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PARTIAL MOLAL VOLUMES AND ADIABATIC COMPRESSIBILITIES OF DODECYLHEXAOXYETHYLENE GLYCOL MONOETHER IN AQUEOUS SOLUTIONS

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The partial molal volume ($\overline{V}_2$) and adiabatic compressibility ($\overline{K}_2$) of dodecylhexaoxyethylene glycol monoether have constant values in the micellar solution. The values of $\overline{V}_2^{\circ}$ and $\overline{K}_2^{\circ}$ (at infinite dilution) of the single molecule could not be determined experimentally because of its low CMC. Their values were calculated from the corresponding values of CH_3, CH_2, CH_2CH_2O, and CH_2OH groups. The changes in $\overline{V}_2$ and $\overline{K}_2$ associated with micelle formation are 10.5 ml/mol and 287×10^{-4} ml/mol•bar at 5°C, and 10.7 ml/mol and 208×10^{-4} ml/mol•bar at 25°C, respectively.

An abrupt change occurs at critical micelle concentration (CMC) in a number of physicochemical properties of surfactant solutions. Several studies on molal volumes and compressibilities of ionic surfactant solutions have been reported,1)-6) but those of nonionic surfactant solutions are very few.7) This work was aimed at the understanding of the micellization process by examining the densities and sound velocities of aqueous solutions of dodecylhexaoxyethylene glycol monoether ($C_{12}E_6$) at 5 and 25°C.

The sample used was 97.8% pure and contained 1.2% dodecylpentaoxyethylene glycol monoether as an impurity, which seems to have little influence on the density and sound velocity of the solution. Solution densities were evaluated to six decimal places by means of a float method. Ultrasonic velocity measurements were made with a sing-around velocimeter, and the accuracy was within ±1 cm/s. The temperature was controlled within ±0.001°C. The densities of pure water were taken as 0.999992 and 0.997075 g/ml at 5 and 25°C, respectively.8) The details of these measurements have been described elsewhere.9) The values of apparent molal volume, ϕ_V, and adiabatic

Table 1. $\overline{V}_2^o$ and $\overline{K}_2^o$ of CH_3, CH_2, CH_2CH_2O, and CH_2OH groups*

	$\overline{V}_2^o$(ml/mol)		$\overline{K}_2^o$(ml/mol•bar)	
	5°C	25°C	5°C	25°C
CH_3	26.3	26.4	-9.5_5	1.3
CH_2	15.5	15.9	-8.0	-1.8
CH_2OH	$28._7$	$28._4$	$6._5$	$6._8$
CH_2CH_2O	36.2_5	37.1	-10	-1.5

*from Ref. 9 and 10.

Table 2. $\overline{V}_2^o$(ml/mol) of alkylsulphinyl alkanols at 25°C

	obs*	calc**
$C_6H_{13}SO(CH_2)_2OH$	166.5	166.3
$C_6H_{13}SO(CH_2)_3OH$	182.3	182.2
$C_6H_{13}SO(CH_2)_4OH$	198.3	198.1
$C_8H_{17}SO(CH_2)_2OH$	198.1	198.1
$C_8H_{17}SO(CH_2)_3OH$	213.9	214.0
$C_8H_{17}SO(CH_2)_4OH$	229.9	229.9

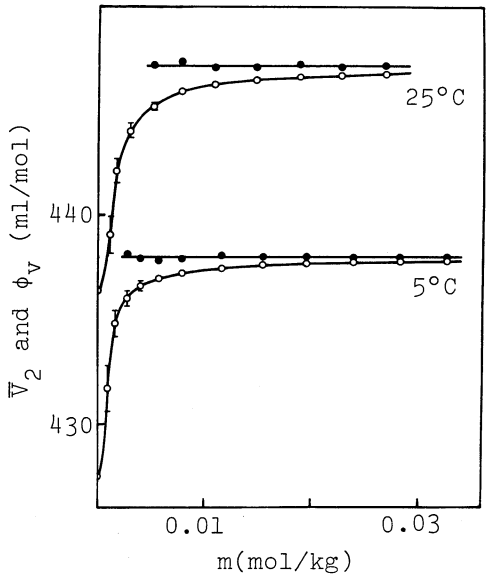
*from Ref. 7.

