

Apparent Molar Volume, Density and Viscometric Studies of Alcohols in Aqueous Solution at Different Temperatures

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Abstract: Densities and viscosities of alcohols at different temperature (298.15, 303.15, 308.15, 313.15K) have been measured from experimental data. The apparent molar volume, limiting apparent molar volume, Jones- doles A and B coefficients were calculated. The results show strong solute- solvent interaction that indicates all selecting alcohols are structure makers in aqueous solution.

Keywords: Density, Viscosity Limiting apparent molar volume, Hepler constant, Jones Dole coefficient

1. Introduction

Apparent and partial molar volumes provide useful information about various types of interactions occurring in solutions¹⁻⁶. These studies are of great help in characterizing the structure and properties of solutions because the solution structure is of great importance in understanding the nature of action of bioactive molecules in the body system⁷⁻⁸. The addition of protic and an aprotic organic solvent to water brings about a sharp change in non – ionic solute molecules. The structure of solution is important to understand the nature of action many alcohols has gained significant popularity as a in the production of bio-diesel trans esterification & relatively safe fuel for flueless, referred as bioethanol fires. Ethanol is used in medical wipes and in most common antibacterial hand sanitizer gelsare, produced industrially on a large scale. Alcohols are used in the production for manufacturing of various chemicals including butyl acrylate, butyl acetate, glycol ethers, and plasticizers it is also used as a direct solvent in paints, dyes, varnishes, coatings, and for other industrial purposes⁹⁻¹¹.

2. Materials And Methods

All the chemical methanol, ethanol and t-butanol were used in the present study of analytical grade. Freshly distilled water with specific conductance of $\sim 10^{-6} \Omega \text{cm}^{-1}$ was used to preparing solution throughout the experiment. The aqueous solution of alcohols was made by weight and molalities were converted in to molarities using the standard expression¹². The densities of solutions were measured at different temperature (298.15, 303.15, 308.15, 313.15 K) using a viscometer made by Borosil glass. The mass measurements were done on digital electronic balance (Sartorius GC103). Viscosity determines with calibrated U shaped Ostwald viscometer with sufficiently long reflux time more than 100 sec. to avoid kinetic energy correction. The viscometer was averaged from three readings for each solution. The calibration of density bottle and viscometer¹²⁻¹³ was done by using doubly distilled water. An average of triplet measurement was taken in to account. Temperature was controlled by thermostatic water – bath.

Method

The apparent molar volume can be calculated from density data using the following equation¹³.

$$\phi_v = M/d_0 - 1000(d-d_0)/d_0c$$

Where d_0 and d are the densities of solvent and solution respectively: c is the molar concentration in gm./lit. and M is molecular weight of solute. The apparent molar volume can be considered to be the sum of the geometric volume of the solute molecules and changes that occur in to the solution due to its interaction with solvent. The data are filled to Masson¹⁴ equation and calculate limiting partial molar volume and experimental slope by least square method.

$$\phi_v = \phi_v^0 + S_v \sqrt{C}$$

Time of flow were determined for carboxylic acids under study at chosen concentration and temperature from 20- 40⁰ C. The viscosity were determined from the formula $\eta / \eta_0 = td / t_0d_0$ were η , t , d are the absolute viscosity, time of flow and density of solution, while η_0 t_0d_0 are same quantities for the solvent water. The viscosity data was analyzed according to Jones- dole equation¹⁵.

$$\eta / \eta_0 = \eta_r = 1 + Ac^{1/2} + Bc$$

Where η_r is relative viscosity, c is molar concentration the constant A is the Falkenhagen coefficient and B is the Jones-dole coefficient related to the solute- solvent and solute – solute interaction respectively. Viscosity data has been analyzed with the help of Jones- dole equation from the linear plots of $[(\eta / \eta_0) - 1] / c^{1/2}$ versus $c^{1/2}$ by computerized least square method. Determination of the free energy of activation of viscous flow of per mole of solute and solvent at different temperatures with a view to obtained additional information, evaluated by the Eyring viscosity relation¹⁵⁻¹⁶.

$$\Delta G^* = RT \ln (\eta_0 V_1 / h N)$$

The values of ΔS^* and ΔH^* were calculated by the relation and summarized.

$$\Delta S^* = -d(\Delta G^* / dT)$$

3. Results and Discussion

The value of apparent molar volume of alcohols at different temperature (298.15, 303.15, 308.15, 313.15 K) given in Table 1.1. It shows Δv is linear function of concentration and obeys Masson's equation.

