Thermodynamic properties of binary mixtures of terpenes and 1-propanol in the temperature range from 288.15 to 323.15 K at atmospheric pressure

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Abstract

Terpenes are the most abundant class of chemical compounds present in essential oils. They are considered green solvents, and come from natural sources such as plants, citrus fruits, but also from tree leaves or pinecones. They find wide commercial uses in food industry as natural flavors and food additives, as well as in pharmaceutical and cosmetics industries. In order to study thermodynamic properties of binary mixtures of terpenes (α-pinene, p-cymene and linalool) with 1-propanol, density and viscosity of these mixtures were determined experimentally. Experimental measurements were done over the temperature range from 288.15 to 323.15 K at atmospheric pressure, over the entire composition range. Excess molar volumes, viscosity deviations and thermal expansion coefficients were calculated based on the experimental results of densities and viscosities. Experimentally measured properties were correlated using the Heritz-Brewer-Jouyban-Acree model, while the Redlich-Kister polynomial was used to correlate the derrived properties. All the experimentally obtained data and the derived values were used to analyze non-ideal behavior of the selected mixtures. The Heritz-Brewer-Jouyban-Acree model successfully correlated the experimental values for all three binary systems, while the Redlich-Kister successfully correlated the derived quantities.

Keywords: Density; viscosity; excess properties; modeling.

1. INTRODUCTION

Most of the current industrial processes rely on organic solvents, which are often highly volatile and toxic. Terpenes, regarded as green solvents, offer a solution to many of these issues. These compounds are present in many natural sources and exhibit a diverse range of chemical structures, leading to varying methods for their extraction and purification. Having that in mind, understanding the thermodynamic properties of various terpenes is crucial. Additionally, incorporating solvents like 1-propanol into terpene mixtures is valuable for advancing extraction techniques [1-3]. Combining 1-propanol with terpenes can enhance extraction efficiency and provide a more environmentally friendly solvent option. Accurate thermodynamic calculations are crucial for predicting the behavior of these mixtures, optimizing the extraction conditions, and preventing issues like phase separation, leading to more effective and sustainable industrial processes.

The first investigated terpene was (*1S*)-(-)-*α*-pinene, later referred as α-pinene (IUPAC: (1S)-2,6,6-trimethylbicyclo-[3.1.1]-hept-2-ene), one of the two possible isomers of pinene. It is a bicyclic monoterpene with a highly reactive ring in its structure, commonly extracted from pine wood remnants and also found in pinecones. *α*-pinene is used in cosmetic and pharmaceutical industries due to its anti-inflammatory and antimicrobial effects. For many years, it has also been used in the treatment of respiratory tract infections. Also, due to many suitable properties of pinene dimers, there is a high possibility of using them in mixtures with renewable, biodegradable biofuels, which could be a green alternative to commercial diesel [4,5].

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p-Cymene (IUPAC: 1-methyl-4-(propan-2-yl)benzene), is an aromatic hydrocarbon consisting of a para-substituted benzene ring with methyl and isopropyl groups. In addition to the only progeneric *p*-cymene, there are also two significantly less common geometric isomers, ortho- and meta-cymene. This terpene is used as an intermediate in various organic syntheses, with a particularly notable application being the addition of p-cymene to liquid fuels that lack other aromatic compounds [6]. Furthermore, *p*-cymene shows significant antimicrobial effect in a wide spectrum of actions [7,8].

Linalool (IUPAC: 3,7-dimethylocta-1,6-dien-3-ol) is a representative of terpene alcohols, which can be found in a large number of different flowers and herbs. It is estimated that over 200 plant species produce this alcohol in nature, while in *Lavandula sp.* [9], *Ocinum Basilicum* L. [10] and *Coriandrum sativum* L. [11] it is present at higher concentrations. It is used as an aroma in the production of soaps, fragrances, various food additives, in a large number of household products, but also in insecticides. Like pinene, it has anti-inflammatory properties, and it can be also converted into suitable dimers for use as a fuel [12].

