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Density and Viscosity of Octyl, Decyl, and Dodecyl Sodium Sulfates in Ethanol

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The density of mixtures of a homologous series of sodium alkyl sulfate ($H(CH_2)_nOSO_3^-Na^+$ surfactants (where $n = 8$, 10, and 12) in ethanol has been measured as a function of concentration and temperature, and the apparent molal volumes have been derived. The calculated partial molal volume of sodium ion ($V°_{Na^+}$) at infinite dilution from the three surfactants is found equal to −14.23, −13.75, and −10.44 cm^3·mol^{-1} at 25, 35, and 45 °C, respectively. The electrostriction of the alcohol molecules by the hydrophobic part $H(CH_2)_nOSO_3^-$ has been found to be almost negligible since the central charge is partially masked by the large hydrocarbon group. The Jones–Dole equation is used to determine the ionic β coefficient from viscosity measurements. The data are interpreted in light of structure-making or structure-breaking phenomena.

Introduction

The partial molal volume of an ion (*1*) can be assumed to be the sum of two parts: (i) the intrinsic volume of the ion and (ii) the volume change due to the change of the system structure by the addition of the ion.

If an ion is inserted into the solvent at infinite dilution, its probable position relative to the cavity or cage space of the solvent can be visualized as one of the following: (a) It can fall in a cavity or cage which is bigger than the ion itself. Because of the strong electrostatic forces operating within the cage, a dipole atmosphere will be created, which will consist of highly structured and oriented solvent molecules. The apparent partial molal ionic volume becomes negative (*2*, *3*) to an external observer, since electrostriction prevails as a result of ion–dipole and dipole–dipole forces in this firm solvation layer. This explains the negative partial molal volume of H^+, Li^+, Na^+, Ag^+, and OH^- ions. These ions belong to group A. (b) The ion size is very large compared to any existing cavity; the solvent network will be ruptured, and solvent molecules will be displaced in order to create a suitable cavity. The apparent partial molal ionic volume becomes positive to an external observer. This is the case for large tetraalkylammonium ions, group B, which do not exert sufficient electrostriction effects on account of their low surface charge density.

The sodium alkyl sulfate surfactant molecule consists of (i) the sodium ion and (ii) the hydrophobic part ($ROSO_3^-$) containing the hydrocarbon chain (R) and the counterion (OSO_3^-). The behavior of these two kinds of ions are very similar to those of the A and B groups.

To analyze the nature of ion–solvent interactions, physical properties such as density and viscosity can be measured to determine the apparent molal volume and the viscosity β coefficient for a series of homologous surfactants of sodium octyl sulfate (SOS), sodium decyl sulfate (SDeS), and sodium dodecyl sulfate (SDoS) in ethanol (EtOH) at different concentrations and at 25, 35, and 45 °C, respectively.

Experimental Section

Ethanol (BDH) was purified as mentioned in the previous works (*4*, *5*). Sodium dodecyl sulfate (*6*) as well as sodium octyl and decyl sulfates (BDH) were purified by recrystallization (twice) from acetone, dried in a vacuum oven, and stored in dark bottles. The stock solutions were prepared by mass. All of the solutions for density measurements were prepared by dilution of the stock solutions on a mass basis with the purified ethanol. All weighings were vacuum-corrected.

Table 1. Densities and Viscosities of Pure Ethanol at 25, 35, and 45 °C

	d_o/(g·cm^{-3})		η/(mPa·s)	
t/°C	obsd	lit.	obsd	lit.
25	0.785 34	0.785 09[a] 0.785 20[b]	1.0850	1.0840[d] 1.0832[a]
35	0.776 82	0.776 87[e]	0.9010	0.9110[b]
45	0.768 19	0.759 7[b] 0.767 98[e]	0.7990	0.8050[b]

[a] Kouris, S.; Panyiotou, C. *J. Chem. Eng. Data* **1989**, *34*, 200. [b] Bruson, R. R.; Byers, C. H. *J. Chem. Eng. Data* **1989**, *34*, 46. [c] Reference 4. [d] Evans, D. F.; Gardam, P. *J. Phys. Chem.* **1968**, *72*, 3281. [e] Reference 5.

