Conductometric and Viscometric Studies on Magnesium Caprylate and Laurate

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ABSTRACT: The conductance of the solutions of magnesium caprylate and laurate in chloroform-propylene glycol mixture has been measured at four different temperatures in order to determine CMC, molar conductance, dissociation constant and thermodynamic parameters viz. enthalpy, free energy and entropy change for both dissociation and micellization processes. The results of conductivity measurements indicate that these soaps behave as weak electrolytes and the micellization process in favoured over the dissociation process. The results also confirm that the CMC remain almost unaffected by the rise in temperature. The experimentally determined density and viscosity data have been analyzed in the light of Einstein, Vands, Mouliks and Jones-Dole equations. These equations confirm that there is a significant interaction between magnesium soaps and solvent molecules.

Keywords: Critical Micellar Concentration (CMC); dissociation constant; molar conductance; specific viscosity and interaction coefficient.

INTRODUCTION: A survey of literature reveals that the physico-chemical studies and micellar behavior of alkaline-earth metal soaps have not yet been studied systematically although these soaps are being widely used in various industries.[1-11] The technological applications of these soaps in industries are based on empirical know-how and the selection of soaps is dependent mainly on economic factors. The physico-chemical characteristics and the structure of metallic soaps depend on the method and conditions of their preparation. The present manuscript deals with the studies on the conductivity and viscosity of magnesium caprylate and laurate in a mixture of 60/40 chloroform-propylene glycol (V/V) at 30°, 35°, 40° and 45°C.

MATERIAL AND METHODS: AnalaR grade caprylic acid, lauric acid, acetone, chloroform and propylene glycol were used for the present investigation. Magnesium soaps were prepared by mixing of the aqueous solution of magnesium sulphate with a slightly excess of hot aqueous solution of potassium soap (potassium caprylate and potassium laurate) with constant stirring at 50-60°C. The white precipitate thus obtained was filtered off and washed with hot distilled water and acetone. After an initial drying in air oven final drying was carried out under reduced pressure. The purity of the soaps was checked by car-

bon and hydrogen analysis and these results were found in good agreement with the theoretically calculated values. The absence of hydroxyl group was confirmed by studying IR spectra of magnesium caprylate and laurate. The purified soaps have the following melting points:

Magnesium caprylate: 147°C
Magnesium laurate: 156°C

The conductance of the solution of magnesium caprylate and laurate in non-aqueous medium was measured with Systronic conductivity Bridge 305 (SR No. 993), and a dipping type conductivity cell with platinized electrodes (cell constant 1.0). All measurements were carried out at 30 to 45°C ($\pm$0.05°C). The viscosity and density of magnesium caprylate and laurate solutions have been measured with the help of Ostwald type viscometer and pyknometer.

RESULTS AND DISCUSSION:

Conductometric Studies: The specific conductance, k, of the solutions of magnesium caprylate and laurate, in 60/40 chloroform-propylene glycol (V/V) mixture increases with increasing concentration as well as temperature. The increase in specific conductance in non-aqueous medium may be due to the fact that these soaps behave as simple electrolyte in dilute

solutions and are ionized into magnesium cations, Mg^{2+} and fatty acid anions $RCOO^-$.

However, the increase in the values of specific conductance at higher soap concentration is probably due to the formation of ionic micelles in non-aqueous medium. The plots of specific conductance vs. soap concentration are characterized by an intersection of two straight lines at the critical micellar concentration (CMC), where the anions begin to associate to form micelles of ionic nature. The increase in temperature and decrease in chain-length of magnesium soap molecules result in the increase of CMC; however, the CMC values were found to be almost independent of the dielectric constant of the solvent mixture. The increase in temperature results in the increase of CMC (Table-1) because the process of micellization is assumed to occur when the energy released as a result of aggregation of hydrocarbon chains of the monomer is sufficient to overcome the electrical repulsion between the ionic head group and to balance the decrease in entropy accompanying aggregation. Therefore, increase in temperature of magnesium soap solution would have been expected to increase the CMC values since the kinetic energy of the monomers has been raised. The increase in specific conductance with soap concentration above the CMC may be due to the

formation of increasing amounts of ionic micelles of high conducting power from the simple ions as reported in the case of rubidium, cesium and potassium soaps.[11 & 12] The values of CMC of magnesium soaps (Table-1) determined by conductivity measurements in 60/40 chloroform- propylene glycol mixture (V/V) are in fair agreement with those obtained from density and viscosity measurements for similar soaps. Unlike the specific conductance, the molar conductance, of the dilute solutions of magnesium soaps in a mixture of 60/40 chloroform- propylene glycol (V/V) increases with dilution. The decrease in molar conductance with increasing concentration may be due to the combined effects of ionic atmosphere, solvation of ions and decrease of mobility and ionization with the formation of ionic micelles. The critical micellar concentration, CMC, cannot be obtained from the plots of molar conductance vs. square root of soap concentration which are concave upward with increasing slope indicating that the Debye-Huckel-Onsager equation is not applicable to these soaps in the mixture of 60/40 chloroform -propylene glycol (V/V). The molar conductance of the dilute soap solutions increases rapidly with dilution, which shows that these soaps behave as weak electrolytes.

