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Application of Flory-Treszczanowicz-Benson model and Prigogine-Flory-Patterson theory to Excess Molar Volume of Binary Mixtures of Ethanol with Diisopropyl Ether, Cyclohexane and Alkanes (C_6-C_9)

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Abstract – Densities (ρ) for binary mixtures of ethanol (1) + diisopropyl ether (DIPE) or cyclohexane or alkane (C_6-C_9) (2) were measured at 298.15 K, 308.15 K and 318.15 K. The excess molar volume (V_m^E) of binary mixtures was calculated using ρ data and correlated with Redlich-Kister polynomial equation. The V_m^E values for binary mixtures of ethanol (1) + cyclohexane or n-alkane (C_6-C_9) (2) were positive, whereas for ethanol (1) + DIPE (2) these were negative. The magnitude of V_m^E values follows the order: cyclohexane > *n*-nonane > *n*-octane > *n*-heptane > *n*-hexane > DIPE. The V_m^E values have been interpreted qualitatively and also quantitatively in terms of Flory-Treszczanowicz-Benson (FTB) model and Prigogine-Flory-Patterson (PFP) theory. The V_m^E values predicted using FTB model agree well with experimental V_m^E values at all mole fractions. But the PFP theory describes well V_m^E data in ethanol-rich region ($x_1 > 0.5$) for all binary mixtures and is able to predict the sign of V_m^E *vs* x_1 curve for ethanol-lean region ($x_1 < 0.5$) except for ethanol (1) + nonane (2) mixtures.

Key words: Excess molar volume, Ethanol, DIPE, Alkanes, FTB, PFP

1. Introduction

Environmental pollution is a major problematic issue these days. One of the major sources of environmental pollution is poisonous gases and components released by the burning of fuels. Therefore, there is a need to develop environment-friendly fuel using oxygenates which have low emission of CO_2 and CO, high-octane rating and high fuel efficiency [1-8]. Oxygenated compounds like ethers and alcohols play an important role in fuel reformulation as they increase octane rating, improve combustion of fuel in engines and reduce environmental pollution. DIPE has high octane number, low toxicity, low production cost and good anti-knocking property [3,9,10]. It is a highly flammable, non-reactive and colorless liquid which is slightly soluble in water but easily miscible with organic compounds. Ethanol is a colorless, low-cost monohydric primary alcohol used as a gasoline additive, gasohol, a mixture of 90% gasoline and 10% ethanol [11,12]. Methyl t-butyl ether (MTBE) was used as a gasoline additive as it increases the octane number. But due to its high solubility in water, it has polluted the groundwater and contaminated soil due to leakage at gas stations. In the replacement for MTBE, ethanol is being used as an additive for petrol [1,13-15]. Ethanol is a renewable fuel produced from plants and agricultural wastes. Due to these reasons, researchers are focused on studying the various interactions taking place in the mixture of oxygenate with the components of gasoline such as alkanes, cycloalkane, and aromatics [16,17]. The thermo-physical properties of the mixture and their deviation from ideal mixture helps in understanding the molecular interaction taking place in the mixture [18]. In the present paper, experimental densities (ρ) along with calculated values of excess molar volume (V_m^E) of binary mixture of ethanol with DIPE or cyclohexane or alkane (C_6-C_9) have been reported from 298.15 K to 318.15 K. FTB model and PFP theory were also used to determine V_m^E values theoretically and to analyze the various molecular interactions taking place in binary solution.

2. Experimental

Ethanol, cyclohexane and n-alkane (C_6–C_8) were supplied by Merck, while n-nonane and DIPE were supplied by Sigma Aldrich and Loba, respectively. Ethanol and n-alkane (C_6–C_9) were simply distilled and their middle fraction was collected. DIPE was purified using standard method [19]. Then all chemicals were kept over molecular sieves (4 Å) for more than 72 hours; their specifications are given in Table 1. Purity of compounds was ensured by measuring the density (ρ) as well as refractive index (n_D) of pure compounds and comparing the measured values with literature data [13-15,20-35] (Table 2). Chemicals were degassed prior to sample preparation.

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Table 1. Chemicals specifications

S. No.	Sample	CAS No.	Make	Mass Fraction Purity	Purification Method
1.	ethanol	64-17-5	Merck	≥0.999	Distillation
2.	diisopropyl ether	108-20-3	Loba	≥0.985	Distillation
3.	n-hexane	110-54-3	Merck	≥0.985	Distillation
4.	cyclohexane	110-82-7	Merck	≥0.990	Distillation
5.	n-heptane	142-82-5	Merck	≥0.990	Distillation
6.	n-octane	111-65-9	Merck	≥0.990	Distillation
7.	n-nonane	111-84-2	Sigma-Aldrich	≥0.990	Distillation

Table 2. Measured densities (ρ/kg m^{-3}) and refractive indices (n_D) of the pure components

