International Research Journal of Natural and Applied Sciences
I F 3.827 Volume 3, Issue 2, February 2016 ISSN: (2349-4077)
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INFLUENCE OF RADII OF TRIVALENT METAL IONS ON THE MICELLAR BEHAVIOUR OF LANTHANIDE SOAPS

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The conductometric measurements have been used to study the premicellar association, formation of micelles, molar conductance at infinite dilution, degree of ionization and ionization constant of lanthanide soaps the results show that the critical micellar concentration(CMC) decreases with decrease in ionic radii of trivalent metal ions of soap molecules in mixture of 50% methanol and50% benzene mixed solvent.

INTRODUCTION

The study of metallic soaps is becoming increasingly important in technological and academic fields.It has been a subject of intense investigations in the recent past on account of its role in diversified fields the application of metal soaps depend largely on their physical state, stability and chemical reactivity together with their volatility and solubility in common solvents, MEHROTRA et al[7]investigated various physicochemical properties of lanthanide & actinide soaps in solid state as wellas in solution. The present paper deals with the determination of CMC, degree of dissociation and dissociation constant of lanthanide soaps in a mixture of 50% methanol and 50%benzene byconductivity measurements

EXPERIMENTAL

All the chemicals used were of BDH/AR grade. All four soaps were prepared by the direct meathesis of corresponding potassium soaps with required amounts of aqueous solutions of lanthanide nitratecerrous chloride, praseodymium nitrate and neodymium nitrate at 50-60°C with vigorous stirring. The soaps were purified by recrystilization with methanol-benzene mixture and the purity was checked by elemental analysis, IR spectra and by the determination of melting points. The purified soaps lanthanum caprylate 108°C cerium caprylate l38°C praseodimiumcaprylate 90°C and neodymium caprylate 105°C respectively. The solutions were prepared by dissolving known weight of the soaps in the mixture50% methanol and 50% benzene and were kept for 2 hours in a thermostat al 40+0.05°C and then used for conductivity measurements. A Toshniwal CL 01.l0A" digital conductivity meter and dipping type conductivity cell with platinized electrodes were used for measuring the conductance of solutions at a constant temperature of 40.-+0. 05°C

RESULT AND DISCUSSION

SPECIFIC CONDUCTANCE IC:

The specific conductance IC, of the solutions of caprylates of lanthanum, cerium, praseodymium and neodymium in mixture of 50% methanol and 50% benezene increases with increasing soap concentration (Tablel to 4). The increase in specific conductance with the increase in soap concentration may be due to the ionization of metal caprylates into simpler metal cations La, Ce, Pr and Nd respectively and fatty anions $C_7H_{15}COO$ in dilute solutions and due to the formation ofmicelles at higher soaps concentrations. The plots of specific conductance vs soap concentrationFig (1) are characterized by an intersection of two straight lines at a definite soap concentration(0.040, 0.035, 0.033, 0.030) respectively corresponding to the CMC of lanthanum caprylate,caprylate, cerium caprylate, praseodymium caprylate and neodymium caprylate respectively in50% methanol and 50% benezene.It is suggested that the soap is considerably ionized in dilutesolutions and anions begin to aggregate to form ionic micelles at the CMC.The result shows thatthe decrease in the size of metal ions result in the decrease in the value of CMC of soapsolution.(Tablesshowsthe results).

MOLAR CONDUCTANCE U AND DISSOCIATION CONSTANT K

The molar conductance, μ of the dilute solutions of lanthanum, cerium, praseodymium andneodymium caprylate in a mixture of 50% methanol and 50% benezene diminishes with increasingsoap concentration (Table 1 to 4).The decrease in molar conductance is attributed to the combinedeffects of ionic atmosphere. Salvation of ions and decrease of mobility and ionization with theformation of micelles. The values of molar conductance of the solutions of lanthanide soaps are inorder of La>Ce>Pr>Nd. The molar conductance of the solutions of lanthanide soaps do not varylinearly with the square root of the soap concentration, $c^{1/2}$ (Fig. 2) indicating that the Debye HuckelOnsager s equation is not applicable to these soap solutions. The molar conductance results show thatthe dilute solutions of lanthanide soaps behave as weak electrolytes. The number of ions for weakelectrolyte is relatively small in dilute solutions and inter-ionic effects are negligible and so theactivities of ions may be taken as almost equal to the concentration and conductance ratio, 1/μ isreasonably good measure for degree of ionization, where μ is the molar conductance at finite dilutionand u_0 is the molar conductance at infinite dilution.