The density measurements were carried out at 25, 35, and 45 °C using pycnometers of 20 cm^3 capacity with a minimum graduation of 0.005 cm^3. Each pycnometer was calibrated several times, and the data were averaged. The precision of the density measurments was within ±0.002%. Absolute viscosity measurements were carried out at the above temperatures using an Ubbelöhde level viscometer which was kept in a closed, dry atmosphere and did not necessitate kinetic energy correction. Runs were repeated until the time of flow using a stopwatch (Citizen) for three determinations within ±10^{-3} s was obtained. The viscosity of each solution was determined within an error of ±0.008%. The equations and procedures used to calculate the absolute density and viscosity of the solutions are reported elsewhere (*5*).

An ultrathermostat was used to adjust the bath temperature within ±0.002 °C, wherein the pycnometers or viscometer was completely immersed and the measurements were performed once the sample solution had reached a constant temperature.

Densites and viscosities at 25, 35, and 45 °C of the ethanol used in the present work with those taken from the literature are listed in Table 1.

Results and Discussion

The apparent molal volume of simple electrolytes and polyelectrolytes in aqueous (*3*), nonaqueous (*7*), and mixed

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Table 2. Density, Apparaent Molal Volume, and Viscosity of Sodium Octyl, Decyl, and Dodecyl Sulfate Solutions in Ethanol at 25, 35, and 45 °C

