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EFFECT OF TEMPERATURE AND CARBON CHAIN LENGTH ON THE ACOUSTIC PARAMETERS OF AMMONIUM SOAPS IN 2-PROPANOL

Abstract

Ultrasonic velocity of ammonium soaps, i.e., laurate, myristate, palmitate and stearate have been measured in 2-Propanaol at temperature 308-323K. Acoustic parameters such as: adiabatic compressibility, molar sound velocity, molar sound compressibility intermolecular free length, relative association constant, specific acoustic impedance, salvation number and apparent molar compressibility have been evaluated in order to determine the micellar aggregation of these ammonium soaps. The effects of temperature and carbon chain length on these parameters have been discussed.

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I. INTRODUCTION

In order to learn crucial information about the structural alterations in soap properties, researchers have examined the impact of temperature on the acoustic characteristics of alkali metal soaps in water (1). In order to investigate micellar aggregation and the soap-solvent interaction, the acoustic characteristics of lithium abietate and oleate in water have been investigated at various frequencies and temperatures (2). According to ultrasonic measurements (3) on gadolinium soap solutions in benzene-methanol mixtures (7:3 v/v), temperature and soap chain length both increase the value of C.M.C. The acoustic behaviour (4) of chromium soap solutions in xylene-methanol mixtures is affected by the chain length. The results indicate that there are significant interactions between the soap and solvent in the diluted solution, and that the soap molecules do not aggregate significantly below the C.M.C.

The current study aims to investigate the impact of temperature and the length of the ammonium soap chain on the acoustic properties of the ammonium soaps (stearate, myristate, palmitate, and lauric acid) in 2-propanol

II. EXPERIMENTAL

Fatty acids (C12–C18) were reacted with ammonium hydroxide to create ammonium soaps after the chemicals were purified. The product was dried at 323K in an air oven after being recrystallized in 2-propanol. Two ingredients were used: freshly prepared conductivity water and distilled 2-propanol (b.p. 355.4K). The density of ammonium soap solutions in methanol and the ultrasonic velocity measurement techniques were previously discussed (5).

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III. RESULT AND DICSUSSION

The ultrasonic velocity, or u, of solutions containing ammonium soap rises as the temperature rises, but it falls as the carbon chain length and ammonium soap concentration rise. The order of variation in ultrasonic velocity is as follows: stearate > palmitate > myristate > laurate. The interaction between two straight lines at C.M.C., or 0.10, 0.04, 0.04, and 0.03M for laurate, myristate, palmitate, and stearate solution, is depicted in the u-C plots (Fig. 1). Concentration showing the C.M.C.'s derived from u-C plots are likewise consistent with what was seen in earlier solvents. As the temperature rises, the C.M.C. values don't change. The following relation can be used to determine the adiabatic compressibility, β, of a solution:

$$\beta = \frac{1}{u^2 d} \qquad \text{----(1)}$$

where ‘d’ is the density of ammonium soaps solution.

As the temperature rises, the adiabatic compressibility β (Table –1) increases, signifying a reduction in the interaction between the ions and solvent. It also decreases as the concentration of ammonium soap and the length of the carbon chain increase. It explains on the basis of ionic head groups close-packing in the micelles, which increases ionic repulsion and, ultimately, internal pressure. As the soap's carbon chain size increases, repulsion likewise increases, leading to a decrease in values of β.

