Study of Molar Volume and Viscosity of Tetracyclin Hydrochloride in Methanol-Water System at 298.15°K

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ABSTRACT

In this research article, we have described to Viscometric properties of Tetracyclin hydrochloride (TCH) are measured in 20% (v/v) methanol-water system 298.15°K. The related parameters are the experimental values of viscosity (η) allow to determine relative viscosity (η_r), viscosity B-coefficient of the Jones-Dole equation, free energies of activation of viscous flow $\Delta\mu_1^{0\neq}$ and $\Delta\mu_2^{0\neq}$ per mole solvent and solute respectively. The excess molar volume, excess viscosity, excess Gibb's free energy, and interaction parameter of Grunberg and Nissan have also been calculated. These studies help in characterizing the structure and properties of solutions. The addition of an organic solvent to water brings about a sharp change in the solvation of ions. The dependence of these properties with temperature are shown. The results are interpreted in terms of solute-solvent interaction.

Keywords: Molar Volume; Viscosity; Tetracyclin hydrochloride; solute-solvent interaction

INTRODUCTION

Thermodynamic and physical properties data have a well recognized importance in design calculations involving chemical separations, fluid flow and heat transfer. Studies on the volumetric and transport properties of binary liquid mixtures provide information on the nature of the interactions between the constituents (Domanska et al, 2003, Sandler et al, 1999, Renon et al 1968, Lorimer et al, 1975, Bard et al 2008, Abrams et al, 2003). Thermodynamic functions of mixtures represent the difference between the functions of actual and ideal solutions, and thus are useful in the study of molecular interactions and arrangements. In particular, they reflect the interactions that take place between solute-solute, solute-solvent, and solvent-solvent (Catalan et al 2000, Marcus et al 1985).

The thermo-physical properties of liquid systems are strictly related to the molecular interactions present in different binary liquid mixtures. The variation of these properties with composition gives us important data about intermolecular interactions and the structure. There is a wide range of possible interactions between the components of a mixture, such as hydrogen bonding, molecular associations, charge transfer, dipole-dipole and dipole-induced dipole interactions.

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Received on: 07-08-2014
Revised on: 27-11-2014
Accepted on: 29-11-2014

As a consequence of these interactions, deviations occur from ideal behaviour of dielectric constant and viscosity. These deviations can be defined by excess dielectric constants and viscosities (Bardwaj et al, 1998, Mandal et al, 2008, Arnett et al, 1966).

Tetracycline is a broad spectrum bacteriostatic antibiotic. It is effective against many gram-positive (e.g. Staphylococcus and Streptococcus) and gram-negative (e.g. Clostridium, Pseudomonas and Haemophilus) bacterial infections, as well as against Rickettsia, Chlamydia, Borrelia, Mycoplasma etc. At higher oral doses tetracycline may produce gastrointestinal irritation, with nausea, vomiting, and diarrhea, as well as renal failure. Bone and teeth discoloration are known to occur in humans under clinical treatment with high levels of tetracycline. The drugs of the tetracycline group may produce renal disease and renal impairment (Varanda et al, 2006). Tetracyclines, particularly demeclocycline, may cause renal medullary toxicity, such as proximal tubular damage with polyuria, glucosuria, and aminoaciduria (Stezowski et al, 1976). In the present investigation following parameters are measured by Viscosity data of TCH is measured in 20%(v/v) methanol-water system 298.15°K is used to determine B-coefficient (B) and constant characteristic of ion-ion interactions (A) excess viscosity (VE), and excess molar free energy of activation of flow (GE). The interaction parameters Gruenberg and Nissan (d) were also calculated and reported. The parameters are analysed to be evaluated to understand solute-solvent interaction.

EXPERIMENT

A stock solution of 0.100M $C_{22}H_{24}N_2O_8 \bullet$ HCl (TCH)is prepared in 20% (v/v) methanol water solvent by direct

Table 1: Viscosities and densities of TCH in 20% (v/v) methanol–water system at 298.15°K

Concentration (moldm−3)	Density (ρ) gm cm⁻³	Viscosity (η) mPa s
0.0100	0.9447	0.9406
0.0200	0.9457	0.9679
0.0300	0.9459	1.0143
0.0400	0.9476	1.0345
0.0500	0.9486	1.1197
0.0600	0.9494	1.1672
0.0700	0.9507	1.2338
0.0800	0.9539	1.3016
0.0900	0.9552	1.3687
0.100	0.9562	1.5005

weighing. Mass dilution technique used for preparation of other concentrations. The concentration of the solutions involved in the experiment was taken in range from 0.010M to 0.100 M. Mass dilution technique was applied to prepare the solution of different concentration. Viscosities were measured by capillary viscometer.

