

Solubilization of Single-Component and Binary Mixtures of Hydrocarbons in Aqueous Micellar Solutions

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The solubilization of hydrocarbon molecules in micellar solutions has been investigated by injecting directly in a gas chromatograph the micellar solutions containing solubilizates. This method was used after an evaluation of the techniques already reported in literature showed that none was as satisfactory for multicomponent hydrocarbon solubilizates. In the single component solubilization experiments, the molar solubilization ratio of seven organic molecules in three different surfactant solutions (cetyl pyridinium chloride, dodecyl ammonium chloride, and sodium dodecyl sulfate surfactants, at 0.1 *M* concentration and at 25°C) have been measured. The data show that the molecular volume of the solubilize and its polarity play an important role in determining the extent of solubilization. The interfacial tension of the solubilize against water was chosen as a measure of its polarity. Correlations between the measured molar solubilization ratios and either the molecular volume or the combined molecular volume-polarity parameter have been developed. In general, a solubilize with smaller molecular volume and some polarity is preferentially solubilized. Solubilization experiments involving binary hydrocarbon mixtures show that selective solubilization of benzene over hexane occurs in all the five surfactant systems examined. The selectivity ratio for benzene increases with decreasing concentrations of benzene in the bulk solubilize phase which is in equilibrium with the aqueous micellar solution. A selectivity ratio as large as 7 occurs in dodecyl trimethyl ammonium chloride solution. However, the systems exhibiting high selectivity ratios do so only at the cost of a decrease in the total solubilization capacities for the different solubilizates. Binary solubilization experiments involving the solubilize pairs benzene + hexane, benzene + cyclohexane and cyclohexane + hexane suggest that the order of selectivity follows that which would be expected from the corresponding pure component molar solubilization ratios. Pairs of solubilizates that have widely different pure component solubilization ratios have the largest selectivity ratio when solubilized as binary mixtures. Finally, the measured molar solubilization ratio for hexane in all the mixed solubilization experiments exhibits an interesting synergistic behavior in the presence of small amounts of benzene. This suggests that surface solubilization of benzene occurs at low amounts of benzene in the micelles.

INTRODUCTION

Hydrophobic molecules which are sparingly soluble in water exhibit enhanced solubility in aqueous micellar solutions. This phenomenon known as solubilization is caused by the availability of a nonpolar microenvironment inside the micelles for the accommodation of the hydrophobic solute molecules. A number of investigations have been carried out over the years toward developing an understanding of this phenomenon of solubilization (1-3). One of the important characteristics of solu-

bilization that is experimentally accessible is the ratio of the maximum number of solubilize molecules to the number of surfactant molecules in a micelle. This ratio, hereafter designated as the molar solubilization ratio, has been measured for a variety of solubilizates in a number of surfactant solutions. These experimental data show that, within a chemical family of solubilizates (such as aliphatic or aromatic hydrocarbons), a rough correlation exists between their molecular volumes and the measured molar solubilization ratios (3-5). These studies pose two interesting

questions: First, one would like to know which of the molecular properties of the solubilizates, in addition to their molecular volume, would permit a more generalized correlation applicable for various chemical families of the solubilizate molecules. Second, could one anticipate that molecules exhibiting different molar solubilization ratios as pure components would give rise to selective solubilization when their binary or multicomponent mixtures are solubilized?

No experiments on the solubilization of hydrocarbon mixtures in common surfactant systems have been reported in the literature. The only reported data (6) on the solubilization of mixtures are for mixtures of benzene + cyclohexane in sodium deoxycholate solutions. In this surfactant, which is both a weakly aggregating and a poorly solubilizing system, no selective solubilization was found.

One of the first problems to be solved in the study of solubilization of mixtures is the choice of a suitable experimental technique. Various techniques have been employed in the past for measuring the molar solubilization ratios of pure solubilizates (1-3). One of the simplest was based on turbidity measurements (1, 5, 7) which take advantage of the fact that a solubilizate added to a surfactant solution in excess of its solubilization capacity forms a dispersion, thus causing a sharp increase in the turbidity of the solution. The turbidity method is simple but cannot be adopted for binary or multicomponent solubilization because the surfactant solution can become turbid even before the solubilization capacity of the micelles in all the components is reached.

The determination of the solubilization capacity by absorption spectrophotometry (1, 3, 8, 9) is applicable for solubilizates which have a characteristic absorbance either in the UV or the visible range. The procedure involves saturating the micellar solution with the solubilizate and then analyzing the surfactant solution with a UV/visible spectrophotometer. The concentration of the solubilizate is determined by comparing the absorbance measurements to the calibration curve for the sol-

ubilizate. The use of this method is limited to solubilizates that have a sufficiently strong characteristic absorbance. In the case of mixtures of solubilizates, the absorbance ranges for the components often overlap with one another. Hence this method is not very useful for the study of solubilization of mixtures.

A stripping technique was developed by Swinnerton *et al.* (10) for determining the water solubilities of gases such as N_2 , O_2 , and CH_4 . The method involves the use of a small glass stripping column into which a few milliliters of the micellar solution is added. The dissolved gases are stripped and concentrated by a carrier gas (N_2 or He) passing through the column. The carrier gas containing the stripped solutes is analyzed using a gas chromatograph. The advantage of this method is that relatively large amounts of aqueous samples can be used (several milliliters), whereas for direct gas chromatographic analysis, the sample size is limited to a few microliters. This constitutes an important factor in systems where the solute concentration is very small. Miller *et al.* (11) have used this technique to determine the solubility of hydrocarbon gases in lipid bilayers. In principle, this method can be used for mixtures of solubilizates as well, since the components can be chromatographically separated and analyzed.

A liquid-liquid extraction procedure followed by mass spectrometric analysis has been used by Thomas and Christian (6) to determine the extent of solubilization of benzene + cyclohexane mixtures in sodium deoxycholate micelles. The solubilizates were extracted from a given volume of the micellar solution by contacting it with a smaller volume of CCl_4 used as extractant. The CCl_4 was then analyzed by a mass spectrometer to determine the amount of benzene and cyclohexane present. It was assumed that all of the benzene and cyclohexane from the micellar solution were extracted into the CCl_4 . This liquid-liquid extraction technique can be used for mixtures of solubilizates since the components can be mass spectrometrically separated and analyzed.

