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論 文

Thermodynamic Properties of (Aerosol OT$+$r$\cdot$H$_2$O) in Cyclohexane at 298.15 K

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Apparent molar volumes V_ϕ, *apparent molar heat capacities* $C_{p,\phi}$, and relative apparent molar enthalpies L_ϕ of the mixed solute {di-2-ethylhexyl sodium sulfosuccinate (Aerosol OT, or AOT) $+$r $\cdot$ H$_2$O} in cyclohexane were determined over the molality range of 0.0002 to 1 mol kg^{-1} at 298.15K. The heats of dilution were measured by using a newly constructed flow-calorimeter. The excess enthalpies for the systems (benzene+cyclohexane) and (chlorobenzene+toluene) at 298.15 K were also measured to test the operating technique for the calorineter. In the system without adding water ($r=0$) the enthalpy of dilution changes from endotherm to exotherm at about 0.2 mol kg^{-1}, and the change in $C_{p,\phi}$ with molality is monotonous. In the systems with $r \geqq 5$ a sharp peak appears at $m=0.001$ mol kg^{-1} in $C_{p,\phi}$ and the enthalpy of dilution increases very sharply at $m<0.01$ mol kg^{-1}. We concluded that the intermolecular interaction of AOT in cyclohexane is moderate, and no micelles are formed. In the systems with $r \geqq 5$ a transition occurs at $m=0.001$ mol kg^{-1} and W/O microemultion is formed.

1. Introduction

Thermodynamically stable, transparent, and single-phase systems composed of three components —amphiphile, water, and hydrocarbon— are called microemultion. It is considered that those mixtures are micellar solutions in which the third component is solubilized in micelles, and alternative words such as "swollen micellar solution", or "solubilized micellar solution" are used. The concept of reverse micelle is accepted to the aggregates of amphiphiles formed in nonaqueous media, and sometimes the critical micellar concentration (CMC) is also assigned. By adding small amount of water the aggregation number increases dramatically and W/O microemultion is formed.[1] Extensive studies of phase diagram for those systems have been reported, and in general the phase of microemultion is identified.[2,3] However, thermodynamic properties for those systems have not been precisely investigated. We have measured apparent molar heat capacities and volumes of {polyoxyethylene glycol monodecyl ether (POE) $+$r$\cdot$H$_2$O} in nonpolar solvents[4,5] and obtained results which are not necessarily coincide with conclusions reported hitherto. We have found that calorimetric study is very useful to understand the aggregation process of amphiphiles in nonpolar solvents as well as in aqueous mixtures. This paper reports apparent molar volumes V_ϕ, apparent molar heat capacities $C_{p,\phi}$, and relative apparent molar enth-

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alpies $L\phi$ for the mixed solute {an ionic amphiphile, di-2-ethylhexyl sodium sulfosuccinate (Aerosol OT, or AOT)+r·H_2O} in cyclohexane at 298.15 K, where r is the ratio of the amount of added water to AOT.

The enthalpies of dilution were measured by using a newly constructed flow-calorimeter.

2. Experimental

2.1 Materials

AOT (American Cyanamide Co.) of 100 g was dissolved in 200 cm^3 of methanol, and 10 cm^3 of water was added. After staying one day the undissolved material was filtered. It was once dried under vacuum at 333K. Then, 5 g of AOT was dissolved in 10 cm^3 of benzene, and dried again under vacuum forming small foams for more than 10 h. The mole fraction of water in the purified AOT was determined by Karl Fisher's method and was 0.03. Cyclohexane and water were fractionally distilled. The density of cyclohexane was 0.773828 to 0.773860 g cm^{-3} at 298.15 K.

The mixtures were prepared by diluting mixed solute (AOT+r·H_2O) with cyclohexane. The value of r was controlled within 0.5 % by using a microsyringe.

2.2 Measurements of mixing enthalpy

A flow calorimeter for determining enthalpies of mixing has been newly constructed. Fig. 1 shows the design of the calorimeter. A stainless steel tube A (2 mm OD, 1.6 mm ID) of 1.5 m is tightly wound and soldered around the copper cylinder B of 40 mm OD×45 mm. A stainless steel tube C (1.5 mm OD, 1.2 mm ID) is inserted in the tube A and coiled together with A for 13 cm length. A stainless steel wire (0.3 mm D) is coiled on two pieces of wire (0.6 mm D×15 mm), and those 15 segments E are installed in the tube A to promote mixing. The calibration heater H made of mananese wire (47 Ω) is wound on B and fixed with insulating varnish (General Electric Co., GE 7031). The electrical power was calculated by measuring the potential drop across the heater and across the standard resistor in series with heater. The air inside the vessel was evacuated through the valve J to the pressure of 1 Pa. The calorimeter was immersed in the water bath, and the temperature of which was controlled within ±0.0002 K. Two HPLC pumps (Waters, Millipore Co. Model 510) were used to flow liquids. The flow rate, which can be changed with a step of 0.01 cm^3 min^{-1}, was determined for each digital setting by measuring the time to fill a calibrated volume of 1 to 3 cm^3 pipettes. The uncertainty of determination of flow rate was 0.1 %. The flow rates were constant within 0.1 % uncertainty for more than 10 months. The liquids are introduced into the calorimeter through the Teflon coupling D after thermostatted during they are flowed in the 50 cm tubes which are located on the calorimeter vessel. The heat flow between the copper cylinder and the heat sink was detected with a thermopile G (Komatsu Electronics Inc., KSM-0671). Its electrical signal was monitored and measured with a

