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Effect of Temperature and Chain Length on the Acoustic Behaviour of Ammonium Soaps in Methanol

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Ultrasonic velocities of ammonum soaps *i.e.* laurate, myristate, palmitate and stearate have been measured in methanol at temperatures 308–323 K. Acoustic parameters such as: adiabatic compressibility, molar sound velocity, molar sound compressibility, intermolecular free length, relative association constant, specific acoustic impedance, solvation number and apparent molar compressibility have been evaluated in order to determine the micellar aggregation of these soaps. The effects of temperature and chain length on these parameters have been discussed.

INTRODUCTION

The effect of temperature on the acoustic properties of alkali metal soaps in water has been studied[1] to obtain important information about the structural changes in properties of soaps. Acoustic properties of lithium abietate and oleate in water have been studied at different frequencies and temperatures[2] to study the micellar aggregation and soap-solvent interaction. Ultrasonic measurements[3] on solutions of gadolinium soaps in benzene-methanol mixture (7 : 3 v/v) show that the value of C.M.C. decreases with increase in chain length of soap and temperature. Effect of chain length on acoustic behaviour[4] of chromium soap solutions in xylene-methanol mixtures show that there is significant soap-solvent interaction in dilute solution and soap molecules do not aggretate appreciably much in dilute soap solutions below C.M.C.

In the present paper an attempt has been made to study the effect of temperature and chain length of soaps on acoustic parameters of ammonium soaps (laurate, myristate, palmitate and stearate) in methanol.

EXPERIMENTAL

The chemicals were purified and the soaps prepared by reacting the fatty acids (C_{12}–C_{18}) with ammonium hydroxide. The product was recrystallized in methanol and dried in an air oven at 323 K. Distilled methanol (b.p. 338 K) and freshly prepared conductivity water were used. The methods of measurements of ultrasonic velocity and density of soap solutions in methanol were described earlier[5].

RESULTS AND DISCUSSION

Ultrasonic velocity, u, of ammonium soap solutions decreases with increase in temperature but increases with increase in chain length and concentration of soap. The u-C plots (Fig. 1) show an intersection of two straight lines at C.M.C. *i.e.* 0.10, 0.04, 0.04 and 0.03 M for laurate, myristate, palmitate and stearate respectively. The C.M.C. values are unaffected with temperature.

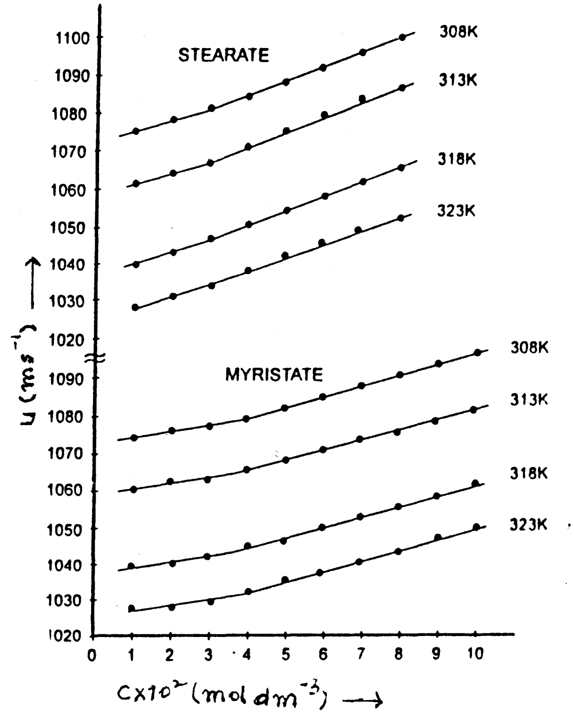

Fig. 1 Plots of ultrasonic velocity, u (m s^{-1}) *vs*. concentration, C (mol dm^{-3}) of ammonium soaps in methanol at 308 K.

The adiabatic compressibility, β, of solution is determined by using the relation:

$$\beta = \frac{1}{u^2 d} \quad (1)$$

where d is the density of solution.