In the present work the applicability of the stripping technique and of the liquid-liquid extraction technique to the solubilization of mixed hydrocarbons has been investigated. It has been found, as will be detailed below, that there are many limitations in the practical use of these techniques. Therefore, a more direct gas chromatographic technique has been developed which is outlined in the next section. Using this procedure molar solubilization ratios have been measured for seven pure solubilizates in three different surfactant solutions. The measured molar solubilization ratios and correlations relating them to the molecular properties of the solubilizates are then presented. Further, results on the solubilization of binary mixtures of benzene + hexane in a number of surfactant systems as well as some data on the solubilization of mixtures of benzene + cyclohexane and of cyclohexane + hexane are presented. The selectivity ratio for the solubilization of benzene over hexane or over cyclohexane is calculated from the measured molar solubilization ratios. In addition, the effect of ionic strength and of the concentration of surfactant on the molar solubilization ratios of the individual components and thus on the selectivity are briefly explored. The last section summarizes the main results.

EXPERIMENTAL

Materials

The following organic liquids have been used as solubilizates: *n*-hexane, cyclohexane, cyclohexene, *n*-decane, benzene, toluene, and carbon tetrachloride. The solubilizates have been chosen such that they cover a large range of molecular volumes and polarities and comprise molecules belonging to at least two chemical families (aromatic and saturated). All organic liquids, obtained from commercial sources in reagent grade, have been used as received.

The surfactants: cetyl pyridinium chloride (CPC (Fluka)), sodium deoxycholate (SDC (Sigma)), dodecyl ammonium chloride (DAC (Eastman)), dodecyl trimethyl ammonium

chloride (DTAC (Eastman)), sodium diamyl sulfosuccinate (Aerosol AY (American Cyanamid)), and sodium dodecyl sulfate (SDS (BDH Chemicals)) have been used without any further purification of the commercial samples. All the above surfactants are highly water soluble and are practically insoluble in nonpolar solvents. Sodium chloride has been used to change the ionic strength of the surfactant solutions in some of the experiments.

Evaluation of the Stripping Method

A stripping column was constructed in order to evaluate the usefulness of the stripping method for determining the molar solubilization ratios for binary solubilizate mixtures. The procedure used was as follows: a few milliliters (1–2 ml) of 0.1 *M* CPC solution containing solubilized benzene and hexane is injected into the sample chamber of the stripping column by means of a gas tight syringe. The carrier gas (He) enters the bottom of the chamber and passes through a coarse glass frit which serves as support for the liquid sample as well as distributor for the carrier gas. The carrier gas bubbles through the liquid sample, stripping the solubilizates. The effluent gas from the column is dried of water vapors by passing through a drying tube containing NaOH. (Drierite was used initially but was found to adsorb the hydrocarbons.) The dried carrier gas containing the stripped solubilizates is then gas chromatographically analyzed.

The experiments have shown that the total time necessary to strip the solubilizates from the sample is too long. Consequently, benzene and hexane enter the chromatographic column over an extended period of time, resulting in very broad overlapping peaks. The difficulties in stripping benzene and hexane efficiently can be attributed to their low volatilities compared to that of the components (CH₄, C₂H₆, C₃H₈, *n*-C₄H₁₀, *cis*-C₄H₈, *iso*-C₄H₁₀, etc.) analyzed successfully by Miller *et al.* (11) by this technique. Because of the above limitation, this technique has been no longer used in this work. The method is, however, ade-

quate to study the solubilization of gases and of very volatile liquids.

Evaluation of the Extraction Method

Thomas and Christian (6) used the liquid-liquid extraction procedure mentioned earlier to analyze the mixed solubilization of benzene and cyclohexane in sodium deoxycholate micelles. The applicability of this technique to common surfactants has been investigated here as follows: a 100-ml solution of 0.1 *M* CPC has been contacted with 20 ml of CCl_4 and allowed to equilibrate. The benzene and hexane solubilized in the CPC solution are assumed to be extracted into the CCl_4 phase. A few microliters of the CCl_4 phase was then chromatographically analyzed to determine the amounts of the two solubilizates. To examine whether any benzene or hexane remained in the CPC solution after the first extraction, the surfactant solution is contacted with fresh CCl_4 and the CCl_4 phase is analyzed again. The analysis shows that large amounts of benzene and hexane still remain in the aqueous phase after the first extraction. It has therefore been concluded that the liquid-liquid extraction technique using CCl_4 as extractant cannot be used as a general procedure for all the surfactant systems. In order to use this technique, one would have to choose proper extractants for specific surfactant systems so as to ensure that the extraction efficiency is sufficiently large. Also two or more extraction stages might be necessary. Because of these limitations this method has not been explored any further.

Direct Injection Gas Chromatography

Trace organics in water can be analyzed by using direct aqueous injection gas chromatography with flame ionization detection (12). This is possible because of the extremely high sensitivity of the flame ionization detector for hydrocarbons and insensitivity toward water. The advantage of direct injection analysis is that it eliminates errors occurring during the stripping or the extraction stages in the pre-

viously described techniques. Because of its simplicity it permits more rapid analysis of samples. In the present work all the measurements have been carried out using this direct injection gas chromatography technique.

Sample Preparation

Samples were prepared by combining 10 ml of the surfactant solution and 10 ml of the organic phase to be solubilized in glass sample bottles which were then sealed to prevent evaporation. The samples were allowed to equilibrate at 25°C for a period of at least 24 hr during which they were shaken periodically. Considerable mixing was necessary in order to achieve equilibrium. Some degree of emulsification was found to occur in a few cases, depending upon the surfactant and solubilizates. When emulsification occurred, the equilibrated samples were either centrifuged or allowed to settle for several days so as to demulsify the systems. In all the binary solubilization experiments, the surfactant solution was contacted with an organic mixture of known composition. The organic phase volume was large enough so that its composition remained essentially unchanged during the solubilization process.

