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

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**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, solvation 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.

**Key Words**: Ultrasonic velocity, Acoustic, myristate, palmitate, solvation number

**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 of acoustic behavior(4) of chromium soap solutions in xylene-methanol mixtures show that there is significant soap-solvent interactions in dilute solution and soap molecules chain carbon length of ammonium soaps on acoustic parameters of ammonium soaps (laurate, myristate, palmitate and stearate) in 2-propanol.

**EXPERIMENTAL:** The chemicals were purified and the 2-propanol soaps prepared by reacting the fatty acids (C12 – C18) with ammonium hydroxide. The product was recrystallized in 2-propanol and dried in an air oven at 323K. Distilled 2-propanol (b.p. 355.4K) and freshly prepared conductivity water were used. The methods of measurements of ultrasonic velocity and density of ammonium soap solutions in methanol were described earlier(5).

**RESULT AND DICSUSSION:** Ultrasonic velocity, u, of ammonium soap solutions decreases with increase in temperature but increases with increase in carbon chain length and concentration of ammonium soap. The ultrasonic velocity varies in different soaps as : stearate > palmitate > myristate > laurate. The u-C plots (Fig. 1) show an interaction of two straight lines at-C.M.C. i.e., 0.10, 0.04, 0.04 and 0.03M for laurate, myristate, palmitate and stearate solution respectively. Concentration indicating the C.M.C.’s obtained from u-c cklots are also the same as observed in previous solvents. The C.M.C. values are remains constant with increase in temperature. The adiabatic compressibility, $β$, of solution is determined by using the relation:

$$β=\frac{1}{u^{2}d}$$

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

The adiabatic compressibility $β$ (Table –1) increase with increase in temperature indicating the decrease in ion-solvent interaction. It also decreases with increase in carbon chain length and concentration of ammonium soap. It explain on the basis of close-packing of ionic head groups in the micelles resulting in an increase in ionic – repulsion and finally internal pressure when the size of carbon chain of the soap increases the repulsion will also increase, thereby a decrease in the values $β$ occurs.



Fig. 3: 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 = u0 + GC --- (2)

where u0 is the ultrasonic velocity for zero soap concentration and ‘G’ is Garnsey’s constant(6). The values of G are 1.00 × 102, 1.33 × 102 and 2.00 × 102, respectively for laurate, myristate, palmitate and stearate respectively. There is no effect of temperature on the value of ‘G’. The values of u0 1.109 × 103, 1.094 × 103, 1.075 × 103 and 1.053 × 103 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 = $\frac{M}{d}$u1/3 = V . u1/3 --- (3)

 where ‘v’ is the molar volume of the soap solution.

**TABLE 1**

**Values of allied parameters adiabatic compressibility,** $β$ **intermolecular free length, lf and relative association constant of ammonium soaps in 2-propanol at different temperatures (308-318k).**

|  |  |  |  |
| --- | --- | --- | --- |
| Conc. C. (mol dm-3) | Adiabatic compressibility ($β×10$10) (m2N-1) | Intermolecular free length (Lf × 10-10) (m)  | Relative association constant (RA)  |
|  | 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 = $\frac{M}{d}β^{-1/7}=V. β^{-1/7}$ ---(4)

where M is the average molecular weight of the soap solution calculated from the relation M = X1M1 + X2M2, where X1 and X2 are mole fractions of solute and solvent of molecular weights M1 and M2.

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, Lf has been calculated by using the following relation:

Lf = $\sqrt{\frac{β}{k}}$ ----(5)

where ‘k’ is temperature dependent Jacobson constant(7). Lf decrease (Table 1 ) with increase in chain length of ammonium soap and temperature. It also decreases 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, RA has been calculated from the relationship:

 RA = $\frac{d}{d\_{0}} \left(\frac{u\_{0}}{u}\right)^{\frac{1}{3}}$ ---(6)

The relative association constant (Table 1) is influenced by either breaking up of solvent molecular in addition of electrolyte or by the salvation of ions and adding soap. The values of RA increases with increase in concentration showing the salvation of ions and aggregation of soaps. The values of RA remain almost constant with increase in temperature. The specific acoustic impedance(8) Z, has been using the equation calculated Z = u.d creases with increase in temperature but increases with increases in carbon chain length and concentration of ammonium 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 the molecules. The values of z decrease with increase in temperature but increase with increase in chain length.

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

 Sn = $\frac{n\_{1}}{n\_{2}} \left[1-\frac{Vβ}{n\_{1}V\_{1}^{0}β^{0}}\right]$ ---(7)

where n1 and n2 are the moles off solvent and solute and V10 is the molar value of solvent respectively and v is the molar volume of solution containing ‘n2’ 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.

 $Φ\_{k}$ = $\frac{1000 [βd\_{0}-β^{0}d]}{d\_{0}}+\frac{βM}{d}$

where ‘M’ is the molecular weight of soap, d0 and $β$0 are densities and compressibilities of the solvent respectively.

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 c1/2 (fig. 2). Show an intersection of two straight lines at e.m.c. The values of $Φ\_{k}$ 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, ‘sn’ of ammonium soaps in 2-propanol at different temperatures (308-323k)**

|  |  |  |
| --- | --- | --- |
| Conc. C (mol dm-3) | Specific acoustic impedance (z)Kgm-2s-2 | Solvation number, (Sn) |
|  | 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 |

The $Φ\_{k}$ is related with soap concentration, C by the relationship:

 $Φ\_{k}$ = $Φ^{0}\_{k}$ + SKC1/2 ---(9)

Where $Φ^{0}\_{k}$ is the limiting apparent molar compressibility and SK is experimental slope. The result show the values of $Φ^{0}\_{k}$ (Table 3) increases with increase in temperature and chain length of soap. The values of SK are negative and differ very much below and C.M.C. showing micellar aggragation. The values of –SK increases in temperature an 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 result are interpreted in terms of solvent-solute and solute-solute interaction. Ultrasonic studies provide a lot of information to understands the molecular behavior and either molecular interaction.13 Ultrasonic velocity, density and viscosity of binary liquid mixture of chloroform and methanol has been measured using ultrasonic interferometer, 30ml gravity bottle and Ostwald’s viscometer respectively at frequency 2MHz and constant temperatures at 295K(14). Density, viscosity and ultrasonic velocity studies of aqueous sodium-propionate at different temperature have been measured(15). Ultrasonic studies on ternary liquid mixtures of some-1-alkanols with metamethoxy phenol and n-hexane at 313 has been experimentally measured. The variation of acoustical parameters with respect to different concentration at constant temperature for the three system have been discussed in the light of molecular interaction(16).



Fit. Plots of $Φ^{0}\_{k}$ vs. C1/2 of ammonium myristate in 2-propanol at different temperatures.

**Table-3**

**Values of** $Φ^{0}\_{k}$ **and sk of ammonium soaps in 2-propanol at different temperatures (308-323k**)

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Ammonium Soap | 308 K  | 313 K | 318 K | 323 K  |
| $Φ^{0}\_{k} $-SK × 1010×1010  a b | $Φ^{0}\_{k} $-SK × 1010×1010  a b | $Φ^{0}\_{k} $-SK × 1010×1010  a b | $Φ^{0}\_{k} $-SK × 1010×1010  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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