On substituting the value of α in the equation of ionization constant for 1:3 electrolytes, one gets;

$$\mu^3 c^3 = \frac{K\mu_0^4}{27\mu} - \frac{K\mu_0^3}{27}$$

The values of K and μ_0 can be obtained from the slope and intercept of the linear part of the plot of$\mu^3 c^3$ vs. 1/μ for dilute soap solutions (Fig 3).The values of limiting molar conductance, $\mu_0$are 2.04,1.97, 1.95 and 1.92 whereas for ionization constant are 4.13, 3.88, 1.82 and 1.53 x 10^5 for

lanthanum, cerium, praseodymium and neodymium caprylates respectively. The values oflimitingmolar conductance, μ0 and ionization constant, K, increase with increasing ionic radii of metal ion.

The values of degree of ionization, α, at different soap concentrations have beencalculated by assuming it as equal to conductance ratio, μ/μ0 and show that the degree of ionizationof lanthanide soaps decreases rapidly with the soap concentration in dilute solutions whereas itdecrease slowly in concentrated solutions. The values of ionization constant, K (Table 1 to 4) againconfirm that these soaps behave as a weak electrolyte in dilute solutions. The values of K exhibits adrift with increasing soap concentration which may be due to the fact that the conductance ratio, μ/μ0 is not exactly equal to the degree of ionization, α, and activity coefficient of ions are notexactly equal to unity and due to the failure of simple Debye _Huckel's activity equation under theseconditions.

The results show that these soaps behave as weak electrolyte in dilute solutions below the

CMC and there is significant interaction between soap solvent molecules in dilute solutions and soapmolecules do not aggregate in dilute solutions.

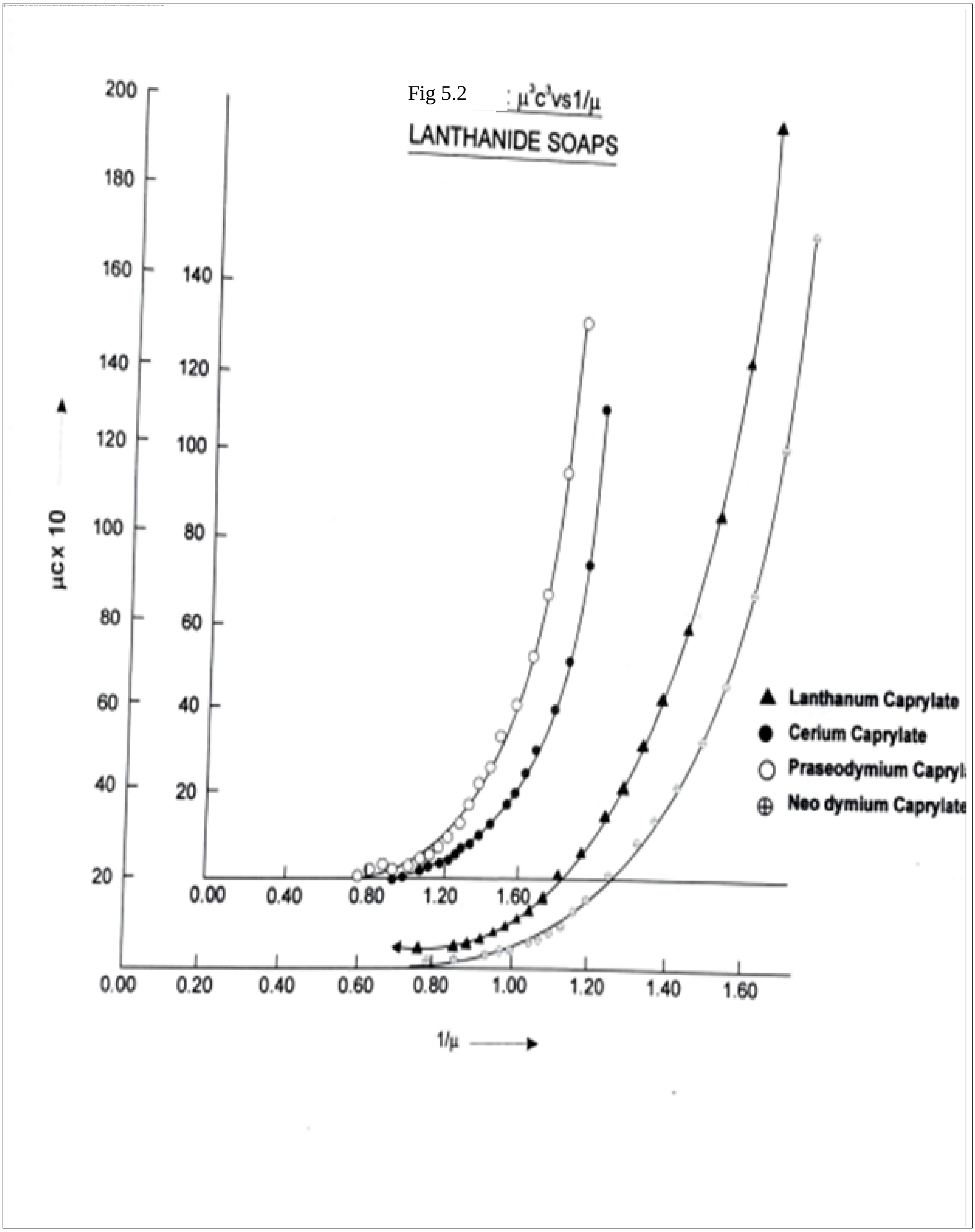
Fig 5.2 : μ³c³vs1/μ
LANTHANIDE SOAPS
μc x 10
1/μ
Lanthanum Caprylate
Cerium Caprylate
Praseodymium Capryl
Neo dymium Caprylate