The Viscometer was calibrated with triple distilled water. Viscosity values were determined using the relation,

$$\eta = \rho \left(Kt - \frac{L}{t} \right), \qquad (1)$$

Where η is a viscosity, ρ is the density of the liquid, t is the flow time, and K and L are constants for given viscometer. The flow time was measured with digital stop watch with accuracy of ± 0.01 sec. The K and L were obtained by measuring the flow time of triple distilled water at temperature298.15°K. All measurements were carried out in triplicate.

RESULT AND DISCUSSION

Viscosities and Densities

The values of viscosities and densities are reported in Table 1 and figure 1A and figure1B. Viscosities of the solution are increasing with the increase in concentration.

Excess Molar Volume and Excess Viscosity

Excess Molar Volume. It is calculated from following expression:

$$V^E = V-(X_1V_1 + X_2V_2) \qquad (2)$$

Where V = Molar volume of solution,

$V1$=Molar volume of mixed solvent,

$V2$ = Molar volume of solute, $X1$ = Mole fraction of solvent, and $X2$ = Mole fraction solute.

The data are shown in Table 2.

Excess Viscosity

The mixing of different compounds give rise to solutions that generally do not behave ideally. The deviation from ideality is expressed by many thermodynamic properties, particularly by excess or residual extensive properties. Excess thermodynamic properties of mixtures correspond with the difference among the actual property and the property if the system behaves ideally and thus are useful in the study of molecular interactions and arrangements. In particular, they reflect the interactions that take place among solute–solute, solute–solvent, and solvent – solvent species. The excess viscosity (η^E) has been evaluated from the observed viscosity of the solution and that of its pure components using the relation (Yadava et al, 2010, Yang et al, 2010, Jones et al, 1929,).

$$\eta^E = \eta - (X_1\eta_1 + X_2\eta_2) \qquad (3)$$

where η^2 = viscosity of solute. The data presented in Table 2 shows that the η^E values are positive in the entire concentration range at both the temperatures. This shows the presence of specific solute –solvent – interactions such as hydrogen bond formation in these systems (Feakins et al 1974).
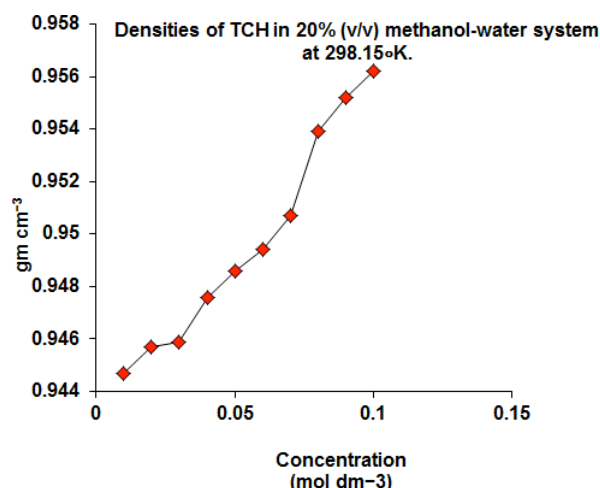

Figure 1a: Densities of TCH in 20% (v/v) methanol–water system at 298.15°K

The Jones-Dole equation was used to analyze the viscosities following the equation (Aralaguppi et al 1991).

$$\eta_r = \eta / \eta 1 = 1 + Ac^{1/2} + Bc, \quad (4)$$

where A = constant characteristic of ion–ion interactions, = constant characteristic of ion–solvent interactions, and c = molar concentrations.
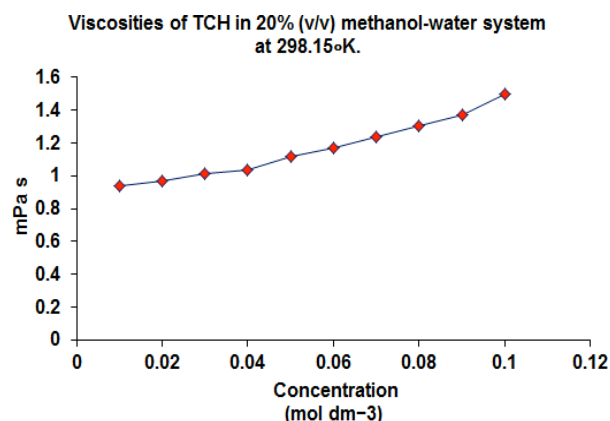

