



VISCOMETRIC STUDIES OF MOLECULAR INTERACTIONS IN BINARY LIQUID MIXTURES OF TETRAHYDROFURAN AND N-PROPANOL AT DIFFERENT TEMPERATURES

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ABSTRACT

Densities and viscosities of binary liquid mixtures of tetrahydrofuran (THF) with polar solvent viz n-propanol have been measured at 303.15, 308.15, 313.15 and 318.15 K. From the density and viscosity data, the values of various properties viz excess molar volume (V^E), excess viscosity (η^E) and excess Gibb's free energy of activation of flow (ΔG^E) have been determined. Further the viscosities of binary mixtures have been correlated to various viscosity models. On the basis of the values of interaction parameters of these viscosity models and also on the basis of the values of various excess properties, the nature of molecular interactions between the components of mixtures have been explained.

Key words: Viscometric studies, Mixed solvent, Binary mixture, Tetrahydrofuran, n-Propanol, Viscosity models.

INTRODUCTION

The thermodynamic and transport properties of tetrahydrofuran and n-propanol have been studied over entire composition range, at 303.15, 308.15, 313.15 and 318.15 K. The present study reveals the nature and extent of interactions between the component molecules in their binary mixtures.

In the present paper, densities (ρ) and viscosities (η) of binary mixtures of THF with n-propanol covering the entire composition range (expressed by mole fraction x of THF) at 305.15, 308.15, 313.15 and 318.15 K are reported. From experimental values of densities and viscosities, excess molar volume (V^E), excess viscosity (η^E), excess free energy of activation of viscous flow (ΔG^E) of n-propanol in THF have been calculated. These

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functions offer a convenient approach for the study of thermodynamic properties of liquid mixtures. The extreme sensitivity of excess functions is due to the size, shape of the molecule and interaction among themselves and gives important information about inter-molecular forces, which are responsible for these interactions.

The several models (equations) have been used from time to time for correlating the viscosity of binary mixtures with those of component liquid systems, and have been used to test the reliability of the results.

EXPERIMENTAL

THF and n-propanol were from S.D. Fine Chemicals (spectroscopic HPLC, A.R. grade) and were further purified according to standard procedures^{1, 2}. The purities were checked by comparing their densities and viscosities with literature values (in the accuracy $\pm 1 \times 10^{-4} \text{ g cm}^3$ and $\pm 3 \times 10^{-3} \text{ mPas}$, respectively).

All the binary mixtures were prepared gravimetrically in stoppard bottles. The densities of pure liquids and their binary mixtures were measured using a single capillary pycnometer (made up of Borosil glass) having bulb capacity of $8 \times 10^{-3} \text{ m}^3$. Viscosity of pure liquid and their binary mixture was measured using Ubbelohde type suspended level viscometer calibrated with tripled distilled water. The viscometers containing the test liquid were allowed to stand for about 30 min in thermostatic bath. The thermostatically controlled water bath, whose temperature was maintained constant by circulating water (Julabo F 25 MP thermostat (made in Germany). It was capable of maintaining constant temperature ($\pm 0.02^\circ\text{C}$).

RESULTS AND DISCUSSION

The excess function is a measure of deviation from the ideal behavior of the mixture, and found to be highly sensitive towards molecular interactions between the component molecules of liquid mixtures. The sign and magnitude of these excess functions from ideality depends on the strength of interaction between unlike molecules.

Excess molar volume (V^E)

The excess molar volume (V^E) of binary mixture was evaluated from the molar volume of mixture (V) and that of pure components (V_1 and V_2) using the following equation³ -

$$V^E = V - (x_1 V_1 + x_2 V_2) \quad \dots(1)$$

The molar volumes V of the binary liquid mixture were calculated from the measured density (ρ) of the mixture using following equation⁴.

$$V = (x_1 M_1) + (x_2 M_2) / \rho \quad \dots(2)$$

Where x_1 and x_2 are the mole fractions of component 1 and 2 of binary liquid mixtures respectively, V_1 is M_1 / ρ_1 and V_2 is M_2 / ρ_2 . ρ_1 and ρ_2 are densities of component 1 and 2.

