The Solubility of Gases in Aqueous Solutions of Decyltrimethyl- and Cetyltrimethylammonium Bromide

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Measurements have been made to determine the solubilities of oxygen, argon, methane, ethane, propane, and carbon tetrafluoride at elevated pressures in aqueous solutions of decyltrimethylammonium bromide and cetyltrimethylammonium bromide. The solubility of each gas follows Henry's law at all surfactant concentrations. Below the critical micelle concentration, the gas solubilities are independent of surfactant concentration and closely approximate the corresponding solubilities in pure water. Above the critical micelle concentration, the gas solubilities increase linearly with surfactant concentration indicating micellar solubilization. The intramicellar solubilities of the individual gases calculated from these latter data are found to be comparable to those determined previously with anionic surfactants of the alkyl sulfate class suggesting that, with ionic surfactants, the nature of the head group is of little consequence in determining the magnitude of intramicellar solubilities. The micellar solubilities of CF_4 in these surfactants are found to be much smaller than the solubilities of hydrocarbon gases in these same micelles indicating that the tendency for mutual exclusion exhibited by fluorocarbons and hydrocarbons in bulk solution is also operative in micellar solubilization. These latter data are used to further test the applicability of the Laplace pressure model for describing the degree of solubilization by various surfactants. © 1985 Academic Press, Inc.

INTRODUCTION

Micellar aggregates present in aqueous solutions of surfactants are capable of solubilizing nonpolar gases in much the same manner as nonpolar solids and liquids. While this phenomenon was noted quite early by McBain and co-workers (1a–c), it has received comparatively little attention over the years as indicated by the paucity of citations in the bibliography contained in Ref. (1). Nevertheless, measurements of gas solubility in micellar solutions are quite useful in that they readily provide information about standard free energy changes associated with solubilization processes. Since gas molecules are small and present at low concentrations in these experiments, it can be assumed with reasonable confidence that the solubilized gas molecules do not perturb the micelles within a solution to any appreciable extent thus facilitating comparisons between solubiliza-

tion equilibria and the corresponding equilibria involving gases dissolved in homogeneous bulk phases. It is this feature that makes gas solubilization measurements particularly useful as a means for studying micelles.

Previous studies in this laboratory have examined how the degree of solubilization in solutions of ionic surfactants depends upon the nature of the gas (1h), the presence of amphiphilic additives (1i), salinity (1j), temperature (1o), and the size of the hydrophobic portion of the anions of alkyl sulfate class surfactants (1m). This paper examines the roles that alkyl chain length and head group play in determining the extent of solubilization. It reports the results of a series of solubility measurements involving six gases of widely differing properties (O_2, Ar, CH_4, C_2H_6, C_3H_8, CF_4) in solutions of two cationic surfactants, decyltrimethylammonium bromide (DTAB) and cetyltrimethylammonium

bromide (CTAB) at 26°C. The results of a series of solubility determinations for CF_4 in micellar solutions of sodium dodecyl sulfate (SDS) at 25°C are also reported. The gas CF_4 is included in this work in order to ascertain whether the extreme positive deviations from ideality exhibited by mixtures of fluorocarbons and hydrocarbons in the bulk phase occur in micelles as well.

EXPERIMENTAL

The method used to determine gas solubilities has been described in detail previously (1h). It differs from other common methods in that it involves measuring the volume of gas released from solutions saturated at elevated pressures. The procedure followed consists of three steps: (i) the solution to be studied is allowed to equilibrate with the gas of interest at an elevated pressure in a thermostated bomb equipped with a magnetically driven stirrer; (ii) the stirrer is stopped and the solution is allowed to become still whereupon the pressure is released; (iii) after a short delay (~1 min) in order for thermal equilibrium to be reestablished following the release of the gas, the magnetic stirrer is again activated and the volume of gas released from the supersaturated solution is measured manometrically at ambient pressure. In this manner one determines the number of moles of gas released, Δn, as the solution proceeds isothermally from what was previously an equilibrium state at the upper pressure to a new equilibrium state at ambient pressure. The difference in pressure between these two equilibrium states, ΔP, is numerically equal to the gauge pressure recorded during the initial equilibration, step (i). The series of steps (i)–(iii) are repeated at one or more different pressures to establish that the ratios $\Delta n/\Delta P$ are independent of pressure. This was found to be the case in every instance so that the average values of $\Delta n/\Delta P$ listed in Table I can be taken to represent gas solubilities in

TABLE I

Gas Solubilities in Surfactant Solutions Expressed Moles Gas per Atmosphere in 1000 g H_2O at 26°C