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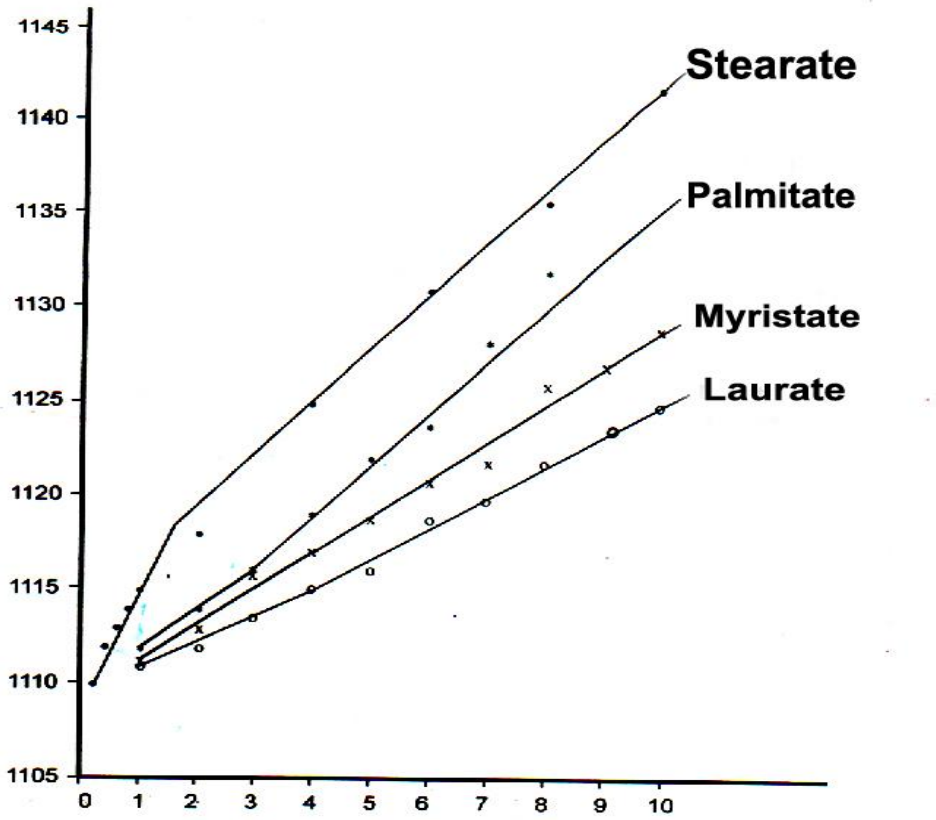

Figure 1: Plots of ultrasonic velocity, u (ms^{-1}) vs. concentration, C ($mol\ dm^{-3}$) of ammonium soaps in 2-propanol at 308K.

The ultrasonic velocity, u is related with ammonium 2-propanol soap concentration, 'C' is:

$$u = u_0 + GC \qquad \text{----(2)}$$

where u_0 is the ultrasonic velocity for zero soap concentration and 'G' is Garnsey's constant**(6)**. The values of G are 1.00×10^2, 1.33×10^2 and 2.00×10^2, respectively for laurate, myristate, palmitate and stearate respectively. There is no effect of temperature on the value of 'G'. The values of u_0 1.109×10^3, 1.094×10^3, 1.075×10^3 and 1.053×10^3 at 308, 313, 318 and 323K 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.

The molar sound velocity, R (Rao's constant) and molar sound compressibility, W (Wada's constant) have been calculated for solutions using the equation:

$$R = \frac{M}{d} u^{1/3} = V.u^{1/3} \qquad \text{----(3)}$$

where 'V' is the molar volume of the soap solution.

Table 1: Values of Allied Parameters Adiabetic Compressibility, β Intermolecular Free Length, L_f and Relative Association Constant of Ammonium Soaps in 2-Propanol at Different Temperatures (308-318k).

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)		
	308K	**313K**	**318K**	**308K**	**313K**	**318K**	**308K**	**313K**	**318K**
Laurate									
0.01	10.460	10.781	11.244	47.8	40.40	33.0	1.0002	1.0002	1.0003
0.03	10.396	10.733	11.172	47.7	40.30	33.90	1.0000	1.0004	1.0002
0.10	10.200	10.592	11.001	47.4	40.0	32.6	1.0019	1.0009	1.0005
0.30	9.980	10.330	10.721	46.7	39.6	32.4	1.0050	1.0052	1.0043
0.50	9.728	10.045	10.451	46.1	39.1	31.7	1.0063	1.0085	1.0086
Myristate									
0.01	10.438	10.757	11.219	47.8	40.40	32.9	1.0001	1.0002	1.0004
0.03	10.386	10.685	11.121	47.7	40.20	32.8	1.0009	1.0007	1.0005
0.04	10.344	10.660	11.095	47.6	40.20	32.7	1.0008	1.0008	1.0007
0.07	10.236	10.528	10.954	47.3	39.9	32.5	1.0007	1.0006	1.0005
0.10	10.129	10.415	10.815	47.1	39.7	32.3	1.0010	1.0009	1.0055
Palmitate									
0.01	10.435	10.735	11.195	47.8	40.3	32.9	1.0004	1.0002	1.0003
0.03	10.324	10.678	11.073	47.5	40.2	32.7	1.0006	1.0013	1.0005
0.04	10.300	10.633	11.026	47.5	40.1	32.6	1.0018	1.0012	1.0009
0.07	10.183	10.474	10.838	47.2	39.8	32.4	1.0021	1.0016	1.0005
0.10	10.034	10.298	10.693	46.9	39.6	32.1	1.0022	1.0023	1.0006
Stearate									
0.01	11.098	10.732	11.193	47.7	40.3	32.9	1.0004	1.0005	1.0005
0.03	11.024	10.653	11.047	47.5	40.2	32.7	1.0009	1.0016	1.0007
0.04	11.954	10.566	10.955	47.4	40.0	32.5	1.0012	1.0013	1.0008

