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INTERFACIAL ADSORPTION OF AN INHALATION ANESTHETIC ONTO IONIC SURFACTANT MICELLES AND ITS DESORPTION BY HIGH PRESSURE

SHOJI KANESHINA *, HIROSHI KAMAYA and ISSAKU UEDA **

Anesthesia Service and Research, Veterans Administration Medical Center, Salt Lake City, UT 84148 and Department of Anesthesia, University of Utah College of Medicine, Salt Lake City, UT 84132 (U.S.A.)

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The effects of pressure and temperature on the critical micelle concentration (CMC) of sodium dodecylsulfate (SDS) were measured in the presence of various concentrations of an inhalation anesthetic, methoxyflurane. The change in the partial molal volume of SDS on micellization, $\Delta\bar{V}_m$, increased with the increase in the concentration of methoxyflurane. The CMC-decreasing power, which is defined as the slope of the linear plot between ln(CMC) vs. mole fraction of anesthetic, was determined as a function of pressure and temperature. Since the CMC-decreasing power is correlated to the micelle/water partition coefficient of anesthetic, the volume change of the transfer (ΔV_p^o) of methoxyflurane from water to the micelle can be determined from the pressure dependence of the CMC-decreasing power. The value of ΔV_p^o amounts 6.5 ± 1.8 $cm^3 \cdot mol^{-1}$, which is in reasonable agreement with the volume change determined directly from the density data, 5.5 ± 0.6 $cm^3 \cdot mol^{-1}$. Under the convention of thermodynamics, this indicates that the application of pressure squeezes out anesthetic molecules from the micelle. The transfer enthalpy of anesthetic from water to the micelle is slightly endothermic. The partial molal volume of methoxyflurane in the micelle (112.0 $cm^3 \cdot mol^{-1}$) is smaller than that in decane (120.5 $cm^3 \cdot mol^{-1}$) and is larger than that in water (108.0 $cm^3 \cdot mol^{-1}$). This indicates that the anesthetic molecules are incorporated into the micellar surface region, i.e., the palisade layer of the micelle in contact with water molecules, rather than into the micelle core.

Introduction

Phospholipid model membranes are often used to probe the mechanisms of the pressure-anesthetic antagonism [1–6]. It is established that the phase-transition temperature of phospholipid membrane is elevated by high pressures and is depressed by anesthetics. Thermodynamic quantities of the phase transition, i.e., dT/dP [5] where T is the absolute temperature of the phase transition and P is the pressure, the changes of volume [3] and enthalpy [7] are reported to be unaffected by the presence of anesthetics.

Although surfactant micelles, which are the macromolecular aggregates with well-defined hydrophobic core and hydrophilic surface, are also regarded to be a suitable model for biological membranes and macromolecules [8–11], few studies have been reported upon the interaction between micelles and anesthetics. Previously, we have shown that the cloud-point temperature of non-ionic surfactant solution is depressed by anesthetics and is elevated by hydrostatic pressure [12].

* On leave from Department of Chemistry, Kyushu University College of General Education, Fukuoka 810, Japan.
** To whom reprint request should be addressed at VA Medical Center.

Abbreviations: CMC, critical micelle concentration; SDS, sodium dodecyl sulfate.

In the present study, the effects of anesthetic, pressure and temperature on the micelle formation are presented. The thermodynamic quantities of micelle formation are determined from the dependences of the critical micelle concentration (CMC) upon pressure and temperature. Since the pressure is an important thermodynamic variable as well as the temperature and concentration, the effect of the anesthetic on the thermodynamic quantities of micellization are expected to give informations to understand the antagonizing action of high pressure against anesthesia. We have previously shown that the CMC-decreasing power by anesthetics is correlated to the partition coefficient of anesthetics between the micelle and water [13]. In this paper, the changes of volume and enthalpy for the transfer of anesthetic molecules from water to the micelle were determined from the dependences of the CMC-decreasing power upon the pressure and temperature. The volume change of the transfer was also directly determined by the solution density measurement and the data were compared with the thermodynamically derived values with reasonable agreement.