The adiabatic compressibility, β increases (Table-1) with increase in temperature indicating the decrease in ion-solvent interaction. It also decreases with increase in chain length and concentration of soap.

The ultrasonic velocity, u is related with soap concentration, C as:

$$u = u_0 + GC \quad (2)$$

where u_0 is the ultrasonic velocity in pure solvent and G is Garnsey's constant[6].

The values of G are 1.00×10^2, 1.75×10^2, 2.00×10^2 and 3.00×10^2, respectively for laurate, myristate, palmitate and stearate respectively. There is no effect of temperature on the values of G. The values of u_0, 1.072×10^3, 1.058×10^3, 1.037×10^3 and 1.026×10^3 at 308, 313, 318, and 323 K, respectively, are in agreement with the experimental values of ultrasonic velocity in methanol. It shows that soap molecules do not aggregate to an appreciable extent below C.M.C.

TABLE-1
VALUES OF ADIABATIC COMPRESSIBILITY, β INTERMOLECULAR FREE LENGTH, L_f AND RELATIVE ASSOCIATION CONSTANT OF AMMONIUM SOAPS IN METHANOL AT DIFFERENT TEMPERATURES (K)

Conc C (mol dm^{-3})	Adiabatic compressibility ($\beta \times 10^{10}$)(m^2N^{-1})			Intermolecular free length ($L_f \times 10^{-10}$)(m)			Relative association constant (R_A)		
	308 K	313 K	318 K	308 K	313 K	318 K	308 K	313 K	318 K
				Laurate					
0.01	11.153	11.505	12.036	49.40	41.73	34.10	1.0002	1.0003	1.0006
0.03	11.143	11.451	11.983	49.38	41.63	33.95	1.0102	1.0005	1.0006
0.10	10.928	11.312	11.786	48.89	41.58	33.74	1.0010	1.0017	1.0011
0.30	10.672	11.034	11.577	48.32	41.14	33.44	1.0080	1.0070	1.0080
0.50	10.403	10.768	11.246	47.77	40.37	32.96	1.0097	1.0120	1.0127
				Myristate					
0.01	11.127	11.478	12.008	49.34	41.68	34.06	1.0002	1.0003	1.0004
0.03	11.051	11.398	11.922	49.17	41.53	33.94	1.0006	1.0007	1.0008
0.04	11.004	11.349	11.871	49.07	41.45	33.86	1.0005	1.0006	1.0007
0.07	10.821	11.158	11.666	48.66	41.09	33.57	1.0001	1.0002	1.0003
0.10	10.623	10.970	11.444	48.21	40.75	33.25	0.9993	0.9998	0.9996
				Palmitate					
0.01	11.465	11.453	11.982	49.38	41.64	34.02	1.0002	1.0003	1.0003
0.03	11.023	11.369	11.868	49.11	41.48	33.86	1.0011	1.0011	1.0009
0.04	10.954	11.318	11.815	48.96	41.39	33.78	1.0008	1.0012	1.0009
0.07	10.686	11.037	11.538	48.36	40.87	33.38	0.9998	1.0002	1.0002
0.10	10.447	10.806	11.312	47.81	40.44	33.06	0.9991	0.9998	1.0002
				Stearate					
0.01	11.098	11.448	11.975	49.28	41.62	34.01	1.0007	1.0008	1.0008
0.02	11.024	11.370	11.893	49.11	41.48	33.89	1.0009	1.0010	1.0010
0.03	10.954	11.297	11.792	48.96	41.35	33.75	1.0008	1.0008	1.0006
0.05	10.788	11.103	11.608	48.58	40.99	33.48	1.0010	1.0007	1.0008
0.08	10.520	10.842	11.329	47.98	40.50	33.08	1.0006	1.0008	1.0009

The molar sound velocity, R and molar sound compressibility, W have been calculated from:

$$R = \frac{M}{d} u^{1/3} \tag{3}$$

$$W = \frac{M}{d} \cdot \beta^{-1/7} \tag{4}$$

where M is the average molecular weight of the solution calculated from the relation $M = X_1M_1 + X_2M_2$, X_1 and X_2 are mole fractions of solute and solvent of molecular weights M_1 and M_2.

