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CONDUCTOMETRIC STUDIES OF COPPER (II) SOAP IN BENZENE – METHANOL AT VARIOUS TEMPERATURES

RASHMI SHARMA*, L. C. HEDA, RENU BHUTRA and K. G. OJHA[a]

Department of Chemistry, S. D. Govt. College, BEAWAR – 305901 (Raj.) INDIA.
[a]Department of Chemistry, M. D. S. University, AJMER – 305001 (Raj.) INDIA

ABSTRACT

The critical micelle concentration and conductivity behaviour of copper (II) soap solution in benzene-methanol mixtures have been determined by the following equation at various temperatures (40, 45, 50 and 55^{0}C):

$$\log \mu = A + B \log c$$

Where A and B are constants, c is concentration of copper soap in g.moles/litre and μ is molecular conductivity. The values of log μ and B generally increase with temperature. Both the values of log μ and B also increase with increase in the volume percent of methanol in the system. The above system obeys the Krauss and Bray type expression and data show that in general, dissociation constant increases and limiting molar conductance decreases with the temperature upto 50% methanol in the solvent mixture. The work has been extended to collect thermodynamic parameters such as the heat of dissociation, ΔH^0, to enable the behaviour of soap solutions to be better understood. In regard to chain length of the soap, the cmc values are in the order: Caprate < Caprylate.

CMC increases with the increase in the methanol percent in the solvent mixture. The results confirm that the change in the nature of micelles from hydrophilic oleomicelles to lipophilic hydromicelles occurs in solutions at about 50% methanol.

Key words: Copper (II), Conductometry

INTRODUCTION

Tremendous developments have taken place in the study of transition metal soaps but references to the investigation of copper (II) soaps are scanty[1–4].

As anionic surfactants containing copper (II) ions possess valuable characteristics

* Author for correspondence

such as toxicity towards fungi, bacteria, pests and are used in lubrication, emulsification etc.[5, 6], present studies at various temperatures will provide revealing interpretations of soap-solvent interaction and structural insight of a micelle in soap-benzene-methanol.

In continuation of our previous study of copper (II) surfactants in ternary system[7–9] conductometric studies have been carried out at four temperatures (40, 45, 50 and 55ºC) to determine the cmc of these soap solutions and to qualitatively determine the effect of the type of solvent on micellar aggregates. The dissociation constant K and the molecular conductance at infinite dilution μ_0 were evaluated to gain insight into the stability and nature of the soap micelles. The heat of dissociation ΔH^0 has been calculated to understand the behaviour of soap solutions at different temperatures.

EXPERIMENTAL

Materials and methods

All reagents used were of LR/AR grade. Fatty acids and chemicals were purified and soaps prepared by the method described in an earlier communication[7]. The purity of the monohydrated soaps was confirmed by their elemental analysis. A Toshniwal conductivity bridge C L 102 A and a Philips dipping type conductivity cell with platinized platinum electrodes were used. All measurements were made in a thermostatic bath (±0.05ºC). The reproducibility of the results was examined by repeating the measurements. The specific and molecular conductance was expressed in mhos cm^{-1} and mhos cm^2 $mole^1$, respectively.

RESULTS AND DISCUSSION

The specific conductance k_{sp} of soap solutions increases with the increase in the concentration of soap in the varying composition of benzene–methanol mixture for both; the caprylate and caprate soaps. This may be ascribed to the formation of ionic micelles of higher conducting power than the simple ions. The plots of specific conductance k_{sp} vs soap concentration c are characterized by an intersection of two straight lines at a definite soap concentration corresponding to cmc of the soap. There is an increase in the values of specific conductance with the rise in temperature (Table 1, Fig. 1).