Compound	T/K	ρ		n_D	
		This work	Literature	This work	Literature
ethanol	298.15	787.08	786.60[15]	1.3612	1.3593[20]
	308.15	778.41	777.94[15]	1.3566	1.3553[21]
	318.15	769.57	769.15[15]	1.3520	1.3512[21]
di-isopropyl ether	298.15	720.12	719.17[13]	1.3654	1.3652[14]
	308.15	709.51	708.12[14]	1.3598	1.3596[22]
	318.15	698.71	-----	1.3541	-----
n-hexane	298.15	655.56	655.13[23]	1.3733	1.3732[24]
	308.15	646.40	646.07[23]	1.3679	1.3672[25]
	318.15	637.12	636.79[23]	1.3628	------
cyclohexane	298.15	773.97	773.92[23]	1.4237	1.4235[26]
	308.15	764.49	764.51[23]	1.4180	1.4175[27]
	318.15	754.89	754.85[23]	1.4123	-----
n-heptane	298.15	679.58	679.78[28]	1.3846	1.3852[28]
	308.15	671.02	671.27[28]	1.3793	1.3800[28]
	318.15	662.34	662.50[29]	1.3740	-----
n-octane	298.15	698.72	698.60[30]	1.3953	1.3951[31] 1.3955[15]
	308.15	690.60	690.42[32]	1.3902	1.3906[15]
	318.15	682.38	682.19[15]	1.3853	1.3849[15]
n-nonane	298.15	713.97	713.96[33]	1.4032	1.4030[33]
	308.15	706.15	706.01[34]	1.3985	1.3989[35]
	318.15	698.36	698.12[34]	1.3934	1.3938[35]

The experimental ρ data for mixtures are reported in Table 3 in the temperature range 298.15 to 318.15 K.

The ρ were measured using Anton Paar Density meter (Model DSA5000M) with uncertainty of 10^{-6} g cm^{-3}. The equipment has two integrated Pt 100 platinum thermometers with a proportional temperature controller which keeps the sample at the required temperature. The apparatus was calibrated at the working temperature with dry air and distilled water. The temperature in the cell was regulated to ±0.001 K with an inbuilt solid-state thermostat by the Peltier method. The density meter performance was ensured by determining the V_m^E values for the binary mixture of benzene (1) + cyclohexane (2) at 298.15 K, and these agree within the experimental limits with corresponding literature. The n_D were measured with refractometer (Abbemat-200) having an accuracy $\pm 1\times10^{-4}$ and temperature controlled within ±0.01 K. All samples were prepared by using a weighing balance (OHAUS, AR224CN) having accuracy ±0.1 mg and the uncertainty in mole fraction was 1×10^{-4}. Experimental ρ values were used to calculate V_m^E.

Table 3. Experimental densities (ρ/g cm^{-3}) and excess molar volume (V_m^E/cm^{3}mol^{-1}) of binary liquid mixtures

x_1	ρ	V_m^E	ρ	V_m^E	ρ	V_m^E
	298.15 K		308.15 K		318.15 K	
ethanol (1) + diisopropyl ether (2)						
0.0000	0.7201	0.0000	0.7095	0.0000	0.6987	0.0000
0.0503	0.7228	-0.2386	0.7126	-0.3098	0.7018	-0.3125
0.0967	0.7251	-0.3892	0.7148	-0.4448	0.7040	-0.4500
0.1303	0.7268	-0.4999	0.7166	-0.5732	0.7059	-0.5872
0.2824	0.7338	-0.7050	0.7240	-0.8077	0.7134	-0.8337
0.3845	0.7392	-0.7936	0.7290	-0.8295	0.7186	-0.8597
0.4857	0.7450	-0.8295	0.7350	-0.8696	0.7248	-0.9048
0.5817	0.7510	-0.8102	0.7412	-0.8527	0.7312	-0.8911
0.6816	0.7581	-0.7352	0.7485	-0.7754	0.7387	-0.8131
0.7276	0.7615	-0.6746	0.7521	-0.7113	0.7424	-0.7463
0.8963	0.7768	-0.3799	0.7678	-0.4000	0.7586	-0.4195
0.9669	0.7836	-0.1303	0.7748	-0.1374	0.7659	-0.1444
1.0000	0.7871	0.0000	0.7784	0.0000	0.7696	0.0000
ethanol (1) + n-hexane (2)						
0.0000	0.6556	0.0000	0.6464	0.0000	0.6371	0.0000
0.0423	0.6575	0.1071	0.6478	0.2244	0.6383	0.2871
0.0731	0.6591	0.1756	0.6494	0.2793	0.6398	0.3535
0.1349	0.6626	0.2712	0.6530	0.3710	0.6435	0.4186
0.2545	0.6707	0.3711	0.6612	0.4427	0.6516	0.5264
0.4113	0.6840	0.4118	0.6745	0.4816	0.6651	0.5204
0.5212	0.6955	0.4041	0.6861	0.4594	0.6768	0.4860
0.5884	0.7036	0.3910	0.6945	0.4003	0.6851	0.4452
0.7429	0.7266	0.3152	0.7176	0.3226	0.7083	0.3495
0.7735	0.7322	0.2759	0.7231	0.2943	0.7138	0.3282
0.8149	0.7402	0.2421	0.7312	0.2534	0.7218	0.2921
0.9620	0.7756	0.0574	0.7669	0.0544	0.7580	0.0572
1.0000	0.7871	0.0000	0.7784	0.0000	0.7696	0.0000
ethanol (1) + cyclohexane (2)						
0.0000	0.7740	0.0000	0.7645	0.0000	0.7549	0.0000
0.0584	0.7730	0.1935	0.7633	0.2291	0.7535	0.2723
0.1136	0.7727	0.2816	0.7630	0.3259	0.7531	0.3812
0.2144	0.7725	0.3978	0.7628	0.4525	0.7529	0.5203
0.3215	0.7725	0.4945	0.7631	0.5236	0.7532	0.5943
0.4034	0.7728	0.5337	0.7634	0.5625	0.7535	0.6329
0.5079	0.7735	0.5523	0.7643	0.5705	0.7545	0.6344
0.6258	0.7748	0.5409	0.7657	0.5453	0.7561	0.6032
0.7355	0.7767	0.4711	0.7682	0.4380	0.7588	0.4758
0.8226	0.7795	0.3322	0.7709	0.3094	0.7617	0.3350
0.9204	0.7832	0.1643	0.7751	0.1125	0.7660	0.1246
0.9598	0.7855	0.0478	0.7767	0.0544	0.7678	0.0549
1.0000	0.7871	0.0000	0.7784	0.0000	0.7696	0.0000