Analysis of Samples

The samples of surfactant solutions containing the solubilizates were analyzed by gas chromatography to determine the extent of solubilization. Two microliters of the aqueous phase were injected into the injection port of a dual column Perkin-Elmer Model 900 gas chromatograph equipped with a flame ionization detector. The columns used were of 1/8-in. I.D. and 12 ft in length. The column packing was 1,2,3-Tris (2-cyanoethoxyl) propane supported on calcined diatomaceous earth (Applied Science, State College, Pa.). Helium was used as the carrier gas at a flow rate of 30 ml/min. The column temperature was kept at approximately 10 to 20°C below the normal boiling point of the solubilizate

being analyzed. The output signal from the detector was recorded on a strip chart recorder, and the peak areas were measured and translated into amounts of solubilizates using the calibrations developed. The water and the surfactant present in the injected sample create no difficulties in the analysis. Because of the insensitivity of the detector toward water a water peak does not form. The surfactant remains at the injection port as a solid residue because of its high boiling point. The amount of residue formed is very small because of the small volumes of the samples (2 μ l) being injected. The residue can be removed periodically by cleaning the injection port.

Estimation of Errors

An error analysis has been carried out (13) taking into account the sources of error and using standard statistical techniques. The sources of error include the presence of minute

emulsion droplets, variations in the sample volumes injected, in the determination of chromatographic peak areas, in the preparation of samples and in the construction of calibration curves. The uncertainty in the reported experimental results are estimated to have an upper bound of 11%.

RESULTS AND DISCUSSION

Experimental Data on Single-Component Solubilization

The molar solubilization ratios of seven hydrophobic liquids have been determined in three surfactant solutions of CPC, DAC, and SDS. The surfactants have been used at 0.1 *M* concentration. All the measurements have been made at 25°C. Table I contains the solubilization data for the systems mentioned above. The results are expressed as molar solubilization ratios which is defined by the relation

molar solubilization ratio

$$= \frac{\text{total moles of solubilizate in the aqueous phase} - \text{moles of singly dispersed solubilizate in the aqueous phase}}{\text{total moles of surfactant in the aqueous phase} - \text{moles of singly dispersed surfactant in the aqueous phase}} \quad [1]$$

The numerator in the above equation accounts for the total number of moles of the solubilizate contained in the micelles, while the denominator refers to the total number of moles of the surfactant present in the form of micelles. The concentration of the singly dispersed solubilizates in the micellar solutions is taken to be the same as its solubility in pure water. In the case of binary solubilization, the concentrations of the singly dispersed solubilizates are taken to be pure component water solubilities multiplied by the mole fraction of the corresponding component in the bulk solubilizate phase (which is in equilibrium with the aqueous micellar phase). This implicitly assumes ideal behavior for binary mixtures of the solubilizates. This is a reasonable as-

sumption for mixtures involving benzene, hexane, and cyclohexane that have been studied here. Moreover, since the number of moles of solubilizates incorporated into the micelles are much larger than those of singly dispersed solubilizates, the results are completely unaffected by the nonidealities (if any) of binary hydrocarbon mixtures. The number of moles of singly dispersed surfactant is assumed to be equal to the critical micelle concentration (CMC) of the surfactant in water. Of course, in the presence of solubilizates, a slight depression in the magnitude of the CMC occurs (1-3). However, the total surfactant concentration used in the experiments is so large that the amount of surfactant present as micelles is relatively unaffected by the small

TABLE I
Molar Solubilization Ratios of Hydrophobic
Molecules at 25°C

Solubilizate	Moles of solubilizate per mole of surfactant in micelles at 25°C		
	0.1 M CPC	0.1 M DAC	0.1 M SDS
<i>n</i> -Decane	0.32	0.42	0.20
<i>n</i> -Hexane	0.77	1.08	0.39
Cyclohexane	1.15	1.68	0.78
Carbon tetrachloride	1.47	1.88	0.69
Cyclohexene	1.72	2.47	1.13
Toluene	2.22	2.51	1.36
Benzene	2.99	3.13	1.68

depression in the CMC. The water solubility and the CMC data used in the calculation of the molar solubilization ratios are tabulated in Tables II and III.

The measured molar solubilization ratios in CPC, DAC, and SDS systems are plotted in Figs. 1–3, respectively, against the molecular volume v of the solubilizate. A reasonable correlation is obtained, with the molar solubilization ratio decreasing as the molecular volume of the solubilizate increases. From the curve fitting of the data, one can obtain the following empirical correlations between the molar solubilization ratio j/g and the molecular volume v (in Å³) of the solubilizates. (Here j refers to the number of solubilizate molecules

in a micelle and g is the number of surfactant molecules in the micelle.)

For CPC,

$$j/g = 1.43 \times 10^6 v^{-2.66}, \quad [2]$$

for DAC,

$$j/g = 8.25 \times 10^5 v^{-2.51}, \quad [3]$$

and for SDS,

$$j/g = 5.39 \times 10^5 v^{-2.58} \quad [4]$$

The data correlated reasonably well with the molecular volume, but there is appreciable scatter. The molecular volumes used in the above correlations have been estimated from liquid density data (14).

One may observe from Figs. 1–3 that some of the molecules show large deviations from the above correlations. The most noticeable is toluene, which has nearly the same molecular volume as cyclohexane but is solubilized to a greater extent in all the three surfactants. More significantly, it appears that the molar solubilization ratios are better correlated independently against the molecular volumes of saturated and aromatic molecules. Indeed such correlations have previously been presented in the literature (1, 4, 5, 15). In order to improve the correlations given by Eqs. [2]–[4], we take into account the polarity of the solubilizate molecules in addition to their molecular volume. The choice of polarity as a

TABLE II
Properties of Solubilizates^a

Solubilizate	Water solubility (moles/liter)	Molecular volume (Å ³ per molecule)	Interfacial tension against water (dynes/cm)
<i>n</i> -Decane	6×10^{-8} (23)	323 (14)	52.00 (25)
<i>n</i> -Hexane	7×10^{-4} (24)	217 (14)	50.70 (25)
Benzene	2.3×10^{-2} (24)	146 (14)	33.93 (25)
Toluene	7.2×10^{-3} (24)	176 (14)	36.10 (25)
Cyclohexane	8.9×10^{-4} (24)	179 (14)	50.20 ^b
Cyclohexene	2.6×10^{-3} (23)	167 (14)	44.2 (25)
Carbon tetrachloride	7.54×10^{-3} (23)	161 (14)	45.00 (25)

^a The reference for a listed value is given in parentheses next to that value.

^b Determined by Wilhelmy Plate method at 25°C in this laboratory.