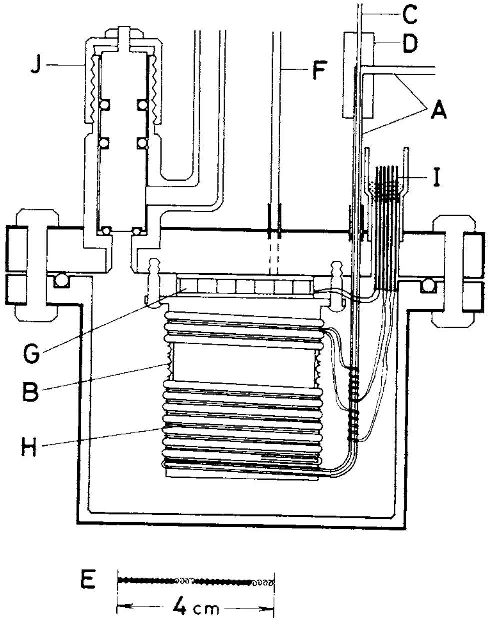

Fig. 1 Schematic diagram of the flow calorimeter for mixing enthalpy.

Table 1 Molar excess enthalpies H^E at 298.15 K

x	$\frac{H^E}{\mathrm{J\ mol^{-1}}}$	x	$\frac{H^E}{\mathrm{J\ mol^{-1}}}$	x	$\frac{H^E}{\mathrm{J\ mol^{-1}}}$	x	$\frac{H^E}{\mathrm{J\ mol^{-1}}}$
			xBenzene + $(1-x)$ Cyclohexane				
0.1000	281.5	0.1928	485.6	0.2874	641.9	0.3188	682.0
0.3854	748.7	0.4693	791.4	0.4693	791.8	0.5489	794.6
0.5489	793.3	0.6117	768.7	0.6186	762.8	0.7093	676.9
0.7093	676.7	0.8566	416.2	0.8870	342.7	0.9300	225.7
0.9583	140.1						
			xChlorobenzene + $(1-x)$ Toluene				
0.1039	−45.84	0.1593	−66.00	0.2113	−82.04	0.2616	−94.66
0.3098	−103.7	0.3098	−104.1	0.3603	−111.4	0.3856	−114.1
0.4354	−117.5	0.4848	−118.7	0.5302	−117.6	0.5518	−116.5
0.6599	−104.0	0.7088	−94.90	0.7374	−88.71	0.8031	−71.64
0.8559	−55.49	0.9041	−38.63	0.9286	−29.18		

recorder after amplification. The base line was kept unchanged with flow rate and also with exchanged liquid inside the usual fluctuation of $\pm 2\ \mu\mathrm{W}$. The linearity of the calibration constant was obtained for the flow rates higer than 0.2 $\mathrm{cm^3\ min^{-1}}$ and also for the heat capacities divided by volume (C_p/V) of liquids. Optimal total flow-rate at which mixing is completely accomplished was found to be 0.4 $\mathrm{cm^3\ min^{-1}}$. The enthalpies of mixing were calculated in the same way described previously⁶⁾.

To test the performance of the calorimeter the molar excess enthalpies H^E for $\{x\text{benzene}+(1-x)\text{cyclohexane}\}$ and $\{x\text{chlorobenzene}+(1-x)\text{toluene}\}$ were measured at 298.15 K. The experimental values are summarized in Table 1. Those were fitted with the smoothing equation

$$H^E/\mathrm{J\ mol^{-1}} = x(1-x)\ \Sigma a_i(1-2x)^{i-1} \quad (1)$$

by the method of least squares. The determined coefficients and the calculated standard deviation for each set are listed in Table 2. More than 60 sets of measurements of H^E for (benzene+cyclohexane) system are found in the handbook⁷⁾. Deviations of the experimental results from the representation (1) for this system are plotted in Fig. 2 along with several sets from literature. Although suitable nonaqueous system for testing exothermic mixing enthalpy has not been established we believe that (chlorobenzene+toluene) is suited for this purpose since the components are stable and easy to purify as has been recommended previously.¹⁰⁾ The deviation plots for this system are shown in Fig. 3. In both cases our present results are in excellent agreement with reliable works reported so far within 0.5 %. The main source of deviation in our earlier work was attributed to the uncertainty in the analog measurements of electrical signal monitored on the recorder.

2.3 Measurements of density

The densities were measured with a vibrating densimeter developed by Picker (Sodev Inc., Canada, Model 01D) and also with a densimeter from Anton Paar (Model DMA 602) to examine the validity of the measurements. The tests and operating procedure for the Picker's densimeter have been accomplished.¹¹⁾ For the densimeter

Table 2 Coefficients a_i for Eqn. (1) and the calculated standard deviation s

System	a_1	a_2	a_3	a_4	$\frac{s}{\text{J mol}^{-1}}$
$x C_6H_6 + (1-x) C_6H_{12}$	3186.6	-164.84	143.35	-48.56	0.84
$x C_6H_5Cl + (1-x) C_7H_8$	-474.9	-31.58	8.14		0.19

