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Density and Viscometric Studies on Magnesium Soaps in Non-Aqueous Medium

Chitra Singh[1*] and S. K. Upadhyaya[2]

[1] *Regional Institute of Education, Bhopal, INDIA*
[2] *S. S. L. Jain P. G. College, Vidisha (M.P.), INDIA*

[*] *Correspondence: E-mail: chitrasingh75@gmail.com*

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ABSTRACT: The density and viscosity measurements of magnesium laurate in the mixture of chloroform - propylene glycol at various temperatures have been carried out in order to determine critical micellar concentration, soap-solvent interactions and to study the nature of the micelles. The density and viscosity results were interpreted in terms of the equation proposed by Root, Einstein, Vands, Moulik and Jones-Dole. These results indicate the CMC values increase with increasing temperature and there is a significant interaction between soap and solvent molecules.

Keywords: CMC; Molar volume; Specific viscosity; Interaction coefficient; Electro -kinetic forces and soap -solvent Interaction.

INTRODUCTION: Carboxylates of metals other than alkali metals are generally insoluble in water and termed as metallic soaps. Metallic soaps are simple carboxylates of alkaline-earth and other polyvalent metals with the general formula $(MO_2CR)_n$ Where M is a metal in oxidation state n and R is an organic radical containing at least six carbon atoms. The density measurement was used to determine the critical micelle concentrations of copper[1] and cobalt[2] soaps of lower fatty acids in non-aqueous media. Mehrotra, *et al.*[3] determine viscosity of the solutions of barium soaps in water and propanol mixtures and showed the presence of two kinds of micelles. Kumar, *et al.*[4] reported results of density and apparent molar volume of alkaline-earth metal soaps in non aqueous medium. Many workers[5-7] used alkaline-earth metal soaps in preparation of paints, varnishes, pigments, lacquers, enamels and inks. Jerzy, *et al.*[8] observed that magnesium soaps can be used as anticorrosion agents in protection of metal during storage. Present paper deals with the results of density and viscosity measurements of magnesium laurate in 60/40 chloroform-propylene glycol mixtures v/v at different temperatures.

MATERIALS AND METHODS: AnalaR grade chemical were used after purification for the present investigation. Magnesium laurate was prepared by metathesis method. The aqueous solution containing stoichiometric amount of magnesium sulphate and potassium laurate were mixed at nearly 80ºC under constant stirring. As evolution of Co_2 ceased and metastatic displacement reaction completed, the desired compound was separated from mother liquor by vacuum filtration. The product was washed several times with distilled water and acetone and oven dried. Viscosity and density of these soap solutions have been measured in a thermostat having thermal stability of $\pm 0.05\,^0C$ using an Ostwald type viscometer and 10 ml bicapillary pyknometer. The viscosities of the soap solutions have been calculated by using the relationship.

$$\frac{\eta_0}{\eta_1} = \frac{\rho_0 t_0}{\rho_1 t_1}$$

Where η_0 $\eta_1 \rho_0 \rho_1$ and t_0 t_1 are the viscosity density and the time flown for solvent and soap solutions, respectively. The measured viscosity and density have an uncertainty of 0.003 cp and 00005g/ml, respectively.

RESULTS AND DISCUSSION: The density, ρ of the solutions of magnesium soaps in 60/40 chloroform-propylene glycol (V/V) mixture increases at first linearly and them rapidly with the increase in soap concentration. The plots of density against the soap concentration (Figure 1) are characterized by an intersection of two straight lines at a point which corresponds to the critical micellar concentration, CMC (Table 1). The plots of density V_s soap concentration have extrapolated to zero soap concentration. The extrapolated values of the density are in agreement with the density of the solvent determined experimentally. The density results have been explained in terms of Root equation:

$$\rho = \rho_0 + AC + BC^{3/2} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (1)$$

Where, C is the concentration of soap (g. mole1^{-1}), ρ and ρ_0 are the densities of soap solution and solvent, respectively. The constants A and B refer to the soap - solvent and soap-soap interactions. The plots of $(\rho - \rho_0)$ /C Vs $C^{1/2}$ shows a linear decrease in the values of $(\rho - \rho_0)$/C upto the CMC and exhibit an increase above the CMC. The values of the CMC are in agreement with the values of CMC determined from other physical technique. (Table 1)

Table 1: Values of CMC and Constants A and B (Root's equation) for Magnesium Laurate in 60/40 chloroform-propylene glycol mixture.