Table 1: Values of critical miseller concentration CMC of Magnesium Caprylate and Laurate.

S. No.	Name of the Soap	CMC $\times 10^3$ (g mol l^{-1})			
		30° C	35° C	40° C	45° C
1	Magnesium Caprylate	12.0	12.4	12.8	13.0
2	Magnesium Laurate	11.9	12.2	12.4	13.6

Table 2: Thermodynamic Parameters for Dissociation and Micellization processes of Magnesium caprylate and laurate at Different Temperatures in 60/40 Chloroform-Propylene Glycol Mixture (V/V).

Name	Dissociation Process								Micellization Process							
	ΔG^o_D KJ mol^{-1}				$\Delta S^o_D \times 10^2$ KJ mol^{-1}				ΔG^o_M KJ mol^{-1}				$\Delta S^o_M \times 10^2$ KJ mol^{-1}			
	30°C	35°C	40°C	45°C	30°C	35°C	40°C	45°C	30°C	35°C	40°C	45°C	30°C	35°C	40°C	45°C
Magnesium Caprylate	16.47	16.70	16.90	17.20	-6.42	-6.39	-6.33	-6.30	-16.25	-16.39	-16.57	-16.76	9.62	8.90	8.80	9.92
Magnesium Laurate	16.80	16.92	17.07	17.22	-11.00	-10.86	-10.71	-10.51	-16.41	-16.52	-16.52	-16.85	9.42	9.31	9.11	9.07

The enthalpy of dissociation, ΔH^o_D for magnesium caprylate and laurate in 60/40 chloroform–propylene glycol mixture are obtained from the slope of linear plots of K_D vs. 1/T. The negative values of enthalpy (magnesium caprylate -3.68 and magnesium laurate -2.67 KJ mole^{-1}) of dissociation suggest that dissociation of magnesium soaps is exothermic in nature. The standard free energy ($\Delta G^o_D = -RT \ln K_D$) and standard entropy change ($T\Delta S^o_D = \Delta H^o_D - \Delta G^o_D$) are also calculated for the dissociation process and their values are recorded in Table-2.

The standard enthalpy change of micellization per mole of monomer, ΔH^o_M is calculated as[13,14,15]

$$ln X_{CMC} = \frac{H^o_M}{2RT} + C$$

The values of ΔH^o_M are determined from the slope of the linear plots of ln X_{CMC} vs 1/T. The values of standard enthalpy change of micellization of magnesium caprylate and laurate was found to be 14.30 and 16.78 KJ mole^{-1}. The positive enthalpy ($\Delta H^o_M > 0$) shows that the micellization is endothermic. The standard entropy change per mole of monomer, $T\Delta S^o_M$ is calculated as $T\Delta S^o_M = \Delta H^o_M - \Delta G^o_M$.

The free energy of micellization (Table-2) per mole of monomer ΔG^{o}_{M} is evaluated as

$$\Delta G^{o}_{M} = 2\ RT \ln X_{CMC}$$

Where; X_{cmc} is the CMC expressed in mole fraction.

The negative enthalpy change of dissociation may compensate for the unfavorable change in free energy and entropy of the dissociation process. The unfavourable entropy change (i.e. $T\Delta S^{o}_{D} < 0$) may rise due to soap solvent interactions, i.e. solvation of the magnesium soap molecules. The negative free energy and positive entropy (Table-2) support micellization and can make up for the unfavourable enthalpy change ($\Delta H^{o}_{M} > 0$) for the micellization process. The positive values of entropy of micellization increase with temperature which indicates that at higher temperature the increased thermal agitation may break up the micelle to cause some randomness in the solutions at higher soap concentrations. It is, therefore, concluded, that magnesium caprylate and laurate behave as weak electrolytes in 60/40 chloroform-propylene glycol mixture in pre micellization region. The thermodynamics results also prove that micellization is a more favourable process for magnesium soap solutions. These results are in agreement with the results of other workers.[16-18]

Viscometric Studies: The viscosity, η of the solutions of magnesium caprylate and laurate in 60/40 chloroform -propylene glycol mixture increases with increasing concentration which may be due to the increasing tendency of the soap molecules to form aggregate with the increase in soap concentration and chain-length of the magnesium soap molecule. 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 soaps 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 and exhibits a break at the critical micellar concentration for magnesium soap. The viscosity results have been explained in the light of Einstein, Vand, Moulik and Jones-Dole equations.