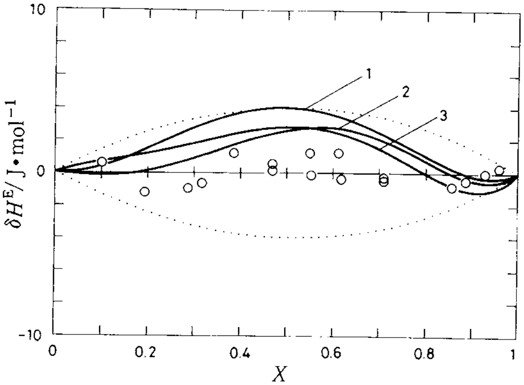

Fig. 2 Deviation plot for excess enthalpies δH^E of {xbenzene+ (1−x) cyclohexane} at 298.15 K ; $\delta H^E = H^E$ (obs) $- H^E$ (eqn.1). ○, present results. Curve : 1, Tanaka et al.[6] : 2, Elliott and Wormald[8] ; 3, Ewing et al.[9]. Dotted curves represent ±0.5% deviation.

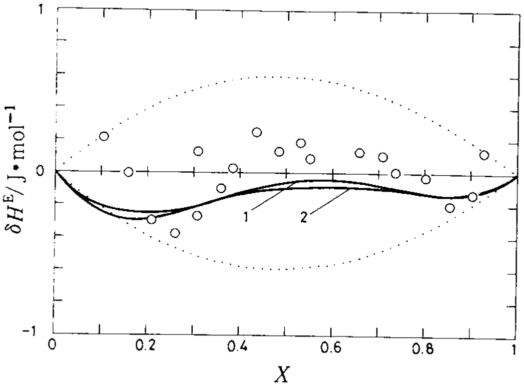

Fig. 3 Deviation plot for excess enthalpies δH^E of {xchlorobenzene + (1−x) toluene} at 298.15 K ; $\delta H^E = H^E$ (obs) $- H^E$ (eqn. 1). ○, present results. Curves : 1, Tanaka et al.[10] ; 2, Kimura and Takagi.[20] Dotted curves represent ±0.5% deviation.

of Anton Paar we have firstly carried out a test to examine the relation between the liquid densities ρ_0 which were determined with Picker's densimeter and the resonance frequency F at 298.15 K. The temperature of circulating water was controlled within ±0.0002 K. The relation between the density ρ and the observed F values were expressed with the equation

$$\rho/\text{g cm}^{-3} = A + BF^2 + CF^4. \qquad (2)$$

In Table 3 the comparison between the values ρ_1 calculated with three parameters determined for all the fluids and the values ρ_2 determined by using N_2 gas and water is indicated. An excellent fitting was obtained with two parameters A and B in the Picker's densimeter, but three parameters were required in the Anton Paar densimeter to express the relation between ρ and F. As is seen an error larger than 5×10^{-5}g · cm^{-3} may occur if the calibration for Anton Paar densimeter is carried out by using only N_2 gas and water, as usually adopted. This error exceeds the precision of our determination with Picker's densimeter ($\pm 3 \times 10^{-6}$ g cm^{-3}) .

2 . 4 Measurements of heat capacity

A Picker's flow calorimeter was used for measuring heat capacities. The test and the operating procedure have been described previously.[12] The heat capacity divided by volume (C_p/V) of cyclohexane was determined by using heptane as standard. It was 1.4337 J K^{-1} cm^{-3} at 298.15 K and used as the reference value.

Table 3 Density values ρ_1 and ρ_2 determined with Anton Paar densimeter calibulated with the ρ_0 values determined by using Picker's densimeter at 298.15 K. The values ρ_1 were calculated with coefficients A, B, and C in eqn. 2 determined by the least squares method ; the values ρ_2 were calculated by the calibulation with water and N_2 gas.

Fluids	ρ_0 / g cm^{-3}	ρ_1 / g cm^{-3}	$(\rho_0-\rho_1)\times10^5$ / g cm^{-3}	ρ_2 / g cm^{-3}	$(\rho_1-\rho_1)\times10^5$ / g cm^{-3}
N_2 gas	0.0011450	0.0011452	-0.02		
Heptane	0.6794877	0.6794865	0.12	0.6794359	5.18
Toluene	0.8621885	0.8621901	-0.16	0.8621633	2.52
Benzene	0.8736036	0.8736033	0.03	0.8735779	2.57
Water	0.9970474[a]	0.9970471	0.03		
Chlorobenzene	1.1010885	1.1010885	0.00	1.1011168	-2.83

[a] Standard value taken from literature.[17)]

3. Results and discussion

3.1 Expression of experimental results

The molar masses M(mix) of the mixed solutes were calculated according to the definition :

$$M(\mathrm{mix}) = M(\mathrm{AOT}) + r\cdot MH_2O \qquad (3)$$

where M(AOT) and M(H_2O) are the molar masses of AOT and water, respectively. The composition of solution was expressed with molality m of the mixed solute in cyclohexane. The apparent molar volumes $V\phi$ and apparent molar heat capacities $C_{p,\phi}$ were calculated from the equations

$$V\phi = M(\mathrm{mix})/\rho + (1/\rho - 1/\rho^*)/m \qquad (4)$$

and

$$C_{p,\phi} = M(\mathrm{mix})\ c_p + (c_p - c_p^*)/m \qquad (5)$$

where c_p is specific heat capacity of solution, and ρ^* and c_p^* are the quantities of cyclohexane. The experimental values of $C_{p,\phi}$ and $V\phi$ are listed in Table 4.

