Aggregation of Dodecyldimethylamine *N*-Oxide Perchlorate in Benzene

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Osmotic coefficients measured by vapour pressure osmometry are reported for solutions of dodecyldimethylamine *N*-oxide perchlorate over the concentration range 0.008—0.38 mol kg^{-1} at 27, 33, 40, and 50 °C. Solute activities decrease rapidly with increasing concentration owing to dipole–dipole association. The non-ideal behaviour of the system is interpreted in terms of an association model, which includes an extended series of multimers, and the association equilibrium constant, enthalpy ($\Delta H° = -3.34$ kcal mol^{-1}) and entropy ($\Delta S° = -10.34$ cal mol^{-1} K^{-1}) are derived.

Surfactants have the general property of being soluble in water as well as in dipolar aprotic and nonpolar solvents. In dilute aqueous solutions they self-associate so as to achieve segregation of their hydrophobic parts from the solvent medium. Various patterns of molecular architecture, such as spherical or globular micelles, large rod-like micelles, and spherical vesicles, result from this self-association.[1] In nonpolar solvents, surfactants form oligomers, which at an appropriate concentration are transformed into cyclic structures ('reversed' or 'inverted' micelles).[2] The reversed micelle structure is generally converse, with the ionic or polar groups surrounding the interior cavity or 'solvent pool' and the hydrophobic hydrocarbon chains extending into and penetrated by the bulk nonpolar solvent. Both types of micelle are known to exhibit considerable catalytic activity, which depends on a variety of factors,[3] as well as acting as solubilizing agents[4] and as model systems for membranes.[4,5]

Salts of long-chain aliphatic amines form micelles in water and reversed micelles in organic solvents and both show catalytic activity.[3b] Extraction with amines has been applied in hydrometallurgy and in processing nuclear fuels.[6]

The properties of *N*-oxides of long-chain aliphatic amines and their salts in aqueous solution have also been extensively investigated and compared with those of the parent amines.[7] Very little is known about their solutions in organic solvents. We report a study of the non-ideality of dodecyldimethylamine *N*-oxide perchlorate (DDAO·HClO$_4$) in benzene solution by vapour pressure osmometry; the results are discussed on the basis of the stepwise aggregation model.

Experimental

Dodecyldimethylamine *N*-oxide monohydrate [m.p. 96—98 °C (from acetone)] was prepared by oxidation of the corresponding amine with hydrogen peroxide.[7a] The perchlorate was prepared by mixing the oxide (0.01 mol) in methanol (10 cm^3) with aqueous perchloric acid (72%; 0.01 mol). The solvent and the excess of water were removed and the residue was crystallized from methanol–ether (5:1); m.p. 71—73 °C (Found: C, 51.3; H, 9.85; N, 4.1. Calc. for $C_{14}H_{32}ClNO_5$: C, 51.0; H, 9.8; N, 4.25%).

A Knauer vapour pressure osmometer was used. The instrumental calibration procedure and method of measurement were similar to those described previously.[8] Osmotic coefficients (Φ) were calculated from equation (1) where V is the measured

$$V = \Phi m k \qquad (1)$$

imbalance (µV), k is the calibration constant determined from benzil reference solutions, and m is the stoicheiometric solute concentration (mol kg^{-1}).

The osmotic coefficients were fitted by least-squares methods to polynomials in m [equation (2)] and $m^{1/2}$ [equation (3)],

$$\Phi = \sum_{i=1}^{n=2.5} A_i m^{i-1} \qquad (2)$$

$$\frac{\Phi - 1}{m^{1/2}} = \sum_{i=1}^{n=3.5} a_i (m^{1/2})^{i-1} \qquad (3)$$

which exactly reproduce all measured data. The coefficients are given in Table 1.

Table 1. Values of the coefficients A_i in equation (2) and a_i in equation (3)

	27 °C	33 °C	40 °C	50 °C
A_1	0.8739	0.9502	0.8661	0.8963
$A_{1.5}$	−7.3718	−8.0106	−5.6167	−5.0618
A_2	32.9964	36.3221	18.0389	14.4622
$A_{2.5}$	−79.5953	−88.7823	−27.4887	−20.1948
A_3	97.2949	109.7241	15.8296	10.9452
$A_{3.5}$	−47.1078	−53.6079		
S_q	0.0017	0.0029	0.0045	0.0049
r	0.999	0.999	0.999	0.999
No. of points	35	34	36	35
Concn. range of m	0.008—0.381	0.008—0.399	0.009—0.381	0.009—0.379
$\bar{n}$	2.3—12.5	2.2—11.1	2.1—9.9	1.9—8.4
a_1	−16.7326	−13.7294	−13.8476	−11.2041
$a_{1.5}$	49.1763	35.0202	37.9364	27.7251
a_2	−55.9622	−33.4088	−41.0479	−27.5894
$a_{2.5}$	22.9902	11.0423	16.3615	10.3798
S_q	0.011	0.014	0.017	0.019
r	0.999	0.999	0.999	0.999

