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To study ultrasonic, volumetric and viscometric study of aqueous electrolyte solutions

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Abstract
For several geological processes in diverse environments, such as geothermal and magmatic hydrothermal settings, aqueous solutions play a critical role. In studying the physio-chemical behaviour and molecular interaction of various liquid mixtures, ultrasonic velocity and its related properties have been very useful. Properties such as relaxation time, relative association, internal pressure enthalpy and relaxation power are assessed from the experimental effects of ultrasonic velocity, density and viscosity and even some of the deviation/excess properties have been assessed in the study.

Keywords: Aqueous solutions, ultrasonic velocity, density and viscosity

1. Introduction

A solution in which the solvent is water is an aqueous solution. Tests of ultrasonic velocity are commonly useful for studying the relationships of ion-solvents in aqueous and non-aqueous solvents. To evaluate the ion-solvent interactions in an aqueous solution containing electrolytes or non electrolytes, this method has been extensively studied [1, 2, 3]. Owing to the association of ions and solvent molecules, the electrolyte applied to the solvent induces volume contraction and this can affect other acoustic properties of the solution. Ultrasonic velocity and its associated properties have been very beneficial in researching the physio-chemical activity and molecular association of different liquid mixtures [4]. An electrolyte alters the structure of water molecules with a heavy electric field of the ions when immersed in water. Water-dissolving electrolytes have been divided into two types: structure producers or structure breakers, based on the density of the charge. Low charge density ions have been reported to be net structure breakers; high charge density ions suggest opposite behaviour and net structure builders. This property of the structure builder or structure breaker of electrolytes has been used to explain the influence of electrolytes on both protein and nucleic acid structure and function [5-8].

For several geological processes in diverse environments, such as geothermal and magmatic hydrothermal settings, aqueous solutions play a critical role. Studies reveals that acoustic parameters are helpful in understanding the nature and strength of liquid mixtures and solutions' molecular interactions. In medicine, chemistry, agriculture, defence and manufacturing, ultrasonic energy is used [9, 10]. The literature includes preliminary findings from viscosity tests of electrolyte concentrations in aqueous solutions and solvent-solvent interactions. The volumetric properties of electrolyte solutions (solute-solvent, solute-solute and solvent-solvent interactions) have been helpful in elucidating the structural interactions in the solution. In their thermodynamic and acoustic properties at low alcohol concentrations, water and alcohol mixtures exhibit unique maxima and minima [11, 12]. Kanhekar *et al* [5] studied thermodynamic properties at various temperatures in the aqueous solution of glycine. Thirumaran and Sathish have been tested in molecular interionic interaction studies of divalent transition metal sulphates in aqueous ethylene glycol at various temperatures [13]. Properties of relaxation time (τ), internal pressure (πi), enthalpy (H) and relaxation strength (α) are assessed from the experimental effects of ultrasonic velocity (u), density (ρ). Deviation/excess characteristics, such as ultrasonic velocity deviation, isentropic compressibility deviation, excess molar volume, excess molar volume, excess molar volume. Often measured are the percentage differences of potential velocities from experimental values.

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In order to study molecular interactions in the solutions, experimental ultrasonic velocity knowledge is used. Viscosity models such as Grunberg and Nissan, Hind *et al.*, Frenkel, correlate the experimental viscosity results of all liquid solutions.
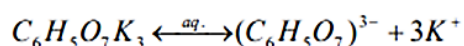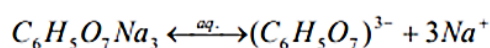
Methodology

The chemicals used in the present study were methanol (purity of mass fraction 0.99), (obtained from LOBA chemicals, Mumbai, INDIA). Tripotassium citrate and trisodium citrate. This have been further purified by normal techniques. Using triply purified deionized water, aqueous tripotassium and trisodium citrate solutions of 0.1 m (molality) were prepared. In exchange, these solutions are used to treat the liquid mixture with the solvent methanol in order to mask the whole composition spectrum (0 to 100% methanol). In specially made glass bottles with air tight stoppers, all the mixtures were prepared and sufficient steps were taken to mitigate the loss of evaporation [14, 15].