The values of R and W increase with increase in chain length and concentration of soap whereas these values are unaffected by the increase in temperature.

The intermolecular free length, L_f has been calculated by using the expression:

$$L_f = \sqrt{\frac{\beta}{k}} \tag{5}$$

where k is temperature dependent Jacobson constant[7]. L_f decreases (Table-1) with increase in chain length of soap and temperature. It also decreases with increase in concentration of soap showing significant interaction between soap and solvent molecules and that the structural arrangement is considerably affected.

The relative association constant, R_A has been calculated from the relationship:

$$R_A = \frac{d}{d_0}\left(\frac{u_0}{u}\right)^{1/3} \tag{6}$$

The relative association constant (Table-1) is influenced by either breaking up of solvent molecules or by the solvation of ions on adding soap. R_A increases with increase in temperature.

The specific acoustic impedence[8], Z, calculated as $Z = du$, decrease with increase in temperature but increases with increase in chain length and concentration of soap solutions (Table-2). The increase in the value of Z with soap concentration can be explained on the basis of lyophobic interaction between soap and solvent molecules which increases the intermolecular distance leaving relatively wider gaps between molecules.

The solvation number[9], S_n has been calculatd from the relationship:

$$S_n = \frac{n_1}{n_2}\left[1 - \frac{v\beta}{nv_1^0\beta^0}\right] \tag{7}$$

where n_1 and n_2 are the mole fraction of solvent and solute and v_1^0 is the molar volume of solvent respectively.

S_n (Table-2) decreases with increase in temperature and cocentration of soap indicating ion-ion interaction.

The apparent molar compressibility, Φ_K has been calculated from the relationship:

$$\Phi_K = \frac{1000[\beta d_0 - \beta d^0]}{dd_0} + \frac{\beta d_0}{d} \tag{8}$$

where M is the molecular weight of soap.

The values of Φ_K increase with increase in temperature and chain length of soap. It also decreases with increase in soap concentration.

TABLE-2
VALUES OF SPECIFIC ACOUSTIC IMPEDANCE, Z AND SOLVATION NUMBER, S_n OF AMMONIUM SOAPS IN METHANOL AT DIFFERENT TEMPERATURES (K)

Conc. (mol dm^{-3})	Specific acoustic impedance (kg m^{-2} s^{-2})				Solvation number, S_n			
	308 K	313 K	318 K	323 K	308 K	313 K	318 K	323 K
				Laurate				
0.01	8.357	8.208	8.004	7.873	2329.4	2317.9	2305.2	2293.2
0.03	8.364	8.231	8.027	7.904	776.3	772.6	768.4	764.5
0.10	8.457	8.314	8.104	7.973	232.9	231.7	230.5	229.3
0.30	8.589	8.431	8.211	8.096	77.6	77.2	76.9	76.4
0.50	8.731	8.567	8.365	8.277	46.5	46.3	46.0	45.8
				Myristate				
0.01	8.367	8.219	8.015	7.891	2329.6	2317.8	2305.4	2293.7
0.03	8.402	8.254	8.049	7.910	776.6	772.7	768.6	764.5
0.04	8.422	8.213	8.069	7.938	582.5	579.6	576.5	573.5
0.07	8.501	8.353	8.148	8.017	333.0	331.3	328.5	327.8
0.10	8.589	8.432	8.236	8.104	233.2	232.0	230.0	229.6
				Palmitate				
0.01	8.378	8.229	8.025	7.894	2329.4	2318.1	2305.6	2294.0
0.03	8.416	8.267	8.071	7.932	776.7	772.8	768.7	764.7
0.04	8.445	8.288	8.091	7.690	582.6	580.1	576.6	573.6
0.07	8.561	8.405	8.199	8.067	333.2	331.5	329.7	328.0
0.10	8.671	8.506	8.292	8.160	233.4	232.2	230.9	229.7
				Stearate				
0.01	8.382	8.233	8.029	7.989	2329.9	2317.9	2305.7	2393.2
0.02	8.414	8.266	8.062	7.939	1165.2	1159.2	1153.1	1196.2
0.03	8.445	8.296	8.099	7.961	776.9	772.9	768.9	797.2
0.05	8.520	8.378	8.173	8.043	466.3	464.0	461.6	478.6
0.08	8.642	8.493	8.288	8.150	291.7	290.2	288.7	299.1

The Φ_K is related with concentration, C of soap by the relationship:

$$\Phi_K = \Phi_K^0 + S_K C^{1/2} \tag{9}$$

where Φ_K^0 is the limiting apparent molar compressibility and S_K is experimental slope.

