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EXCESS AND DEVIATIONS PROPERTIES FOR THE BINARY SOLVENT MIXTURES OF TETRAHYDROFURFURYL ALCOHOL WITH SOME AROMATIC HYDROCARBONS AT 298.15K

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ABSTRACT. In this work, excess properties (e.g. excess molar volume (V^E), excess viscosity (η^E), excess Gibbs free energy of activation of viscos flow (ΔG^{*E}) and molar refraction changes (Δn_D) of binary solvent mixtures of tetrahydrofurfuryl alcohol (THFA) with aromatic hydrocarbons (benzene, toluene and p-xylene) have been calculated. This was achieved by determining the physical properties including density ρ, viscosity η and refraction index n_D of liquid mixtures at 298.15K. Results of the excess parameters and deviation functions for the binary solvent mixtures at 298.15 K have been discussed by molecular interactions that occur in these mixtures. Generally, parameters showed negative values and have been found to fit well to Redlich-Kister equation which has been used to obtain the coefficients and evaluate the standard error.

Keywords: *Binary systems, Tetrahydrofurfuryl alcohol, Deviations and excess properties, Density, Viscosity.*

INTRODUCTIONS

Interest in studying the theoretical and experimental properties of solvents mixtures has been significantly increased in the last two decades. The thermodynamic and transport information (e.g. fluids flow, heat and mass transfer) of mixtures systems are important in many chemical industries,

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solution theories and biological processes [1-4]. Moreover, for profound understanding the interaction properties between component molecules of liquid mixture, in terms of nature, strength of interaction and behavior of solution, the experimental excess properties are very important [5-8].

Tetrahydrofurfuryl alcohol (THFA), benzene, toluene and p-xylene are widely used in chemical industries. These solvents have been used in fuel, perfumes, cosmetics, lubricants, paints, dyes, printing ink, drugs, gums, resins, etc. [9,10]. The excess properties for these organic solvents are useful in investigating the molecular motion and packing, and interaction in their mixtures [11].

In this study, physical properties such as density, viscosity and refractive index were determined over a range of binary systems ((THFA+ Benzene), (THFA +Toluene) and (THFA+P-Xylene)) concentrations at 298.15K. Excess molar properties including V^E η^E, ΔG^{*E} and refractive index deviation were derived. Up to our knowledge, those binary solvent mixtures have not been studied for $V^{E,}$ η^E, ΔG^{*E}, and Δn_D at any temperature.

RESULTS AND DISCUSSION

In this work the retrieved data from experimentally obtained density (ρ) for binary systems (THFA + benzene, THFA + toluene and THFA + p-xylene) at 298.15 K were used to calculate V^E for binary solvent mixtures using following equation (1) [12]:

$$\mathrm{V^E} = \frac{X_1M_1 + X_2M_2}{\rho_{12}} - \frac{X_1M_1}{\rho_1} - \frac{X_2M_2}{\rho_2} \tag{1}$$

where X_1 and X_2 are the mole fractions, M_1 and M_2 are the molar masses and ρ_1, ρ_2 are densities of solvents 1 and 2; while ρ_{12} is the density of the mixture. Values of V^E and ρ of the binary solvent systems at a range of mole fractions of THFA with benzene, toluene and p-xylene are presented in Table 1. Excess viscosities were obtained using equation (2) [13]:

$$\eta^E = \eta_{12} - (X_1\eta_1 + X_2\eta_2) \tag{2}$$

where η_1 and η_2 are viscosities of solvents 1 and 2, respectively, η_{12} is the viscosity of mixture. The results are listed in Table 1.

Equation 3 was used to calculate (ΔG^{*E}) [14]:

$$\Delta \mathrm{G^{*E}} = \mathrm{RT}[\ln(\eta_{12}\mathrm{V}_{12}) - (\mathrm{X}_1\ln\eta_1\mathrm{V}_1) - (\mathrm{X}_2\ln\eta_2\mathrm{V}_2)] \tag{3}$$

where R is gases universal constant and T is the absolute temperature (K). V_1, V_2 are the molar volumes of solvents 1 and 2; while V_{12} is the molar volume for binary system. Table 1 shows the values of ΔG^{*E} determined from equation 3. V_{12} has been obtained from the below equation:

