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Studies on miceller properties on the soaps of beryllium

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ABSTRACT

The conductance of the solution of beryllium soaps has been measured at 30°C + 0.05°C in pure benzene with a view to determined the critical miceller concentration (CMC), molar conductance at infinite dilution. The results show that the specific conductance of the solutions of a soap increases whereas the molar conductance decreases with the increase in the soap concentration but increases with increasing chain length of the soap. The value of CMC decreases with the increase in the chain length of soap. The viscosity measurements confirm that the soap molecules does not aggregate appreciably below the CMC and the results has been interpreted in terms of Einstein, Vand, Moulik, and Jones-Dole equations. The values of molar volume are in agreement.

Key words: Miceller properties, soaps of beryllium.

INTRODUCTION

The alkaline earth metal soaps are of great significance of their uses in various industries under different conditions. The soaps are widely used in industries as antibacterials[1], dryers, fungicides, stabilizers[2-4], cosmetic[5], binding insulators, adhesives and to improve the heat resistance and binding capacity[6-7]. The methods of preparation and physico chemical properties provide the basis of the selection of metal soap for industrial use. The methods of preparation metal soap were described by several workers[8-15]. The Infra-red spectra, X-ray diffraction and thermal analysis of Magnesium soaps were investigated by Chitra *et al.*[16]. The thermodynamics of dissociation of Calcium and Lithium soaps were investigated by Updhyaya[17] and Verma *et al.*[18]. The ultrasonic velocity measurements of Lithium soaps were made by Upadhaya[19] and the ultrasonic, conductivity and viscosity measurements of Strontium and Barium soaps were made by Rawat *et al.*[20,21]. From the literature it has been revealed that Berrylium soap has not been thoroughly investigated in splite of the large number of application of alkaline earth metal soaps in industry. The present work includes molar volume, viscosity and conductivity measurements of beryllium soaps to study the micelles properties in pure benzene.

EXPERIMENTAL

Preparation of soap

The soaps of beryllium (Caprate, Laurate and Myristate) were prepared by direct metathesis of corresponding potassium soaps with the required amount of aqueous solution of beryllium sulphate at 50-55°C under vigorous stirring. The precipitated soaps were washed several times with of distilled water and acetone to remove the excess of fatty acid and metal sulphate. The soaps were purified by recrystallisation, dried in an air over at 50-60°C and the final drying of the soaps were carried out under reduced pressure. The absences of hydoxyl group in the soaps were confirmed by studying its Infrared absorption spectrum. The basis of making the solution of these soaps is the maximum solubility in polar and non-polar organic solvents. The best solubility of Beryllium soaps in pure Benzene.

Measurements

Conductivity

The conductivity of the solution was measured by using a "TOSHNIWAL DIGITTAL CONDUCTIVITY METER" (Model CL 01, 10A) and a dipping type conductivity cell with platinized electrodes at a constant temperature, 30±0.05°C.

Viscosity

An Oswald's type viscometer was used for measuring the viscosity of the soap solutions. The viscosities of the soap solutions were calculated by using relationship.

$$\frac{\eta_1}{\eta_2} = \frac{\rho_1 t_1}{\rho_1 t_2}$$

where η_1, η_2, ρ_1, ρ_2 and t_1, t_2 are the viscosity, density and time of flow of solvent and solution, respectively, All measurements were made at a constant temperature 30±0.05°C in a thermostat.

RESULTS AND DISCUSSION

Conductivity

The specific conductance, k of the solution of Beryllium soaps (Caprate, Laurate, Myristate) in pure Benzene increases with the increase in soaps concentration, C (Table-1). The increase in specific conductance with the increase in soaps concentration may be due to the ionization by Beryllium soaps into a simple as metal cation M^{2+} and fatty acids anions $RCOO^-$ (Where M is Beryllium and R is C_9H_{19}, $C_{11}H_{23}$ and $C_{13}H_{27}$ for caprate. Laurate and Myristate, respectively) in solutions and also due to the formation of micelles at higher soap concentration. The plots of specific conductance vs the soap concentration (Fig.1) are characterized by an intersection of two straight lines at a definite soap concentration, which corresponds to the CMC, indicating the formation of ionic micelles at this soap concentration. The value fo CMC for Beryllium soaps are recorded in (Table-2). The results show that the CMC decreases with increasing chain-length of soap molecules.