** $\overline{V}_2^o$ of SO group was estimated to be 16.1 ml/mol.

Table 3. $\overline{V}_2$ and $\overline{K}_2$ of $C_{12}E_6$

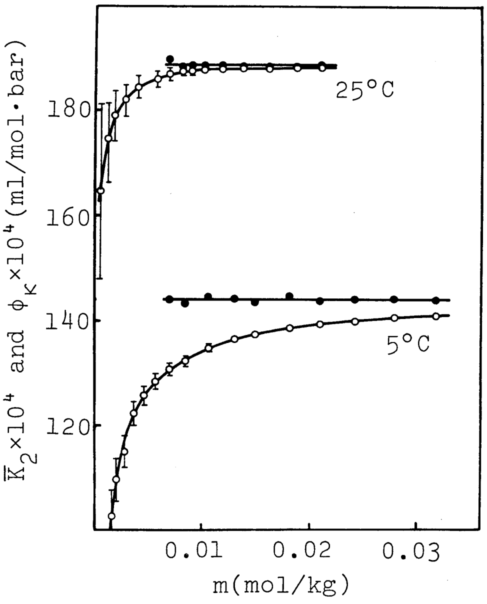
	$\overline{V}_2$ (ml/mol)			$\overline{K}_2\times10^4$ (ml/mol•bar)		
	$\overline{V}_2^o(=\phi_V^o)$	$\overline{V}_2^m$	$\overline{V}_2^m-\overline{V}_2^o$	$\overline{K}_2^o(=\phi_K^o)$	$\overline{K}_2^m$	$\overline{K}_2^m-\overline{K}_2^o$
5°C	427.5	438.0±0.2	$10._5$	-143	$144._0\pm1$	287
25°C	436.4	447.1±0.2	$10._7$	$-18._9$	$188._6\pm1$	208

Fig. 1. $\overline{V}_2$ and ϕ_V of $C_{12}E_6$



● : $\overline{V}_2$, ○ : ϕ_V.

Fig. 2. $\overline{K}_2$ and ϕ_K of $C_{12}E_6$



● : $\overline{K}_2$, ○ : ϕ_K.

compressibility, ϕ_K, were calculated from the following equations :

$$\phi_V = \frac{1000(d_o - d)}{m d_o d}, \quad \phi_K = \frac{1000(\kappa - \kappa_o)}{m d_o}, \quad \kappa = \frac{1}{u^2 d}$$

where d_o is the density of water ; d, that of the solution ; M, the molecular weight of the solute ; m, its molality ; u, the sound velocity in the solution ; κ_o, the coefficient of the adiabatic compressibility of water, and κ, that of the solution.

Figures 1 and 2 show the plots of ϕ_V and ϕ_K vs. molality, respectively, with the corresponding partial molal quantities calculated from the following equations : $\overline{V}_2 = \phi_V + m(\partial\phi_V/\partial m)$ and $\overline{K}_2 = \phi_K + m(\partial\phi_K/\partial m)$. The partial quantities are less accurate than the apparent ones because of the ambiguity in determination of the $\partial\phi_V/\partial m$ and $\partial\phi_K/\partial m$ values, and could not be determined in the low concentration range on account of the less accuracy in the values of ϕ_V and ϕ_K. In spite of this situation, it is noteworthy that the $\overline{V}_2^m$ and $\overline{K}_2^m$, the $\overline{V}_2$ and $\overline{K}_2$ in the micellar solutions, have constant values as are shown in Figs. 1 and 2. This finding implies the constancy of the micellar structure and the lack of interaction among the micelles.

The values of ϕ_V^o ($=\overline{V}_2^o$) and ϕ_K^o ($=\overline{K}_2^o$) could not be determined by the extrapolation of the experimental data because of the low CMC of the surfactant (8.7×10^{-5} mol/l at 25°C[11]). However, assuming that the values of $\overline{V}_2^o$ and $\overline{K}_2^o$ of a solute are the sum of the independent factors characteristic of the constituent groups of the molecule, we can calculate these thermodynamic quantities of the solute itself. This additivity has been discussed previously, and the values of $\overline{V}_2^o$ and $\overline{K}_2^o$ for CH_3, CH_2, CH_2CH_2O, and CH_2OH groups are given in Table 1[9],[10]. An example for the additivity of $\overline{V}_2^o$ is shown below. The partial molal volumes for a homologous series of n-alkylsulphinyl alkanols below the CMC were experimentally determined by Corkill et al.[7], and are given in Table 2 (column 2) with our calculated values (column 3) from our data in Table 1. The experimental and calculated values are in good agreement. It is concluded that the additivity for $\overline{V}_2^o$ holds for moderately large nonionic compounds. Other authors have also tested this additivity with success.[12],[13] As in the case of $\overline{V}_2^o$ we also assume the additivity for $\overline{K}_2^o$, although there have been few studies to examine it.[5],[9] Thus, the $\overline{V}_2^o$ and $\overline{K}_2^o$ values of $C_{12}E_6$ were calculated as are given in Table 3. The changes in both $\overline{V}_2$ and $\overline{K}_2$ associated with micelle formation are positive.