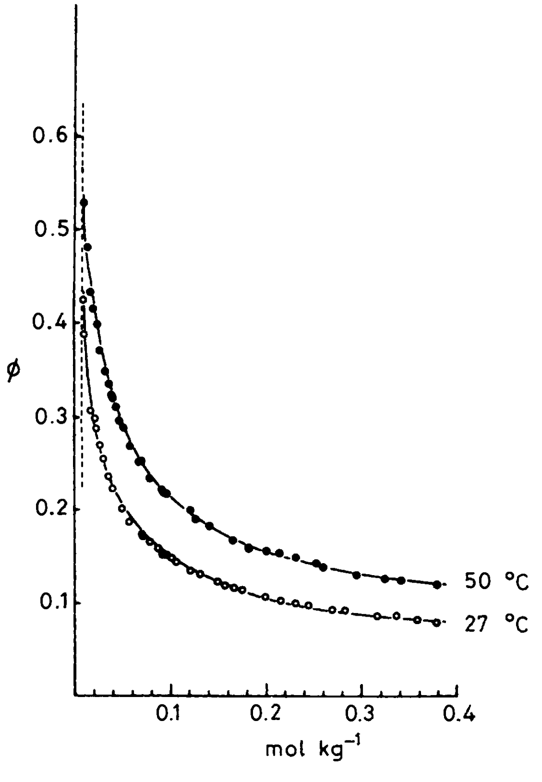

Figure 1. Molal osmotic coefficients of solutions of dodecyldimethylamine *N*-oxide perchlorate in benzene at 27 and at 50 °C

Results and Discussion

Figure 1 shows the molal osmotic coefficients of DDAO·$HClO_4$ in benzene solution as a function of the molal concentration. The solid lines are drawn on the basis of equation (2), using the coefficients from Table 1. The vertical dotted line at 0.008 mol kg^{-1} indicates the concentration limit below which precise measurements were not possible.

Assuming that the dipole moment of the complex investigated is high and dissociation to ions in non-polar and low dielectric constant benzene is negligible, and that the extent of non-specific deviation and non-ideality due to solute–solvent interaction is equally insignificant, the deviation from ideal behaviour ($\Phi = 1$) must be due to the formation of aggregates.

The aggregation of DDAO·$HClO_4$ can be described by the stepwise aggregation model,[2,8,9] where it is assumed that dimers and all higher species coexist in each solution with one equilibrium constant, K [equation (4)]. In this equation m is the

$$K = (m - \Phi m)/(\Phi m)^2 \qquad (4)$$

$$m = m_1 + \sum_{i=2}^{n=20} iK^{i-1}(m_1)^i \qquad (4a)$$

$$\Phi m = m_1 + \sum_{i=2}^{n=20} K^{i-1}(m_1)^i \qquad (4b)$$

stoicheiometric concentration, Φm is the osmometric concentration, and m_1 is the free monomer concentration. The values of equilibrium constants are given in Table 2. Examples of the population distributions computed for DDAO·$HClO_4$ at 27 and at 50 °C are shown in Figure 2 (for details see ref. 8). The standard enthalpy, $\Delta H°$, and entropy, $\Delta S°$, for the stepwise aggregates were calculated from equation (5) and are listed in Table 2.

Table 2. Values of the aggregation constants and thermodynamic parameters for DDAO·$HClO_4$ in benzene

T/°C	K/kg mol⁻¹	$-\Delta H°$/kcal mol⁻¹ [a]	$-\Delta S°$/cal mol⁻¹ K⁻¹ [a]
27	384.0 ± 8.0	3.34 ± 0.32	10.34 ± 1.05
33	294.7 ± 9.2		
40	243.6 ± 8.9		
50	171.2 ± 7.1		

[a] 1 cal = 4.184 J.

