Conductometric Analysis of Nickel (Ni) Butyrte, Caproate, And Caprylate Soaps in Benzene-Methanol Mixture

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ABSTRACT

Several researchers reported the uses and significant role of metallic soaps. In this paper, the conductometric analysis of nickel soaps (butyrate, caprote and caprylate) were investigated in benzene-methanol mixture at different temperatures. The results showed that nickel soaps behave as weak electrolytes in benzene-methanol below the CMC. The thermodynamics of dissociation and micellization process may be satisfactorily explained. The results also shown that the dissociation process of these soaps was found to be endothermic while micellization was exothermic in nature.

Key Words: *azelates, critical micelle concentration, dilute, electrolyte, oleates, platinised.*

I.INTRODUCTION

The importance of metal soaps, recently become increasing in technological uses as well as in academic studies. Lanthanoide soaps behave as weak electrolyte in dilute solutions. Viscometric and conductometrc titrations of polymethylacrylic acid with alkali metal and quaternary ammonium bases reported by Harry and revealed that the reduced specific viscosity of polymethylacrylic acid increased with counter ion size at the same degree of neutralization for the cations sodium < tetramethyl ammonium < tetraethylammonium < tetrapropylammonium < tetrabutylammonium [1]. Upadhyay studied the conductometric and acoustical studies and compressibility behavior of cobalt caprate in dimethylformamide and results showed that cobalt caprte behave as weak electrolytes in dimethylformamide and the micellization process is dominant over the dissociation process [2]. Conductometric studies and thermodynamics of dissociation and micellization of praseodymium and neodymium linoleates in mixed organic solvents showed that the praseodymium and neodymium linoliates behave as a weak electrolytes in dilute solutions (60 % benzene + 40 % methanol v/v) below the critical miceller concentrations and the conductance results can be explained on the basis of Ostwaald's formula and Debye- Huckel's theory of weak electrolytes [3].

Micellization and conductometric investigation on some lanthanod metal oleates in a mixture of 60 % benzene and 40 % methanol were investigated and the results showed that these soaps behave as weak electrolytes in dilute solutions and the values of CMC increase with the increasing temperatures [4]. In addition, conductometric, viscometric and acoustical studies on gadolium caprylate and caprate in non-aqueous medium showed that the soaps behave as weak electrolytes in dilute solutions below the CMC and the micellization process of these soaps has been found to be predominant over the dissociation process [5]. The solubility products of 32 metallic carboxylates resulting from the precipitation of seven cations (Cd, Co, Cu, Mn, Ni, Pb and Zn) with six linear saturated carboxylates such as heptanoate, octanoate, nonanote, decanoate, dodecanoate and octadecanoate were also reported[6].The conductometic , viscometric, and ultrasonic velocity measurements of the solutions of terbium laurate in benzene-methanol mixture were carried out at 40C and the conductivity results showed that the soaps behaves as a weak electrolytes in dilute solutions[7]. Additionally, conductivity measurements of solutions of terbium soaps in benzene-methanol mixture shown that these soaps behave as weak electrolytes in dilute solutions and Debye-Onsangers equations is not applicable to these soaps solutions [8]. The conductance of non-aqueous medium of magnesium myristate and palmitate was measured at different temperatures and shown that these soaps behave as weak electrolytes in chloroform-propylene glycol mixture below the CMC [9]. The studies of electrolytic behavior of the solution of dysprosium cproate and caprylate in mixture of benzene and methanol were employed and found that soaps behaves as a weak electrolytes below the CMC [10].