The excess viscosity (η^E) of the given binary liquid mixture was calculated from the observed viscosity of mixture and that of its pure components using following equation⁵ -

$$\eta^E = \eta - (x_1 \eta_1 + x_2 \eta_2) \quad \dots(3)$$

Where η is viscosity of binary mixture, η_1 and η_2 are the viscosities of pure component 1 and 2, respectively and x_1 and x_2 are the mole fraction of the component 1 and 2, respectively.

The excess Gibb's free energy of flow (ΔG^E) for the binary liquid mixture was computed from the Eyring equation⁶ -

$$\Delta G^E = RT (\ln \eta V - x_1 \ln \eta_1 V_1 - x_2 \ln \eta_2 V_2) \quad \dots(4)$$

Where the symbols have their usual significance.

The values of density (ρ), viscosity (η), molar volume (V) and excess thermodynamic properties viz excess molar volume (V^E), excess viscosity (η^E), excess Gibb's free energy of activation of flow (ΔG^E) at various temperatures 303.15, 308.15, 313.15 and 318.15 K as a function of composition of binary mixtures have been presented in Table 1.

A perusal of Table 1 shows that the values of V^E of binary mixture of THF + n-propanol are negative over entire range of composition and for all experimental temperatures. The Fig. 1 exhibits the variation of V^E with mole fraction x_1 of n-propanol at 303.15, 308.15, 313.15 and 318.15 K. Increase in temperature from 303.15 to 318.15 K results in a decrease in the V^E for THF + n-propanol.

Table 1: Densities, viscosities, excess properties and interaction parameters (d_{12} , T_{12} , H_{12}) of binary liquid mixtures of n-propanol and THF at 303.15, 308.15, 313.15 and 318.15 K.

S. No.	x_1	ρ (g cm ⁻³)	η (m Pas.)	η^E (m Pas.)	v^E (cm ³ mol ⁻¹)	ΔG^E (J mol ⁻¹)	d_{12}	T_{12}	H_{12}
303.15 K									
1.	0.0000	0.87900	0.4380	0.000	0.0000	0.00	0.0000	0.0000	0.0000
2.	0.0594	.87526	0.5038	0.003	-0.0760	167.08	1.1998	0.0029	0.9935
3.	0.1176	0.87141	0.5683	0.006	-0.1380	289.10	1.1184	0.0100	0.9954
4.	0.1747	0.86745	0.6337	0.011	-0.1857	385.80	1.0742	0.0194	1.0048
5.	0.2307	0.86341	0.6968	0.015	-0.2216	450.90	1.0202	0.0296	1.0086
6.	0.4440	0.84659	0.9253	0.018	-0.2604	505.00	0.8216	0.0594	1.0029
7.	0.6420	0.82937	1.1316	0.015	-0.1980	401.39	0.7005	0.0532	0.9991
8.	0.8276	0.81227	1.3188	0.006	-0.0966	215.45	0.6045	0.0212	0.9876
9.	0.9153	0.80401	1.4095	0.004	-0.0481	112.74	0.5816	0.0064	0.9925
10	1.0000	0.79590	1.4950	0.000	0.0000	0.00	0.0000	0.0000	0.0000
308.15 K									
1.	0.0000	0.86540	0.4060	0.000	0.0000	0.00	0.0000	0.0000	0.0000
2.	0.0594	0.86208	0.4743	0.004	-0.0656	199.35	1.4021	0.0028	0.9831
3.	0.1176	0.85881	0.5412	0.008	-0.1307	342.20	1.2980	0.0097	0.9853
4.	0.1747	0.85536	0.6070	0.012	-0.1772	445.16	1.2156	0.0189	0.9885
5.	0.2307	0.85186	0.6716	0.016	-0.2128	517.10	1.1476	0.0290	0.9920
6.	0.4440	0.83699	0.9044	0.018	-0.2436	569.53	0.9083	0.0584	0.9834
7.	0.6420	0.82176	1.1156	0.015	-0.1866	449.91	0.7699	0.0525	0.9795
8.	0.8276	0.80653	1.3075	0.006	-0.0912	241.07	0.6631	0.0210	0.9682
9.	0.9153	0.79911	1.3994	0.003	-0.0418	124.17	0.6272	0.0063	0.9666
10	1.0000	0.79190	1.4880	0.0000	0.00000	0.00	0.0000	0.0000	0.0000

Cont...