TABLE III
Critical Micelle Concentrations (CMC) of Surfactants

Surfactant	Chemical formula	CMC at 25°C (M)	References
Dodecyl ammonium chloride, DAC	$\text{CH}_3(\text{CH}_2)_{11}\text{N}^+\text{H}_3\text{Cl}^-$	1.2×10^{-2}	(18, 19)
Dodecyl trimethyl ammonium chloride, DTAC	$\text{CH}_3(\text{CH}_2)_{11}\text{N}^+(\text{CH}_3)_3\text{Cl}^-$	2×10^{-2}	(19, 20)
Sodium dodecyl sulfate, SDS	$\text{CH}_3(\text{CH}_2)_{11}\text{SO}_4^-\text{Na}^+$	8.1×10^{-3}	(2)
Cetyl pyridinium chloride, CPC	$\text{CH}_3(\text{CH}_2)_{15}\text{N}^+(\text{CH})_5\text{Cl}^-$	9×10^{-4}	(21)
Sodium diamyl sulfosuccinate, Aerosol AY	$\text{CH}_2-\text{COOC}_5\text{H}_{11}$ $\text{CH}-\text{COOC}_5\text{H}_{11}$ SO_3^-Na^+	3×10^{-2}	(22)

molecular parameter is based on the fact that the aromatic molecules differ somewhat in their polarity (due to aromaticity) from the saturated molecules and, as shown by theory

(16), this polarity difference is partly responsible for the differences in their solubilization capacity. Anyone of a number of physical properties of the solubilizates may probably

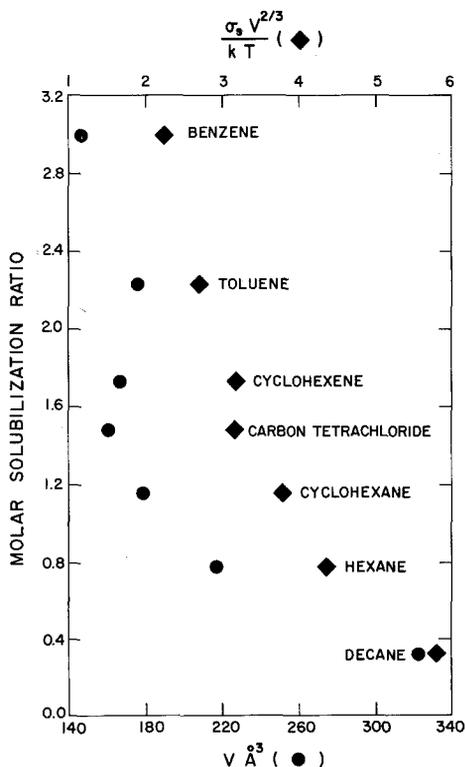


FIG. 1. Molar solubilization ratio of hydrophobic solubilizates in 0.1 M CPC solution against the molecular volume v and against the volume-polarity parameter $\sigma_s v^{2/3}/kT$ of the solubilizate.

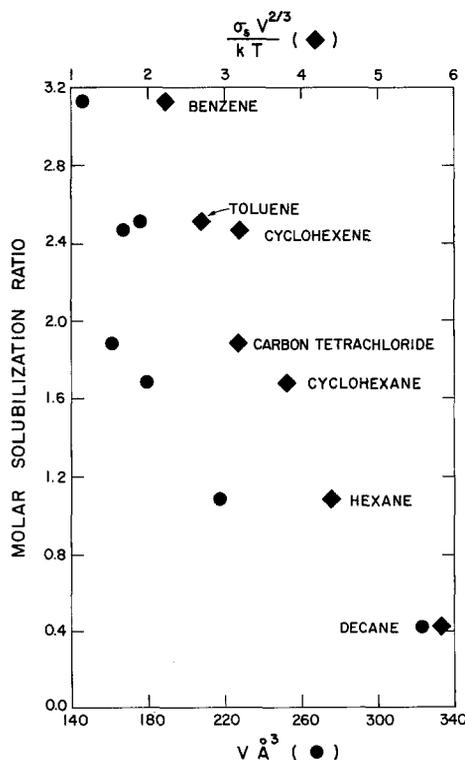


FIG. 2. Molar solubilization ratio of hydrophobic solubilizates in 0.1 M DAC solution against the molecular volume and against the volume-polarity parameter of the solubilizate.

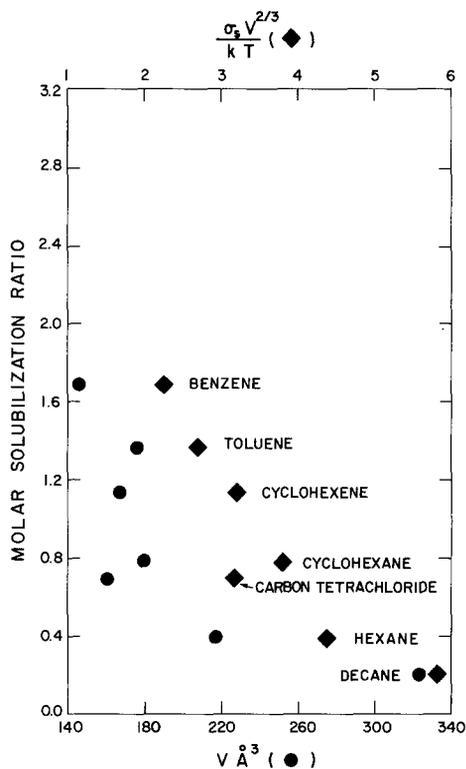


FIG. 3. Molar solubilization ratio of hydrophobic solubilizes in 0.1 *M* SDS solution against the molecular volume and against the volume–polarity parameter of the solubilize.