The molar conductance, μ of the soaps solution of Beryllium soaps (Caprate, Laurate, Myristate) in pure Benzene decreases with the increasing soaps concentration, (Table-1). The decrease in molar conductance with the increase in soaps concentration may be due to the combine effects of ionic atmosphere, salvation of ions, decrease of mobility and ionization with the formation of micelles. The plot of molar conductance, μ against the square root of the soap concentration, is not linear which indicates that the soap behave as simple electrolyte in these solution. The molar conductance, μ cannot be obtained by the usual extrapolation method, as the Debye Huckel equation is not applicable to these soap solution.

Assuming that the soap are completely dissociated into M^{2+} and RCOO ions. The dissociation of metal soaps my be represented as:

$$(RCOO)_2M \quad = \quad M^{2+} + 2RCOO^- \qquad ...(1)$$
$$C(1-\alpha) \quad = \quad C\alpha \; 2(C\alpha)$$

where M stand for Beryllium R is C_9H_{19}, $C_{11}H_{25}$ and $C_{13}H_{27}$ for caprate. Laurate and Myristate, respectively, α and C are the degree of dissociation and concentration of soap respectively. The dissociation constant, K can be written as:

$$K = \frac{[M^{2+}][RCOO^-]^2}{[M(RCOO)_2]} \qquad ...(2)$$

$$= \frac{C\alpha(2C\alpha)^2}{C(1-\alpha)} = \frac{4C^2\alpha^3}{1-\alpha} \qquad ...(3)$$

Assuming that the solutions do not deviate appreciably from their ideal behaviour, the activities of ions can be taken almost equal to concentration. Thus α may be defined by conductance ratio μ/μ_0 where μ is the molar conductance at finite concentration, that is attributed to the ions formed by the dissociation of metal soaps and μ_0 is the limiting molar conductance of theses ions.

Table-1: Conductivity Measurements of Beryllium Soaps in pure Benzene at 30°C ± 0.05°C

S. No.	Conductance C × 10^3 (mol/L)	Beryllium Caprate		Beryllium Laurate		Beryllium Myristate	
		Specific Conductance K × 10^6 mhos cm^{-1}	Molar Conductance μMhos cm^2 mol^{-1}	Specific Conductance K × 10^6 mhos cm^{-1}	Molar Conductance μ mhos cm^2 mol^{-1}	Specific Conductance K × 10^6 mhos cm^{-1}	Molar Conductance μmhos cm^2 mol^{-1}
1.	20.0	22.5	1.1250	23.4	1.1700	24.4	1.2200
2.	18.1	21.6	1.1934	22.0	1.2155	23.3	1.2873
3.	16.6	20.0	1.2048	21.9	1.2831	22.0	1.3253
4.	15.3	19.1	1.2484	20.4	1.3333	21.1	1.3791
5.	14.2	18.6	1.3099	19.2	1.3521	20.7	1.4577
6.	13.3	17.8	1. 3383	18.6	1.3985	19.8	1.4887
7.	12.5	17.0	1.3600	18.0	1.4400	19.3	1.5440
8.	11.7	16.4	1.4017	17.4	1.4872	18.7	1.5983
9.	11.1	16.0	1.4414	17.0	1.5315	18.3	1.6486
10.	10.5	15.5	1.4762	16.8	1.6000	18.0	1.7143
11.	10.0	15.2	1.5200	16.2	1.6200	17.5	1.7500
12.	9.5	14.8	1.5579	15.8	1.6632	17.2	1.8105
13.	9.1	14.3	1.5714	15.3	1.6813	16.8	1.8462
14.	8.6	14.0	1.6279	14.9	1.7320	16.5	1.9186
15.	8.3	13.7	1.6506	14.5	1.7469	16.0	1.9177
16.	8.0	13.3	1.6625	14.1	1.7625	15.7	1.9625
17.	7.6	12.7	1.6711	13.6	1.7895	15.2	2.0000
18.	7.1	12.3	1.7324	13.3	1.8732	14.7	2.0704
19.	6.8	11.9	1.7500	12.8	1.8824	14.3	2.1029
20.	6.6	11.7	1.7727	12.5	1.1839	13.9	2.1061