S. No.	x_1	ρ (g cm ⁻³)	η (m Pas.)	η^E (m Pas.)	v^E (cm ³ mol ⁻¹)	ΔG^E (J mol ⁻¹)	d_{12}	T_{12}	H_{12}
313.15 K									
1.	0.0000	0.85431	0.3750	0.00	0.00000	0.00	0.0000	0.0000	0.0000
2.	0.0594	0.85139	0.4442	0.004	-0.0632	228.06	1.5769	0.0027	0.9596
3.	0.1176	0.84850	0.5131	0.009	-0.1292	394.81	1.4714	0.0095	0.9673
4.	0.1747	0.84545	0.5797	0.013	-0.1745	508.26	1.3638	0.0184	0.9687
5.	0.2307	0.84232	0.6452	0.017	-0.2115	586.83	1.2795	0.0283	0.9717
6.	0.4440	0.82897	0.8813	0.019	-0.2407	638.95	1.0013	0.0571	0.9623
7.	0.6420	0.81516	1.0956	0.016	-0.1840	502.07	0.8441	0.0515	0.9586
8.	0.8276	0.80128	1.2903	0.007	-0.0882	268.93	0.7270	0.0207	0.9483
9.	0.9153	0.79450	1.3825	0.003	-0.0385	137.07	0.6809	0.0062	0.9428
10	1.0000	0.78790	1.4725	0.0000	0.0000	0.00	0.0000	0.0000	0.0000
318.15 K									
1.	0.0000	0.84612	0.3460	0.000	0.0000	0.00	0.0000	0.0000	0.0000
2.	0.0594	0.84328	0.4172	0.005	-0.0533	267.75	1.8176	0.0026	0.9480
3.	0.1176	0.84056	0.4872	0.01	-0.1145	455.00	1.6654	0.0093	0.9520
4.	0.1747	0.83770	0.5548	0.014	-0.1590	580.26	1.5293	0.0179	0.9521
5.	0.2307	0.83476	0.6213	0.018	-0.1927	665.69	1.4256	0.0272	0.9544
6.	0.4440	0.82224	0.8612	0.02	-0.2242	716.43	1.1028	0.0550	0.9442
7.	0.6420	0.80928	1.0790	0.017	-0.1733	559.63	0.9244	0.0510	0.9406
8.	0.8276	0.79617	1.2770	0.008	-0.0797	299.81	0.7959	0.0205	0.9316
9.	0.9153	0.78979	1.3708	0.004	-0.0345	153.65	0.7493	0.0058	0.9292
10	1.0000	0.78360	1.4613	0.0000	0.0000	0.00	0.0000	0.0000	0.0000

The negative values of V^E are due to the chemical or specific interactions, which can result in decrease in volume and these includes possible depolymerisation of self associated alcohol by the addition of THF or formation of new bonds (hydrogen bond) between THF and alcohol and other complex forming interactions,

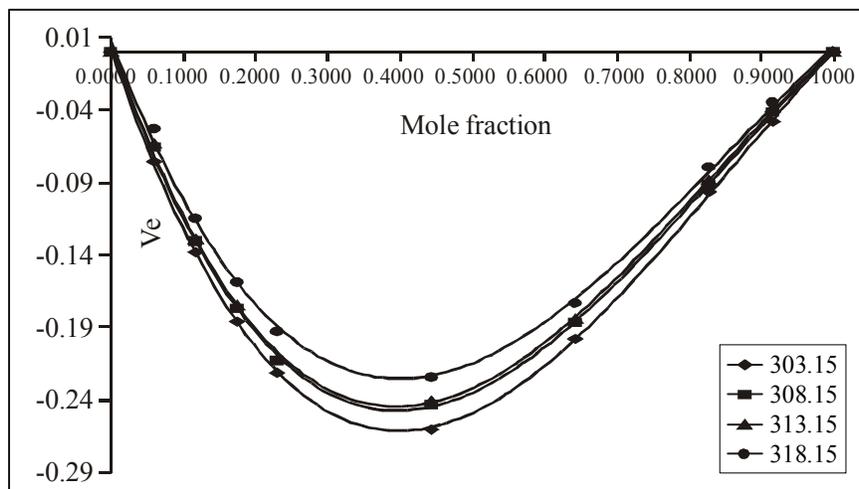


Fig. 1: Variation of excess molar volumes (V^E) with mole fraction (x_1) for n-propanol (1) + THF (2) at 303.15, 308.15, 313.15 and 318.15 K.

