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Effect of Temperature on the Sodium 1-Hexyl Sulfate−Water System

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Electrical conductivity measurements for aqueous solutions of sodium 1-hexyl sulfate (SHS) have been carried out from (293.15 to 313.15) K. From the molar conductivity at infinite dilution values the transport numbers of SHS anions have been obtained for each temperature. Densities of the binary system water sodium 1-hexyl sulfate were measured at 298.15 K and 308.15 K. Excess volumes have been evaluated at concentrations above and below the critical micellar concentration.

Introduction

The self-association of sodium *n*-hexyl sulfate (SHS) in aqueous solution has been investigated as a function of the temperature. Several authors have reported systematic studies on the micellar behavior of the sodium 1-alkyl sulfate series with 8, 10, 12, 14, and 16 carbon atoms in the alkyl chain (Van Os, 1993). Preliminary evidence suggesting the possibility of self-association of this surfactant was from the apparent solubilization of the water-insoluble dye Sudan IV by concentrated aqueous solutions of SHS. A value of 0.517 mol L^{-1} for the critical micelle concentration (cmc) of SHS has been reported (Suarez, 1999).

It has been generally recognized that studies of thermodynamic and transport properties of surfactants are important for understanding their behavior in solutions (Kresheck, 1975). In this article we report results on electrical conductivity, the apparent and partial molal volumes, and excess volumes of sodium 1-hexyl sulfate in aqueous solution at various temperatures.

Materials and Methods

Sodium 1-hexyl sulfate (SHS) (purity ≥ 99%) from Lancaster (No. 6245) was used without further purification. All concentrations were determined by mass using distilled and degassed water.

The conductance was measured by using a conductivity meter (Kyoto Electronic type C-117), the cell of which was calibrated with KCl solutions in the appropriate concentration range. SHS solutions of known concentration were progressively added to water using an automatic pump (Dosimat 665 Metrohm). The measuring cell was immersed in a thermostat bath, maintaining the temperature control within ±0.01 K. The automatic pump and the temperature control were achieved using a Hewlett-Packard Vectra computer.

The densities of all solutions were measured with an Anton Paar DMA 60/602 density meter with an accuracy of $\pm 1.5 \times 10^{-6}$ g cm^{-3}. The temperature was kept constant within ±0.01 K by a proportional temperature controller HETO and checked with a digital precision thermometer Anton Paar DT 100-30. The densimeter was calibrated at each temperature with air at known pressure and water, where the density of air-saturated water was assumed to be 0.997 043 g cm^{-3} and 0.994 030 g cm^{-3} at 298.15 K and 308.15 K, respectively.

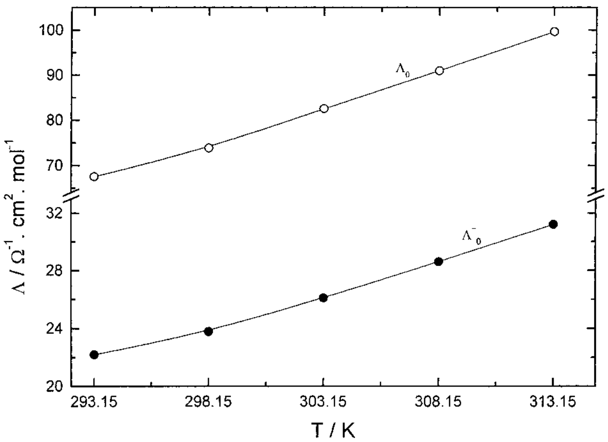

Figure 1. Variation of the molar conductivity at infinite dilution of sodium 1-hexyl sulfate, Λ_0, and 1-hexyl sulfate anion, Λ_0^-, with the temperature.

Results and Discussion

Table 1 shows the specific conductivity of SHS as a function of concentration. The molar conductivity of SHS at infinite dilution, Λ_0, is plotted vs temperature in Figure 1. By subtracting from the values of Λ_0 the corresponding conventional value for the sodium cation, $\Lambda_0^{Na^+} = 45.4$, 50.1, 56.5, 62.4, and 68.5 Ω^{-1} cm^2 mol^{-1} at 293.15 K, 298.15 K, 303.15 K, 308.15 K, and 313.15 K, respectively, the values of Λ_0^- for surfactant anions were obtained. As expected, the values slightly increase with the increase in temperature. From Λ_0 and Λ_0^- values the transport numbers of sodium 1-hexyl sulfate anions, $t_0^- = \Lambda_0^-/\Lambda_0$, can be calculated. The obtained results are summarized in Table 2. These values compare with the literature (Vanýsek, 1996): 0.367, 0.342, and 0.324 for the anions octyl sulfate, decyl sulfate, and dodecyl sulfate, respectively.

