

Measurement and Modeling of Phase Equilibrium, Volumetric Properties and Molar Refractivity of 2-Methylpropan-2-ol + Ethane-1,2-diol

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Abstract 2-Methylpropan-2-ol, an important fine chemical, may be dehydrated during extractive distillation with glycols as entrainer. Experimental isobaric phase equilibrium studies were carried out on binary mixtures of 2-methylpropan-2-ol with ethane-1,2-diol, as an entrainer, at the local atmospheric pressure of 94.99 kPa and at sub-atmospheric pressures of 19.99, 39.99, 59.99, 78.79 kPa using a Sweitoslawski-type ebulliometer. The Wilson and NRTL activity coefficient models were used to correlate the experimental results and the binary interaction parameters were obtained using the Generalized Reduced Gradient optimization technique. UNIFAC was also used to predict the deviations in bubble temperatures. Moreover, the variation in density, refractive index values and other derived properties (excess molar volumes, partial molar volumes and deviations in molar refractivity) were explored at 303.15, 313.15, 323.15 and 333.15 K to understand the shift of equilibrium with the variation in the mixture composition for the conformational state of the molecules. The Redlich–Kister polynomial equation was used to correlate the excess molar volumes and deviations from molar refractivity. Different theoretical mixing rules (Lorentz–Lorenz, Wiener, Heller, Gladstone–Dale and Arago–Biot) are investigated and reported in terms of average percentage deviation. Furthermore, the Prigogine–Flory–Patterson theory was used to predict the trend of the dependence of excess molar volumes on composition for the present system.

Keywords 2-Methylpropan-2-ol · Ethane-1 · 2-diol · VLE · Densities · Refractive index values

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1 Introduction

The ability of biodiesel to contribute to the solutions of problems and concerns from air pollution, global warming, environmental improvements and other sustainability issues, has led to its widespread production. The bio-fuel so produced has resulted in the abundant availability of bio-glycerol, a by-product of the biodiesel industry [1]. This bio-glycerol finds an application in the etherification of 2-methylpropan-2-ol to produce *tert*-butyl ethers of glycerol (high content of the di-ethers), which are potential alternatives to diesel fuel, with high gasoline octane booster capabilities [2, 3]. 2-Methylpropan-2-ol, being an important etherification reagent, has a major dehydration issue, mainly due to the formation of a minimum boiling azeotrope with water that restricts its industrial applicability [4, 5]. Among the various alternatives, extractive distillation with the aid of glycols as an entrainer is a promising method for the dehydration of 2-methylpropan-2-ol [6, 7]. Ethane-1,2-diol is found to dehydrate 2-methylpropan-2-ol efficiently, due to its water-like hydrogen bond network structure and lower molar mass.

In the design of extractive distillation, knowledge of phase equilibrium data at ambient and low pressures is vital to establish appropriate relation between temperature and pressure as well as to determine the capacity of the solvent [8, 9]. Further, the volumetric properties of liquid mixtures provide information about the character the of the solute–solute, solvent–solvent and solute–solvent pair interactions in a mixture. The properties also shed light on packing effects which arise due to different sizes of the molecules [10, 11].

A literature survey reveals that various thermo-physical properties of the systems 2-methylpropan-2-ol + water, water + ethane-1,2-diol and 2-methylpropan-2-ol + water + ethane-1,2-diol have been reported [5, 6, 12–16]. However, to the best of our knowledge, there is no report of data for the phase equilibria of the binary system 2-methylpropan-2-ol + ethane-1,2-diol and so this system has been studied in the present work. Additionally, the densities (ρ) and refractive index values (n_D) have been measured and the excess molar volumes (V_m^E), deviations in molar refractivity (ΔR) and partial molar volumes (\bar{V}_1 and \bar{V}_2) are calculated. The phase equilibria of 2-methylpropan-2-ol + ethane-1,2-diol were measured at sub-atmospheric (19.99, 39.99, 59.99, 78.79 kPa) and local atmospheric pressure of 94.99 kPa over the entire composition range. The activity coefficient models, Wilson [17] and NRTL [18] models for activity coefficient were used to model the experimental phase equilibrium data. Non-linear regression analysis was performed using the generalized reduced gradient optimization technique, to find out the optimum binary interaction parameters for the binary mixture. The universal functional activity coefficient model (UNIFAC) was employed to predict the bubble temperature of the 2-methylpropan-2-ol + ethane-1,2-diol mixtures.

The densities, refractive indices and the derived excess properties of the binary mixtures of 2-methylpropan-2-ol + ethane-1,2-diol were measured at 303.15, 313.15, 323.15, and 333.15 K under local atmospheric pressure of 94.99 kPa over the entire composition range. The derived excess properties; excess molar volumes (V_m^E) and deviations in molar refractivity (ΔR) were correlated with the Redlich–Kister polynomial equation [19]. Generally, the refractive index values are measured at sodium D light wavelength i.e. 589.3 nm, however, the refractive index values at other wavelengths (404.7, 435.8, 486.1, 546.1, 587.6, 632.8, 644.0 and 706.5) nm were also explored, since it is convenient in the field of optics and for processes that are phase matched [20].

Furthermore, to predict the refractive indices of the binary liquid mixtures, the Lorentz–Lorentz (L–L), Weiner (W), Gladstone–Dale (G–D), Argo–Biot relation (A–B) and Heller (H) theoretical mixing rules were applied and the deviations are reported in terms of average percentage deviation [21–23]. The Prigogine–Flory–Patterson theory was used to predict the excess molar volumes of binary mixtures of 2-methylpropan-2-ol + ethane-1,2-diol.

2 Experimental Section

2.1 Materials

2-Methylpropan-2-ol (>99.5 mass%, AR) provided by Sigma–Aldrich, India was dried over molecular sieves (Aldrich, type 4Å, 1.6 mm pellets) and ethane-1,2-diol (>99.5 mass%, AR) was provided by SD Fine Chemical Ltd, India. The solvents were double distilled to remove trace impurities and were stored in desiccators to prevent moisture absorption. The water content of these chemicals was measured using a Karl Fischer titrator, Metrohm 797. The final purities of 2-methylpropan-2-ol and ethane-1,2-diol were analyzed using Shimadzu Gas Chromatograph, GC-17A, with with a flame ionization detector and an Agilent CP-Wax 57 CB column (0.53 mm × 25 m) at 373 K initially, followed by a ramping of 10 K per minute to 473 K. The injector and detector temperature was maintained at 423 K. The sample analyses were carried out in triplicate. The specifications (density and refractive index) of the pure components used in the present study have been measured at different temperatures and compared to those of literature values in Table 1 [24–32].

2.2 Isobaric Phase Equilibria Measurements

The phase equilibria were measured using a Sweitoslawski-type ebulliometer, similar to that described by Hala et al. [33]. A detailed description of the construction of the experimental setup and the procedure followed in the present study was described by Kumari et al. [34]. The Sweitoslawski-type ebulliometer is connected to a vacuum pump and a nitrogen gas cylinder, along with a closed end U-tube mercury in-line manometer to maintain the pressure within 0.50 kPa of the desired value. The pressure was adjusted manually using the needle valve of the gas cylinder or by opening the bypass line of the vacuum pump. A Lutron barometer, PHB-318, was used to measure the local atmospheric pressure. A high precision WIKA digital thermometer, Model CTH6200 calibrated by point-to-point by comparison to a WIKA hand-held calibrator, Model CEP3000, was used for measuring the equilibrium temperatures with an accuracy of 0.01 K. The thermometer is placed in the thermo-well containing glycerol to measure the equilibrium temperature of the mixture impinging on the thermo-well from the Cottrell tube of the ebulliometer. The samples used were prepared gravimetrically using a Shimadzu balance, AUW120D which can record weights with an uncertainty of 0.00001 g and thereafter charged into the ebulliometer. The average uncertainty in the measurement of mole fractions were determined to be 5×10^{-5} .