All the values of V^E are fitted to Redlich -Kister type polynomial⁷.

$$V^E = x_1 x_2 \sum a_i (x_1 - x_2)^i \quad \dots(5)$$

The values of parameters obtained by least square method are included in Table 2

The standard deviation (σ) calculated as -

$$\sigma (V^E) = [(\sum V^E_{\text{experimental}} - V^E_{\text{calculated}})^2 / (D - N)]^{1/2} \quad \dots(6)$$

Where D is number of experimental data points and N is number of parameters.

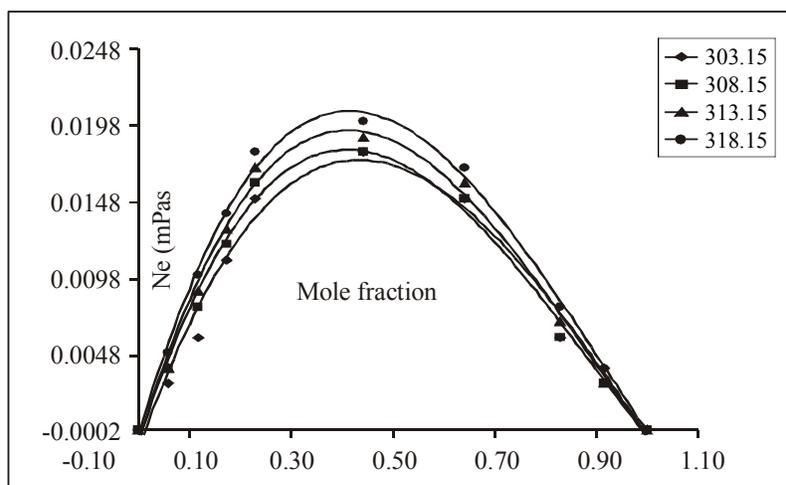
The values of standard deviation at different temperatures for n- propanol are of the order 10^{-3} .

Excess viscosity (η^E)

A perusal of Table 1 shows that the values of η^E are positive over entire range of composition and at all experimental temperatures. The negative of η^E suggest that dispersion type of forces are predominant in these mixtures⁸, while positive values may be attributed to the presence of strong interactions⁹. The plot of η^E verses x_1 (mole fraction of alcohol) for the binary mixtures have been presented in Fig. 2.

Table 2: Redlich- Kister coefficient of excess molar volume and standard deviation for n-propanol (1) + THF (2) at 303.15, 308.15, 313.15, and 318.15 K.

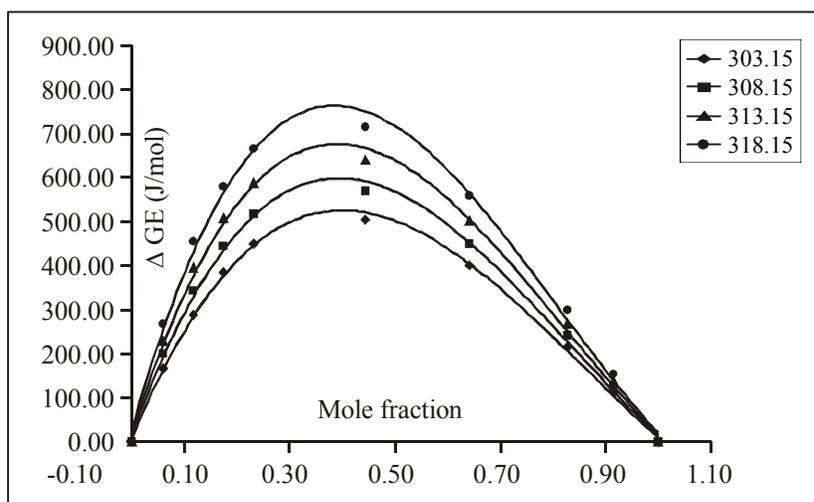
Temp. (K)	A ₀	A ₁	A ₂	σ
303.15	-1.00078	0.46445	0.03256	9.5 x 10 ⁻³
308.15	-0.94936	0.95229	0.86482	3.4 x 10 ⁻³
313.15	-0.94462	0.45040	0.04409	2.5 x 10 ⁻³
318.15	-0.87866	0.40682	0.13806	3.4 x 10 ⁻³

