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Molecular Interaction and Compressibility Behaviour of Beryllium Soaps in Non-Aqueous Medium

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The ultrasonic measurements were made on beryllium soaps (caprate, laurate and myristate) in pure benzene with a view to determine the critical miceller concentration (CMC), soap-solvent interaction and various acoustic parameters. The value of CMC decreases with the increase in the chain-length of soap. The results of ultrasonic velocity, adiabatic compressibility, intermolecular free length, specific acoustic impedence, apparent molar compressibility, relative association and solvation number suggested that there is a significant interaction between soap and solvent molecules.

Key Words: Ultrasonic velocity, metal soaps, interaction parameters.

INTRODUCTION

The study of metallic soaps is becoming increasingly important in technological and academic fields. It has been a subject of intense investigations in the recent past on account of its role in such diversified fields as detergents, softeners, stabilizers, plasticizers, lubricants, cosmetics, medicines, emulsifiers, insecticides and water-proofing agents. The technological applications of these soaps are mostly based on empirical know-how and the selection of the soap is dependent largely on economic factors.

The methods of preparation and uses of metal soaps were reviewed by several researchers[1-9]. The study of molecular interactions has been a subject of extensive investigations by Raman[10], NMR[11,12], infrared[13,14] and ultrasonic absorption[15-20] measurements.

The present work deals with the ultrasonic velocity measurements of beryllium soaps (caprate, laurate and myristate) in pure benzene with a view to evaluate various allied parameters related to the acoustical properties of soap solutions.

EXPERIMENTAL

All the chemicals used were of AR grade. The beryllium soaps (caprate, laurate and myristate) was prepared by direct metathesis of corresponding potassium soap with the required amount of aqueous solution of beryllium sulphate at 50-55 ºC under vigorous stirring. The precipitated soaps were washed with water and acetone and dried under reduced pressure. The purity of the soaps was checked by elemental analysis, IR spectrum and determination of their melting points.

The densities of the solvent and the solutions were measured with a dilatometer. The ultrasonic velocity measurements was recorded on a multi-frequency ultrasonic interferometer at 30 ± 0.05 ºC using a crystal of 1 MHz frequency.

Various acoustic parameters namely adiabatic compressibility (β), intermolecular free length (L_f)[21], specific acoustic impedance (Z)[22], apparent molar compressibility (ϕ_k)[23], relative association (R_A)[24] and solvation number (S_n)[25,26] were calculated using the following relationships:

$$\beta = \rho^{-1}V^{-2} \tag{1}$$

$$L_f = \sqrt{B/K} \tag{2}$$

$$Z = \rho V \tag{3}$$

$$\phi_k = \frac{1000}{C\rho_o}(\rho_o\beta - \beta\rho_o) + \frac{\beta_o M}{\rho_o} \tag{4}$$

$$R_A = \left(\frac{\rho}{\rho_o}\right)\left(\frac{v_o}{v}\right)^{1/3} \tag{5}$$

$$S_n = \frac{n_o}{n}\left(1 - \frac{\beta}{\beta_o}\right) \tag{6}$$

where, ρ_o, ρ, β_o, β, v_o and v are the density, adiabatic compressibility and ultrasonic velocity of solvent and solutions, respectively and n_o, n, M_o and M are the number of moles and molecular weight of solvent and solute, respectively, K and C are the temperature dependent Jacobson's constant and concentration, respectively.

RESULTS AND DISCUSSION

The density, ρ of the solutions of beryllium soaps of caprate, laurate and myristate in pure benzene increases first slowly and then rapidly with increasing soap concentration (Table-1). The plots of density, ρ *vs.* C (Fig. 1) are characterized by an intersection of two straight lines at definite soap concentration which corresponds to the CMC of soap.