In accordance with the Hala et al. [33], the mixture is placed into the ebulliometer and vacuum is gradually applied. The heating rate is slowly increased and adjusted to produce the required boil-up rate, so that a drop count of about 30 drops per minute is achieved. The

Table 1 Specifications of the chemicals and comparison of refractive index (n_D) and density (ρ) of pure components with the literature data

Chemical (IUPAC name)	Source	Initial mass purity	Purification method	Final mass purity	Analysis method	T/K	Refractive index (n_D)		Density (ρ) g·cm ⁻³	
							Present work	Literature	Present work	Literature
2-Methyl propan-2-ol	Sigma-Aldrich	0.995	Dried over molecular sieves	0.9999	GC	303.15	1.38216	–	0.77547	0.77948 ^a , 0.77521 ^b
						313.15	1.37781	–	0.76486	0.76484 ^a , 0.76469 ^b
						323.15	1.37374	–	0.75394	0.75401 ^b , 0.75394 ^{a,c,d}
Ethane-1,2-diol	SD Fine	0.995	Simple vacuum distillation	0.9995	GC	333.15	1.36971	–	0.74270	0.74270 ^{a,c,d}
						303.15	1.42910	1.4284 ^d , 1.4287 ^e	1.10668	1.10651 ^e , 1.10625 ^h , 1.10636 ⁱ
						313.15	1.42623	1.4254 ^d , 1.4254 ^c	1.09988	1.09974 ^e , 1.09917 ^h , 1.09839 ⁱ
						323.15	1.42325	1.4229 ^d	1.09236	1.09212 ^d , 1.09294 ^e , 1.09105 ⁱ
						333.15	1.41988	1.4200 ^d	1.08524	1.08490 ^c , 1.08601 ^g , 1.08478 ^h

Standard uncertainties u are: $u(T) = 0.01$ K, $u(\rho) = 0.000125$ g·cm⁻³, $u(n_D) = 0.00015$

^a Ref. [24]

^b Ref [25]

^c Ref [26]

^d Ref [27]

^e Ref [28]

^f Ref [29]

^g Ref [30]

^h Ref [31]

ⁱ Ref [32]

equilibrium temperature is recorded after the system reaches a steady-state condition, judged by the constancy of temperature and uniformity of the drop rate over at least 30 min. The phase equilibrium experiment was initially performed at the lowest pressure and after the measurement of the equilibrium temperature, the vacuum was released and pressure regulated to the next higher value to be studied. Experimental phase equilibrium data were measured at constant pressures of 19.99, 39.99, 59.99, 78.79 and 94.99 kPa and the standard uncertainty in pressure was found to be 0.50 kPa.

2.3 Volumetric Property and Molar Refractivity Measurements

The densities and refractive indices of the 2-methylpropan-2-ol + ethane-1,2-diol binary mixtures were measured using a Rudolph Research analytical automatic densitometer (Model DDM 2911) and Schmidt + Haensch refractometer (Model DSR λ), respectively. The densitometer and refractometer were switched on an hour prior to the start of experimentation to allow the instruments to stabilize. A regular calibration of the instruments was carried out with the standard samples provided by the manufacturers to ensure the accuracy of measurements. The U-tube of the densitometer was cleaned with acetone and the air pump was switched on to remove the solvent. Thereafter, the temperature of the densitometer was increased to 353.15 K and left for almost 15 min to remove the traces of solvent. The traces were also removed by the air pump and density of air is measured at 353.15 and 293.15 K. This procedure was repeated until the air density conformed to the standard values at the corresponding temperatures. Then, the sample tube was rinsed with the sample to be measured. After the measurements, the same procedure was followed to clean the sample U-tube.

For the measurement of refractive indices, the housing or sample well of the instrument was cleaned with acetone to remove any impurities. Subsequently, it was rinsed with a small amount of the sample, whose refractive index is to be measured. The measurement was performed by placing the required amount of sample to the well at the desired temperature. The uncertainties in measurements of density and refractive index were determined to be $0.00125 \text{ g}\cdot\text{cm}^{-3}$ and 0.00150, respectively. The densities and refractive index values of the binary mixture were measured at 303.15, 313.15, 323.15 and 333.15 K over the entire composition range at a local atmospheric pressure of 94.99 kPa.

3 Results and Discussion

3.1 Isobaric Phase Equilibria

The experimental isobaric phase equilibrium data for the 2-methylpropan-2-ol (1) + ethane-1,2-diol (2) binary system were measured at sub-atmospheric pressures of 19.99, 39.99, 59.99, 78.79 and local atmospheric pressure of 94.99 kPa and are reported in Table 2. The vapor phase mole fraction (y_1) of 2-methylpropan-2-ol was predicted using the non-random two liquid activity (NRTL) coefficient model and the results are included in Table 2. It can be observed that with an increase in the mole fraction of 2-methylpropan-2-ol, the bubble point temperature also increased. Moreover, the mixture did not show any azeotropic behavior. The pure component data and the Antoine constants used for vapor

Table 2 Experimental and derived phase equilibrium data of 2-methylpropan-2-ol (1) + 1,2 dihydroxethane (2) at different pressures using the NRTL model

x_1^a	$T(K)^b$	γ_1^c	γ_2^d	y_1^e	x_1^a	$T(K)^b$	γ_1^c	γ_2^d	y_1^e
$p/kPa = 19.99$					$p/kPa = 39.99$				
0.00000	422.77	2.19060	1.0000	0.00000	0.00000	441.72	1.88495	1.00000	0.00000
0.02501	386.89	2.09691	1.0006	0.79435	0.02501	411.46	1.81986	1.00044	0.69029
0.07003	363.63	1.94561	1.0043	0.94135	0.07003	386.66	1.71347	1.00345	0.90254
0.14976	348.29	1.72400	1.0194	0.97711	0.14976	368.64	1.55446	1.01557	0.96388
0.19970	343.33	1.60990	1.0342	0.98519	0.19970	362.57	1.47097	1.02750	0.97565
0.29952	337.10	1.42659	1.0766	0.99190	0.29952	354.81	1.33418	1.06135	0.98550
0.40986	332.75	1.27756	1.1438	0.99259	0.40986	349.40	1.22025	1.11463	0.99105
0.50395	330.10	1.18396	1.2193	0.99602	0.50395	346.00	1.14727	1.17392	0.99353
0.60024	327.82	1.11288	1.3159	0.99729	0.60024	343.14	1.09103	1.24886	0.99492
0.69918	325.78	1.06081	1.4380	0.99992	0.69918	340.66	1.04933	1.34236	0.99973
0.80010	323.78	1.02572	1.5901	1.00000	0.80010	338.27	1.02096	1.45697	0.99997
0.85995	322.64	1.01235	1.6953	1.00000	0.85995	336.92	1.01008	1.53512	0.99998
0.94004	321.12	1.00221	1.8557	1.00000	0.94004	335.17	1.00181	1.65287	0.99999
0.97324	320.49	1.00044	1.9295	1.00000	0.97324	334.46	1.00036	1.70647	0.99999
1.00000	320.01	1.00000	1.9924	1.00000	1.00000	333.91	1.00000	1.75182	1.00000
$p/kPa = 59.99$					$p/kPa = 78.79$				
0.00000	453.81	1.78432	1.00000	0.00000	0.00000	462.40	1.68065	1.00000	0.00000
0.02501	426.26	1.72864	1.00040	0.62920	0.02501	437.11	1.63414	1.00035	0.57885
0.07003	400.92	1.63707	1.00312	0.87369	0.07003	411.81	1.55715	1.00276	0.84735
0.14976	381.40	1.49884	1.01408	0.95345	0.14976	391.12	1.43971	1.01250	0.94273
0.19970	374.67	1.42553	1.02490	0.96844	0.19970	383.87	1.37677	1.02213	0.96207
0.29952	366.03	1.30425	1.05562	0.98206	0.29952	374.47	1.27154	1.04949	0.97983
0.40986	359.96	1.20197	1.10402	0.98890	0.40986	367.76	1.18163	1.09260	0.98653
0.50395	356.16	1.13575	1.15787	0.99237	0.50395	363.60	1.12276	1.14056	0.99104
0.60024	352.98	1.08430	1.22589	0.99458	0.60024	360.12	1.07661	1.20106	0.99372
0.69918	350.23	1.04587	1.31065	0.99960	0.69918	357.13	1.04187	1.27632	0.99872
0.80010	347.60	1.01956	1.41438	0.99982	0.80010	354.30	1.01792	1.36822	0.99915
0.85995	346.13	1.00943	1.48501	0.99990	0.85995	352.74	1.00866	1.43066	0.99977
0.94004	344.23	1.00169	1.59129	0.99994	0.94004	350.72	1.00156	1.52441	0.99983
0.97324	343.46	1.00033	1.63960	0.99997	0.97324	349.91	1.00031	1.56696	0.99990
1.00000	342.86	1.00000	1.68046	1.00000	1.00000	349.26	1.00000	1.60291	1.00000
$p/kPa = 94.99$									
0.00000	468.23	1.58017	1.00000	0.00000	0.60024	365.30	1.06873	1.17598	0.99259
0.02501	444.97	1.54218	1.00031	0.53620	0.69918	362.11	1.03776	1.24185	0.99813
0.07003	420.19	1.47887	1.00240	0.82423	0.80010	359.10	1.01624	1.32217	0.99830
0.14976	398.71	1.38117	1.01088	0.93625	0.85995	357.47	1.00786	1.37666	0.99943
0.19970	390.93	1.32821	1.01928	0.95723	0.94004	355.36	1.00142	1.45837	0.99966
0.29952	380.74	1.23865	1.04320	0.97504	0.97324	354.52	1.00028	1.49540	0.99983
0.40986	373.48	1.16099	1.08096	0.98251	1.00000	353.84	1.00000	1.52667	1.00000

Table 2 continued

x_1^a	$T(K)^b$	γ_1^c	γ_2^d	y_1^e	x_1^a	$T(K)^b$	γ_1^c	γ_2^d	y_1^e
0.50395	368.99	1.10950	1.12298	0.98765					