$$V_{12}= (X_1M_1 + X_2M_2)/ \rho_{12} \qquad (4)$$

Molar refraction (n_D) was calculated using the Lorentz-Lorenz equations (5,6, and 7) [15]

$$n_D=\left(\frac{n_{12}^2-1}{n_{12}^2+2}\right)\frac{X1M1+X2M2}{\rho_{12}} \qquad (5)$$

$$n_{D1} = \left(\frac{n_1^2-1}{n_1^2+2}\right)\frac{X1M1}{\rho_1} \qquad (6)$$

$$n_{D2} = \left(\frac{n_2^2-1}{n_2^2+2}\right)\frac{X2M2}{\rho_2} \qquad (7)$$

where n_{12} is the refractive index of the mixture; whereas n_1 and n_2 are the refractive index of solvent 1 and 2, respectively. The deviation from a molar fraction average of the molar refraction was computed according to the equation (8) [16,17]:

$$\Delta n_D=n_D-X_1n_{D1}-X_2n_{D2} \qquad (8)$$

where Δn_D represents the deviation value from molar fraction. Table 1 lists experimental n_D and $\Delta \mathbf{n_D}$ for the binary solvent mixtures.

For binary solvent mixtures, the excess function was determined using Redlich-Kister model equation (9) [18]:

$$X^E=X_iX_j\sum_{K=0}^{n} A_K(X_i - X_j)^k \qquad (9)$$

where X^E may represent V^E, η^E, ΔG^{*E} or Δn_D. X_i and X_j are the mole fractions of the components i and j, respectively. n is the degree of polynomial expansion and A_k denotes the polynomial coefficients.The equation (10) was used to calculate standard deviation (σ) for the excess parameters [19]:

$$\sigma = [\sum(X_{exp}^E - X_{calc}^E)^2/(M - n)]^{1/2} \qquad (10)$$

where *M* is the number of data points and *n* is the number of estimated parameters. The values of these coefficients and the standard deviation are given in Table 2.

For all the studied systems, the negative values of V^E, η^E, $\Delta G^{*E,}$ Δn_D follow the order: Benzene > Toluene > p-xylene. Fig.1 shows the deviations in molar volume for all the systems (THFA+ benzene), (THFA+ toluene) and (THFA+ p-xylene). The obtained negative values of V^E can be attributed to the interactions of dipolar-induced forces between the benzene ring of the aromatic hydrocarbons and hydroxyl group (OH) or oxygen of the THFA, which results the formation of electron donor-acceptor complexes and the breaking of the self-associations existing in pure solvents [20,21].

Table 1. Experimentally obtained and calculated values of density, viscosity and refractive index, $V^{E,}$ η^E, ΔG^{*E}, n_D and Δn_D for binary solvent mixtures of THFA+benzene, THFA+ toluene and THFA+ p-xylene at 298.15K.

X_1 THFA + X_2 benzene at 298.15K

X_1	ρ(g.cm^{-3})	V^E cm^{3}mol^{-1}	η	η^E mpa.s	ΔG^{*E} (J.mol^{-1})	n_D	Δn_D
0.0000	0.87372	0.00000	0.59951	0.00000	0.0000	1.4975	0.0000
0.0867	0.89294	-0.11763	0.65845	-0.08836	-218.2600	1.4882	-0.2377
0.2012	0.91623	-0.16936	0.81019	-0.12150	-299.6432	1.4754	-0.5832
0.3078	0.93673	-0.19441	0.99374	-0.14121	-348.0611	1.4664	-0.7895
0.3622	0.94663	-0.18579	1.10746	-0.14713	-362.5572	1.4636	-0.8175
0.5033	0.97132	-0.16189	1.48353	-0.15119	-372.4340	1.4581	-0.8077
0.5528	0.97965	-0.15214	1.65007	-0.14877	-366.4779	1.4571	-0.7589
0.6664	0.99804	-0.11675	2.13172	-0.13130	-323.4082	1.4552	-0.6238
0.8307	1.02332	-0.06816	3.09948	-0.10213	-251.8803	1.4545	-0.3136
0.9082	1.03474	-0.04150	3.77085	-0.06886	-169.9206	1.4536	-0.1879
1.0000	1.04761	0.00000	4.89883	0.00000	0.0000	1.4532	0.0000