The site of incorporation of the anesthetic molecules into the micelle is predicted from the partial molal volumes of the anesthetic in water, micelle and decane, since the partial molal volume is dependent upon the solvent property surrounding the solute molecules.

Materials and Methods

Materials. Sodium dodecylsulfate (SDS) was obtained from Eastman (Rochester, NY) and recrystallized three times from acetone/water (95:5, v/v). The CMC determined by the conductivity method was $8.23 \cdot 10^{-3}$ molal at 298.15 K, which was in good agreement with that in the literature [14]. Inhalation anesthetic, methoxyflurane (2,2-dichloro-1,1-difluoroethyl methyl ether) was a gift from Abbott Laboratories (North Chicago, IL). Water was purified by triple distillation, once from alkaline potassium permanganate solution. The specific conductivity of water was $1.1 \cdot 10^{-6}$ $ohm^{-1} \cdot cm^{-1}$. Decane was obtained from Sigma. The density of decane measured by Anton-Paar oscillation densitometer was 0.726413 at 298.15 K, which was in good agreement with the literature value [15].

Determination of CMC. The CMC with and without anesthetic was measured by the conductivity method. It was taken as a break point on a plot between the specific conductivity vs surfactant concentration. The conductivity cell for pressure studies was made by fusing platinized-platinum electrodes to a 5 ml glass syringe. The cell constant was 0.4883 cm^{-1} at an atmospheric pressure. The effect of pressures on the cell constant was checked by measuring the conductivity of a 0.01 D KCl standard solution under high pressures and by comparing with the molal conductivities at various pressures in the literature [16].

The high pressure vessel of Parr Instrument Co. (Moline, IL), which was made of 316SS with the dimension of 1 inch (inner diameter) $\times$ 5.5 inches, was used for the measurement of the specific conductivity under high pressure. A pair of cones were fitted into the high pressure vessel to wire electrical leads and epoxy resin was used for the insulator of the high pressure leads.

Pressures were generated by a hand-operated hydraulic pump and measured within an accuracy of ± 10 lb/inch^2 (0.7 bar) by a Heise pressure gauge. Ligroin was used as the pressure transmitting medium.

The specific conductivity of the surfactant solution was measured by a Beckman conductivity bridge Model RC-18A (Cedar Grove, NJ), equipped with a Type 1419-K Decade Capacitor of GenRad (Concord, MA). The temperature of the water bath, in which the high pressure vessel was immersed, was kept at 298.15 and 308.15 $\pm$ 0.01 K.

The anesthetic was added to the surfactant solutions in glass ampules with microsyringes. The added amount was checked by weighing the ampule by an analytical balance. In order to minimize the escape of the anesthetic vapor into the gas phase, the ampules were filled to the neck and were flame sealed close to the solution. The sealed ampules were incubated at 313 K for 24 h in a shaking water bath to ensure equilibration of the anesthetic.

Density measurement and estimation of partial molal volume. The densities of solutions including various amounts of the anesthetic were measured

using an Anton Paar oscillation densimeter DMA60/601HT (Mettler, Hightstown, NJ) at 298.15 ± 0.005 K. The densimeter was calibrated with water and air. The reproducibility of the density measurements was within $\pm 1 \cdot 10^{-6}$ g · cm^{-3}.

The partial molal volume is designated by $\bar{V}$ and using subscripts 1 and 2 for the solvent and solute, respectively, the total volume V is expressed:

$$V = n_1\bar{V}_1 + n_2\bar{V}_2 \tag{1}$$

where n_1 and n_2 are the number of moles of solvent and solute, respectively.

The apparent model volume of the solute, ϕ_2, is defined

$$\phi_2 = (V - n_1V_1^o)/n_2 \tag{2}$$

where V_1^o is the molal volume of the solvent in the pure state. Then,

$$V = n_1V_1^o + n_2\phi_2 \tag{3}$$

By definition of the partial molal volume:

$$\bar{V}_2 = \left(\frac{\partial V}{\partial n_2}\right)_{T,P,n_1} = \phi_2 + n_2\left(\frac{\partial \phi_2}{\partial n_2}\right)_{T,P,n_1}$$

$$= \phi_2 + \left(\frac{\partial \phi_2}{\partial \ln n_2}\right)_{T,P,n_1} \tag{4}$$

At infinite dilution, the partial molal volume and the apparent molal volume are equal ($\phi_2^o = \bar{V}_2^o$).