Expanding the database of thermodynamic properties is vital for designing industrial processes, as the accuracy of calculations depends heavily on the consistency of the available data. Furthermore, these properties enhance understanding of molecular interactions in binary systems [13], as solvent mixtures often deviate from ideal behavior. In this work, densities and viscosities for three binary mixtures of terpenes (α-pinene, p-cymene and linalool) with 1-propanol were determined over the entire composition range, for T = 288.15 to 323.15 K and at atmospheric pressure. Furthermore, the excess properties and deviations, the excess molar volumes, the viscosity deviations and thermal expansion coefficients were calculated from the obtained density and viscosity data. The densities and viscosities were correlated by using the Heric-Brewer-Jouyban-Acree single mathematical model, while the excess properties were correlated as a function of the mole fraction by using the Redlich-Kister equation.

2. EXPERIMENTAL

2. 1. Materials

Within this work pure terpenes (*α*-pinene, *p*-cymene and linalool) were products supplied by Acros Organics (Belgium), while the pure solvent 1-propanol was purchased from Fisher Scientific (United Kingdom) (Table 1). The supplied chemicals were used without additional purification.

Table 1. *Sample details*

Chemical name	Supplier	Molar mass, g mol^{-1}	CAS registry N°	Initial mass fraction purity
(*1S*)-(-)-*α*-pinene	Acros organics	136.23	7785-26-4	0.98
p-cymene	Acros organics	134.21	99-87-6	0.99
linalool	Acros organics	154.25	78-70-6	0.97
1-propanol	Fisher scientific	60.09	71-23-8	0.99

2. 2. Apparatus and procedure

Density (ρ) and viscosity (η) of binary mixtures of selected terpenes (*α*-pinene, *p*-cymene, linalool) with 1-propanol were measured by using an Anton Paar SVM 3000/G2 viscometer (Anton Paar, Austria) with rotating cylinders. Measurements were performed in the temperature range from 288.15 to 323.15 K with 5 K increment. A detailed explanation of the characteristics of the apparatus and measurement methods used can be found in our previous work [14].

All chemicals were stored in dark bottles in a separate room when not used, due to terpenes sensitivity to the direct light. The mixtures were prepared gravimetrically using a Mettler AG 204 balance (Mettler Toledo, Switzerland) with a precision of 0.10 μg in the whole range of compositions with the step of 0.01 μg. The standard uncertainty in the mole fraction calculation was less than ±10^{-4}, with all molar quantities derived from the IUPAC relative atomic mass table. The combined expanded uncertainties in the density and viscosity measurements are estimated to 2 kg m^{-3} and 0.007 mPa s, respectively.

2. 3. Comparison with literature

Experimental values of densities and viscosities for pure terpenes and 1-propanol were compared with literature data at several temperatures. Table 2 provides the experimental data and literature values, including their percent deviations.

Table 2. *Experimental and literature values of densities, viscosities of the pure components and deviation at atmospheric pressure*