Perusal of Table 1.2. Show that the value of Δv^0 for all alcohols is positive in water but decreases with increasing temperatures again since Δv^0 is a measure of solute solvent interaction, the positive value indicate strong solute solvent interaction which suggest that the overall structural order is enhanced in aqueous solution. The presence of ion solvent interaction between the molecules promotes the structure making effect of solutes in water. Δv^0 is a limiting apparent molar volume of the solute also called the apparent molar volume at infinite dilution. It is evident from table that the values of S_v are positive for all alcohols in aqueous solution at different temperature. Since S_v is a measure of ion-ion interaction so the results indicate the presence of weak ion-ion interaction. The Δv value in water is present investigation has good agreement with reported value²¹⁻²³. According to Gurney co-sphere overlap model always produce overlap of the co-sphere of two ions or polar group or an ion with hydrophilic group positive volume change. On the other hand overlap of the co-sphere of an ion with that of hydrophilic groups result a negative volume change. Results indicate that ion-hydrophilic and hydrophilic interactions predominate over the ion-hydrophobic and hydrophobic-hydrophobic interactions.

$$\Delta v^0 = a_0 + a_1 T + a_2 T^2$$

Where T is temperature in Kelvin. The value of coefficient a_0, a_1 and a_2 are given in table, calculated by differentiating above equation with respect to temperature.

$$\Delta v^0_E = (\delta^2 \Delta v^0 / \delta T^2)_p$$

The Limiting apparent molar expansibilities for alcohols in aqueous solution obtain at different temperature are calculated. It is found that Δv^0_E value increase with rise in temperature, this increase Δv^0_E with temperature ascribed to the presence of caging effect¹⁶. The structure making / breaking capacity of solute in aqueous solution may be interpreted with the help of Hepler¹⁷ equation on the basis of sign of giving expression.

$$(\delta \Delta v^0_E / \delta T)_p = (\delta \Delta v^0 / \delta T^2)_p = -a_2$$

The sign of $(\delta^2 \Delta v^0 / \delta T^2)_p$ second derivative of limiting apparent molar volume of solution with respect to temperature at constant pressure, which correspond to structure making of breaking properties of solution was determined. The determined value of $(\delta^2 \Delta v^0 / \delta T^2)_p$ has been found to be positive for all three alcohols structure making properties.

The value of viscosity of all studied of three alcohols at different temperatures (298.15, 303.15, 308.15, 313.15 K) given in table 1.1. Viscosity of aqueous solution of alcohols has been determined as a function of their concentrations. The values of coefficients A and B of the Jones - Dole equation have been determined by computerized least square method and the result has been showed in Table 1.3. "B" coefficient are constant and characteristics of ion-ion and

ion solvent interaction respectively. The value of A coefficients are negative and very small for all the three alcohols indicating the presence of weak ion-ion interaction.

Perusal of table 1.3 shows that the value of B- coefficient for all alcohols in aqueous solution is positive, since B is measure of solute-solvent interaction and its value depend on size and shape of solute. Positive B value indicates the existence of ion solvent interaction. A decrease in the value of B- coefficient with the rise of temperature represents structure promoting effect. This is due to ordering and a sort of enforcement of hydrogen bonded structure around the solute. At higher temperature, the surrounded sheath of solvent molecule around the water is broken and ion-solvent interaction is weakened. That further supporting earlier conclusion drawn from Δv^0 and S_v . Recently it has been emphasized by many workers¹⁸ that (dB/dT) is a better decisive factor for determine structure making / breaking nature of any solute rather than the B- coefficient. The value of (dB/dT) were calculated from the slope of the curve obtained by plotting B- coefficient value against temperatures and these values given in table 1.3. Table 1.3 shows at higher temperature B is less and Δv is higher than at low temperature. (dB/dT) is negative underline the greater hydration at higher temperature¹⁹⁻²⁰. Higher B and negative (dB/dT) disclose the structure making capacity of carboxylic acids. These are in identical agreement with the conclusion drawn from Hepler equation as discussed earlier. According to volumetric and viscometric behavior these non electrolyte solute act overall as water structure builder due to hydrophobic hydration and hydrogen bonding between solute and water molecules. Similar explanation had drawn from stereo chemical, kinetic and thermo dynamical studies²¹⁻²³ alcohols. Hydrophobic hydration of alcohols depends on their confirmation and configuration of hydroxy group. The hydration of alcohols has been explained with the help of concept of compatibility through specific hydration model²⁴⁻²⁶.