By means of the experimentally measured density, d, and the molecular weights, M_1 and M_2 of the solvent and the solute, respectively, the total volume is written:

$$V = (n_1M_1 + n_2M_2)/d \tag{5}$$

By designating d_1 for the density of the solvent at its pure state, V_1^o is expressed:

$$V_1^o = M_1/d_1 \tag{6}$$

It is convenient to use molal concentration of the solute, m_2, for the calculation of the apparent molal volume and:

$$m_2 = (n_2/n_1M_1) \times 1000 \tag{7}$$

From Eqns. 2 and 5–7, it follows:

$$\phi_2 = \frac{1}{m_2}\left(\frac{1000 + m_2M_2}{d} - \frac{1000}{d_1}\right) \tag{8}$$

The apparent molal volume was measured at several molal concentrations of the solute. The partial molal volume was obtained by extrapolating the value to infinite dilution.

Results

The specific conductivity measured at a constant pressure and concentration of the anesthetic was plotted against the concentration of the surfactant which resulted in two straight lines. The CMC was taken as the intersection point of the two straight lines obtained by the least-squares method.

The CMC values of SDS in the presence of various concentrations of methoxyflurane at 298.15 and 308.15 K are shown in Figs. 1 and 2, respectively, as a function of pressure. The application of

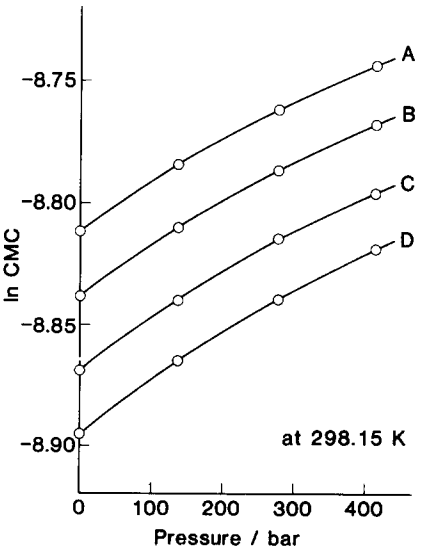

Fig. 1. The logarithm of the CMC as a function of pressure at 298.15 K. The concentration of methoxyflurane: A, zero; B, $0.33 \cdot 10^{-4}$; C, $0.69 \cdot 10^{-4}$, and D, $1.03 \cdot 10^{-4}$ in mole fraction.

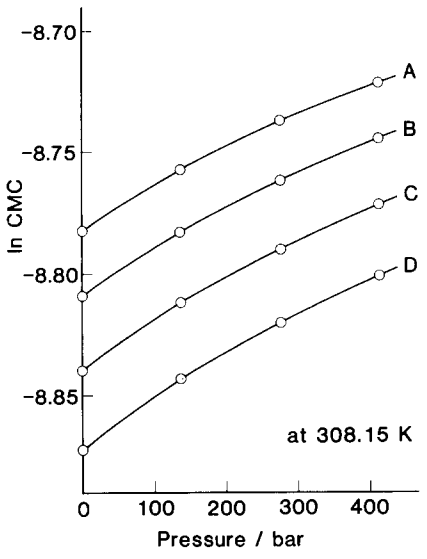

Fig. 2. The logarithm of the CMC as a function of pressure at 308.15 K. The concentration of methoxyflurane: A, zero; B, $0.33 \cdot 10^{-4}$; C, $0.69 \cdot 10^{-4}$, and D, $1.03 \cdot 10^{-4}$ in mole fraction.

hydrostatic pressure non-linearly elevated the CMC both in the absence and the presence of methoxyflurane. The slopes of the CMC vs. pressure curves were dependent upon the methoxyflurane concentration; the higher the concentration of methoxyflurane, the steeper the slope at atmospheric pressure. The CMC was increased with the elevation of the temperature at any pressure and at any concentration of methoxyflurane studied.

The values of the partial molal volume of methoxyflurane in various solvents were measured by fluid densimetry and were summarized in Table I.