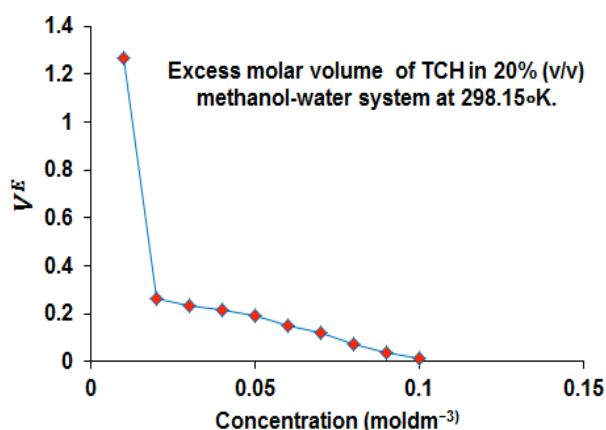**Figure 1b: Viscosities of TCH in 20% (v/v) methanol–water system at 298.15°K**

Figure 2a: Excess molar volume of TCH in 20% (v/v) methanol–water system at 298.15°K
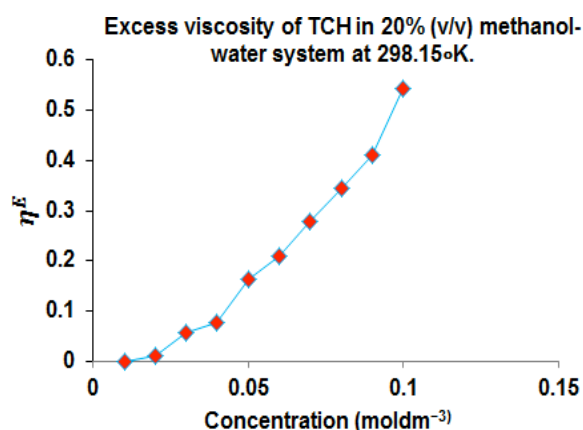

Figure 2b: Excess viscosity of TCH in 20% (v/v) metha---nol–water system at 298.15°K

The values of relative viscosities are presented in Table 3. The Falkenhagan coefficient A is also given for electrolytes. The B–coefficients obtained as slope of straight line have been recorded in Table 3.

Einstein (Pal et at al 2003) proposed an equation

$$\eta = \eta 1 (1 + 2.5\,v), \quad (5)$$

Where **v** = aggregate volume of the particles in a unit volume of solution.

The previous equation describes the concentration dependence of the relative viscosity of solution of electrolyte. The term 2.5 is taken to be valid for electrolyte and it is equivalent to the product in BC in the Jone–Doles equation. The data are presented in Table 3.

Activation Parameter: The viscosity data have also been analyzed on the basis of a transition state theory of relative viscosity as suggested by Rama Rao et al. 2004. The viscosity B–coefficient is expressed by equation

$$B = \frac{\left(\overline{V}_1^0 - \overline{V}_2^0\right)}{1000} + \frac{\left[\left(\overline{V}_1^0/1000\right)\Delta\mu_2^{0\neq} - \Delta\mu_1^{0\neq}\right]}{RT}, \quad (6)$$

where V_1^0 = partial molar volume of solvent, V_2^0 = partial molar volume of solute, $\Delta\mu_1^{0\neq}$ = free energy of activation per mole of solvent, $\Delta\mu_2^{0\neq}$ = free energy of activation per mole of solute, B = viscosity B–coefficient. R = universal Gas constant (8.314 JK−1 mol−1), and T = temperature (298.15°K).

Solvent Activation Parameter: $(\Delta\mu_1^{0\neq})$, $\Delta\mu_1^{0\neq}$ is calculated from equation proposed by Eying et al.

$$\Delta\mu_1^{0\neq} = RT\,\ln\left(\frac{\eta_1\overline{V}_1^0}{HN}\right), \quad (7)$$

Where N = Avogadro's number (6.023 × 10^{23} gm·atom), h = Planck's constant (6.626 × 10^{-34} J·sec), and $\eta 1$ = viscosity of solvent.

