Physico-Chemical Study of Tetrabutylammonium Bromide Solutions in Methanol and Ethanol at Different Temperatures

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Abstract

Viscosity and density measurements at concentration range (0.0040-0.1661mole/L) for the tetrabutylammonium bromide (TBABr) solutions in methanol and ethanol at various temperatures (298.15, 303.15 and 308.15 K) are reported. The viscosity A and B coefficient was calculated from the Jones–Dole equation and found to be decreased from methanol to ethanol. The Gibbs free energy of viscons flow of (TBABr) solutions in methanol and ethanol we're calculated from experimental viscosity measurements using Eyring equation. The apparent molal volumes ϕ_v for these solutions at different temperatures we're also obtained from experimental density measurements.

Keywords : Tetrabutylammonium bromide, Jones–Dole equation.

Introduction

Viscosities of electrolyte solutions were among the earliest studies in the field of solution chemistry and have influenced the developments of our view of the solution process. The viscosity of a solution is a measure of its resistance to flow, which is fundamentally a kinetic process. Viscosities of electrolytic solutions have long been used as an indication of amount of structure within a solution [4]. The relative viscosity η_r of an electrolytic solution is given by the well known Jones–Dole equation [1, 2].

$$\eta_r = \frac{\eta}{\eta_\circ} = 1 + A\sqrt{c} + Bc \quad \text{.................................(1)}$$

Where η and $\eta_\circ$ are the viscosity of the solution and pure solvent, respectively, and c represents the solute concentration. The A coefficient takes account of ion-ion interactions and can be calculated from ionic interaction theory [2], while the B coefficient reflects the effect of solute–solvent interaction on solution viscosity. The Jones-Dole equation normally used in its linear form as follows

$$(\eta_r - 1)/\sqrt{c} = A + B\sqrt{c} \quad \text{................................(2)}$$

Many articles have been written concerning the effect of the halide and tetraalkylammonium ions on transport properties of aqueous solutions [6-9]. In this paper we are reporting viscosity and density measurements and calculating Jones-Dole coefficients and apparent molar volume of TBABr solutions in methanol and ethanol at three temperatures 289.15, 303.15 and 308.15 K.

Experimental

Materials: Methanol and ethanol were obtained from Aldrich with a purity of (>99.8 mol %). Tetrabutylammonium bromide was obtained from Fluka with a purity of (>99 mol %). These products were subjected to no further purification but the solvents were dehydrated with activated molecular sieve (type 4A) that produced by Union Carbide Company then filtered before use.

Measurement Techniques

An Ubbelohde–type glass capillary tube viscometer with a Schott – Gerate automic measuring unit model AVS300 was used. The time was recorded automatically with accuracy of ± 0.01 s. For density measurements, digital type (DMA 60/602) Anton Paar densimeter. Temperature was controlled with ± 0.01 K using water bath model Schott–Gerate CT 1150. Full details about the two instruments are reported in previous works [14, 13]. Preparation of tetrabutylammonium bromide solutions in alcohols with concentration range (0.0040 – 0.1661) mole/L were obtained by dissolving the salt in methanol or ethanol, and the solutions were homogenized and used after (24) hrs.

Results and Discussion

Kinematics viscosity (ν) and density (ρ) were experimentally measured in concentration range (0.0040–0.1661) mole/L for tetrabutyl-ammonium bromide (TBABr) solutions in methanol and ethanol at (298.15, 303.15 and 308.15 K). As shown in the tables below. Where Tables (1) and (2) showed the measured density and absolute viscosity data. In Figs. (1) and (2) were shown relationship between concentration and absolute viscosity for these solutions.