Table -2: Values of CMC, μ_0 and log K for Beryllium Soaps at 30±0.05°C

Metal Soap	CMC (Mol 1^{-1})	μ_0	-log K
Beryllium Caprate	9.8 0× 10^{-3}	4.5	2.96
Beryllium Laurate	9.5× 10^{-3}	5.0	3.09
Beryllium Myristate	9.1× 10^{-3}	5.8	3.11

On substituting the values of in equation (3) and rearranging we obtains:

$$\mu^2C^2 = \frac{K\mu_0^3}{4\mu} - \frac{\mu_0^2K}{4} \qquad ...(4)$$

The plots $\mu_2 C_2$ vs 1/μ of are plotted and the intercept and slope are equal to $\frac{\mu_0^2K}{4}$ and $\frac{K\mu_0^3}{4\mu}$ respectively. The value of the dissociation constant, K and limiting molar conductance, μ_0 for dilute solutions below the CMC have been calculated from the slope and intercept of these plot of $\mu_2 C^2$ vs 1/μ. The value of the limiting molar conductance, μ_0 and dissociation constant, K are depicted in (Table-2). The conductivity results confirm that the soaps behave, as a simple electrolyte in these solution and Debye Huckel equation is not applicable to these solutions.

Viscosity

The viscosity, η and specific viscosity, η_{sp} of the e solution of Beryllium soaps (Caprate. Laurate and Myristate) in pure Benzene increases with increasing soap concentration (Table-3). The increase in the viscosity may be due to the increasing tendency of the soap molecule to form aggregates with the increase in the soap concentration. The plot of η vs soap concentration, C (Fig. -2) and η_{sp} vs soap concentration (Fig. 3) are characterized by an intersection of two straight lines at a definite soap concentration, which corresponds to the CMC of the soaps are 0.0099 mol/L, 0.0095 mol/L, 0.0091 mol/L for Caprate. Laurate and Myristate, respectively. The plots of viscosity η_{vs}. C below the CMC has been extrapolated to zero soap concentration. The extrapolated value (Table- 4). The viscosity results confirm that there is no appreciable aggregation of the soap molecules below the CMC where as there is a sudden increase in the aggregation at this soap concentration.

The viscosity results have been interpreted in the light of equations proposed by Einstein[22], Vand[23], Moulik[24] and Jones-Dole[25].

$$Einstein \rightarrow \eta_{sp} = 2.5\bar{V}C$$

$$Vand \rightarrow 1/C = \left[\frac{0.921}{V}\right]\frac{1}{\log(\eta/\eta_0)} + \phi\bar{V}$$

$$Moulik \rightarrow (\eta/\eta_0)^2 = M + K^1C^2$$

$$Jones\ -\ Dole \rightarrow \eta_{sp}/\sqrt{C} = A + B\sqrt{C}$$

where, V, C, ϕ , η, η_0 and η_{sp} are the molar volume, concentration of he soap (mol 1^{-1}), interaction coefficient, viscosity of the solution, viscosity of the solvent and specific viscosity respectively. M and K are Moulik's constants and A and B are the Jones-Doles constants.