Solute Activation Parameter: $(\Delta\mu_2^{0\neq})$ Solute activation parameter, $\Delta\mu_2^{0\neq}$, is derived from following expression:

$$\Delta\mu_2^{0\neq} = \Delta\mu_1^{0\neq} + \left(\frac{RT}{\overline{V}_1^0}\right)\left[1000B - \overline{V}_1^0 - \overline{V}_2^0\right]. \quad (8)$$

The values of solvent $\Delta\mu_1^0$ and solute $\Delta\mu_2^0$ and activation free energies are given in Table 4.

According to Feakins model, the greater the value of $\Delta\mu_2^{0\neq}$ the greater the structure ability of the solute. The values of $\Delta\mu_2^{0\neq}$ are very large as compared to those of $\Delta\mu_1^{0\neq}$, which suggests that the formation of transition state is accompanied with breaking and distortion of inter molecular bonds.

Excess Free Energy of Activation for Viscous Flow GE and Interaction Parameter d

Excess Free Energy of Activation for Viscous Flow GE.

The extra–thermodynamic property, excess Gibb's free energy of activation of flow (G^E) for the solution has been computed from the Eyring equation (Grunberg et al, 1954 Grunberg et al, 1949).

Table 2: Excess molar volume and excess viscosity of TCH in 20% (v/v) methanol-water system at 298.15°K

Concentration (moldm^{-3})	Excess molar volume (V^E)	Excess viscosity (η^E)
0.0100	1.2692	−0.0257
0.0200	0.2648	0.0112
0.0300	0.2351	0.0578
0.0400	0.2148	0.0781
0.0500	0.1946	0.1633
0.0600	0.1537	0.2106
0.0700	0.1208	0.2772
0.0800	0.0734	0.3451
0.0900	0.0387	0.4121
0.100	0.0158	0.5440

Table 3: B-coefficient, *A*, *B* of TCH in 20% (v/v) methanol-water system at 298.15°K

Concentration (moldm^{-3})	B_C	A	B
0.0100	−0.0056		
0.0200	−0.0457		
0.0300	−0.0959		
0.0400	−0.1179		
0.0500	−0.2098	0.1029	−6.5589
0.0600	−0.2613		
0.0700	−0.3330		
0.0800	−0.4066		
0.0900	−0.4788		
0.100	−0.6215		

Table 4: Activation parameters of TCHin 20% (v/v) methanol-water system at298.15°K

Concentration (moldm^{-3})	$\Delta\mu_1^{0\neq}$(in kJmol^{-1}) 10^5	$\Delta\mu_2^{0\neq}$(in kJmol^{-1}) 10^5
0.0100	2.6245	−6.4835
0.0200	2.6284	−6.4799
0.0300	2.6330	−6.4753
0.0400	2.6347	−6.4733
0.0500	2.6427	−6.4655
0.0600	2.6468	−6.4614
0.0700	2.6523	−6.4559
0.0800	2.6576	−6.4504
0.0900	2.6625	−6.4457
0.100	2.6715	−6.4366

$$G^E = RT [\ln \eta\ V − (X_1\ln \eta_1 V_1 + X_2\ln \eta_2 V_2)] \quad (9)$$

The values are listed in Table 5. The value of G^E increases with the increase in concentration of solute and also increases with the increase in temperature suggesting the interactions became stronger.

Interaction Parameter (d). The impact of solute on viscosity is understood in terms of parameter d, which is regarded as a measure of the strength of interaction between components of solution. It has been estimated using relationship proposed by Gruenberg and Nissan [23]

$$\ln \eta = X_1\ln \eta_1 + X_2\ln \eta_2 + X_1 X_2 d, \quad (10)$$

where d = Grunberg and Nissan parameter: da$W$RT, (11)where$W$= interaction energy. The values of d are reported in Table 5.

$$d \propto \frac{W}{RT} \quad (11)$$

In figure 3 shows that the density of Tetracycline hydrochloride decreases slightly with increase in % of mixed solvent. The viscosity increases slowly up to 50% solvent and them sharply increases. The excess molar volume decreases sharply up to 20% and then slightly decreases up to 80 %.Excess viscosity remains no change up to 20% and then increases with higher % of solvent.

