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STUDY OF EXCESS ULTRASONIC VELOCITY AND EXCESS GIBB'S FREE ENERGY IN BINARY LIQUID MIXTURES AT FOUR DIFFERENT TEMPERATURES T=(303.15,308.15,313.15 AND 318.15)K

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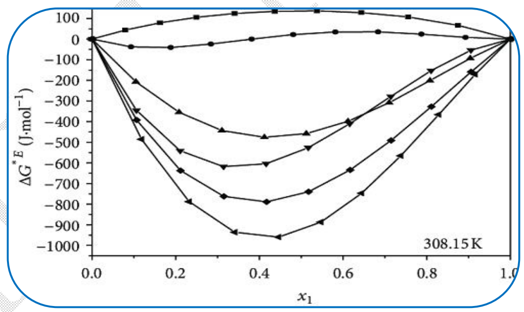
ABSTRACT :
Excess ultrasonic velocity (U^E) and excess Gibb's free energy of activation function (G^{*E}) have been calculated at four temperatures T=(303.15,308.15,313.15 and 318.15)K in binary liquid mixtures of methanol with quinoline by using the experimentally measured data of ultrasonic sound velocities, viscosities and densities. All these excess parameters have been fitted to Redlich-Kister polynomial expression. These results have been explained on the basis of molecular interactions present in the liquid mixtures.



KEYWORDS : *Excess viscosity; excess molar volume; quinoline; methanol.*

INTRODUCTION

The study of excess parameters is much important [1,2] for chemical separations, heat transfer, fluid flow. The knowledge of excess parameters in binary liquid mixtures has been useful in elucidating the structural properties [3-7] and various types of intermolecular interactions in liquid mixtures [8]. Quinoline is a hetero cyclic aromatic organic compound with the chemical formula C_9H_7N. Methanol, also known as methyl alcohol with chemical formula CH_3OH. In the present work, study of molecular interactions between the component molecules of binary liquid mixtures containing methanol with quinoline have been reported at four temperatures T=(303.15,308.15,313.15 and 318.15)K using excess parameters such as excess Gibb's free energy of activation function (G^{*E}) and excess ultrasonic velocity (U^E) over the entire mole fraction range of quinoline.

EXPERIMENTAL

The chemicals used for the present work are of AR grade (Quinoline from SDFCL and Methanol from MERCK) and they are purified with standard procedure [9]. The liquid mixtures of different concentrations are made by changing mole fractions with respect to Job's method.For preserving these liquid mixtures Stoppard conical flasks are used and they are left undisturbed to get thermal equilibrium. Ultrasonic interferometer (Mittal enterprises, India) is used for the measurement of velocities at a fixed frequency of 3MHz. Temperature controlled water bath is used for changing the temperature of the pure liquids and liquid mixtures by circulating water around the liquid cell. Densities of pure liquids and liquid mixtures are measured by specific gravity bottle. Shimadzu AUY220 electronic weighing balance is used for the measurements of mass of pure liquids and liquid mixtures with precision of + or - 0.1 mg. Ostwald's viscometer is used for the measurement of viscosity of pure liquids and liquid mixtures. The time of flow of liquid in the viscometer is measured with an electronic stopwatch with a precision of 0.01s.

THEORY

Excess ultrasonic velocity and excess Gibb's free energy of activation function are evaluated from the experimentally measured values of ultrasonic velocity (u), viscosity (η) and density (ρ) by using the following equations [10-13].

$$U^E = U_{exp} - (X_1U_1 + X_2U_2) \quad m.s^{-1} \quad \text{------(1)}$$

$$G^{*E} = RT\left[\ln(V\eta) - \sum_{i=1}^{N} x_i \ln(V_i\eta_i)\right] \quad J.mol^{-1} \quad \text{------(2)}$$

Here G^{*E} and U^E represent excess values of thermo-acoustical parameters such as Gibb's free energy of activation function and ultrasonic velocity respectively. X represent the molefraction with 1 and 2 indicate first and second component respectively. And also these excess parameters are fitted to the following Redlich-Kister equations [10-13]

$$A^E = x_1(1-x_1) - \sum_{i=1}^{N} A_i(2x_2-1)^i \quad \text{------(3)}$$

Here the values of A_i are calculated by the method of least square fit. The values of these parameters of each studied system are used to identify the standard deviation of the experimental and theoretical values. The standard deviation values are summarized by the following relation [10-13]

$$\sigma = \left[\sum (x_{exp} - x_{cal})^2 / (n-p)\right]^{1/2} \quad \text{------(4)}$$

Here n represent the number of experimental points, p is the number of parameters, X_{exp} and X_{cal} are experimental and calculated parameters.

RESULTS AND DISCUSSION

Experimentally measured values of ultrasonic velocities, densities and viscosities of pure liquids together with the literature values are given in **Table-1**.

Table-1: The values of ultrasonic velocities (U), densities (ρ) and viscosities (η) of pure liquids along with the literature values at temperature T=303.15K.

Liquid	Ultrasonic velocity U($m.s^{-1}$)		Density ρ($Kg.m^{-3}$)		Viscosity η ($N.s.m^{-2}$)	
	Exp	Lit	Exp	Lit	Exp	Lit
quinoline	1553.68	1547.00[14]	1085.45	1085.79[14]	2.9320	2.9280[14]
methanol	1084.14	1084[15]	795.18	795.1[15]	0.5068	0.5070[15]

The variations of excess parameters such as G^{*E} and U^E for the above binary liquid mixtures containing methanol with quinoline at four different temperatures T=(303.15,308.15,313.15 and 318.15)K are represented in **Fig-1** and **Fig-2** respectively. The Redlich–Kister coefficients (A_0, A_1,

A_2,A_3, A_4) and their standard deviations(σ) of all the evaluated excess parameters at four different temperatures T=(303.15,308.15,313.15 and 318.15)K are represented in **Table-2.**

Table-2: Values of Redlich –Kister coefficients (A_0, A_1, A_2,A_3, A_4) and their standard deviations(σ) of all the evaluated excess parameters in a binary liquid mixture of (quinoline + methanol) at temperatures 303.15,308.15,313.15 and 318.15K .