4. Conclusion

Densities and viscosities of methanol, ethanol, t-butanol (0.05-0.2m) in aqueous at 298.15, 303.15, 308.15 and 313.15K. The experimental value of density and viscosity were used to evaluate partial molar volume, limiting apparent molar volume, experimental slope, partial molar expansibility, Hepler constant, Falkenhagen coefficient, Jones-Dole coefficient and dB/dT coefficient. Free energy of activation of per mole of solute & solvent, activation enthalpies and entropy also have been calculated by the using equation and explains structure making tendency in terms of transition state theory. The value of activation energy ΔG^* , activation enthalpy ΔH^* were found to be positive while activation entropy ΔS^* were found to be negative at all, causes experimental temperatures suggesting that the transition state is associated with bond making ability with increased order. Using this value partial molar transfer of alcohol has been studied in terms of co-sphere overlap model. The experimental viscosity data is in good agreement with the Jones-dole and Modified Jones-Dole equation. On according to further discussion these all alcohols are behave as structure promoter solute & their capacity in the order of methanol < ethanol < t-butanol.

Table 1.1(A) Densities (d) Viscosities(η) and Apparent molar volume(ϕ_v) of **Methanol + Water Mixture** at different temperature.

Alcohols C mol.dm ⁻³	298.15 K			303.15 K			308.15 K			313.15 K		
	d (g.cm ⁻³)	η (cp)	ϕ_v (cm ³ mol ⁻¹)	d (g.cm ⁻³)	η (cp)	ϕ_v (cm ³ mol ⁻¹)	d (g.cm ⁻³)	η (cp)	ϕ_v (cm ³ mol ⁻¹)	d (g.cm ⁻³)	η (cp)	ϕ_v (cm ³ mol ⁻¹)
Methanol + H₂O												
0.00	0.9970	0.8937		0.9956	0.8007		0.9940	0.7225		0.9922	0.6560	
0.05	0.9980	0.9089	50.19	0.9966	0.9041	49.26	0.9950	0.9006	48.35	0.9909	0.8962	47.44
0.10	0.9983	0.9293	45.01	0.9968	0.9224	44.21	0.9952	0.8560	43.27	0.9910	0.8324	42.35
0.15	0.9984	0.9495	40.14	0.9970	0.9419	39.19	0.9954	0.8354	38.25	0.9911	0.8203	37.32
0.20	0.9985	0.9702	36.16	0.9972	0.9622	35.18	0.9956	0.8282	34.24	0.9912	0.8134	33.30
Ethanol+ H₂O												
0.05	0.9987	0.9662	56.54	0.9968	0.9582	54.93	0.9932	0.9424	52.34	0.9927	0.9336	50.85
0.10	0.9988	0.9706	54.21	0.9969	0.9696	52.10	0.9934	0.9591	48.54	0.9928	0.9443	48.54
0.15	0.9989	0.9870	52.18	0.9970	0.9787	49.85	0.9936	0.9641	46.56	0.9929	0.9565	46.56
0.20	0.9990	0.9987	50.41	0.9974	0.9842	48.28	0.9938	0.9772	45.58	0.9930	0.9602	45.58
t-Butanol+ H₂O												
0.05	0.9992	0.9769	66.24	0.9973	0.9475	64.34	0.9952	0.9343	62.43	0.9944	0.9275	59.55
0.10	0.9995	0.9893	60.82	0.9974	0.9501	58.30	0.9953	0.9439	56.48	0.9945	0.9324	53.68
0.15	0.9996	0.9921	56.81	0.9975	0.9627	54.28	0.9955	0.9536	52.36	0.9946	0.9482	49.46
0.20	0.9997	0.9992	53.17	0.9976	0.9987	50.78	0.9957	0.9682	48.85	0.9947	0.9554	45.65