Standard uncertainties u are $u(x_i) = 0.00005, u(T) = 0.05K, u(p) = 0.50$ kPa

^a Mole fraction of 2-methylpropan-2-ol in the liquid phase

^b Temperature in K

^c Activity coefficients of component 1

^d Activity coefficients of component 2

^e Predicted mole fractions of component 1 in the vapor phase

pressure calculations are reported in Table 3 [35–37]. The equilibrium data were correlated with the activity coefficient (Wilson and NRTL) and UNIFAC predictive models.

$$\text{Wilson model : } \ln \gamma_i = \ln(x_i + A_{ij}x_j) + x_j \left[\left\{ \frac{A_{ij}}{A_{ij}x_j + x_i} \right\} - \left\{ \frac{A_{ij}}{A_{ij}x_i + x_j} \right\} \right] \quad (1)$$

$$\text{NRTL Model : } \ln \gamma_i = x_j^2 \left\{ \tau_{ji} \left(\frac{G_{ji}}{G_{ji}x_j + x_i} \right)^2 + \left(\frac{G_{ij}\tau_{ij}}{(x_i + x_iG_{ij})^2} \right) \right\} \quad (2)$$

where $G_{ij} = \exp(-\alpha_{ij}\tau_{ij})$, $\tau_{ij} = a_{ij} + \frac{b_{ij}}{T}$, $\tau_{ij} \neq \tau_{ji}$, and $\alpha_{ij} = \alpha_{ji}$ where T is the absolute temperature, x_i is the mole fraction, and γ_i is the activity coefficient of component i . A_{ij} is the binary interaction parameter for the Wilson model, α_{ij} is the non-randomness factor, τ_{ij} is the binary interaction energy parameter and G_{ji} is the local binary parameter for the NRTL model.

$$\text{UNIFAC model : } \ln \gamma_i = \ln \gamma_i^C + \ln \gamma_i^R \quad (3)$$

where $\ln \gamma_i^C$ and $\ln \gamma_i^R$ are the combinatorial and residual components of the activity for the i th molecule:

$$\ln \gamma_i^C = \ln \frac{\phi_i}{x_i} + \frac{z}{2} q_i \ln \frac{\theta_i}{x_i} + l_i \frac{\phi_i}{x_i} \sum_j x_j l_j \quad (4)$$

where θ_i, ϕ_i and l_i are the molar weighted segment, area fractional components and a compound parameter of coordination number z , for the i th molecule in the system.

$$l_i = \frac{z}{2}(r_i - q_i) - (r_i - 1); z = 10; \theta_i = \frac{q_i x_i}{\sum_j q_j x_j}; \phi_i = \frac{r_i x_i}{\sum_j r_j x_j} \quad (5)$$

where, q_i and r_i are calculated from the group surface area and volume contributions.

$$\ln \gamma_i^R = \sum_k^n v_k^{(i)} [\ln \Gamma_k - \ln \Gamma_k^{(i)}] \quad (6)$$

where $\ln \Gamma_k$ is the activity of an isolated group in a solution consisting only of molecules of type i . The total pressure equation used in the calculations for the binary data reduction by Barker’s method is as follows:

Table 3 Physical properties and Antoine constants for pure components

Component	T_c/K	p_c	z_c	ω	A^a	B^a	C^c	D^d
2-methylpropan-2-ol	506.20 ^b	39.73 (bar) ^b	0.260 ^b	0.613 ^b	-8.47927 ^b	2.47845 ^a	-9.27918 ^b	-2.53992 ^b
Ethane-1,2-diol	718.15 ^c	76 (atm) ^c	0.239 ^c	-	4.97012 ^d	1914.95 ^d	-84.996 ^d	-

^a Antoine constants: 2-methylpropan-2-ol: $\ln(p) = \ln(p_c) + \{(T_c/T) * (A\tau + B\tau^{1.5} + C\tau^{2.5} + D\tau^5)\}$

where, $\tau = (1 - T/T_c)$; ethane-1,2-diol : $\log_{10} p = A - B/(C + T)$; p in bar and T in K

^b Ref. [35]

^c Ref. [36]

^d Ref. [37]

Table 4 Binary interaction parameters of 2-methylpropan-2-ol (1) + ethane-1,2-diol (2) at various pressures based on Wilson, NRTL and UNIFAC models

Parameters	Wilson ^a	NRTL ^b	UNIFAC	Parameters	Wilson ^a	NRTL ^b	UNIFAC
<i>p</i> = 19.99 kPa				<i>p</i> = 39.99 kPa			
<i>A</i> ₁₂	0.58432	2.47764	–	<i>A</i> ₁₂	0.63781	2.35372	–
<i>A</i> ₂₁	0.74878	– 1.90395	–	<i>A</i> ₂₁	0.81334	–1.90928	–
α^c	–	– 0.03291	–	α^c	–	–0.03289	–
RMSD (<i>T</i>) ^c	0.03724	0.02807	1.84169	RMSD (<i>T</i>) ^c	0.02748	0.02292	3.559250
<i>p</i> = 59.99 kPa				<i>p</i> = 78.79 kPa			
<i>A</i> ₁₂	0.66222	2.28947	–	<i>A</i> ₁₂	0.69107	2.24623	–
<i>A</i> ₂₁	0.83038	–1.87174	–	<i>A</i> ₂₁	0.84776	–1.86311	–
α^c	–	–0.02974	–	α^c	–	–0.02618	–
RMSD (<i>T</i>) ^c	0.03468	0.02747	4.457733	RMSD (<i>T</i>) ^c	0.03213	0.02714	5.34137
<i>p</i> = 94.99 kPa							
<i>A</i> ₁₂	0.73455	2.20450					
<i>A</i> ₂₁	0.85057	–1.85355					
α^c	–	–0.02142					
RMSD (<i>T</i>) ^c	0.10206	0.10346	6.19036				

^a *A*_{*ij*} = *A*_{*ij*}

^b *A*_{*ij*} = τ_{ij} are binary interaction parameters

^c α is the non randomness factor

^d Root mean square deviation (RMSD) = $\left(\sum_{i=1}^k \frac{(Z_i - ZM_i)^2}{k} \right)^{0.5}$ where *Z* is a regressed property value, *ZM* is the corresponding experimental values from the data set and *k* is the number of data points

$$p_{cal}/kPa = (p_1^0/kPa)x_1\gamma_1F_1 + (p_1^0/kPa)x_2\gamma_2F_2 \tag{7}$$

where *p*_{*i*}⁰ indicates the vapor pressures of the pure components, *x*_{*i*} is the liquid-phase mole fractions, and γ_i is the activity coefficient. According to Reid et al. [38] the vapor phase non-ideality correction factor, *F*_{*i*} in Eq. 7, is close to unity for low and ambient pressures. Hence Eq. 7 can be reduced as:

$$p_{cal}/kPa = (p_1^0/kPa)x_1\gamma_1 + (p_1^0/kPa)x_2\gamma_2 \tag{8}$$

The optimum binary interaction parameters of the activity coefficient models were obtained by minimizing the following objective function Φ based on Generalized Reduced Gradient (GRG) optimization technique as described by Edgar and Himmelblau [39].

$$\Phi = \left(\frac{p_{cal} - p_{exp}}{p_{exp}} \right)^2 \tag{9}$$

The results of the correlations of the experimental data with the local composition models (Wilson and NRTL) and that predicted by the UNIFAC group contribution method [40, 41] are presented in Table 4. The deviations in bubble temperatures predicted by the different models from the experimental values are expressed in terms of root mean square deviation (RMSD). The results showed that the deviations obtained from the predicted values of UNIFAC model were substantially larger. Among the models used in the study, the 2-methylpropan-2-ol + ethane-1,2-diol binary system was best represented by the NRTL

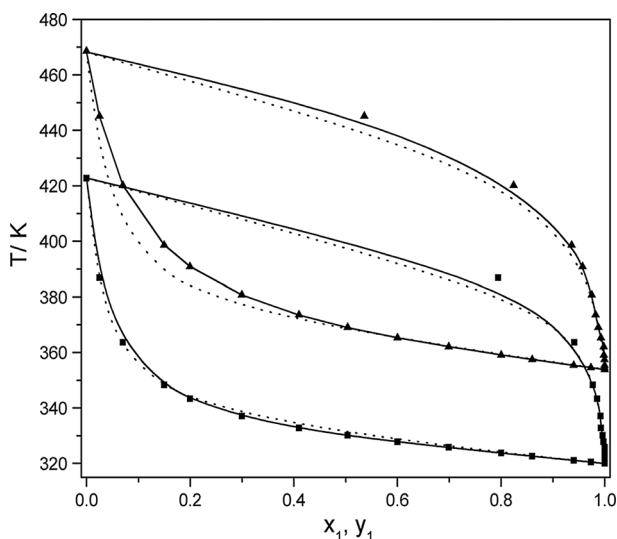


Fig. 1 Phase equilibrium data of 2-methylpropan-2-ol (1) + ethane-1,2-diol (2) experimental data at pressure p : 19.99 kPa, filled square; 94.99 kPa, filled triangle; solid curve (dashed lines), fitted to NRTL model; (filled circles), predicted by UNIFAC