Table 3. Continued

x_1	ρ	V_m^E	ρ	V_m^E	ρ	V_m^E
ethanol (1) + n-heptane (2)						
0.0000	0.6796	0.0000	0.6710	0.0000	0.6623	0.0000
0.0511	0.6809	0.1861	0.6722	0.2271	0.6633	0.2778
0.1461	0.6846	0.3481	0.6758	0.4116	0.6668	0.4902
0.2322	0.6890	0.3937	0.6800	0.4644	0.6709	0.5542
0.3469	0.6956	0.4582	0.6866	0.5320	0.6774	0.6258
0.4291	0.7012	0.4774	0.6922	0.5497	0.6830	0.6413
0.5270	0.7092	0.4762	0.7002	0.5412	0.6910	0.6245
0.6178	0.7182	0.4377	0.7092	0.4934	0.7000	0.5644
0.7247	0.7310	0.4007	0.7221	0.4422	0.7129	0.4960
0.8191	0.7454	0.3261	0.7365	0.3541	0.7274	0.3903
0.9086	0.7625	0.2442	0.7538	0.2575	0.7448	0.2765
0.9563	0.7749	0.0837	0.7662	0.0894	0.7573	0.0972
1.0000	0.7871	0.0000	0.7784	0.0000	0.7696	0.0000
ethanol (1) + n-octane (2)						
0.0000	0.6987	0.0000	0.6906	0.0000	0.6824	0.0000
0.0568	0.6998	0.1842	0.6915	0.2274	0.6830	0.2799
0.1097	0.7012	0.2789	0.6928	0.3363	0.6843	0.4066
0.1951	0.7039	0.3788	0.6955	0.4484	0.6868	0.5349
0.3033	0.7082	0.4539	0.6996	0.5306	0.6909	0.6256
0.3855	0.7121	0.4814	0.7035	0.5599	0.6947	0.6562
0.4825	0.7177	0.4970	0.7090	0.5703	0.7002	0.6621
0.5882	0.7251	0.4938	0.7164	0.5641	0.7075	0.6370
0.6833	0.7333	0.4879	0.7246	0.5436	0.7157	0.6127
0.8047	0.7479	0.3690	0.7392	0.4055	0.7302	0.4521
0.9025	0.7638	0.2521	0.7551	0.2713	0.7462	0.2956
0.9655	0.7778	0.1003	0.7691	0.1072	0.7603	0.1156
1.0000	0.7871	0.0000	0.7784	0.0000	0.7696	0.0000
ethanol (1) + n-nonane						
0.0000	0.7140	0.0000	0.7062	0.0000	0.6984	0.0000
0.0528	0.7147	0.1378	0.7068	0.1616	0.6988	0.2147
0.1125	0.7156	0.2908	0.7078	0.2940	0.6996	0.3814
0.1835	0.7172	0.3790	0.7093	0.4010	0.7010	0.5042
0.3158	0.7210	0.4928	0.7127	0.5920	0.7043	0.6959
0.4069	0.7244	0.5335	0.7158	0.6586	0.7074	0.7522
0.5128	0.7292	0.5552	0.7209	0.6104	0.7123	0.7149
0.6268	0.7361	0.5240	0.7279	0.5515	0.7195	0.6024
0.7219	0.7438	0.4583	0.7360	0.4151	0.7273	0.4860
0.8029	0.7522	0.3783	0.7442	0.3530	0.7354	0.4085
0.8992	0.7657	0.2490	0.7579	0.1939	0.7490	0.2235
0.9700	0.7803	0.0354	0.7716	0.0454	0.7628	0.0488
1.0000	0.7871	0.0000	0.7784	0.0000	0.7696	0.0000

3. Results

The V_m^E values were calculated by using Eq. (1) and recorded in Table 3:

$$V_m^E = \frac{(x_1M_1 + x_2M_2)}{\rho_m} - \frac{x_1M_1}{\rho_1} - \frac{x_2M_2}{\rho_2} \quad (1)$$

where V_m^E and ρ_m represents excess molar volume and density of binary mixture. The ρ_1 and ρ_2 represent density of pure components. The calculated V_m^E values were correlated with Redlich-Kister polynomial Eq. (2) [36].