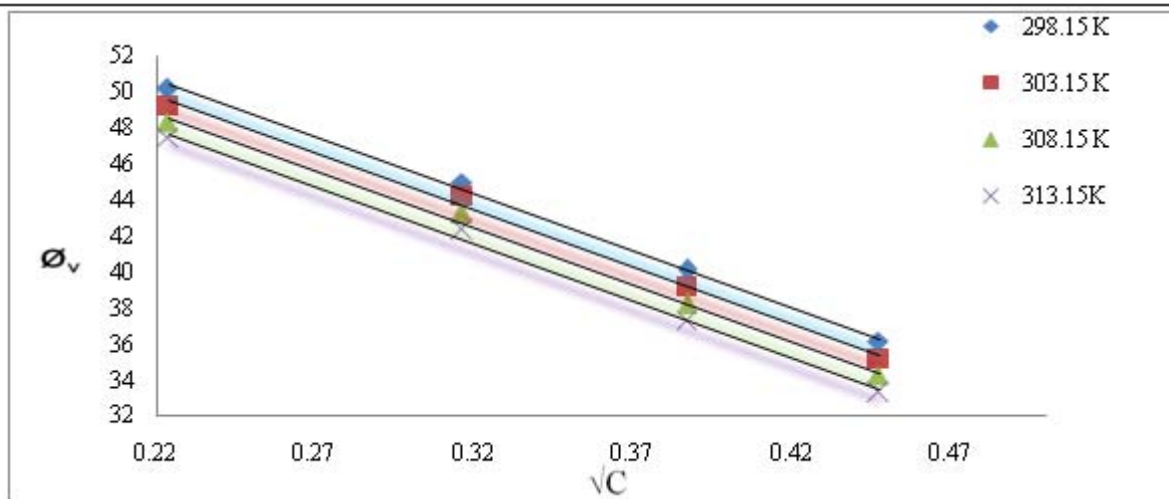


Figure 1.1 (A): Plots of ϕ_v versus \sqrt{C} of Methanol in aqueous solution at different temperatures

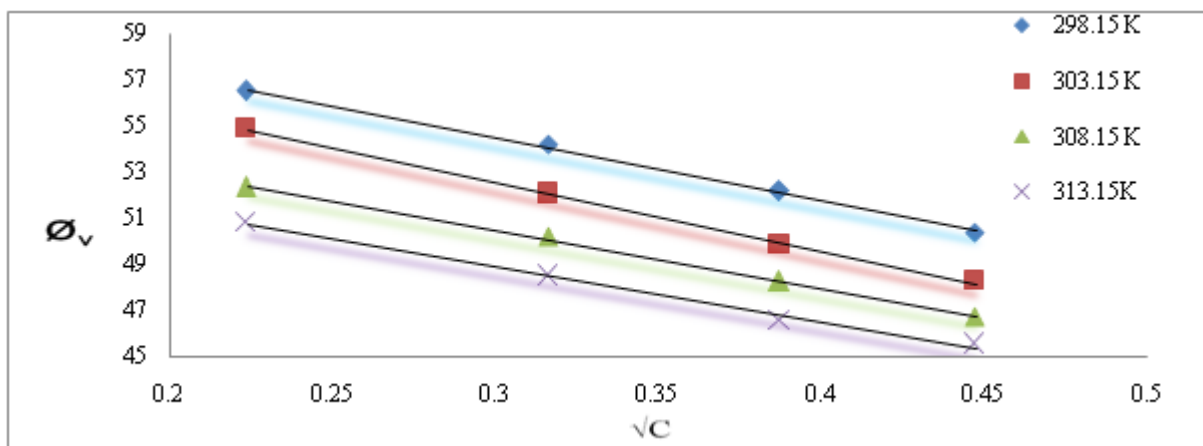


Figure 1.1(B): Plots of ϕ_v versus \sqrt{C} of Ethanol in aqueous solution at different temperatures