Table 1. Specific conductivity k_{sp} of copper caprylate (caprate) solutions in benzene-methanol mixtures

Conc.	30% Methanol				70 % Methanol			
(g mol L^{-1})	40°C	45°C	50°C	55°C	40°C	45°C	50°C	55°C
0.00	0.710	1.123	1.735	2.147	3.079	5.038	5.535	6.117
	(0.710)	(1.123)	(1.735)	(2.147)	(3.079)	(5.038)	(5.535)	(6.117)
0.01	1.120	1.517	2.230	2.533	5.676	6.635	7.747	8.423
	(0.572)	(0.582)	(0.594)	(0.660)	(4.219)	(5.515)	(6.016)	(7.231)
0.02	1.949	2.089	2.527	2.756	7.700	9.595	10.535	14.033
	(0.638)	(0.673)	(0.683)	(0.688)	(5.947)	(8.463)	(9.529)	(11.890)
0.03	2.453	2.673	2.982	3.176	9.625	13.333	15.143	20.010
	(0.682)	(0.698)	(0.706)	(0.724)	(8.233)	(11.887)	(13.831)	(17.705)
0.04	2.971	3.266	3.308	3.615	11.550	17.028	19.538	25.912
	(0.726)	(0.738)	(0.748)	(0.755)	(9.999)	(15.155)	(17.544)	(23.093)
0.05	3.562	3.744	4.059	4.150	13.860	20.780	23.783	31.356
	(0.759)	(0.777)	(0.785)	(0.790)	(11.571)	(18.347)	(21.783)	(28.455)
0.06	3.992	4.357	4.453	4.996	16.170	23.980	29.125	38.200
	(0.800)	(0.824)	(0.836)	(0.843)	(12.969)	(21.923)	(26.167)	(34.955)
0.08	4.283	4.791	4.921	5.107	17.930	28.710	36.500	47.521
	(0.814)	(0.858)	(0.869)	(0.878)	(16.156)	(25.819)	(32.700)	(43.916)
0.1	4.547	5.162	5.239	5.465	22.000	35.200	45.500	58.200
	(0.836)	(0.887)	(0.910)	(0.922)	(19.424)	(30.795)	(39.713)	(53.649)
0.12	5.167	5.640	5.819	6.027	23.088	40.000	52.521	68.510
	(0.902)	(0.935)	(0.957)	(0.965)	(22.242)	(35.801)	(46.686)	(62.860)

Table 2. Molecular conductance μ of copper caprylate (caprate) solutions in benzene-methanol mixtures ($\mu \times 10^6$ in mhos cm^2 $mole^{-1}$)

Conc. (g mol L^{-1})	$\sqrt{c}$	30% Methanol				70 % Methanol			
		40ºC	45ºC	50ºC	55ºC	40ºC	45ºC	50ºC	55ºC
0.01	0.10	11.200	15.170	22.300	25.330	56.766	66.350	77.470	84.230
		(5.822)	(5.822)	(5.940)	(6.060)	(42.190)	(53.150)	(47.645)	(72.310)
0.02	0.14	9.745	10.445	12.635	13.780	38.500	47.975	52.765	70.165
		(3.199)	(3.365)	(3.415)	(3.490)	(59.786)	(42.315)	(45.642)	(59.490)
0.03	0.17	8.049	8.821	9.840	10.481	31.762	44.000	49.899	66.033
		(2.250)	(2.303)	(2.330)	(2.382)	(27.169)	(39.224)	(43.360)	(58.426)
0.04	0.20	7.353	8.165	8.270	9.038	28.575	42.570	48.845	64.780
		(1.815)	(1.845)	(1.870)	1.887	(24.997)	(37.887)	(43.360)	(57.730)
0.05	0.22	7.124	7.748	8.118	8.300	27.720	41.580	47.566	62.780
		(1.518)	(1.554)	(1.570)	(1.580)	(23.142)	(36.694)	(43.566)	(56.810)
0.06	0.24	6.387	6.971	7.120	7.993	25.272	38.368	46.600	61.140
		(1.280)	(1.318)	(1.337)	(1.348)	(20.752)	(33.476)	(41.859)	(55.928)
0.08	0.28	5.353	5.988	6.151	6.384	22.413	35.880	45.625	59.400
		(1.018)	(1.072)	(1.086)	(1.097)	(20.195)	(32.270)	(40.900)	(59.896)
0.10	0.31	4.547	5.162	5.239	5.465	22.000	35.200	44.500	58.200
		(0.836)	(0.887)	(0.910)	(0.922)	(19.426)	(30.795)	(39.913)	(53.649)
0.12	0.34	4.304	4.698	4.847	5.020	20.892	33.320	43.732	51.068
		(0.751)	(0.779)	(0.797)	(0.804)	(18.527)	(29.822)	(38.889)	(52.363)

