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Viscosity Measurements of Zirconyl Soaps in Benzene-Methanol Mixture

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ABSTRACT

The density and viscosity measurements of the solutions of Zirconyl soaps (caprylate and caprate) in benzene-methanol mixture (4:1 v/v) have been used to determine the critical micelle concentration and other viscosity parameters. The viscosity results have been interpreted in terms of equations proposed by Einstein, Vand, Moulik and Jones-Dole. The values of molar volume are in agreement with each other and the soap molecules do not aggregate appreciably below the CMC.

Keywords- Zirconyl soaps, viscosity, CMC, Molar volume.

I. INTRODUCTION

Metal soaps are termed as surfactant because they have lyophillic and lyophobic moieties in the same molecules which lend them unique characteristics and make them useful for many applications in industries [1-10]. However, the applications of metal soaps are based on empirical knowledge and the selection of the soap for a specific purpose is mainly governed by economic factors.

The present work deals with study of viscosity of the solution of zirconyl soaps (caprylate and caprate) in benzene-methanol mixture (4:1 v/v).

II. EXPERIMENTAL

All the chemical used were of AR/BDH grade. Zirconyl soaps (caprylate and caprate) were prepared by direct metathesis of the corresponding potassium soaps with slight excess of the solution of zirconium oxychloride under vigorous stirring. The precipitated soaps were washed with water, methanol and acetone to remove excess of metal salt. The purity of the soaps was confirmed by m.p. (caprate, 137ºC and caprate 146ºC) elemental analysis and ir spectra. The solutions of different concentrations of zirconyl soaps were prepared in benzene-methanol mixture (4:1 v/v). The viscosity and density of the solutions of zirconyl soaps were measured with Ostwald's viscometer and dilatometer respectively at 40±05ºC.

III. RESULT AND DISCUSSION

The density, ρ of the solution of zirconyl soaps (caprylate and caprate) in benzene-methanol mixture (4:1 v/v) increases with increasing soap concentration as well as with the chain length of soap (Table 1). The plots of density, ρ Vs soap concentration, C are characterized by an intersection of two straight lines at a definite soap concentration (caprylate 0.044 M and caprate 0.040 M) which correspond to the critical micelle concentration (CMC) of these soaps in solutions. The results show that the values of the CMC of zirconyl soaps in benzene-methanol mixture (4:1 v/v) decreases with increasing chain length of soap.

The plots of ρ Vs C for dilute solutions were extrapolated to zero soap concentration and the extrapolated values, ρ_0 of density were found to be in agreement with experimental value of the density of the solvent mixture (845.2 kgm^{-3}) (Table-2).

The viscosity, η and specific viscosity, η_{sp} of solutions of zirconyl soaps in the benzene-methanol mixture (4:1 v/v) increases with increasing soap concentration and chain length of the soap (Table 1). The increase in viscosity with increasing chain length of the soap may be due to the increasing solvation of anions and aggregation in solutions. The aggregation is mainly causes by the energy change due to dipole-dipole interaction.

The plots of viscosity, η Vs soap concentration, C (Fig.-1) and specific viscosity, η_{sp} Vs C are characterized by the intersection of two straight lines at definite soap concentration (caprylate 0.043 M and caprate 0.041 M) which correspond to the critical micelle concentration (CMC) for these soaps in solutions. The viscosity results confirm that there is no appreciable aggregation of the soap molecules below the CMC whereas there is a sudden change in the aggregation at this soap concentration.

The plots of η Vs C for dilute soap solutions were extrapolated to zero soap concentration and the extrapolated values η_0 of viscosity were found to be in agreement with the experimental value of the viscosity of the solvent mixture (0.4515 Pas) (Table-2).

