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Viscometric Investigations on Zirconyl Soaps in Benzene-Chloroform Mixture

M. Anis
Department of Chemistry, School of Chemical Sciences, St. John's Colelge, Agra-282002, INDIA

ABSTRACT

The density and viscosity of the solutions of Zirconyl soaps (hexanoate, octanoate, decanoate and dodecanoate) in a benzene-chloroform (4:1 v/v) mixture were measured at a constant temperature 40±05ºC. The density and viscosity results were explained on the basis of equations proposed by Einstein, Vand, Moulik and Jones-Dole. The values of molar volume evaluates by using Einstein's and Vand's equations were found to be in close agreement. The result of Jones-Dole equation confirm that soap molecules do not aggregate appreciably in dilute solutions. The values of CMC for Zirconyl soaps from density and viscosity measurements were in agreement.

Keywords--Density, Viscosity, CMC, Benzene-Chloroform Mixture.

I. INTRODUCTION

The importance of metal soaps are well known owing to their recognized usefulness in various industries. However, the applications of metal soaps are based on our empirical knowledge and selection of the soap for a specific purpose is mainly governed by economic factors. Kapoor and Mehrotra [1] prepared tetracarboxylates of Zirconium by the reaction of Zirconiumn Chloride with fatty acids in refluxing benzene. R.C. Paul et al [2] prepared Zirconium (IV) carboxylates by the reaction of Zirconium (IV) Chloride and Carboxylic acids. V.D. Makhev et al [3] developed the solid phase synthesis of Zirconium Carboxylates under mechanical activation by the reactions of Zirconium tetrachloride with metal carboxylate such as isobutyrate and palmitate.

Hirosawa [4] and Miyoshi [5] reported Zirconium soaps as water proofing agents. Zirconium Carboxylates are useful as dryer catalysts in paints and coating and to increase the viscosity of oil and to form greases [6].

The present work deals with the density and viscosity measurements of the solution of zirconyl soaps (hexanoate, octanoate, decanoate and dodecanoate) in benzene-chloroform (4:1 v/v) mixture. The results have been used to study the soap-solvent interaction, to evaluate the CMC and various parameters.

II. EXPERIMENTAL

All the chemical used were of AR/BDH grade. Zorconyl soaps (hexanoate, octanoate, decanoate and dodecanoate) 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. (hexanoate, 137ºC; octanoate 146ºC; decanoate, 158ºC; and dodecanoate 167ºC), elemental analysis and ir spectra. The solutions of different concentrations of Zirconyl soaps were prepared in benzene-chloroform (4:1 v/v) mixture. The densities were determined with a dilatometer at 40±05ºC. An Ostwald Viscometer was used for measuring the viscosity at 40±05ºC.

III. RESULT AND DISCUSSION

The density ρ of the solution of zirconyl soaps (hexanoate, octanoate, decanoate and dodecanoate) in benzene-chloroform (4:1 v/v) mixture increases with increasing soap concentration as well as with the chain length of soap (Table 1.1-1.2) The plots of density, ρ Vs soap concentration, C are characterized by an intersection of two straight lines at a definite soap concentration (hexanoate, 0.050 M; octanoate, 0.047 M; decanoate, 0.043 M and dodecanoate, 0.039 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 chloroform (4:1 v/v) mixture decreases with increasing chainlength 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 (988.80 kgm^{-3}) (Table-2).

The viscosity η and specific viscosity η_{sp} of solutions of zirconyl soaps in the benzene-chloroform (4:1 v/v) mixture increases with increasing soap concentration and chain length of the soap (Table 1.1 & 1.2). 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.

Table 1.1 : Density and viscosity of zirconyl Hexanoate and Octanoate in benzene-chloroform (4:1 v/v) mixture at (40±0.05) °C

