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RESEARCH ARTICLE

THERMODYNAMIC AND PHYSICO CHEMICAL INVESTIGATION OF RUBIDIUM SOAPS IN ALKANOLS

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ABSTRACT

Imperative to evolve thermodynamic characteristic of Rubidium carboxylate (caprylate, caprate and laurate) apparent molar volume insight from density studies have been measured in alkanols. Limiting apparent molar volume and experimental slopes S_v tooaredetermined from Masson equation $\varphi_v = \varphi_v^0 + S_v$. φ_v^0 has been interpreted in terms of solute-solvent interaction. Ion-solvent interaction and solvent- solvent interaction are quite stronger in alkanols an insight in the structure making or breaking capacity of individual ions.

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INTRODUCTION

Amphiphilic carboxylates of alkali, alkaline earth and transitional metals are of special molecular structure effective for readily association of surfactant molecules naturally find enormous applications in industry and medicinal area. In this venture metal alkanoates of dicarboxylic acids were synthesized and investigated to reveal their ability for the stability of PVC (Burrows *et al*., 2010; Liu *et al*., 2007; Barbara and Lacz, 2007; Shukla *et al*., 2010). The molecular inter –action of metal alkanoates (Mehrotra and Anis, 1997) in non- aqueous solvent has crucial role for their application as stabilizer, fungicide, pesticide, foaming, wetting, lubricating, grease, catalyst and emulsifier. The metal carboxylates are characterized (Mehrotra *et al*., 1996; Sharma *et al*., 2006; Sandeep *et al*., 2003) by physico-chemical studies which give insight to their structure valuable for biological processes. In this paper, we have tried to get information about physical characters specially interaction between anionic head group and metal ion, solute-solvent inter-action, solvent- solvent inter action, apparent molar volume of rubidium soaps in alkanols may be relevant for material sciences.

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MATERIALS AND METHODS

The materials used for synthesis were of BDH/AR grade, soaps were purified, dried and characterized by IR spectra, elemental analysis as in previous article (Mehrotra and Saroha, 1979)

RESULTS AND DISCUSSION

Critical micelle concentration CMC of rubidium soaps in alkanols is obtained from the calculated values of apparent

molar volume using equation…….. (1)

$Øv = M/d_0 -1000(d-do)/d_0\ c$ ………. (1)

Where Øv is apparent molar volume (solute–solvent interaction), M is the molecular mass of soap, d and d_0 are the density of solvent and solution respectively and C is the molar concentration. The interaction of solute and solvent mostly in amphiphilic soaps brings a change in the volume of solution, this along with the volume of solute is known as apparent molar volume. The apparent molar volume is a linear function of the square root of molar concentration Fig.1(A,B,C). Plot of apparent molar volume and the square root of molar concentration are linear, show a break at definite soap concentration critical micelle concentration CMC Table 1A.

Table 1A. Critical micelle concentration from graph of Øv vs √C g mol L^{-1}

Soap	Critical micelle concentration		
	Methanol	Butanol	Pentanol
Caprylate	0.044	0.045	0.045
Caprate	0.045	0.046	0.045
Laurate	0.044	0.045	0.044

Table 1B. Parameters from $Ø_V$ vs √C graphs

Parameters	Rubidium soaps								
	Caprylate			Caprate			Laurate		
	Methanol	Butanol	Pentanol	Methanol	Butanol	Pentanol	Methanol	Butanol	Pentanol
φ^{v}_{01} cm^3 mol^{-1}	340.1	203.2	251.0	154	111	160	168.3	36.1	48.3
φ^{v}_{02} cm^3 mol^{-1}	71.0	12	199.7	59.8	104.5	159.8	59.8	1.1	7.9
$S_v cm^3$ $mol^{-3/2}$	-1.1	-0.84	-0.67	-0.34	-0.39	-0.31	-0.42	-0.071	-0.069