$$V_m^E = x_1(1-x_1)\left[\sum_{n-1}^{4} V^{(n)}(2x_1-1)^{(n-1)}\right] \quad (2)$$

where $V^{(n)}$ represents adjustable parameters. The standard deviations $\sigma(V_m^E)$ were calculated using Eq. (3).

$$\sigma(V_m^E) = \{[\Sigma(V_m^E - V_{calcd.(Eq.(2))}^E)^2]/(m-n)\}^{1/2} \quad (3)$$

where m and n represent the number of measured data points and number of adjustable parameters, respectively. The choice of n to have 1-4 values was determined by the consideration that the maximum deviation $\sigma(V_m^E)$ of V_m^E as calculated using Eq. (3) from corresponding experimental V_m^E values satisfied the relation $\sigma_{max}(V_m^E) \le 2\sigma(V_m^E)$. The adjustable parameters $V^{(n)}$ and standard deviations $\sigma(V_m^E)$ are given in Table 4. The experimental V_m^E data for binary mixtures agree well with literature [14,37,38] at 298.15 K as shown in Fig. 1. Effect of temperature on the V_m^E values of binary system is shown in Fig. 2.

4. Discussion

The V_m^E values for binary systems of ethanol (1) + cyclohexane or n-alkane (C_6-C_9) (2) are positive, whereas for ethanol (1) + DIPE (2) mixtures these are negative as shown in Fig. 1 (b). Magnitude of V_m^E values follows the sequence: cyclohexane > n-nonane > n-octane > n-heptane > n-hexane > DIPE. The H-bonds in self-associated ethanol broke due to involvement of nonpolar n-alkanes and cycloalkane, resulting in increase in volume [39,40]. The V_m^E values increased with increase in chain length of n-alkane due to weakening of bonding between the unlike molecules. The positive value of V_m^E in ethanol

Table 4. Values of adjustable parameters ($V^{(n)}$) of Redlich-Kister equation and standard deviation $\sigma(V_m^E)$

Property	T/K	$V^{(1)}$	$V^{(2)}$	$V^{(3)}$	$V^{(4)}$	$\sigma(V_m^E)$
ethanol (1) + diisopropyl ether (2)	298.15 K	-3.2547	0.0312	-1.4847	0.4979	0.0001
	308.15 K	-3.4218	0.1807	-2.0621	0.8437	0.0002
	318.15 K	-3.5680	0.1240	-2.0730	0.8135	0.0002
ethanol (1) + n-hexane (2)	298.15 K	1.6371	-0.2304	0.602	-0.4902	0.0001
	308.15 K	1.7833	-0.3352	1.2358	-1.6966	0.0003
	318.15 K	1.9226	-0.3783	1.799	-2.2322	0.0006
ethanol (1) + cyclohexane (2)	298.15 K	2.2354	0.3941	0.4649	-1.4407	0.0001
	308.15 K	2.2988	0.1424	0.4588	-1.9006	0.0000
	318.15 K	2.5559	0.0468	0.6157	-2.2085	0.0001
ethanol (1) + n-heptane (2)	298.15 K	1.8517	-0.0858	1.3939	-0.4038	0.0003
	308.15 K	2.1140	-0.2088	1.5698	-0.6555	0.0004
	318.15 K	2.4485	-0.3666	1.7887	-0.9383	0.0004
ethanol (1) + n-octane (2)	298.15 K	1.9869	0.1821	1.2997	-0.4890	0.0001
	308.15 K	2.2771	0.0990	1.4776	-0.7611	0.0001
	318.15 K	2.6214	-0.0455	1.7340	-1.0039	0.0001
ethanol (1) + n-nonane (2)	298.15 K	2.1945	0.046	0.7168	-0.3986	0.0002
	308.15 K	2.5049	-0.7420	-0.0654	0.3928	0.0002
	318.15 K	2.8520	-0.9552	0.3468	0.1788	0.0002

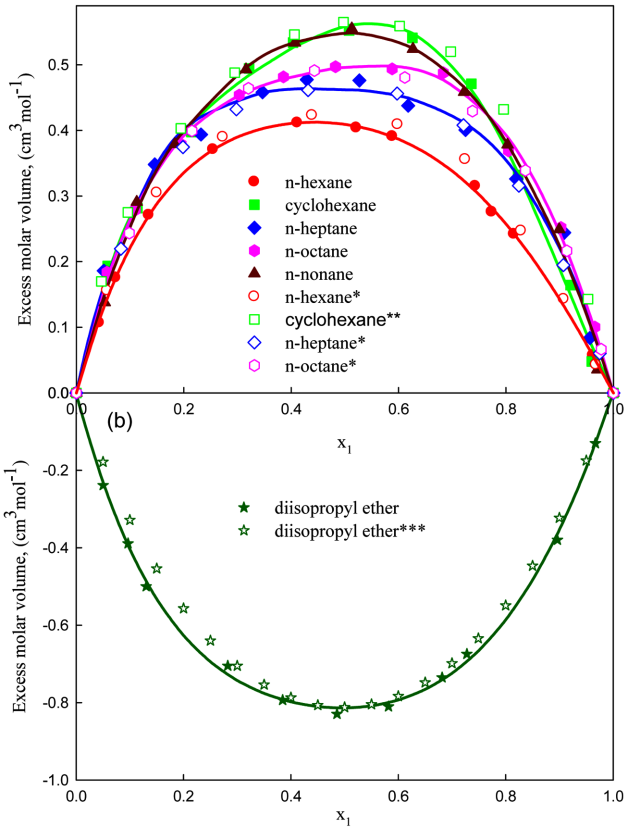

Fig. 1. Excess molar volume of ethanol (1) + diisopropyl ether or cyclohexane or alkane (C_6-C_9) (2) as function of mole fraction of ethanol at 298.15 K; solid symbols represent experimental values, lines represent values calculated from Redlich-Kister equation and hollow symbols represent the literature values *[37], **[38], *[14].**

