

Electrical Conductance of Sodium Dodecyl Sulfate in Calcium Nitrate Tetrahydrate + Acetamide Melts

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The specific conductance of sodium dodecyl sulfate (SDS) in molten mixtures of calcium nitrate tetrahydrate (CNTH) and acetamide was measured at 38 °C. In these molten mixtures SDS undergoes micellization and the values of the critical micelle concentration (cmc) were estimated. The shape of the specific conductance versus concentration of SDS isotherm depends on the relative amounts of the hydrated salt and acetamide present in the molten mixture. The slope of this isotherm is positive in the acetamide-rich (>~73 mass % acetamide) melt, and it changes to a negative value in the hydrated salt-rich melt.

Introduction

Although micellization of surfactants can take place in molten salt media, such reports are very few in the literature,^{1–7} owing to (1) poor solubility of surfactants in ionic melts and (2) thermal decomposition of surfactants due to the high working temperature of ionic melts. Therefore, selecting a suitable molten solvent so as to overcome the above difficulties is a prerequisite for undertaking a study on the micellization behavior of surfactants in molten salt media. Room-temperature molten salts, which are emerging as potential solvents for synthesis,^{8–14} can be expected to act as potential molten solvents for micellization studies. Hydrate melts form one category of room-temperature ionic liquids.¹⁵ However, pure hydrate melts cannot be employed as solvents for studying the micellization properties of surfactants due to their negligible solubility in such melts. A new molten salt system consisting of a mixture of calcium nitrate tetrahydrate (CNTH) and acetamide has been reported by us and others.^{16–18} Since this room-temperature molten salt system is a mixture of an inorganic hydrated salt and an organic compound, it may dissolve inorganic and organic compounds as well as surfactants. In fact, the micellization behavior of surfactants in a pure acetamide melt has been studied recently. It is therefore considered to be worthwhile to take up the study of the micellization behavior of surfactants in a CNTH + acetamide melt, and the results of a conductance study of sodium dodecyl sulfate (SDS) made in this particular melt at 38 °C are reported for the first time in this communication.

Experimental Section

SDS (Sigma, 99%) and CNTH (E. Merck) were used without additional purification. Acetamide (E. Merck) was purified as described earlier.⁷ Different molten mixtures of CNTH and acetamide containing 78.30 (melt A), 73.47 (melt B), 70.18 (melt C), 68.38 (melt D), and 34.68 (melt E) mass % of acetamide were prepared as described elsewhere.¹⁶

For conductance measurement a weighed amount of any one of the molten mixtures was taken in a sample tube

and into it a dip-type conductivity cell of cell constant = 121.11 m⁻¹ was introduced. The sample tube was then closed airtight and kept in an oil bath maintained at (38 ± 0.1) °C (INSREF thermostat). After the thermal equilibrium electrical conductance of the melt was measured at 1 kHz using a Wayne Kerr B905 Automatic Precision Bridge, a weighed amount of SDS was added to the melt in the sample tube and was allowed to dissolve. When the molten mixture became homogeneous, the conductance reading was recorded. Similarly, conductance readings were taken for subsequent additions of SDS till the molten mixture became saturated with SDS. Measurements were repeated to ensure the reproducibility of the conductance data, which was found to be within ±0.5%. Although the solubility of SDS in the pure acetamide melt at 89 °C is very good (~2.1 mol·kg⁻¹), it is found to be considerably less in the molten mixtures of CNTH and acetamide at 38 °C. For example, SDS is soluble in melt A, which contains 93.5 mol % acetamide, only about 0.12 mol·kg⁻¹, and this solubility decreased by about 3 times in melt E. Sometimes SDS was dissolved in the melt by heating the sample to higher temperature and then cooling the sample to the required temperature. The surfactant, once dissolved in the melt at higher temperatures, remains in the dissolved state even at lower temperatures. Such solutions are termed as supercooled surfactant solutions by Franses et al.¹⁹ In melts containing less than 34.68 mass % acetamide, the solubility of SDS was found to be negligible.

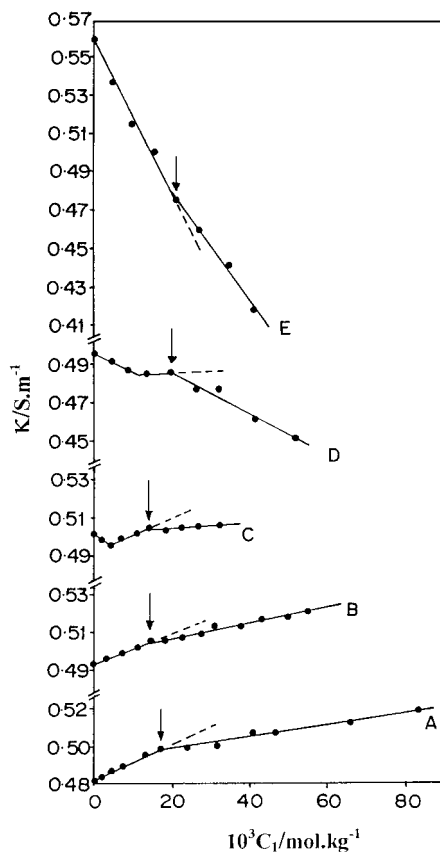
Results and Discussion

The specific conductances, κ , of SDS in the different CNTH + acetamide melts are given in Table 1, and the variation of κ with concentration of SDS, C_1 , is shown in Figure 1. From Figure 1 it is apparent that the nature of the behavior of κ with respect to SDS concentration is dependent on the amount of acetamide present in the molten mixture. The shape of the κ versus concentration of SDS plots in melts A and B is similar to that in the pure acetamide melt.⁷ This type of variation of κ with ionic surfactant concentration is common in water and polar organic solvents. Thus, SDS may be considered to micellize in melts A and B, and the values of cmc of SDS in these molten mixtures are found to be (0.017 and 0.014) mol·kg⁻¹, respectively. It is interesting to note that the cmc value of SDS in melt A is close to the value (0.016 mol·kg⁻¹)

