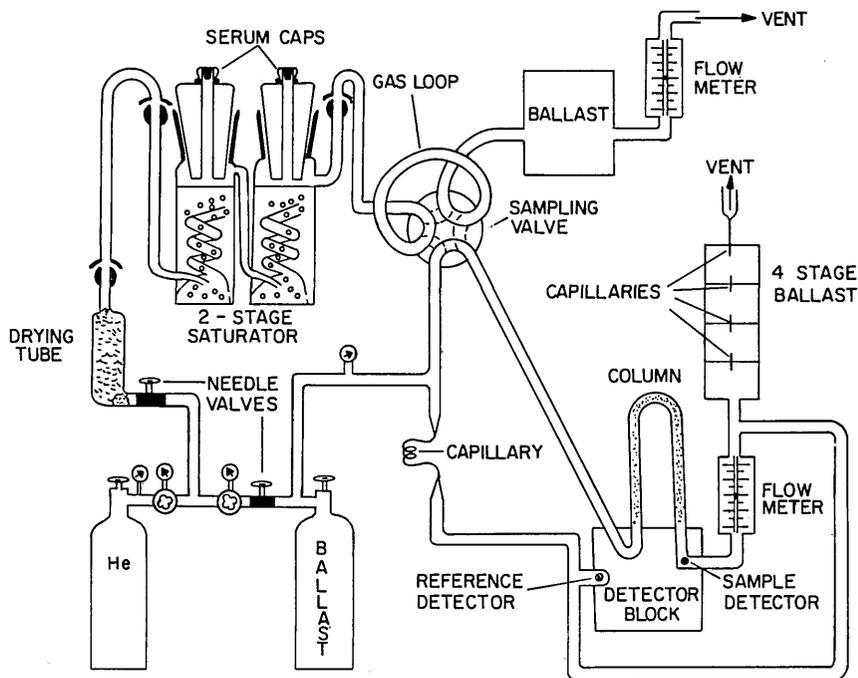


Fig. 1 - Modified experimental arrangement for studying vapors by gas chromatography

When a soap solution was being studied, only the second stage of the saturator was charged with a soap solution. The first stage was charged with a toluene solution of the solubilize in the proper concentration to yield the same vapor composition as that issuing from the second stage. This procedure conserved the valuable supply of soap without losing the advantages of two-stage saturation. The requisite concentration of solubilize in the first stage was estimated from data obtained in advance with binary solutions of solubilize and solvent. By underestimating the solubilize concentration in the first stage, an adjustment can be made after a preliminary determination by a hypodermic injection of additional solubilize through the serum cap of the first stage. The experimental arrangement used here facilitated the execution of measurements with three concentrations of solubilize in one working day with one portion of soap. Additions of solubilize were injected into the second stage of the saturator for successive determinations. Appropriate adjustment were made at the first stage for each addition to the second stage.

Calculations concerning the degree of solubilization in the second stage of the saturator were made according to the following scheme. Weight fractions are computed from the weights of the solvent (toluene) and solubilize (additive), excluding the soap.

T = total weight of toluene in the soap solution

A_t = total weight of solubilize (additive) in the soap solution

F_t = total weight fraction of solubilize in the soap solution = $\frac{A_t}{A_t + T}$

F_o = weight fraction (observed) indicated by the chromatograms by comparison with a calibration curve derived from soapless solutions

A_o = weight of solubilize (observed) which is not solubilized

L = weight of solubilize lost to the soap, or solubilized

$$F_o = \frac{A_o}{T + A_o} \quad (1)$$

Solving for A_o in Eq. (1)

$$A_o = \frac{F_o T}{1 - F_o} \quad (2)$$

$$L = A_t - A_o \quad (3)$$

substituting for A_o in Eq. (3) from Eq. (2)

$$L = A_t - \frac{F_o T}{1 - F_o} \quad (4)$$

Thus L is the weight of solubilize which has interacted with or has been solubilized by the soap. The ratio of L to the quantity of soap present is the degree to which solubilization occurs. This quantity can be computed as moles of solubilize per equivalent weight of soap as in Figs. 2 and 3.