Component	T^b / K	ρ^c / g m^{-3}		η^d / mPa s		Deviation at atmospheric pressure^a, %	
		Exp.	Lit.	Exp.	Lit.	Density	Viscosity
(1S)-(-)-α-pinene	288.15	0.8643	0.862393 [15]	1.548	1.5542 [15]	0.22	0.40
	293.15	0.8603	0.858276 [15] 0.8585 [16]	1.410	1.4403 [15]	0.24 0.21	2.15
	298.15	0.8562	0.854151 [15] 0.8548 [16] 0.85403 [17]	1.288	1.3096 [15] 1.293 [21]	0.24 0.16 0.25	1.68 0.39
	303.15	0.8521	0.850019 [15] 0.8519 [16]	1.182	1.2110 [15]	0.24 0.02	2.45
	308.15	0.8480	0.845876 [15] 0.8469 [16] 0.84579 [17]	1.087	1.1223 [15]	0.25 0.13 0.26	3.25
	313.15	0.8438	0.841722 [15] 0.8429 [16]	0.999	1.0423 [15]	0.25 0.11	4.33
	318.15	0.8396	0.837556 [15] 0.8394 [16] 0.83864 [17]	0.9248	0.9711 [15]	0.24 0.02 0.11	5.01
	323.15	0.8354	0.833377 [15] 0.8352 [16]	0.859	0.9065 [15]	0.24 0.02	5.53
p-cymene	288.15	0.8614	0.860963 [15]	0.917	0.9358 [15]	0.05	2.05
	293.15	0.8575	0.856962 [15] 0.8561 [16]	0.847	0.8719 [15]	0.06 0.16	2.94
	298.15	0.8536	0.852953 [15] 0.8521 [16] 0.85347 [17]	0.793	0.8073 [15] 0.798 [21]	0.08 0.18 0.02	1.80 0.63
	303.15	0.8496	0.848934 [15] 0.8486 [16]	0.744	0.7595 [15]	0.08 0.12	2.08
	308.15	0.8456	0.844907 [15] 0.8445 [16]	0.697	0.7126 [15]	0.08 0.13	2.24
	313.15	0.8415	0.840873 [15] 0.8406 [16]	0.647	0.6672 [15]	0.07 0.11	3.12
	318.15	0.8374	0.836826 [15] 0.83846 [17]	0.613	0.6321 [15]	0.07 0.13	3.12
	323.15	0.8334	0.832768 [15] 0.8326 [16]	0.579	0.5971 [15]	0.08 0.10	3.13
linalool	293.15	0.8613	0.8618 [18]	5.431	5.53 [18]	0.06	1.82
	298.15	0.8572	0.8577 [18] 0.85809 [20] 0.85760 [21]	4.362	4.47 [18] 4.3493 [19] 4.4640 [20] 4.3810 [21]	0.06 0.10 0.05	2.48 0.29 2.34 0.44
	303.15	0.8531	0.8533 [18]	3.584	3.63 [18]	0.02	1.28
	313.15	0.8446	0.8448 [18] 0.84543 [21]	2.505	2.541 [18] 2.552 [20]	0.02 0.10	1.44 1.88
	323.15	0.8359	0.8362 [18]	1.844	1.868 [18]	0.04	1.30
1-propanol	288.15	0.8074	0.80754 [22]	2.502	2.5150 [23]	0.02	0.52
	293.15	0.8035	0.80362 [24]	2.194	2.198 [25]	0.01	0.18
	298.15	0.7996	0.79956 [22] 0.79941 [24]	1.968	1.970 [25]	0.01 0.02	0.10
	303.15	0.7956	0.79527 [24]	1.750	1.745 [24]	0.04	0.29
	308.15	0.7915	0.79146 [22]	1.560	1.5050 [23]	0.01	3.53
	313.15	0.7875	0.78662 [24]	1.366	1.361 [25]	0.11	0.37
	318.15	0.7832	0.78319 [22]	1.250	1.2253 [26]	<0.01	1.98
	323.15	0.7791	0.77391 [24]	1.125	1.115 [25]	0.67	0.89

Standard uncertainties *u* for each variable are: $^a u(p)$ = 0.005 MPa, $^b u(T)$ = 0.01 K and the combined expanded uncertainties U_c are $^c U_c(\rho)$ = 2 kg m^{-3}, $^d U_c(\eta)$ = 0.007 mPa s with 0.95 level of confidence (k = 2)

The results show that the largest density deviation of 0.67 % occurs for 1-propanol at 323.15 K, whereas the smallest deviation of less than 0.01 % is observed for 1-propanol at 318.15 K. Conversely, the largest viscosity deviation of 5.53 % is observed for α-pinene at 323.15 K, while the smallest deviation of 0.10 % is recorded for 1-propanol at 298.15 K.

3. RESULTS AND DISCUSSION

Experimentally determined densities and viscosities for binary mixtures at different temperatures in the investigated temperature range are shown in the Table S1 (Supplementary material) and represented graphically in Figures 1 and 2, respectively.

