Original Research Article

Ultrasonic, viscometric and volumetric studies of some bioapplicable system with pyrazinamide (antitubercular drug)

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Abstract

Ultrasonic, Viscometric and volumetric studies of Nickel(II), Copper(II), Cobalt(II), Iron(II) and Zinc(II) chlorides involving pyrazinamide (Drug) in aqueous medium at different concentration and temperatures have been done. The value of apparent molar volume (Φ_v), acoustic impedance, adiabatic compressibility, inter molecular free length and molar sound velocity have been calculated from ultrasonic, relative viscosity (η_{rev}) and density data. The viscosity data have been analyzed in the light Jones-Dole equation. The structure making and breaking behavior of the interacting compounds and electrolytes have been studied.

Keywords: Ultrasonic, Density, Viscosity, Molar volume, Binary electrolytes.

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INTRODUCTION

Ultrasonic technique is very effective powerful and reliable tool to investigate the properties of solution[1-4]. From the physical parameters characterizing the ultrasound propagation in tissues important information about anatomical functions of the biological tissues or the foreign bodies and tumors can be evidenced. So, the study of the propagation is very important for biology, biophysics and medicine. On the other hand, the domain of the ultrasounds bond vast fields of knowledge from physics, biology, chemistry or bioengineering which contribute to the understanding of the complex, phenomena of ultrasound interaction with living systems. Viscosity and density data provide useful information regarding the solute-solute and solute-solvent interactions. These studies are of great help for interpreting the interaction behavior and structural solutions. 3d-transition metal ions play a vital role in life systems because of their natural presence in vitamins, enzymes and proteins viz (Co, Ni, Cu, Fe, Zn) etc. The role of metal ions in vital function of living organisms and for was being of living organisms are well-established. Various types of interaction occur between the ions and molecules in solutions. The ion-ion, solute-solute and solute-solvent. Interactions are of current interest in solution chemistry. These interactions help in better understanding the nature of solute and solvent whether the solute modifies or distorts the structure of solvent and vice-versa. Akhtar *et al* have utilized density and viscosity data to deduce thermodynamic properties of electrolyte solution. An attempt has been made here to study the densities and viscosities of solution of transition metal chlorides in binary aqueous solutions of pyrazinamide (antitubercular (drug) at 303 K. A number of parameters have been deduced from these data.

Experimental

Salts of metal chlorides. viz $CoCl_2.6H_2O$, $NiCl_2.6H_2O$, $CuCl_2.2H_2O$, $ZnCl_2$ of A.R. grade were used pyrazinamide was taken as such without further purification conductivity water was used for preparing binary aqueous solutions.

The pyrazinamide and metal salt's solution of varing concentration were prepared in water. The relative viscosity was measured using an Ostwald suspended level type viscometer with a flow time 240s for water at 303.15 K. Runs were repeated until three successive determinations were obtained within ± 1 s. Because all the flow times were greater then 100 s. The kinetic energy correction was not necessary. The density and viscosity values were accurate with in ± 0.1% Kgm^{-3} and 0.1% $Kgm^{-1}s^{-1}$ respectively.

The ultrasonic velocity of the solution was measured by using M-84 (Mittal Enterprises; New Delhi) instrument of a frequency of 2 MHZ with an accuracy of 0.03% at 303.15 K.

Theoretical

The ultrasonic velocity and density data described many parameters for understanding solvent interaction and structural effect. The parameters have been computed using the following relation.

$$\phi_v = \frac{m_2}{d_1} - \frac{d_2 - d_0}{C \times d_1}$$

$$R = V \times U^{1/3}$$

$$\beta_s = \frac{1}{U^2 \times d_0}$$

$$L_f = K.\ \beta_s$$

$$Z = U \times d_0$$

Where R, V, U, βs^o, K, L_f, and Z are the molar sound velocity molar volume, ultrasonic velocity, adiabatic compressibility of solution, adiabatic compressibility of solvent, Jacobson constant, inter molecular free length and acoustic impedance, respectively.

The experimental data are analysd in the light of Masson's equation.

$$\Phi v = \Phi v^0 + S_v C^{1/2} \quad \text{.....(2}$$

Where S_v is the experimental slope and Φ_v^0 is the partical molar volume. The viscosity data was analysed in the light of Jones- Dole equation.

$$\frac{\eta}{\eta^0} = 1 + A\sqrt{C} + BC \quad \text{.....(3)}$$

Where A and B are the viscosity coefficients characteristic of solute-solute and solute-solvent interactions respectively.

RESULT AND DISCUSSION

The apparent molar volume (Φ v) was calculated from the density data using eq (1). It was found to vary linearly with the square root of the concentration. This is in conformity with the Masson's equation. Densities, relative viscosities and apparent molar volumes of electrolyte solutions are presented in table I.

Table I - Values of density, relative viscosity and apparent molar volume for metal chlorides in pyrazinamide water at 303 K.