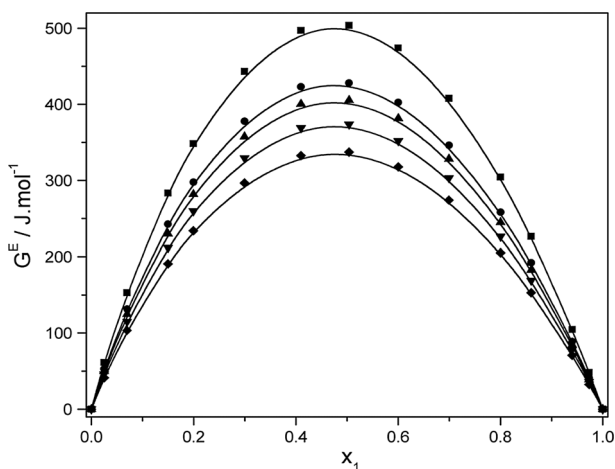


Fig. 2 Excess Gibbs energy G^E as a function of the mole fraction of the first component for the binary mixture formed by 2-methylpropan-2-ol (1) + ethane-1,2-diol (2) at 19.99 kPa, filled square; 39.99 kPa, filled circle; 59.99 kPa, filled triangle; 78.79 kPa, filled inverted triangle; 94.99 kPa, filled diamond

model, followed closely by the Wilson activity coefficient model. These results can be observed from Fig. 1, where the phase equilibrium data have been plotted with modeled values of NRTL and UNIFAC model at 19.99 and 94.99 kPa. Further, the optimum model parameters were used to calculate the activity coefficients (γ_1 and γ_2) and excess Gibbs energy (G^E). It was observed from the activity coefficients in Table 2 that the system 2-methylpropan-2-ol(1) + ethane-1,2-diol (2) exhibits non-ideal behavior with positive deviations from Raoult's law, which was mainly attributed to the presence of strong

Table 5 Densities, ρ ($\text{g}\cdot\text{cm}^{-3}$) of 2-methylpropan-2-ol (1) + ethane-1,2-diol at different temperatures (T /K) at 94.99 kPa

x_1	T/K				x_1	T/K			
	303.15	313.15	323.15	333.15		303.15	313.15	323.15	333.15
0.00000	1.10668	1.09988	1.09236	1.08524	0.50402	0.90417	0.89705	0.88741	0.87941
0.02501	1.09453	1.08775	1.08008	1.07292	0.55837	0.88746	0.88019	0.87038	0.86219
0.06920	1.07358	1.06681	1.05895	1.05175	0.59726	0.87599	0.86859	0.85868	0.85035
0.07004	1.07319	1.06641	1.05855	1.05135	0.65371	0.86004	0.85247	0.84237	0.83382
0.14986	1.03678	1.02982	1.02193	1.01458	0.69916	0.84779	0.84001	0.82979	0.82105
0.19961	1.01528	1.00823	1.00027	0.99283	0.75073	0.83450	0.82633	0.81606	0.80710
0.25748	0.99153	0.98444	0.97626	0.96873	0.80946	0.82010	0.81136	0.80103	0.79180
0.30452	0.97321	0.96614	0.95769	0.95009	0.85711	0.80888	0.79965	0.78921	0.77972
0.37730	0.94649	0.93947	0.93052	0.92281	0.90271	0.79839	0.78855	0.77810	0.76827
0.39988	0.93858	0.93157	0.92247	0.91472	0.95964	0.78532	0.77502	0.76424	0.75378
0.40111	0.93815	0.93114	0.92204	0.91428	0.97840	0.78094	0.77047	0.75962	0.74886
0.46431	0.91691	0.90986	0.90039	0.89250	1.00000	0.77547	0.76486	0.75394	0.74270

Standard uncertainties u are $u(x_i) = 0.00005$, $u(\rho) = 0.00125\text{g}\cdot\text{cm}^{-3}$ $u(T) = 0.01\text{K}$, $u(V_m^E) = 0.03758\text{cm}^3\cdot\text{mol}^{-1}$

hydrogen bonding. Also, the excess Gibbs energies of the mixtures were found to be positive. The plot of G^E as the function of mole fraction of the more volatile component is presented in Fig. 2. The plot shows that G^E is symmetric with respect to the mole fraction for the mixture of 2-methylpropan-2-ol and ethane-1,2-diol, which indicates the highly non-ideal behavior of the binary mixtures. The excess Gibbs energy was observed to be positive over the entire composition range with maximum value at $x_1 = 0.5$.

3.2 Volumetric Properties and Molar Refractivity

Volumetric properties reflect the intermolecular interactions between the components studied. In the 2-methylpropan-2-ol (1) + ethane-1,2-diol (2) mixtures 1–1, 1–2 and 2–2 hydrogen bonding plays an imperative role and fluctuations in the volume depend on the relative energies of the hydrogen bonds. 2-Methylpropan-2-ol consists a hydrophilic –OH group that is able to form strong hydrogen bonds with molecules of ethane-1,2-diol and three hydrophobic –CH₃ groups that display solvophobic effects, which strengthen the interactions of solvent molecules in the solvation shell [42]. Ethane-1,2-diol has a water-like hydrogen bond network with inter and intramolecular hydrogen bonds. The number of weakly polar methylene groups is equal to the number of hydroxyl groups and thereby have a considerable influence on the volumetric properties with the association of hydrogen bond. Further, it exhibits 27 different conformations and, depending on the temperature and aggregation state, it exists in gauche- and trans-conformations with the predominance of gauche at room temperature and atmospheric pressure conditions [43].

The experimental volumetric properties and densities of the 2-methylpropan-2-ol (1) + ethane-1,2-diol (2) binary system were measured at 303.15, 313.15, 323.15 and 333.15 K at local atmospheric pressure of 94.99 kPa over the entire composition are summarized in Table 5. The derived property, excess molar volumes (V_m^E) for the present binary mixtures at different molar compositions, were evaluated according to the following equation:

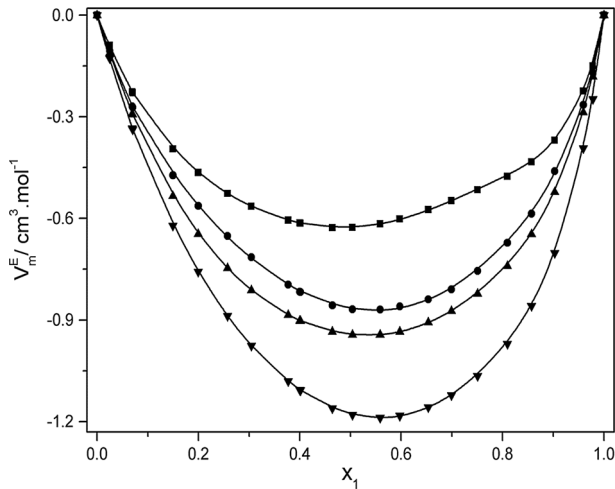


Fig. 3 Excess molar volume V_m^E of 2-methylpropan-2-ol (1) + ethane-1,2-diol (2) at constant temperature: experimental data at 303.15 K, filled square; 313.15 K, filled circle; 323.15 K, filled triangle; 333.15 K, filled inverted triangle; solid curve—calculated from Redlich–Kister parameters

$$V_m^E = x_1 M_1 (1/\rho - 1/\rho_1) + x_2 M_2 (1/\rho - 1/\rho_2) \quad (10)$$

where x_1, x_2 are the mole fractions, M_1, M_2 are the molecular weights and ρ_1, ρ_2 are the densities of pure 2-methylpropan-2-ol (1) and ethane-1,2-diol (2), respectively; ρ is the density of the mixture. The excess molar volumes (V_m^E) of the binary mixtures were found to be negative over the entire composition range as illustrated in Fig. 3. The negative values of excess molar volumes reflect the strong intermolecular interactions and the packing effect between 2-methylpropan-2-ol and 1, 2-dihydroxyethane. It is also clear from Fig. 3 that, with an increase in the temperature of the mixture, the intermolecular interactions strengthen, which leads to the more negative values of the excess molar volumes (V_m^E) with a minimum at $x_1 = 0.58$ and 333.15 K.