RESULTS AND DISCUSSION

The particular solubilizes used here were selected for their variety of representative functional groups and for their volatility, which suited them to the experimental

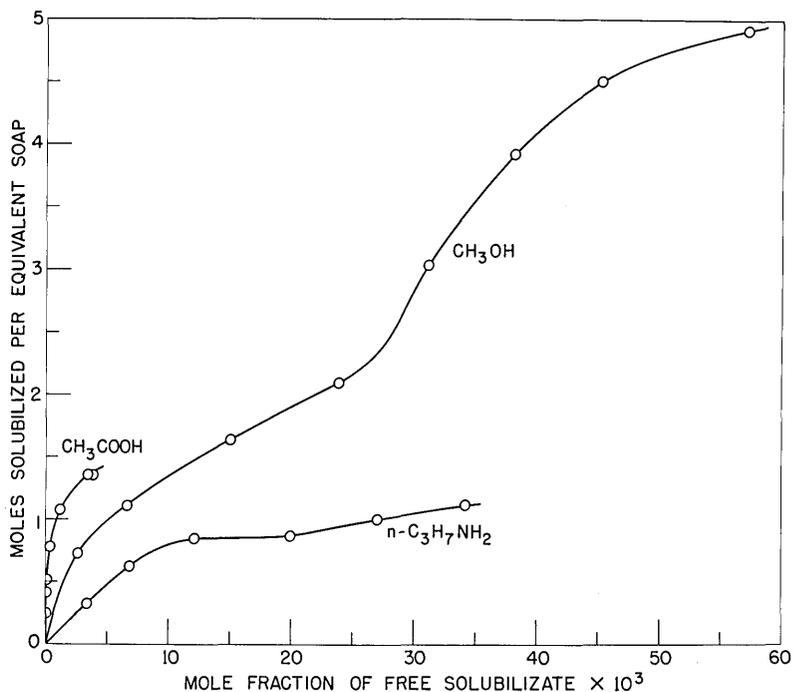


Fig. 2 - Solubilization of organic species by sodium dinonylnaphthalene sulfonate in toluene at 25°C

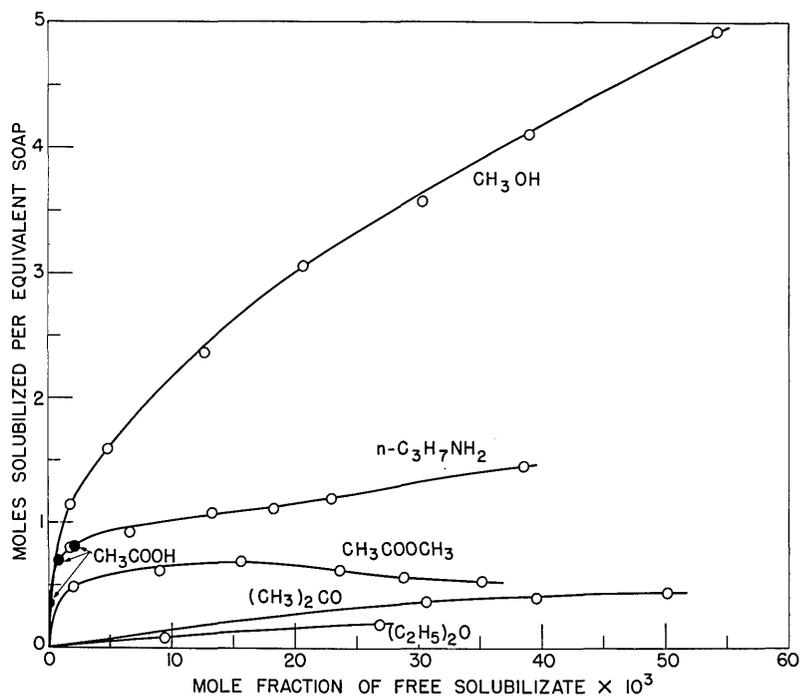
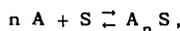


Fig. 3 - Solubilization of organic species by magnesium dinonylnaphthalene sulfonate in toluene at 25°C

method. Figures 2 and 3, respectively for NaDNNS and Mg(DNNS)₂, display the data derived from the measurements. Included for comparison are data previously obtained for the solubilization of methanol (2,3) under strictly comparable conditions and for acetic acid in benzene (6) under somewhat different conditions of soap concentration.

Concentrations of soap in the solutions studied here were 3.6×10^{-3} and 1.8×10^{-3} (mole fraction) for NaDNNS and Mg(DNNS)₂, respectively. Results are compared with benzene solutions of the same soaps whose concentrations were both 1.6×10^{-3} (mole fraction) in the acetic acid study. However, the functions plotted here reconcile these differences to a first approximation, as demonstrated by the following considerations.