serve as an index of their polarity. However, theories for micelle formation and solubilization (16) show that an important contribution to the free energy of micellization is provided by the interfacial free energy of the micellar core–water interface. This interfacial free energy is likely to be affected by the extent of solubilization and by the interfacial tension between solubilize and water which depends on polarity. Therefore, a quantitative measure of polarity can be provided by the interfacial tension of the solubilize against water, σ_s . The dimensionless quantity $\sigma_s v^{2/3}/kT$, where k is the Boltzmann constant and T is the absolute temperature, includes the effects of both molecular volume and the polarity of the solubilize and is used as the combined molecular volume–polarity parameter. The molar solubilization ratios are plotted against the

combined volume–polarity parameter in Figs. 1–3 for CPC, DAC, and SDS micellar systems. The data in the figures show that the correlations are somewhat improved. Using a regression analysis, the following correlations are obtained:

for CPC,

$$j/g = 22.9[\sigma_s v^{2/3}/kT]^{-2.3}, \quad [5]$$

for DAC,

$$j/g = 29.5[\sigma_s v^{2/3}/kT]^{-2.3}, \quad [6]$$

and for SDS,

$$j/g = 13.2[\sigma_s v^{2/3}/kT]^{-2.3}. \quad [7]$$

In the above correlations kT is expressed in ergs, v is expressed in \AA^3 and σ_s in dynes per centimeter. The data show an improved correlation against the combined volume–polarity parameter rather than against the molecular volume alone. The above correlations also make it clear that the molar solubilization ratios are dependent on the type of the surfactant as well. CPC and DAC are better solubilizers than SDS. Since DAC and SDS have identical hydrocarbon tail lengths, the difference in the solubilization capabilities of the two surfactants is primarily due to differences between their polar head groups.

Solubilization of Binary Hydrocarbon Mixtures

The correlations shown in Figs. 1–3 suggest that selective solubilization may occur for a binary mixture composed of a slightly polar solubilize having a small molecular volume and a nonpolar solubilize having a larger molecular volume. Preferential solubilization is expected for the slightly polar solubilize of smaller molecular volume. The binary systems chosen to examine the existence of selective solubilization are benzene + hexane, benzene + cyclohexane, and cyclohexane + hexane. One may note that the solubilization of benzene + cyclohexane mixtures in sodium deoxycholate surfactant solutions showed total absence of selectivity (6). This only result available in literature on binary

hydrocarbon solubilization will be interpreted below in the light of the present experimental data.

Solubilization of benzene + hexane mixtures. The molar solubilization ratios for benzene + hexane mixtures solubilized in five different surfactant systems have been determined against the composition of the bulk solubilize phase which is in equilibrium with the aqueous phase. The surfactants that have been studied include 0.1 M CPC, 0.1 M DAC, 0.1 M SDS, 0.1 M DTAC, and 0.3 M Aerosol AY. The data are plotted in Figs. 4–8. The measured molar solubilization ratios have been used to calculate the selectivity ratio of benzene over hexane defined as

selectivity ratio for benzene

$$= \frac{j/g \text{ for benzene in micelle}}{j/g \text{ for hexane in micelle}}, \quad [8]$$

$$= \frac{X_{\text{benzene}}}{X_{\text{hexane}}} \text{ in bulk solubilize phase}$$

where X_{benzene} and X_{hexane} are the mole frac-

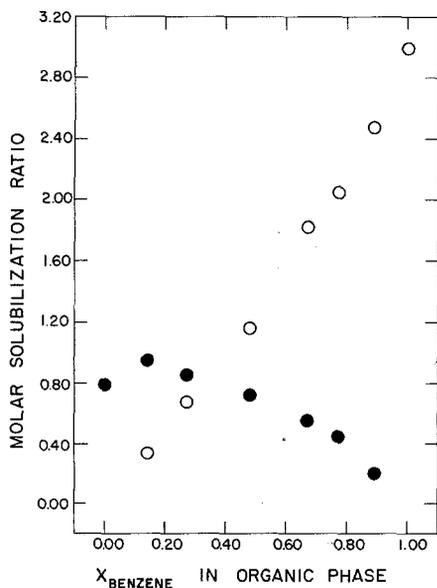


FIG. 4. Molar solubilization ratio of benzene and hexane in 0.1 M CPC solution as a function of the composition of the bulk solubilize phase: ●, hexane; ○, benzene.

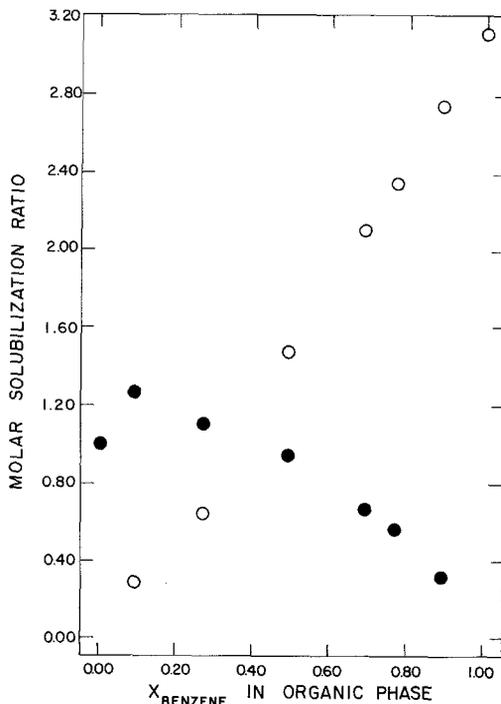


FIG. 5. Molar solubilization ratio of benzene and hexane in 0.1 M DAC solution as a function of the composition of the bulk solubilize phase: ●, hexane; ○, benzene.

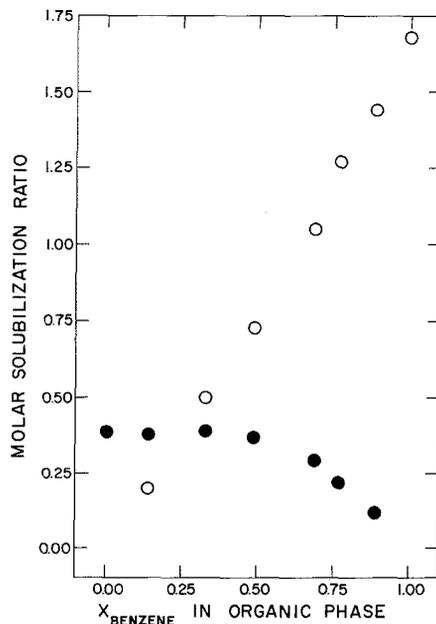


FIG. 6. Molar solubilization ratio of benzene and hexane in 0.1 M SDS solution as a function of the composition of the bulk solubilize phase: ●, hexane; ○, benzene.