The experimental refractive index (n) of the 2-methylpropan-2-ol + ethane-1,2-diol system were measured at different wavelengths (404.7, 435.8, 486.1, 546.1, 587.6, 589.3, 632.8, 644.0 and 706.5 nm) for the binary mixtures at 303.15, 313.15, 323.15 and 333.15 K over the entire compositions at local atmospheric pressure and are reported in Table 6. Instead of deviations in refractive index, the deviations in molar refractivity (ΔR) are evaluated, since this provides the electronic perturbation of molecular orbital resulting from mixing the components [44]. The deviations in molar refractivity (ΔR) have been evaluated by following equation [45]:

$$\Delta R (\text{cm}^3 \cdot \text{mol}^{-1}) = R_m - \sum_i \phi_i R_i \quad (11)$$

The Lorentz–Lorenz equation was used to investigate R_m values for the binary mixture:

$$R_m = \left(\frac{n_\lambda^2 - 1}{n_\lambda^2 + 2} \right) \left(\frac{\sum_i x_i M_i}{\rho_m} \right) \quad (12)$$

Table 6 Refractive indices n_λ of 2-methylpropan-2-ol (1) + ethane-1,2-diol (2) for different wavelengths and temperatures^a

x_1	n_λ								
	404.7	435.8	486.1	546.1	587.6	589.3	632.8	644	706.5
$T/K = 303.15$									
0.00000	1.44111	1.43873	1.43452	1.43085	1.42916	1.42910	1.42743	1.42709	1.42560
0.02501	1.43941	1.43675	1.43284	1.42949	1.42785	1.42774	1.42619	1.42584	1.42463
0.06920	1.43698	1.43429	1.43041	1.42710	1.42546	1.42537	1.42383	1.42350	1.42232
0.07004	1.43694	1.43425	1.43036	1.42706	1.42542	1.42533	1.42378	1.42345	1.42228
0.14986	1.43263	1.42989	1.42605	1.42282	1.42119	1.42112	1.41959	1.41929	1.41819
0.19961	1.43000	1.42723	1.42342	1.42023	1.41861	1.41854	1.41703	1.41674	1.41568
0.25748	1.42700	1.42420	1.42042	1.41726	1.41565	1.41559	1.41410	1.41382	1.41281
0.30452	1.42459	1.42177	1.41801	1.41489	1.41329	1.41323	1.41175	1.41149	1.41050
0.37730	1.42094	1.41810	1.41437	1.41129	1.40970	1.40964	1.40819	1.40794	1.40699
0.39988	1.41982	1.41697	1.41326	1.41019	1.40860	1.40854	1.40710	1.40685	1.40592
0.40111	1.41976	1.41691	1.41320	1.41013	1.40854	1.40848	1.40704	1.40679	1.40586
0.46431	1.41668	1.41382	1.41014	1.40710	1.40551	1.40545	1.40404	1.40379	1.40289
0.50402	1.41478	1.41192	1.40825	1.40523	1.40364	1.40358	1.40218	1.40194	1.40105
0.55837	1.41222	1.40936	1.40571	1.40270	1.40113	1.40105	1.39967	1.39944	1.39857
0.59726	1.41042	1.40755	1.40392	1.40093	1.39935	1.39927	1.39791	1.39767	1.39682
0.65371	1.40785	1.40499	1.40137	1.39839	1.39682	1.39672	1.39539	1.39515	1.39431
0.69916	1.40582	1.40296	1.39936	1.39638	1.39482	1.39471	1.39340	1.39316	1.39232
0.75073	1.40355	1.40070	1.39711	1.39415	1.39259	1.39246	1.39118	1.39093	1.39009
0.80946	1.40102	1.39819	1.39462	1.39165	1.39010	1.38995	1.38869	1.38844	1.38760
0.85711	1.39901	1.39620	1.39263	1.38967	1.38812	1.38795	1.38672	1.38645	1.38562
0.90271	1.39712	1.39433	1.39077	1.38780	1.38625	1.38606	1.38486	1.38458	1.38374
0.95964	1.39481	1.39204	1.38850	1.38552	1.38397	1.38376	1.38258	1.38229	1.38144
0.97840	1.39406	1.39130	1.38776	1.38478	1.38324	1.38301	1.38184	1.38155	1.38070
1.00000	1.39323	1.39047	1.38690	1.38394	1.38241	1.38216	1.38102	1.38071	1.37989
$T/K = 313.15$									
0.00000	1.43755	1.43488	1.43109	1.42796	1.42629	1.42623	1.42476	1.42442	1.42317
0.02501	1.43633	1.43354	1.42978	1.42663	1.42498	1.42491	1.42346	1.42312	1.42203
0.06920	1.43384	1.43105	1.42730	1.42416	1.42251	1.42244	1.42100	1.42066	1.41958
0.07004	1.43379	1.43100	1.42726	1.42411	1.42247	1.42240	1.42096	1.42062	1.41954
0.14986	1.42937	1.42659	1.42285	1.41973	1.41809	1.41802	1.41660	1.41626	1.41519
0.19961	1.42666	1.42388	1.42016	1.41705	1.41542	1.41534	1.41394	1.41360	1.41253
0.25748	1.42355	1.42079	1.41707	1.41398	1.41235	1.41228	1.41088	1.41054	1.40949
0.30452	1.42106	1.41831	1.41460	1.41152	1.40990	1.40983	1.40844	1.40810	1.40706
0.37730	1.41727	1.41454	1.41084	1.40778	1.40618	1.40611	1.40472	1.40439	1.40336
0.39988	1.41611	1.41338	1.40970	1.40664	1.40504	1.40497	1.40359	1.40325	1.40223
0.40111	1.41605	1.41332	1.40963	1.40658	1.40498	1.40491	1.40353	1.40319	1.40216
0.46431	1.41285	1.41013	1.40646	1.40342	1.40183	1.40177	1.40039	1.40006	1.39904
0.50402	1.41087	1.40816	1.40450	1.40147	1.39989	1.39982	1.39845	1.39812	1.39711
0.55837	1.40819	1.40551	1.40185	1.39884	1.39727	1.39721	1.39583	1.39551	1.39451
0.59726	1.40630	1.40363	1.39999	1.39699	1.39543	1.39537	1.39398	1.39367	1.39268

Table 6 continued

x_1	n_λ								
	404.7	435.8	486.1	546.1	587.6	589.3	632.8	644	706.5
0.65371	1.40360	1.40095	1.39732	1.39434	1.39280	1.39273	1.39135	1.39104	1.39006
0.69916	1.40146	1.39883	1.39521	1.39224	1.39071	1.39065	1.38926	1.38896	1.38799
0.75073	1.39907	1.39646	1.39286	1.38990	1.38839	1.38833	1.38693	1.38663	1.38568
0.80946	1.39639	1.39381	1.39023	1.38728	1.38579	1.38573	1.38432	1.38404	1.38310
0.85711	1.39426	1.39170	1.38813	1.38519	1.38372	1.38367	1.38225	1.38197	1.38104
0.90271	1.39225	1.38971	1.38615	1.38323	1.38178	1.38172	1.38029	1.38002	1.37911
0.95964	1.38978	1.38728	1.38374	1.38082	1.37940	1.37935	1.37790	1.37764	1.37674
0.97840	1.38898	1.38649	1.38295	1.38004	1.37862	1.37857	1.37712	1.37687	1.37597
1.00000	1.38806	1.38558	1.38205	1.37915	1.37774	1.37769	1.37623	1.37598	1.37509
$T/K = 323.15$									
0.00000	1.43436	1.43180	1.42819	1.42495	1.42331	1.42325	1.42182	1.42147	1.42008
0.02501	1.43293	1.43037	1.42671	1.42356	1.42191	1.42184	1.42038	1.42006	1.41896
0.06920	1.43069	1.42813	1.42443	1.42129	1.41958	1.41951	1.41804	1.41773	1.41663
0.07004	1.43064	1.42809	1.42439	1.42125	1.41953	1.41946	1.41800	1.41769	1.41659
0.14986	1.42659	1.42403	1.42027	1.41717	1.41537	1.41528	1.41383	1.41352	1.41243
0.19961	1.42405	1.42150	1.41772	1.41464	1.41279	1.41270	1.41125	1.41095	1.40986
0.25748	1.42109	1.41854	1.41476	1.41170	1.40982	1.40973	1.40829	1.40798	1.40690
0.30452	1.41867	1.41613	1.41236	1.40933	1.40743	1.40733	1.40590	1.40560	1.40452
0.37730	1.41492	1.41240	1.40866	1.40567	1.40375	1.40364	1.40224	1.40194	1.40088
0.39988	1.41376	1.41124	1.40751	1.40454	1.40262	1.40251	1.40111	1.40082	1.39976
0.40111	1.41369	1.41117	1.40745	1.40448	1.40256	1.40245	1.40105	1.40076	1.39970
0.46431	1.41042	1.40792	1.40426	1.40133	1.39941	1.39929	1.39793	1.39764	1.39659
0.50402	1.40836	1.40586	1.40225	1.39935	1.39744	1.39733	1.39598	1.39570	1.39465
0.55837	1.40553	1.40305	1.39952	1.39666	1.39478	1.39466	1.39334	1.39306	1.39203
0.59726	1.40350	1.40103	1.39757	1.39474	1.39288	1.39276	1.39147	1.39119	1.39017
0.65371	1.40055	1.39810	1.39475	1.39197	1.39015	1.39003	1.38878	1.38850	1.38749
0.69916	1.39817	1.39573	1.39248	1.38974	1.38797	1.38784	1.38663	1.38635	1.38535
0.75073	1.39546	1.39304	1.38991	1.38723	1.38551	1.38539	1.38421	1.38394	1.38295
0.80946	1.39236	1.38996	1.38700	1.38437	1.38274	1.38261	1.38149	1.38122	1.38025
0.85711	1.38984	1.38746	1.38465	1.38207	1.38050	1.38038	1.37931	1.37904	1.37808
0.90271	1.38742	1.38506	1.38240	1.37987	1.37838	1.37826	1.37723	1.37697	1.37602
0.95964	1.38439	1.38206	1.37961	1.37714	1.37576	1.37564	1.37467	1.37441	1.37347
0.97840	1.38339	1.38107	1.37869	1.37624	1.37490	1.37478	1.37383	1.37357	1.37264
1.00000	1.38212	1.38005	1.37752	1.37515	1.37385	1.37374	1.37280	1.37253	1.37167
$T/K = 333.15$									
0.00000	1.43115	1.42842	1.42470	1.42159	1.41994	1.41988	1.41844	1.41810	1.41706
0.02501	1.42996	1.42735	1.42362	1.42050	1.41889	1.41882	1.41758	1.41723	1.41624
0.06920	1.42768	1.42507	1.42136	1.41828	1.41666	1.41660	1.41537	1.41502	1.41403
0.07004	1.42764	1.42503	1.42131	1.41824	1.41662	1.41656	1.41532	1.41498	1.41399
0.14986	1.42350	1.42089	1.41722	1.41424	1.41260	1.41254	1.41133	1.41100	1.41000
0.19961	1.42091	1.41830	1.41467	1.41174	1.41009	1.41004	1.40884	1.40852	1.40753
0.25748	1.41788	1.41529	1.41170	1.40884	1.40718	1.40713	1.40595	1.40563	1.40465