TABLE-1

DENSITY, ULTRASONIC VELOCITY AND OTHER ACOUSTIC PARAMETERS OF BERYLLIUM SOAPS IN BENZENE AT 30 ± 0.05 ºC

AA	BB	CC	DD	EE	FF	GG	HH	II
Caprate								
0.002	0.8640	1037	10.752	12.754	8.959	20.206	0.9969	3.922
0.004	0.8643	1039	10.714	12.731	8.980	11.149	0.9966	4.317
0.006	0.8647	1042	10.651	12.694	9.010	8.569	0.9961	4.973
0.008	0.8652	1046	10.552	12.635	9.049	7.745	0.9954	6.003
0.010	0.8655	1049	10.491	12.598	9.079	6.845	0.9948	6.637
0.012	0.8662	1055	10.367	12.524	9.138	6.812	0.9938	7.927
0.014	0.8669	1061	10.243	12.448	9.198	6.789	0.9927	9.217
0.016	0.8676	1065	10.154	12.394	9.239	6.554	0.9922	10.143
0.018	0.8683	1070	10.054	12.333	9.291	8.665	0.9915	11.183
0.020	0.8689	1075	9.955	12.272	9.341	6.322	0.9906	12.213
Laurate								
0.002	0.8645	1040	10.688	12.716	8.991	23.728	0.9965	4.783
0.004	0.8647	1042	10.651	12.694	9.010	12.854	0.9961	5.184
0.006	0.8650	1045	10.578	12.650	9.039	9.850	0.9955	5.976
0.008	0.8653	1049	10.493	12.599	9.077	8.499	0.9946	6.898
0.010	0.8658	1053	10.407	12.548	9.117	7.723	0.9939	7.831
0.012	0.8665	1059	10.283	12.473	9.176	7.545	0.9928	9.175
0.014	0.8673	1064	10.181	12.411	9.228	7.269	0.9922	10.282
0.016	0.8681	1069	10.075	12.346	9.279	7.088	0.9916	11.431
0.018	0.8687	1074	9.969	12.281	9.329	9.340	0.9907	12.581
0.020	0.8694	1079	9.869	12.219	9.381	6.784	0.9899	13.666
Myristate								
0.002	0.8647	1043	10.628	12.679	9.019	26.862	0.9958	5.676
0.004	0.8652	1044	10.599	12.662	9.033	14.323	0.9961	6.007
0.006	0.8654	1047	10.539	12.626	9.061	10.595	0.9954	6.689
0.008	0.8656	1051	10.455	12.577	9.097	9.019	0.9943	7.633
0.010	0.8662	1057	10.333	12.503	9.156	8.519	0.9931	9.023
0.012	0.8670	1061	10.242	12.448	9.199	7.985	0.9928	10.045
0.014	0.8676	1067	10.119	12.373	9.257	7.733	0.9916	11.431
0.016	0.8683	1072	10.019	12.312	9.308	7.450	0.9909	12.567
0.018	0.8691	1077	9.918	12.249	9.360	9.758	0.9902	13.715
0.020	0.8697	1083	9.797	12.174	9.419	7.166	0.9891	15.094

AA = Concentration C mol dm^{-3}; BB = Density $\rho \times 10^{-3}$ kg m^{-3}; CC = Velocity *vs.* ms^{-1}; DD = Adiabatic compressibility $\beta \times 10^{10}$ m^2 N^{-1}; EE = Inter molecular free length L_f Å ; FF =Specific acoustic impedance $Z \times 10^{-5}$ m^{-2} s^{-1}; GG = Apparent molar compressibility $-\phi_k \times 10^6$ m^5 N^{-1} (k mol)$^{-1}$; HH = Relative association R_A; II = Solvation number S_n.