Molarity (Mol L^{-1}) M L	Density ρ x 10^{-3} Kg m^{-3}	Relative viscosity η x 10^{-3} kg $m^{-1}s^{-1}$	App.molar volume Φ v x $10^6 m^3 mole^{-1}$
Cobalt chloride + Pyrazinamide + water			
0.009 + 0.001	0.9964	0.8733	170.7582
0.007+0.003	0.9963	0.8560	160.1741
0.005+0.005	0.9962	0.8481	150.5623
0.003+0.007	0.9961	0.8398	131.8169
0.001+0.009	0.9959	0.8313	113.4063
Nickel chloride + Pyrazinamide + Water			
0.009 + 0.001	0.9962	0.8733	169.42
0.007+0.003	0.9961	0.8560	159.66
0.005+0.005	0.9960	0.8481	149.93
0.003+0.007	0.9959	0.8398	128.24
0.001+0.009	0.9958	0.8313	108.16
Copper chloride + Pyrazinamide + water			
0.009 + 0.001	0.9958	0.8527	104.139
0.007+0.003	0.9956	0.8454	94.017
0.005+0.005	0.9953	0.8416	85.037
0.003+0.007	0.9951	0.8339	65.756
0.001+0.009	0.9949	0.8312	48.684
Iron chloride + Pyrazinamide + water			

0.009 + 0.001	0.9950	0.8519	95.942
0.007+0.003	0.9947	0.8440	84.274
0.005+0.005	0.9944	0.8414	74.318
0.003+0.007	0.9942	0.8336	58.451
0.001+0.009	0.9940	0.8312	41.379
Zinc chloride + Pyrazinamide + water			
0.009 + 0.001	0.9948	0.8483	64.0095
0.007+0.003	0.9947	0.8436	61.6771
0.005+0.005	0.9945	0.8394	52.897
0.003+0.007	0.9940	0.8346	39.440
0.001+0.009	0.9940	0.8314	24.377

Table 2: Values of ultrasonic velocity (U), acoustic impedance (Z), adiabatic compressibility (ßs), Rao's Constant (R)

Molarity (Mol L^{-1}) M L	U (ms^{-1})	ßs X 10^{11} (m^2 n^{-1})	ZX10^{-3} Kgm^{-2} S^{-1}	RX 1^{06}	L_f A^0
Cobalt chloride + Pyrazinamide + water					
0.009 + 0.001	1510	99.64	1504.56	1958.93	.6237
0.007+0.003	1508	99.63	1502.42	1836.74	.6237
0.005+0.005	1507	99.62	1501.27	1726.15	.6235
0.003+0.007	1504	99.61	1498.13	1510.18	.6236
0.001+0.009	1502	99.59	1495.84	1298.68	.6236
Nickle chloride + Pyrazinamide + water					
0.009 + 0.001	1509	99.62	1503.26	1943.24	.6237
0.007+0.003	1507	99.61	1501.12	1830.48	.6236
0.005+0.005	1504	99.60	1497.98	1717.79	.6236
0.003+0.007	1501	99.59	1494.84	1468.30	.6238
0.001+0.009	1498	99.58	1491.70	1237.57	.6235
Cuppor chloride + Pyrazinamide + water					
0.009 + 0.001	1496	99.58	1489.71	1190.93	.6235
0.007+0.003	1480	99.56	1473.48	1072.02	.6235
0.005+0.005	1477	99.53	1470.05	968.34	.6234
0.003+0.007	1471	99.51	1463.79	747.76	.6233
0.001+0.009	1468	99.49	1460.51	552.80	.6233
Iron chloride + Pyrazinamide + water					
0.009 + 0.001	1482	99.50	1474.59	1093.82	.6233
0.007+0.003	1476	99.47	1468.17	959.47	.6232
0.005+0.005	1474	99.44	1465.74	845.69	.6230
0.003+0.007	1470	99.42	1461.47	664.59	.6230
0.001+0.009	1465	99.40	1456.21	469.85	.6230
Zinc chloride + Pyrazinamide + water					
0.009 + 0.001	1476	99.48	1468.32	728.68	.6232
0.007+0.003	1472	99.47	1464.19	701.52	.6232
0.005+0.005	1468	99.45	1459.92	601.10	.6231
0.003+0.007	1463	99.40	1454.22	447.73	.6230
0.001+0.009	1460	99.40	1451.24	276.46	.6230

The value of density and viscosity of these systems varies with increase in concentration of electrolytes. The change in structure of solvent and solutions as a result of hydrogen bond formation or disruption leads to decrease or increase in intermolecular force length. Hydrophobic (structure making) or hydrophilic (structure breaking) character of solute hydrogen bond forming or disrupting properties can thus be correlated with change in density and viscosity. Solutes can occupy the interstitial spaces in solvent or get solvated forming new weaker bonds. The ultrasonic velocity (U), acoustic impedance (Z), molar sound velocity (R), Compressibility, and inter Molecular free length are decrease. The decrease in the value of density has been attributed to decrease in hydrophobic interaction. It can also be seen that increase structural properties of solute. Therefore the solute that increase the ultrasonic velocity are the structure maker and those decrease the sound velocity are structure breakers. Compressibility gives account of extent of ion solvent molar interaction and