X_1 THFA + X_2 toluene at 298.15K

X_1	ρ(g.cm^{-3})	V^E cm^{3}mol^{-1}	η	η^E mpa.s	ΔG^{*E} (J.mol^{-1})	n_D	Δn_D
0.0000	0.86224	0.00000	0.55464	0.00000	0.0000	1.4950	0.0000
0.0801	0.87733	-0.17517	0.55817	-0.16815	-416.0727	1.4855	-0.3714
0.2024	0.89945	-0.27578	0.67662	-0.24213	-598.5265	1.4750	-0.7081
0.3004	0.91712	-0.30678	0.82295	-0.25982	-641.8989	1.4670	-0.9415
0.3968	0.93436	-0.28668	1.01161	-0.26343	-650.4906	1.4624	-0.9856
0.5022	0.95335	-0.24312	1.27016	-0.26543	-655.2431	1.4581	-0.9821
0.5867	0.96872	-0.19668	1.55083	-0.24986	-616.8046	1.4562	-0.8887
0.7005	0.98983	-0.13909	2.08992	-0.19942	-492.1386	1.4553	-0.6653
0.7915	1.00704	-0.09509	2.64994	-0.16026	-395.4876	1.4547	-0.4714
0.8996	1.02791	-0.04847	3.57807	-0.09546	-235.6671	1.4539	-0.2334
1.0000	1.04761	0.00000	4.89883	0.00000	0.0000	1.4532	0.0000

X_1 THFA + X_2 p-xylene at 298.15K							
X_1	ρ(g.cm^{-3})	V^E cm^{3}mol^{-1}	η	η^E mpa.s	ΔG^{*E} (J.mol^{-1})	n_D	Δn_D
0.0000	0.85676	0.00000	0.61225	0.00000	0.0000	1.4945	0.0000
0.1074	0.87474	-0.20439	0.66272	-0.14414	-350.8699	1.4859	-0.5063
0.2045	0.89176	-0.38483	0.73091	-0.24813	-604.0360	1.4773	-0.9615
0.2921	0.90681	-0.42023	0.84477	-0.28553	-693.5423	1.4710	-1.2382
0.3968	0.92537	-0.43209	1.02825	-0.30671	-743.5405	1.4669	-1.3145
0.5168	0.94742	-0.40192	1.29614	-0.32474	-787.1356	1.4629	-1.2905
0.6108	0.96535	-0.35118	1.59703	-0.31146	-754.8408	1.4602	-1.1920
0.7255	0.98808	-0.25996	2.08926	-0.28134	-682.6599	1.4585	-0.9179
0.7811	0.99944	-0.20241	2.43108	-0.24543	-595.6440	1.4577	-0.7568
0.8856	1.02173	-0.10211	3.30304	-0.15625	-379.6321	1.4548	-0.4554
1.0000	1.04761	0.00000	4.89883	0.00000	0.0000	1.4532	0.0000

The results of deviations in viscosity (η^E) for mixtures (THFA+ benzene), (THFA+ toluene) and (THFA+ p-xylene) are illustrated in Fig.2. Interaction between components molecules believed to be due dispersion or weak dipole-dipole forces [22]. Moreover, THFA contains molecules with high polarity while aromatic hydrocarbon are non-polar molecules having π - electrons on the ring. THFA molecules would induce a small dipole moment in the aromatic hydrocarbon molecule when mixed. A formation of a weak dipole-induced dipole interaction between the component molecules is also expected. In addition, donor acceptor interaction between π-electrons of benzene ring and oxygen of O-H group of THFA results in negative values of η^E [11].

The plots of ΔG^{*E} versus mole fractions (X_1) at 298.15K for all the three binary systems (THFA + benzene, THFA + toluene and THFA + p-xylene) are presented in Fig.3. Values of ΔG^{*E} were found to be negative for all the systems under study. The experimentally obtained negative ΔG^{*E} and η^E values for all binary solvents mixtures show weak interactions between unlike molecules and indicate that flow is easier for the binary solvent mixtures when compared with that of pure solvents [23,24].

The deviations in Δn_D (molar refraction) was found to be negative for all binary systems over the composition range at investigated temperature (Fig.4). Generally, the negative values of Δn_D suggest weak interactions between the component molecules in the system [15]. For all binary solvent mixtures, the interactions of self-association are stronger than the specific interaction of unlike molecules, and the average interaction strength in mixture is weaker than that in the pure solvents.