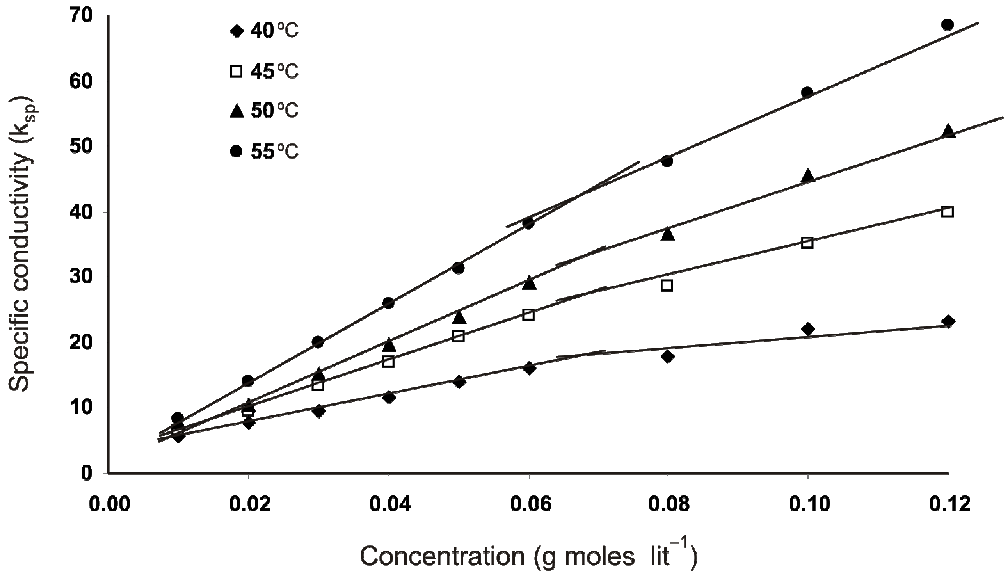

Fig. 1: Plots of specific conductivity v/s concentration of copper caprylate at various temperatures in 70% methanol

It is apparent from the results that cmc values are higher for caprylate than caprate and also dependent on the composition of the solvent mixture. The value of cmc (Table 2) in the solution upto 50% methanol is lower as compared with the cmc values at higher methanol concentration. This may be attributed to favourable interaction between polar groups of the soap molecules and the hydrogen-bonded solvent (methanol) causing micellization to occur at a relatively higher concentration. It is also known that the degree of ionization of micellar units changes with the solvent composition and in the solvent of high dielectric constant, micelles of relatively enhanced size and compactness are formed. More over it is contemplated that in such systems, predominance of micelles markedly affect the organizational features of the aggregates[10–12].

The molecular conductance μ of the soap solution decreases as the concentration of the soap in the system: benzene-methanol increases. The molecular conductance (μ) values at four different temperatures (40, 45, 50, 55 ^{0}C) are given in (Table 2). The decrease in molar conductance, μ, with increasing soap concentration is due to the combined effects of ionic atmosphere, solvation of ions and decrease in mobility as well as ionization with the onset of micellization.

This decrease seems to be due to the tendency of the soap to form aggregates at higher soap concentration. Further it has also been suggested that the mobility of the soap anion decreases with increase in the size of the micelle.[13]

Table 3. Values of the cmc (g mole L^{-1}) for copper caprylate (caprate) solutions in benzene-methanol mixtures