The plots η_{sp} vs. C (fig-2) are linear below the CMC with the intercept almost equal to zero, which show shat Einstein's equation is applicable to these soap solutions. The values of molar volume of soaps, V calculated from the slope of the Einstein's plot. (Table -5). The plot of 1/C v 1/log (η/η_0) are linear below the CMC which shows that Vand's equations is applicable to these solution of Beryllium soaps in pure Benzene. The values of interaction coefficient, ϕ and molar volume obtained from the intercept and slope of the plots of 1/C vs. 1/log (η/η_0) are recorded in (Table -5). The values are inclose agreement with the values obtained from Einstein's equation.

The plot of $(\eta/\eta_0)^2$ Vs C^2 shows as break at a definite soap concentration, which corresponds, to the CMC of the soap. The value of Moulik's constant, M and K obtained from the Intercept and

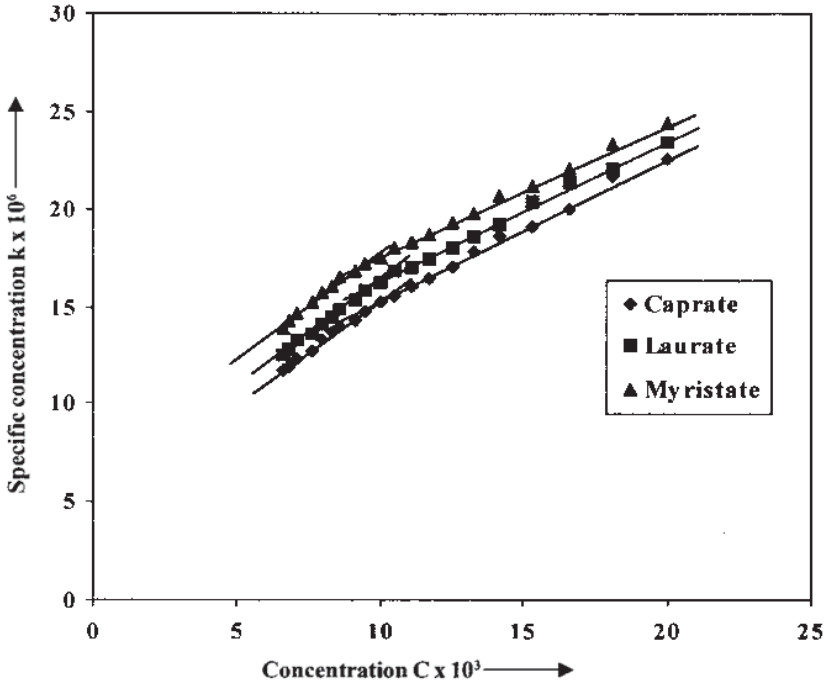

Fig. - 1: Specific concentration vs concentration

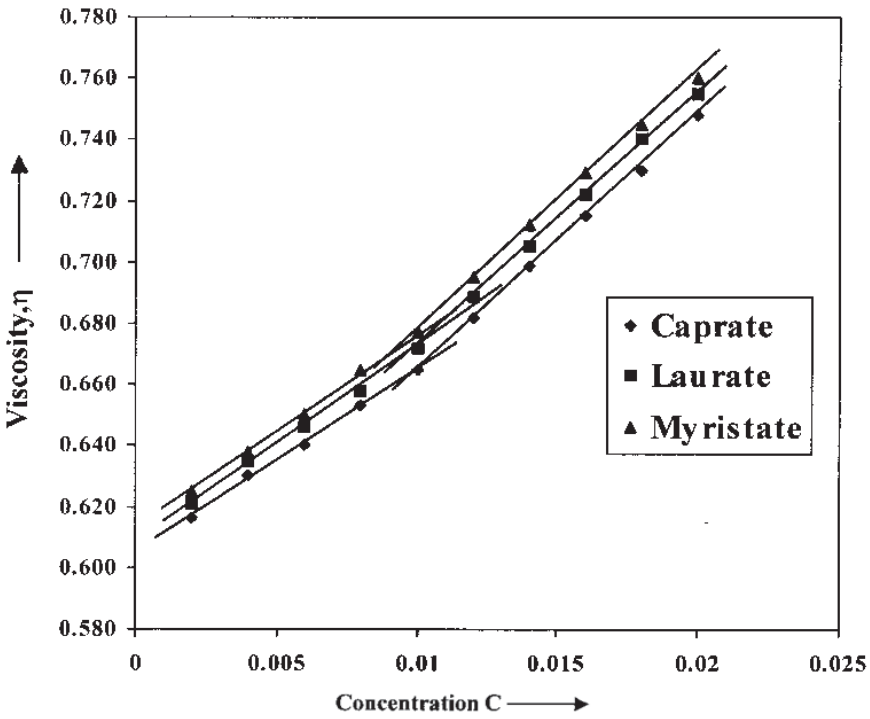

Fig. - 2: Viscosity vs concentration

