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SOLUTE-SOLUTE AND SOLUTE-SOLVENT INTERACTIONS OF SOME ORGANIC ACIDS IN DIOXANE-WATER MIXTURES

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Abstract: Apparent molal volume (ϕ_v) and apparent molal compressibility (ϕ_k) have been evaluated by measuring ultrasonic sound velocities and densities in 20, 30, 40, 50, 60, 70, 80% dioxane-water mixture at 303K. Data obtained is utilised to explain the ion-solvent and ion-ion interaction in solution with increasing percentage of organic solvent.

Keywords: Solute-Solute, Solute-Solvent, Organic Acids

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INTRODUCTION

In recent ultrasonic velocity and absorption studies in case of electrolyte solution have leads to a new insight to the process of Ion association and complex form.[1-6] The study of molecular interaction in liquid provides valuable information regarding internal structure, molecular association, complex formation reactions.[7-8] Ultrasonic parameters are directly related to large number of thermodynamic parameters. The study of apparent molal volume (ϕ_v) and apparent molal compressibility (ϕ_k) can furnish useful information about solute-solvent interaction.[9-14] The present study is undertaken to examine the interaction between some organic acids and water and various proportion of water-dioxane mixture at 303K.

EXPERIMENTAL

Pure sample of adipic acid (ADP), malonic acid (MAL), phthalic acid (PHT) and salicylic acid (SAL) are used without further purification. Water-dicxane mixture of composition 30, 40, 50, 60, 70 and 80 wt% were prepared by mixing appropriate weight of water and dioxane in stopperd bottle. In all compositions the 0.05 molar solution are prepared. Double distilled water, sp. conductance: 0.8 x 10^{-6} $ohm^{-1}an^{-1}$ is used. Densities are measured with an 15 cm^3 bicapillary pycnometer which is precalibrated. The accuracy in density measurement found to be ± 0.0001 g cm^1. A variable path single crystal interferrometer (Mittal Enterprises, Model MX-3) working at 1 MHz with accuracy of ± 0.03% is used to obtain the sound velocity in study of acoustic properties of solution.

RESULTS AND DISCUSSION

The apparent molal adiabatic compressibility (ϕk) has been calculated by using eqn. (1):

$$\phi k = \frac{1000\,(\beta d_0 - \beta_0 d)}{c\,d\,d_0} + \frac{\beta M}{d} \quad \text{... (1)}$$

where. β, β_0 are adiabatic compressibility of solute and solvent respectively. The apparent molal volume ϕ_v has been calculated from the relation :

$$\phi_v = \frac{1000\,(d_0 - d)}{c\,d\,d_0} + \frac{M}{d} \quad \text{... (2)}$$

$$\phi_v = \phi_v^0 + S_v C \quad \text{... (3)}$$

where S_v is experimental slope or limiting slope.

Adiabatic compressibility β is calculated by using eqn. :

$\beta = l00/U^2d$

where, U and d are ultrasonic velocity and density of solution respectively.

$\eta_r = dt / d_0 t_0$

where, d and t are density and time flow for solution and do, to are corresponding value for solvent.

Other acoustic parameters like free path length (Lt), relative association (ra) and specific acoustic impedance (Z) are computed by using eqn.

$Z = Us\ ds$

$R_A = (ds/d_0)(U_0/Us)^{1/3}$

The ultrasonic studies have been carried out for adipic acid, malonic acid, phthalic acid, salicylic acid in various concentration of water-dioxane mixture and in pure dioxane shows non-linear increase in the velocity with concentration which is attributed to the increasing cohesion of the water molecules due to addition of electrolyte. The observed absorption increases with increase in concentration of dioxane which reflects on the fact that water acts as bridge to join the ions dipole in mixtures. The addition of electrolyte to the polar solvent can have two effects, (i) The ion may be act as acceptor as they can be compete with the protons for the lone pair of electrons on oxygen atom. This leads to the formation of solvation sheath around the ions, (ii) The equilibrium between two structures forms get disturb and hence it may be suggested that both of the effect contributes to the change in acoustic parameters. The increase in free length (L_f) indicates that solute-solvent interactions increases due to decreasing ion number and thus such type of interactions results in the association. With water molecule[15,16] β_s value increase indicate the presence of solvent molecule around the ions. The higher value of β_s in some concentration range suggested that there exists a strong tendency of association between component molecules. In this molecules[17] the behaviour of solute is influenced by three solvation parameters like nucleophilicity, polarability which a adiabatic of the solvent to stabilize the dipole and charge. According to solvation model, it may be suggested that negative value of β_S indicates the solvation of ion due to nucleophilicity of the solvation[18]. Relative association (R_A) is a property used to understand the interaction of solvent. When the solute is added which may leads to breaking of solvent structure and solvation of solute which takes place simultaneously in the solution. It is observed that for ADP the value of R_A decreases with increasing percentage of dioxane and in MAL the reverse trend observed which may be due to increasing chain length of dicarboxylic acid. For SAL R_A increases as compared to PHT, this suggests that salicylate ions is more stable as compared to phthalic acid. The positive value of ϕK i.e. compressibility of solvent molecule is due to weak electrostatic forces in the vicinity of ions. It may be concluded that solute-solute interaction in solution is due to linking of dicarboxylic ions by water molecules.