0.07	11.788	10.328	10.703	47.0	39.5	32.1	1.0018	1.0010	1.0009
0.10	11.520	10.262	10.630	46.9	39.4	32.0	1.0020	1.0012	1.0010

$$W = \frac{M}{d}\beta^{-1/7} = V.\beta^{-1/7} \quad \text{----(4)}$$

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

The value of R and W increase with increase in soap concentration and also increase with increase in carbon chain length but are unaffected by temperature.

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

$$L_f = \sqrt{\frac{\beta}{k}} \quad \text{----(5)}$$

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

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

$$R_A = \frac{d}{d_0}\left(\frac{u_0}{u}\right)^{\frac{1}{3}} \quad \text{----(6)}$$

Either the solvent molecules are broken up in the presence of electrolyte, or the ions are saved and soap is added, affecting the relative association constant (Table 1). The values of RA rise as

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concentration rises, indicating that soaps aggregate and ions are saved. As temperature rises, RA values essentially stay the same. According to the formula Z = u.d, the specific acoustic impedance (8) Z rises with temperature but decreases with carbon chain length and ammonium soap solution concentration (Table 2). Lyophobic interaction between solvent and soap molecules increases the intermolecular distance between molecules, leaving relatively wider gaps between them, which explains why the value of Z increases with soap concentration. As temperature rises, Z values fall, but as chain length increases, they rise.

The solvation number **(9)**, Sn has been calculated by using Passynsky's relation.

$$S_n = \frac{n_1}{n_2}\left[1 - \frac{V\beta}{n_1 V_1^0 \beta^0}\right] \qquad \text{----(7)}$$

where n_1 and n_2 are the moles of solvent and solute and V_1^0 is the molar value of solvent respectively and V is the molar volume of solution containing 'n_2' moles of solute.

S_n (Table – 2) decrease with increase in temperature and concentration of ammonium soap indicating ion-ion interaction. The higher values of salvation number suggest a considerable dissociation of ammonium soaps.

The apparent molar compressibility, Φ_k of the solution has been calculated by using the relation.

$$\Phi_k = \frac{1000\ [\beta d_0 - \beta^0 d]}{d d_0} + \frac{\beta M}{d}$$

where 'M' is the molecular weight of soap, d_0 and β^0 are densities and compressibilities of the solvent respectively.

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The values of Φ_k increase with increase in temperature and carbon chain length of soap. The value of Φ_k decreases with increase in soap concentration. The plots of Φ_k against $C^{1/2}$ (Fig. 2). Show an intersection of two straight lines at C.M.C. The values of Φ_k^0 are positive which shows considerable soap-solvent interaction below C.M.C.

Table 2: Values of Allied Parameter, Specific Acoustic Impedance, 'Z' and Solvation of Number, 'S_n' of Ammonium Soaps in 2-Propanol at Different Temperatures