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Table 1 : Density and viscosity of zirconyl soaps in benzene-methanol mixtur (4:1 v/v) at (40+0.05)°C

S.No.	Concentration c (mol dm^{-3})	Density, ρ (kg m^{-3})	$(\rho-\rho_o)/c$	Viscosity $\eta\times10^3$ (Pascal-sec)	Specific viscosity $\eta_{sp}\times10^2$	$\eta_{sp}/c^{1/2}$	$(\eta/\eta_o)^2$	$1/\log(\eta/\eta_o)$
CAPRYLATE								
1.	0.01	845.8	60.0	0.4563	1.06	0.106	1.021	217.74
2.	0.02	846.2	50.0	0.4615	2.21	0.157	1.045	105.11
3.	0.03	846.7	50.0	0.4658	3.17	0.183	1.064	73.85
4.	0.04	847.1	47.5	0.4705	4.21	0.210	1.086	55.86
5.	0.05	847.8	52.0	0.4768	5.60	0.255	1.115	42.23
6.	0.06	848.7	58.3	0.4836	7.11	0.290	1.147	33.52
7.	0.07	849.5	61.4	0.4906	8.66	0.327	1.181	27.12
8.	0.08	850.4	65.0	0.4978	10.25	0.362	1.220	23.59
9.	0.09	851.2	66.7	0.5050	11.18	0.395	1.252	20.56
10.	0.10	852.0	68.0	0.5125	13.51	0.428	1.291	18.17
CAPRATE								
1.	0.01	846.0	80.0	0.4570	1.22	0.122	1.025	190.17
2.	0.02	846.6	70.0	0.4626	2.46	0.174	1.050	94.81
3.	0.03	847.2	66.7	0.4682	3.70	0.214	1.075	63.40
4.	0.04	847.8	65.0	0.4741	5.01	0.250	1.103	47.14
5.	0.05	848.9	74.0	0.4814	6.62	0.301	1.137	35.91
6.	0.06	849.7	75.0	0.4897	8.46	0.345	1.176	28.35
7.	0.07	850.6	77.1	0.4970	10.08	0.380	1.212	23.98
8.	0.08	851.6	80.0	0.5052	11.89	0.420	1.252	20.49
9.	0.09	852.6	82.2	0.5125	13.51	0.450	1.288	18.17
10.	0.10	853.5	83.0	0.5206	15.30	0.484	1.330	16.17

Table 2 : CMC, experimental and extrapolated values of density, ρ_o and viscosity, η_o of zirconyl soaps in benzene-methanol (4:1 v/v) mixture at (40$\pm$0.05)°C

Soap	CMC x 10^2 (mol dm^{-3})		ρ_o (kg m^{-3})		η_o x 10^3 (Pascal-Sec)	
	ρ Vs c	η Vs c	Experimental	Extrapolated	Experimental	Extrapolated
Caprylate	4.4	4.3	845.2	845.3	0.4515	0.4518
Caprate	4.0	4.1	845.2	845.3	0.4515	0.4515

Table 3 : Molar volume, $\bar{V}$; Interaction coefficient, ∅; constants M and K (from Moulik's equation; A and B (from Jones-Dole's equation).

Zirconyl soap	$\bar{V}$ (l mol^{-1})		∅	Moulik's equation		Jones-Dole's equation	
	Einstein's equation	Vand's equation		M	K	A	B
Caprylate	0.40	0.42	-0.78	1.020	41.25	0.000	1.05
Caprate	0.51	0.52	-1.92	1.023	48.33	0.000	1.26

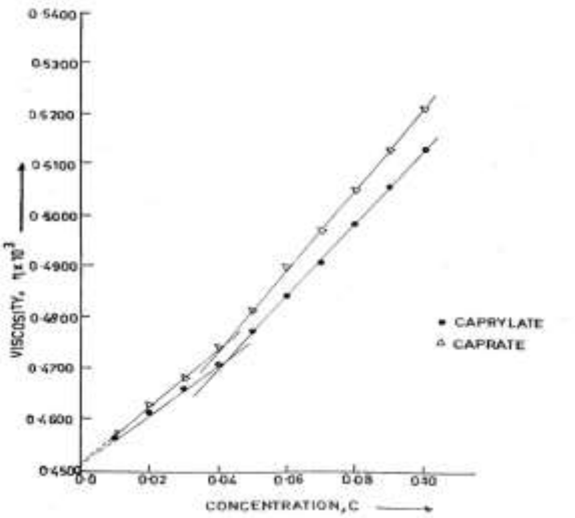

Fig. 1 : Viscosity Vs concentration of zirconyl soaps in benzene-methanol mixture (4:1 v/v) at (40±0.05)ºC

