J. Chem. Eng. Data **2004,** *49,* 339−340

Specific Conductivity Maxima of Ionic Surfactants in Acetamide Melt

S. Dev, D. Das, and K. Ismail*

Department of Chemistry, North Eastern Hill University, Shillong 793022, India

The specific conductivity of sodium dodecyl sulfate, cetyl pyridinium chloride, and sodium nitrate in acetamide melt was measured at 89 °C up to (2.067, 1.599, and 3.705) mol·kg^{-1}, respectively. The specific conductivity maximum has been observed for sodium nitrate as well as for the two ionic surfactants. This is the first report on the observation of a specific conductivity maximum for any ionic surfactant, which is otherwise a general feature of a normal electrolyte in aqueous or nonaqueous media. In acetamide melt, the concentrations of sodium dodecyl sulfate and cetyl pyridinium chloride corresponding to their conductivity maxima are found to be less than that of sodium nitrate, which is probably due to micellization of ionic surfactants.

Introduction

The electrical conductivity method is widely used for studying the micellization behavior of ionic surfactants in aqueous and nonaqueous media. In this method critical micellization concentration (cmc) values of ionic surfactants are determined generally by plotting specific conductivity versus concentration.[1,2] Besides this graphical approach, different analytical approaches are also used to determine the micellization parameters of ionic surfactants from their specific conductivity data.[2,3−9] Since cmc values of surfactants lie in the low concentration region, normally measurement of specific conductivity of ionic surfactants in different media is made in the low concentration region only. Extension of specific conductivity measurements of ionic surfactants to the high concentration region is, however, restricted due to low solubility of these surfactants, especially in water and pure nonaqueous liquids. Therefore, although the occurrence of a conductivity maximum is a general feature of normal electrolytic solutions, until now, to our knowledge, conductivity maxima have not been reported for ionic surfactants in any solvent. Reported here, therefore, are conductivity maxima for an anionic surfactant [sodium dodecyl sulfate (SDS)], a cationic surfactant [cetyl pyridinium chloride (CPC)], and a normal electrolyte ($NaNO_3$) in acetamide melt at 89 °C.

Experimental Section

SDS (Sigma, 99%) and CPC (SISCO, extra pure grade) were used without further purification. Acetamide (E. Merck) was recrystallized from its solution in doubly distilled acetone whereas $NaNO_3$ (SD) was recrystallized from its solution in doubly distilled water. Electrical conductance measurements were made at 1 kHz using a Wayne Kerr B905 automatic precision bridge and a dip-type cell of cell constant 121.11 m^{-1}. A thermostated oil bath (INSREF make) was used to maintain the temperature at (89 ± 0.1) °C. The method of preparing the molten mixtures and measuring their electrical conductances is similar to that described in our earlier work.[10] The uncertainty in the measured specific conductivity (κ) values was found to be ±0.5%.

Table 1. Specific Conductivity, κ, Values for SDS in Acetamide Melt at 89 °C

m/mol·kg^{-1}	κ/S·m^{-1}	m/mol·kg^{-1}	κ/S·m^{-1}	m/mol·kg^{-1}	κ/S·m^{-1}
0.0011	0.0026	0.0022	0.0051	0.0027	0.0065
0.0033	0.0079	0.0040	0.0094	0.0049	0.0116
0.0058	0.0136	0.0064	0.0151	0.0073	0.0171
0.0082	0.0192	0.0092	0.0215	0.0103	0.0241
0.0110	0.0252	0.0119	0.0274	0.0138	0.0319
0.0150	0.0340	0.0158	0.0363	0.0180	0.0401
0.0233	0.0513	0.0266	0.0577	0.0376	0.0790
0.0416	0.0883	0.0497	0.1031	0.0554	0.1127
0.0626	0.1251	0.0799	0.1572	0.2090	0.3197
0.3333	0.4156	0.5744	0.5304	0.5844	0.5362
0.5931	0.5375	0.5993	0.5408	0.6039	0.5432
0.6396	0.5533	0.7334	0.5746	1.0219	0.5892
1.2326	0.5828	1.3006	0.5788	1.3278	0.5656
1.3778	0.5565	1.5134	0.5404	1.7714	0.5095
2.0665	0.4699				