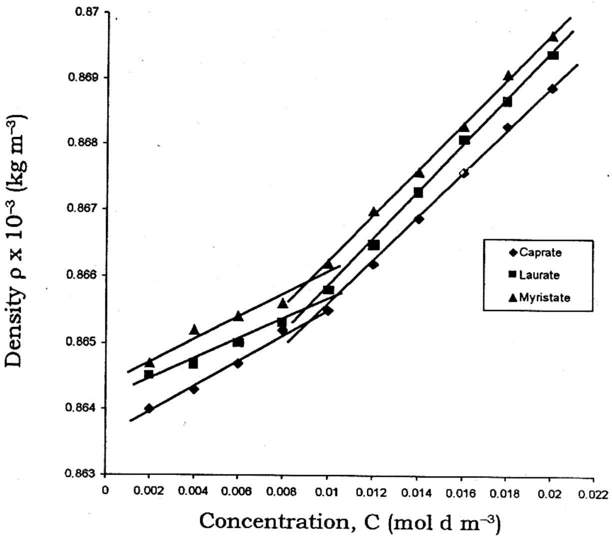

Fig. 1. Density ρ *vs.* concentration, C

The results show that the CMC values decrease with increasing chainlength of the soap molecules (Table-2). The plots of ρ *vs.* C below the CMC have been extrapolated to zero concentration and extrapolated values of the density, ρ_o are in agreement with experimental values of the density of pure solvent. It is, further, concluded that the soap molecules do not show appreciable aggregation below the CMC whereas there is a marked change in aggregation of the soap molecules at the definite soap concentration.

TABLE-2
VALUES OF CMC, CONSTANT (A AND B) OBTAINED FROM DENSITY MEASUREMENTS AT 30 ± 0.05 °C

Metal soaps	CMC (mol dm^{-3})	A	B
Be caprate	0.0098	0.84	-5.00
Be laurate	0.0095	0.96	-6.36
Be myristate	0.0089	1.29	-9.00

The density results have also been explained in terms of Root's equation:

$$\rho = \rho_o + AC - BC^{3/2}$$

where, C is the concentration (mol/L) and ρ and ρ_o are the densities of soap solution and solvent, respectively. The constants A and B refer to the solute-solvent and solute-solute interactions, respectively.

The plots of $\rho-\rho_o/C$ *vs.* $C^{1/2}$ indicate a break at a definite soap concentration, which corresponds to the CMC of the soap. The values of constants A and B have been obtained from the intercept and slope of the plots of $\rho-\rho_o/C$ *vs.* $C^{1/2}$ below the CMC and are recorded in Table-2. The values of the constant A are higher than constant B, which shows that the solute-solvent interaction is larger than the solute-solute interaction in soaps solutions. It is, therefore, concluded that the soap molecules do not show appreciable aggregation below the CMC and there is marked increase in aggregation of the soap molecules at this definite soap concentration.

The ultrasonic velocity (v) of beryllium soap (caprate, laurate and myristate) solutions increases with the increasing concentration and chainlength of the soaps (Table-1). The variation in ultrasonic velocity with concentration (dv/dC) depends on the concentration derivatives of density (ρ) and adiabatic compressibility (β).

$$\frac{dv}{dC}=\frac{v}{2}\left[\frac{1}{\rho}\left(\frac{d\rho}{dC}\right)+\frac{1}{\beta}\left(\frac{d\beta}{dC}\right)\right]$$

The quantity $d\rho/dC$ is always positive while $d\beta/dC$ is negative since the values of $1/\beta(d\beta/dC)$ are higher than $1/\rho(d\rho/dC)$ for these soap solutions, the quantity dv/dC is positive, *i.e.*, the ultrasonic velocity increases with increasing soap concentration. These results are in agreement with the results of other workers[27,28] for electrolytic solutions indicating that these soaps behave as simple electrolytes in solution.

The plots of ultrasonic velosity *vs.* soap concentration (Fig. 2) are characterized by an intersection of two straight lines at a definity soap concentration which corresponds to the CMC of these soaps. The CMC values of beryllium soaps decrease with increasing chain-length of the soap molecules (Table-3). The values are in agreement with the values obtained from density measurements.

TABLE-3
VALUES OF VARIOUS CONSTANT OBTAINED FROM ULTRASONIC MEASUREMENTS AT 30 ± 0.05 ºC

	Be caprate	Be laurate	Be myristate
CMC (mol/dm^{-3})	0.0098	0.0094	0.0090
G	1923.0700	2000.0000	2083.3300
$A \times 10^{10}$	-174.0000	-215.0000	-240.0000
$B \times 10^{10}$	1125.0000	1571.4300	1800.0000
$\phi_k \times 10^6$	-14.6000	-16.9000	-20.5000
$S_k \times 10^6$	81.8182	88.8890	140.0000