Table 6 continued

x_1	n_λ								
	404.7	435.8	486.1	546.1	587.6	589.3	632.8	644	706.5
0.30452	1.41541	1.41283	1.40929	1.40648	1.40481	1.40476	1.40359	1.40328	1.40231
0.37730	1.41157	1.40901	1.40557	1.40282	1.40115	1.40109	1.39995	1.39965	1.39870
0.39988	1.41037	1.40783	1.40441	1.40169	1.40002	1.39995	1.39882	1.39853	1.39759
0.40111	1.41031	1.40776	1.40435	1.40163	1.39996	1.39989	1.39876	1.39847	1.39752
0.46431	1.40695	1.40443	1.40112	1.39845	1.39678	1.39671	1.39560	1.39532	1.39440
0.50402	1.40483	1.40233	1.39909	1.39646	1.39479	1.39470	1.39362	1.39334	1.39244
0.55837	1.40191	1.39946	1.39632	1.39373	1.39206	1.39196	1.39090	1.39063	1.38976
0.59726	1.39982	1.39739	1.39434	1.39177	1.39011	1.39000	1.38896	1.38870	1.38784
0.65371	1.39678	1.39439	1.39146	1.38894	1.38727	1.38716	1.38614	1.38589	1.38507
0.69916	1.39431	1.39197	1.38915	1.38665	1.38499	1.38486	1.38386	1.38363	1.38284
0.75073	1.39151	1.38921	1.38652	1.38406	1.38241	1.38226	1.38129	1.38106	1.38031
0.80946	1.38830	1.38606	1.38353	1.38111	1.37947	1.37930	1.37835	1.37814	1.37743
0.85711	1.38569	1.38350	1.38111	1.37871	1.37708	1.37689	1.37597	1.37577	1.37510
0.90271	1.38318	1.38104	1.37880	1.37642	1.37480	1.37459	1.37370	1.37350	1.37288
0.95964	1.38004	1.37797	1.37591	1.37355	1.37195	1.37171	1.37085	1.37067	1.37010
0.97840	1.37900	1.37695	1.37496	1.37261	1.37101	1.37076	1.36992	1.36974	1.36919
1.00000	1.37791	1.37588	1.37393	1.37153	1.36997	1.36971	1.36893	1.36875	1.36826

^a Standard uncertainties u are $u(x_i) = 0.00005$, $u(T) = 0.01\text{K}$, $u(n_\lambda) = 0.00150$, $u(\Delta R) = 0.0551\text{cm}^3 \cdot \text{mol}^{-1}$

$$R_i = \left(\frac{n_{\lambda,i}^2 - 1}{n_{\lambda,i}^2 + 2} \right) \left(\frac{M_i}{\rho_i} \right) \tag{13}$$

$$\varphi_i = \frac{x_i V_i}{\sum_k x_k V_k} \tag{14}$$

where n_λ and $n_{\lambda,i}$ are the refractive index values of the mixture and pure components, respectively, and φ_i are the volume fractions of 2-methylpropan-2-ol + ethane-1,2-diol. The deviations in the molar refractivity (ΔR) at 589.3 nm (sodium D line) was evaluated and found to be negative over the entire range of composition; this is shown in Fig. 4. The negative values of ΔR indicate greater dispersive forces in the mixtures than pure components and become more negative with increasing temperature.

The excess molar volumes (V_m^E) and deviations in molar refractivity (ΔR) were modeled with Redlich–Kister equation:

$$V_m^E / \Delta R = x_2(1 - x_2) \sum_{i=0}^{i=n} A_i(1 - 2x_2)^i. \tag{15}$$

The order of the polynomial is determined based on the F-test. The deviations in experimental and predicted values of V_m^E or ΔR was calculated using the equation stated below:

$$\sigma = \left[\sum \left((V_m^E / \Delta R)_{\text{exp}} - (V_m^E \text{ or } \Delta R)_{\text{cal}} \right)^2 / (N - (n + 1)) \right]^{0.5} \tag{16}$$

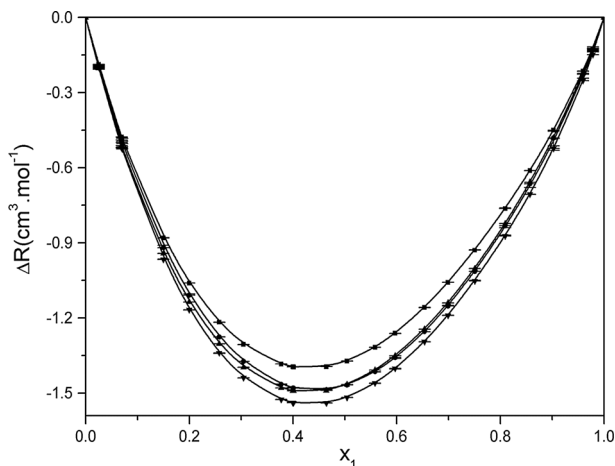


Fig. 4 Deviation in molar refractivity ΔR of 2-methylpropan-2-ol (1) + ethane-1,2-diol (2) at: 303.15 K; filled square, 313.15 K; filled circle, 323.15 K; filled triangle, 333.15 K; filled inverted triangle, Solid curve—calculated from Redlich–Kister parameters and (dashed lines) standard error bar

where N is the total number of experimental points, n is the order of the polynomial and $n + 1$ is a number of coefficients (A_i). The Redlich–Kister parameters for excess molar volumes (V_m^E) and molar refractivity (ΔR) with their standard error $\sigma(V_m^E/\Delta R)$ and the overall standard deviations at each temperature are summarized in Table 7. The correlation results for V_m^E and ΔR using the Redlich–Kister equation are relatively good and are graphically presented in Figs. 3 and 4, respectively.

Additionally, the measured refractive indices were further considered using the Lorentz–Lorenz, Wiener, Heller, Gladstone–Dale and Arago–Biot mixing models [44–48]. These rules are based on the electromagnetic theory of light, which treats the molecules as dipoles or assemblies of dipoles in an external field [49]. The following equations were used for the prediction of the refractive index of binary mixtures:

$$\begin{aligned} \text{Lorentz–Lorenz (L–L) relation : } n_\lambda^2 - 1/n_\lambda^2 + 2 \\ = \left(n_{\lambda,1}^2 - 1/n_{\lambda,1}^2 + 2 \right) \varphi_1 + \left(n_{\lambda,2}^2 - 1/n_{\lambda,2}^2 + 2 \right) \varphi_2 \end{aligned} \quad (17)$$

$$\text{Wiener (W) relation : } n_\lambda^2 - n_{\lambda,1}^2/n_\lambda^2 + 2n_{\lambda,1}^2 = \left(n_{\lambda,2}^2 - n_{\lambda,1}^2/n_{\lambda,2}^2 - 2n_{\lambda,1}^2 \right) \varphi_2 \quad (18)$$

$$\text{Heller (H) relation : } n_\lambda - n_{\lambda,1}/n_{\lambda,1} = \frac{3}{2} \left(\left(n_{\lambda,2}/n_{\lambda,1} \right)^2 - 1 / \left(n_{\lambda,2}/n_{\lambda,1} \right)^2 + 2 \right) \varphi_2 \quad (19)$$

$$\text{Gladstone–Dale (G–D) relation : } n_\lambda - 1/\rho = \left(n_{\lambda,1} - 1/\rho_1 \right) w_1 + \left(n_{\lambda,2} - 1/\rho_2 \right) w_2 \quad (20)$$

$$\text{Arago–Biot (A–B) relation : } n_\lambda = n_{\lambda,1} \varphi_1 + n_{\lambda,2} \varphi_2 \quad (21)$$

where w_1 and w_2 are the weight fractions of component 1 and 2, respectively.