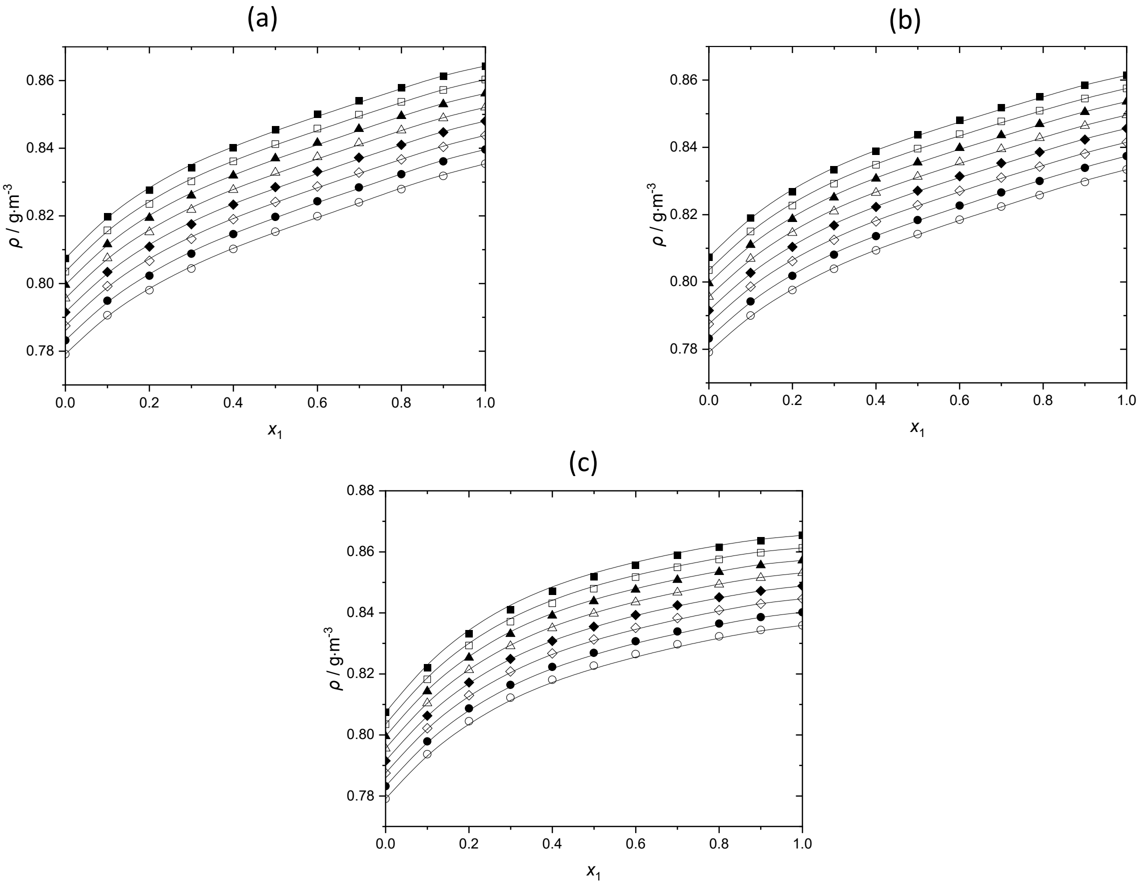

Figure 1. *Experimental values of density ρ as a function of molar fraction x_1 for the binary systems: (a) α-pinene (1) + 1-propanol (2); (b) p-cymene (1) + 1-propanol (2); (c) linalool (1) + 1-propanol (2); at following temperatures: ■ -288.15 K, □ - 293.15 K, ▲ - 298.15 K, Δ - 303.15 K, ♦ - 308.15 K, (◊) 313.15 K, ● - 318.15 K, ○ - 323.15 K; —- predictions by the Heric-Brewer-Jouyban-Acree model*

From the Figure 1 it is apparent that for all three systems density decreases with increasing temperature but increases as the amount of a terpene in the binary mixture increases. All the systems investigated show similar density values following the same trend.