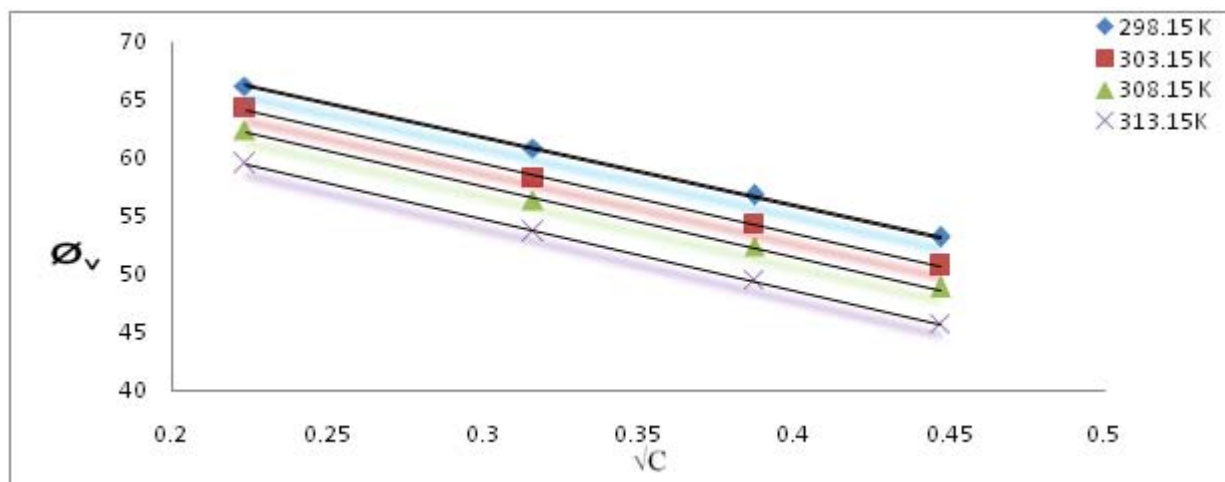


Figure: 1.1 (C) Plots of ϕ_v versus \sqrt{C} of t-Butanol in aqueous solution at different temperatures.

Table 1.2 (A): Least square fit values of Limiting Apparent Molar Volume (ϕ_v^0), Experimental Slope (S_v), ϕ_E^0 and Hepler constant $(\delta^2 \phi_E^0 / \delta T^2)_p$ of Alcohols + Water Mixture at different temperature.

Temp (°K)	ϕ_v^0 (cm ³ mol ⁻¹)	S_v (cm ³ lit ^{1/2} mol ^{-3/2})	ϕ_E^0 (cm ³ mol ⁻¹ K ⁻¹)	$(\delta^2 \phi_E^0 / \delta T^2)_p$
Methanol+ H₂O				
298.15	51.20	6.71	1.04	1.907x10 ⁻¹
303.15	50.14	6.72	1.05	2.009 x10 ⁻¹
308.15	49.92	6.73	1.06	2.015 x10 ⁻¹
313.15	48.00	6.81	1.19	2.015 x10 ⁻¹
Ethanol+ H₂O				
298.15	57.14	8.72	1.18	1.503 x10 ⁻¹
303.15	55.03	8.73	1.21	1.509 x10 ⁻¹
308.15	53.11	8.75	1.28	1.509 x10 ⁻¹
313.15	51.22	8.76	1.31	1.512 x10 ⁻¹
t- Butanol + H₂O				
298.15	67.11	14.06	1.20	2.341 x10 ⁻¹
303.15	65.74	14.16	1.24	2.347 x10 ⁻¹
308.15	63.89	14.19	1.29	2.349 x10 ⁻¹
313.15	60.05	14.21	1.34	2.351 x10 ⁻¹

Table 1.3 (A): Least square fit values of coefficient A and B of Jones – Dole Equation and Standard Deviation of Alcohols + Water

Temp (°K)	A (m ² mol ⁻¹)	B (m ³ mol ⁻¹)	S.D.
Methanol+ H₂O			
298.15	0.1615	0.201	0.17
303.15	0.1400	0.207	0.16
308.15	0.1310	0.239	0.14
313.15	0.1246	0.277	0.13
Ethanol+ H₂O			
298.15	0.1900	0.204	0.15
303.15	0.1800	0.212	0.13
308.15	0.1700	0.460	0.11
313.15	0.1600	0.535	0.10
t- Butanol + H₂O			
298.15	0.2020	0.205	0.21
303.15	0.1910	0.279	0.19
308.15	0.1820	0.496	0.17
313.15	0.1750	0.537	0.15