The plot of Φ_K against $C^{1/2}$ (Fig. 2) are characterised by intersection of two straight lines at C.M.C. The results show that the values of Φ_K^0 (Table-3) increases with increase in temperature and chain length of soap. The values of $-S_K$ differ very much above and below C.M.C. showing micellar aggragation. It increases with increase in temperature and chain length of soap.

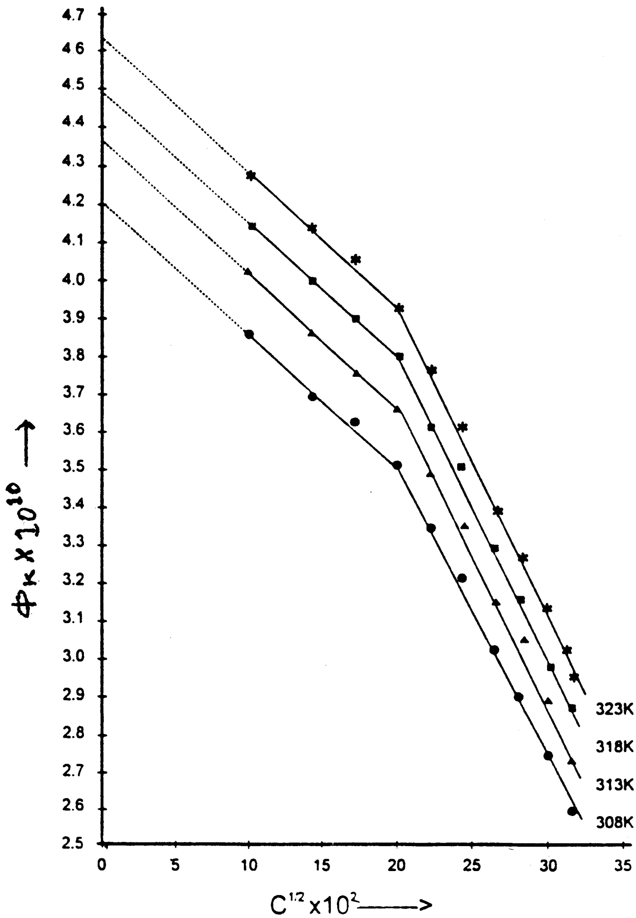

Fig. 2 Plot of Φ_K vs. $C^{1/2}$ of ammonium in methanol at different temperatures

TABLE-3

VALUES OF Φ_K^0 AND S_K OF AMMONIUM SOAPS IN METHANOL AT DIFFERENT TEMPERATURES

Soap	308 K			313 K			318 K			323 K		
	$\Phi_K^0 \times 10^{10}$	$-S_K \times 10^{10}$ a	b	$\Phi_K^0 \times 10^{10}$	$-S_K \times 10^{10}$ a	b	$\Phi_K^0 \times 10^{10}$	$-S_K \times 10^{10}$ a	b	$\Phi_K^0 \times 10^{10}$	$-S_K \times 10^{10}$ a	b
Laurate	3.17	3.0	1.0	3.28	3.2	1.1	3.44	3.3	1.2	3.54	3.4	1.3
Myristate	3.67	5.5	2.1	3.79	5.6	2.3	3.94	6.0	2.4	4.14	6.3	2.7
Palmitate	4.21	7.7	3.4	4.37	8.1	3.5	4.49	8.2	3.6	4.64	8.3	3.7
Stearate	4.59	7.8	4.0	4.78	8.2	4.4	5.01	8.4	4.6	5.18	8.8	4.8

a: Values above C.M.C., b: Values below C.M.C.

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