TABLE I

THE PARTIAL MOLAL VOLUME OF METHOXYFLURANE IN VARIOUS SOLVENTS AT 298.15 K

Solvent	Partial molal volume ($cm^3 \cdot mol^{-1}$)
Water	108.0±0.4
SDS solution (mmolal)	
2.01	107.2±1.5
4.10	106.6±0.6
6.13	106.4±0.6
12.05	111.9±0.6
16.02	112.0±0.5
20.06	112.1±0.4
Methoxyflurane (pure state)	116.4±0.05
Decane	120.5±0.4

Discussion

Anesthetic effect on micelle formation

The interaction of anesthetics with surfactant micelles can be studied thermodynamically in two ways. The first approach is to determine the thermodynamic quantities of micelle formation in the presence of anesthetics. The second approach is to analyze the changes induced upon anesthetic molecules by the interaction with micelles. In this section, we discuss the effect of the anesthetic on the thermodynamic quantities of micelle formation.

The change in the partial molal volume of surfactant on micellization, $\Delta\bar{V}_m$, can be determined from the pseudo-phase separation model [17] by the following equation [18]:

$$\Delta\bar{V}_m = \bar{V}_m - \bar{V}_s = (1+\beta)\, RT\left(\frac{\partial \ln(\mathrm{CMC})}{\partial P}\right)_T \quad (9)$$

where β is the constant which indicates the ratio of the number of the counter-ion to that of the surfactant ion in a micelle, and $\bar{V}_m$ and $\bar{V}_s$ are the partial molal volume of the surfactant in the micellar and singly dispersed states, respectively.

The logarithm of the CMC (in mole fraction) shown in Figs. 1 and 2 can be expressed as a function of pressure by a polynomial:

$$\ln(\mathrm{CMC}) = A + BP + CP^2 + DP^3 \quad (10)$$

Constants A, B, C and D were determined by the method of least-squares.

The values of $\Delta\bar{V}_m$ calculated from Eqn. 9 are summarized in Table II. The value of β was taken from the previous paper [13] and shown in Table II. In the absence of the anesthetic, the value of $\Delta\bar{V}_m$ is in good agreement with the value in the literature [18–21]. As shown in Table II, the value of $\Delta\bar{V}_m$ increased with the increase in the concentration of methoxyflurane.

TABLE II

THE CHANGE OF PARTIAL MOLAL VOLUME OF SURFACTANT ON MICELLE FORMATION IN THE PRESENCE OF VARIOUS CONCENTRATIONS OF METHOXYFLURANE

Mole fraction of methoxyflurane	β	$\Delta\bar{V}_m$ ($cm^3 \cdot mol^{-1}$)	
		298.15 K	308.15 K
0	0.762	9.1±0.5	8.4±0.5
$0.33 \cdot 10^{-4}$	0.760	9.4±0.5	8.8±0.5
$0.69 \cdot 10^{-4}$	0.759	9.7±0.5	9.2±0.5
$1.03 \cdot 10^{-4}$	0.758	10.0±0.5	9.7±0.5

TABLE III

THE CHANGE OF PARTIAL MOLAL ENTROPY OF SURFACTANT ON MICELLE FORMATION AT VARIOUS PRESSURES AND VARIOUS ANESTHETIC CONCENTRATIONS

Mole fraction of methoxyflurane	$-\Delta\bar{S}_m$ ($J \cdot K^{-1} \cdot mol^{-1}$), pressure (bar)			
	0	137.9	275.8	413.7
0	12.9	11.8	10.7	9.7
$0.33 \cdot 10^{-4}$	12.9	11.9	10.9	10.2
$0.69 \cdot 10^{-4}$	13.0	12.4	10.9	10.5
$1.03 \cdot 10^{-4}$	10.3	9.7	8.4	7.8

Høiland and Vikingstad [22] reported that $\Delta\bar{V}_m$ decreased linearly as β increased. This means that the release of counter-ions from the micellar surface causes the increase of $\Delta\bar{V}_m$. In our previous paper [13], we have shown that the addition of anesthetics and alcohols decreased β of the ionic surfactant micelles. It was theorized that the decrease of the effective surface potential of the micelle by anesthetics was responsible for the increase of $\Delta\bar{V}_m$ and decrease of β.