S.No.	Concentration c (mol dm^{-3})	Density, ρ (kg m^{-3})	$(\rho-\rho_o)/c$	Viscosity $\eta \times 10^3$ (Pascal sec)	Specific viscosity $\eta_{sp} \times 10^2$	$\eta_{sp}/c^{1/2}$	$(\eta/\eta_o)^2$	$1/\log(\eta/\eta_o)$
Hexanoate								
1.	0.01	989.1	30.0	0.6985	0.57	0.058	1.012	400.94
2.	0.02	989.4	30.0	0.7066	1.74	0.123	1.035	133.31
3.	0.03	984.6	26.7	0.7130	2.66	0.154	1.054	87.59
4.	0.04	989.8	25.0	0.7200	3.67	0.184	1.075	63.86
5.	0.05	990.0	24.0	0.7278	4.79	0.214	1.098	49.16
6.	0.06	991.1	38.3	0.7440	7.12	0.291	1.148	33.44
7.	0.07	992.3	50.0	0.7619	9.70	0.367	1.203	24.86
8.	0.08	993.3	56.3	0.7796	12.25	0.433	1.260	19.92
9.	0.09	994.5	63.3	0.7980	14.90	0.497	1.320	16.58
10.	0.10	995.5	67.0	0.8144	17.26	0.546	1.375	14.46
Octanoate								
1.	0.01	989.3	50.0	0.7022	1.10	0.111	1.022	208.83
2.	0.02	989.7	45.0	0.7129	2.64	0.187	1.054	88.06
3.	0.03	990.0	40.0	0.7230	4.10	0.237	1.084	57.25
4.	0.04	990.3	37.5	0.7330	5.54	0.277	1.114	42.68
5.	0.05	991.0	44.0	0.7450	7.27	0.325	1.151	32.80
6.	0.06	992.6	63.3	0.7660	10.29	0.420	1.217	23.49
7.	0.07	994.0	74.3	0.7882	13.49	0.510	1.288	18.19
8.	0.08	995.4	82.5	0.8100	16.63	0.588	1.360	14.97
9.	0.09	997.0	91.1	0.8320	19.79	0.660	1.435	12.75
10.	0.10	998.5	97.0	0.8542	22.99	0.728	1.513	11.13

Table 1.2 : Density and viscosity of zirconyl Decanoate and Dodecanoate in benzene-chloroform (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 $\eta \times 10^3$ (Pascal sec)	Specific viscosity $\eta_{sp} \times 10^2$	$\eta_{sp}/c^{1/2}$	$(\eta/\eta_o)^2$	$1/\log(\eta/\eta_o)$
Decanoate								
1.	0.01	989.5	70.0	0.7062	11.68	0.169	1.034	137.83
2.	0.02	990.0	60.0	0.7180	3.38	0.239	1.069	69.19
3.	0.03	990.5	56.7	0.7310	5.26	0.303	1.108	44.95
4.	0.04	990.9	52.5	0.7435	7.05	0.353	1.146	33.77
5.	0.05	992.3	68.0	0.7677	10.54	0.471	1.222	22.98
6.	0.06	994.0	86.7	0.7897	13.71	0.560	1.293	17.92
7.	0.07	996.0	102.9	0.8164	17.55	0.663	1.382	14.24
8.	0.08	997.7	111.3	0.8421	21.25	0.752	1.470	11.95
9.	0.09	999.6	120.0	0.8662	24.72	0.824	1.556	10.42
10.	0.10	1001.5	127.0	0.8890	28.01	0.886	1.639	9.33
Dodecanoate								
1.	0.01	989.7	90.0	0.7110	2.37	0.238	1.048	98.06
2.	0.02	990.4	80.0	0.7280	4.82	0.341	1.099	48.88
3.	0.03	991.0	73.3	0.7456	7.35	0.425	1.153	32.43
4.	0.04	991.6	70.0	0.7640	10.00	0.500	1.210	24.14
5.	0.05	993.8	100.0	0.7932	14.21	0.636	1.304	17.33
6.	0.06	995.8	116.7	0.8216	18.30	0.747	1.399	13.70
7.	0.07	998.2	134.3	0.8450	21.67	0.819	1.480	11.74
8.	0.08	1000.4	145.0	0.8746	25.93	0.917	1.586	9.99
9.	0.09	1002.5	152.2	0.9012	29.76	0.992	1.684	8.84
10.	0.10	1004.9	161.0	0.9264	33.39	1.057	1.779	7.99

Table 2 : CMC, experimental and extrapolated values of density, ρ_o and viscosity, η_o of ziroconyl soaps in benzene-chloroform (4:1 v/v) mixture at (40±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
Hexanoate	5.0	5.1	988.80	988.90	0.6945	0.6920
Octanoate	4.7	4.8	988.80	989.00	0.6945	0.6930
Decanoate	4.3	4.2	988.80	989.05	0.6945	0.6940
Dodecanoate	3.9	3.9	988.80	989.05	0.6945	0.6960