Table (1)

Density ρ, Viscosity η and Apparent Molal Volume ϕ_v for the TBABr in methanol at different temperatures.

c/ mole L^{-1}	ρ / g cm^{-3}	η / cP	ϕ_v / cm^{-3} $mole^{-1}$
T= 298.15 K			
0.0042	0.78666	0.539	293
0.0107	0.78811	0.544	191
0.0149	0.78933	0.547	146
0.0228	0.79099	0.551	144
0.0285	0.79213	0.552	145
0.0444	0.79466	0.563	165
0.0808	0.79547	0.582	261
0.1221	0.79600	0.604	318
0.1661	0.79630	0.629	328
T= 303.15			
0.0042	0.77864	0.531	953
0.0107	0.80056	0.535	107
0.0149	0.80519	0.537	96
0.0228	0.80970	0.541	73
0.0285	0.81016	0.544	119
0.0444	0.81275	0.553	157
0.0808	0.82121	0.572	260
0.1221	0.83890	0.589	280
0.1661	0.84002	0.616	295
T= 308.15 K			
0.0042	0.76613	0.523	407
0.0107	0.76034	0.524	143
0.0149	0.76765	0.527	85
0.0228	0.77054	0.530	60
0.0285	0.77309	0.534	111
0.0444	0.77932	0.539	127
0.0808	0.79635	0.555	240
0.1221	0.79801	0.579	255
0.1661	0.81012	0.597	274

Table (2)

Density ρ, viscosity η and apparent molal volume ϕ_v for the TBABr in ethanol at different temperatures.

c/ mole L^{-1}	ρ /gcm^{-3}	η / cP	ϕ_v / cm^{-3} $mole^{-1}$
T= 298.15 K			
0.0042	0.78875	1.103	175
0.0079	0.78932	1.113	149
0.0114	0.79128	1.120	8
0.0150	0.79219	1.127	26
0.0314	0.79275	1.156	203
0.0500	0.79277	1.184	279
0.0748	0.79552	1.218	273
0.0996	0.79700	1.247	287
0.1241	0.79964	1.279	282
T=303.15 K			
0.0042	0.78438	0.997	573
0.0079	0.78458	1.003	481
0.0114	0.78719	1.009	162
0.0150	0.78769	1.013	171
0.0314	0.78885	1.033	248
0.0500	0.79076	1.054	258
0.0748	0.79227	1.079	281
0.0996	0.79701	1.101	250
0.1241	0.79731	1.128	277
T= 308.15 K			
0.0042	0.77849	0.902	2812
0.0079	0.78095	0.907	1279
0.0114	0.78256	0.911	831
0.0150	0.78300	0.916	693
0.0314	0.78483	0.933	470
0.0500	0.78641	0.950	406
0.0748	0.78836	0.971	373
0.0996	0.79310	0.991	319
0.1241	0.79361	1.012	330

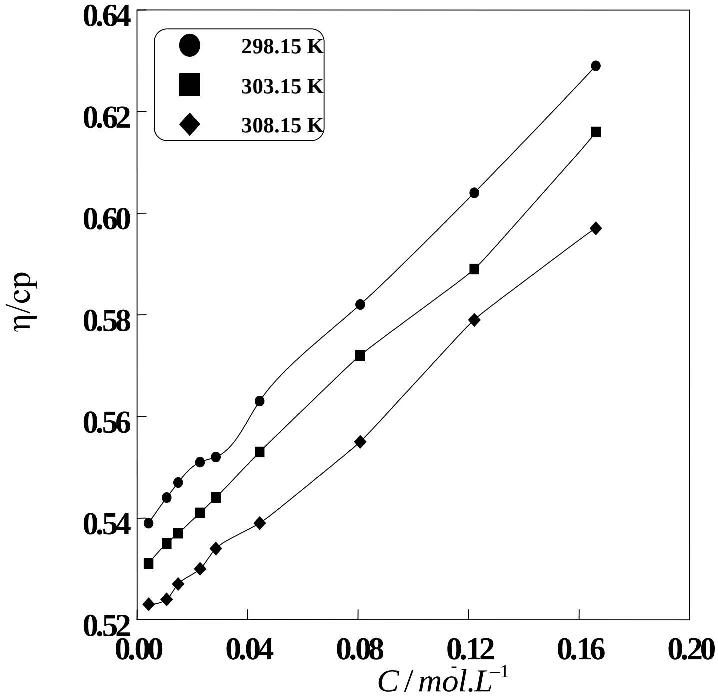

Fig.(1) The viscosity η as a function of molar concentration c for TBABr in methanol solvent at different temperatures.

