



Studies of ultrasonic of KBr in dioxan and water solvent mixture at 303.15K

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Abstract

Various acoustic parameters like isentropic compressibility (β_s), intermolecular free length (L_f), apparent molar volume (ϕ_k), molar sound velocity (R), acoustic impedance (Z) of KBr in 10%, 20%, 30% and dioxan and water solvent mixture at 303.15K have been determined from ultrasonic velocity (V), density (ρ) and relative viscosity (η_r) of the solution. These parameters are related with the molar concentration of the solution and reflects the distortion of the structure of the solvent in dioxan and water mixture when the solute is added to it.

Keywords: Ultrasonic, viscosity, density, molar concentration, KBr solution, dioxan and water solvent mixture at 303.15K

Introduction

The dissolution of electrolyte in various solvents is responsible for structure maker or structure breaker [1]. Viscosity and density data leads an insight to the state of association of the solute and the extent of interaction of the solute with the solvent. The present work mainly deals with the reflects the ion-ion, ion-solvent and solvent-solvent interaction KBr solution in 10%,20% and 30% in dioxan and water mixture.

Materials and methods

The solvents used were purified by appropriate method. Dioxan was used in AR grade, sample and water was triple distilled. Purity was about 99.9% which was in good

agreement with the standard values of density, viscosity etc. The solvents of different Dioxan content were prepared by taking required volume of dioxan in distilled water, For the preparation of different concentration of solution, the required amount of KBr was weighed and dissolved in a 250 ml measuring flask. In the present work the ultrasonic velocity of the solution was measured by a commercially available ultrasonic interferometer of frequency 5 MHZ manufactured by Mital enterprisers.

Results and discussion

The experimental data of density (ρ) and relative viscosity (η_r) for the solute in different concentration of the dioxan and water solvent mixture at 303.15 K are given in Table-1.

Table 1: Physical properties of KBr of different concentration in 10%,20% and 30% dioxan and water solvent mixture at 303.15K

| concentration | η_r | Pgm ml ⁻¹ | ϕ_k Gm ³ ml ⁻¹ |
|-----------------------|----------|----------------------|---|
| i) 10% dioxan+water | | | |
| 0.1000 | 1004.987 | 1.017551 | 21.82058 |
| 0.0750 | 1003.984 | 1.015130 | 21.76424 |
| 0.0500 | 1002.931 | 1.012706 | 21.6974 |
| 0.0250 | 1001.839 | 1.010280 | 21.61029 |
| 0.0100 | 1000.961 | 1.008822 | 21.53300 |
| 0.0075 | 1000.789 | 1.008579 | 21.51518 |
| 0.0050 | 1000.622 | 1.008336 | 21.49405 |
| 0.0025 | 1000.418 | 1.008093 | 21.46650 |
| 0.0010 | 1000.247 | 1.007947 | 21.44206 |
| 0.0000 | 1000.112 | 1.007849 | - |
| ii) 20% dioxan+water | | | |
| 0.1000 | 1006.794 | 1.025492 | 24.38067 |
| 0.0750 | 1005.331 | 1.023141 | 24.31627 |
| 0.0500 | 1003.810 | 1.020788 | 24.23988 |
| 0.0250 | 1002.198 | 1.018431 | 24.14033 |
| 0.0100 | 1001.121 | 1.017014 | 24.05200 |
| 0.0075 | 1000.913 | 1.016768 | 24.03164 |
| 0.0050 | 1000.685 | 1.016542 | 24.00748 |
| 0.0025 | 1000.441 | 1.016305 | 23.97600 |
| 0.0010 | 1000.253 | 1.016163 | 23.94807 |
| 0.0000 | 1000.168 | 1.016069 | - |
| iii) 30% dioxan+water | | | |
| 0.1000 | 1008.299 | 1.032302 | 24.80913 |
| 0.0750 | 1006.583 | 1.029966 | 24.74092 |
| 0.0500 | 1004.792 | 1.027628 | 24.66001 |
| 0.0250 | 1002.854 | 1.025286 | 24.55456 |
| 0.0100 | 1001.528 | 1.023878 | 24.46100 |

| | | | |
|--------|----------|----------|----------|
| 0.0100 | 1001.239 | 1.023643 | 24.43943 |
| 0.0075 | 1000.953 | 1.023409 | 24.41364 |
| 0.0050 | 1000.624 | 1.023174 | 24.28050 |
| 0.0025 | 1000.362 | 1.023033 | 24.35091 |
| 0.0010 | 1000.198 | 1.022938 | - |
| 0.0000 | | | |

From the result it is clear that the relative viscosity (η_r) [2] increases with the increase in volume percentage of dioxan. Such characteristics indicates the more extent of H-bonding of O(CH₂)₄O. With the increase in volume percentage of O(CH₂)₄O. With the increase in concentration of the solute the relative viscosity increases which is in good agreement [3]. The apparent molar volume (ϕ) were determined from

$$\phi = \frac{M(r-r_0)}{\rho_0 \rho c}$$

the equations and are given in Table - 1 Where M is the molecular wt. of the solute, ρ_0 is the density of the solvent, ρ is the density of the solutions, c is the molar

concentration of the solution.