(1) + cyclohexane (2) system is due to rupture of hydrogen bonding in ethanol and breakage of cohesive forces in cyclohexane [38]. Positive value of V_m^E in ethanol (1) + n-alkane (2) is due to breakage of hydrogen bonding in ethanol on mixing with nonpolar n-alkanes (C_6-C_9). Longer the chain of alkanes, weaker is the interaction between the unlike molecules, as straight chain alkanes get fitted into linearly associated ethanol. Therefore, the V_m^E for binary mixture of ethanol (1) + n-alkane (2) are lower as compared to the V_m^E for binary mixture of ethanol (1) + cyclohexane (2). The V_m^E values for ethanol (1) + DIPE (2) are negative because ethers have an oxygen atom connected to two alkyl groups. Interactions between a polar component (alcohol) and ether form a complex compound containing strong n-π interactions [1]. There is a temperature effect also on V_m^E values. The V_m^E values become more positive as temperature increases from 298.15 K - 318.15 K for all binary systems as represented in Fig. 2. This is due to the increase in randomness with increase in temperature as intermolecular forces weaken with temperature rise.

4-1. Prigogine-Flory-Patterson (PFP) theory

Further, PFP theory [41-43] was applied to predict V_m^E theoretically, according to which V_m^E is the resultant of three factors: interaction between unlike molecules, free volume change and change in internal pressure as given in Eq. (4).

$$V^E = V^E_{inter} + V^E_{free\ vol} + V^E_{P^*} \tag{4}$$

$$\frac{V^E}{x_1V_1^* + x_2V_2^*} = \frac{(\tilde{V}^{-1/3}-1)\tilde{V}^{2/3}\psi_1\theta_2(\chi_{12}^*/P_1^*)}{((4/3)\tilde{V}^{-1/3}-1)}$$

$$-\frac{(\tilde{V}_1-\tilde{V}_2)^2((14/9)\tilde{V}^{-1/3}-1)\psi_1\psi_2}{((4/3)\tilde{V}^{-1/3}-1)} + +\frac{(\tilde{V}_1-\tilde{V}_2)(P_1^*-P_2^*)\psi_1\psi_2}{P_2^*\psi_1+P_1^*\psi_2} \tag{5}$$

where all the terms used in Eq. (5) have their standard meaning [41-43]. The pure component parameters used in PFP theory calculations are given in Table 5 [19,30,44-48]. The V^E_{inter}, $V^E_{free\ vol}$ and $V^E_{P^*}$ values at equimolar composition along with interactional parameter χ_{12}^* are given in Table 6. PFP theory is able to predict the sign and shape of the V_m^E curve. The V_m^E values computed using Eq. (5) are tabulated in Table 7. The V_m^E values predicted using PFP theory agree well with the experimental data in region with mole fraction $x_1 >$ 0.5 for all binary mixtures except for ethanol (1) + nonane (2) for which PFP theory is able to predict only sign and shape of V_m^E curve as shown in Fig. 3 and Table 7. For the studied binary systems $P_1^* > P_2^*$ and $\tilde{V}_1 < \tilde{V}_2$, which results in a large negative contribution of $V^E_{P^*}$ except in case of ethanol (1) + cyclohexane (2). The V^E_{inter} is positive for all the binary mixtures except for ethanol (1) + DIPE (2) and the $V^E_{free\ vol}$ is positive for all binary systems. Patterson et al. [41-43] postulated that the discrepancies between theoretical and experimental values may arise due to additional factors which occur during mixing because PFP theory does not consider all the possible interactions existing in binary mixture. That's why the Flory-Treszczanowicz-Benson (FTB) model was applied to predict the V_m^E values, because this model was established for binary mixtures of alkanol (1) + alkane (2).

4-2. Flory-Treszczanowicz-Benson (FTB) model

Treszczanowicz-Benson established a model for alkanol (1) + alkane (2) binary mixtures where alkanol is self-associated by Mecke-Kempter (MK) type association and alkanes behave like inert species. As per FTB model, the V_m^E is due to combination of two terms: physical contribution term and chemical contribution term [42,49,50].

$$V_m^E = V^E_{MK} + V^E_{Phys} \tag{6}$$

The chemical contribution of V^E_{MK} is expressed as [42,49]

$$V^E_{MK} = \Delta v^{\circ}_H x_1 h(K^{\phi}, \phi_1) \tag{7}$$

where x_1, Δv^0_H represents mole fraction and the increase in volume per mole of bonds formed between associating molecules (ethanol).