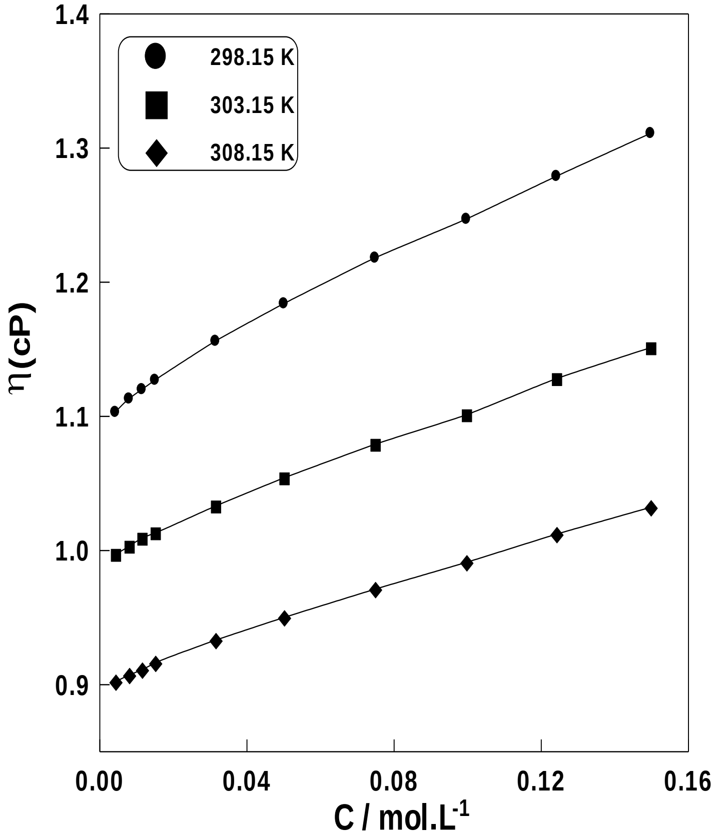

Fig.(2) The viscosity η as a function of molar concentration (c) for TBABr in ethanol solvent at different temperatures.

It can be observed that density, kinematic viscosity and absolute viscosity decrease with increasing temperatures and from methanol to ethanol in the same concentration and temperature. The viscosity of a liquid decrease markedly as temperature is raised [8]. As the temperature increased, more molecules are able to escape from the potential wells provided by their neighbors and so the liquid becomes more fluid. Fig.(3) and (4) were illustrated plotting of $(\eta_r - 1)/\sqrt{c}$ versus $\sqrt{c}$ for solutions at different temperatures. The constants (A) and viscosity coefficient (B) were obtained respectively from the intercept and slope of these Figures and are listed in Table (3).