The data obtained have been found to agree with the

Masson's equation [4] as the plot of ϕ vs $c^{1/2}$ is linear -

$$\phi_0 = \phi_0 + S_v c^{1/2}$$

The value of the limiting apparent molar value ϕ_0 obtained from the extrapolation of the above plot to zero concentration. The limiting slope S_v is a constant dependent on charge and salt type and can be related ion-ion interaction. The value of ϕ_0 and S_v are listed in Table-2.

Table 2: Limiting apparent molar volume (ϕ_0), limiting slope (S_v) A and B for KBr in 10%, 20%, 30%, dioxan and water solvent mixture at 304.15 K

| Parametre | 10% | 20% | 30% |
|--|------|------|------|
| ϕ_0 (cm ³ mol ⁻¹) | 21.4 | 23.9 | 24.3 |
| S_v (cm ^{9/2}) | 1.33 | 1.52 | 1.61 |
| Ax 10 ⁻² (cm ^{1/2} It ^{1/2}) | 6.16 | 6.33 | 5.50 |
| B (mol ⁻¹ It) | 10.0 | 12.2 | 16.0 |

Ultrasonic Studies of KBr in dioxan and water solvent mixture at 303.15K.

The limiting slope (S_v) is positive suggestion ion-ion interaction. This increases with the increases in non-aqueous solvent. The increase in ϕ_0 with increase in O(CH₂)₄O content may be attributed to low surface charges. density as a result of which the electrostatic attraction is more in a medium of low dielectric constant and hence ion-solvent interaction would also be more. The plot of $(\eta_r - 1)/c^{1/2}$ is linear, which is in good agreement with the Jones-Dole equation.[5]

$$\eta_r = 1 + A\sqrt{c} + BC$$

$$\frac{\eta_r - 1}{c^{1/2}} = A + Bc^{1/2}$$

The values of A and B are obtained from the graph and are recorded in Table-2. The result reveals that the value of A increases in O(CH₂)₄O content, which also supports the increase in electrostatics attraction in a medium of low dielectric constant and also the increase in ion solvent interaction. The increase in B values with increase in O(CH₂)₄O content is due to large size of the solvent molecule and also the strong association between water and organic solvent through H-bonding.

The ultrasonic velocity (V [6,7]), isentropic compressibility (β_s) [8], Molar compressibility (w), Molar sound velocity (R), Acoustic impedance (Z) [9], inter molecular free length (L_f) and Apparent molar compressibility (ϕ_k) of KBr in 10%, 20% and 30% O(CH₂)₄O + h₂O at 303.15K are recorded in Table-3.

Table 3 : Variation of U, β_s , W, R, Z, L and ϕ_k with concentration of KBr in 10%, 20%, and 30% dioxan and water solvent mixture at 303.15K