Compactness. The positive values of the apparent molar volume at different molarities are given in table 1. The magnitude of positive values of Φv for all the ions indicate greater solute-solvent interactions . The Φv value decrease with decrease in concentration of metal salts (ions) which may be attributed to the ionic concentration and electrostriction effect. This may be accounted to the associative interaction among the molecules and ions and also increase in stacking interaction between the metal ions and pyrazinamide molecules. The value of viscosity and relative viscosity decrease with decrease in concentration of electrolytic solutions, because the ions are surrounded by water molecules and the degree of cluster formation is greater. They behave as structure makers. The value of A and B coefficients have been computed by the least square method. A and B coefficient of the electrolytes were obtained from the intercepts and slopes of the linear plots of $\frac{\eta}{\eta^0} - 1/\sqrt{C}. /vs/\sqrt{C},$ The value of A,B, Sv and Φv^0 are presented in table-II.

Table II

metal Ion + ligand	A	B	Sv	Φv^0
$COCl_2$ +Pyrazinamide	-0.0684	0.626	-24.873	146.943
$NiCl_2$ + Pyrazinamide	-0.069	0.627	88.391	137.43
$CuCl_2$+ Pyrazinamide	-0.0670	0.599	597.650	43.277
$FeCl_2$+ Pyrazinamide	-0.0681	0.609	818.785	18.470
$ZnCl_2$+ Pyrazinamide	-0.0672	0.590	681.507	05.863

A perusal of table II shows that the value of A coefficient are negative showing the weak to very weak ion-ion interactions. On the other hand the value of A coefficient solute-solute/ion-ion interaction in solution increases in the order Nickle chloride<Cobalt chloride<Iron chloride<Zinc chloride<Copper Chloride. A comparison of coefficient. A values, reflect that the extent of ion-ion interaction is more in copper chloride. It is also evident from the data that the value of coefficient B are positive and fairly large in cases of the all the four transition metal chloride-pyrazinamide systems studied at different concentration at 303 K. This show the presence of ion-solvent interactions. The value of B coefficient (ion-solvent) is a measure of order or disorder introduced by ions.

It is evident from table -2 that the B-coefficient is positive for all the electrolytes their by suggesting that all the electrolytes (metal chlorides) introduce an order to the various concentrations of pyrazinamide. Hence all the electrolytes behave as structure makers.

The viscosity data have also been analysed on the basis of transition state treatment of relative viscosity of electrolyte solutions as suggested by Feakins *et al.,*. According to this theory, B-coefficient is given by eq.

$$B = \frac{V_1^0 - V_2^0}{1000} + \frac{V_1^0}{1000}\left[\frac{\Delta\mu_2^{0\#} - \Delta\mu_1^{0\#}}{RT}\right] \ldots\ldots\ldots\ldots\ldots\ldots (4)$$

Here V_1^0 is the mean volume of the solvent. and V_2^0 is the partial molar volume of the solute.

The energy of activation per mole of the solvent $\Delta\mu_1^{0\#}$ and the free energy of activation per mole of solute $\Delta\mu_2^{0\#}$ were calculated with the help of Eyring viscosity relation.

$$\Delta\mu_1^{0\#} = RT \ln (n_0 V_1^0/hN) \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (5)$$

$$\Delta\mu_2^{0\#} = \Delta\mu_1^{0\#} + (RT/V_1^0)[1000B - (V_1^0 - V_2^0)] \ldots\ldots\ldots\ldots (6)$$

Where R is the universal gas constant and T is the absolute temperature, h is the planck's constant and N the Avogadro's number.

Table III

$V_1^0(\mathrm{dm^3mol^{-1}})$, $V_2^0(\mathrm{dm^3mol^{-1}})$, $\Delta\mu_n^0(\mathrm{KJ\ mol^{-1}})$ and $\mu_2^{o\#}(\mathrm{KJ\ mol^{-1}})$ for Transition metal chlorides in pyrazinamide + water

Metal chlorides	V_2^0	$\mu_2^{o\#}$
Cobalt chloride	146.9434	66.9488
Nickel chloride	137.4309	69.0248
Copper chloride	43.2773	41.0567
Iron chloride	18.4707	63.3013
Zinc chloride	05.8639	54.2561

$V_1^0 = 123.64$

$\Delta\mu_1^{0\#} = 14.4095$

The activation energy of a reaction is defined as the additional energy which reactant molecules must aquire in order to form in intermidate activated complex for the reaction. The reacting molecules possessing sufficient energy approach each other and there is redistribution of energy and bonds so that the activated complex acquires, energy to form the intermolecular bonds. The positive values show that the formation of transition state is less favoured in the presence of pure systems. The formation of transition state is accompanied by the breaking and distortion of the intermolecular bonds. Moreover the smaller values suggested that all electrolytes behave as structure breakers in aqueous solutions.

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