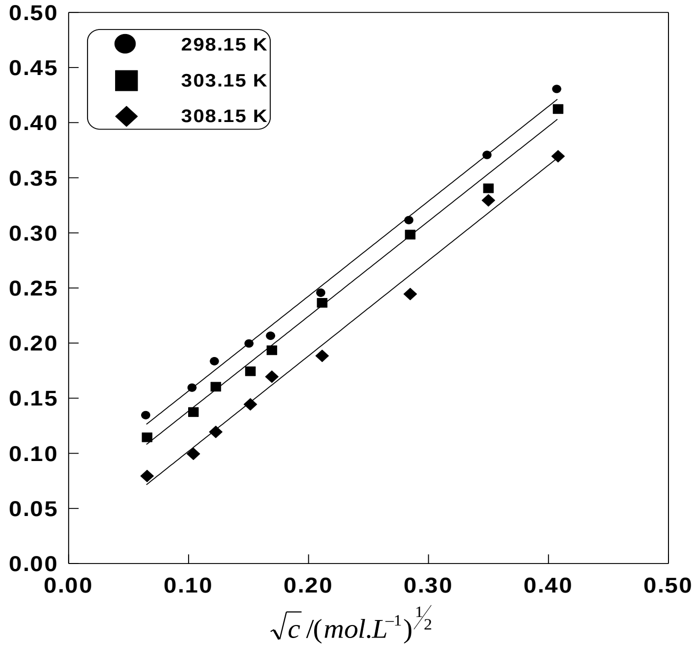

Fig.(3) The parameter η_{rel} -1/ $\sqrt{c}$ as a function of $\sqrt{c}$ for TBABr in methanol solvent at different temperatures.

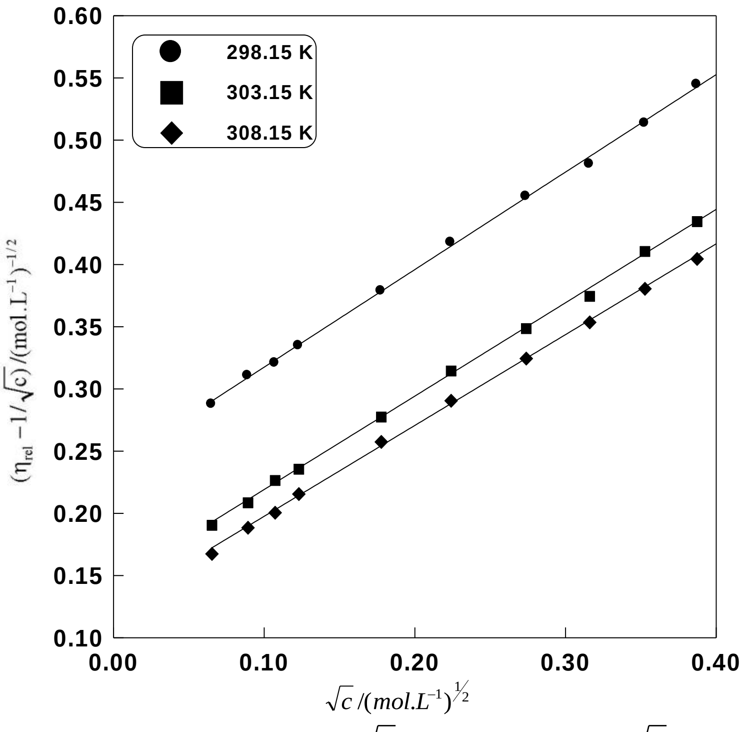

Fig.(4) The parameter $(\eta_{rel}$ -1)/ $\sqrt{c}$ as a function of $\sqrt{c}$ for TBABr in ethanol solvent at different temperatures.

Table (3)
Jones-Dole constants A and B values for TBABr solutions in methanol and ethanol at different temperatures.

T/ K	*A/(mole $L^{-1})^{-1/2}$*	*B/ L $mole^{-1}$*
TBABr in Methanol		
298.15	0.041	0.860
303.15	0.052	0.862
308.15	0.015	0.865
TBABr in Ethanol		
298.15	0.024	0.784
303.15	0.014	0.750
308.15	0.012	0.730