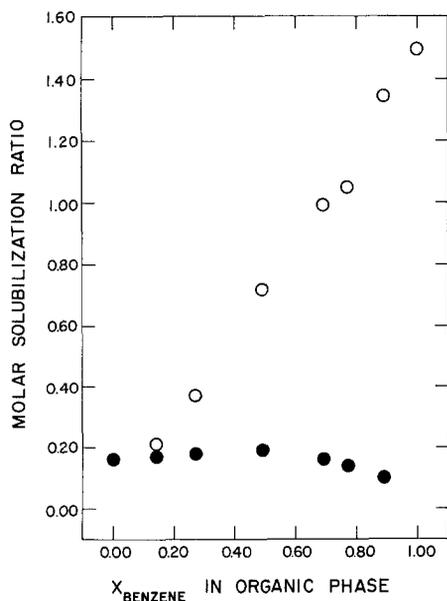


FIG. 7. Molar solubilization ratio of benzene and hexane in 0.1 M DTAC solution as a function of the composition of the bulk solubilize phase: ●, hexane; ○, benzene.

tions of benzene and hexane in the bulk solubilize phase. The calculated selectivity ratios are plotted against the composition of the sol-

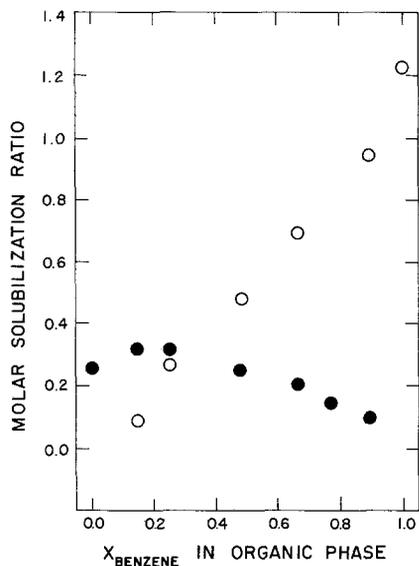


FIG. 8. Molar solubilization ratio of benzene and hexane in 0.3 M Aerosol AY solution as a function of the composition of the bulk solubilize phase: ●, hexane; ○, benzene.

ubilize phase for the five surfactant systems mentioned above (Fig. 9). The selectivity ratios displayed by the five surfactants are significantly different from one another. The greatest selectivity ratio of about 7 is found in DTAC. The least selective surfactant is DAC with the remaining surfactants showing intermediate selectivity ratios. The selectivity ratio increases with decreasing concentration of benzene in the bulk solubilize phase.

DTAC, SDS, and DAC have the same hydrocarbon chain lengths. Thus, the nature of their polar head groups strongly affects the selectivity ratio for benzene. The high selectivity for benzene seems to be accompanied by the low molar solubilization ratios for both benzene and hexane. The selectivity for benzene increases in the order: DAC < CPC < SDS \approx Aerosol AY < DTAC, while the solubilization capacity decreases in the same order.

Relationship of selectivity to pure component solubilization behavior. The molar solubilization ratios of the binary systems, benzene + cyclohexane and cyclohexane + hexane

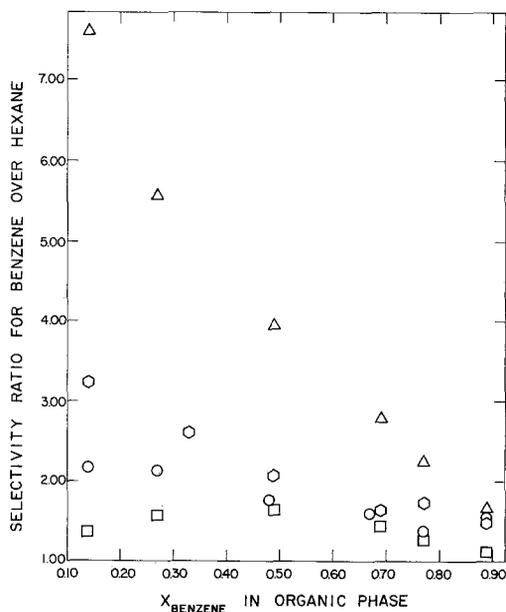


FIG. 9. Selectivity ratio for benzene as a function of the composition of the bulk solubilize phase: ○, CPC; □, DAC; ◇, SDS; △, DTAC; ○, Aerosol AY.

have been determined in 0.1 M CPC as a function of the composition of the solubilize phase. The results are presented in Figs. 10 and 11. A plot of the selectivity ratio versus organic phase composition is shown in Fig. 12. Also included, for comparison, are the selectivity ratios for the benzene + hexane system. The magnitude of the selectivity ratios for the three systems follow the order which is expected from the pure component solubilization data in CPC (Table I). The molar solubilization ratios of the pure components are 2.99, 1.15, and 0.77 for benzene, cyclohexane, and hexane, respectively. From these pure component values one can expect the system benzene + hexane to show the highest selectivity for benzene, since the two solubilizes have widely different molar solubilization ratios. For the same reasons, the system cyclohexane + hexane should exhibit the least selectivity for cyclohexane. The present experimental results shown in Fig. 12 follow exactly this trend. Thus it is apparent that the pure component molar solubilization ratios

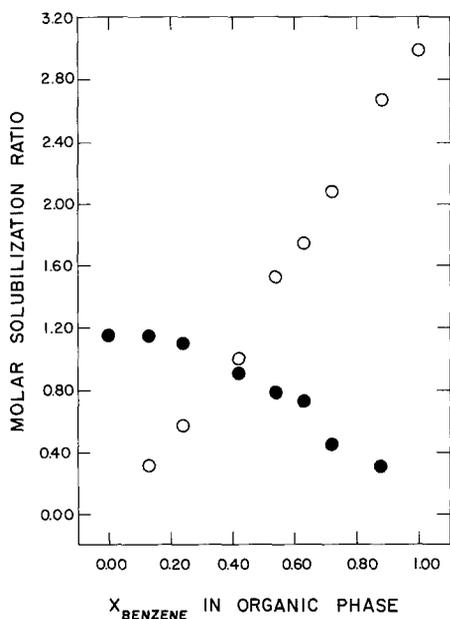


FIG. 10. Molar solubilization ratio of benzene and cyclohexane in 0.1 M CPC solution as a function of the bulk solubilize phase composition: ●, cyclohexane; ○, benzene.