Surfactant	Surfactant concentration (m)	Gas solubility $(m) \times 10^3$ [a]					
		O_2	Ar	CH_4	C_2H_6	C_3H_8	CF_4
Decyltrimethylammonium bromide	0	1.41[b]	1.51[b]	1.55[b]	1.76[b]	1.42[c]	0.27
	0.04	1.45	1.52	1.50	1.78	1.4	0.29
	0.10	1.41	1.56	1.56	2.07	2.2	0.28
	0.20	1.46	1.65	1.71	2.88	4.3	0.36
	0.30	1.54	1.72	1.93	3.70	6.2	0.41
	0.40	1.61	1.75	2.06	4.53	8.6	0.43
	0.50	1.66	1.88	2.25	5.25	10.4	0.45
Cetyltrimethylammonium bromide	0.10	1.52	1.68	1.79	3.39	6.2	0.42
	0.20	1.58	1.79	2.08	4.87	11.4	0.42
	0.30	1.72	1.92	2.41	6.42	15.6	0.56
	0.40	1.79	2.02	—	—	—	—
Sodium dodecyl sulfate[c]	0.10	—	—	—	—	—	0.37
	0.30	—	—	—	—	—	0.48
	0.50	—	—	—	—	—	0.58

[a] Average errors of solubilities measured in this experiment for O_2, Ar, CH_4, C_2H_6, C_3H_8, and CF_4 are $\pm 2 \times 10^{-5}$, $\pm 3 \times 10^{-5}$, $\pm 2 \times 10^{-5}$, $\pm 7 \times 10^{-5}$, $\pm 2 \times 10^{-4}$, and $\pm 2 \times 10^{-5}$ m, respectively.
[b] Data taken from Ref. (1m).
[c] $T = 25$°C.

the respective solutions at a partial pressure of 1 atm with Henry's law being satisfied for each system.

The cetyltrimethylammonium bromide used in experiments was purchased from Aldrich Chemical Company (Cat. No. 85,582-0, Lot No. 5814AJ), having a quoted purity of 95%. The decyltrimethylammonium bromide was from Eastman–Kodak Company (Lot No. A10E and A10F), with no quoted purity. The sodium dodecyl sulfate was BDH Prod. No. 44244 (Lot No. 9088113C), purchased from Gallard-Schlesigner Chemical Mfg. Corporation, having a quoted purity of 99.0%. Each surfactant was recrystallized once from 2-propanol and dried *in vacuo* before use. Gas chromatographic analysis of the alcohol resulting from acid-catalyzed hydrolysis of the sodium dodecyl sulfate revealed that the SDS was better than 99% pure with respect to alkyl chain length. No chemical analyses were performed on the trimethylammonium surfactants. However, sharp, well-defined CMC values of 9×10^{-4} and 5.5×10^{-2} M were obtained with the recrystallized CTAB and DTAB, respectively, using the surface tension method. The close agreement between the experimental CMC values and those recommended in the literature (2) suggests that the CTAB and DTAB surfactants used here were very pure with respect to chain length of the alkyl groups. All gases used were CP grade or the equivalent, having quoted purities of 99.0% or better for the hydrocarbon gases, and 99.7% or better for tetrafluoromethane, oxygen, and argon. The oxygen and argon were obtained from Selox Corporation while the remaining gases were purchased from Matheson. Doubly distilled water was used to make up all solutions.

RESULTS AND DISCUSSION

The gas solubilities determined in these experiments are listed in Table I. The Krafft temperature of CTAB is relatively high (~20°C) (3). Therefore, in order to avoid precipitation at higher concentrations, solu-

tions of CTAB (and DTAB) were maintained at 26°C for these experiments. Previous experiments have shown that the heats of solution of propane in micelles of sodium octyl sulfate and SDS are quite small (1o). Therefore micellar gas solubilities can be expected to be relatively insensitive to temperature so that values obtained at 26°C can be compared directly with similar data at 25°C, e.g., the solubilities of CF_4 in SDS in Table I, without introducing any appreciable error.

