

Theoretical and Experimental Methods for Study of Binary mixtures viscosity at T= 303.15

Mohammad Almasi *

Department of Applied Chemistry, Faculty of Science, Malayer University, Malayer, 65174, Iran.

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ABSTRACT

Molecular interactions in binary mixtures composed of a xylene and selected 1-butanol 1-pentanol, 1-hexanol, 1-heptanol and 1-octanol was investigated by measuring the viscosity at T= 303.15 K. From experimental data, viscosity deviation was calculated. Values of viscosity deviations for all binary mixtures are negative and increase with increase of alcohols chain length. Obtained data were interpreted based on the type and magnitude of the physico-chemical interactions in the binary liquid systems. free volume theory was applied to correlate the viscosities of binary mixtures and correlated values by this model were good enough and obtained data were within the uncertainty region

1. Introduction,

The non-ideal behaviour of binary mixtures containing a self-associated component is primarily due to the specific interactions arising from the hydrogen bond between the polar groups of the component molecules. When two liquids are mixed together, the resulting changes in physical and thermodynamic properties can be considered as a sum of several contributions due to free volume change, change in energy, change in molecular orientations and steric hindrances.¹ Alcohols are of important class of hydrogen-bonded solvents and their -OH group participates in hydrogen bond formation as donor and acceptor of electrons. Our initial studies on the thermodynamics of alcohols solutions were motivated by a desire to better understand the interactions among the various functional groups with alcohols.²⁻⁴ Moreover, this work contributes to test the compatibility of free volume theory model to correlate the experimental viscosities.

2. Results and discussion

The experimental values of viscosities for binary mixtures at T= 303.15K are listed in Table 1. Binary viscosities increase with increasing the alcohols chain length. The viscosity deviation can be calculated as

$$\Delta\eta = \eta - x_1\eta_1 - x_2\eta_2 \quad (1)$$

where η is the mixture viscosity and η_1 and η_2 are the viscosities of pure components. Values of viscosity deviations were correlated by the Redlich – Kister⁵

$$\Delta\eta = x_1(1-x_1) \sum_{k=0}^N A_k (1-2x_1)^k \quad (2)$$

where x is the mole fraction of one component of mixture, A_k is the adjustable parameter and k is the order of polynomial. Values of viscosity deviations are presented in Table 1. Figure 1 indicates the $\Delta\eta$ values for binary mixtures xylene + 1-alkanol at T= 303.15 K. This figure shows that the viscosity deviations for xylene + 1-alkanol are negative and systematically tends to the larger negative values with an increase in the size of 1-alkanol. The algebraic values of $\Delta\eta$ fall in the order: 1-octanol > 1-heptanol > 1-hexanol > 1-pentanol > 1-butanol.

When the chain length of the alcohol increases, the hydrophobic character of the 1-alkanol amplifies and the interactions between unlike molecules weaken, resulting in a negative contribution to $\Delta\eta$. In alcohols with higher chain length, the relative volume contributions of the polar OH versus the non-polar alkyl chain for the alcohols decrease and the viscosity deviation increases.

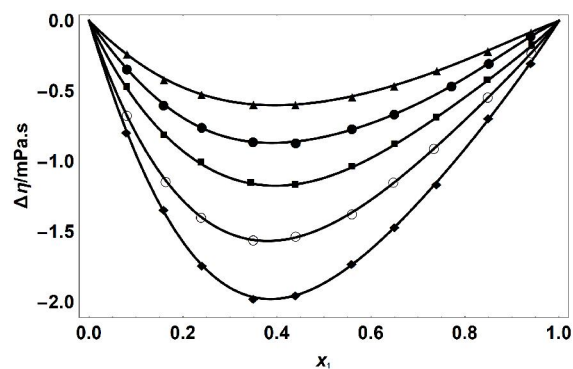


Fig 1. Viscosity deviations $\Delta\eta$ vs. mole fraction of xylene for binary mixtures of xylene with (▲) 1-butanol, (●) 1-pentanol, (■) 1-hexanol, (○) 1-heptanol, (◆) 1-octanol at T= 303.15 K.

* Corresponding Author:

E-mail address: m.almasi@malayeru.ac.ir (M. Almasi)

Table 1 Viscosities η and viscosity deviation $\Delta\eta$ for the binary mixtures at 303.15 K.

T/K = 323.15					
Viscosities(mPa.s) for Xylene +					
x_1	1-Butanol	1-Pentanol	1-Hexanol	1-Heptanol	1-Octanol
0	2.2708	3.0373	3.9379	5.0329	6.4073
0.081	1.9007	2.4971	3.1964	3.9530	5.0946
0.1595	1.5853	2.0483	2.5876	3.1599	4.1620
0.2395	1.3474	1.6918	2.1304	2.5724	3.2711
0.3501	1.1051	1.3231	1.6640	1.9684	2.3981
0.4397	0.9378	1.1220	1.3315	1.5998	1.9180
0.5601	0.7897	0.8996	1.0310	1.2000	1.4266
0.6497	0.7180	0.8000	0.8818	1.0050	1.1577
0.7404	0.6725	0.7240	0.7916	0.8480	0.9421
0.8492	0.6306	0.6521	0.6743	0.7110	0.7570
0.9407	0.6088	0.6289	0.6083	0.6193	0.6369
1	0.5893	0.5893	0.5893	0.5893	0.5893
$\Delta\eta$					
0	0	0	0	0	0
0.081	-0.234	-0.342	-0.473	-0.672	-0.793
0.1595	-0.417	-0.600	-0.817	-1.145	-1.342
0.2395	-0.521	-0.757	-1.010	-1.398	-1.74
0.3501	-0.592	-0.859	-1.155	-1.559	-1.975
0.4397	-0.594	-0.868	-1.170	-1.532	-1.951
0.5601	-0.539	-0.767	-1.040	-1.375	-1.729
0.6497	-0.46	-0.663	-0.880	-1.149	-1.467
0.7404	-0.353	-0.464	-0.690	-0.909	-1.162
0.8492	-0.212	-0.302	-0.425	-0.544	-0.692
0.9407	-0.080	-0.107	-0.176	-0.228	-0.301
1	0	0	0	0	0