Table 1 **Conductivity of Lanthanum caprylate in Mixture of 50% benzene and 50% methanol at 40±0.05°C.**

S.No	Concentration $Cx10^{2}$	specific conductance $Kx10^{6}$	Molar conductance (μ)	1/μ	$μ^{2}C^{2}x10^{6}$	Degree of dissociation α	Dissociation constant $Kx10^{6}$
1.	1.00	14.2	1.42	0.70	2.86	0.696	2.08
2.	1.18	15.4	1331	0.77	3.65	0.642	2.11
3.	1.43	16.6	1.16	0.86	4.57	0.569	1.92
4.	1.54	17.4	1.13	0.89	5.27	0.554	2.08
5.	1.65	18.1	1.10	0.92	5.93	0.538	2.22
6.	1.91	19.6	1.03	0.97	7.53	0.505	2.47
7.	2.07	20.7	1.00	1.00	8.87	0.490	2.71
8.	2.26	22.0	0.97	1.03	10.65	0.475	3.02
9.	2.49	23.4	0.94	1.06	12.81	0.461	3.49
10.	2.77	25.2	0.91	1.10	16.00	0.446	4.10
11.	3.12	27.3	0.88	1.14	20.35	0.431	4.97
12.	3.57	30.3	0.85	1.18	27.82	.417	6.26
13.	4.16	33.1	0.80	1.26	36.26	0.392	7.55
14.	4.54	35.1	0.77	1.29	43.24	0.377	8.06
15.	4.99	37.5	0.75	1.33	52.763	0.368	9.74
16.	5.55	40.2	0.72	1.38	64.96	0.353	11.08
17.	6.24	43.6	0.70	1.43	82.88	0.343	11.09
18.	7.14	47.7	0.67	1.50	108.53	0.328	16.93
19.	8.33	52.8	0.63	1.58	147.20	0.309	20.59
20.	10.00	58.8	0.59	1.70	203.30	0.289	26.49

Table 2 Conductivity of cerium Carpylate inmixture of 50% benzene and 50% metmethanol at 40±0.5°C

S.No	Concentration $C\times10^2$ c	specific conductance $K\times10^6$	Molar conductance (μ)	1/μ	$\mu^3C^3\times10^6$	Degree of dissociation α	Dissociation constant $K\times10^6$
1.	1.00	12.5	1.25	.80	1.95	0.635	0.12
2.	1.18	13.6	1.15	0.87	2.52	0.589	0.13
3.	1.43	15.0	1.05	0.95	3.38	0.532	0.14
4.	1.54	15.6	1.01	0.99	3.80	0.514	0.14
6.	1.91	17.8	0.93	1.07	5.64	0.473	0.18
7.	2.07	18.9	0.91	1.10	6.75	0.463	0.20
8	2.26	20.3	0.90	1.11	8.37	0.456	0.25
9.	2.49	21.6	0.87	1.15	10.08	0.440	0.28
10.	2.77	23.3	0.84	1.19	12.65	0.427	0.33
11.	3.12	25.4	0.81	1.23	16.39	0.413	0.41
12.	3.57	28.2	0.79	1.27	22.43	0.400	0.52
13.	4.16	31.0	0.75	1.34	29.79	0.378	0.64
14.	4.54	33.1	0.73	1.37	36.26	0.370	0.76
15.	4.99	35.3	0.71	1.41	43.99	0.359	0.87
16.	5.55	38.0	0.69	1.46	54.87	0.348	1.04
17.	6.24	41.0	0.66	1.52	68.92	0.334	1.23
18.	7.14	45.0	0.63	1.59	91.13	0.320	1.52
19.	8.33	50.0	0.60	1.67	125.00	0.305	1.94
20.	10.00	56.0	0.56	1.79	175.62	0.284	2.45

