Solubility of Gases in Micellar Solutions

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Measurements have been made to determine the solubilities of compressed He, O_2, Ar, CH_4, and C_2H_6 in aqueous solutions of sodium dodecylsulfate (SDS) and cetyltrimethylammonium bromide (CTAB) using a simple manometric technique. The solubility of each gas follows Henry's law and increases linearly with surfactant concentration above the critical micelle concentration. Values for the intramicellar solubility and associated ΔG for transfer of dissolved gas from water to the micellar interior are calculated from the data. The intramicellar solubility of each gas is found to be less than that in a typical hydrocarbon. The discrepancy can be explained using a simple phase separation model in which the hydrocarbon-like interior of a micelle is considered to be compressed by interfacial tension at the micelle surface.

INTRODUCTION

Solubilization of normally insoluble organic substances in aqueous solutions of colloidal electrolytes plays an important role in innumerable biological and industrial processes. As a consequence a great amount of research has been devoted to this topic as described in several comprehensive reviews (1). It is somewhat surprising, however, that the role such substances play in solubilizing gases and low-molecular-weight vapors has received comparatively little attention, with refs. (2–7) constituting a reasonably complete bibliography on this subject. As noted much earlier by McBain (1b, p. 45), studies of this nature allow one to freely vary the chemical potential of the solubilizate under isothermal conditions, thus providing a sensitive probe for examining the equilibria involved in solubilization processes.

This paper reports results obtained at 25°C with a series of gases having widely differing solubilities: He, O_2, Ar, CH_4, and C_2H_6. Solutions of an anionic surfactant (SDS) as well as one of the cationic type (CTAB) were used.

EXPERIMENTAL

The experimental equipment and procedures used in these studies are very simple. The apparatus consists of a thick-walled cylindrical brass bomb which has an observation window on the side and is jacketed such that water pumped from a remote constant temperature bath makes contact with the major portion of its external surface. The bomb rests on a variable-speed magnetic stirrer, thus allowing the agitation produced by a magnetic stirring bar in the interior of the bomb to be controlled externally. The bottom of the bomb is constructed so that the water used to control temperature passes between the top surface of the stirring motor and the pressure supporting surface at the base of the bomb proper, thus preventing conduction of heat from the motor assembly to the interior of the bomb.

An inlet line to the bomb is connected to a gas manifold through an ordinary needle valve, thus allowing the bomb to be evacuated, loaded with the gas desired, and subsequently vented to the atmosphere. Bourdon gauges, accurate to 0.25% of full scale,

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were used to record pressure. These were periodically checked against a dead weight tester to ensure their accuracy. An exit line, also attached to the bomb through a needle valve, is connected to a Warburg manometer filled with water.

The solution to be studied is made up in a glass liner which makes a close fit with the interior walls of the bomb. A clean stirring bar is added, and the liner containing the solution is placed inside the bomb. After sealing, the bomb is evacuated to a pressure somewhat above the vapor pressure of water, and the solution is allowed to outgas with stirring for several hours. The gas to be studied is introduced over the solution at the desired pressure, and the solution is allowed to equilibrate with the dense gas for a minimum of 5 hr. The stirrer is then stopped, and the solution is allowed to become still.

TABLE I

Moles of Gas Absorbed per Atmosphere in 1000 g of H_2O with Added Colloidal Electrolytes at 25°C

Solute	Gas	Moles solute	Solubility (moles gas/atm) $\times 10^3$
SDS	He	0	0.54
		0.300	0.55
	O_2	0	1.41
		0.100	1.47
		0.200	1.61
		0.300	1.70
	Ar	0	1.51
		0.100	1.63
		0.200	1.74
		0.300	1.82
	CH_4	0	1.55
		0.150	1.88
		0.300	2.09
	C_2H_6	0	1.76
		0.150	3.46
		0.300	4.99
CTAB	O_2	0.100	1.50
		0.200	1.64
		0.300	1.82
	Ar	0.100	1.63
		0.200	1.80
		0.300	1.97

The dense gas is vented through the manifold leaving the supersaturated solution under a gaseous environment at atmospheric pressure. The solution is allowed to remain this way for a measured period of time, usually between 30 sec and 1 min, in order to restore thermal equilibrium, after which the valve leading to the manometer is opened and the one to the manifold is shut. The rate of evolution from the unstirred solution is first recorded in order to correct for gas lost during the period allowed for thermal equilibration. The stirrer is then activated, thus initiating a rapid evolution of gas from the supersaturated solution. After the gas evolution has ceased as indicated by the manometer, the total volume of gas that escaped from the solution is recorded along with the atmospheric pressure and ambient temperature. Allowance is made, of course, for the partial pressure of water vapor in converting the volume recorded in the buret to moles of gas.