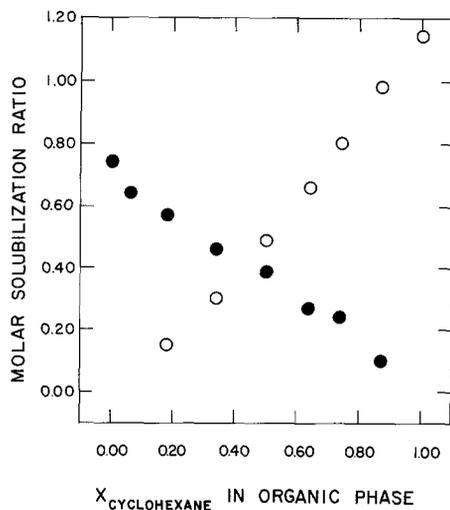


FIG. 11. Molar solubilization ratio of cyclohexane and hexane in 0.1 M CPC solution as a function of the bulk solubilize phase composition: ●, hexane; ○, cyclohexane.

can be used to anticipate the order of selectivity for any one component present in a mixture of solubilizes.

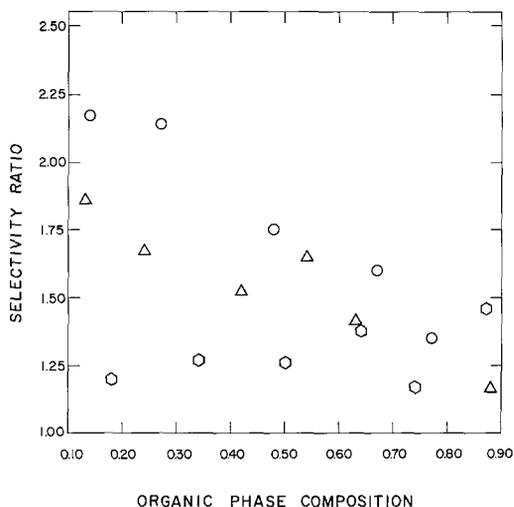


FIG. 12. Selectivity ratio of benzene over hexane (○), benzene over cyclohexane (Δ), and cyclohexane over hexane (○) in 0.1 M CPC solution as a function of the bulk solubilize composition. The abscissa refers to the mole fractions of benzene (in benzene + hexane), benzene (in benzene + cyclohexane), and cyclohexane (in cyclohexane + hexane), respectively.

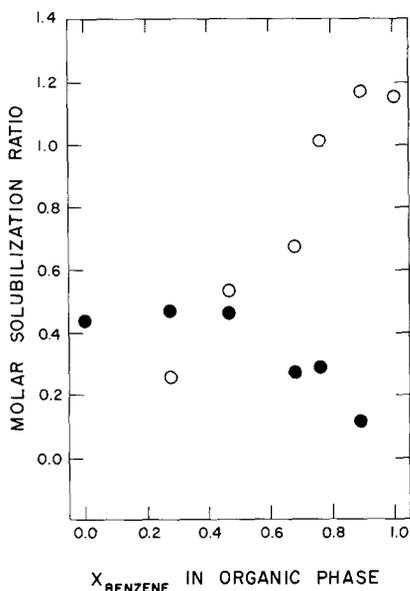


FIG. 13. Molar solubilization ratios of benzene and cyclohexane in 0.3 M Aerosol AY solution as a function of the bulk solubilize phase composition: ●, cyclohexane; ○, benzene.

Similar results are shown for the Aerosol AY in Figs. 13 and 14. The molar solubilization ratios of benzene and cyclohexane are plotted in Fig. 13 and the selectivity ratios in Fig. 14, against the composition of the bulk solubilize phase. Again the data indicate a higher selectivity ratio for benzene over hexane than for benzene over cyclohexane; this is consistent with the pure component molar solubilization ratios. These results also explain the observed absence of selectivity for benzene over cyclohexane in solutions of sodium deoxycholate. In sodium deoxycholate micelles which are made of very small primary aggregates, the molar solubilization ratios of both benzene and cyclohexane as pure solubilizes are practically comparable. Consequently, when their mixtures are solubilized one would expect no selectivity for benzene over cyclohexane.

Effect of surfactant and electrolyte concentrations on selectivity. Molar solubilization ratios for the solubilization of benzene + hexane in 0.05 M CPC and in 0.1 M CPC + 0.1 M

NaCl solutions have been measured to determine whether the preferential solubilization of benzene is affected by the decrease in the surfactant concentration and by the addition of the electrolyte. Figures 15 and 16 show the molar solubilization ratios under these two conditions. The results are compared with those obtained for the solubilization in 0.1 M CPC. One can observe that the effectiveness of the surfactant to solubilize is increased by the addition of the electrolyte. When the surfactant concentration is lowered from 0.1 to 0.05 M, the molar solubilization ratio of hexane is somewhat decreased, while that of benzene remains practically unaltered. Increased molar solubilization ratios in the presence of electrolytes and decreased ratios in the presence of lower concentrations of surfactant have been reported in literature (4, 5), consistent with the present observations. Plots of selectivity ratios against the solubilize phase composition are shown in Fig. 17. The addition of the electrolyte causes a slight decrease in the selectivity ratio, whereas the decrease

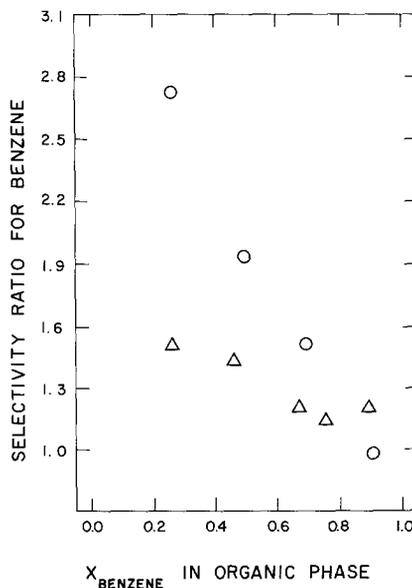


FIG. 14. Selectivity ratios for benzene over hexane (○) and for benzene over cyclohexane (Δ) in 0.3 M Aerosol AY solution as a function of the composition of the bulk solubilize phase.