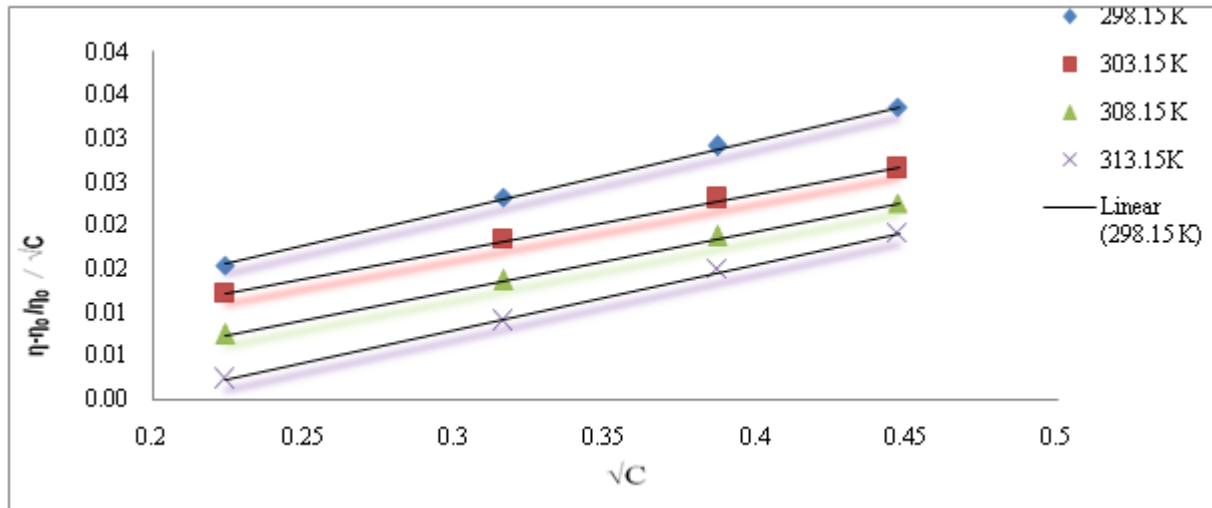


Figure 1.1 (a): Plots of $(\eta - \eta_0) / \eta_0 / \sqrt{C}$ versus \sqrt{C} of Methanol in aqueous solution at different temperatures.