Conc. (C) (mol dm^{-3})	**Specific acoustic impedance (Z) Kg m^{-2}s^{-2}**				**Solvation number, (S_n)**			
	308K	**313K**	**318K**	**323K**	**308K**	**313K**	**318K**	**323K**
Laurate								
0.01	8.613	8.463	8.265	8.055	1290.5	1284.1	1277.4	1270.8
0.03	8.643	8.485	8.296	8.086	430.2	428.0	425.8	423.6
0.10	8.701	8.552	8.370	8.145	129.0	128.4	127.7	127.1
0.30	8.859	8.682	8.526	8.297	43.0	42.8	42.6	42.4
0.50	9.001	8.826	8.667	8.449	25.8	25.7	25.5	25.4
Myristate								
0.01	8.623	8.474	8.276	8.066	1290.5	1284.1	1277.4	1270.8
0.03	8.651	8.508	8.318	8.101	430.2	428.0	425.8	423.6
0.04	8.670	8.520	8.330	8.120	322.6	321.1	319.3	317.7
0.07	8.722	8.581	8.390	8.180	184.3	183.4	182.5	181.6
0.10	8.776	8.634	8.452	8.249	129.0	128.4	127.7	127.1
Palmitate								
0.01	8.626	8.484	8.286	8.076	1290.5	1284.1	1277.4	1270.8
0.03	8.679	8.514	8.339	8.129	430.2	428.0	425.8	423.6
0.04	8.692	8.534	8.359	8.148	322.6	321.0	319.3	317.7
0.07	8.752	8.609	8.442	8.231	184.3	183.4	182.5	181.6
0.10	8.828	8.677	8.525	8.322	129.0	128.4	27.7	127.1
Stearate								
0.01	8.636	8.486	8.288	8.085	1290.5	1284.1	1277.4	1270.8
0.03	8.685	8.526	8.351	8.148	430.2	428.0	425.8	423.6
0.04	8.715	8.565	8.390	8.187	322.6	321.0	319.3	317.7
0.07	8.804	8.676	8.502	8.322	184.4	183.4	182.5	181.6
0.10	8.836	8.709	8.533	8.364	161.3	160.5	158.1	127.1

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The Φ_k is related with soap concentration, "C" by the relationship:

$$\Phi_k = \Phi^0{}_k + S_K C^{1/2} \quad \text{----(9)}$$

Where $\Phi^0{}_k$ is the limiting apparent molar compressibility and S_K is experimental slope. The result show the values of $\Phi^0{}_k$ (Table 3) increases with increase in temperature and chain length of soap. The values of S_K are negative and differ very much below and above C.M.C. showing micellar aggragation. The values of $-S_K$ increases with increase in temperature and carbon chain length of soap. Measurements of allied parameters (densities, ultrasonic velocities and viscosities) have been carried out for binary mixtures of 2-methyl aniline with 1-alcohols (1-Propanol, 1-butanol, 1-pentanol, 1-hexanol) at different temperatures**(10)**. Allied Parameters (ultrasonic-velocity, density and viscosity) of binary liquid mixtures with Acetone with Toluene, chlorobenzene and nitrobenzene measured at 303K**(11)**. The studies on ultrasonic velocity, density and viscosity in binary liquid mixture have been used to evaluate the different thermo acoustical parameters along with the excess properties from these parameters molecular interaction such as existence of strong molecular association and weak interaction among the molecular liquids has been observed in present study.12 By using ultrasonic velocity, density and concentration data various Acoustic parameter are calculated and results are explained in terms of the interaction between the solute and the solvent. Many insights into the behaviour and interactions of molecules can be gained from ultrasonic studies.(13) The ultrasonic interferometer, 30 ml gravity bottle, and Ostwald's viscometer were used to measure the ultrasonic velocity, density, and viscosity of the binary liquid mixture of methanol and chloroform at a frequency of 2 MHz and constant temperature of 295 K, respectively(14). Measurements have been made of the density, viscosity, and ultrasonic velocity of aqueous sodium propionate at various temperatures (15). Experimental measurements have been

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made using ultrasonic research on ternary liquid mixtures of certain-1-alkanols with metamethoxy phenol and n-hexane at 313K. In light of molecular interaction, the variation of acoustical parameters with respect to different concentration at constant temperature for the three systems has been discussed (16).