	25 °C			35 °C			45 °C		
c/(mol·L^{-1})	d/(g·cm^{-3})	ϕ_v/(cm^3·mol^{-1})	η/(mPa·s)	d/(g·cm^{-3})	ϕ_v/(cm^3·mol^{-1})	η/(mPa·s)	d/(g·cm^{-3})	ϕ_v/(cm^3·mol^{-1})	η/(mPa·s)
$H(CH_2)_8OSO_3^-Na^+$									
	±0.002%		±0.008%	±0.002%		±0.008%	±0.002%		±0.008%
0.043	0.785 49	290.0(0.03)	1.0852	0.776 84	298.0(0.09)	0.9010	0.768 20	302.0(0.06)	0.799 01
0.065	0.785 58	289.7(0.7)	1.0853	0.776 87	279.5(0.07)	0.9010	0.768 22	301.5(0.07)	0.799 03
0.086	0.785 66	289.5(0.04)	1.0854	0.776 92	297.0(0.06)	0.9011	0.768 28	300.5(0.07)	0.799 09
0.108	0.785 80	288.6(0.05)	1.0856	0.776 97	296.7(0.05)	0.9011	0.768 35	299.7(0.09)	0.799 17
0.133	0.785 93	288.3(0.04)	1.0858	0.777 04	296.2(0.05)	0.9012	0.768 48	298.5(0.06)	0.799 30
0.152	0.786 03	288.1(0.02)	1.0859	0.777 11	295.7(0.06)	0.9013	0.768 57	298.0(0.05)	0.799 39
0.171	0.786 15	287.8(0.02)	1.0861	0.777 19	295.3(0.06)	0.9014	0.768 71	297.0(0.08)	0.799 54
0.200	0.786 31	287.5(0.03)	1.0863	0.777 28	295.0(0.07)	0.9015	0.768 94	295.7(0.08)	0.799 78
0.250	0.786 66	286.7(0.04)	1.0868	0.777 59	293.6(0.08)	0.9018	0.769 41	293.6(0.10)	0.800 27
0.330	0.787 19	286.0(0.02)	1.0875	0.778 12	292.0(0.07)	0.9025	0.770 34	290.5(0.08)	0.801 24
0.390	0.787 72	285.0(0.03)	1.0883	0.778 55	291.0(0.06)	0.9030	0.771 23	288.0(0.07)	0.802 16
$H(CH_2)_{10}OSO_3^-Na^+$									
0.090	0.785 50	328.5(0.03)	1.0852	0.776 88	334.0(0.04)	0.901 07	0.768 20	338.6(0.05)	0.799 01
0.110	0.785 57	328.0(0.05)	1.0854	0.776 96	333.0(0.06)	0.901 16	0.768 25	337.9(0.05)	0.799 06
0.136	0.785 66	327.5(0.04)	1.0854	0.777 14	331.0(0.04)	0.901 37	0.768 37	336.5(0.04)	0.799 19
0.155	0.785 75	327.0(0.06)	1.0856	0.777 28	330.0(0.08)	0.901 53	0.768 48	335.5(0.03)	0.799 30
0.175	0.785 88	326.2(0.04)	1.0857	0.777 45	328.8(0.06)	0.901 73	0.768 62	334.5(0.06)	0.799 45
0.200	0.786 04	325.5(0.03)	1.0859	0.777 75	327.0(0.07)	0.902 07	0.768 76	333.8(0.06)	0.799 59
0.260	0.786 46	324.0(0.03)	1.0865	0.779 53	323.5(0.06)	0.904 14	0.769 39	330.5(0.05)	0.800 25
0.290	0.786 75	323.0(0.02)	1.0869	0.779 04	321.5(0.05)	0.903 57	0.769 79	328.8(0.08)	0.800 66
0.340	0.787 17	322.0(0.06)	1.0875	0.779 96	318.5(0.04)	0.904 64	0.770 51	326.3(0.07)	0.801 41
0.374	0.787 61	320.7(0.07)	1.0881	0.780 71	316.3(0.06)	0.905 51	0.771 09	324.5(0.08)	0.802 01
0.400	0.787 91	320.0(0.08)	1.0885	0.781 35	314.5(0.03)	0.906 25	0.772 05	323.5(0.08)	0.203 01
$H(CH_2)_{12}OSO_3^-Na^+$									
	±0.002%		±0.008%	±0.002%		±0.008%	±0.002%		±0.008%
0.072	0.785 30	360.0(0.04)	1.0849	0.776 63	375.5(0.08)	0.900 78	0.768 10	377.8(0.05)	0.798 91
0.100	0.785 39	366.2(0.06)	1.0850	0.776 76	372.2(0.06)	0.900 93	0.768 30	373.5(0.03)	0.799 11
0.130	0.785 55	364.5(0.03)	1.0853	0.776 98	369.0(0.05)	0.901 18	0.768 62	369.5(0.04)	0.799 45
0.170	0.785 86	362.0(0.04)	1.0857	0.777 45	364.7(0.05)	0.901 73	0.769 37	363.0(0.05)	0.800 22
0.200	0.786 18	360.0(0.05)	1.0861	0.777 93	361.5(0.06)	0.902 28	0.769 97	359.5(0.06)	0.800 85
0.250	0.786 81	357.0(0.03)	1.0870	0.778 97	356.0(0.07)	0.903 49	0.771 39	352.2(0.05)	0.802 33
0.280	0.787 24	355.3(0.06)	1.0876	0.779 68	353.0(0.06)	0.904 31	0.772 43	347.8(0.03)	0.803 41
0.310	0.787 76	353.4(0.06)	1.0883	0.780 48	350.0(0.04)	0.905 24	0.773 58	343.5(0.06)	0.804 61
0.340	0.788 35	351.5(0.07)	1.0891	0.780 52	346.5(0.03)	0.905 29	0.775 18	337.5(0.06)	0.806 27
0.362	0.788 83	350.0(0.07)	1.0898	0.782 28	343.8(0.06)	0.907 33	0.787 89	334.0(0.04)	0.809 49
0.396	0.789 68	347.5(0.05)	1.0909	0.783 35	341.0(0.07)	0.908 57	0.778 04	329.0(0.03)	0.819 24

solvents (*8–10*) has been the subject of extensive studies of ion–solvent interactions. The following equation (*11*) is used to calculate the apparent molal volume ϕ_v for the three surfactant solutions studied:

$$\phi_v = \frac{1000(d_o - d)}{cdd_o} + \frac{M}{d} \tag{1}$$

where, d_o, d, M, and c are, respectively, the density of the pure solvent, the density of the solution, the molecular weight, and the molality at a given temperature. The measured densities related to ϕ_v values are given with their probable errors in Table 2. The concentration dependence of the apparent molal volume can be compared to Masson's equation (*12*):