Table 3 Conductivity of Praseodymium caprylate in mixture of 50% benzene and 50% methanol at 40±0.05°C

S.No	Concentration $C \times 10^2$	specific conductance $K \times 10^6$	Molar conductance (μ)	$1/\mu$	$\mu^3 C^3 \times 10^6$	Degree of dissociation α	Dissociation constant $K \times 10^6$
1.	1.00	11.5	1.15	0.87	1.52	0.590	7.98
2.	1.18	12.6	1.07	0.94	2.00	0.549	8.94
3.	1.43	13.8	0.97	1.04	2.63	0.497	9.58
4.	1.54	14.4	0.94	1.07	2.99	0.482	10.28
5.	1.65	15.1	0.92	1.09	3.44	0.472	11.40
6.	1.91	16.6	0.87	1.15	4.57	.446	13.44
7.	2.07	17.7	0.86	1.17	5.55	0.441	16.20
8.	2.26	18.9	0.84	1.20	6.75	0.431	18.90
9.	2.49	20.0	0.80	1.25	8.00	0.410	19.96
10.	2.77	21.7	0.78	1.28	10.22	0.400	24.48
11.	3.12	23.4	0.75	1.33	12.81	0.385	29.30
12.	4.16	29.0	0.73	1.37	17.58	0.374	38.40
13	4.54	30.3	0.70	1.43	24.39	0.359	50.37
14.	4.99	32.5	0.67	1.40	27.82	0.345	54.65
15.	5.55	35.0	0.65	1.54	33.70	0.333	61.85
16.	6.24	37.9	0.63	1.59	42.88	0.323	74.21
17.	6.24	37.9	0.61	1.65	54.44	0.313	91.65
18.	7.14	41.2	0.58	1.73	69.93	0.297	108.77
19.	8.33	46.1	0.55	1.81	97.97	0.282	137.46
20.	10.00	51.3	0.52	1.95	135.01	0.267	187.20

Table 4 Conductivityof Neodymuim caprylate in mixture of 50% benzene and 50% methanol at 40±0.05°C

S.No	Concentration $Cx10^2$	specific conductance $Kx10^6$	Molar conductance (μ)	1/μ	$\mu^3C^3x10^6$	Degree of dissociation α	Dissociation constant $Kx10^6$
1.	1.00	10.4	1.04	0.96	1.13	0.542	5.09
2.	1.178	11.2	0.95	1.05	1.41	0.495	5.27
3.	1.43	12.7	0.89	1.13	2.05	0.463	6.76
4.	1.54	13.4	0.87	1.15	2.41	0.453	7.59
5.	1.65	14.0	0.85	1.18	2.74	0.443	8.39
6.	1.91	15.2	0.80	1.23	3.51	0.417	9.76
7.	2.26	17.3	0.77	1.30	5.18	0.401	10.34
8.	2.26	17.3	0.77	1.30	5.18	0.401	10.34
9.	2.49	18.5	0.74	1.35	6.33	0.385	14.89
10.	2.77	19.8	0.72	1.40	7.76	0.375	18.16
11.	3.12	24.6	0.69	1.45	10.08	0.6359	21.25
12.	3.57	23.8	0.65	1.53	13.48	0.339	25.31
13.	4.16	26.2	0.63	1.59	17.98	0.328	33.48
14.	4.54	237.9	0.62	1.63	21.72	0.323	40.62
15.	4.99	29.8	0.60	1.68	26.46	0.313	46.87
16.	5.55	32.2	0.58	1.72	33.39	0.303	55.82
17.	6.24	35.0	0.56	1.78	42.88	0.292	67.36
18.	7.14	38.0	0.53	1.88	54.87	0.276	78.77
19.	8.33	45.2	0.51	1.97	75.15	0.266	106.45
20.	10.00	47.0	0.47	2.13	103.82	0.245	128.85

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