The solubilities of the various gases dissolved in solutions of DTAB and CTAB are shown plotted as a function of surfactant concentration in Figs. 1 and 2. The data in Fig. 1 reveal several features of interest. As noted above, the CMC for DTAB is 0.055 M. Therefore, the fact that the solubilities measured for each gas in 0.04 m solutions of DTAB are, within experimental error, the same as the corresponding solubilities in pure water reflects the absence of micelles neces-
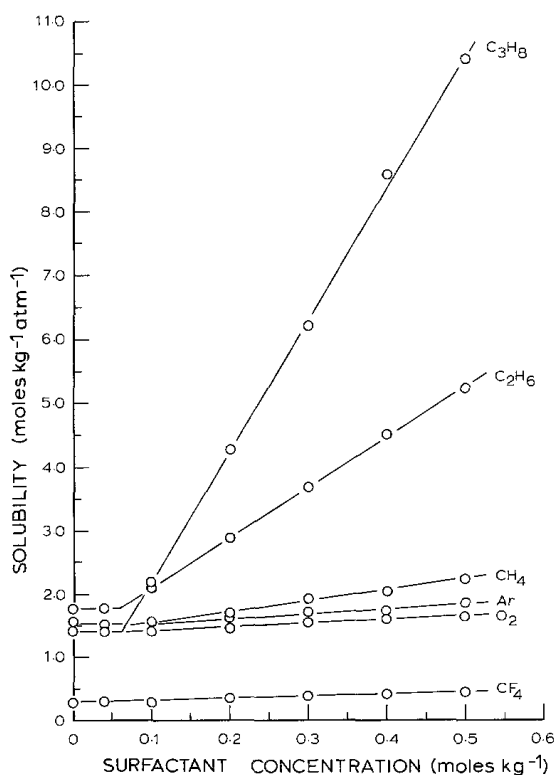

FIG. 1. Moles of gas absorbed per atmosphere in 1000 g of H_2O with added decyltrimethylammonium bromide shown as a function of surfactant concentration at 26°C.
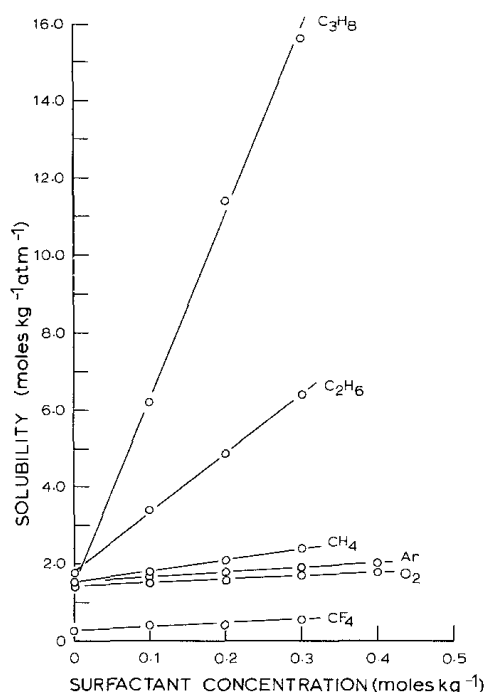
FIG. 2. Moles of gas absorbed per atmosphere in 1000 g of H$_2$O with added cetyltrimethylammonium bromide shown as a function of surfactant concentration at 26°C.

sary to induce solubilization. Above the CMC, the solubilities of each gas are seen to increase with surfactant concentration. The linearity of the rising portions of these curves indicates that while micelle concentration, hence solubilization, increases with added surfactant, the ability of micelles of DTAB to solubilize the various gases is insensitive to surfactant concentration, even at concentrations as large as 0.6 m. As seen in Fig. 2, the data obtained with CTAB exhibit the same characteristics although the extent to which the gas solubilities are enhanced by added surfactant is much greater, indicating that micelles of CTAB solubilize gases more effectively than those of DTAB. With the exception of CF$_4$, the extent to which the individual gases are solubilized in the two surfactants increases with critical temperature of each gas, as is normally the case for solutions in nonpolar solvents.[1] CF$_4$ represents a special case in

[1] The critical temperatures of O$_2$, Ar, CH$_4$, C$_2$H$_6$, and C$_3$H$_8$ fall in the sequence: 154 $\simeq$ 151 < 190 < 305 < 370 K. The critical temperature of CF$_4$ is 228 K.

view of the well-known anomalies exhibited by solutions of highly fluorinated gases such as CF$_4$ and SF$_6$ in hydrocarbon solvents (4).

If it is assumed that surfactant monomer concentration remains effectively constant above the CMC, then the slopes of the upward rising portions of the solubility data shown in Figs. 1 and 2 can be taken to be ratio of solubilized gas molecules to micellized surfactant ions present in each solution.[2] The solubilized gases constitute a highly dilute system so that the mole ratios defined by these slopes approximate mole fraction solubilities of the individual gases in micellar DTAB and CTAB at 1 atm, X_g^m. Micellar solubilities thus derived from the upward rising slopes of the data of Figs. 1 and 2 are listed for each gas in Table II. One-atmosphere solubilities of these same gases in water and various normal alkanes are included in Table II for comparison.