The interaction of acid with soap molecules can be represented by the equilibrium



where n = the number of acid molecules reacting with one soap molecule, A represents an acid molecule and S represents a soap molecule.

Thus,

$$\frac{[A_n S]}{[A]^n [S]} = K, \quad (5)$$

where the brackets denote concentration and K is the equilibrium constant. Rearranging and adding $[S]$ to both sides of the equation,

$$[S] + [A_n S] = (K [A]^n + 1) [S]. \quad (6)$$

The degree of solubilization in moles A solubilized per mole of soap present is equal to

$$\frac{n [A_n S]}{[A_n S] + [S]}.$$

By substitution from Eqs. (5) and (6) this function becomes

$$\frac{n K [A]^n [S]}{(K [A]^n + 1) [S]} \text{ or } \frac{n K [A]^n}{K [A]^n + 1}.$$

Thus, for any assigned value of $[A]$, the concentration of unsolubilized acid, such as $[A]_1$, the expression is independent of the concentration of S . It is also evident that this is true regardless of the value of n . The curves in Figs. 2 and 3 are plotted in analogous terms, and should therefore be reasonably comparable despite the fact that different soap concentration was used in the acetic acid study. The use of benzene as the solvent in the acetic acid study should not be considered a serious deviation from toluene.

The abscissas are concentrations of unsolubilized solute remaining in equilibrium with that bound by the soap. The ordinates are ratios of bound solubilizate to soap present, in moles per equivalent or per gram-anion. Plotting in these coordinates maintains a practical comparability irrespective of cation valence if one is interested in the ultimate solubilization, but it distorts the impression obtained concerning the effect of the cation in the lower concentration range, which falls below 3 to 5×10^{-3} for these plots. Had the ordinates been plotted on the mole or gram-cation basis, they would be unchanged in Fig. 2, but doubled in Fig. 3.

Of the solutes shown in Fig. 3, methanol is most vigorously solubilized by Mg(DNNS)₂, once the initial stage is passed. Differentiation is not clear between the amine, acid, and alcohol in the very dilute region. For these three solubilizates it is concluded that in the initial stage nearly all the solute present is coordinated by the magnesium moiety of the soap because of the strong coordinating tendency of that cation. Discrimination between

these solubilizates is consequently marginal or absent because nearly all the available solubilizate has interacted in each case. In Fig. 2 for NaDNNS, there is a clear differentiation between these solubilizates because the more weakly coordinating sodium ion does not interact as vigorously. These data are consistent with earlier observations (4), wherein it has been demonstrated that $Mg(DNNS)_2$ micelles are more firmly bound together than those of NaDNNS because of the charge-radius functions of the respective cations. In the upper concentration range, the ordinates and slopes both show that methanol is the most strongly and extensively solubilized of the solutes shown if acetic acid is excluded from consideration because of the limited data. This effect is attributed to the nature of the anion, common to both soaps. Coordination of amine with the cation appears to be the principal reason for its solubilization by both soaps, and a lesser interaction with the anion is indicated than for methanol, which is solubilized at higher concentrations by a hydrogen-bonding effect.

Acetone and diethyl ether are both very feebly bound by $Mg(DNNS)_2$, and although data are not available, it should be expected that NaDNNS would solubilize these compounds to a lesser extent than would $Mg(DNNS)_2$. It is probable that the ether and ketone both interact principally by coordination with the cation. The curve for methyl acetate suggests that the ester is solubilized exclusively by the cation. The initial slope distinctly differentiates the ester from the ether and ketone.

REFERENCES

1. McBain, M.E.L., and Hutchinson, E., "Solubilization and Related Phenomena," Academic Press, New York, N. Y., 1955
2. Kaufman, S., J. Colloid Sci. 17:231 (1962)
3. Kaufman, S., "Solubilization of Methanol by Soap Micelles in Toluene as Measured by Gas Chromatography," NRL Report 5639, July 26, 1961
4. Kaufman, S., and Singleterry, C.R., J. Colloid Sci. 12:465 (1957)
5. Ford, T.F., Kaufman, S., and Nichols, O., "Ultracentrifugal Studies of Barium Dinonylnaphthalenesulfonates-Benzene Systems," American Chemical Society 147th National Meeting, Philadelphia, Pa., Apr. 1964
6. Bascom, W.D., and Singleterry, C.R., J. Colloid Sci. 13:569 (1958)