$$\phi_v = \phi°_v + S_v c^{1/2} \tag{2}$$

where the intercept $\phi°_v$ is the limiting partial molal volume of the salt, while S_v is the concentration dependence slope of the apparent molal volume. From ϕ_v vs $c^{1/2}$ plots for the given surfactant in ethanol, $\phi°_v$ (=$V°$) can be obtained by extrapolation to zero concentration. The utility of electrolytes in studying ion–solvent interactions lies in the additivity rule as, for our salts, $\phi°_v$ is equal to the sum of its ionic components ($V°_{Na^+}$ + $V°_-$). Conway et al. (*13*) obtained a straight line from the plots of the $V°$ of the tetraalkylammonium halides R_4NX in water vs the molecular weight of the cation R_4N^+; the $V°$ for X^- is obtained by extrapolating to zero cationic molecular weight. Millero and Drost-Hansen (*14*) have also used this method. Similarly in this work, Figure 1 shows the experimental $\phi°_v$ values obtained from applying eq 2 for the three surfactants (SOS, SDeS, and SDoD) at 25, 35, and 45 °C, respectively. These values are plotted against the molecular weight of the corresponding hydrophobic part (M^-). In each case a straight line was obtained in agreement with the Conway assumption. The intercept (obtained by the least-squares method) is found equal to the common limiting partial molal volume ($V°_{Na^+}$) at a given temperature from which $V°_-$ of the hydrophobic part can be calculated by subtraction. Both $V°_{Na^+}$ and $V°_-$ values at 25, 35, and 45 °C are recorded in Table 3. In addition, literature $V°_{Na^+}$ values

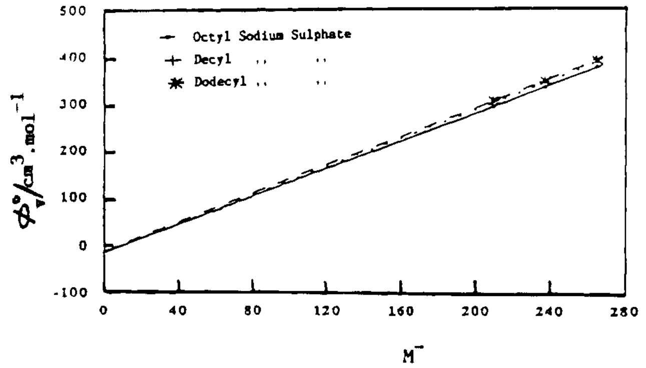

Figure 1. Variation of $\phi°_v$ against the hydrophobic molecular weight of the anion (M^-) of octyl, decyl, and dodecyl sodium sulfates at different temperatures.

Table 3. Limiting Partial Molal Volume $\bar{V}°$ ($cm^3 \cdot mol^{-1}$) for Na^+ in Ethanol and Other Solvents at 25 °C and Those for Octyl, Decyl, and Dodecyl Sulfates in Ethanol at Different Temperatures

		$\bar{V}°$/($cm^3 \cdot mol^{-1}$)				
		25 °C			35 °C	45 °C
ion	solvent	H_2O	MeOH	EtOH	EtOH	EtOH
Na^+		−5.7[a]	−12.6[b]	−14.75 −10.50[c]	−13.75	−10.44
OS^-				305.47	312.64	314.54
DeS^-				345.58	353.76	353.82
DoS^-				387.40	396.50	398.73

[a] Reference 16a. [b] Reference 16b. [c] Reference 1.

Table 4. Temperature Dependence of the Viscosity β Coefficient for Different Electrolytes in Ethanol

	β/($L \cdot mol^{-1}$)		
salt	25 °C	35 °C	45 °C
SOS	0.90	0.88	0.82
SDeS	1.10	1.06	0.99
SDoS	1.15	1.01	1.00

in other solvents (only at 25 °C) are also recorded.

The $V°_{Na^+}$ value at 25 °C in ethanol is −14.23 $cm^3 \cdot mol^{-1}$ in good agreement with Kawaizumi et al. (*15*); the other values are −13.5 and −10.44 $cm^3 \cdot mol^{-1}$ at 35 and 45 °C, respectively. As noted above, group A ions have negative apparent partial molal ionic volumes while those of group B have positive values. Accordingly, Na^+ is considered a structure-making ion while the hydrophobic part is considered structure-breaking.