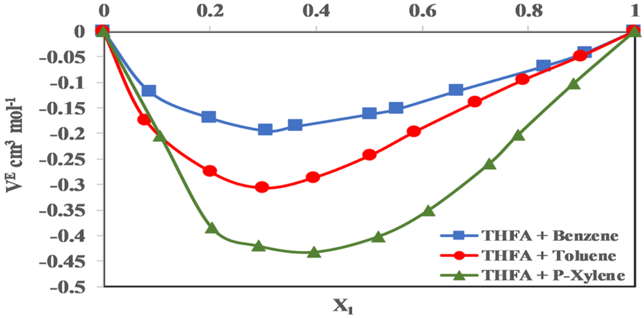

Figure 1. V^E versus X_1 for (■) X_1 THFA +X_2 benzene, (●) X_1 THFA + X_2 toluene and (▲) X_1 THFA + p-xylene at 298.15K**.**

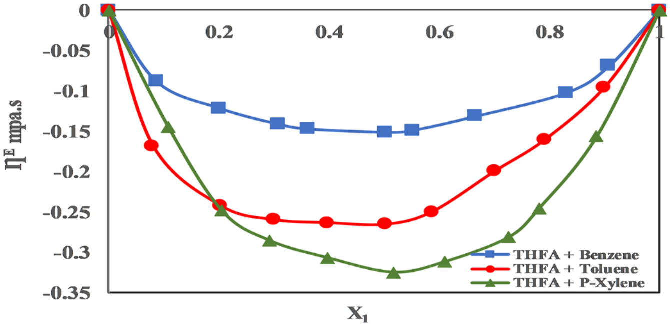

Figure 2. η^E versus X_1 for (■) X_1 THFA+ X_2 benzene, (●) X_1 THFA+ X_2toluene and (▲) X_1 THFA + X_2 p-xylene at 298.15K.

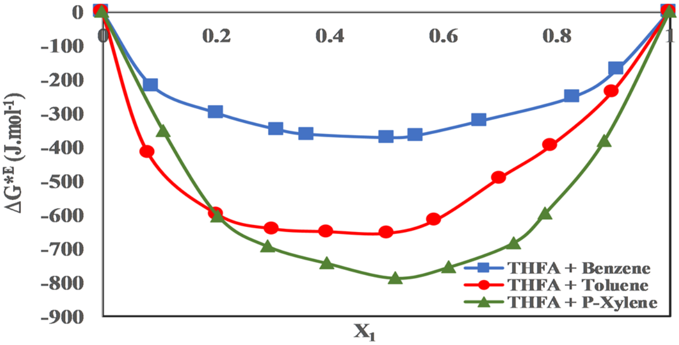

Figure 3. ΔG^{*E} versus X_1 for (■) X_1 THFA + X_2 benzene,(●) X_1 THFA+ X_2 toluene and (▲) X_1 THFA +X_2 p-xylene at 298.15K.

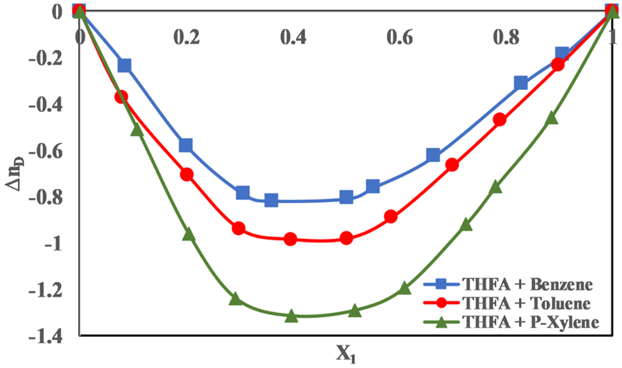

Figure 4. Excess refractive index versus X_1 for (■) X_1 THFA + X_2 benzene, (●) X_1 THFA+X_2 toluene and (▲) X_1 THFA + X_2 p-xylene at 298.15K.

Table 2. Polynomial coefficients (A_k) and standard deviations (σ) for binary solvent mixtures at 298.15K.