The relative apparent molar enthalpies $L\phi$ were expressed as relative values by taking the enthalpy of dilution extrapolated at $m=0$, $\Delta_{\mathrm{dil}}H^\infty$ as the standard value :

$$L\phi = \Delta_{\mathrm{dil}}H - \Delta_{\mathrm{dil}}H^\infty, \qquad (6)$$

where the enthalpies of dilution $\Delta_{\mathrm{dil}}H$ were measured by diluting original mixtures of 0.8 and 0.06 mol kg^{-1} with cyclohexane. The observed enthalpies $L\phi$ are listed in Table 5. Each set was divided into some groups and smoothed by the least squares method fitting to polynomial equation.

3.2 Apparent molar volumes

The experimental results for $V\phi$ are plotted in Fig. 4. In all systems the $V\phi$ values are constant over the investigated molality within the imprecision of measurements of about 0.5 cm^3 mol^{-1}. It is very interesting to compare the present results with those for (POE+H_2O+hydrocarbon) in which significant decreases in $V\phi$ with increasing molality were observed[4,5)]. From the differences between the $V\phi$ for (AOT+r·H_2O) and that for AOT (r=0) the molar volume of water solubilized in the swollen micelles of AOT was calulated to be 17.5±0.5 cm^3 mol^{-1}. This value is reasonable since it is comparable with that of bulk water, 18 cm^3 mol^{-1} at 298.15 K.

Except for the system of r=0 we observed

Table 4 Apparent molar heat capacities $C_{p,\phi}$ and apparent molar volumes V_ϕ of (AOT + r · H_2O) in cyclogexane at 298.15 K ($m^0=1$ mol kg^{-1}, $C^0=1$ J K^{-1} · mol^{-1}, $V^0=1$ cm^3 mol^{-1})

$\frac{m}{m^0}$	$\frac{C_{p,\phi}}{C^0}$	$\frac{V_\phi}{V^0}$	$\frac{m}{m^0}$	$\frac{C_{p,\phi}}{C^0}$	$\frac{V_\phi}{V^0}$	$\frac{m}{m^0}$	$\frac{C_{p,\phi}}{C^0}$	$\frac{V_\phi}{V^0}$
				r = 0				
0.000500	2350	-	0.000798	1920	401.0	0.001549	1410	401.0
0.001715	1260	401.0	0.002269	1200	398.2	0.003065	1010	-
0.00373	1040	396.8	0.004567	1020	395.9	0.008657	904.7	396.3
0.01161	880.7	395.4	0.01612	808.5	395.0	0.01742	843.0	395.3
0.02008	833.6	394.2	0.03030	813.1	394.9	0.03171	799.9	395.9
0.04150	795.8	395.9	0.04180	805.1	394.8	0.04917	805.6	395.7
0.06301	794.1	395.8	0.1019	796.4	395.8	0.1280	793.2	396.0
0.2134	793.3	395.7	0.2629	793.4	395.9	0.3689	793.1	395.5
0.4198	793.4	395.8	0.5846	793.7	395.6	0.6865	791.1	395.2
0.7610	794.6	395.4	0.8930	789.8	395.0	1.0261	787.4	394.5
				r = 1.0				
0.000394	2800	-	0.000784	2510	-	0.001274	2200	-
0.002532	1800	417.4	0.003831	1570	-	0.004778	1440	415.7
0.006441	1320	414.5	0.008371	1240	414.1	0.01651	1100	413.1
0.02473	1050	412.7	0.03324	1020	412.5	0.04483	993	412.4
				r = 3.0				
0.000258	2660	-	0.000653	2860	-	0.001569	2370	-
0.003186	1850	453.6	0.004812	1770	448.3	0.006409	1540	-
0.007977	1490	446.9	0.01616	1250	454.8	0.02492	1190	452.2
0.03353	1140	455.0	0.04576	1110	455.1			
				r = 4.0				
0.000400	3070	-	0.001134	2850	-	0.004161	2230	462.8
0.006082	1950	464.3	0.01002	1680	463.6	0.02140	1380	463.1
0.05640	1230	463.4	0.10788	1179	463.7	0.2152	1157	463.6
0.3661	1147	463.7	0.51697	1140	463.7	0.6639	1137	463.7
0.7585	1172	463.6						
				r = 5.0				
0.000420	2820	-	0.000823	3690	-	0.001647	3830	-
0.003292	2980	487.9	0.004623	2540	487.4	0.006514	2210	487.3
0.008280	2020	484.3	0.01656	1640	482.9	0.02501	1500	482.2
0.03312	1440	481.8	0.04268	1390	481.8			

Table 4 —Continued

$\frac{m}{m^0}$	$\frac{C_{p,\phi}}{C^0}$	$\frac{V_\phi}{V^0}$	$\frac{m}{m^0}$	$\frac{C_{p,\phi}}{C^0}$	$\frac{V_\phi}{V^0}$	$\frac{m}{m^0}$	$\frac{C_{p,\phi}}{C^0}$	$\frac{V_\phi}{V^0}$
				r = 6.0				
0.000224	2980	-	0.000667	3870	-	0.001057	4290	-
0.001523	4090	-	0.001893	3890	-	0.002181	3710	-
0.002796	3320	-	0.003692	2850	503.8	0.006822	2180	499.9
0.01239	1780	499.2	0.02209	1560	498.7	0.03168	1470	498.1
0.04165	1420	498.2						
				r = 10.0				
0.001089	5520	-	0.001682	5290	-	0.001988	4520	-
0.001993	4510	-	0.002638	3680	-	0.003455	3070	-
0.004973	2550	565.3	0.006431	2260	570.4	0.007684	2150	569.5
0.01205	1890	569.5	0.02079	1740	568.9	0.02343	1760	568.8
0.03055	1660	568.8	0.03976	1620	568.8	0.05556	1620	568.9
0.1156	1648	569.6	0.2721	1600	569.5	0.4320	1588	569.4
0.5932	1604	569.2	0.7376	1662	569.2	0.8682	1642	569.0