The SDS used in these experiments, obtained from Aldrich Chemical Company, Inc., was recrystallized from ethanol and dried *in vacuo* before use. The CTAB (Eastman technical grade) was recrystallized from an ethyl acetate–ethanol mixture and also dried *in vacuo*. All gases used were C.P. grade or the equivalent, having quoted purities of 99.0% or higher for the hydrocarbon gases and 99.5% or better for the others. Laboratory-distilled water was used without further purification.

RESULTS AND DISCUSSION

The data obtained in these experiments are the moles of gas released by a known amount of solution when the pressure is dropped from some initial elevated value to atmospheric pressure. The highest initial pressures in these experiments were the order of 10–15 atm with most data taken at pressures half this great. Henry's law can be assumed to hold under these conditions so that the moles of gas released divided by gauge pressure when normalized to the

same amount of solution constitutes a reciprocal Henry's law constant. For the purposes of this study, it proved more convenient to normalize the data to a constant amount of water, and the solubilities listed in Table I are recorded as moles of gas dissolved per atmosphere in solutions containing varying amounts of surfactant dissolved in 1 kg of water. Each value listed is the average of three experimental measurements, all taken at different pressures. The average error associated with each entry is $\pm 0.03 \times 10^{-3}$ moles of gas/atm. The accuracy of these results depends upon the fact that the evolution of gas from an unstirred supersaturated solution is sufficiently slow that any correction attributed to it is small. In these experiments which typically involved the order of 100 ml of solution, the rate of gas evolution seldom exceeded 0.6 ml/min. The total volume collected was typically 20–30 ml. Thus the correction accounting for gas that escaped during thermal equilibration following the pressure release amounted to only 1% of the recorded volume.

The solubilities of Table I are shown in Fig. 1 plotted as a function of concentration of surfactant in micellar form, $C_m = m - CMC$. Here m represents formal surfactant concentration expressed as molality and CMC denotes the critical micelle concentration. Values of 8×10^{-3} and 9×10^{-4} m were used as CMC values for SDS and CTAB, respectively, in these calculations (8). The straight lines shown in Fig. 1 were fitted to each set of data by the method of least squares, and the resulting coefficients are listed in part A of Table II. The intercept "b" for each gas represents the solubility of that gas in pure water at a partial pressure of 1 atm and is recast in the more familiar mole fraction units in part B of Table II: $X_{H_2O}^g = b/55.35$. A comparison with the values recommended by Wilhelm *et al.* (9) for these systems indicates that solubilities obtained in these experiments are quite accurate. Similarly, if the small ef-
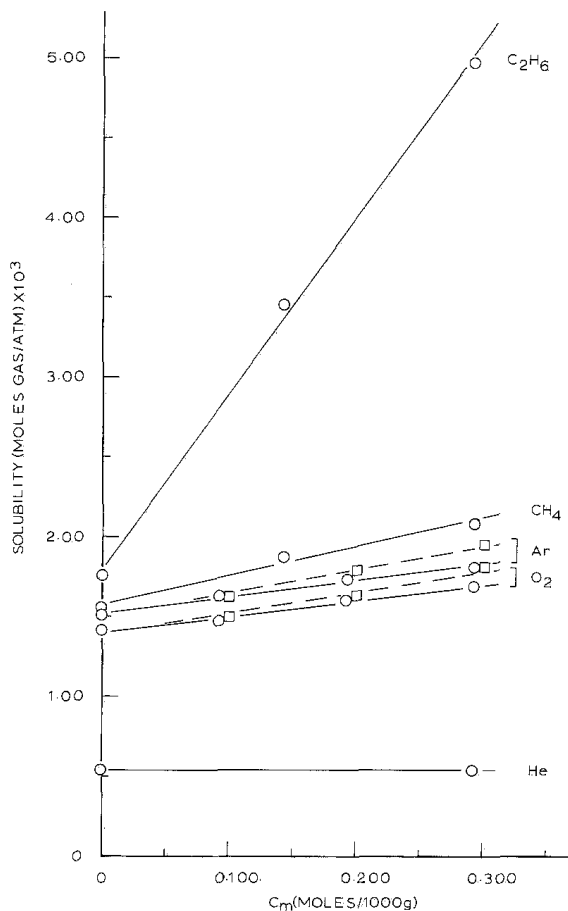