The viscosity results have been interpreted in terms of equations proposed by Einstein [11], Vand [12], Moulik [13] and Jones-Dole [14]:

$$\textbf{Einstein}: \quad \eta_{sp} = 2.5\ \bar{V} C$$

$$\textbf{Vand}: \frac{1}{C} = \left(\frac{0.921}{\bar{V}}\right)^{-1} \frac{1}{\log\left(\eta/\eta_0\right)} + \emptyset\,\bar{V}$$

$$\textbf{Moulik}: \left(\frac{\eta}{\eta_0}\right)^2 = M + KC^2$$

$$\textbf{Jones - Dole}: \left(\frac{\eta_{sp}}{\sqrt{C}}\right) = A + B\sqrt{C}$$

Where $\bar{V}$ (1 mol^{-1}, C (mol dm^{-3}), $\emptyset$, η (Pas), η_0 (Pas) and η_{sp} are the molar volume, concentration, interaction coefficient, viscosity of the solution, viscosity of solvent and specific viscosity respectively. M and K are the Moulik constants and constants A and B of the Jones-Dole equation refer to soap-soap and soap-solvent interactions respectively.

The plots of specific viscosity, η_{sp} against the soap concentration C are linear below the CMC with the intercept almost equal to zero which shows that Einstein's equation is applicable to dilute solutions of zirconyl soaps in the benzene-methanol mixture (4:1 v/v). The values of molar volume, $\bar{V}$ were calculated from the slop of Einstein's plots (η_{sp} Vs C) for dilute solutions and were found to be 0.40 mol^{-1} and 0.51 mol^{1-} for zirconyl caprylate and caprate respectively.

The plots (Vand 1/C Vs 1/log η/η_0; Moulik $(\eta/\eta_0)^2$ Vs C^2; Jones-Dole $\eta_{sp}/\sqrt{C}$ Vs $\sqrt{C}$) are also characterized by an intersection of two straight lines at concentrations which correspond to the CMC for these soaps in solutions.

The calculated values of molar volume, $\bar{V}$ from the slope of the Vand plots (1/C Vs 1/log η/η_0) for dilute solutions (caprylate 0.40 mol^{-1} and caprate 0.51 mol^{-1}) were found to be in close agreement with those obtained from the Einstein plots (Table-3).

The values of interaction coefficient ϕ calculated from the intercept of the Vand's plots were 0.78 and – 1.92 for caprylate and caprate respectively. The results show that the molar volume increases while interaction coefficient decreases with increasing chain length of soap molecules.

The values of the Moulik constant M (1.020 and 1.023 for caprylate and caprate, respectively) obtained from the intercepts of the plots of $(\eta/\eta_0)^2$ Vs C^2 are almost constant while those of K (41.25 and 48.33) evaluated from the slope of the Moulik Plots increase with increasing chain length of the soap. The values of the Jones-Dole constant A (0.00 and 0.00) and B (1.05 and 1.26) for caprylate and caprate respectively were calculated from the intercept and slope of the plots of $\eta_{sp}/\sqrt{C}$ for dilute solutions. The values of the constant B (soap-solvent interaction) are larger than those of A (soap-soap interaction), which confirms that the soap molecules do not aggregate below the CMC and there is a sudden change in aggregation at a definite concentration of these soaps.

The density and viscosity measurements of the solution of zirconyl soaps (caprylate and caprate) in a mixture of benzene-methanol (4:1 v/v) were used to determine the critical micelle concentration (CMC) of the soaps and the results were explained in terms of equations proposed by Einstein, Vand, Moulik's and Jones-Dole. The values of CMC and the molar volume of the zirconyl soap obtained by using these equations are in agreement. It is therefore concluded that the viscosity results for solutions of zirconyl soaps may be satisfactorily explained in terms of these equations.

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