From the density data, apparent molal volumes, V_ϕ, of the surfactant in water were calculated using the equation

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Table 1. Specific Conductivity, κ, for the System 1-Hexyl Sulfate Water at Different Temperatures

c/mol dm^{-3}	κ/mS cm^{-1}	c/mol dm^{-3}	κ/mS cm^{-1}	c/mol dm^{-3}	κ/mS cm^{-1}
		$T = 293.15$			
0.1066	6.0	0.2908	14.1	0.5645	23.4
0.1200	6.6	0.3199	15.2	0.5998	24.5
0.1371	7.5	0.3309	15.7	0.6398	25.7
0.1600	8.5	0.3428	16.1	0.6855	27.0
0.1745	9.2	0.3555	16.6	0.7383	28.6
0.1919	10.0	0.3691	17.1	0.7998	30.2
0.2133	10.6	0.4799	20.8	0.8725	32.2
0.2399	12.0	0.5051	21.6	0.9597	34.5
0.2666	13.1	0.5332	22.5	1.0664	37.1
		$T = 298.15$ K			
0.0999	5.7	0.3107	16.5	0.4753	22.9
0.1010	6.3	0.3232	17.1	0.5050	24.0
0.1346	8.2	0.3366	17.6	0.5386	25.1
0.1616	10.1	0.3513	18.2	0.5771	26.5
0.2020	11.5	0.3672	18.8	0.6215	27.9
0.2308	12.9	0.3847	19.5	0.6733	29.5
0.2525	13.9	0.4040	20.3	0.7245	31.3
0.2693	14.7	0.4252	21.1	0.8079	33.4
0.2885	15.5	0.4489	22.0	0.8977	35.9
		$T = 303.15$ K			
0.0273	2.1	0.1577	10.4	0.3906	22.0
0.0328	2.5	0.1745	11.3	0.4100	22.9
0.0410	3.1	0.1953	12.5	0.4317	23.8
0.0513	3.8	0.2158	13.5	0.4557	24.8
0.0586	4.3	0.2412	14.9	0.4825	25.9
0.0683	4.9	0.2563	15.6	0.5126	27.0
0.0745	5.3	0.2734	16.4	0.5468	28.4
0.0820	5.8	0.2929	17.5	0.5858	29.8
0.0911	6.4	0.3155	18.6	0.6309	31.4
0.0965	6.7	0.3281	19.2	0.6835	33.2
0.1093	7.5	0.3417	19.9	0.7456	35.3
0.1262	8.5	0.3566	20.6	0.8202	37.7
0.1414	9.4	0.3728	21.2	0.9113	40.7
		$T = 308.15$ K			
0.0140	1.2	0.1747	12.5	0.3882	24.2
0.0349	2.7	0.1888	13.3	0.4110	25.2
0.0582	4.7	0.2117	14.8	0.4367	26.4
0.0699	5.5	0.2329	15.9	0.4358	27.8
0.0822	6.4	0.2588	17.4	0.4991	29.2
0.0932	7.2	0.2795	18.5	0.5375	30.9
0.1075	8.2	0.3038	19.9	0.5823	32.7
0.1270	9.5	0.3327	21.5	0.6352	34.8
0.1397	10.3	0.3494	22.3	0.6987	37.7
0.1553	11.3	0.3678	23.1	0.7764	40.2
		$T = 313.15$ K			
0.0886	7.5	0.2214	16.6	0.4429	29.5
0.0996	8.4	0.2416	17.8	0.4689	30.8
0.1063	8.9	0.2657	19.4	0.4982	32.1
0.1134	9.5	0.2847	20.5	0.5314	33.7
0.1226	10.1	0.3066	21.9	0.5694	35.6
0.1329	10.8	0.3322	23.6	0.6132	37.4
0.1449	11.7	0.3623	25.2	0.6643	39.6
0.1594	12.7	0.3796	16.1	0.7247	42.0
0.1733	13.6	0.3986	27.0	0.7972	45.2
0.1993	15.2	0.4196	28.3	0.8858	48.4

Table 2. Transport Numbers of 1-Hexyl Sulfate Anion, t_0^-, and Transport Numbers of Sodium Cation, t_0^+

T/K	t_0^-	t_0^+	T/K	t_0^-	t_0^+
293.15 K	0.328	0.672	308.15 K	0.314	0.686
298.15 K	0.321	0.679	313.15 K	0.313	0.687
303.15 K	0.316	0.684			

Table 3. Densities, ρ, Apparent Molal Volumes, V_ϕ, Excess Volumes, V_ϕ^{EX}, and Partial Molal Volumes, $\bar{V}_2$, for the System 1-Hexyl Sulfate Water at two Different Temperatures