Similarly to density, viscosities also decrease with the increase in temperature for all the analyzed systems. Among all the investigated terpenes only pure linalool shows higher viscosity than 1-propanol (Figure 2c), consequently viscosities increase with increasing the concentration of linalool in mixtures. For the other two systems viscosities decrease as the amount of a terpene increases.

Experimental thermodynamics properties (density and viscosity) of the investigated binary mixtures were mathematically described using the Heric-Brewer-Jouyban-Acree model, Equation (1) [27,28]:

$$\ln Y_{\mathrm{m},T} = x_1 \ln Y_{1,T} + x_2 \ln Y_{2,T} + J_0\left[\frac{x_1 x_2}{T}\right] + J_1\left[\frac{x_1 x_2 \left(x_1 - x_2\right)}{T}\right] + J_2\left[\frac{x_1 x_2 \left(x_1 - x_2\right)^2}{T}\right] \tag{1}$$

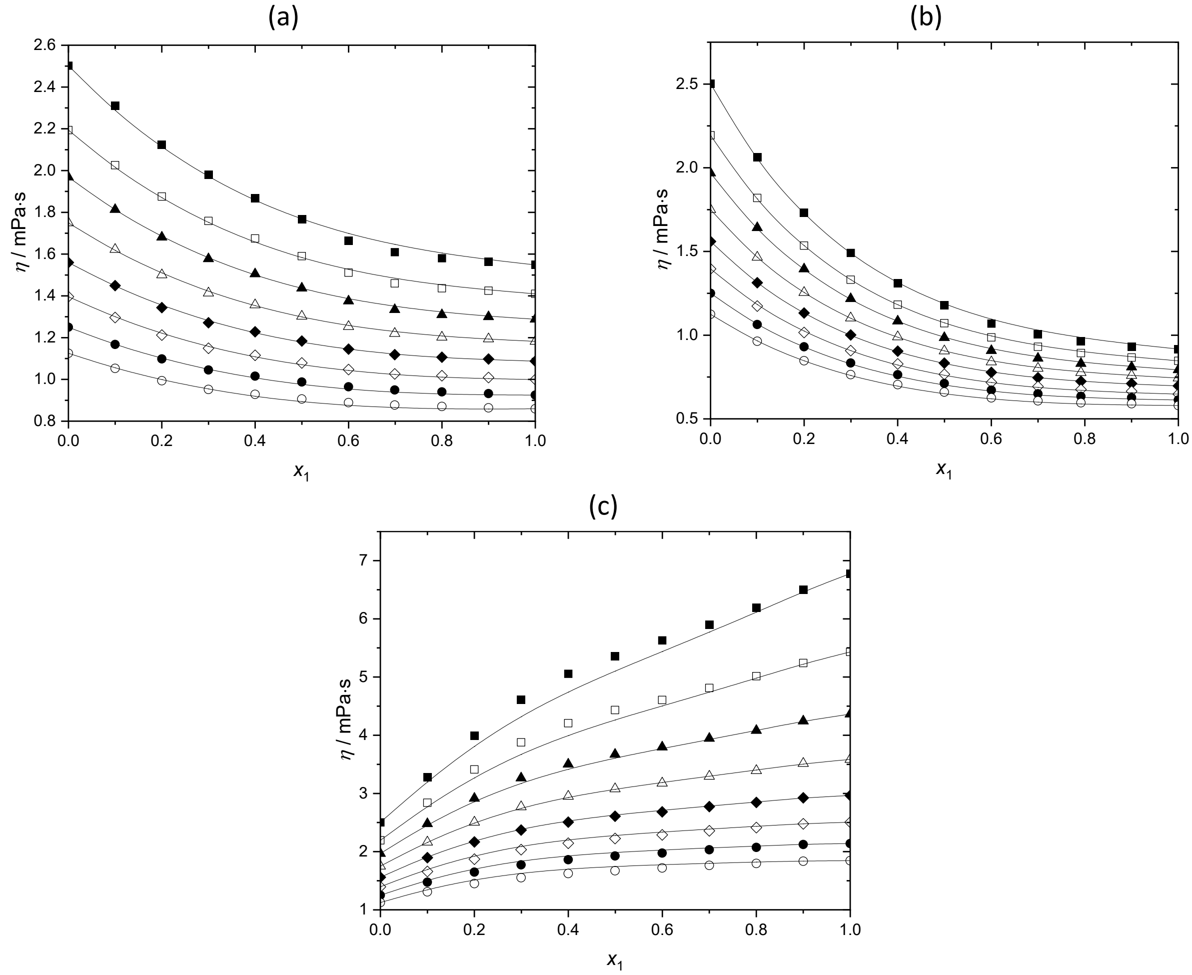

Figure 2. *Experimental values of dynamic viscosity η as a function of molar fraction x_1 for the binary systems: (a) α-pinene (1) + 1-propanol (2); (b) p-cymene (1) + 1-propanol (2); (c) linalool (1) + 1-propanol (2); at following temperatures: ■ - 288.15 K, □ - 293.15 K, ▲ - 298.15 K, Δ - 303.15 K, ♦ - 308.15 K, ◊ - 313.15 K, ● - 318.15 K, ○ - 323.15 K; ── - predictions by the Heric-Brewer-Jouyban-Acree model*

$Y_{m,T}$, $Y_{1,T}$ and $Y_{2,T}$ represent the values of the corresponding property at the temperature T. The subscript m denotes a mixture, while 1 and 2 correlate to the pure components of the mixtures (terpene and 1-propanol). The J_i is the model parameters obtained with the use of the least squares method, where the optimal degree of the polynomial was determined based on the minimum value of the standard deviation of the correlation, Equation (2):