Table 3: Values of Molar Volume ($\overline{V}$) and Moulik's Constants (M&K$^{/}$) Determined form Einstein and Moulik's Equations in 60/40 Chloroform-Propylene Glycol Mixture (V/V) at Different Temperatures.

Name	Molar Volume, $\overline{V}$								Moulik's Constants							
	Einstein's Equation				Vand's Equation				M				K^1 x 10^{-3}			
	30°C	35°C	40°C	45°C	30°C	35°C	40°C	45°C	30°C	35°C	40°C	45°C	30°C	35°C	40°C	45°C
Magnesium Caprylate	16.0	15.0	14.5	12.0	7.5	7.3	7.1	7.0	1.14	1.14	1.14	1.15	0.50	0.47	0.41	0.40
Magnesium Laurate	16.8	15.5	15.0	13.3	9.0	8.8	8.6	8.8	1.15	1.14	1.15	1.14	0.50	0.48	0.43	0.41

Table 4: Values of Constants A and B and Interaction Coefficient (Ø) determined form Jones-Dole and Vand's Equations in 60/40 Chloroform-Propylene Glycol Mixture (V/V) at Different Temperatures.

Name	Constant - A				Constant - B				Interaction Coefficient			
	30°C	35°C	40°C	45°C	30°C	35°C	40°C	45°C	30°C	35°C	40°C	45°C
Magnesium Caprylate	0.65	0.60	0.58	0.56	11.5	10.0	8.6	8.7	71.8	-71.6	-71.5	-71.4
Magnesium Laurate	0.68	0.60	0.58	0.57	13.4	11.5	10.6	10.4	-49.8	-45.7	-45.7	-45.5

The molar volume has been determined by Einstein's equation.[19]

$$\eta_{sp} = 2.5\ \overline{V}C$$

Where; η_{sp}, $\overline{V}$ and C are respectively, specific viscosity, molar volume of soap and concentration in gm moles/ litre. 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 soap in non-aqueous medium and there is

no aggregation of the soap molecules below this concentration. The values of molar volume, $\overline{V}$ obtained from the plots of η_{sp} vs. C (Einstein's equation) are summarized in Table-3. The values of molar volume and interaction coefficient, $\emptyset$ have also been determined by using Vand's Equation.[20]

$$1/C = (0.921/\overline{V})^{-1} \times 1/\log (\eta/\eta_o) + \emptyset\overline{V}$$

Where; C, $\overline{V}$, η, η_o and $\emptyset$ are respectively, concentration of soap, molar volume, viscosity of soap solution, viscosity of solvent mixture and interaction coeffi-

cient. The values of molar volume calculated from Einstein's equation are somewhat larger than the values determined from Vand's Equation. The molar volume $\bar{V}$ decreases with increasing temperature. The values of the interaction coefficient $\emptyset$, calculated from the intercept of the plots of $1/C$ vs. $1/\log (\eta/\eta_o)$ are also summarized in Table-4. The results of viscosity have also been analysed in the light of Moulik Equation.[21]

$$(\eta/\eta_o)^2 = M + K'C^2$$

Where; M and K' are Moulik constants. The value of the Moulik constants M and K' have been obtained from the plots of $(\eta/\eta_o)^2$ vs C^2 are linear below the CMC which shows that Moulik's Equation is applicable to the dilute solutions of magnesium soaps in a mixture of 60/40 chloroform -propylene glycol (V/V) at different temperatures. The values of Moulik's constants decrease with increasing temperature. The values of constants A & B for magnesium caprylate and laurate (Table-4) have been calculated from the plots of $(\frac{\eta}{\eta_o} - 1)/\sqrt{C}$ Vs $\sqrt{C}$ (Jones-Dole equation).[22] It is observed that the values of constant A and B decrease with the rise in temperature due to more violent thermal agitation at higher temperatures, thereby resulting in the weakening of the force of attraction .The values of constant A increase with increasing chain length of magnesium soap molecules. A perusal of Table-4 indicates that the B coefficients for all the magnesium soaps are positive indicating the existence of strong ion-solvent interactions. The magnitude of constant B, decrease with the rise in temperature indicating that ion-solvent interactions decrease with increasing temperature.[23-25] The values of constant B (Table-4) differ widely below and above the CMC which may be attributed to the fact that the aggregation of the soap molecule in the post micellization region boosts up the electrokinetic-forces causing more intake of the solvent resulting in increasing viscosity of the system.

CONCLUSION: Magnesium caprylate and laurate behave as weak electrolytes in 60/40 chloroform-propylene glycol mixture. The thermodynamics results also prove that micellization is a more favourable over dissociation process. The values of various constants obtained from Einstein, Vand, Moulik and Jones-Dole equations indicate that there is significant interaction between soap and solvent molecules in soap solutions.

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