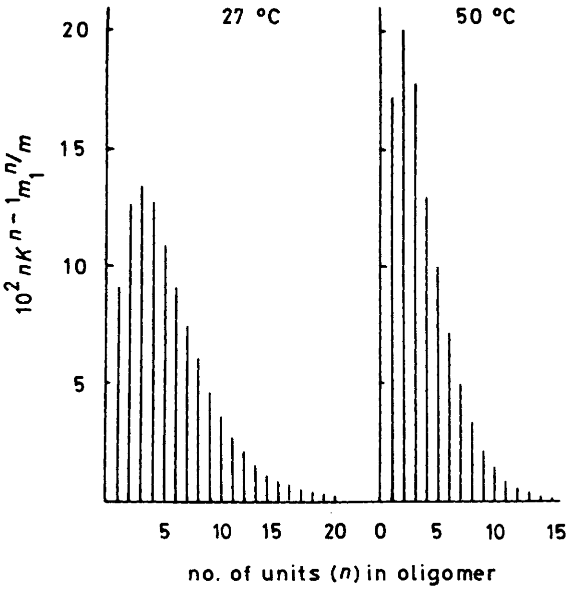

Figure 2. Examples of the population distribution in aggregations of dodecyldimethylamine *N*-oxide perchlorate in benzene at 27 and at 50 °C; concentration m = 0.02 mol kg⁻¹; m_1 calculated from equations (4a) and (4b)

$$\ln K = -\Delta H°/RT + \Delta S°/R \qquad (5)$$

Our results can be compared with those for dodecylammonium propionate;[10] in the case of DDAO·$HClO_4$ enthalpy is three times and entropy five times smaller than for dodecylammonium propionate. The difference is probably caused by the bulk factor of the polar groups. As in the case of dodecylammonium propionate, we confirmed the apparent failure of a monomer–oligomer association to describe the observed self-association.

It is apparent from the thermodynamic functions listed in Table 2 that the aggregation is exothermic, since $\Delta H°$ is negative. The negative value of $\Delta S°$ reflects, in part, the increase due to self-association. The fact that the observed self-association of DDAO·$HClO_4$ decreases with increasing temperature tends to rule out hydrophobic interactions as the predominant cause of the self-association, since hydrophobic interactions generally increase with increasing temperature.[11,12] However, the temperature effect on the self-association is consistent with a dipole–dipole-type interaction.[8,13,14]

Activity coefficients γ_2 are obtained from Φ with the help of the Gibbs–Duhem equation (6).[15] The difficulty with this pro-

$$\ln \gamma_2 = \Phi - 1 + \int_0^{m^{1/2}} \frac{\Phi - 1}{m^{1/2}} dm^{1/2} \qquad (6)$$

cedure is that it is necessary to assume values of the function

Table 3. Osmotic and activity coefficients of dodecyldimethylamine *N*-oxide perchlorate in benzene solution

		27 °C		33 °C		40 °C		50 °C	
$m^{1/2}$	m	Φ	$\gamma_2{}^*$	Φ	$\gamma_2{}^*$	Φ	$\gamma_2{}^*$	Φ	$\gamma_2{}^*$
0.1	0.01	0.396	1	0.434	1	0.459	1	0.516	1
0.15	0.0225	0.288	0.686	0.318	0.691	0.345	0.700	0.400	0.714
0.2	0.04	0.223	0.519	0.249	0.525	0.270	0.532	0.318	0.548
0.25	0.0625	0.184	0.418	0.207	0.423	0.222	0.429	0.262	0.442
0.3	0.09	0.157	0.350	0.177	0.354	0.191	0.360	0.223	0.370
0.35	0.1225	0.136	0.300	0.155	0.304	0.169	0.310	0.195	0.319
0.4	0.16	0.119	0.263	0.135	0.267	0.152	0.272	0.173	0.280
0.45	0.2025	0.106	0.234	0.121	0.237	0.136	0.242	0.156	0.249
0.5	0.25	0.097	0.211	0.110	0.214	0.121	0.218	0.141	0.224
0.55	0.3025	0.090	0.192	0.103	0.195	0.109	0.198	0.129	0.204
0.6	0.36	0.083	0.176	0.095	0.179	0.104	0.182	0.122	0.188

$(\Phi - 1)/m^{1/2}$ from the lowest concentration measured to infinite dilution. This is particularly difficult in the present case. In contrast to osmotic coefficients, however, only the ratio $\gamma_2(m^{1/2})/\gamma_2(m^{1/2} = 0.1) = \gamma_2^*$ relative to the values of $m^{-1/2} = 0.1$ mol kg^1 can be calculated using equation (7).[16,17] Relative activity coefficients γ_2^* evaluated by this method are listed in Table 3.

$$\ln \gamma_2^* = \Phi(m^{1/2}) - \Phi m^{1/2} = 0.1 + \int_{m^{1/2} = 1.0}^{m^{1/2}} \frac{\Phi - 1}{m^{1/2}} \mathrm{d}m^{1/2} \quad (7)$$

Acknowledgements

We acknowledge financial support from the Polish Academy of Sciences.

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Received 13*th July* 1987; *Paper* 7/1254