m/mol kg^{-1}	ρ/ (g cm^{-3})	V_ϕ/ (cm^3 mol^{-1})	V_ϕ^{EX}/ (cm^3 mol^{-1})	$\bar{V}_2$/ (cm^3 mol^{-1})
		$T = 298.15$ K		
0.2556	1.011 99	143.86	−0.30	144.3
0.2904	1.013 92	143.92	−0.30	144.7
0.3380	1.016 53	144.07	−0.24	145.0
0.4095	1.020 34	144.24	−0.18	145.2
0.4437	1.022 13	144.33	−0.14	145.4
0.4865	1.024 34	144.43	−0.10	146.4
0.5607	1.027 99	144.81	0.19	148.6
0.6663	1.032 81	145.61	0.86	150.3
0.7197	1.035 15	145.99	1.18	150.7
0.8159	1.039 29	146.53	1.62	150.6
0.8843	1.042 17	146.84	1.87	151.0
0.9436	1.044 58	147.13	2.09	151.5
1.0476	1.048 71	147.57	2.43	151.3
1.1849	1.054 05	147.96	2.71	152.1
1.2578	1.056 68	148.26	2.95	152.8
1.3751	1.060 87	148.62	3.21	152.3
1.4589	1.063 80	148.83	3.35	152.4
1.6301	1.069 60	149.19	3.58	152.9
1.8302	1.076 00	149.58	3.83	152.7
2.0000	1.081 20	149.85	3.99	152.8
2.1868	1.086 68	150.10	4.11	152.9
2.4316	1.093 46	150.40	4.26	153.0
2.6564	1.099 40	150.60	4.33	153.2
2.9181	1.105 80	150.88	4.46	153.2
3.2556	1.113 75	151.08	4.48	152.9
3.6013	1.121 40	151.22	0.48	152.9
		$T = 308.15$ K		
0.1305	1.002 61	145.68	−0.40	146.2
0.2441	1.007 94	145.93	−0.41	146.6
0.3197	1.010 73	146.17	−0.31	146.9
0.3954	1.016 55	146.31	−0.29	147.2
0.4481	1.018 56	146.44	−0.24	147.5
0.5065	1.021 47	146.57	−0.19	147.7
0.5479	1.023 50	146.67	−0.15	149.0
0.5729	1.024 66	146.82	−0.03	150.9
0.6031	1.026 00	147.06	0.17	151.9
0.6596	1.028 47	147.49	0.53	152.5
0.7792	1.033 49	148.31	1.21	152.9
0.8946	1.038 15	148.92	1.70	153.0
1.0445	1.044 13	149.50	2.13	153.5
1.1370	1.047 62	149.87	2.41	153.7
1.2330	1.051 08	150.13	2.58	153.5
1.4422	1.058 23	150.67	2.95	153.7
1.6932	1.066 66	151.10	3.18	153.7
1.9818	1.075 38	151.50	3.37	154.1
2.2577	1.083 21	151.85	3.53	154.4
2.5324	1.090 52	152.12	3.63	154.4

(Harned and Owen, 1958):

$$V_\phi = \frac{M}{\rho} - \frac{10^3(\rho - \rho_0)}{m\rho\rho_0} \qquad (1)$$

where m is the molality of the solution, M is the molecular weight of the solute (204.22 g mol^{-1}), and ρ and ρ_0 represent the densities for the solution and solvent (water), respectively. The apparent molal volumes of SHS in water at 298.15 K and 308.15 K together with the experimental values of density are summarized in Table 3.

The partial molal volumes, $\bar{V}_2$, of the surfactant have been computed from V_ϕ by the equation

$$\bar{V}_2 = V_\phi + m\left(\frac{\partial V_\phi}{\partial m}\right)_{T,P} \qquad (2)$$

The values of $\bar{V}_2$ so obtained are tabulated at various molalities, m, and at 298.15 K and 308.15 K, in Table 3. The concentration and temperature dependence of $\bar{V}_2$ is similar to that of other surfactants (Desnoyers et al., 1979).

The excess volumes, V_ϕ^{EX}, calculated by the expression

$$V_\phi^{\mathrm{EX}} = V_\phi - A_v m^{1/2} - V_\phi^0 \qquad (3)$$

where V_ϕ^0 is the standard (infinite dilution) apparent

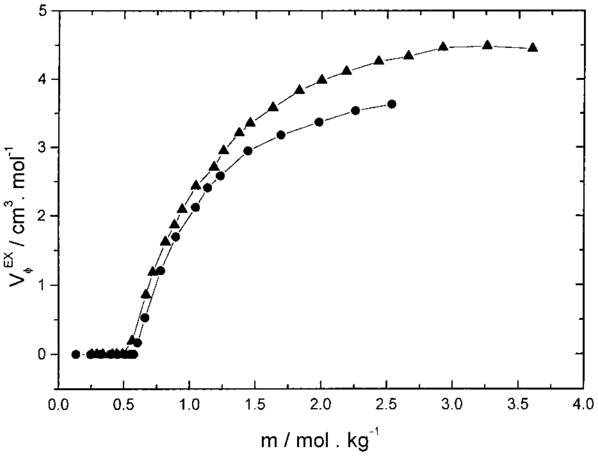

Figure 2. Variation of the excess volume of SHS with molality: (●) 298.15 K; (▲) 308.15 K.

molal volume and A_v (1.865 cm^3 kg$^{1/2}$ mol$^{-3/2}$ for 1:1 electrolyte at 298.15 K) is the Debye−Hückel limiting law coefficient, are plotted in Figure 2 for each temperature (Musbally et al., 1974; Desnoyers et al., 1987). Table 3 includes too the V_ϕ^{EX} values obtained by eq 3. The concentration dependence of V_ϕ^{EX} is similar to that of other surfactants (De Lisi et al., 1979; Desnoyers et al., 1979). The increase of V_ϕ^{EX} with temperature is typical of hydrophobic solutes in water (De Lisi et al., 1980).

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