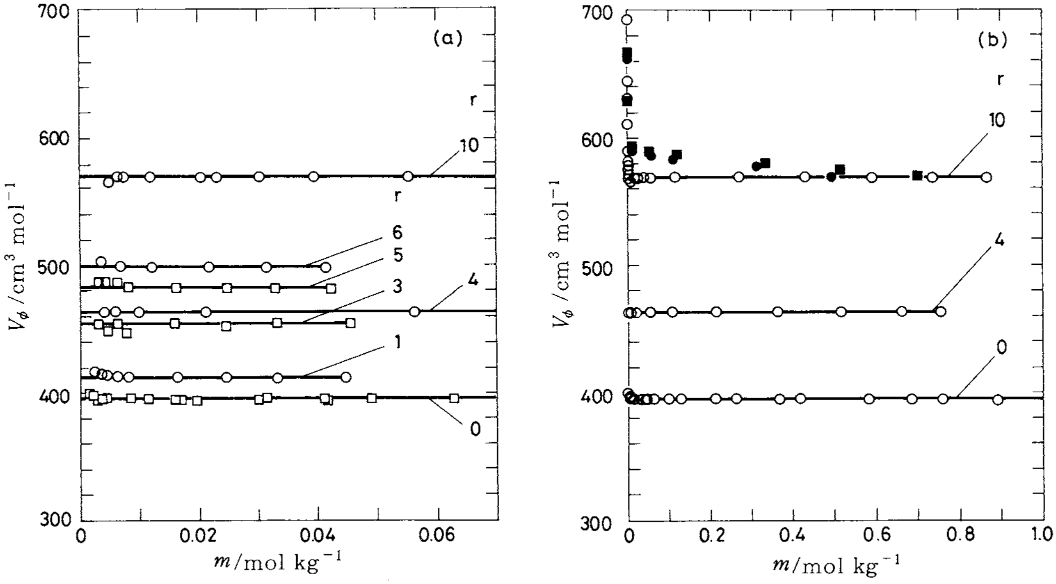

Fig. 4 Apparent molar volumes of $(AOT+r\cdot H_2O)$ in cyclohexane at 298.15 K. Marks : ○, □, measured within 3h after preparation ; ●, measured by Anton Paar densimeter 1 d after preparation ; ■, measured by Picker's densimeter 2 d after preparation.

Table 5 Relative apparent molar enthalpies L_ϕ of (AOT + r · H_2O) in cyclohexane at 298.15 K ($m^\circ=1$ mol kg^{-1}, $L_\phi=1$ kJ mol^{-1})

$\frac{m}{m^0}$	$\frac{L_\phi}{L^0}$	$\frac{m}{m^0}$	$\frac{L_\phi}{L^0}$	$\frac{m}{m^0}$	$\frac{L_\phi}{L^0}$	$\frac{m}{m^0}$	$\frac{L_\phi}{L^0}$
r = 0							
0.01607	2.057	0.03331	3.564	0.06778	4.404	0.1027	4.671
0.1726	4.868	0.2251	4.931	0.2621	4.954	0.3547	4.975
0.4632	4.979	0.5675	4.968	0.7979	4.938		
r = 1.0							
0.00335	-6.382	0.00473	-8.600	0.00631	-10.85	0.01106	-12.41
0.01719	-13.71	0.02327	-14.32	0.03082	-14.87	0.03298	-15.00
0.03982	-15.17	0.04697	-15.33	0.06436	-15.67	0.09894	-15.96
0.1642	-16.25	0.2497	-16.46	0.3385	-16.58	0.5438	-16.77
0.7678	-16.89						
r = 4.0							
0.00219	-30.02	0.00252	-33.78	0.00267	-35.56	0.00304	-37.25
0.00311	-37.80	0.00317	-38.44	0.00325	-40.64	0.00334	-39.46
0.00448	-45.95	0.00459	-47.15	0.00613	-51.43	0.00766	-54.44
0.01074	-58.30	0.02995	-63.64	0.03871	-64.33	0.04567	-64.83
0.04606	-64.75	0.06342	-65.39	0.1463	-66.43	0.3717	-67.03
0.5444	-67.20	0.7744	-67.34				
r = 5.0							
0.00149	-38.25	0.00320	-67.65	0.00619	-81.29	0.00930	-86.45
0.01537	-90.59	0.02285	-92.70	0.03026	-93.83	0.03264	-94.23
0.04616	-94.89	0.06379	-95.60	0.1636	-96.16	0.2497	-96.41
0.3400	-96.62	0.5516	-96.85	0.7858	-99.00		
r = 10.0							
0.00092	-102.0	0.00137	-135.5	0.00295	-165.7	0.005701	-177.3
0.00856	-181.5	0.01416	-185.0	0.01540	-184.5	0.02105	-186.8
0.02789	-187.1	0.03200	-187.3	0.03554	-187.7	0.04291	-188.0
0.06541	-188.7	0.09957	-189.2	0.1690	-189.6	0.2221	-189.7
0.2598	-189.8	0.3563	-190.0	0.4727	-190.1	0.5881	-190.1
0.8561	-190.2						