Association constant K^{ϕ} is calculated by using equation

$$\ln K^{\phi} = 1 + \ln(K_H/r_1) \tag{8}$$

$$K_H = \exp[-(\Delta h^0_H - T\Delta s^0_H)/RT] \tag{9}$$

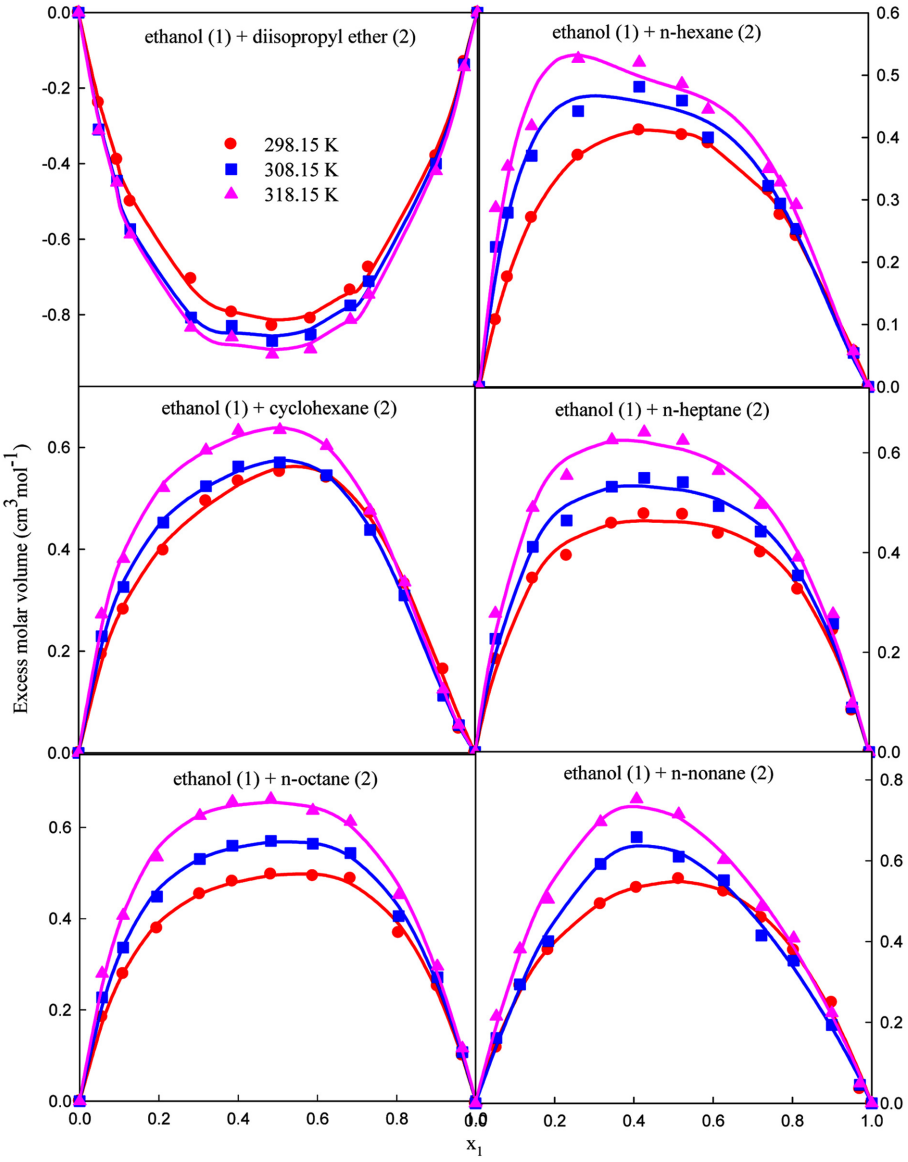

Fig. 2. Excess molar volume of ethanol (1) + DIPE or cyclohexane or alkane (C_6-C_9) (2) as functions of mole fraction of ethanol at T=298.15 K, 308.15 K and 318.15K.

$$r_1 = (V_1^*/17.12 \ \ cm^3 mol^{-1}) \tag{10}$$

where r_1 is the number of segments in a molecule of first component, V_1^* is the characteristic or core molar volume of first component. The values of association parameters Δv_H^o, Δh_H^o, and Δs_H^o used to calculate V_{MK}^E are -10 cm^3mol^{-1}, -24400 $J\ mol^{-1}$ and -33 $J\ K^{-1}mol^{-1}$, respectively [50].

$$V_{Phys}^E = V_{Flory}^E = V_{Interaction}^E + V_{Free\ volume}^E \tag{11}$$

$$V_{Flory}^E = V^*[\tilde{V} - (\tilde{V}_1\phi_1 + \tilde{V}_2\phi_2)] \tag{12}$$

The parameters used to calculate V_{Phys}^E from Flory theory are recorded in Table 5. The binary association parameters K^{ϕ} along with interaction parameters χ_{12} are in Table 6.

$$\tilde{T}\tilde{V}^{4/3} - \tilde{V}^{1/3} + 1 = 0 \tag{13}$$

$$\tilde{T} = \frac{\sum_{i=1}^{2}(\phi_i P_i^* \tilde{T}_i)}{\left(\sum_{i=1}^{2}(\phi_i P_i^*) - \phi_2\theta_1\chi_{12}\right)} \tag{14}$$