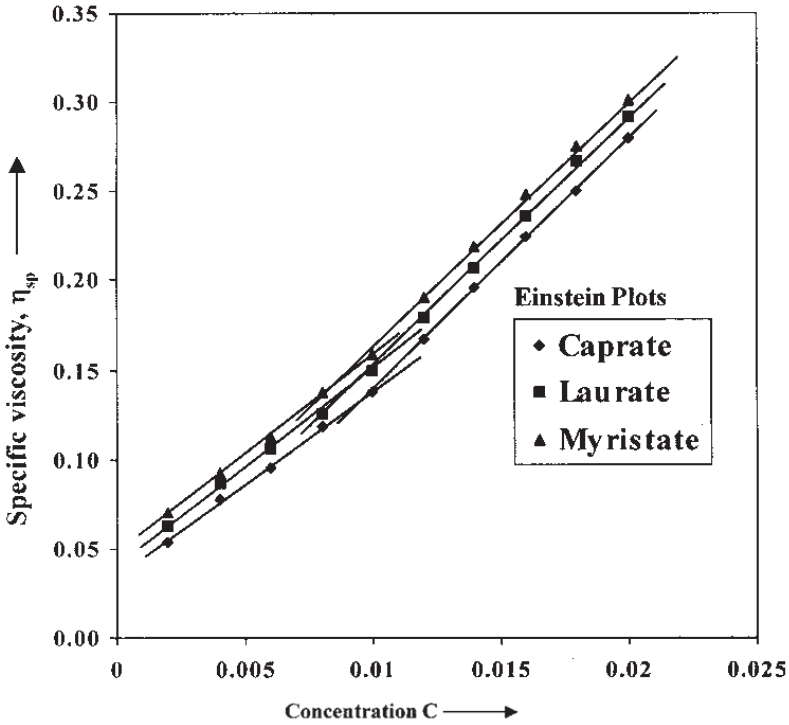

Fig. - 3: Specific viscosity vs concentration $\sqrt{C}$

slope of the plots of $(\eta/\eta_0)^2$ Vs C^2 are recorded in (Table -5).

The viscosity data have also been explained in the light of Jones-Dole's equation. The plot of $\eta_{sp}/$ vs is characterized by an intersection of two straight lines at a definite soap concentration. The values of the constant A and B calculated from the intercept and slope of plots of $\eta_{sp}/$ vs $\sqrt{C}$ are recorded in (Table -5). The small value of A (soap-soap interaction), compared with B (soap-solvent interaction) confirm that there is no appreciable aggregation of the soap molecules in dilute solution below the CMC. This may be attributed to the fact that the aggregation of soap molecules above the CMC boosts up the electro-kinetic forces causing more intake of one solvent resulting in the increased viscosity of the system.

The results show that the CMC values obtained from viscosity measurements are in agreement with those obtained from conductivity method.