A METTER TOLEDO (Switzerland made) ABB5-S/FACT digital balance with an accuracy of 0.01 mg was used to measure solutions. Using a multi-frequency ultrasonic interferometer (M-82 Model) at a fixed frequency of 2MHz, the ultrasonic velocity of pure liquids and their binary mixtures is measured. Using a 5 cm3 two-stem double-walled Parker & Parker type pyknometer, the densities of pure liquids and their mixtures were determined [16]. The pyknometer is calibrated with water from a triple distiller. To assess the viscosity of the liquid mixture, an Ostwald viscometer was used. The experiment was conducted at 308.15 K.

Results and Discussion

The differences of experimental values u, ρ and η with the mole fraction of methanol are plotted in fig 1 and 2. From the above estimates, it has been found that with methanol concentration, the ultrasonic velocity and viscosity initially increased and reached a limit and then decreased. The density for both processes decreases non-linearly with an increase in the mole fraction of methanol. On the basis of the flickering cluster model, the above variations can be explained [17, 18]. According to this model, water is a complex mixture formed by hydrogen bonding and tight packed structures (monomer water molecules) of open structures (water molecular aggregates). In water molecules, partial negative charges of water molecules form on the oxygen atom and partial positive charges of water molecules develop on the hydrogen atoms due to the electro-negativity on the oxygen atom. One hydroxyl group includes trisodium citrate and tripotassium citrate. When dissolved these in water, these citrates dissociates into citric anion and sodium/potassium cations.

$$C_6H_5O_7Na_3 \xleftrightarrow{aq.} (C_6H_5O_7)^{3-} + 3Na^+$$

$$C_6H_5O_7K_3 \xleftrightarrow{aq.} (C_6H_5O_7)^{3-} + 3K^+$$

Because of attractions between partial charges produced on oxygen and hydrogen atoms of water molecules and ions formed due to electrolyte dissociation in water, these ions undergo hydration, i.e. water molecules surround these ions. In addition to this, hydrogen bonding occurs between the citrate ions and water molecules through the hydroxyl group. The population of monomer water molecules (close packed structures) reduces in the solution due to the hydration of ions and the formation of new hydrogen bonds between the citrate ions and the water molecules. We may tell from all this that solute interacts intensely with water, such that the solution rises in the long-range order.
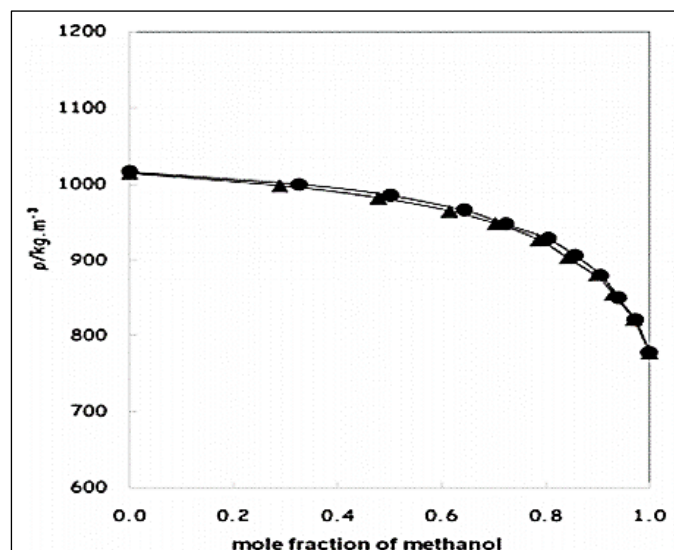