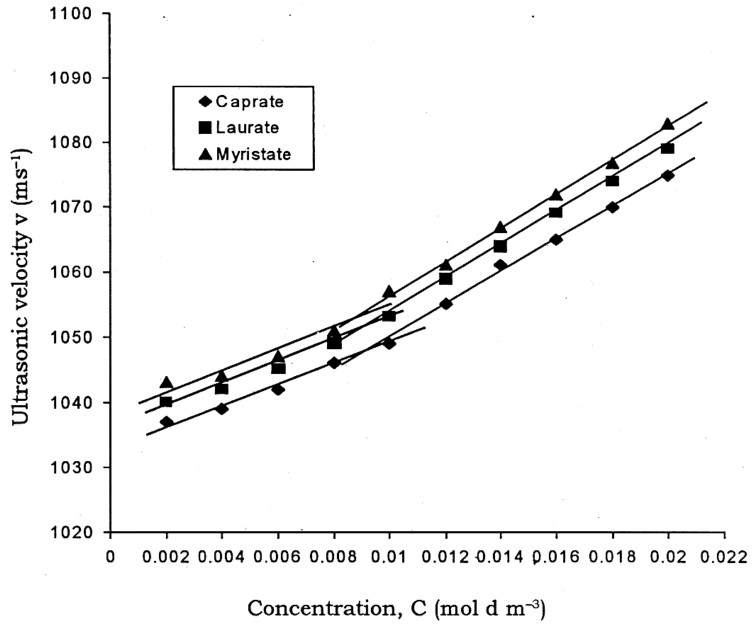

Fig. 2. Ultrasonic velocity (v) *vs.* concentration (C)

The extrapolated values of velocity (v_o) (1031.5, 1034 and 1035 m/s for caprate, laurate and myristate, respectively) are in close agreement with the experimental values of velocity (1030 m/s) of solvent, indicating that the soap molecules do not aggregate upto appreciable extent below the CMC.

The variation of ultrasonic velocity, v with soap concentration, C follows the relationship

$$v = v_o + GC$$

where, v_o is the ultrasonic velocity in pure solvent and G is Garnsey's constant[29]. The values of G (Table-3) has been calculated from the slopes of the plots of v *vs.* C. The values of G increases with increasing chain-length of soap molecules.

The adiabatic compressibility, β of these soap solutions decreases with increasing the soap concentration (Table-1). The decrease in adiabatic compressibility, β is attributed to the fact, that the molecule of beryllium soaps (caprate, laurate and myristate) in dilute solutions are considerably ionized into metal cations and fatty acid anions. These ions are surrounded by a layer of solvent molecules firmly bound and oriented towards the ions. The orientation of solvent molecules around the ions is attributed to the influence of their electrostatic field and the internal pressure increases lowering the compressibility of the solutions, *i.e.*, the solution becomes more difficult to compress[30].

The plots of β *vs.* C indicate a break at a definite soap concentration which corresponds to the CMC of the soap. The extrapolated values of adiabatic compressibility, β_o (10.82×10^{10}, $10.74 \times \times 10^{10}$ and 10.70×10^{10} $m^2 N^{-1}$ for caprate, laurate and myristate, respectively) are in close agreement with experimental value (10.90×10^{10} $m^2 N^{-1}$) of solvent.

The results of adiabatic compressibility have been explained in term of Bachem's equation[31]:

$$\beta = \beta_o + AC + BC^{3/2}$$

where A and B are constants, C is the molar concentration and β and β_o are the adiabatic compressibility of the solutions and solvent, respectively. The values of A and B (Table-3) have been obtained from the intercept and slope of the plots of $(\beta - \beta_o)/C$ *vs.* $C^{1/2}$.

The intermolecular free length, L_f decreases while specific acoustic impedance, Z increases with increasing soap concentration (Table-1) indicating that there is significant interaction between the soap and solvent molecules which considerably affects the structural arrangement. The increase in the values of Z with increase in concentration can be explained on the basis of lyophobic interaction between soap and solvent molecules which increases the intermolecular distance. The plot of L_f *vs.* C (Fig. 3) and Z *vs.* C show a break at a definite soap concentration which corresponds to the CMC of these soaps.