abnosmally large V_ϕ at molalities lower than 0.0005 mol kg^{-1} as shown in Fig. 4 (b) for the case of r=10. In order to examine this abnormality we carried out some measurements with Anton Paar densimeter to see possible affection caused from the material used for the cell tube, and also tested the dependence of V_ϕ on the stored period of mixtures after preparation. As are shown in Fig. 4 (b) the region of abnormally large volumes is extended to a higher molality for the sets of mixtures stored more than one day. This occurred with both densimeters of Picker and Anton Paar. We concluded, therefore, that those abnormal results were attributed to a slight decrease in density due to absorption of added water onto the glass wall of vessels during the samples were stored for a long period because the solubilized water is less stable in dilute region. From this consideration the abnormally large volumes that observed generally at $m<0.0005$ mol kg^{-1} have been omitted. Unless, we can not explain such large values at infinite dilution. The points of dilute region were measured within 2h after preparation, and the loss in density for those mixtures was estimated to be less than 3×10^{-5} g cm^{-3}.

3 . 3 Apparent molar heat capacity

The experimental results of $C_{p,\phi}$ are plotted in Fig. 5. It appears in literature that AOT, to which no water is added, forms reverse micells in nonpolar hydrocarbons passing through very small CMC, for instance, 0.2 mmol dm^{-3} from a spectroscopic[13] and light scattering methods[14]. However, it is seen that the present results accompany no maximum in $C_{p,\phi}$ up to 1 mol · kg^{-1}, which are attributed to the thermal relaxation due to intermolecular aggregation as have been observed in the systems of (alcohol + alkane).[15] We suppose that those values assigned as CMC are the lowest composition at which AOT molecules begin to interact each other forming very small size aggregates.

The $C_{p,\phi}$ for the system of r=0 increases with decreasing molality in the region of $m<0.005$ mol kg^{-1}. This increase in $C_{p,\phi}$ suggests the thermal relaxation due to a change in conformation of AOT as the intermolecular interactions of both long and short ranges among AOT molecules are broken in very dilute region. When the amount of water, r is increased to the

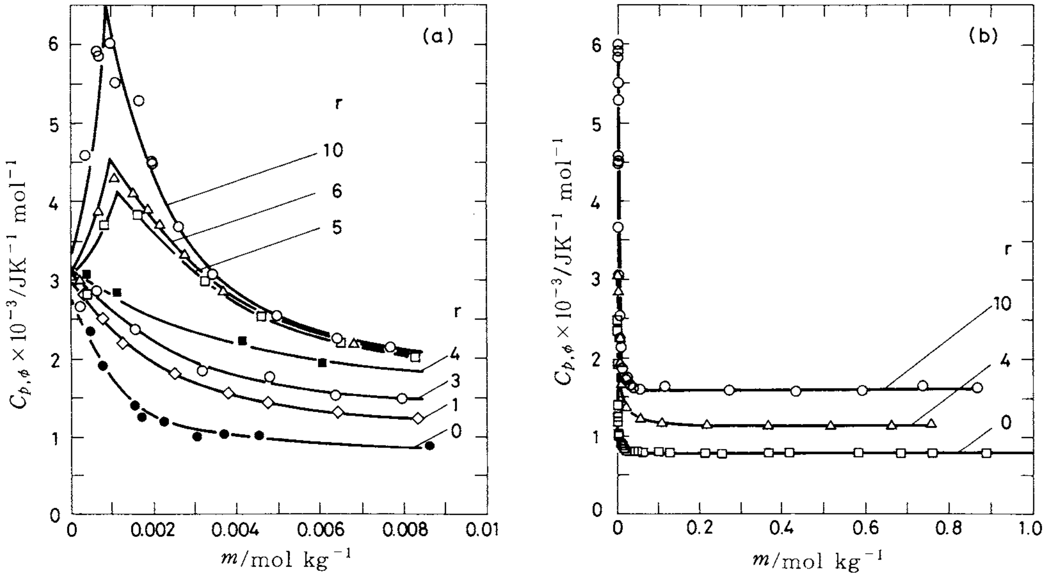

Fig. 5 Apparent molar heat capacities of (AOT + r·H_2O) in cyclohexane at 298.15 K.

value larger than 4 a sharp peak appears at about 0.001 mol kg^{-1}. Similar changes were also observed in cases of nonionic amphiphiles[4,5]. This means that a drastic shift in the equilibrium between monomers and associated AOT occurs around the molality where the peak appears. Thus, in the present systems a transition occurs at 0.001 mol kg^{-1} and swollen micelles are formed with the help of water when the ratio of amount of water to AOT exceeds 4. This composition where a peak appears may be assigned to the 'CMC' of forming swollen micelles. Recently Kon-no[16] found that the solubitity curve of water in (AOT+cyclohexane) solution at 298 K is clearly broken at 8 mmol kg^{-1}. In our observation this composition corresponds to that where the $C_{p,\phi}$ reaches nearly constant value with increasing molality so that no more significant change in the fraction of monomeric AOT occurs. The changes in $C_{p,\phi}$ with molality become very small at $m>0.1$ mol kg^{-1}.