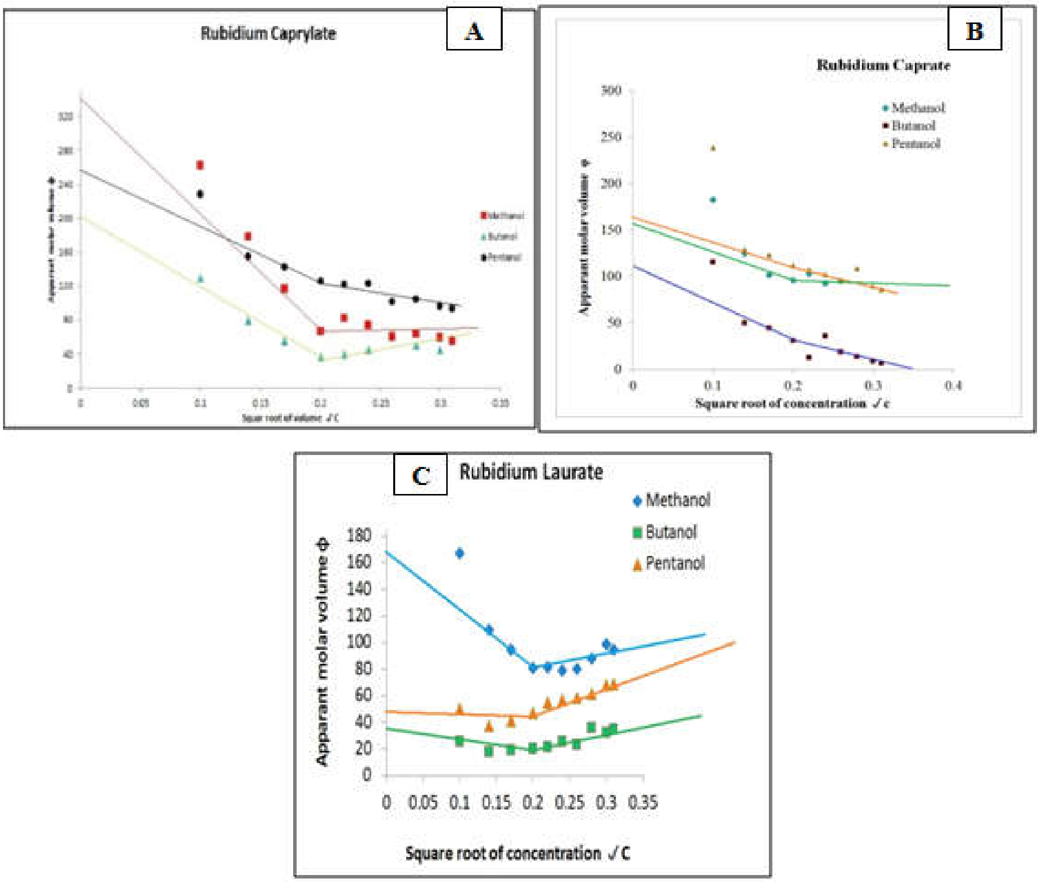

Figure 1. Apparent molar volume Øv cm^3mol^{-1} vs square root of concentration g mol L^{-1}

The value of CMC is independent of hydrocarbon chain in soaps. The existence of polar head group of soap molecule causes change in the energy of solution and micellization takes place. It can be argued that a change in overall structure cannot be over ruled.

Massion equation Øv = Øv_0 + S_v √C is applicable to curve Øv vs √C.

The value of Øv_0 is obtained from the intercept of the line and that of S_v from the slop of the line, Øv_0 and S_v are the measure of solute- solvent and solvent- solvent interaction respectively.Øv apparent molar volume is positive and show sharp decrease with the increase of soap concentration below c mc and slight increase above c mc fig.1, 2 and 3. Øv, apparent molar volume is solute-solvent inter action, the positive value indicates strong solute- solvent inter action, a progress for overall structural order in alkanols. The soaps in alkanols behave actively as structure making agent. The decline inØv is as soaps molecules in dilute solution ionise considerably in to cation Rb^+ and anion hydrocarbon which are encircled completely by a layer of solvent molecules, firmly bounded by Vander Walls' forces and dipol-dipol interaction which are oriented towards the ions. Change in overall structure is evident.

The apparent molar volume is extrapolated to zero soap concentration in the graph of Øv vs √C, to get limiting apparent molar volume φ^0_vie as follows.

Øv = Øv^∞ = lim(m →0) Øv

Massion equation is applicable to the system below cmc as well as above c mc, two values of Ø $^0{}_V$are possible Ø $^0{}_{V1}$ belowcmc and Ø $^{0}{}_{V2}$ above cmc. It is a measure of solute- solvent interaction below cmc and its positive value with higher magnitude Table 1B verifies quantitatively strong solute – solvent interaction leading to change in overall structural order, The structure breaking effect of soap due to ion-solvent inter action between the molecules may be visualized. It is concluded that interaction of soap and solvent is higher below cmc whereas soap- soap interaction exists due to its low value. Experimental slop S_v has values, Sv_1 below c mc and Sv_2 above c mc. Sv_1 comes out negative pointing towards weak ion-ion inter action as a result of inter ionic penetration Table 1B where as Sv_2 is positive. The Sv_2 may have positive value due to appreciable ionization of soap at higher concentration. The solute–solute inter action is appreciably strong as the concentration of soap in solution increases due to micellisztion process

Conclusion

The rubidium soaps considerably ionize in solution to form anion hydrocarbon (caprylate, caprate, laurate) giving rise to hydrogen bonding favoring condition and resonance. Massion equation $Øv = Øv_0 + S_v \surd C$ is applicable to the dilute solution of soaps under investigation. The value of Ø $^{0}{}_{V1}$ and Ø $^{0}{}_{V2}$ apparent molar volume below cmc and above cmc depend on the chain length of the soaps. The positive value&deceasing character of apparent molar volume indicates strong ion-solvent interaction and shows structure breakingcapacity of soaps in alkanols.

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