Table 5: Excess molar free energy of activation of flow (G^E) and Grunberg and Nissan constant TCH in 20% (v/v) methanol-water system at 298.15°K

Concentration (moldm⁻³)	Excess molar free energy of activation of flow (G^E)	Grunberg and Nissan (d)
0.0100	16.9677	0.0001
0.0200	56.1699	0.0004
0.0300	103.0464	−0.0011
0.0400	122.8587	−0.0006
0.0500	202.7111	−0.0004
0.0600	243.5636	−0.0002
0.0700	299.0244	−0.0002
0.0800	351.6796	−0.0003
0.0900	401.7945	-0.0001
0.100	494.6974	−0.0001
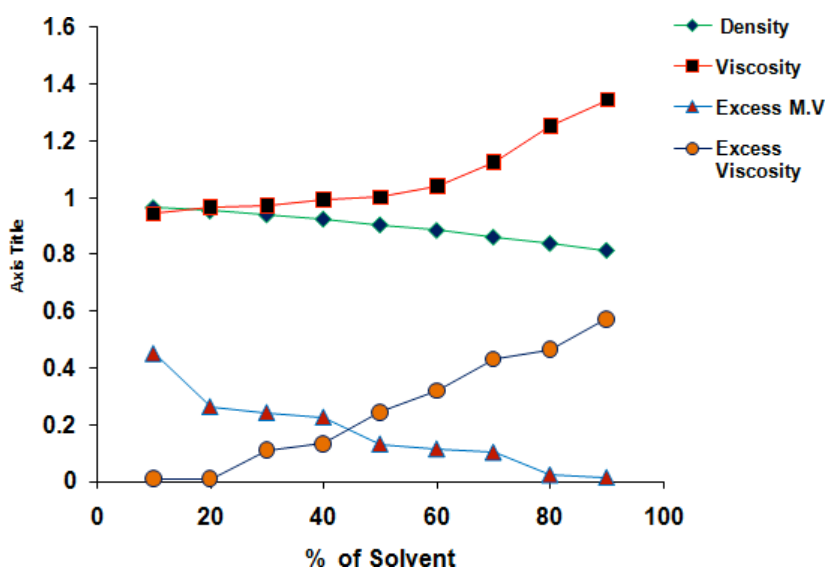
Figure 3: Density , Viscosity & Excess properties of different % of methanol-water at 0.002 M
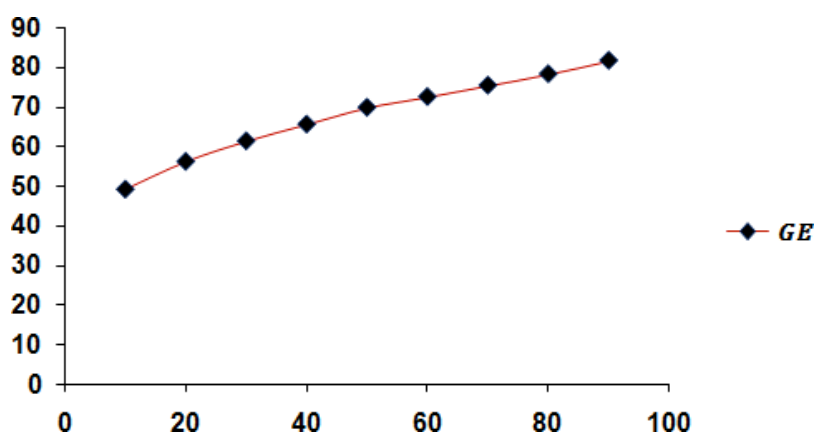
Figure 4: Gibbs free energy of different % of methanol-water at 0.002M

In figure 5 observed that Gibb's free energy of TCH in methanol-water solvent increases gradually with % of solvent. All these observations indicate there is a steady interaction between solvent and substrate up to 20% solvent (V/V) without any structure breaking. The ion- solvent interaction starts after 20% more effectively up to 50% and then structure breaking starts.

CONCLUSION

The present study shows the experimental data of transport properties is important in all these applications to understand the molecular interactions. Viscosity increases as a function of concentration and decreases in increase in temperatures. The values of B-coefficient show solute-solvent interactions in the present systems.Thevalues,$\Delta\mu_2^{0\neq}$, are very large as

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compared to those of $\Delta\mu_1^{0\neq}$ whichsuggests that the formation of transition state is accompanied with breaking and distortion of intermolecular bonds. Volumetric data are used to test molecular theories or models of solution to extend our understanding about molecular interactions among components.

ACKNOWLEDGMENTS

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