Table 3 lists the limiting partial molal volumes $V°$ with their probable errors. If one compares the $V°_{Na^-}$ value for ethanol at 25 °C to those for water and methanol (*16*) and if the negativity of their values is deemed a function of solvation power in different media, then one concludes that the power increases from water to ethanol (i.e., decreasing dielectric constant of the solvent).

From Table 3 the $V°$ values for $ROSO_3^-$ salts (R = O, De, or Do) at any given temperature increase directly with the alkyl chain length, and their values are almost equal to their related molecular weight, indicating the unsolvation behavior of the hydrophobic chain. If we consider that this part of the surfactant is similar to a polymer chain with an uncharged state, then Tanford (*17*) considered the volume of the sphere is less than 1.0% of the total volume, the rest being solvent.

Moreover, the solvation shell is then mainly the result of short-range forces, since the polymer chain bears only a small charge density. Thus, the amount of solvent with this hydrophobic part appears sufficient to ensure only a solvation of the counterion group of the anion.

Millero (*18*) proposed that the partial molal volume of an ion at infinite dilution $V°_{ion}$ can be obtained from the relation

$$(\bar{V}°_{ion} - \bar{V}°_{crys}) = \bar{V}°_{elect} + \bar{V}°_{disord} + \bar{V}°_{caged} \qquad (3)$$

where $V°_{crys}$ is the crystal partial molal volume, $V°_{elect}$ is the contribution of the electrostrictional effect of the solvent, $V°_{disord}$ is a negative term corresponding to the accommodation of the ion in a cavity of the solvent, and $V°_{caged}$ is the caged partial molal volume (due to formation of caged or structured solvent around ions with a hydrophobic part). The resulting $V°_{ion} - V°_{crys}$ value depends on the balance between the electrostatic and the structure contributions.

It has been suggested for ions in aqueous solutions (*19*) that when the term $V°_{ion} - V°_{crys}$ is negative, the $V°_{disord}$ region in the above equation is greater than the $V°_{elect}$ region and the ion can be classified as a structure-making or positive solvating one (*20*). Assuming that this assumption is extended to nonaqueous solutions, the calculated $V°_{Na^+} - V°_{crys}$ values in ethanol ($V°_{crys}$ = 2.1 $cm^3 \cdot mol^{-1}$) (*21*) are −16.33, −15.85, and 12.54 $cm^3 \cdot mol^{-1}$ at 25, 35, and 45 °C, respectively. These values give a strong indication that, by raising the temperature, the ethanol structure is modified mainly by the presence of that ion and the structure-making behavior is decreased. When the term $V°_{Na^+} - V°_{crys}$ was compared in ethanol at 25 °C with those of other solvents taken from the literature (*16*) such as in MeOH, H_2O, ethylene glycol (EG), and *n*-methylpropionamide (NMP), the calculated values of the above term showed a gradual decrement in the following order, EtOH > MeOH > H_2O > EG > NMP, indicating that the structure-making character is decreased in the same direction.

Viscosity β Coefficient. The viscosity of different solutions at different temperatures is reported in Table 3. The Jones−Dole equation (*22*) is used to define the viscosity β coefficient as follows:

$$(\eta_r - 1)/c^{1/2} = A + \beta c^{1/2} \qquad (4)$$

where η_r is the relative viscosity of dilute solutions with molar concentration c, A is the ion−ion interaction parameter which can be calculated from Debye−Hückel theory, and β reflects the effects of ion−solvent interactions. When $(\eta_r - 1)/c^{1/2}$ vs $c^{1/2}$ is plotted against $c^{1/2}$ for the electrolytes at different temperatures, straight lines are obtained with intercepts equal to A, and the slopes yield the viscosity β coefficient. Table 4 shows β values for SOS, SDeS, and SDoS at 25, 35, and 45 °C, respectively. The β coefficient for a given salt is positive and decreases with increasing temperature. These positive values of β are associated with structure-making phenomena. The weak temperature dependence of β in ethanol is found to be similar to those obtained in pure nonaqueous solvents like methanol, acetonitrile (*23*), and dimethyl sulfoxide (*24*).

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