All the terms used in above equations have their usual meaning [41,42,50]. V_{Flory}^E is calculated using Eq. 12, which includes the effect due to nonspecific interaction between real species in the mixture along with the free volume term. Flory's equation of state (Eq. 13) was solved to find the value of reduced volume ($\tilde{V}$). The reduced temperature ($\tilde{T}$) value needed to solve Flory's equation of state was calculated using Eq. 14. The interaction parameter (χ_{12}) value was calculated using Eq. (12)-(14) by employing equimolar V_m^E values and using various parameters of pure components (Table 6) [51]. The V_m^E values calculated by FTB model are in good agreement

Table 5. Molar volume (V/cm^{3}mol^{-1}), isobaric expansivity (10^3 α/K^{-1}), isothermal compressibility (10^6 k_T/cm^{3}J^{-1}), characteristic pressure (P*/Jcm^{-3}), characteristic molar volume (V*/cm^{3}mol^{-1}) and characteristic temperature (T*/K) and specific heat at constant pressure (C_p/Jmol^{-1}K^{-1}) obtained from Flory theory for the pure liquids at 298.15 K

Compound	V	α	k_T	P*	V*	T*	C_p
ethanol	58.53	1.095	1153	454.44	46.20	4981.73	113.30
diisopropyl ether	141.89	1.446	1817	421.29	106.49	4353.70	216.10
n-hexane	131.46	1.381	1673	424.17	99.44	4436.06	195.42
cyclohexane	108.74	1.215	1120	538.39	84.28	4724.33	155.90
n-heptane	147.46	1.247	1459	428.12	113.76	4664.39	224.78
n-octane	163.49	1.164	1297	438.56	127.68	4826.98	254.15
n-nonane	179.56	1.094	1177	453.46	141.43	4948.714	284.34

Table 6. PFP interaction parameter (χ_{12}^*) and values of the various contributions at (x_1=0.5) to excess volume as well as Flory-Treszczanowicz-Benson (FTB) association model parameters (K^ϕ) and (χ_{12}) at 298.15 K

System	V_{Inter}^E	$V_{Free\ vol}^E$	$V_{P^*}^E$	χ_{12}^*	K^ϕ	χ_{12}
ethanol (1) + diisopropyl ether (2)	-0.6272	0.1052	-0.0813	-35.43	358.32	-44.69
ethanol (1) + n-hexane (2)	0.5424	0.0725	-0.0607	32.58	358.32	24.70
ethanol (1) + cyclohexane (2)	0.5128	0.0114	0.0574	41.90	358.32	32.29
ethanol (1) + n-heptane (2)	0.5136	0.0215	-0.0292	32.56	358.32	23.18
ethanol (1) + n-octane (2)	0.5096	0.0047	-0.0082	33.79	358.32	22.99
ethanol (1) + n-nonane (2)	0.5489	0.0002	-0.0001	38.00	358.32	25.67