Viscosity coefficient (B), the ion – solvent parameter represents the higher terms of the long – range columbic forces, hydrodynamic or size and shape effect, solvation effect and chemical structural effects. The intercept (A) values were small and contributed very little to the concentration dependence of viscosity. This term in the viscosity equation is interpreted as the contribution from interionic forces that tend to interfere with the flow of one layer of solution past another. And because of the little effect of (A) values, logically can be neglected (according to [5], (A) values ranged between (0.01) for aqueous solutions to (0.02) for non-aqueous solutions). The tetraalkylammonium ions expected to be hydrophobic, and so their anomalous B-coefficient in water should be a reflection of the ions hydrophobic [3]. The properties of such hydrophobic solutes arose from the solvent – solvent interactions in a region of structurally rigidified water around the alkyl surface of the solute [5]. Thus, it is assumed that the structurally region is one of higher viscosity, accordingly for the large B- coefficient and their increase with size of the tetraalkylammonium ions. Viscosity coefficient B for TBABr in aqueous solutions is (1.24) [5] are larger than the corresponding values in methanol solutions and the latter is larger than this in ethanol solutions. These effects must be due to the large tetrabutylammonium ions (Bu_4N^+), since the contribution to the B value from the bromide ion is very small (B for Bu_4N^+ is 1.28 and for Br^- is -0.04 at 25 ^oC) [5]. This could be due to that water reinforcement about the hydrocarbon side chains of Bu_4N^+ ions forms a larger moving entity and, at the same time, increases the bulk viscosity by increasing the degree of hydrogen bonding in their vicinity. Since, hydrogen bonding forces decreases as the alkyl chains of alcohol increase the B value decreases from methanol to ethanol solutions. (B) Coefficient decreases with increased temperatures for aqueous solutions, whereas the values are about constant for methanol and ethanol solutions. The changing of temperatures had no effect on (B) values which agrees with literature. [11]. to calculate the activation energy of a viscous flow (ΔG^*) for the prepared alcoholic solutions, Eyring equation [12] had been applied. From the obtained data, ΔG^* for methanol and ethanol solutions respectively are 115 and 854 J/mole, we concluded that solvents process was more in methanol than ethanol. Apparent molal volume had been calculated by using equation (3):-

$$\phi_v = M/\rho + 1000(\rho^\circ - \rho)/m\rho\rho^\circ \quad ....(3)$$

Where (ρ°) and (ρ) are the densities of the pure solvent and solution, respectively. M, (molecular weight of the solute) (m), molality of solvent Tables (1) and (2) were listed the apparent molal volume data of solutions at different temperatures. According to the equation (4), the linear relationship between (ϕ_v) values and ($\sqrt{c}$) can be represented [15] as follows:

$$\phi_v = \phi_v^\circ + S_v\sqrt{c} \quad ....(4)$$

Where, (ϕ_v°) apparent molar volume at infinite dilution, or limiting apparent molar volume, (S_v) limiting slope. The calculated data from linear plots refers to the clathrate like structure [10] between TBABr ions and alcohol molecules. Extrapolated values of (ϕ_v°) at finite dilutions are not used due to difficulty of obtaining the true value from the curvature line. In contrast, (S_v) values obtained from the slope, of the straight line could be used to support the viscometers behavior.

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الخلاصة

تم القياس العملي للزوجة والكثافة على مدى تركيز (٠.٠٠٤٠ – ٠.١٦٦١ mole / L) لبروميد tetrabutylammonium (TBABr) في محاليل الميثانول والايثانول في درجات حرارة مختلفة (٢٩٨.١٥، ٣٠٣.١٥ ٣٠٨.١٥ و K). + تم حساب معامل اللزوجة B من المعادلة جونز دول James Dole وجدت انها انخفضت من الميثانول إلى الإيثانول. حسبت طاقة جيبس الحرة للجريان اللزج لمحلولي (TBABr) في الميثانول والايثانول من قياسات اللزوجة العلمية باستخدام المعادلة Eyring. وتم أيضا الحصول على الحجم المولي الظاهري في درجات حرارة مختلفة من القيم العلمية لكثافة المقاسة.

الكلمات الرئيسية: بروميد Tetrabutylammonium، جونز دول المعادلة، جيبس الحرة والطاقة، وحجم مولالي ظاهر، vicosity، Eyring المعادلة.