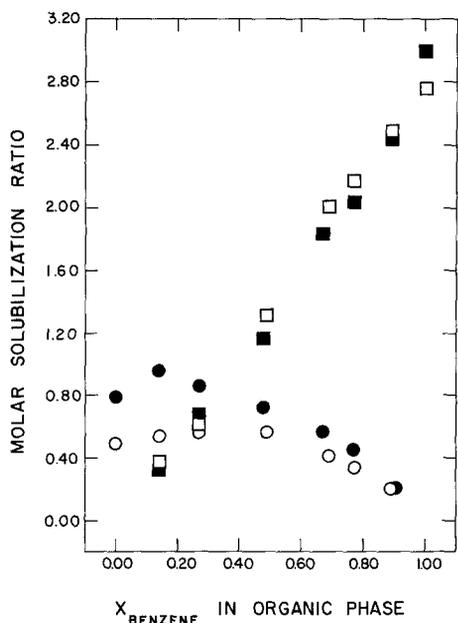


FIG. 15. Influence of concentration of surfactant on the molar solubilization ratio of benzene and hexane in the CPC solutions as a function of the composition of the bulk solubilize phase: ●, ○, hexane; ■, □, benzene; ●, ■, 0.1 M CPC; ○, □, 0.05 M CPC.

in the surfactant concentration causes an increase in the selectivity ratio.

Synergistic solubilization of hexane. The binary solubilization results presented in Figs. 4–8 for benzene + hexane system show that the amount of hexane solubilized increases slightly or remains constant even as the mole fraction of hexane in the bulk solubilize phase is decreased. For example, in Fig. 4, the amount of hexane solubilized at a bulk solubilize composition of 0.14 mole fraction benzene is greater than the amount of hexane solubilized when the solubilize phase is pure hexane. Thus, it appears that the solubilization of small amounts of benzene has a synergistic effect in increasing the amount of hexane solubilized. This synergism is observed in all the surfactant systems studied, though with varying degrees. This synergism was examined from a theoretical point of view in Refs. (16) and (17) with the conclusion that some of the benzene molecules solubilized are likely to be

located at the micellar surface, especially when the concentration of benzene in the micelles is very small.

CONCLUSIONS

A direct aqueous injection gas chromatographic method has been employed in order to determine the extent of solubilization of single component and binary mixtures of hydrocarbons in aqueous surfactant solutions. This technique is more versatile, simple to use, and reliable than the other available techniques, especially for mixtures of solubilizates.

Correlations of molar solubilization ratio against the molecular volume of the solubilizates and against a combined molecular volume–polarity parameter for the solubilizates have been obtained for three surfactant systems. The interfacial tension of the solubilize against water is taken as a measure of the polarity in developing the correlations. These correlations clearly show that, in general, molecules which have a smaller molecular volume and a slight polarity are preferentially solubilized.

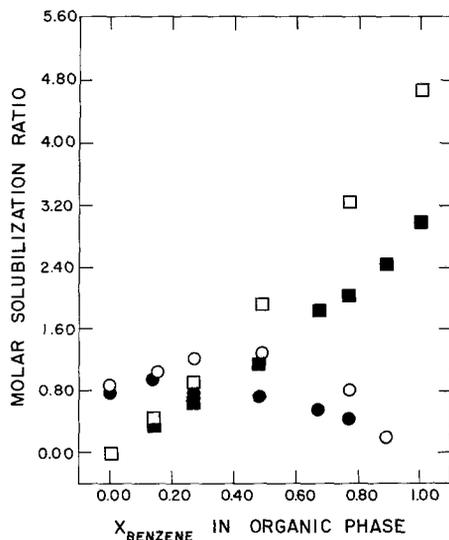


FIG. 16. Influence of electrolyte concentration on the molar solubilization ratio of benzene and hexane in 0.1 M CPC solutions, as a function of the bulk solubilize phase composition: ●, ○, hexane; ■, □, benzene; ●, ■, 0 NaCl; ○, □, 0.1 M NaCl.

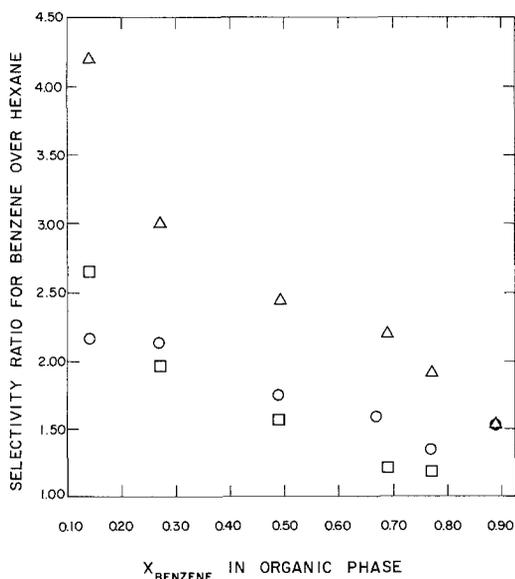


FIG. 17. Selectivity ratio for benzene over hexane in CPC solutions as a function of the composition of the bulk solubilize phase: \circ , 0.1 M CPC, 0 NaCl; \triangle , 0.05 M CPC, 0 NaCl; \square , 0.1 M CPC, 0.1 M NaCl.

Molecules having different molar solubilization ratios as pure components exhibit selective solubilization of one molecule over another when they are solubilized as mixtures. This has been demonstrated for the solubilization of benzene + hexane mixtures in five different surfactant solutions. A selectivity ratio for benzene has been determined as a function of the composition of the bulk solubilize phase. This selectivity ratio is found to be the largest at low concentrations of benzene in the bulk phase. It is also found that the surfactants which have the highest selectivity also have the lowest capacity for solubilization. The selectivity for benzene over hexane can be understood in terms of its smaller molecular volume and aromaticity. The results for two other binary mixtures involving benzene, hexane, and cyclohexane show that the selective solubilization behavior in binary systems parallels the behavior that would be anticipated from the corresponding pure component molar solubilization ratios. That is, the largest selectivity is found to occur in systems in which the cor-

responding pure component molar solubilization ratios differ the most.

The addition of electrolyte to a surfactant system is found to increase the molar solubilization ratios for both benzene and hexane, while very slightly decreasing the selectivity ratio for benzene. Decreasing the surfactant concentration results in an increase in the selectivity ratio for benzene, primarily because of a decrease in the molar solubilization ratio of hexane. Further, all of the solubilization data for binary mixtures indicate the existence of a synergistic effect on the solubilization of hexane in the presence of small amounts of benzene, the extent of which is different for various surfactants.

ACKNOWLEDGMENT

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