| Conc. Mole dm ⁻³ | U m/sec | $\beta_s^* 10^{-2} \text{ cm}^2 \text{ Dync}^{-1}$ | W | R | $Z^* 10^{-5} \text{ cm}^2 \text{ Dync}^{-1}$ | $L_f^* 10^{-6} \text{ m}$ | ϕ_k |
|-----------------------------|---------|--|-----------|-----------|--|---------------------------|----------|
| 10% dioxan + water | | | | | | | |
| 0.1000 | 1550 | 40.9054 | 3564.6928 | 1353.4264 | 1.57720 | 6.39573 | -1.44344 |
| 0.0750 | 1547 | 41.1621 | 3570.0024 | 135.7784 | 1.57044 | 6.41577 | -1.61346 |
| 0.0500 | 1545 | 41.3675 | 3576.0037 | 1358.4377 | 1.56463 | 6.43176 | -2.0558 |
| 0.0250 | 1542 | 41.6284 | 3581.3728 | 1360.8178 | 1.55785 | 6.45201 | -3.16048 |
| 0.0100 | 1540 | 41.7969 | 3584.4796 | 1362.1951 | 1.55259 | 6.46505 | -6.3539 |
| 0.0075 | 1538 | 41.9158 | 3583.8886 | 1361.9332 | 1.55120 | 6.47424 | -6.91714 |
| 0.0050 | 1535 | 42.0899 | 3582.6302 | 1361.3751 | 1.54780 | 6.48767 | -6.93961 |
| 0.0025 | 1532 | 42.2651 | 3581.3679 | 1360.8176 | 1.54440 | 6.50116 | -6.96302 |
| 0.0100 | 1530 | 42.3818 | 3580.4761 | 1360.4202 | 1.54216 | 6.51013 | -5.87441 |
| 0.0000 | 1529 | 42.4414 | 3580.1054 | 1360.2560 | 1.54100 | 6.51471 | - - - |
| 20% dioxan + water | | | | | | | |
| 0.1000 | 1574 | 40.3637 | 3543.8319 | 1349.8419 | 1.614124 | 6.35324 | -1.99792 |
| 0.0750 | 1571 | 40.5180 | 3550.0395 | 1352.0835 | 1.607354 | 6.36538 | -1.15882 |
| 0.0500 | 1568 | 40.6732 | 3556.2798 | 1354.3370 | 1.600595 | 6.37755 | -1.47859 |
| 0.0250 | 1566 | 40.7771 | 3563.2113 | 1356.8940 | 1.594862 | 6.38569 | -2.64245 |
| 0.0100 | 1564 | 40.8815 | 3566.8728 | 1358.2059 | 1.590609 | 6.3986 | -5.7123 |
| 0.0075 | 1560 | 40.0914 | 3565.1266 | 1357.3753 | 1.586158 | 6.41026 | -4.84575 |
| 0.0050 | 1558 | 41.1970 | 3564.6119 | 1357.0966 | 1.583772 | 6.41849 | -5.21498 |
| 0.0025 | 1556 | 41.3029 | 3564.1358 | 1356.8320 | 1.581370 | 6.42673 | -6.29272 |

| | | | | | | | |
|-----------------------|------|---------|-----------|-----------|----------|---------|-----------|
| 0.0025 | 1555 | 41.3561 | 3563.9784 | 1356.7308 | 1.580133 | 6.43087 | -10.5608 |
| 0.0100 | 1553 | 41.4627 | 3562.9976 | 1356.2744 | 1.577955 | 6.43915 | - - - |
| 0.0000 | | | | | | | |
| 30% dioxan + water | | | | | | | |
| 0.1000 | 1585 | 38.5598 | 3543.5227 | 1344.0536 | 1.636198 | 6.20365 | -1.10273 |
| 0.0750 | 1584 | 38.6961 | 3549.7697 | 1346.8186 | 1.631466 | 6.22062 | -1.32167 |
| 0.0500 | 1582 | 38.8822 | 3555.4083 | 1349.3145 | 1.625707 | 6.23556 | -1.65983 |
| 0.0250 | 1581 | 39.0204 | 3561.7239 | 1352.1116 | 1.620977 | 6.24663 | -2.86527 |
| 0.0100 | 1580 | 39.1235 | 3565.2777 | 1353.6855 | 1.617727 | 6.25488 | -5.27871 |
| 0.0075 | 1575 | 39.3813 | 3562.7518 | 1352.5664 | 1.612237 | 6.27545 | -4.96667 |
| 0.0050 | 1573 | 39.4906 | 3562.1558 | 1352.3058 | 1.609822 | 6.28415 | -5.31338 |
| 0.0025 | 1571 | 39.6003 | 3561.5622 | 1362.0399 | 1.607406 | 6.29288 | -6.33592 |
| 0.0100 | 1570 | 39.6562 | 3561.3353 | 1351.9393 | 1.606162 | 6.29732 | -10.39560 |
| 0.0000 | 1568 | 39.7611 | 3560.3222 | 1351.4905 | 1.603966 | 6.30564 | - - - |

The values of U.W.R. & ϕ_k increases and β_s , Z, L_f decreases in $O(CH_2)_4O$ content in the solvent, suggest the powerful interaction between $O(CH_2)_4O$ and water. The increase in value of U, Z, and decrease in values of β_s , w, R, L_f with the increase in concentration of the solute represents the decrease in cohesive force. The decrease in cohesive force is due to the structure breaking nature of the solute. The H-bond exists between dioxan and water is disrupted by the solute molecule and there by formation of new bonding between solute and solvent molecules has occurred.

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