Table I : Acoustic properties of aliphatic carboxylic acid in different composition of dioxane-water.

ADP							
% Dioxane	30%	50%	60%	70%	80%	90%	100%
β_s (bar^{-1}) 10^{-6}	72.79	75.78	77.38	79.43	80.23	80.97	83.76
L_f(A°) 10^{-1}	3.68	3.77	3.84	3.19	3.94	3.96	4.05
ϕ_v(m^{3}mol^{-1}) 10^{-1}	3.81	3.72	3.53	3.44	3.34	3.25	3.21
$\phi K_{(s)}$ (m^{3}mo^{-1}bar^{-1})10^{-6}	97.23	102.92	106.72	111.09	1 12.35	113.46	119.98
R_A	-0.6763	-0.66	-0.65	-0.64	-40.64	-0.53	-0.62
Z (kgm^{-2}s^{-1}) x 10^{6}	-1.02	-0.48	-0.49	-0.50	-0.50	-0.51	-0.53
MAL							
% Dioxane	30%	50%	60%	70%	80%	90%	1 00%
β_s (bar^{-1}) 10^{-6}	50.33	49.22	48.67	47.99	47.48	47.07	46.96
L_f(A°) 10^{-1}	2.64	2.59	2.57	2.54	2.52	2.50	2.50
ϕ_v (m^{3}mol^{-1}) 10-^{1}	-1.022	-1.15	-1.28	-1.37	-1.45	-1.50	-1.52
$\phi K_{(s)}$ (m^{3}mor^{-1}bar) 10^{-6}	56.8140	59.1210	61.7810	67.2210	68.80	69.2002	71.6221
R_A	0.632	0.64	0.65	0.66	0.47	0.67	0.68
Z (kgm^{-1}V^{-1}) x 10^{6}	0.2911	0.28	0.28	0.27	0.27	0.26	0.26

Table II: Acoustic properties of aromatic carboxylic acid in different composition of dioxane-water.

PHT							
% Dioxane	30%	50%	60%	70%	80%	90%	100%
β_s (bar^{-1}) 10^{-6}	54.45	56.47	57.80	59.40	60.69	61.15	61.96
L_f (A°) 10^{-1}	2.04	2.12	2.17	2.24	2.28	2.30	2.33
ϕ_v (m^{3}mol^{-1}) 10^{-1}	2.96	2.78	2.70	3.43	3.36	3.22	3.14
$\phi K_{(s)}$ (m^{3}mol^{-1}bar^{1}) 10^{-6}	53.05	57.10	59.99	62.41	65.20	65.42	66.92
R_A	-1.71	-1.70	-1.70	-1.68	-1.68	1.67	-1.67
Z (kgm^{-2}s^{-1}) x 10^{6}	-1.33	-1.34	-1.35	-1.36	-1.37	-1.37	-1.38
SAL							
% Dioxane	30%	50%	60%	70%	80%	90%	100%
β_s (bar^{-1}) 10^{-6}	58.8842	59.2120	61.4201	62.0211	63.10	63.1810	68.7210
L_f (A°) 10^{-1}	3.8120	3.8510	3.8840	3.9266	3.9570	3.9880	4.1579
ϕ_v (m^{3}mol^{-1}) 10^{-1}	5.7550	5.7620	5.8210	5.6220	5.5300	5.1890	4.8110
$\phi K_{(s)}$ (m^{3}mol^{-1}bar^{1}) 10^{-6}	63.2770	68.1180	70.2198	72.8990	81.0110	82.9120	83.002
R_A	1.2210	1.3180	1.3182	1.5210	1.6720	1.6242	1.64
Z (kgm^{-2}s^{-1}) x 10^{6}	1.1810	1.2210	2.2510	2.4016	2.6110	2.8100	2.8421

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