The gases listed in Table II are arranged in the order of increasing solubility in hydrocarbon solvents. The micellar gas solubilities for a given surfactant follow the same order. The gases are seen to be orders of magnitude more soluble in micelles than in water. On the other hand, the micellar gas solubilities are themselves substantially smaller than corresponding solubilities in bulk hydrocarbons. Furthermore, in contrast to the individual gas solubilities in hydrocarbons, which do not vary appreciably from one hydrocarbon to the next, the micellar solubility of each gas decreases markedly as the length of the

[2] Measurements of the electrochemical potential of solutions of DTAB using ion selective electrodes by Kale et al. (5), show that the activity of the decyltrimethylammonium cation decreases by roughly 50% of its value at the CMC as the surfactant concentration increases from the CMC to 0.6 M. Assuming that this decrease is the result of a decrease in monomer concentration accompanied by a corresponding increase in micellized ions, the discrepancy between the resulting concentration of micellized cations and that predicted assuming a constant monomer concentration is less than 3% at 0.6 M, the highest DTAB concentration used here. The discrepancy is expected to be even less with CTAB in view of its lower CMC.

TABLE II

Gas Solubilities at 26°C and 1 atm (Mole Fraction $\times 10^4$)

Gas	Surfactants and bulk solvents				
	CTAB[a]	DTAB[a]	SDS[b]	Water[b]	n-Alkane/carbon No.[b]
CF_4	9	4	5	0.049 (0.038)[e]	21.5/7[f], 19.7/8[g], 20.0/8[h], 18.7/10[h]
O_2	10	7	(10)[c]	0.25 (0.23)[e]	21.6/7[i], 20.9/8[i], 21.2/9[i]
Ar	13	7	(11)[d]	0.27 (0.25)[e]	25.3/6[j], 25.0/7[j], 24.5/8[j], 24.5/9[j], 24.8/10[j], 25.5/12[j], 25.9/14[j]
CH_4	29	17	(19)[c]	0.28 (0.25)[e]	50.8/6[k]
C_2H_6	155	80	(110)[c]	0.32 (0.33)[e]	325/6[l], 329/7[i], 337/8[i], 336/9[i]
C_3H_8	480	210	(320)[c]	0.26 (0.27)[e]	1160/6[m], 1160/6[n], 1170/7[n], 1200/8[m], 1230/12[n], 1265/16[n]

[a] Estimated errors: CF_4, $\pm 2 \times 10^{-4}$; O_2, Ar, CH_4, $\pm 1 \times 10^{-4}$, C_2H_6, $\pm 5 \times 10^{-4}$; C_3H_8, $\pm 10 \times 10^{-4}$.
[b] $T = 25°C$, estimated error: $\pm 2 \times 10^{-4}$.
[c] Ref. (1m).
[d] Ref. (1h).
[e] Recommended values from Wilhelm, E., Battino, R., and Wilcock, R. J., *Chem. Rev.* **77,** 219 (1977).
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alkyl chain of the surfactant ion becomes shorter. This suggests that, while the interior of a micelle is basically hydrocarbon-like in nature, the change in free energy associated with bringing a gas molecule from the gas phase to the interior of a micelle is more positive than for the equivalent process in which the gas molecule is transferred into a bulk hydrocarbon solvent, with the discrepancy becoming more pronounced as the alkyl group of the surfactant ion decreases in size.

A previous paper on this subject (1m) points out that the trends noted above can be reconciled in a quantitative manner by invoking a simple model in which the interior of a micelle is considered to resemble a submicroscopic spherical droplet of oil which is compressed by Laplace forces acting across the curved micelle–water interface. This model was first invoked by Mukerjee (6) in order to explain the odd–even alternation in free energies of micellization observed with sodium alkyl sulfates. The effect of this compression is to create a pressure difference of $P_L = 2\gamma/r$ between the micelle interior and the surrounding aqueous phase, where γ denotes the interfacial tension at the micelle surface and r is the radius of the micelle. The Laplace pressure acts to raise the chemical potential of a solubilized gas molecule, component i, by an amount $2\gamma \bar{V}_i/r$ where $\bar{V}_i$ denotes the molar volume of the solubilized gas so that the chemical potential of gas i residing in the interior of a micelle μ_i^m becomes

$$\mu_i^m = \mu_i^* + RT \ln X_i^m + 2\gamma \bar{V}_i/r. \quad [1]$$

Here R and T symbolize the universal gas constant and temperature while X_i^m denotes the mole fraction of gas i dissolved in the micelle, and μ_i^* is the chemical potential of gas i solubilized in a highly dilute Henry's law standard state. To the extent that the micelle interior can be treated as ordinary

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