The change in the partial molal entropy of surfactant on micellization, $\Delta\bar{S}_m$, can be determined by the following equation [18]:

$$\Delta\bar{S}_m = \bar{S}_m - \bar{S}_s$$

$$= -(1+\beta)\, RT\left(\frac{\partial \ln(\mathrm{CMC})}{\partial T}\right)_P \qquad (11)$$

where $\bar{S}_m$ and $\bar{S}_s$ are the partial molal entropy of the surfactant in the micellar and singly dispersed states, respectively. From the data shown in Figs. 1 and 2, $\Delta\bar{S}_m$ was calculated at the mean temperature, 303.15 K. The value of the CMC has neither minimum nor maximum in the temperature range between 298.15 and 308.15 K [23,24]. The values of β at atmospheric pressure were used in the place of those under high pressure because the micellar charge is little affected by pressure [25]. The values of $\Delta\bar{S}_m$ thus obtained from Eqn. 11 are tabulated in Table III. In the present experimental range of temperature, pressure and concentration of methoxyflurane, the sign of $\Delta\bar{S}_m$ was negative. The value of $\Delta\bar{S}_m$ increased with the increase in pressure at any concentration of methoxyflurane, while it was little affected with the increase of methoxyflurane concentration at any pressure.

Although the CMC decreased significantly in the presence of the anesthetic, the thermodynamic quantities of micelle formation, $\Delta\bar{V}_m$ and $\Delta\bar{S}_m$, were little affected by the anesthetic. In the case of phospholipid vesicles, the phase-transition temperature of vesicles was depressed by anesthetics. However, the thermodynamic quantities of the phase transition, i.e., dT/dP [5] and the changes of volume [3] and enthalpy [7] were reported to be unaffected by the presence of anesthetics. Therefore, in order to elucidate the pressure-anesthetic antagonism by using the model membranes, it is necessary to analyze the changes induced upon anesthetic molecules by the interaction with model membranes other than the changes occurring in the membrane.

Transfer of anesthetic from water to micelle

The partition coefficient is one of the thermodynamic equilibrium constants and is, therefore, a function of temperature and pressure. With regard to the depression of CMC by alcohols, several authors [26–28] discussed quantitatively the relation between the micelle/water partition coefficient of alcohol and the 'CMC decreasing power' which is defined as $-d\ln(\mathrm{CMC})/dY_a$ where Y_a is the mole fraction of additives (alcohols) in the aqueous phase. Shirahama and Kashiwabara [26]

proposed a relationship between the CMC-decreasing power and the partition coefficient (K) as

$$-(\mathrm{d}\ln(\mathrm{CMC})/\mathrm{d}Y_a) = \theta K \qquad (12)$$

where θ is a constant. The term 'ISA (interaction of surfactant and additive) coefficient' was designated for $-\theta$ by Hayase and Hayano [27]. The physical meaning of θ has been described in detail by Manabe et al. [28]. Previously, we have shown that Eqn. 12 holds between the CMC-decreasing power of anesthetics and the micelle/water partition coefficient, and the value of θ for several anesthetics is estimated to be 0.52 ± 0.04 [13]. Since θ is specific to the combination of the micellar surfactant and the ligands, the pressure and temperature dependence of θ may be negligible.

The effect of pressure on the CMC-decreasing power leads to the volume change of the transfer of an anesthetic (ΔV_p^o) from the aqueous to the micellar phase via the pressure dependence of K as follows:

$$\left(\frac{\partial \ln\left(-\frac{\mathrm{d}\ln(\mathrm{CMC})}{\mathrm{d}Y_a}\right)}{\partial P}\right)_T \simeq \left(\frac{\partial \ln K}{\partial P}\right)_T = -\frac{\Delta V_p^o}{RT} \qquad (13)$$

The CMC of SDS was depressed linearly with the increase in the concentration of methoxyflurane at any pressure studied (Fig. 3). The CMC-decreasing power at various pressures was estimated from the slope in Fig. 3, which was replotted from Fig. 1. Fig. 4 shows that the logarithm of the CMC-decreasing power decreases linearly with the increase in pressure. In other words, the partition coefficient decreases with the increase in pressure. The volume change of the transfer of methoxyflurane from the aqueous to the SDS micellar phase can be obtained from the slope in Fig. 4 and Eqn. 13, and the value was 6.5 ± 1.8 cm$^3 \cdot$ mol^{-1} at 298.15 K. According to the principle of Le Chatelier, the pressure transforms the equilibrium of a system to the direction of the volume reduction. In the present system, the application of hydrostatic pressure squeezes out anesthetic molecules from the surfactant micelle.