FIG. 1. Moles of gas absorbed per atmosphere in 1000 g of H_2O with added colloidal electrolyte as a function of moles of solute in micellar form at 25°C. $\bigcirc$,——SDS; $\square$,——CTAB.

fects expected from salting out and premicellar equilibria are ignored, the coefficient "a" can be identified with the gas solubility within the micelle proper, $X_{micelle}^g$. These are listed in Table IIB along with values for the distribution coefficient, K, and corresponding free energy of transfer, $\Delta G_{TR}^m = -RT \ln K$, for each system. The ΔG_{TR}^m for ethane with SDS obtained here (-3.47 kcal/mole) agrees well with that found by Wishnia for C_2H_6 with SDS in 0.1 M NaCl ($\Delta G_{TR}^m = -3.45$ kcal/mole) (6).

The gases listed in Table II are arranged in order of increasing critical temperature. Since they are all nonpolar, one expects an increasing contribution of London dispersion forces to the overall potential energy

TABLE II

A. Least-Squares Results

$$S = aC_m + b, \qquad S \approx \frac{\text{Moles gas/atm}}{1000 \text{ g } H_2O + C_m \text{ solute}}$$

Gas	Solute	$a \times 10^3$	$b \times 10^3$	$\sigma_a \times 10^{3a}$
He	SDS	0.0(3)	0.54	0.03
O_2	SDS	1.04	1.40	0.09
Ar	SDS	1.06	1.52	0.08
CH_4	SDS	1.8(5)	1.57	0.3
C_2H_6	SDS	11.1	1.80	0.5
O_2	CTAB	1.4	1.39	0.1
Ar	CTAB	1.5(5)	1.50	0.09

B. Solubilities of Gases at 25°C and 1 atm Expressed as Mole Fraction

Gas	Solute	$X^g_{H_2O} \times 10^4$	$X^g_{micelle} \times 10^4$	$K = \dfrac{X^g_{micelle}}{X^g_{H_2O}}$	$-\Delta G^m_{TR}$ (kcal/mole)	$K_c = \dfrac{[gas]_{micelle}}{[gas]_{H_2O}}$
He	SDS	0.09 (0.07)[b]	~0	—	—	—
O_2	SDS	0.25 (0.23)	10	40	2.20	2.9
A	SDS	0.27 (0.26)	11	41	2.20	3.0
CH_4	SDS	0.28 (0.25)	19	68	2.50	5.0
C_2H_6	SDS	0.32 (0.33)	111	350	3.47	26
O_2	CTAB	0.25	14	56	2.38	2.8
Ar	CTAB	0.27	16	59	2.42	2.9

[a] Standard deviation.
[b] Recommended values from Ref. (9).

determining the solubility as one proceeds down the list. It is seen that, as might be expected, the partitioning of gas into the micelle is favored as the critical temperature increases. A comparison of Ar and O_2 solubilities in SDS to those in CTAB shows that CTAB solubilizes more gas than SDS on a mole fraction basis.

Partial molar volumes have been measured above and below the critical micelle concentration for both CTAB and SDS (10). Above the CMC, the partial molar volumes for CTAB and SDS are found to be $\bar{v} = 365.4$ and 246.4 ml/mole, respectively. Thus without recourse to any specific model of a micelle, one can use these values to convert the distribution coefficients of Table II based on mole fractions to distribution coefficients based on concentrations: $K_c = [gas]_{micelle}/[gas]_{H_2O} = K(18/\bar{v})$. A comparison of the values listed in Table II for Ar

and O_2 in the two surfactants reveals that on a volume basis both Ar and O_2 are about equally concentrated in the micellar interiors, taken as a whole, of each surfactant.

In a recent paper (11), Mukerjee calls attention to the role that Laplace forces play in determining intramicellar properties. It is interesting therefore to examine these data in terms of a simple phase separation model in which the micellar interior is considered to be a long chain hydrocarbon which is subjected to a hydrostatic pressure generated by the surface tension forces at the curved micelle–water interface. Gas solubility in such a micellar interior would be expected to be less than that in an equivalent hydrocarbon at atmospheric pressure.