Our next objective in this study is the correlation of the binary mixtures viscosity applying the free volume theory. In the free volume theory [6,7], the viscosity is expressed as the sum of two terms

$$\eta = \eta_0 + \Delta\eta^{res} \quad (3)$$

η_0 is the viscosity in the dilute gas limit, while the residual viscosity $\Delta\eta^{res}$ describes deviations from the dilute gas. For

η_0 the form proposed by Chung et al was used

$$\eta_0 = 40.785 \frac{\sqrt{M_w T}}{v_c^{2/3} \Omega^*} F_c \quad (4)$$

Ω^* is the reduced collision integral and F_c is an empirical factor. The residual viscosity is described by a generalized dumbbell model

$$\Delta\eta^{res} = 10^{-14} \rho N_a \zeta L^2 \quad (5)$$

Where ρ is the density, ζ is the friction coefficient and N_a is Avogadro's number and L^2 is an average quadratic length related to the size of the molecule. On the other hand, the viscosity depends on free spaces among the molecules defined as a free volume fraction f_V through the exponential relation

$$\Delta\eta^{res} = A \exp\left(\frac{B}{f_V}\right) \quad (6)$$

The combination of eqs 5 and 7 leads to the following equation

$$\Delta\eta^{res} = 10^{-14} \rho N_a L^2 \zeta_0 \exp\left(\frac{B}{f_V}\right) \quad (7)$$

ζ_0 is a friction coefficient related the mobility of the molecule and B is a parameter related to the free-volume overlap among the molecules. The final equation includes three adjustable parameters related to the structural and energetic properties of the fluid: L_V , α and B. The theory can be applied to mixtures by employing mixing rules for the three parameters. We applied a linear compositional mixing rule of the Lorentz type for the three parameters of the dense fluid term:

$$\alpha_{mix} = \sum_{i=1}^n \alpha_i x_i \quad (8)$$

$$B_{mix} = \sum_{i=1}^n B_i x_i \quad (9)$$

$$L_{V,mix} = \sum_{i=1}^n L_{V,i} x_i \quad (10)$$

Table 2 Optimized parameters of the Free-volume theory along with ADD

Entry	Compound	$\alpha \times 10^3$	B X10	L_V	AAD (%)
1	Xylene	14.3	1.4	0.37	2.17
2	2-Butanol	180.19	3.81	0.025	2.43
3	2-Pentanol	161.12	2.14	0.021	2.66
4	1-Hexanol	143.17	2.37	0.018	1.89
5	1-Heptanol	122.3	3.12	0.014	2.68
6	1-Octanol	109.71	4.16	0.011	1.93

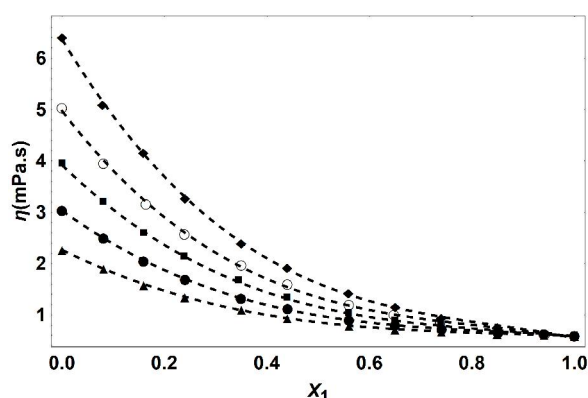


Fig 2. Experimental and calculated viscosities of xylene with (▲) 1-butanol, (●) 1-pentanol, (■) 1-hexanol, (○) 1-heptanol, (◆) 1-octanol at $T = 303.15$ K. (.....) Free volume theory

Here, it is remarkable that no binary adjustable parameters are used for the viscosity of mixtures. Three viscosity parameters were fitted to viscosity data of the pure fluid and adjustable parameters of the free volume theory are presented in Table 2 along with AAD. Comparison between the calculated viscosities

and experimental data are shown in Figure 2. The Agreement between experimental and calculated values is satisfactory.

3. Conclusion

This paper reports the viscosities and viscosity deviations for binary mixtures of xylene with selected 1-alkanols. Analyses suggest the presence of weak interaction in all binary mixtures due to the scattering forces. Free volume theory has been used to modeling the viscosities of pure state and binary mixtures.

4. Experimental

Xylene and all 1-alkanol were analytical grade and purchased from Merck with purity greater than 99 % of mass fraction and used as received without further purification. The measured viscosities for pure materials were compared with the literature values and results show the measurements are in agreement with literature. Viscosity measurements have been performed with an Anton-Paar SVM 3000 viscometer that corrects automatically viscosity related errors in the density by measuring the damping of the U-tubes oscillation. Prior to each series of measurements, the apparatus was calibrated using doubly distilled degassed water and dry air at the atmospheric pressure. Pure fluids used in the binary mixtures were degasified before the preparation of the samples using an ultrasonic bath.

The solutions were prepared by mass, using a digital balance (Mettler AE 163, Switzerland) with the precision ± 0.01 mg and stored in airtight stopped bottles to prevent evaporation of the samples. To minimize evaporation during the sample preparation, the less volatile component was charged first. The relative uncertainty is 0.04 for viscosity measurements and the uncertainty in the mole fraction was $\pm 1 \times 10^{-3}$.

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