II. METHODOLOGY

In this study, first the fatty acids were purified by distilling under reduced pressure. The purity of acids was checked by determining their boiling points, melting points. Then used solvent benzene was purified by keeping over sodium for a couple of days and then distilling. The distillate was refluxed over sodium metal and then redistilled. Methanol was purified by keeping over KOH for twenty four hours and then distilling. The distillate was refluxed with 1% of calcium metal for about eight hours and redistilled. Sodium soaps (butyrate, caproate and caprylate) was prepared by refluxing equivalent amounts of corresponding fatty acid aqueous solution of sodium hydroxide for 6-8 hours on a water bath. The soaps were purified by recrystallization with methanol and dried under reduced pressure. The purity of soaps was checked by the determination of their melting points. Nickel butyrate, caproate and caprylate soaps were prepared by direct metathesis of the corresponding sodium soap with slight excess of the solution of nickel nitrate under vigorus stirring. The precipitated soaps were washed with water, methanol and acetone to remove the excess of metal salts, sodium soap and unreacted fatty acid. The soap thus obtained was dried in an air oven and the final drying of the soaps were carried out under reduced pressure. The soaps were purified by recrystallization with benzene-methanol mixture. The purity of the soaps were confirmed by determination of their melting point. Further, the nickel soaps (butyrate, cproate and caprylate) were investigated by conductivity measurements of these soaps in benzene and methanol with a Toshniwal Digital Conductivity Meter using 'Type CL 01.10 ^ using dipping type conductivity cell with platinised electrodes at different temperatures in a thermostate.

III. RESULTS AND DISCUSSIONS

The specific conductance , k of the dilute solutions of nickel soaps (butyrate, caproate and caprylate) in benzene – methanol increase with increase in the soap concentrations and the temperatures, while decrease with increasing chain length of the fatty acids of the soap molecules shown in Table- 1-9. This increase in the specific conductancce

Table-1 Conductivity measurements of Nickel Butyrate in Benzene- Methanol mixture at (20^0C)

S.No.	Concentration C X 10^4	Specific conductance k x 10^6	Molar conductance μ	$μ^2$ x 10^5	1/μ	Degree of dissociation ά	Dissocaton constant K x 10^6
1.	1.0	2.27	28.70	0.824	0.035	168.82	1.15
2.	2.0	4.06	20.30	1.648	.049	119.40	2.30
3.	3.0	5.23	17.42	2.731	0.057	102.47	3.82
4.	4.0	7.56	16.20	4.199	0.062	95.29	5.87
5.	5.0	9.32	15.64	6.115	0.064	92.00	8.56
6.	6.0	11.0	15.03	8.132	0.067	88.41	11.38
7.	7.0	12.26	14.51	10.316	0.069	85.35	14.45
8.	8.0	13.01	14.06	12.652	0.071	82071	17.73
9.	9.0	13.65	13.77	15.359	0.073	81.00	21.52
10	10.0	14.23	13.53	18.306	0.074	79.59	25.66

may be due to ionization of nickel soaps into simple metal cations Ni^{2+} and fatty acids anions $RCOO^-$ and due to the formation of micelles at higher concentrations.

Table-2- Conductivity measurements of Nickel Butyrate in Benzene- Methanol mixture at (30^0C)

S.No.	Concentration C X 10^4	Specific conductance k x 10^6	Molar conductance μ	$μ^2$ x 10^5	1/μ	Degree of dissociation ά	Dissocaton constant K x 10^6
1.	1.0	2.51	30.10	0.906	0.033	150.50	0.91
2.	2.0	4.49	22.45	2.016	0.045	112.25	2.03
3.	3.0	6.36	19.20	3.318	0.052	96.00	3.35
4.	4.0	8.23	18.08	5.230	0.055	90.40	5.27

5.	5.0	10.11	17.42	7.586	0.057	87010	7.67
6.	6.0	12.01	16.92	10.306	0.059	84.60	10.43
7.	7.0	13.47	15.9415.64	12.450	0.063	79.70	12.61
8.	8.0	14.11	14.87	15.55	0.064	78.20	15.86
9.	9.0	14.76	14.43	17.920	0.067	74.35	18.15
10	10.0	15.43		20.822	0.069	72.15	21.12

Table-3 Conductivity measurements of Nickel Butyrate in Benzene- Methanol mixture at (40^0C)

S.No.	**Concentration C X 10^4**	**Specific conductance k x 10^6**	**Molar conductance μ**	**$\mu^2 \times 10^5$**	**1/μ**	**Degree of dissociation ά**	**Dissocaton constant K x 10^6**
1.	1.0	2.75	31.50	0.992	0.032	131.25	0.69
2.	2.0	4.76	23.80	2.265	.0.042	99.17	1.59
3.	3.0	6.73	20.43	3.756	0.049	85.13	2.64
4.	4.0	8.65	19.63	6.165	0.051	81.79	4.33
5.	5.0	10.72	18.74	8.779	0.053	78.08	6.18
6.	6.0	12.51	17.85	11.470	0.056	74.38	8.08
7.	7.0	14.27	16.89	13.978	0.059	70.38	9.85
8.	8.0	14.88	16.46	17.399	0.061	68.58	12.23
9.	9.0	15.37	15.98	20.684	0.063	66.58	14.58
10	10.0	16.01	15.61	24.367	0.064	65.04	17.19