Table III lists the solubilities of these gases in n-dodecane and various other long chain n-alkanes. Experimentally it is found that on a mole fraction basis gas solubilities

do not change appreciably with size of the *n*-alkane beyond a carbon number of six (12). Consequently, the solubilities listed can be taken as reasonable estimates of gas solubility in the interior of a micelle in the absence of any Laplace pressure. It is seen that for each gas the solubility and associated free energy of transfer, ΔG_{TR}^h, from water to hydrocarbon is greater than that for the micelle (Table II). Within the framework of this model, the difference between the free energy of transfer to the micelle and that to the hydrocarbon can be equated to a positive contribution to the chemical potential of the solubilized gas molecule resulting from the Laplace pressure of the micelle interior, P,

$$\Delta G_p = \Delta G_{TR}^m - \Delta G_{TR}^h$$

$$= RT \ln (X_h^g / X_m^g) = P\bar{v}_g; \qquad [1]$$

where $\bar{v}_g$ denotes the partial molar volume of dissolved gas, taken to be constant with respect to pressure. Values for partial molar volumes of the gases are listed in Table III along with the ratio of $\Delta G_p / \bar{v}_g = P$ calculated for each gas. It is seen that although the range in partial molar volumes is not extremely great, the values calculated for Laplace pressure are remarkably constant and assume an average value of 400 atm.

The Laplace pressure inside a body enclosed by a convex surface having a surface tension γ is given by the well-known formula

$$P = \gamma[1/r_1 + 1/r_2]; \qquad [2]$$

where r_1 and r_2 denote radii of curvature of the surface. In his discussion concerning this factor, Mukerjee chose a sphere having a diameter of 30 Å and a surface tension of 20 dyn/cm as his model, thus estimating a pressure of 250 atm for micelle interiors. At the relatively high surfactant concentrations used here, it is likely that a significant fraction of the micelles assume an elliptical shape. Thus one expects the Laplace pressure encountered in this work

TABLE III

Gas Solubility in Hydrocarbons and Laplace Pressures

Gas solvent	$X_h^g \times 10^4$	$-\Delta G_{TR}^h$ (kcal/mole)	$\bar{v}_g$ (cm³/mole)	P (atm)
He/C$_{12}$	2.24[a]	1.90	48[d]	—
O$_2$/C$_9$	21.2[b]	2.63	56[d], 46[e]	319[d], 400[e]
Ar/C$_{12}$	25.5[a]	2.69	52[d], 48[f]	388[d], 420[f]
CH$_4$/C$_6$	50.8[c]	3.08	60[d,f]	400
C$_2$H$_6$/C$_9$	336[b]	4.12	68[d], 69[g]	410

[a] Reference (12).

[b] Thomsen, E. S., and Gjaldbaek, J. Chr., *Acta. Chem. Scand.* **17**, 127 (1963).

[c] Lannung, A., and Gjaldbaek, J. Chr., *Acta. Chem. Scand.* **14**, 1124 (1960).

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[f] Walkley, J., and Jenkins, W. I., *Trans. Faraday Soc.* **64**, 19 (1968).

[g] Gjaldbaek, J. Chr., and Hildebrand, J. H., *J. Amer. Chem. Soc.* **72**, 1077 (1950).

to lie within the range $\gamma/r < P < 2\gamma/r$. Thus taking a radius of 15 Å to be common to both types of micelles, one finds that the tension at the micellar surface necessary to generate 400 atm falls between 30 and 60 dyn/cm, which are surprisingly high values. It should be noted, of course, that any factor that serves to reduce gas solubility, for example, water penetration in the micelle, will be reflected as an increase in Laplace pressure as it is treated here.

There is other evidence of a similar nature that suggests that Laplace pressure plays a significant role in solubilization phenomena. It is well known that for a given surfactant the mole ratio of solubilized paraffin to surfactant decreases with increasing molar volume of solubilizate; and that among surfactants having a common head group, the amount solubilized per mole of surfactant increases with length of the hydrophobic group of the surfactant. It is reasonable to expect alkanes larger than pentane to form ideal solutions in the hydrophobic interior of a micelle. Thus, if the incorporation of

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