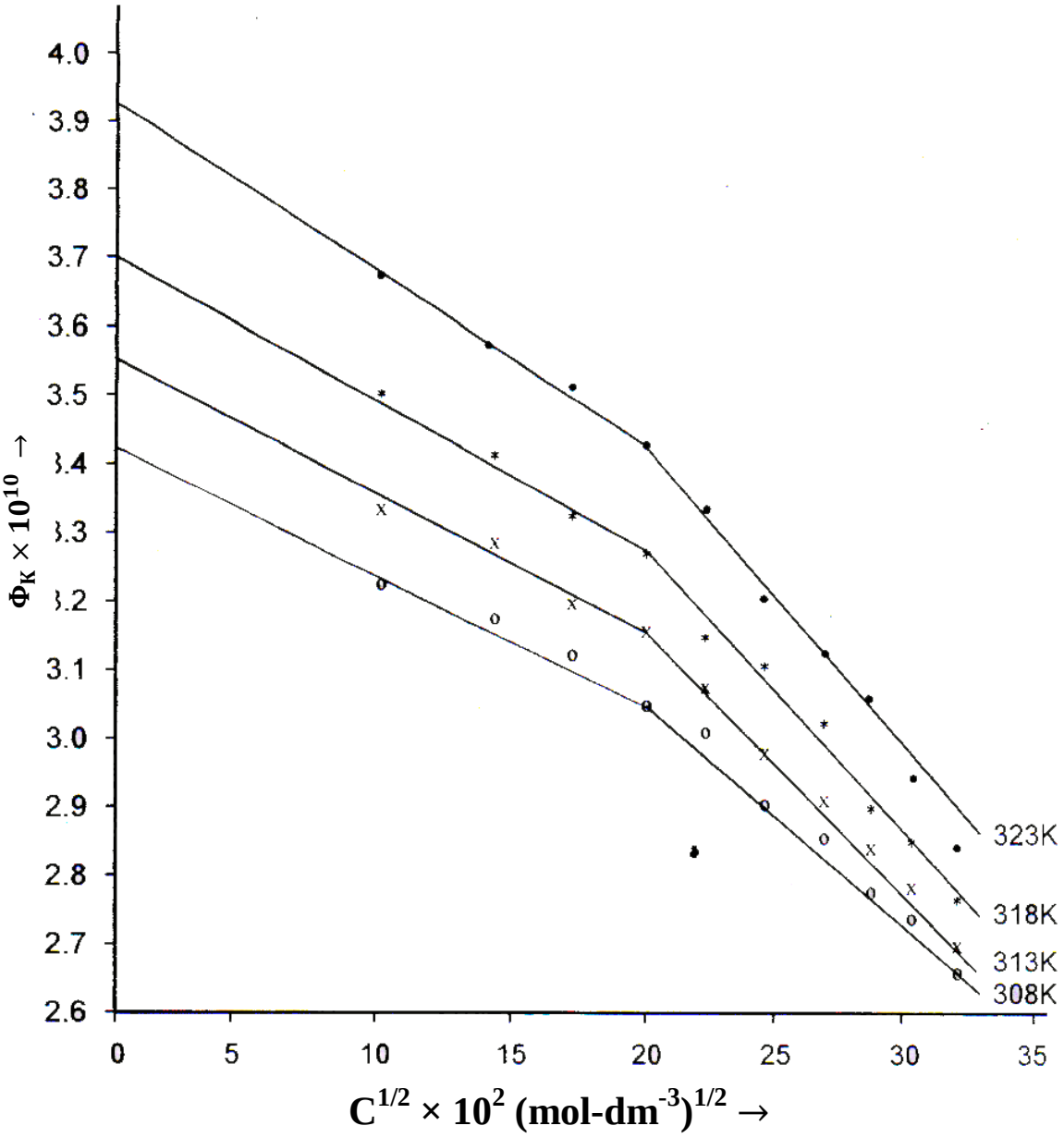

Figure 2: Plots of Φ_k vs. $C^{1/2}$ of ammonium myristate in 2-propanol at different temperatures (308-323K).

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Table 3: Values of Φ^0_k and S_k of Ammonium Soaps in 2-Propanol at Different Temperatures (308-323k)

Ammonium Soap	308 K			313 K			318 K			323 K		
	$\boldsymbol{\Phi^0_k}$ $-S_K \times 10^{10}$			$\boldsymbol{\Phi^0_k}$ $-S_K \times 10^{10}$			$\boldsymbol{\Phi^0_k}$ $-S_K \times 10^{10}$			$\boldsymbol{\Phi^0_k}$ $-S_K \times 10^{10}$		
	$\times$ ——— 10^{10}	a	b	$\times$ ——— 10^{10}	a	b	$\times$ ——— 10^{10}	a	b	$\times$ ——— 10^{10}	a	b
Laurate	3.05	1.6	2.95	3.20	1.8	3.15	3.34	1.9	3.20	3.50	2.0	3.30
Myristate	3.44	1.9	3.5	3.57	2.0	4.0	3.72	2.2	4.2	3.94	2.5	4.7
Palmitate	3.86	2.5	4.5	4.01	2.6	5.0	4.18	3.2	5.2	4.41	3.5	6.6
Stearate	4.25	2.8	5.6	4.43	3.0	7.0	4.65	4.0	7.2	4.89	4.2	8.4

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

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