Table -3: Viscosity parameters of Beryllium soaps (Caprate, Laurate and Myristate) in pure Benzene at 30 ± 0.05°C

S. No.	Cocnetration C (mol L^{-1})	Viscosity η Centipoise	Specific vicosity η_{sp}	$\eta_{sp}/\sqrt{C}$	$(\eta/\eta_0)^2$	$\frac{1}{\log \frac{\eta}{\eta_o}}$
Beryllium Caprate						
1.	0.002	0.616	0.05479	1.2253	1.11259	43.1628
2.	0.004	0.630	0.07876	1.2453	1.16374	30.3696
3.	0.006	0.640	0.09589	1.2379	1.20097	25.1465
4.	0.008	0.653	0.11815	1.3210	1.25026	20.6184
5.	0.010	0.665	0.13869	1.3869	1.29664	17.7277
6.	0.012	0.682	0.16781	1.5319	1.36378	14.8431
7.	0.014	0.699	0.19692	1.6643	1.43261	12.8099
8.	0.016	0.715	0.22432	1.7732	1.49895	11.3774
9.	0.018	0.730	0.25000	1.8629	1.56250	10.3139
10.	0.020	0.748	0.28082	1.9857	1.64050	9.3033
Beryllium Laurate						
1.	0.002	0.621	0.06336	1.4167	1.13072	37.4831
2.	0.004	0.635	0.08733	1.3807	1.18228	27.5020
3.	0.006	0.646	0.10616	1.3706	1.22359	22.8209
4.	0.008	0.658	0.12671	1.4167	1.26948	19.3002
5.	0.010	0.672	0.15068	1.5069	1.32014	16.4052
6.	0.012	0.689	0.17979	1.6414	1.39192	13.9263
7.	0.014	0.705	0.20719	1.7511	1.45731	12.2285
8.	0.016	0.722	0.23630	1.8679	1.52844	10.8549
9.	0.018	0.740	0.26712	1.9904	1.60560	9.7258
10.	0.020	0.755	0.29281	2.0705	1.67135	8.9658
Beryllium Myristate						
1.	0.002	0.625	0.07021	1.5699	1.14339	33.9361
2.	0.004	0.638	0.09247	1.4619	1.19348	26.0363
3.	0.006	0.650	0.11301	1.4589	1.23879	21.5059
4.	0.008	0.665	0.13869	1.5507	1.29663	17.7278
5.	0.010	0.677	0.15925	1.5924	1.34385	15.5822
6.	0.012	0.695	0.19006	1.7357	1.41626	13.2325
7.	0.014	0.712	0.21917	1.8524	1.48639	11.6188
8.	0.016	0.729	0.24828	1.9627	1.55822	10.3826
9.	0.018	0.745	0.27568	2.0543	1.62737	9.4569
10.	0.020	0.760	0.30137	2.1310	1.69356	8.7412

Table -4: Value of η_0 and η_{osp} of Soaps obtained from the plots of η vs. C and η_{sp} vs C.

S. No.	Metal	Caprate		Laurate		Myristate	
		η_0	η_{osp}	η_0	η_{osp}	η_0	η_{osp}
1.	Beryllium	0.604	0.034	0.609	0.040	0.613	0.046

Table -5: Values of various parameters obtained from viscosity measurements at 30 ± 0.05°C

Metal Soaps	Molar Volume V (L mol^{-1})		ϕ	Mouliks's Constant			Jone-Doles Contant	
	Einstein's Equation	Vand's Equation		M	K × 10^{-4}	A	B Above CMC	B Below CMC
Beryllium Caprate	4.30	5.26	17.5	1.13	0.1666	1.10	13.75	3.00
Beryllium Laurate	4.50	5.75	18.0	1.15	0.1785	1.70	12.50	3.21
Beryllium Myristate	4.60	6.14	17.0	1.16	0.1944	1.23	12.00	3.57

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