Results and Discussion

The micellization behavior of different ionic surfactants in acetamide melt was studied by measuring their specific conductivity (κ) values, and their cmc values were reported.[11,12] The highest molality of ionic surfactant covered during those specific conductivity measurements was about 0.25 mol·kg^{-1} or less. The specific conductivity values of KI, KBr, KCl, and $NaNO_3$ in acetamide melt were also reported,[12,13] and the highest molarity of electrolyte covered in those studies was about 0.225 mol·dm^{-3} or less. We observed that molten acetamide can dissolve high concentrations of SDS and CPC, and therefore, the κ values of these two ionic surfactants were measured at 89 °C up to (2.067 and 1.599) mol·kg^{-1}, respectively, and are listed in Tables 1 and 2. We could also measure κ of $NaNO_3$ in acetamide melt up to 3.705 mol·kg^{-1} at 89 °C, and these values are given in Table 3. From Figure 1 it is obvious that the two ionic surfactants, SDS and CPC, exhibit conductivity maxima in acetamide melt just like the normal electrolyte $NaNO_3$. The values of concentration (C_{max}) at which conductivity maxima occur are (1.232, 1.406, and 2.530) mol·kg^{-1} for SDS, CPC, and $NaNO_3$, respectively.

---

* To whom correspondence should be addressed. E-mail: kismail@nehu.ac.in.

10.1021/je034187w CCC: $27.50

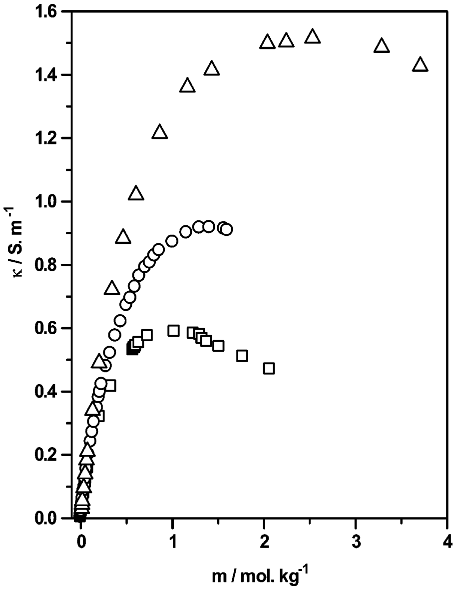

Figure 1. Plot of specific conductivities of SDS, CPC, and $NaNO_3$ versus their concentration in acetamide melt at 89 °C: □, SDS; ○, CPC; △, $NaNO_3$.

Table 2. Specific Conductivity, κ, Values for CPC in Acetamide Melt at 89 °C

m/mol·kg^{-1}	κ/S·m^{-1}	m/mol·kg^{-1}	κ/S·m^{-1}	m/mol·kg^{-1}	κ/S·m^{-1}
0.0012	0.0035	0.0019	0.0056	0.0024	0.0071
0.0031	0.0093	0.0045	0.0131	0.0056	0.0162
0.0065	0.0189	0.0080	0.0229	0.0112	0.0319
0.0124	0.0351	0.0157	0.0442	0.0233	0.0637
0.0347	0.0863	0.0518	0.1239	0.0667	0.1545
0.0899	0.2001	0.1122	0.2405	0.1298	0.2711
0.1501	0.3032	0.1794	0.3472	0.2005	0.3805
0.2129	0.3979	0.2315	0.4222	0.2812	0.4790
0.3254	0.5203	0.3803	0.5747	0.4390	0.6201
0.5019	0.6716	0.5450	0.6947	0.5959	0.7299
0.6414	0.7644	0.7091	0.7910	0.7587	0.8062
0.8081	0.8281	0.8597	0.8446	1.0046	0.8716
1.1582	0.9012	1.2994	0.9158	1.4063	0.9166
1.5676	0.9132	1.5992	0.9085		

Table 3. Specific Conductivity, κ, Values for $NaNO_3$ in Acetamide Melt at 89 °C

m/mol·kg^{-1}	κ/S·m^{-1}	m/mol·kg^{-1}	κ/S·m^{-1}	m/mol·kg^{-1}	κ/S·m^{-1}
0.0092	0.0309	0.0130	0.0442	0.0168	0.0546
0.0310	0.0964	0.0461	0.1395	0.0618	0.1838
0.0723	0.2103	0.1268	0.3401	0.1997	0.4903
0.3395	0.7209	0.4631	0.8830	0.6005	1.0207
0.8619	1.2141	1.1623	1.3604	1.4292	1.4142
2.0386	1.4984	2.2440	1.5035	2.5297	1.5153
3.2870	1.4862	3.7055	1.4267		