Table-4- Conductivity measurements of Nickel Caproate in Benzene- Methanol mixture at (20^0C)

S.No.	Concentration $C \times 10^4$	Specific conductance $k \times 10^6$	Molar conductance μ	$\mu^2 \times 10^5$	$1/\mu$	Degree of dissociation ά	Dissocaton constant K $\times 10^6$
1.	1.0	1.92	19.20	0.368	0.052	128.00	0.66
2.	2.0	3.69	18.45	1.361	.0.054	123.00	2.44
3.	3.0	5.38	17.93	2.893	0.056	119.53	5.19
4.	4.0	7.03	17.58	4.945	0.057	117.20	8.87
5.	5.0	8.35	16.70	6.972	0.060	111.33	12.51
6.	6.0	9.52	15.87	9.067	0.063	105.80	16.27
7.	7.0	10.26	14.66	10.531	0.068	97.70	18.90
8.	8.0	10.88	13.60	11.837	0.074	90.67	21.28
9.	9.0	11.41	12.68	13.023	0.079	84.53	23.43
10	10.0	12.11	12.11	14.665	0.083	80.73	26.40

Table-5- Conductivity measurements of Nickel Caproate in Benzene- Methanol mixture at (30^0C)

S.No.	Concentration $C \times 10^4$	Specific conductance $k \times 10^6$	Molar conductance μ	$\mu^2 \times 10^5$	$1/\mu$	Degree of dissociation ά	Dissocaton constant K $\times 10^6$
1.	1.0	2.09	20.90	0.437	0.048	116.00	0.54
2.	2.0	3.86	19.30	1.490	.0.052	107.22	1.86
3.	3.0	5.65	18.83	3.191	0.053	104.61	3.98
4.	4.0	7.41	18.52	5.488	0.054	102.89	6.84
5.	5.0	9.03	18.06	8.154	0.055	100.33	10.17

6.	6.0	10.68	17.80	11.406	0.056	98.89	14.23
7.	7.0	11.89	16.99	14.144	0.059	94.39	17.65
8.	8.0	12.43	15.54	15.455	0.064	83.33	19.30
9.	9.0	13.08	14.53	17.101	0.069	80.72	21.38
10	10.0	13.69	13.69	18.742	0.073	76.06	23.45

Table-6- Conductivity measurements of Nickel Caproate in Benzene- Methanol mixture at (40^0C)

S.No.	**Concentration C X 10^4**	**Specific conductance k x 10^6**	**Molar conductance μ**	**μ^2 x 10^5**	**1/μ**	**Degree of dissociation ά**	**Dissocaton constant K x 10^6**
1.	1.0	2.23	22.30	0.497	0.045	106.19	0.45
2.	2.0	4.29	21.45	1.840	.0.047	93.26	1.41
3.	3.0	6.22	20.73	3.868	0.048	90.13	2.96
4.	4.0	7.99	19.98	6.387	0.050	86.87	4.89
5.	5.0	9.55	19.10	9.120	0.052	83.04	6.98
6.	6.0	11.31	18.85	12.792	0.053	81.96	9.79
7.	7.0	12.76	18.23	16.284	0.055	79.26	12.47
8.	8.0	13.73	17.16	18.846	0.058	74.70	14.48
9.	9.0	14.51	16.12	21.048	0.062	70.09	16.15
10	10.0	15.16	15.16	22.983	0.066	65.91	17.64

Table-7- Conductivity measurements of Nickel Caprylate in Benzene- Methanol mixture at (20^0C)