Function	System	A_0	A_1	A_2	σ
VE (cm3.mol^{-1})	THFA + Benzene	-0.64840	0.50722	-0.41527	0.00005
VE (cm3.mol^{-1})	THFA + Toluene	-0.96620	0.99681	-0.58565	0.02326
VE (cm3.mol^{-1})	THFA + P-Xylene	-1.65665	0.87340	-0.07943	0.02937
Function	System	A_0	A_1	A_2	σ
η^E (mPa.s)	THFA + Benzene	-0.58614	0.07922	-0.45357	0.02414
η^E (mPa.s)	THFA + Toluene	-1.02289	0.43810	-0.70071	0.03616
η^E (mPa.s)	THFA + P-Xylene	-1.29209	0.00408	-0.47842	0.01902
Function	System	A_0	A_1	A_2	σ
Δn_D (cm^3.mol^{-1})	THFA + Benzene	-3.26617	1.03140	0.76222	0.03357
Δn_D (cm^3.mol^{-1})	THFA + Toluene	-3.89318	1.43064	0.49336	0.03873
Δn_D (cm^3.mol^{-1})	THFA + P-Xylene	-5.29561	1.18722	0.44150	0.03461
Function	System	A_0	A_1	A_2	σ
ΔG^{*E} (J.mol^{-1})	THFA + Benzene	-1443.65	196.1852	-1124.19	1.20126
ΔG^{*E} (J.mol^{-1})	THFA + Toluene	-2524.99	1086.265	-1737.40	1.80019
ΔG^{*E} (J.mol^{-1})	THFA + P-Xylene	-3131.71	15.89403	-1185.48	0.94697

EXPERIMENTAL SECTION

Chemicals

All solvents in this study (THFA, benzene, toluene and p-xylene) were purchased from Sigma-Aldrich and with purity of ≥99%, therefore, no further purifications were needed. Density ***ρ***, viscosity Ƞ and refractive index n_D for solvents have been checked and examined against those listed in the literature (Table 3).

Measurements

The densities (ρ) were calculated (an average of three replicates) with accuracy of (±0.00001 $g.cm^{-3}$) using a digital density meter (Anton paar, Model DMA 60/602). A controlled temperature suspended-level Ubbelohde viscometer was used for the measurement of viscosity (η) under atmospheric pressure at 298.15± 0.01K.

The determinations of refractive indices for pure solvents and their binary solvent mixtures were performed using a digital Abbe refractometer (model: BOE 32400). For refractometer calibration, double distilled water used at 298.15.

Table 3. Experimental and literature physical properties [density (ρ), viscosity (Ƞ) and refractive index (n_D)] of pure solvents at 298.15K.

Compound	T/ K	ρ ($g.cm^{-3}$)		Ƞ mpa.s		n_D	
		Exp.	Lit.[ref]	Exp.	Lit.[ref]	Exp.	Lit.[ref]
THFA	298.15	1.04761	1.04761[25]	4.89883	4.89883 [25]	1.4532	1.45322[25]
Benzene	298.15	0.87372	0.87357 [26] 0.87361[27] 0.87360 [28] 0.87342[29]	0.59951	0.6038[26] 0.604 [28]	1.4975	1.4980[27] 1.4971[29]
Toluene	298.15	0.86224	0.86301[26] 0.86236[27] 0.86220 [28] 0.86226[29]	0.55464	0.5540 [26] 0.556 [28]	1.4950	1.4942[27] 1.4931[29]
p-xylene	298.15	0.85676	0.85670 [26] 0.85682 [27] 0.85662 [28] 0.85670[29]	0.61225	0.6078[26] 0.611 [28]	1.4945	1.4933[27] 1.4926[29]

Exp.: experimental, Lit.: literature, [ref]: reference

CONCLUSIONS

The values of ρ, η, and n_D were calculated in binary solvent mixtures THFA with benzene, toluene and p-xylene over a range of mole fractions. Various excess properties like V^E, η^E, $\Delta G^{*E,}$ Δn_D were calculated from experimentally obtained thermodynamic values. For the binary solvent mixtures studied, benzene showed the most negative values of (V^E, η^E, $\Delta G^{*E,}$ Δn_D) while *p*-xylene showed the least.

The experimental values of V^E, η^E, $\Delta G^{*E,}$ Δn_D were fitted well to Redlich-Kister equation. For all binary solvent mixtures, the interactions of self-association are stronger than the specific interaction of unlike molecules, while, the average interaction strength in mixture is weaker than that in the pure solvents.

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