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

Soap	$\bar{V}$ (1 mol^{-1})		Ø	Moulik's equation		Jones-Dole's equation	
	Einstein's equation	Vand's equation		M	K	A	B
Hexanoate	0.41	0.35	11.42	1.01	45	-0.080	1.40
Octanoate	0.59	0.52	5.76	1.02	70	-0.065	1.70
Decanoate	0.78	0.71	1.41	1.03	90	-0.035	1.95
Dodecanoate	1.00	0.92	0.54	1.04	130	-0.020	2.55

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 (hexanoate, 0.051 M; octanoate, 0.048 M; decanoate, 0.042 M and dedecanoate 0.039 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 (0.6945 Pas) (Table-2).

The viscosity results have been interpreted in terms of equations proposed by Einstein [7], V and [8], Moulik [9] and Jones-Dole [10]:

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

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

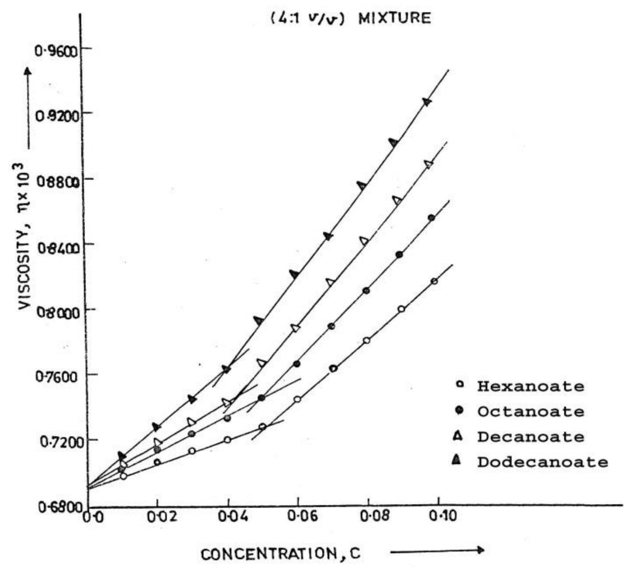
$$Moulik: \left(\frac{\eta}{\eta_0}\right)^2 = M + KC^2$$

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

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

FIG. 1 VISCOSITY Vs CONCENTRATION
SOLVENT: BENZENE-CHLOROFORM
(4:1 v/v) MIXTURE



equation is applicable to dilute solutions of zirconyl soaps in the benzene-chloroform (4:1 v/v) mixture. 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 0.41 mol^{-1}, 0.59 mol^{1-}, 0.78 mol^{-1} and 1.00 mol^{-1} for zirconylhexanoate, octanoate, decanoate and dodecanoate respectively. The differences in the values of molar volume for these soaps (hexanoate and octanoate, 0.18 mol^{-1}; octanoate and decanoate, 0.19 mol^{-1}; decanoate and dodecanoate, 0.22 mol^{-1}) suggest that each – CH_2 group makes a definite contribution to the molar volume of soaps and the contribution of each – CH_2 group to molar volume is about 0.09 – 0.11 mol^{-1} [11].

The plots (Vand 1/C Vs 1/log η/η_0; Moulik $\left(\eta/\eta_0\right)^2$ 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 (hexanoate 0.35 mol^{-1}, octanoate 0.52 mol^{-1}, decanoate 0.71 mol^{-1} and dodecanoate 0.92 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 11.42, 5.76, 1.41 and 0.54 for hexanoate, octanoate, decnoate and dodecanoate respectively. The values of the Moulik constant M (1.01, 1.02, 1.03 and 1.04 for hexanoate, octanoate, decanoate and dodecanoate respectively) obtained from the intercepts of the plots of $\left(\eta/\eta_0\right)^2$ Vs C^2 are almost constant while those of K (45, 70, 90 and 130) evaluated from the slope of the Moulik Plots increase with increasing chain length of the soap. The values of the Jones-Dole constant A (- 0.08, - 0.06, - 0.04 and – 0.02) and B (1.40, 1.70, 1.95 and 2.55) for hexanoate, octanoate, decanoate and dodecanoate 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 data obtained from the viscosity measurement for dilute soap-solutions of zirconyl soaps show that it can be satisfactorily explained in terms of equations proposed by Einstein, Vand, Moilik and Jones-Dole and the values of molar volume and CMC obtained by using these equations are in close agreement.

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