S.No.	Concentration C X 10^4	Specific conductance k x 10^6	Molar conductance μ	μ^2 x 10^5	1/μ	Degree of dissociation ά	Dissocaton constant K x 10^6
1.	1.0	1.81	18.10	0.328	0.055	129.28	0.67
2.	2.0	3.48	17.40	1.211	.0.057	124.29	2.49
3.	3.0	4.84	16.13	2.342	0.062	115.21	4.82
4.	4.0	6.63	15.32	3.755	0.065	109.43	7.73
5.	5.0	7.36	14.72	5.417	0.068	105.14	11.16
6.	6.0	8.48	14.13	7.188	0.071	100.93	14.82
7.	7.0	9.20	13.14	8.460	0.076	93.86	17.45
8.	8.0	9.74	12.18	9.494	0.082	87.00	19.60
9.	9.0	10.54	11.71	11.107	0.085	83.64	22.94
10	10.0	11.15	11.15	12.432	0.090	79.64	25.69

Table-8 Conductivity measurements of Nickel Caprylate in Benzene- Methanol mixture at (30^0C)

S.No.	Concentration C X 10^4	Specific conductance k x 10^6	Molar conductance μ	μ^2 x 10^5	1/μ	Degree of dissociation ά	Dissocaton constant K x 10^6
1.	1.0	1.98	19.80	0.392	0.051	116.47	0.54
2.	2.0	3.83	19.15	1.467	.0.052	112.65	2.05
3.	3.0	5.64	18.80	3.181	0.053	110.59	4.44
4.	4.0	7.08	17.72	5.024	0.056	104.24	7.02
5.	5.0	8.52	17.04	7.259	0.059	100.24	10.15

6.	6.0	9.70	16.17	9.412	0.062	95.12	13.18
7.	7.0	10.80	15.43	11.666	0.065	90.76	16.33
8.	8.0	11.69	14.61	13.660	0.068	85.94	19.13
9.	9.0	12.24	13.60	14.982	0.074	80.00	20.99
10	10.0	12.78	12.78	16.333	0.078	75.18	22.91

Table-9- Conductivity measurements of Nickel Caprylate in Benzene- Methanol mixture at (40^0C)

S.No.	**Concentration C X 10^4**	**Specific conductance k x 10^6**	**Molar conductance μ**	**μ^2 x 10^5**	**1/μ**	**Degree of dissociation ά**	**Dissocaton constant K x 10^6**
1.	1.0	2.95	21.50	0.462	0.047	102.38	0.42
2.	2.0	4.07	20.35	1.656	.0.049	96.90	1.52
3.	3.0	5.99	19.97	3.589	0.050	95.09	3.29
4.	4.0	7.58	18.95	5.746	0.053	90.24	5.27
5.	5.0	9.19	18.39	8.455	0.054	87.57	7.76
6.	6.0	10.51	17.51	11.038	0.057	83.38	10.13
7.	7.0	11.85	16.93	14.045	0.059	80.62	12.90
8.	8.0	13.04	16.30	17.004	0.061	77.62	15.62
9.	9.0	13.57	15.08	18.420	0.066	71.81	16.94
10	10.0	13.95	13.95	19.460	0.071	66.43	17.92

The values of CMC decrease with increase in chain length of the soaps while increase with increase n temperature. The molar conductance ,μ of the dilute solutions of nickel soaps decrease with increasing soap concentratons(Table-1-9). The decrease in molar conductance may be due to combined effects of ionic atmosphere, salvations of ions and decrease of mobility and the ionization with the formation of micelles. Mathematically, we concluded that these soaps behave as weak electrolytes n dilute solutions and not obey the Debye-Huckel's Onsanger's equation. The values of limiting molar conductance and dissociation constant, K for dilute solutions were recorded (Table-1-9).

The results showed that the values of limiting molar conductance decrease with chain-length of soap molecule while increase with increasing temperature.

Table- 10 Values of the CMC (gmol dm^{-3}) C X 10^4 at various Temperatures

S.No.	Nickel Soaps	20 ^{0}C	30 ^{0}C	40 ^{0}C
1.	**Butyrate**	6.13	6.52	6.81
2.	**Caproate**	5.92	6.24	6.70
3.	**Caprylate**	5.80	6.10	6.55

IV. CONCLUSIONS

Finally, it was concluded that , nickel soaps behave as weak electrolyte in benzene-methanol below the CMC. The thermodynamics of dissociation and micellizaion process may be satisfactorily explained. The results shown that the dissociation process of these soaps was found to be endothermic while the micellization process was found exothermic in nature.

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