Plots	Temp. (°C)	Volume percent of methanol in the solvent mixture					
		30%	40%	50%	60%	70%	80%
k_{sp} vs c	40	0.063 (0.054)	0.064 (0.055)	0.065 (0.056)	0.066 (0.062)	0.068 (0.062)	0.070 (0.064)
	45	0.062 (0.053)	0.064 (0.056)	0.065 (0.056)	0.065 (0.058)	0.068 (0.058)	0.071 (0.059)
	50	0.062 (0.053)	0.063 (0.054)	0.065 (0.056)	0.066 (0.057)	0.068 (0.057)	0.070 (0.058)
	55	0.062 (0.052)	0.063 (0.053)	0.064 (0.054)	0.066 (0.055)	0.067 (0.056)	0.070 (0.057)
μ vs $\sqrt{c}$	40	0.064 (0.053)	0.064 (0.054)	0.065 (0.056)	0.067 (0.058)	0.067 (0.062)	0.069 (0.062)
	45	0.063 (0.053)	0.063 (0.055)	0.064 (0.055)	0.066 (0.057)	0.068 (0.061)	0.069 (0.063)
	50	0.063 (0.052)	0.062 (0.055)	0.063 (0.055)	0.065 (0.056)	0.067 (0.061)	0.068 (0.063)
	55	0.063 (0.052)	0.062 (0.055)	0.063 (0.054)	0.064 (0.055)	0.066 (0.061)	0.068 (0.063)

The plots of μ vs square root of concentration $\sqrt{c}$, are characterized by an intersection of two straight lines corresponding to cmc of the soap (Fig. 2 and Table 3). The results are in complete agreement with the values of cmc obtained from k_{sp} vs c plots and other physical properties studied by us.[1,7]

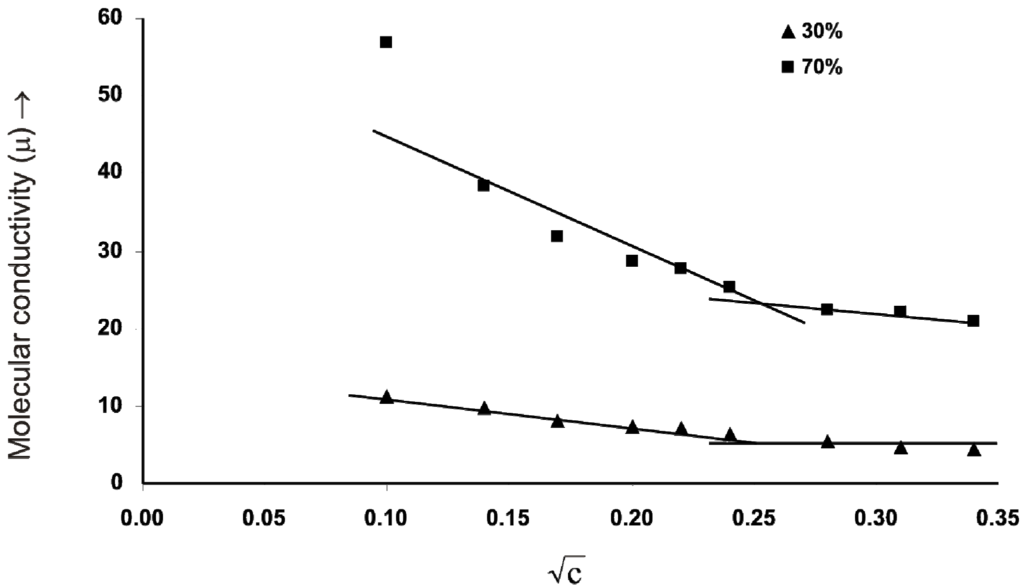

Fig. 2: Plots of molecular conductivity of copper caprylate v/s square root of soap concentration in benzene - methanol at 40°C