Excess Parameter	Co-efficients	Temperatures			
		303.15K	308.15K	313.15K	318.15K
G^{*E}x10^3	A_0	1.7384	2.1919	2.7775	3.3403
	A_1	0.9192	1.2923	1.7420	2.2753
	A_2	-0.4963	0.6152	-0.8853	1.2118
	A_3	-0.3704	-0.4737	-0.7205	-0.7072
	A_4	2.4741	3.9798	6.6535	9.8794
	σ	0.0043	0.0006	0.0012	0.0026
U^Ex10^2	A_0	4.8842	4.7252	4.5068	4.3171
	A_1	3.0226	3.3351	3.5536	3.5022
	A_2	4.2531	3.4673	3.3263	3.1622
	A_3	2.3358	1.6036	2.1273	2.4957
	A_4	-3.3220	-1.7653	-2.3470	-2.8930
	σ	0.0021	0.0018	0.0013	0.0009

Fig-1: Variations of excess Gibb's free energy of activation function (G^{*E}) in binary liquid mixture of (quinoline + methanol) with the mole fraction of quinoline at temperatures T=(303.15,308.15,313.15 and 318.15)K.

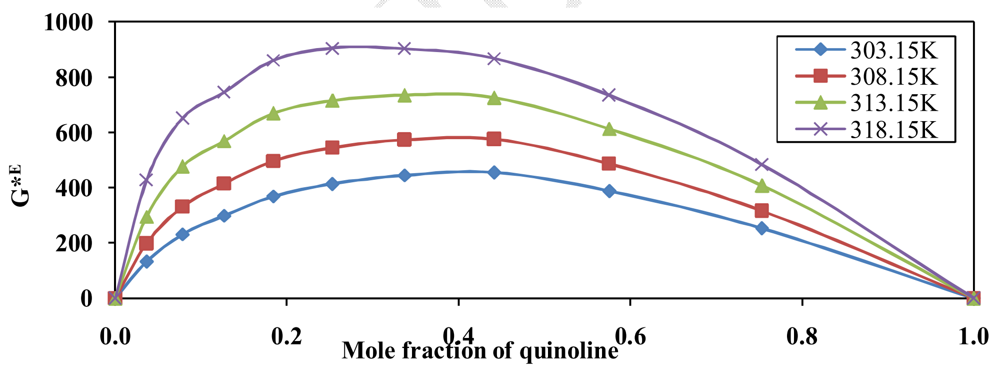
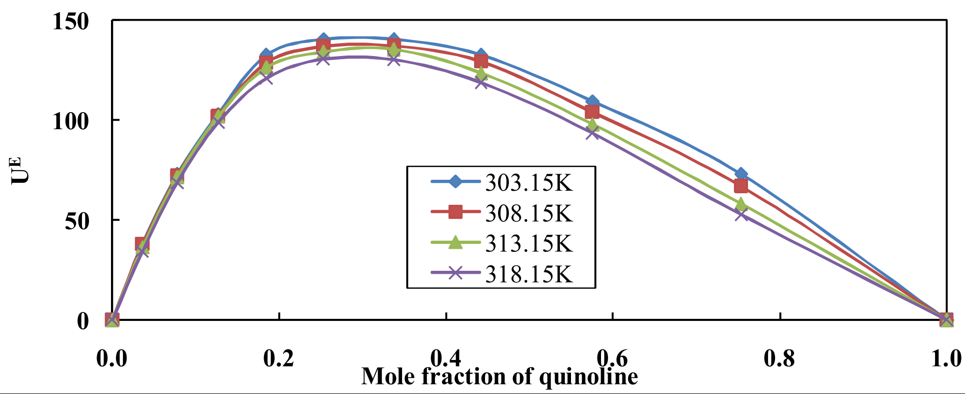


Fig-2: Variations of excess ultrasonic velocity (U^E) in binary liquid mixture of (quinoline + methanol) with the mole fraction of quinoline at temperatures T=(303.15,308.15,313.15 and 318.15)K.



The variation of excess Gibb's free energy of activation (**G^{*E}**) for the binary liquid mixture methanol with over the entire mole fraction range of quinoline at different temperatures is as shown in **Fig-3**.From **Fig-3** it is observed that, **G^{*E}** values are positive. According to Oswal *et al.*[16] and Reed *et al.*[17] the positive **G^{*E}** may be attributed to specific interactions and the positive values of **G^{*E}** show strong interactions.

Excess ultrasonic velocity (**U^E**) variations at different temperatures is as shown in **Fig-4**.It is observed from **Fig-4** is that, **U^E** values are positive .This produces negative values of excess compressibility. According to Reddy *et al* [18], the positive values of **U^E** show strong interactions. Also the positive values of U^E decrease with increase of temperature which show that strength of the interaction decreases with the increase of temperature in the binary liquid mixture studied.

CONCLUSIONS

Excess parameters such as excess Gibb's free energy of activation function (G^{*E}) and excess ultrasonic velocity (U^E) have been calculated. An analysis of these results suggests the presence of strong intermolecular interactions in binary liquid mixtures.

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