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Table 1. Specific Conductance, κ , Values for Sodium Dodecyl Sulfate in CNTH + Acetamide Melts at 38 °C

$C_1/\text{mol}\cdot\text{kg}^{-1}$	$\kappa/\text{S}\cdot\text{m}^{-1}$	$C_1/\text{mol}\cdot\text{kg}^{-1}$	$\kappa/\text{S}\cdot\text{m}^{-1}$	$C_1/\text{mol}\cdot\text{kg}^{-1}$	$\kappa/\text{S}\cdot\text{m}^{-1}$
Melt A (78.30 mass % Acetamide)					
0.0	0.4809	0.0019	0.4844	0.0044	0.4858
0.0074	0.4907	0.0132	0.4959	0.0168	0.4986
0.0239	0.4982	0.0316	0.4992	0.0407	0.5068
0.0467	0.5069	0.0658	0.5112	0.0841	0.5188
Melt B (73.47 mass % Acetamide)					
0.0	0.4924	0.0031	0.4954	0.0068	0.4988
0.0108	0.5005	0.0145	0.5061	0.0181	0.5054
0.0233	0.5077	0.0278	0.5090	0.0315	0.5133
0.0383	0.5127	0.0436	0.5174	0.0500	0.5178
0.0553	0.5214				
Melt C (70.18 mass % Acetamide)					
0.0	0.5017	0.0019	0.4995	0.0044	0.4957
0.0071	0.4994	0.0107	0.5011	0.0141	0.5044
0.0186	0.5036	0.0255	0.5037	0.0271	0.5057
0.0325	0.5054				
Melt D (68.38 mass % Acetamide)					
0.0	0.4951	0.0045	0.4927	0.0089	0.4876
0.0133	0.4840	0.0197	0.4853	0.0262	0.4768
0.0321	0.4765	0.0411	0.4603	0.0521	0.4512
Melt E (34.68 mass % Acetamide)					
0.0	0.5593	0.0048	0.5355	0.0102	0.5144
0.0159	0.5009	0.0212	0.4743	0.0273	0.4581
0.0349	0.4405	0.0413	0.4170		

**Figure 1.** Plot of specific conductance versus concentration of SDS in CNTH + acetamide molten mixtures of different composition at 38 °C: values of mass % of acetamide are (A) 78.30, (B) 73.47, (C) 70.18, (D) 68.38, and (E) 34.68. Arrows indicate the cmc values.

reported in the pure acetamide melt at 89 °C.⁷ In melt C, the cmc of SDS is found to be 0.014 mol·kg⁻¹ and the dependence of κ on SDS concentration above the cmc is seen to be similar to that found in melts A and B (Figure 1). However, the increase in κ with SDS concentration in melt C above the cmc is not significant. On the other hand, in melt C below the cmc, κ initially decreases with the

addition of SDS up to ~ 0.004 mol·kg⁻¹ and, above this concentration, it starts increasing, thereby exhibiting a minimum. In melt D, κ decreases with the addition of SDS up to ~ 0.012 mol·kg⁻¹, remains almost constant in the concentration range from (~ 0.012 to ~ 0.020) mol·kg⁻¹, and then decreases continuously above 0.020 mol·kg⁻¹. The cmc of SDS in melt D is found to be 0.020 mol·kg⁻¹. In melt E, κ decreases monotonically by the addition of SDS, and the cmc value is found to be 0.021 mol·kg⁻¹. The error limit of all the cmc values of SDS in CNTH + acetamide melts is estimated to be ± 0.002 mol·kg⁻¹. It is worthwhile to note that the nature of the κ versus surfactant concentration isotherm in melt E is different from that in melts A and B but is similar to that of cetyldimethylbenzylammonium chloride in molten pyridinium chloride at 155 °C.¹ In ionic liquids such as hydrate melts, κ is known to decrease by the addition of an inorganic or organic solute.^{16,20}

In light of the above, it is apparent that in the CNTH + acetamide melt if κ increases with solute concentration, then acetamide controls the conductance behavior of the added solute and this happens when the amount of acetamide in the molten mixture is $> \sim 73$ mass %. On the other hand, if κ decreases with an increase in solute concentration, then the conductance behavior of the solute is governed by CNTH. When both CNTH and acetamide control the conductance behavior of the added ionic surfactant, a minimum occurs in the κ versus concentration plot below the cmc. This happens when the amount of acetamide in the binary melt is in the range from ~ 70 to 68 mass %. Thus, in the CNTH + acetamide mixture both CNTH and acetamide exhibit their relative influence in controlling the conductance behavior of a solute, which is in accordance with the reported fact that a binary molten mixture of a hydrated salt and an inorganic/organic solute behaves like an ideal mixture of hydrate melt and supercooled solute.^{16,21} The cmc of SDS in the molten mixture at 38 °C seems to decrease with an increase in the amount of CNTH up to ~ 30 mass % CNTH in the melt. Thus, the effect of the addition of CNTH on the cmc of SDS in the acetamide-rich molten mixture is similar to the effect of added electrolyte on the cmc in an aqueous medium.^{22,23} Such an effect on the cmc is explained as due to the reduction caused by the added counterions in the repulsive interaction between the ionic heads residing on the micellar surface. The cmc of SDS in the molten mixture appears to exhibit an increase on further addition of CNTH above ~ 30 mass % CNTH. Above the cmc, κ either increases (acetamide dominating region), remains constant (both acetamide and CNTH control κ), or decreases (CNTH dominating region) with an increase in surfactant concentration.

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