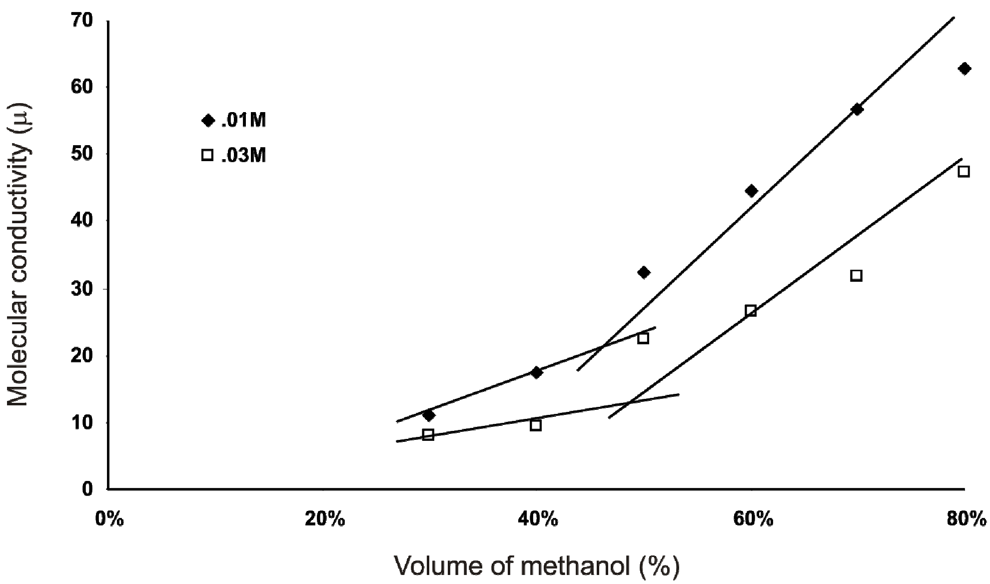

Fig. 3: Molecular conductivity v/s volume percent of methanol for copper caprylate in benzene - methanol at 40°C

With respect to solvent composition, it has been noticed that the nature of the curves (μ vs volume percent of methanol) shows a change at 50 % methanol concentration for these plots (Fig. 3). This may be due to the combined effect of the variation of dielectric constant, viscosity and degree of aggregation of the soap with the change in the composition of the solvent mixtures.

It may be pointed out that the plots of log μ vs log c (Fig. 4) for the solutions of the copper caprylate and caprate are linear for all the compositions of the solvent mixtures and this behaviour may be exhibited by the expression: log μ= A + B log c, where A and B are constants and c refers to the concentration of the soap (g mole L^{-1}).

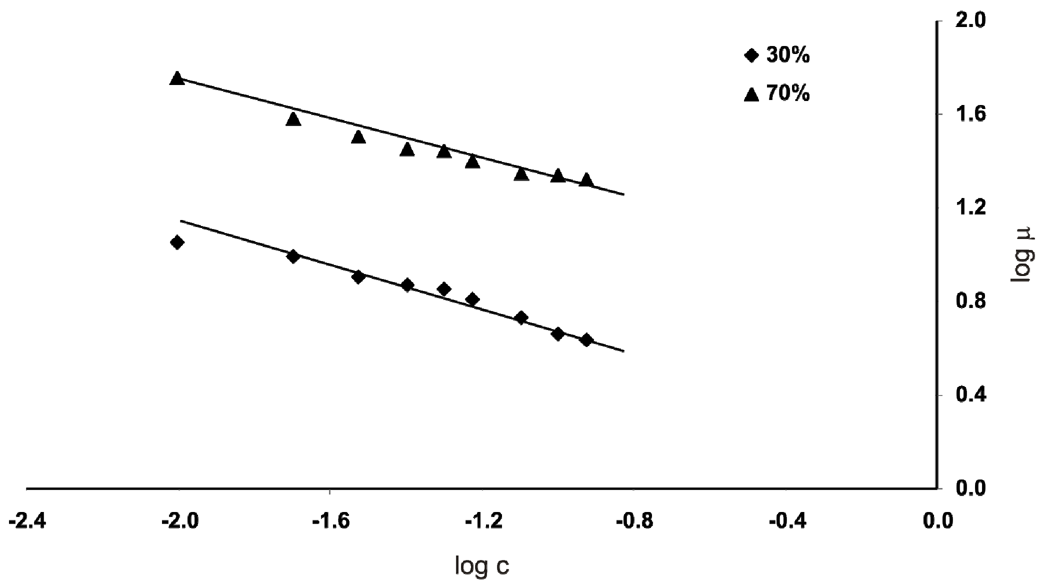

Fig. 4: Plots of specific conductivity v/s concentration of copper caprylate at various temperatures in 70% methanol

The values of log μ for zero value of log c (i.e. log $\mu_{c=1}$) are given in the Table 4. The values of log $\mu_{c=1}$ and B generally increase with temperature. The values of log $\mu_{c=1}$ and B also increase with increase in the volume percent of methanol in the system. This may be due to the low degree of association of soap molecules in the soap solution as the volume percent of methanol in the system increases[14,15].