The molar heat capacity of water at the infinite dilution can be estimated from the difference between the value of $C_{p,\phi}$ for r=0 and that of r=10 by assuming an additive for the molar heat capacity of mixed solutes. Although it is a rough value because of uncertainty of determination the molar heat capacity of water is about 50 J K^{-1} mol^{-1}. Since this value is closer to that of gaseous water, 37 J K^{-1} mol^{-1} [17] it is reasonable to understand that the water molecules are separated each other, partially binding on the hydrophilic part of AOT and partially solved in cyclohexane. On the other hand the difference between $C_{p,\phi}$ for r=10 and that for r=0 at $m>0.1$ mol kg^{-1} is 805 J K^{-1} mol^{-1}. This is close to 10 times of the molar heat capacity of bulk water, 75 J K^{-1} mol^{-1}.[17]This result supports the accepted concept that the water is incorporated in the hydrophilic micellar core of AOT and takes bulky state. The corresponding calculation for r=4 gives 87.6 J K^{-1} mol^{-1} as the molar heat capacity of water.

3.4 Relative apparent molar enthalpy

The experimental results of L_ϕ are plotted in

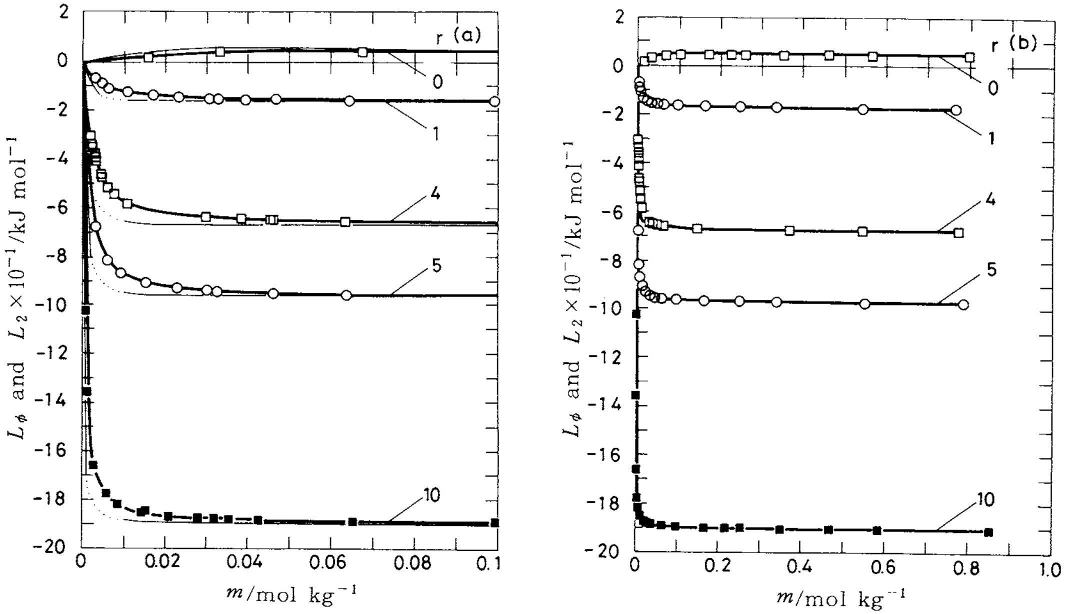

Fig. 6 Relative molar enthalpies of (AOT+r·H_2O) in cyclohexane at 298.15 K. Marks and heavy lines represent apparent molar quantities. Fine lines represent partial molar quantities.

Fig. 6. It is very interesting to see that the relative enthalpies for the system of r=0 are positive. In the actual measurements the enthalpy of dilution is slightly endothermic down to 0.2 mol kg^{-1}, then changes exotherm at the lower molalithes. Generally the enthalpy of diluting polar liquids with nonpolar solvents is endothermic because of the breakdown of attractive intermolecular interactions among the polar molecules, unless attractive forces act between solutes and solvent molecules forming molecular complexes upon mixing. A specific interaction which gives negative enthalpies of mixing has been suggested for the systems of (globular molecule+long chain hydrocarbon).[18] This effect is explained in terms of the "condensation" of a chain molecule onto a globular one. However, the enthalpies of mixing of (cyclohexane+long chain hydrocarbon) are positive.[19] Therefore, the negative sign of the enthalpies of dilution for the present case cannot be attributed to the effect of "condensation". We speculate that sodium ion is stabilized in the polar medium formed in the associated AOT molecules but favorable to make ion pair with sulfonium ion in a very dilute region where the associated AOT molecules are separated into monomeric ones. The endothermic heat of dilution due to van der Waal's forces among polar parts of AOT and the exothermic heat due to ionic interaction are canceled each other, and the net heat of dilution is exotherm in the dilute region. The fact that the enthalpy depends on molality suggests, more or less, the existence of intermolecular interactions among AOT molecules, however, we believe that the intermolecular attractive-force of AOT-AOT is moderate and only small size of aggregates are formed. Accordingly, it is unreasonable to conclude that "reverse micelles" are formed without adding water. This conclusion is consistent with that obtained from heat capacity measurements.