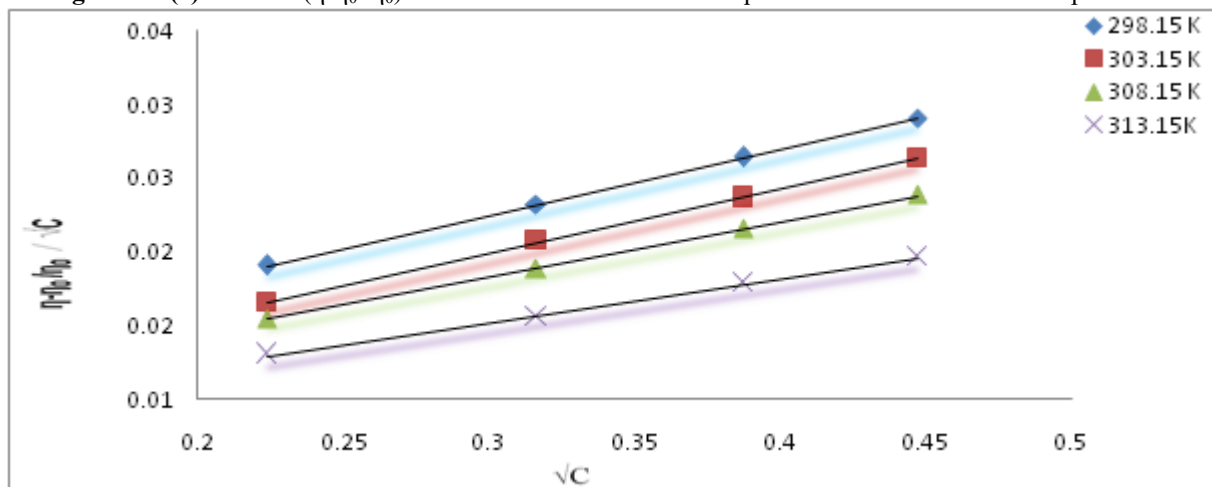


Figure 1.1(b): Plots of $(\eta - \eta_0) / \eta_0 / \sqrt{C}$ versus \sqrt{C} of Ethanol in aqueous solution at Different temperatures

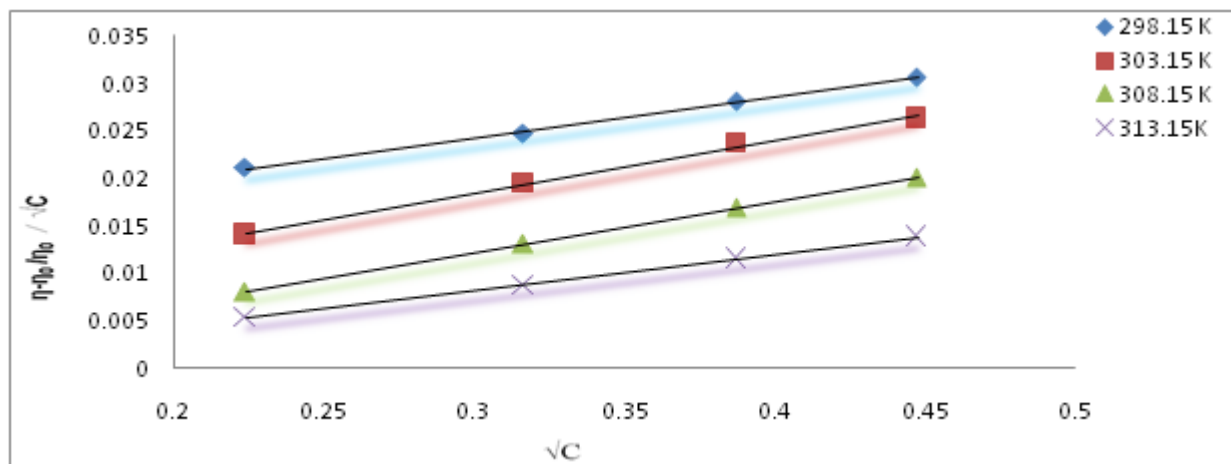


Figure 1.1 (c): Plots of $(\eta - \eta_0) / \eta_0 / \sqrt{C}$ versus \sqrt{C} of t-Butanol in aqueous solution at different temperatures.

Table 1.4 (A) Thermodynamic Parameters ΔG^* , ΔH^* and ΔS^* of Alcohols + Water Mixture in aqueous solution.

Alcohols C mol.dm ⁻³	ΔG^* (KJ mol ⁻¹ K ⁻¹)				ΔH^* (KJ mol ⁻¹ K ⁻¹)	$-\Delta S^*$ (J mol ⁻¹ K ⁻¹)
	298.15K	303.15K	308.15K	313.15K		
Methanol + H₂O						
0.05	13.483	13.388	13.235	13.146	10.230	-23.963
0.10	14.949	14.858	14.771	14.486	11.563	-24.759
0.15	16.300	16.213	16.110	16.092	12.369	-25.986
0.20	16.427	16.327	16.273	16.243	13.897	-26.358
Ethanol + H₂O						
0.05	16.692	15.457	14.208	13.879	11.492	-26.356
0.10	18.431	17.350	16.073	15.704	12.986	-26.981
0.15	20.114	18.834	17.667	17.362	13.869	-27.869
0.20	21.409	20.788	19.045	18.761	14.254	-28.975
t- Butanol + H₂O						
0.05	17.726	17.236	16.329	16.186	13.566	-27.865
0.10	18.810	18.608	18.302	17.737	14.256	-28.875
0.15	19.890	19.760	19.532	18.969	15.236	-29.856
0.20	21.907	21.603	20.556	20.271	16.352	-30.587

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