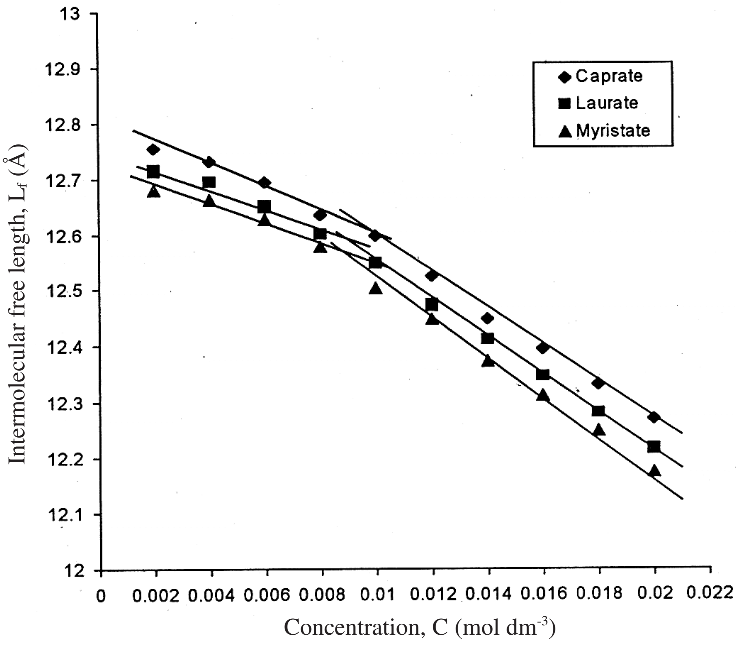

Fig. 3. Intermolecular free length (L_f) *vs.* concentration (C)

The values of apparent molar compressibility, ϕ_k increases with increasing soap concentration (Table-1). The ϕ_k is related to the molar concentration, C by the relationship:

$$\phi_k = \phi^o_k + S_k C^{1/2}$$

where ϕ^o_k and S_k are the limiting apparent molar compressibility and a constant, respectively. The values of ϕ^o_k and S_k have been obtained from the intercept and slope of the plots of ϕ_k and $C^{1/2}$ (Fig. 4) below the CMC and are recorded in Table-3.

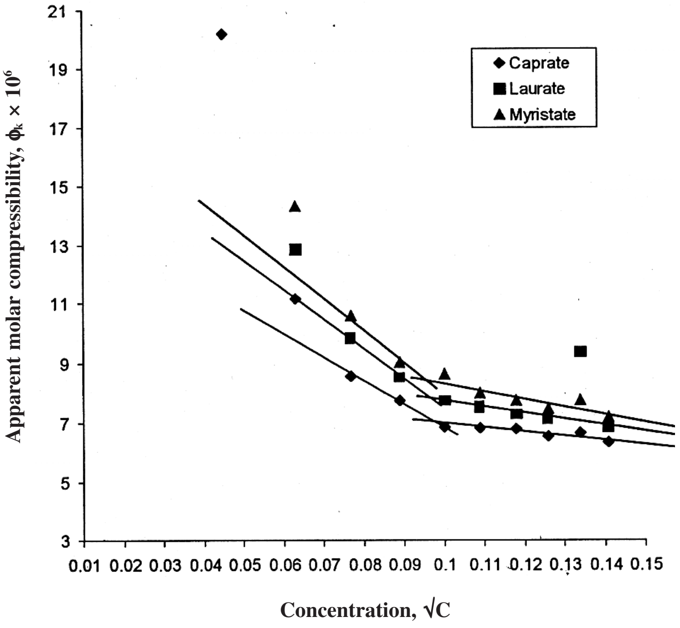

Fig. 4. Apparent molar compressibility ϕ_k *vs.* concentration C

The values of relative association (R_A) decreases while solvation number, S_n increases with increasing soap concentrations (C) are characterized by a break at the CMC.

The ultrasonic velocity results show that beryllium soaps (caprate, laurate and myristate) behaves as a simple electrolyte in solutions. The result confirms that there is a significant interaction between the soap and solvent molecule in dilute solutions and the soap molecule do not aggregate appreciably below the CMC. The CMC values are in agreement with the values obtained from other parameters.

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