Fig 1: Variation of density (ρ) with mole fraction of methanol on aqueous tripotassium citrate and trisodium citrate solutions.
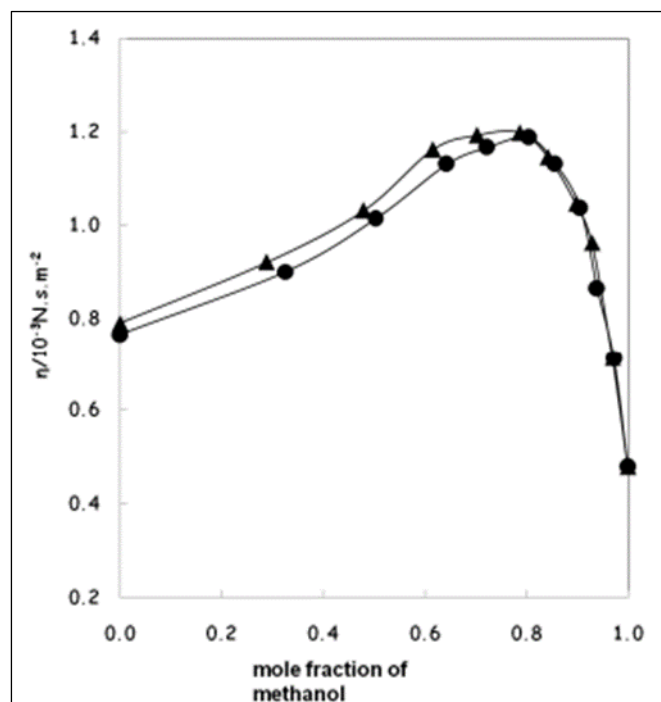

Fig 2: Variation of viscosity with mole fraction of methanol in aqueous tripotassium citrate and trisodium citrate solutions.

From Figure 1, the maximum (ultrasonic velocity) observed in the low methanol concentration area is attributed to the long-range order set when citrate is inserted into water. There are various cavities in such a hydrogen bonded structure [19], and these cavities can accommodate solvent molecules, i.e. methanol. The marked variation in molar volume between the components of the solution further favours this. Methanol molecules appear to dominate the cavities of water molecular aggregates (open structures) and water + citrate structures, as methanol is added to the

aqueous tripotassium citrate/trisodium citrate. This results in a denser bundle of molecules that contributes to an improvement in ultrasonic velocity. Till all cavities are filled, this process continues. The addition of methanol to the solution further strengthens the monomer structures in the solution. Thus with increasing methanol concentration in the methanol-rich region, the solution structure becomes more and more loosely packed. As such, ultrasound velocity decays. It is obvious from the above discussion that intermolecular complex formation is taking place in the solution's low alkanol concentration region.

From Figure 2, with increasing methanol concentration, the viscosity increases and reaches a maximum value. A further increase in the concentration of methanol has resulted in a decline in system viscosity. In literature, several instances of such maximums are recorded. In the viscosity figure, a well-defined peak is an indicator of strong particular interactions involving dipole-dipole relations, interactions of the acceptor-donor kind and other complex formation that favour interactions between component molecules [20-22].

Alcohol molecules are polar and they can accept protons and donate them as well. Therefore in addition to the hydrogen bonding interactions in the existing structures, dipole- dipole interactions and donor-acceptor type interactions are possible [23].

Table 1 presents the measured properties of molar volume, isentropic compressibility, free length and acoustic impedance. In Table 2, free volume, internal strain, relaxation time, enthalpy, relative interaction and strength of relaxation are seen. The duration of viscous relaxation and enthalpy increased gradually with concentration and reached a high value, with additional changes in methanol concentration resulting in a drop in the time of viscous relaxation and enthalpy. Relaxation strength (α) decreases first with methanol mole fraction, then increases with methanol concentration. This variance confirms the above discussion that in the mixtures investigated, strong particular interaction is active, resulting in complex development. From table 2, it is found that with an increase in the mole fraction of methanol, RA decreases.