S. No.	Temperature	CMC (g. mol. l^{-1})	Constant A	Constant B
1.	30°C	11.9	2.25	16.43
2.	35°C	12.2	2.00	15.20
3.	40°C	12.4	1.76	13.80
4.	45°C	13.6	1.73	11.75

The values of Constants A and B have been obtained from the intercept and slope of the plots of $\rho - \rho_0 / C$ Vs $C^{1/2}$. The values of the constant A are higher than constant B which shows that the soap-solvent interactions are larger than the soap-soap interactions in dilute solutions of magnesium soap. The values of constant A increase with increasing chain - length of the soap molecules. It is therefore, concluded that the molecules of magnesium soaps do not show an appreciable aggregation below the CMC and there is a marked increase in aggregation of the soap molecule at this concentration.

The viscosity of magnesium laurate has been measured in 60/40 chloroform-propylene glycol mixture (V/V) with the help of Ostwald type viscometer at different temperatures. The viscosity, η of the solution of magnesium laurate in the mixture of chloroform and propylene glycol increase with increasing concentration, which may be due to the increasing tendency of the soap molecules to from aggregate with the increase in soap concentration and chain-length of the soap. The plots of viscosity, η against the soap concentration, C, are characterized by an intersection of two straight lines, which corresponds to the critical micellar concentration (CMC). It may be pointed out that the viscosity of the solutions of magnesium laurate increases with the increase in chain - length of the anion or hydrophobic part of the magnesium soap molecules. The values of CMC are also affected by the chain length of the soap molecules. The values of CMC of magnesium soaps are in good agreement with the values obtained from other micellar properties.

The specific viscosity of η_{sp} of the soap solutions increases with the increase in soap concentration. The plot also shows a break at the critical micellar concentration for magnesium laurate.

The molar volume has been determined by using Einstein equation:

$$\eta_{sp} = 2.5\bar{V}C \text{———————} (2)$$

Where η_{sp}, $\bar{V}$ and C and respectively, specific. viscosity, molar volume of soap and concentration in gm/ liter. The plots of specific viscosity, η_{sp}, against soap concentration, C are linear below the CMC with intercept equal to zero which shows that Einstein's equation is applicable to the solutions of magnesium laurate and there is no appreciable aggregation of the soap molecules below this concentration.

The values of molar volume, $\bar{V}$ obtained from the plots of η_{sp} Vs C (Einstein's equation) are summarized in Table -2 .The values of molar volume and interaction coefficient ϕ have also been determined by using Vand's equation.[10]

$$1/C = (0.921\bar{V})^{-1} \times 1/\log \eta/\eta_0) + \phi\bar{V} \text{———————} (3)$$

Where, C , $\bar{V}$, η, η_0 and ϕ are respectively, concentration of magnesium soap, molar volume, viscosity of soap solutions viscosity of solvent mixture and interaction coefficient. The values of molar volume calculated using Einstein's equation are somewhat larger than the values determined from Vand's equation. The molar volume $\bar{V}$ decreases with increasing temperatures (Table 2). The plots of η_{sp}/C against C have been extrapolated to zero soap concentration and the extrapolated value is intrinsic viscosity. The values of the interaction coefficient, ϕ, calculated from the intercept of the plots of I/C Vs 1/log (η/η_0) are summarized in Table 3. The plots of I/C Vs 1/log (η/η_0) are also characterized by an intersection of two straight lines at a concentration which corresponds to the CMC of the magnesium laurate. The results of viscosity have also been analyzed in the light of Moulik's equation.[11]

$$\left(\frac{\eta}{\eta_0}\right)^2 = M+K'C^2 \text{ --------------------------(4)}$$

Where, M and K^1 are Moulik's constants.

The values of the Moulik's constants M and K (Table 2) have been obtained from the plots of $\left(\frac{\eta}{\eta_0}\right)^2$ Vs C^2 are linear below the CMC which shows that Moulik's equation is applicable to the dilute solutions of magnesium laurate in 60/40 chloroform and propylene glycol mixture at different temperatures. The values of Moulik's constants decrease with increasing temperature.