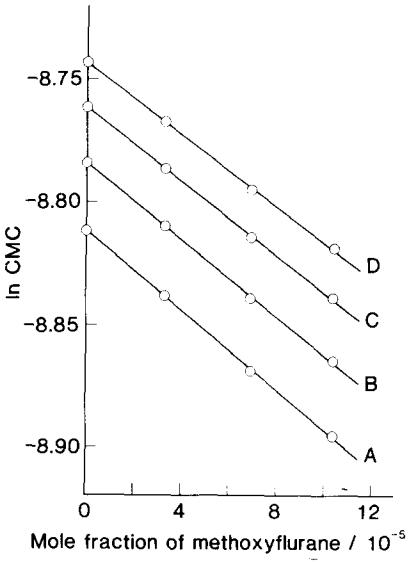

Fig. 3. The logarithm of the CMC as a function of mole fraction of methoxyflurane at 298.15 K. Pressure: A, atmospheric pressure; B, 137.9 bar; C, 275.8 bar, and D, 413.7 bar.

The enthalpy of transfer of an anesthetic (ΔH_p^o) from the aqueous to the micellar phase can be determined in analogy with Eqn. 13 from the temperature dependence of the CMC-decreasing power by the following equation:

$$\Delta H_p^o = RT^2\left(\frac{\partial \ln K}{\partial T}\right)_P \simeq RT^2\left(\frac{\partial \ln\left(-\frac{\mathrm{d}\ln(\mathrm{CMC})}{\mathrm{d}Y_a}\right)}{\partial T}\right)_P \qquad (14)$$

The CMC-decreasing power at 308.15 K was calculated from the results shown in Fig. 2. The value of ΔH_p^o was obtained from Eqn. 14 and the CMC-decreasing power at 298.15 and 308.15 K, and is summarized in Table IV. As shown in Table IV, ΔH_p^o has a small positive value and decreases with the increase in pressure. The process of transfer of anesthetic molecules from the aqueous to the micellar phase was slightly endothermic.

The standard Gibbs free energy of transfer

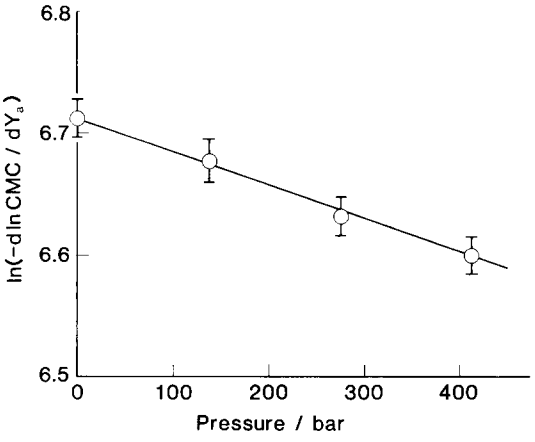

Fig. 4. The logarithm of the 'CMC-decreasing power' as a function of pressure at 298.15 K.

(ΔG_p°) was calculated from the expression:

$$\Delta G_p^\circ = -RT \ln K \tag{15}$$

where the value of K was estimated from Eqn. 12 in which the value of θ was taken as 0.52 [13]. The entropy change of transfer (ΔS_p°) was obtained from the thermodynamics relation:

$$\Delta G_p^\circ = \Delta H_p^\circ - T\Delta S_p^\circ \tag{16}$$

The values of ΔG_p°, and ΔS_p° were obtained from Eqns. 15 and 16, respectively, and are summarized in Table IV together with the value of ΔH_p°. As shown in Table IV, the large negative value of ΔG_p° is attributable to the large positive value of ΔS_p°. Consequently, the process of the transfer of anesthetic molecules from the aqueous to the micellar phase is predominantly entropic. Simon et al. [29] examined the temperature dependence of the partition coefficient of halothane into phospholipid bilayers and also reported that the enthalpy of transfer showed a small endothermic value and the entropy change showed a large positive value. Note that the partition behavior of anesthetic molecules between water and micelles resembles to that between water and phospholipid vesicles.