The average percentage deviation (APD) obtained from these models is presented in Table 8. The G–D model resulted in the lowest deviation. It was also observed that the Arago–Biot relation had similar deviations to the Lorentz–Lorenz relation at all the

Table 7 Redlich–Kister parameters, standard deviation (SD) and error (σ) for excess molar volumes (V_m^E) and deviations in molar refractivity (ΔR) of 2-methylpropan-2-ol (1) + ethane-1,2-diol (2) at different temperatures

T/K	($\text{cm}^3 \cdot \text{mol}^{-1}$)	A_0	A_1	A_2	A_3	A_4	A_5	A_6	SD
303.15	V^E	-2.50490	0.09591	-0.65989	0.29491	-1.04258	-2.08681	-1.61821	0.00379
	$\sigma(V^E)$	0.00783	0.03415	0.14693	0.19754	0.54787	0.23841	0.51107	
	ΔR	-5.50148	1.42952	-0.60108	0.20262	-0.36283	-0.64816	-0.51994	0.00125
313.15	$\sigma(\Delta R)$	0.00258	0.01126	0.04844	0.06513	0.18063	0.07860	0.16849	
	V^E	-3.46265	-0.55671	-0.89825	0.27901	-0.05542	-1.27826	-2.23203	0.00647
	$\sigma(V^E)$	0.01334	0.05820	0.25042	0.33669	0.93381	0.40636	0.87108	
323.15	ΔR	-5.88104	1.27370	-0.66021	0.22200	-0.14334	-0.43335	-0.57698	0.00520
	$\sigma(\Delta R)$	0.00450	0.01964	0.08449	0.11360	0.31507	0.13711	0.29391	
	V^E	-3.76975	-0.35581	-1.39206	0.07152	-0.17505	-1.70405	-1.64225	0.00353
333.15	$\sigma(V^E)$	0.00728	0.03176	0.13665	0.18372	0.50956	0.22174	0.47533	
	ΔR	-5.87732	1.49409	-0.85358	0.08531	-0.14515	-0.35735	-0.43643	0.00072
	$\sigma(\Delta R)$	0.00148	0.00646	0.02779	0.03736	0.10361	0.04509	0.09665	
333.15	V^E	-4.70815	-0.82331	-1.53351	-0.09821	-0.66476	-2.41002	-2.13389	0.00463
	$\sigma(V^E)$	0.00956	0.04169	0.17938	0.24117	0.66888	0.29107	0.62395	
	ΔR	-6.08184	1.44583	-0.89478	0.19039	-0.33180	-0.93688	-0.51056	0.00200
	$\sigma(\Delta R)$	0.00414	0.01804	0.07762	0.10436	0.28943	0.12595	0.26999	

Table 8 Average percentage deviations in mixing rules of 2-methylpropan-2-ol(1) + ethane-1,2-diol (2) at different temperatures

T/K	L-L	W	H	G-D	A-B
303.15	0.19292	0.18785	0.19316	0.02324	0.18490
313.15	0.20475	0.19936	0.20505	0.01522	0.19618
323.15	0.25524	0.24966	0.25559	0.01718	0.24634
333.15	0.31270	0.30701	0.31311	0.02399	0.30358

temperatures studied. Positive deviations were observed for all the mixing rules considered. In general, for binary systems, the dispersion and dipolar interactions are inactive where deviations are found to be positive [44].

Furthermore, the partial molar volumes (\bar{V}_1 and \bar{V}_2) of 2-methylpropan-2-ol (1) + ethane-1,2-diol (2) system were calculated by differentiation of Eq. 15 with respect to x_2 (sixth order polynomial) and the combination of differentiation resulted in Eqs. 22 and 23:

$$\bar{V}_1 = V_1^0 + V_m^E - x_2(\partial V_m^E/\partial x_2) \quad (22)$$

$$\bar{V}_2 = V_2^0 + V_m^E + (1 - x_2)(\partial V_m^E/\partial x_2) \quad (23)$$

where V_1^0 and V_2^0 are molar volumes of pure components 1 and 2, respectively. The derived equations for the calculation of partial molar volumes are:

$$\bar{V}_1 = V_1^0 + x_2^2 \sum_{i=0}^{i=n} A_i(1 - 2x_2)^i + 2x_2^2(1 - x_2) \sum_{i=0}^{i=n} A_i(i)(1 - 2x_2)^{i-1} \quad (24)$$

$$\bar{V}_2 = V_2^0 + (1 - x_2)^2 \sum_{i=0}^{i=n} A_i(1 - 2x_2)^i - 2x_2(1 - x_2) \sum_{i=0}^{i=n} A_i(i)(1 - 2x_2)^{i-1}. \quad (25)$$

The results for the derived volumetric properties, partial molar volumes for 2-methylpropan-2-ol (1) + ethane-1,2-diol (2) with respect to the mole fraction of 2-methylpropan-2-ol, are shown in Fig. 5a and b.

The partial molar volume of 2-methylpropan-2-ol (\bar{V}_1) increases with increasing 2-methylpropan-2-ol concentration, while the partial molar volume of ethane-1,2-diol (\bar{V}_2) decreased over the entire temperature range under consideration. The variation in partial molar volumes (\bar{V}_1 and \bar{V}_2) for both the components was prominent at higher temperatures as is evident from Fig. 5. The increase in temperature decreases in the average length of the H-bond of 2-methylpropan-2-ol and increases the translatory motion. The sharp decrease in the partial molar volumes for ethane-1,2-diol (\bar{V}_2) is primarily due to the contributions of intra- and intermolecular H-bonds amongst the total intermolecular interactions in the 2-methylpropan-2-ol (1) + ethane-1,2-diol (2) system. The addition of a small quantity of 2-methylpropan-2-ol to ethane-1,2-diol lowers the contribution from intramolecular H-bonds in ethane-1,2-diol and increases the contribution from its intermolecular H-bonds.

3.3 Prigogine–Flory–Patterson (PFP) Theory

For estimation and analysis of excess molar volumes, the Prigogine–Flory–Patterson (PFP) theory has been used. Patterson and coworkers have presented a detailed discussion of the

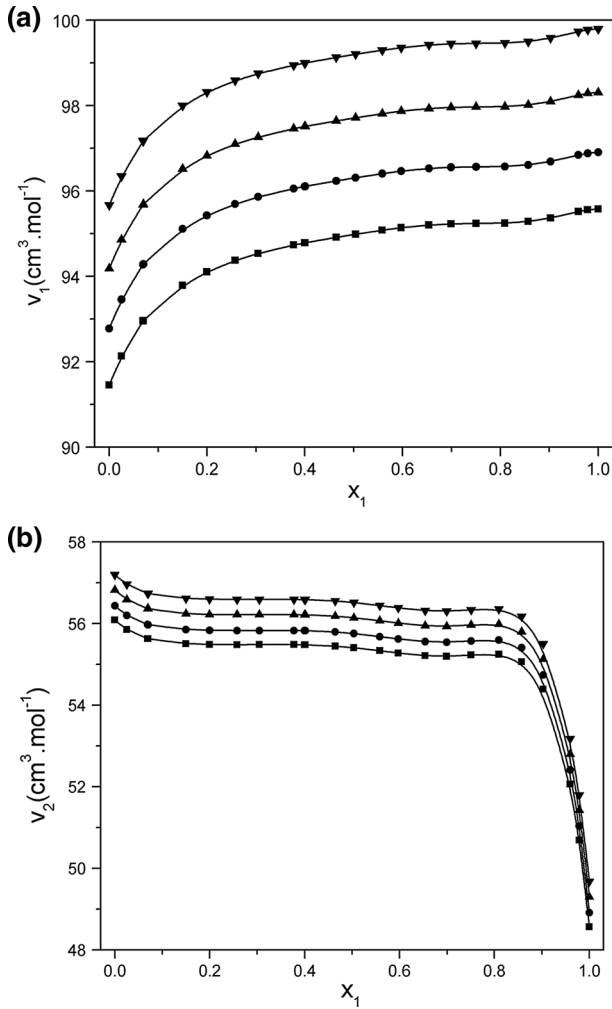


Fig. 5 Dependences of partial molar volumes \bar{V}_1, \bar{V}_2 for 2-methylpropan-2-ol (1) + ethane-1,2-diol (2) mixtures, respectively, at different temperatures: 303.15 K, *filled square*; 313.15 K, *filled circle*; 323.15 K, *filled triangle*; 333.15 K, *filled inverted triangle*

PFP theory [48]. This theory establishes the relative importance of different contributions to the experimental excess molar volumes. The PFP theory considers V_m^E as a sum of three contributions: an interactional term calculated from the interactional parameter (χ_{12}), a free volume contribution and a p^* term reflecting a pressure contribution, which arises from the differences in the internal pressures, and the reduced volumes of the pure components and is directly proportional to $(\bar{v}_1 - \bar{v}_2)(p_1^* - p_2^*)$. The resulting equation is [50]:

Table 9 Flory parameters of the pure components at the different temperatures from 303.15 K to 333.15 K