Thus, for the ionic surfactants the concentration at which the conductivity maximum occurs is almost half the value of that for the normal electrolyte. The concentration and mobility of the ionic species determine the electrical conductivity of a solution. In any electrolyte solution the general explanation given for the occurrence of a conductivity maximum is that the concentration of ionic species controls κ along the ascending portion of the plot of κ versus concentration whereas the mobility of the ionic species and ion pairing control κ along the descending portion of that plot. This general explanation for the occurrence of a conductivity maximum perhaps holds good in the present systems under study also. As mentioned above, SDS and CPC are reported[11,12] to form micelles in acetamide melt, and with an increase in the concentration of the surfactants, the aggregation number of these micelles may increase, similar to the behavior well-known in aqueous media.[14,15] Thus, low values for $C_{\max}$ of SDS and CPC compared to that of $NaNO_3$ are probably attributable to the presence of micelles in the respective solutions of these two ionic surfactants in acetamide melt. Furthermore, in aqueous media an inverse relation between $C_{\max}$ and the radii of hydrated ions was suggested by Claes and Glibert.[16] This type of relation appears to be operating in acetamide melt also, since solvated ionic micelles of SDS and CPC have a larger size than solvated ions of $NaNO_3$, thereby resulting in lower $C_{\max}$ values for the ionic surfactants.

Literature Cited

(1) Evans, H. C. Alkyl Sulphates. Part I. Critical Micelle Concentrations of the Sodium Salts. *J. Chem. Soc.* **1956**, 579−586.
(2) Goddard, E. D.; Benson, G. C. Conductivity of Aqueous Solutions of Some Paraffin Chain Salts. *Can. J. Chem.* **1957**, *35*, 986−991.
(3) Kimizuka, H.; Satake, I. Estimation of Micellar Charge from Conductivity Data of Aqueous Detergent Solutions. *Bull. Chem. Soc. Jpn.* **1962**, *35*, 251−253.
(4) Nishikido, N. Estimation of Micellar Charge or Aggregation Number from Conductivity and Counterion-Activity Measurements. *J. Colloid Interface Sci.* **1983**, *92*, 588−591.
(5) Shanks, P. C.; Franses, E. I. Estimation of Micellization Parameters of Aqueous Sodium Dodecyl Sulfate from Conductivity Data. *J. Phys. Chem.* **1992**, *96*, 1794−1805.
(6) Moroi, Y.; Matsuoka, K. Electric Conductivity Analysis of Micellar Solution of Sodium Dodecyl Sulfate. *Bull. Chem. Soc. Jpn.* **1994**, *67*, 2057−2061.
(7) Moroi, Y.; Yoshida, N. A New Approach to Micellization Parameters: Its Application to Sodium Dodecyl Sulfate Micelle. *Langmuir* **1997**, *13*, 3909−3912.
(8) Paul, B. C.; Islam, S. S.; Ismail, K. Effect of Acetate and Propionate Co-ions on the Micellization of Sodium Dodecyl Sulfate in Water. *J. Phys. Chem.* **1998**, *102*, 7807−7812.
(9) Manabe, M.; Kaneko, M.; Miura, T.; Akiyama, C.; Kawamura, H.; Katsuura, H.; Shiomi, M. Counterion Release of Ionic Surfactant Micelles Induced by Solubilized Amphiphiles: Size Effect of a Polar Headgroup. *Bull. Chem. Soc. Jpn.* **2002**, *75*, 1967−1972 and references therein.
(10) Dev, S.; Ismail, K. Electrical Conductance of Sodium Dodecyl Sulfate in Calcium Nitrate Tetrahydrate + Acetamide Melts. *J. Chem. Eng. Data* **2001**, *46*, 574−576.
(11) Akhter, M. S. Studies on Micelle Formation and Enthalpy of Micellization in Molten Acetamide. *Colloids Surf., A* **1995**, *99*, 255−258.
(12) Dev, S.; Gunaseelan, K.; Ismail, K. Micellization of Surfactants in Acetamide Melt. *Langmuir* **2000**, *16*, 6110−6113.
(13) Wallace, R. A. Equivalent Conductivity of Potassium Halides in Molten Acetamide. *J. Phys. Chem.* **1971**, *75*, 2687−2690.
(14) Quina, F. H.; Nassar, P. M.; Bonilha, J. B. S.; Bales, B. L. Growth of Sodium Dodecyl Sulfate Micelles with Detergent Concentration. *J. Phys. Chem.* **1995**, *99*, 17028−17031.
(15) Molinero, I.; Sierra, M. L.; Valiente, M.; Rodenas, E. Physical Properties of Cetyl Pyridinium Chloride Micelles and Their Behaviour as Reaction Media. *J. Chem. Soc., Faraday Trans.* **1996**, *92*, 59−63.
(16) Claes, P.; Glibert, J. In *Ionic Liquids*; Inman, D., Lovering, D. G., Ed.; Plenum Press: New York, 1981.

Received for review September 23, 2003. Accepted December 20, 2003.

JE034187W