**Fig. 2: Variation of excess viscosity (η^E) with mole fraction (x_1) for n-propanol (1) + THF (2) at 303.15, 308.15, 313.15 and 318.15 K.****Excess Gibb's free energy activation of flow (ΔG^E)**

The values of ΔG^E for binary mixtures THF and alcohol have been presented in Table 1. It is seen that the values of ΔG^E are positive over entire range of composition for n-propanol. The values of ΔG^E for above binary mixtures have been plotted against x_1 and the plots have been represented in Fig. 3. The plots are parabolic in shape. The negative values of ΔG^E may be attributed to the dominance of dispersion forces while positive one to the size effect of the mixing components¹⁰. According to Mayer¹¹, ΔG^E may be considered a reliable measure to detect the presence of interaction between the molecule. Positive values of ΔG^E can be seen in binary mixtures, where specific interactions (hydrogen bonding) between the molecules are dominant where as negative ΔG^E indicates characteristic behavior of mixture in which dispersion forces are dominant¹².

Table 3: Redlich- Kister coefficient of excess molar viscosity and standard deviation for n-propanol (1) + THF (2) at 303.15, 308.15, 313.15, and 318.15 K.

Temp. (K)	A ₀	A ₁	A ₂	σ
303.15	0.07324	-0.02041	-0.02964	7.9 x 10 ⁻³
308.15	0.07322	-0.02940	-0.02128	5.0 x 10 ⁻³
313.15	0.07762	-0.03039	-0.01877	5.7 x 10 ⁻³
318.15	0.08104	-0.03039	-0.00784	4.8 x 10 ⁻³

**Fig. 3: Variation of excess Gibb's free energy of activation of flow (ΔGE) with mole fraction (x_1) for n-propanol (1) + THF (2) at 303.15, 308.15, 313.15 and 318.15 K.**

Viscosity models and interaction parameters

The several models (equation) have been put forth for correlating the viscosity of binary liquid mixtures with those of component liquid with a view to interpreting the molecular interaction in the liquid mixture in terms of interaction parameter of the viscosity model.

Grunberg and Nissan¹³ have suggested the following logarithmic relation between viscosity of the binary liquid mixture and pure components -

$$\ln \eta = x_1 \ln \eta_1 + x_2 \ln \eta_2 + x_1 x_2 d_{12} \quad \dots(7)$$

Where d_{12} is constant proportional to interaction energy. It is approximate measure of strength of the molecular interaction between the mixing components.

Tumara and Kurata¹⁴ developed the following equation for the viscosity of binary mixture.

$$\eta = x_1\Phi_1\eta_1 + x_2\Phi_2\eta_2 + 2(x_1x_2\Phi_1\Phi_2)^{0.5} T_{12} \quad \dots(8)$$

Where T_{12} is interaction parameter and it depends on temperature and composition of mixture. Φ_1 ; Φ_2 are the volume fractions and x_1 ; x_2 are mole fractions; η_1 and η_2 are viscosities of pure components 1 and 2, respectively.

Hind et al.¹⁵ suggests the following equation for the viscosity of binary mixtures.

$$\eta = x_1^2 \eta_1 + x_2^2 \eta_2 + 2 x_1 x_2 H_{12} \quad \dots(9)$$

Where x_1 and x_2 are the mole fraction, η_1 and η_2 are the viscosities of liquid component 1 and 2, respectively. η is viscosity of binary mixture and H_{12} is Hind interaction parameter.

According to Fort and Moore¹⁶, the value of d_{12} (vide equation⁷) provides better measure of strength of interaction. The variation with composition is large where strong specific interaction might be expected, which vary with composition.

The negative values of d_{12} indicate the domination of dispersion forces¹⁷. On the other hand, the positive values of d_{12} may be attributed to presence of strong interactions. A perusal of the values of d_{12} shows that these are positive for all binary mixture showing strong specific interactions.

The values of T_{12} and H_{12} ¹⁸⁻²⁴ (vide equations 8 and 9) for the given mixture do not show very different variation expect where there is a strong interaction between the components.

A perusal of values of T_{12} and H_{12} shows that they are positive for all the binary mixtures, showing strong specific interactions.

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