T/K	2-methylpropan-2-ol (1)			ethane-1,2-diol (2)		
	V*	p*/(J·cm ⁻³)	T*/K	V*	p*/(J·cm ⁻³)	T*/K
303.15	71.80	570.23	955.96	47.90	685.36	1600.80
313.15	71.82	568.59	950.20	47.91	684.71	1596.03
323.15	71.85	565.15	945.72	47.93	683.37	1591.76
333.15	71.95	559.78	942.42	47.94	681.33	1587.97

$$\begin{aligned}
 \frac{V_m^E}{V_1^*x_1 + x_2V_2^*} = & \frac{(\bar{v}^{\frac{1}{3}} - 1)\bar{v}_1^2\psi_1\theta_2}{\left(\frac{4}{3}\bar{v}^{-\frac{1}{3}} - 1\right)P_1^*} \chi_{12}(\text{interactional}) \\
 & - \frac{(\bar{v}_1 - \bar{v}_2)^2\left(\frac{14}{9}\bar{v}^{-\frac{1}{3}} - 1\right)\psi_1\psi_2}{\left(\frac{4}{3}\bar{v}^{-\frac{1}{3}} - 1\right)\bar{v}} (\text{Free volume}) \\
 & + \frac{(\bar{v}_1 - \bar{v}_2)(P_1^* - P_2^*)\psi_1\psi_2}{\psi_1P_2^* + \psi_2P_1^*} (P^* \text{ effect})
 \end{aligned} \tag{26}$$

where V_1^* is the characteristic volume ($V_i^* = \frac{V_i}{\bar{v}_i}$). The reduced volume, \bar{v}_i , and characteristic pressure, P_i^* , are calculated according to following equations:

$$\bar{v}_i = \left(\frac{1 + \frac{4}{3}\alpha_i T}{1 + \alpha_i T} \right)^3 \tag{27}$$

$$P_i^* = \frac{\bar{v}_i^2 \alpha_i T}{k_i} \tag{28}$$

The \bar{v}_i of a binary mixture in Eq. 27 is approximated by:

$$\bar{v} = \psi_1\bar{v}_1 + \psi_2\bar{v}_2 \tag{29}$$

where ψ_i , Φ_i and θ_1 represent the molecular contact energy fraction, hard-core volume fraction, and molecular surface site fraction, respectively, and are evaluated as follows:

$$\psi = 1 - \psi_2 = \left(\frac{\Phi_1 P_1^*}{\Phi_1 P_1^* + \Gamma_2 P_2^*} \right) \tag{30}$$

$$\Phi_1 = 1 - \theta_2 = \left(\frac{\Phi_1 V_1^*}{\Phi_1 V_1^* + \Phi_2 V_2^*} \right) \tag{31}$$

$$\theta_1 = 1 - \theta_2 = \frac{\Phi_1 s_1}{\Phi_1 s_1 + \Phi_2 s_2} \tag{32}$$

where s_i is the molecular surface to volume ratio, which is determined by the Abe and Flory theory:

$$\frac{s_1}{s_2} = \left(\frac{V_1^*}{V_2^*} \right)^{-\frac{1}{3}} \tag{33}$$

Table 10 Calculated parameters of excess molar volume from the PFP theory with interaction parameter (χ_{12})

T/K	χ_{12} /($\text{J}\cdot\text{cm}^{-3}$)	V_m^E /($\text{cm}^3\cdot\text{mol}^{-1}$) at $x = 0.5$		Calculated contribution		
		Exp.	PFP	V_m^E (int)	V_m^E (fv)	V_m^E (p^*)
303.15	67.85	-0.6268	-0.5604	0.0114	0.0147	-0.0072
313.15	66.01	-0.8688	-0.8688	0.0103	0.0170	-0.0078
323.15	63.35	-0.9438	-0.9438	0.0124	0.0196	-0.0084
333.15	57.58	-1.1800	-1.0052	0.0121	0.0225	-0.0093

The values of the different parameters of the pure components necessary in the PFP theory (Eq. 26) were obtained using the Flory model and are listed in Table 9. PFP theory requires experimental, V_m^E , thermal expansion coefficient, α_p and isothermal compressibility, κ_T and α_p ; κ_T required in the calculation were taken from literature [27, 51, 52]. The values of α_p , κ_T at other than 298.15 K were calculated from the following relation [11]:

$$\alpha = \alpha_0 + \alpha_0^2(7 + 4\alpha_0 T) \left(\frac{T - T_0}{3} \right) \tag{34}$$

$$\gamma = \gamma_0 - \gamma_0(1 + 2\alpha_0 T) \left(\frac{T - T_0}{T} \right), T_0 = 298.15 \text{ K} \tag{35}$$

where $\kappa_T = \frac{2p}{\gamma}$, γ and γ_0 are the thermal pressure coefficient at the desired temperature and reference temperature, respectively. To predict the V_m^E according to the PFP theory, the energy interaction parameter, χ_{12} was calculated by fitting the Eq. 26 to experimental V_m^E at equimolar composition. The χ_{12} along with three PFP interactional contributions, free volume, p^* effect, and experimental and calculated (using PFP theory) V_m^E values near the

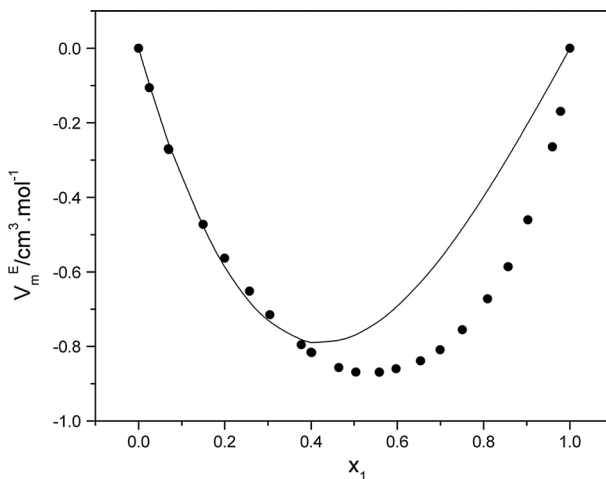


Fig. 6 Comparison of experimental and theoretical excess molar volume as a function of mole fraction (x_1) for 2-methylpropan-2-ol (1) + ethane-1,2-diol (2) mixtures: 313.15 K, filled circle solid line calculated using PFP theory

equimolar composition are presented in Table 10. Study of the data revealed that the interactional and free volume contributions are positive, whereas p^* (characteristic pressure) contributions are negative for the system studied. For the binary mixtures, the free volume contribution dominates over the other two contributions. Table 9 shows that the characteristic pressure p_i^* of ethane-1,2-diol is larger than that of 2-methylpropan-2-ol, while the value of the reduced volume, \bar{v}_i ; for 2-methylpropan-2-ol is higher than for ethane-1,2-diol, which results in a negative contribution from the p^* term, resulting from the large negative $(p_1^* - p_2^*)$ and positive $(\bar{v}_1 - \bar{v}_2)$ values. The p^* term makes little contribution to V_m^E for the binary mixtures in comparison with the other terms.

Furthermore, the χ_{12} value calculated at the equimolar composition was used to check whether the PFP theory can predict V_m^E correctly over the entire composition range. The theoretical values are plotted in Fig. 6 along with the experimental results. It is clear from the figure that the theoretical results agree adequately with the experimental V_m^E values in the ethane-1,2-diol rich region, but the agreement is poor at higher mole fractions of 2-methylpropan-2-ol. The discrepancies between theory and experimental values arise at higher mole fraction of 2-methylpropan-2-ol from additional factors that happen through mixing of two components. As Patterson and co-workers suggested that the PFP theory does not consider all the factors existing in a binary mixture, i.e., it turns out the main features of experimental data are represented using only one parameter [50].

4 Conclusions

Isobaric experimental data for 2-methylpropan-2-ol + ethane-1,2-diol were measured at sub-atmospheric and local atmospheric pressures using a modified Sweitoslawski-type ebulliometer. The experimental phase equilibria results are modelled by activity coefficient Wilson and NRTL models to obtain the optimized binary interaction parameters. The lower RMSD values for the NRTL model suggest a better representation of experimental data. Furthermore, density and refractive index values for pure components and the binary mixtures were studied at temperatures from (303.15 to 313) K at 10 K intervals over the entire composition range. The excess properties, excess molar volumes (V_m^E), partial molar volumes (\bar{V}_i), and deviations in molar refractivity (ΔR) were evaluated to study the effect on these derived properties with varying temperature and molar composition. Excess molar volumes and deviation in molar refractivity were found to be negative at all the temperatures investigated. The negative values of V_m^E indicate that a more attractive interaction or structural accommodation of components occurred on mixing the components. Moreover, negative values of ΔR can be attributed to the dominance of dispersive forces in mixtures compared to those of the pure components. Partial molar volumes of both components showed opposite behavior, i.e., with increasing partial molar volume of 2-methylpropan-2-ol (\bar{V}_1), the partial molar volume of ethane-1,2-diol (\bar{V}_2) decreases. Moreover, different mixing rules were explored to accurately predict the refractive index values of the binary mixture 2-methylpropan-2-ol + ethane-1,2-diol. It was found that the Gladstone–Dale model gives good agreement with the experimental values. The PFP theory correctly represents the main characteristics of experimental excess molar volumes.

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