Table 1: Calculated properties of molar volume, $V_m/10^{-5}$ m 3.mol^{-1}, isentropic compressibility, $k_s/10^{-10}$Pa^{-1}, inter molecular free length, $L_f/10^{-10}$m and acoustic impedance, $Z/10^6$ kg.m^{-2}.s^{-1} with mole fraction, x of methanol in aqueous solutions of tripotassium citrate and trisodium citrate at 308.15 K

x	V.	k.	1.1	Z
0.1 m aqueous tripotassium citrate				
0.0000	16.8476	4.1591	0.4271	15631
03263	12.5831	4.0997	0.4241	15616
0.5026	10.2807	4.1103	0.4246	15480
0.6430	8.4633	4.2027	0.4293	15158
0.7228	7.4525	4.4594	0.4423	1.4577
0.8044	63845	4.7660	0.4572	13955
0.8563	5.7424	5.4219	0.4877	12928
0.9057	5.1327	6.0531	05153	12057
0.9392	4.7734	7.1453	0.5598	1.0897
0.9728	43701	8.5603	0.6128	0.9786
1.0000	4.1255	11.1904	0.7006	0.8331
0.1 m aqueous trisodium citrate				
0.0000	15.1845	4.1490	0.4266	1.5637
0.2885	11.9102	4.1306	0.4256	1.5543
0.4792	9.7326	4.11%	0.4251	1.5439
0.6155	8.1849	4.1833	0.4284	1.5185
0.7024	7.2066	4.4088	0.4397	1.4667
0.7865	6.2659	4.7524	0.4566	1.3966
0.8425	5.6728	5.2172	0.4784	1.3160
0.8973	5.0664	6.0646	0.5158	1.2045
0.9290	4.7680	7.1249	0.5590	1.0946
0.9693	43609	8.5538	0.6125	0.9794
1.0000	4.1255	11.1910	0.7006	0.8331

Table 2: Calculated properties of free volume, $V_f/10^{-7}$ m^3.mol^{-1}, internal pressure, $\pi_i/10^6$ Pa, relaxation time, $\tau/10^{-12}$ s, enthalpy, H/J.mol^{-1}, Relative Association (RA) and relaxation Strength, (α) with mole fraction of methanol in aqueous solutions of tripotassium citrate and trisodium citrate at 308.15 K

X	V,	a.	r	H	RA	a
0.1 m aqueous tripotassium citrate						
0.0000	7.2133	18730	0.4242	31555.6	1.0000	0.0758
03263	3.6435	285.70	0.4920	35949.9	0.9788	0.0469
0.5026	2.2239	38537	0.5552	39618.7	0.9623	0.0351
0.6430	13661	516.12	0.6332	43680.8	0.9438	0.0375
0.7228	1.0156	620.14	0.6933	46215.9	0.9324	0.0756
0.8044	0.7344	765.95	0.7543	48902.1	0.9203	0.1170
0.8563	0.6006	879.04	0.8176	50478.0	0.9144	0.2050
0.9057	0.5214	993.06	0.8361	50970.8	0.9000	0.2666
0.9392	0.5276	103823	0.8231	49558.9	0.8867	0.3557
0.9728	0.5280	1100.88	0.8104	48109.6	0.8779	0.4434
1.0000	0.6864	1048.17	0.7147	43242.3	0.8618	0.5506

		0.1 m aqueous trisodium citrate				
0.0000	5.8960	214.69	0.4365	32599.6	1.0000	0.0720
02885	3.2235	308.71	0.5067	36768.0	0.9802	0.0523
0.4792	1.9872	414.99	0.5663	40389.3	0.9616	0.0344
0.6155	1.2510	543.47	0.6476	44482.5	0.9442	0.0320
0.7024	0.9430	650.03	0.7007	46845.1	0.9338	0.0658
0.7865	0.7051	786.19	0.7591	49261.9	0.9207	0.1133
0.8425	0.5946	889.20	0.7965	50442.5	0.9076	0.1714
0.8973	0.5032	1013.63	0.8458	51354.6	0.9022	0.2679
0.9290	0.4513	1094.52	0.9139	52186.7	0.8947	0.3578
0.9693	0.5247	1104.70	0.8120	48174.9	0.8807	0.4434
1.0000	0.6864	1048.17	0.7147	432423	0.8638	0.5506

Conclusions

Mixtures are prepared from methanol with aqueous tripotassium and trisodium citrate solution. At 308.15 K, the ultrasonic speed, density and viscosity are measured. Properties such as relaxation time, relative association, internal pressure enthalpy and relaxation power are assessed from the experimental effects of ultrasonic velocity, density and viscosity and even some of the deviation/excess properties have been assessed.

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