TABLE IV

THE TRANSFER FREE ENERGY, ENTHALPY AND ENTROPY OF METHOXYFLURANE FROM WATER TO THE SDS MICELLE AT VARIOUS PRESSURES

Pressure (bar)	$-\Delta G_p^\circ$ (kJ·mol^{-1})	$-\Delta H_p^\circ$ (kJ·mol^{-1})	ΔD_p° (J·K^{-1}·mol^{-1})
0	18.3±0.2	1.8±1.1	67±4
137.9	18.2±0.2	1.2±1.1	65±4
275.8	18.1±0.2	0.8±1.1	63±4
413.7	18.0±0.2	0 ±1.1	60±4

Partial molal volume of anesthetic and the site of adsorption

The partial molal volume of a solute varies according to the difference in the solvent property surrounding the solute molecule. The change of the partial molal volume of anesthetic by adsorbing to the micelle would report the physical property of the site of the adsorption.

The values of the partial molal volume of methoxyflurane in various solvents are summarized in Table I. The partial molal volumes of methoxyflurane in the SDS solutions below and above the CMC are depicted in Fig. 5 as a function of SDS concentration. It increases abruptly at the CMC.

From Fig. 5, the volume change of the transfer of the anesthetic from the singly-dispersed surfactant solution into the micelle was estimated to be 5.5 ± 0.6 cm^3 · mol^{-1}, which is in reasonable agreement with the value of ΔV_p° calculated from Eqn. 13, 6.5 ± 1.8 cm^3 · mol^{-1}.

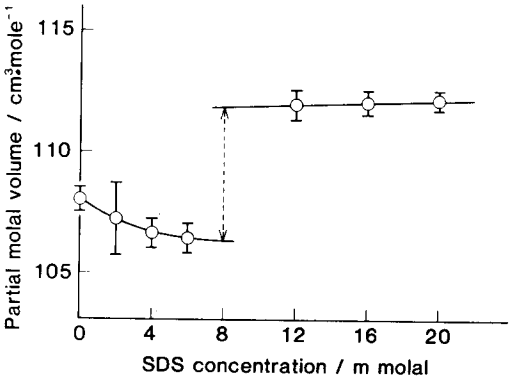

Fig. 5. The partial molal volume of methoxyflurane as a function of SDS concentration at 298.15 K.

It is established that the interior of micelles approximates the state of liquid hydrocarbons [30]. If the anesthetic is solubilized into the micelle core, the partial molal volume of anesthetic in the micelle should resemble that in hydrocarbons such as decane. As shown in Table I, however, the partial molal volume in the micelle is much smaller than that in decane, and is larger than that in water. The above results are consistent with the idea that the anesthetic molecules are located in the hydrophilic environment in the micelle rather than in the nonpolar core of the micelle. It is concluded that the anesthetic molecules are incorporated into the micellar surface region in contact with water. By the use of proton nuclear magnetic resonance spectroscopy, we have shown that methoxyflurane does not penetrate deep into the hydrophobic core of surfactant micelles and the proton of the ethylene moiety stays at the interfacial region [31].

The molal volume of methoxyflurane, which was calculated from the density of pure methoxyflurane, is smaller than the partial molal volume in decane by 4.1 $cm^3 \cdot mol^{-1}$. This reduction in volume at its pure state is ascribed to the self association among methoxyflurane molecules by hydrogen bonding. The volume change of the hydrogen-bond formation is known to be in the range of -3.0 to -7.0 $cm^3 \cdot mol^{-1}$ [32–34]. The hydrogen bonding between anesthetic molecules has been recognized by the infrared spectroscopy [35,36].

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