Table 4. Values of log $\mu_{c=1}$ and constant B for copper soaps in bezene-methanol mixtures

Parameters	Name of Soap	Temp (°C)	Volume percent of methanol in the solvent mixture					
			30%	**40%**	**50%**	**60%**	**70%**	**80%**
log $\mu_{c=1}$	Caprylate	40	0.23	0.24	0.62	0.85	0.94	1.24
		45	0.30	0.30	0.62	0.80	1.28	1.42
		50	0.38	0.37	0.64	0.86	1.40	1.52
		55	0.42	0.41	0.65	0.89	1.48	1.62
	Caprate	40	-1.34	0.01	0.38	0.52	0.67	0.86
		45	-1.12	0.07	0.39	0.54	0.70	0.90
		50	0.01	0.19	0.41	0.57	0.73	0.98
		55	0.08	0.26	0.43	0.60	0.76	0.02
B	Caprylate	40	-0.44	-0.48	-0.46	-0.38	-0.36	-0.26
		45	-0.44	-0.46	-0.50	-0.46	-0.26	-0.23
		50	-0.42	-0.44	-0.46	-0.42	-0.26	-0.21
		55	-0.42	-0.44	-0.44	-0.40	-0.28	-0.17
	Caprate	40	-0.83	-0.57	-0.57	-0.46	-0.40	-0.36
		45	-0.78	-0.53	-0.50	-0.44	-0.38	-0.32
		50	-0.75	-0.50	-0.48	-0.42	-0.40	-0.30
		55	-0.75	-0.48	-0.46	-0.42	-0.38	-0.28

Dissociation constant (K) and limiting molecular conductivity (μ_0)

Krauss and Bray[16] derived an expression for the dissociation constant of the soap with the assumption that the soap behaves as a weak electrolyte in dilute solution. It is thus anticipated that such system obeys the Krauss and Bray type expression. Using the following expression, values of K and limiting molar conductance were obtained at four temperatures for copper caprylate and copper caprate in benzene and methanol mixtures:

$$c^2\mu^2 = \frac{K\mu_0^3}{4\mu} - \frac{\mu_0^2 K}{4}$$

Where μ_0 is the limiting molar conductance. It is observed that the plots of $c^2\mu^2$ against μ^{-1} are linear. The values of K and μ_0 for copper soaps in benzene- methanol mixtures of varying compositions have been obtained form the intercept and slopes of these plots at different temperatures. The average value of K and μ_0 were found to be (-0.8259×10^6) and (-5.8875×10^{-2}), respectively for copper caprylate soap.

The result suggests that in general, dissociation constant increases and limiting molar conductance decreases with the rise in temperatures. It may be due to the change in the viscosity of the solvent mixture. The values of μ_0 decreases upto 50% methanol concentration and thereafter, this pattern disappears at higher concentration of methanol and values of μ_0 and K at 70% and 80% methanol (above cmc) are difficult to study.

This may be due to the change in the nature of micelles from hydrophilic oleomicelles to lipophilic hydromicelles occurring at 60% methanol.[17] It is further underlined that the dissociation constant K does not show any particular trend with the increase in volume percent of methanol.

This is presumably due to the collection of counter ion in the vicinity of micelles at higher soap concentration.[18]

The heat of dissociation ΔH^0 as calculated from the slopes of linear plots of log K vs 1/T (Table 5) decreases upto 60% methanol concentration and then the trend vanishes, showing the change in the nature of the micelles at about this concentration. The negative enthalpy of dissociation ($\Delta H^0 < 0$) suggests that the dissociation of these metal soaps is exothermic. Negative enthalpy change of dissociation may be compensating for the unfavourable change in free energy and entropy of the dissociation process. The unfavourable entropy change may be attributed due to ion–solvent interactions i.e.

solvation of the soap molecules[13,19,20].

Table 5. Values of heat of dissociation, ΔH^o in (K cal mole^{-1}) of copper soaps in benzene-methanol mixtures

Percentage of methanol	Name of soap	
	Caprylate	Caprate
30%	-0.0174	-0.1228
40%	-0.0349	-0.1405
50%	-0.0524	-0.1584
60%	-0.0699	-0.1763
70%	-0.0349	-0.1405
80%	-0.0174	-0.1228

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