The $L\phi$ curves for the solute to which water is added are quite unique. In the dilute region less than 0.005 mol kg^{-1} the value of $L\phi$ decreases very sharply with increasing molality. On the other hand, at $m>0.05$ mol kg^{-1} $L\phi$ takes nearly constant value and expressed with slightly concave curve. In the case of associated solutions, the apparent molar heat capacity reflects the shifting rate of fractions of species between monomers and aggregates with the change of composition, and the enthalpy reflects the fraction of monomeric or associated species exist at the composition. The sharp decreases in enhalpy at $m<0.005$ mol kg^{-1} suggest that the aggregation of AOT is in progress very sharply with increasing molality with the help of water,but the aggregation number reaches a saturated one indicating a nearly constant enthalpy value at $m>0.05$ mol kg^{-1}. The value of $L\phi/r$ for $m>0.05$ mol kg^{-1} is -19.3 ± 0.4 kJ K^{-1} mol^{-1} independently of r. Since the enthalpy change due to AOT-AOT interaction is very small this value is assigned to the stabilization enthalpy of water which is transferred from the state of infinite dilution in to the polar core of the swollen micelles. The calculated value corresponds to the enthalpy to form 1 mol of hydrogen bondings.

Fig. 6 (a) shows the changes in $L\phi$ at low molalities along with the relative partial molar enthalpies L_2. The L_2 for the systems of $r\geqq5$ decreases with a straight line up to 0.002 mol kg^{-1} and then, turns to horizontal one at $m>0.02$ mol kg^{-1}. Smooth curve of L_2 between those two straight lines could not be determined because the slope of $L\phi$ curve changes abruptly. Dotted lines show approximate values.

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References

1) J. C. Ravey, M. Buzier, C. Picot, *J. Colloid Interface Sci.* **97**, 9 (1984).
2) P. L. Luisi, B. E. Straub (ed.) ,"*Reverse Micelles*", Plenum Press, New York (1984).
3) H. L. Rosano, M. Clausse (ed.) , "*Micloemulsion Systems*", Marcel Dekker, Inc., New York (1987).
4) R. Tanaka, *J. Colloid Interface Sci.* **122**, 220 (1988).
5) R. Tanaka, A. Saito, *J. Colloid Interface Sci.* **134**, 82 (1990).
6) R. Tanaka, P. J. D'Arcy, G. C. Benson, *Thermochim. Acta* **11**, 163 (1975).
7) J. J. Christensen, R. W. Hanks, R. M. Izatt, "*Handbook of Heats of Mixing*", Wiley-Interscience, New York (1982).
8) K. Elliott, C. J. Wormald, *J. Chem. Thermodyn.* **8**, 881 (1976).
9) M. B. Ewing, K. N. Marsh, R. H. Stokes, C. W. Tuxford, *J. Chem. Thermodyn.* **2**, 751 (1970).
10) R. Tanaka, G. C. Benson, *J. Chem. Eng. Data* **21,** 320 (1976).
11) R. Tanaka, *Netsu Sokutei* **6**, 2 (1979) .
12) R. Tanaka, *J. Chem. Thermodyn.* **14**, 259 (1982).
13) S. Muto, K. Meguro, *Bull. Chem. Soc. Jpn.* **46**, 1316 (1973).
14) M. Kotlarchyk. J. S. Huang, S. H. Chen, *J. Phys. Chem.* **89**, 4382 (1985).
15) R. Tanaka, S. Toyama, S. Murakami, *J. Chem. Thermodyn.* **18**, 63 (1986).
16) K. Kon-no, *Newsletter* **14**, 9 (1989); published from Division of Colloid and Surface Chemistry, Chem. Soc. Jpn.
17) J. A. Riddick, W. B. Bunger, "*Techniques of Chemistry*" Vol. II (A. Weissberger, ed.), Wiley-Interscience, New York (1970).
18) P. St. Romain, H. Tra Van, D. Patterson, *J. Chem. Soc. Faraday Trans* I, **75**, 1700 (1979) .
19) V. T. Lam, P. Picker, D. Patterson, P. Tancrēde, *J. Chem. Soc. Faraday Trans* II, **70**, 1465 (1974).
20) T. Kimura, S. Takagi, *J. Fac. Sci. Technol. Kinki Univ.* **18**, 49 (1983).

要　旨

混合溶質 {di-2-ethylhexyl sodium sulfosuccinate (Aerosol OT, 又は AOT) $+r\cdot H_2O$} の見かけのモル体積 $V\phi$, モル熱容量 $C_{p,\phi}$, 相対モルエンタルピー $L\phi$ をシクロヘキサン中 298.15 K で, 0.0002 から 1 mol kg^{-1} の範囲で測定した。希釈熱は新しく作ったフロー型熱量計で測定した。この熱量計をテストするために（ベンゼン＋シクロヘキサン）と（クロロベンゼン＋トルエン）の 298.15 K における過剰エンタルピーを測定した。

水を添加しない系では, 希釈熱が0.2 mol kg^{-1} で吸熱から発熱に変わる。そして, 熱容量の濃度に対する変化は単調である。$r \geqq 5$ の系では $m=0.001$ mol kg^{-1} に熱容量の鋭いピークが現れる。そして, 希釈熱は $m=0.01$ mol kg^{-1} 以下の濃度で鋭く増加する。AOT はシクロヘキサン中での分子間相互作用は弱くミセルを形成しないが, $r \geqq 5$ の系では $m=0.001$ mol kg^{-1} で転移が生じて W/O マイクロエマルションが生成されると結論した。