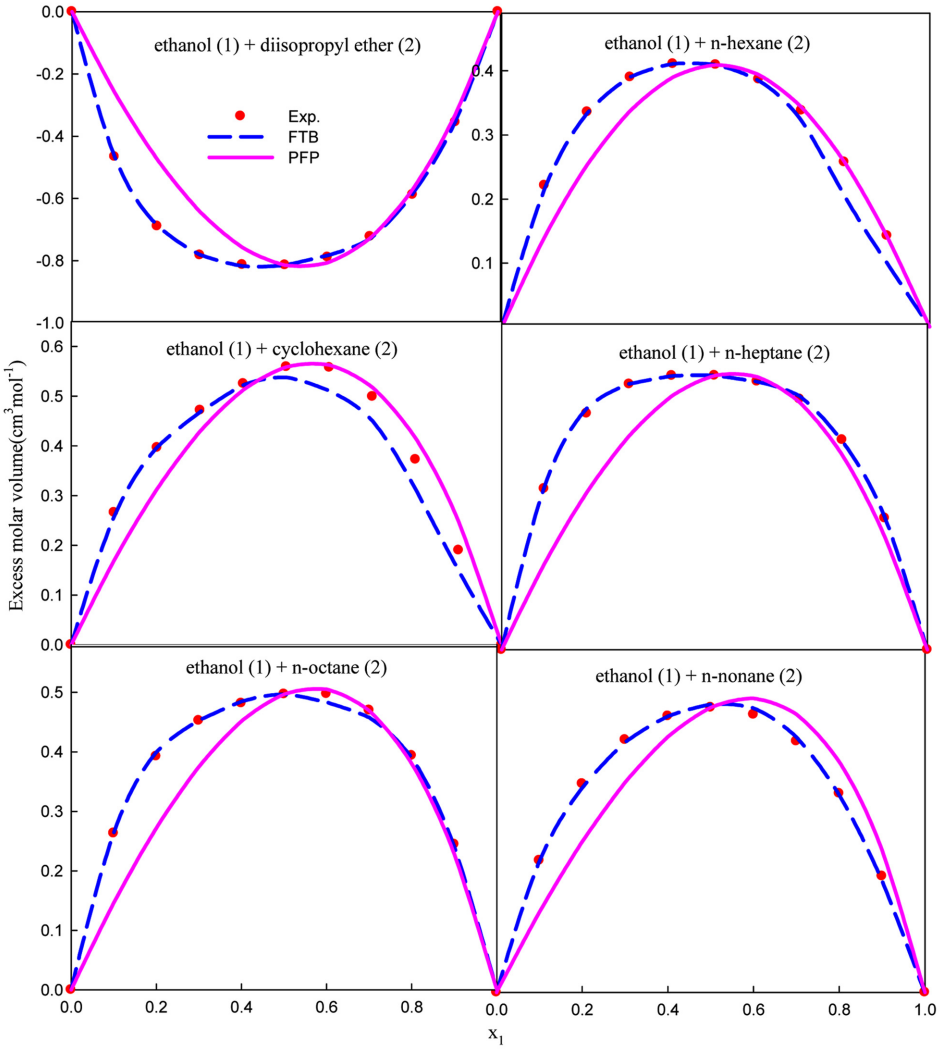

Fig. 3. Excess molar volume of ethanol (1) + DIPE or cyclohexane or alkane (C_6-C_9) (2) as function of mole fraction of ethanol at 298.15 K.

Table 7. Comparison of excess molar volume (V_m^E) values calculated from Flory-Treszczanowicz-Benson association model and Prigogine-Flory-Patterson theory with their corresponding experimental values at 298.15 K

x_1	V_m^E/cm^{3}mol^{-1}					
	Exptl.	FTB	PFP	Exptl.	FTB	PFP
ethanol (1) + diisopropyl ether (2)				ethanol (1) + n-hexane (2)		
0.1	-0.4036	-0.4046	-0.2585	0.2212	0.2248	0.1406
0.2	-0.6265	-0.6393	-0.4740	0.3357	0.3339	0.2538
0.3	-0.7427	-0.7631	-0.6418	0.3900	0.3819	0.3376
0.4	-0.7978	-0.7927	-0.7569	0.4107	0.4204	0.3900
0.5	-0.8137	-0.8141	-0.8137	0.4093	0.4020	0.4093
0.6	-0.7929	-0.7902	-0.8058	0.3867	0.3845	0.3939
0.7	-0.7241	-0.7479	-0.7269	0.3381	0.3225	0.3434
0.8	-0.5861	-0.6139	-0.5701	0.2576	0.2062	0.2582
0.9	-0.3533	-0.3741	-0.3293	0.1428	0.1004	0.1414
ethanol (1) + cyclohexane (2)				ethanol (1) + n-heptane (2)		
0.1	0.2660	0.2906	0.1699	0.2717	0.2737	0.1442
0.2	0.3964	0.3835	0.3142	0.3988	0.4072	0.2656
0.3	0.4713	0.4599	0.4297	0.4483	0.4488	0.3614
0.4	0.5248	0.5016	0.5128	0.4627	0.4675	0.4284
0.5	0.5589	0.5246	0.5589	0.4629	0.4629	0.4629
0.6	0.5571	0.5103	0.5626	0.4529	0.4547	0.4609
0.7	0.4988	0.4502	0.5174	0.4231	0.4280	0.4178
0.8	0.3725	0.3130	0.4156	0.3544	0.3525	0.3291
0.9	0.1900	0.1496	0.2471	0.2222	0.2245	0.1906
ethanol (1) + n-octane (2)				ethanol (1) + n-nonane (2)		
0.1	0.2631	0.2655	0.1457	0.2538	0.2520	0.1542
0.2	0.3922	0.4024	0.2717	0.4018	0.3938	0.2901
0.3	0.4522	0.4447	0.3749	0.4864	0.4815	0.4042
0.4	0.4815	0.4846	0.4515	0.5321	0.5317	0.4922
0.5	0.4967	0.4967	0.4967	0.5486	0.5545	0.5486
0.6	0.4971	0.4831	0.5050	0.5350	0.5472	0.5663
0.7	0.4696	0.4575	0.4691	0.4834	0.4916	0.5358
0.8	0.3933	0.3902	0.3803	0.3830	0.3805	0.4442
0.9	0.2443	0.2408	0.2281	0.2237	0.2149	0.2739
0.8	0.2631	0.2655	0.1457	0.2538	0.2520	0.1542
0.9	0.3922	0.4024	0.2717	0.4018	0.3938	0.2901

with experimental values at all mole fractions as shown in Fig. 3. FTB model correctly predicted the sign and shape of V_m^E *vs* x_1 curves. The characteristic skewing of V_m^E toward high concentration of ethanol (x_1 > 0.5) is well described by this model. In this model, only one associating compound (an alkanol) is taken into account, showing maximum at the high alkanol concentration area (Fig. 3) [52].

5. Conclusions

The ρ values of ethanol (1) + DIPE, cyclohexane or alkane (C_6-C_9) (2) were measured at 298.15 K, 308.15 K and 318.15 K. The measured ρ values were used to compute V_m^E of binary mixtures. The V_m^E for binary systems of ethanol (1) + cyclohexane or alkanes (C_6-C_9) (2) are positive, whereas the V_m^E for ethanol (1) + DIPE (2) are negative. The V_m^E data has been interpreted quantitatively and qualitatively in terms of PFP theory and FTB model. The values predicted by PFP theory agree well with the experimental V_m^E data in region with mole fraction x_1 > 0.5 for all six binary systems, while PFP theory was only able to describe the sign of V_m^E values at mole fraction x_1 < 0.5. The V_m^E values calculated by FTB model are in good agreement with experimental values over the whole composition range for all the studied binary systems.

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