Table 2: Values of Molar Volume ($\bar{V}$) and Moulik's Constants constants (M&K') Determined from Einstein and Moulik's Equations in 60/40 Chloroform-Propylene glycol mixture.

S. No.	Temperature	Molar Volume ($\bar{V}$)		Moulik's Constant	
		Einstein Equation	Vand's Equation	M	$K' \times 10^{-3}$
1.	30°C	16.8	9.0	1.15	0.50
2.	35°C	15.5	8.8	1.14	0.48
3.	40°C	15.0	8.6	1.15	0.43
4.	45°C	13.3	8.8	1.14	0.41

Table 3: The Values of Constant – A and B Interaction coefficient – (∅) Determined from Jone's–Dole and Vand's Equations in 60/40 Chloroform-Propylene glycol mixture.

Temperature	Constant – A	Constant – B	Interaction coefficient, ∅
30°C	0.68	13.4	-49.8
35°C	0.60	11.5	-45.7
40°C	0.58	10.6	-45.7
45°C	0.57	10.4	-45.5

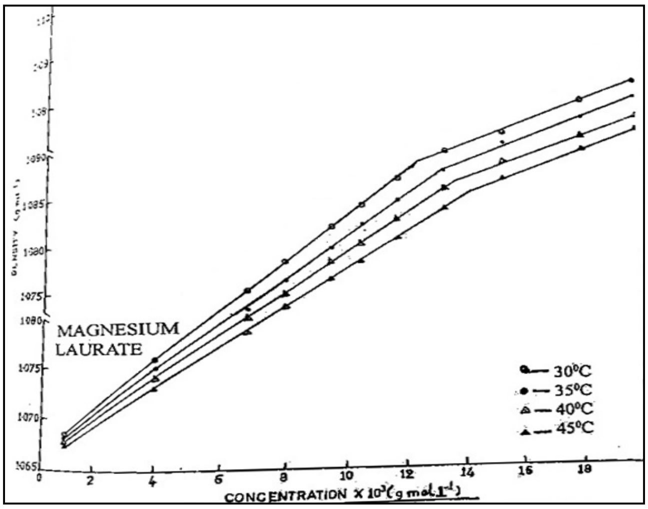

Figure 1: Density Vs Concentration of Magnesium Laurate in 60/40 Chloroform-Propylene Glycol (V/V) at different temperature.

The relative viscosities have been analyzed in terms of Jones-Dole equation.[12]

$$\left(\frac{\eta}{\eta_0^{-1}}\right)\sqrt{C} = A + B\sqrt{C}$$

$$\frac{\eta_{sp}}{C^{1/2}} = A + BC^{1/2} \ldots\ldots\ldots\ldots\ldots\ldots..(5)$$

The values of the constant A and B have been calculated from the plots of η_{sp}/C Vs $C^{1/2}$ the positive values of constant A indicates that strong ion-ion interactions whereas positive values of constant B indicate that these interactions are strong. The values of constant A decrease with increasing temperature due to more violent thermal agitation at higher temperatures, Table 3. Thereby resulting in the weakening of the force of attraction. The values of constant B differ widely below and above the CMC boosts up the electrokinetic force causing more intake of the solvent resulting in an increasing viscosity of the system. The positive values of constant A and B increase with the increase in chain-length of the soaps. These results are in agreement with the results of the solutions of copper soaps[13] and surfactants[14] in non-aqueous medium. It is therefore concluded that the equations proposed by Einstein, Vand, Moulik and Jones - Dole are applicable to the non-aqueous solutions of magnesium laurate. The viscosity results show that there is a marked change in the aggregation of the soap molecules at the CMC and the values of CMC of magnesium laurate increase with increasing temperature. These results also indicate that there is a significant interaction between the molecules of soaps and non-aqueous solvent mixture.

CONCLUSION: It is concluded that the equations of Roots, Einstein, Vand, Moulik and Jones-Dole have a similar probability of fitting the experimental data of magnesium laurate in a mixture of 60/40 Chloroform-Propylene glycol mixture. The density and viscosity measurements of magnesium laurate solutions indicate that there is a marked change in the aggregation of the anionic species at the critical micellar concentration, the value of CMC increases with increasing temperature and results are in good agreement with other data [15-17]. The values of various constants calculated from above cited well known equations indicate that there is a significant interaction between magnesium laurate and solvent molecules.

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