Although the partial molal adiabatic compressibility assigned to the hydrophilic group in the micellar state, $\overline{K}_2^m$(EO), is perhaps different from that at infinite dilution, $\overline{K}_2^o$(EO), it was still assumed that $\overline{K}_2^m$(EO) is approximated by $\overline{K}_2^o$(EO), so that

$\overline{K}^m_2-\overline{K}^m_2(EO)$, i.e., the compressibility of the dodecyl group in the micellar state, approximately corresponds to $\overline{K}^m_2-\overline{K}^o_2(EO)$. The molal compressibility of n-dodecane at 25°C was obtained to be 187×10^{-4} ml/mol•bar from the interpolation of the data at 20°C and 30°C by Weissler et al.14). The $\overline{K}^m_2-\overline{K}^o_2(EO)$ value was found to be 189×10^{-4} ml/mol•bar at 5 and 25°C. This agreement supports the idea that the interior of the micelle resembles liquid hydrocarbons. However, it is unreasonable that the compressibilities, which correspond to those in the interior of the micelle, had the same value at 5 and 25°C. This seems to result from the rough assumption that $\overline{K}^m_2-\overline{K}^m_2(EO)$ was taken as $\overline{K}^m_2-\overline{K}^o_2(EO)$.

The large increments in both $\overline{V}_2$ and $\overline{K}_2$ on micellization are explained as follows :

1) The alkyl chains of the molecularly dispersed surfactants are affected by high hydrocarbon-water interfacial tension tending to reduce the surface area. Accordingly, they are under the condition of high compression. As the hydrocarbon-water contact is eliminated on micellization, the chains are more free to expand.15) In other words, the larger free volumes should be assigned to the chains in the micelles as compared to the case of the single surfactants.

2) Hydrophobic hydration effect should be also taken into account. It has been generally accepted that icebergs are formed around hydrophobic solutes and with rising temperature the hydrophobic hydration is progressively destroyed. The fact that $\overline{K}^o_2$ is largely negative at 5°C could be mainly attributed to the pronounced hydrophobic hydration.9)

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References

1) G.M.Musbally, G.Perron, and J.E.Desnoyers, J.Colloid Interface Sci., 48, 494 (1974).
2) K.Shinoda and T.Soda, J.Phys.Chem., 67, 2072 (1963).
3) F.Franks and H.T.Smith, ibid., 68, 3581 (1964).
4) F.Franks, M.J.Quickenden, J.R.Ravenhill, and T.H.Smith, ibid., 72, 2668 (1968).
5) K.Shigehara, Bull.Chem.Soc.Japan, 38, 1700 (1965), 39, 2332, 2643 (1966).
6) T.Sasaki and K.Shigehara, IVth International Congress of Surface Activity, B/IV. 13, Brussels, Belgium (1964).
7) J.M.Corkill, J.F.Goodman, and T.Walker, Trans.Faraday Soc., 63, 768 (1967).
8) G.S.Kell, J.Chem.Eng.Data, 12, 66 (1967).
9) T.Nakajima, T.Komatsu, and T.Nakagawa, Bull.Chem.Soc.Japan, 48, 783, 788 (1975).
10) T.Nakajima, Manuscript in preparation.
11) J.M.Corkill, J.F.Goodman, and R.H.Ottewill, Trans.Faraday Soc., 57, 1627 (1961).
12) J.E.Desnoyers and M.Arel, Can.J.Chem., 45, 359 (1967).
13) M.Sakurai, Bull.Chem.Soc.Japan, 46, 1596 (1973).
14) A.Weissler and V.A.Del Grosso, J.Am.Chem.Soc., 72, 4209 (1950).
15) R.F.Tuddenham and A.E.Alexander, J.Phys.Chem., 66, 1839 (1962).

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