$$\sigma = \left(\frac{\left(\sum_{i=1}^{n} Y_i^{\exp} - Y_i^{cal} \right)^2}{n\text{-}m} \right)^{1/2} \tag{2}$$

The accuracy of the used model was evaluated by the average percent deviation, Equation (3):

$$D = \frac{100}{N} \sum_{i=1}^{n} \left(\frac{Y_i^{\exp} - Y_i^{cal}}{Y_i^{\exp}} \right) \tag{3}$$

In Equations (2) and (3), N stands for number of data points in each set, n is the number of experimental data, m is the number of model parameters, while Y_{cal} and Y_{exp} are the calculated and experimental values of the observed property, respectively.

Table 3 shows Heric-Brewer-Jouyban-Acree model parameters together with standard deviation σ and the average percent deviation D.

Table 3. *Heric-Brewer-Jouyban-Acree model parameters for density and viscosity, predictions, standard deviation, and the average deviations, at T = 288.15 to 323.15 K*

Function	A_0	A_1	A_2	σ	Deviation, %
α-pinene (1) + 1-propanol (2)					
ρ / g m^{-3}	13.287	-9.1360	7.6862	0.0004	0.0449
η / mPa·s	-122.97	19.160	11.456	0.0113	0.6518
p-cymene (1) + 1-propanol (2)					
ρ / g m^{-3}	13.142	-9.0732	6.1676	0.0003	0.0335
η /mPa·s	-279.78	57.438	25.299	0.0079	0.6464
linalool (1) + 1-propanol (2)					
ρ / g m^{-3}	23.416	-13.133	7.2450	0.0006	0.0591
η /mPa·s	247.13	-186.05	104.77	0.0941	1.9800

By the analysis of the obtained results of density and viscosity modeling (Fig. 1 and Table 3) it is apparent that the Heric-Brewer-Jouyban-Acree model with three parameters was successfully used to correlate both properties over the entire temperature range, showing a very good agreement with experimental values. All the given parameters are temperature dependent. Average percent deviations show smaller deviations for densities than for viscosities, where the highest deviation is for the system linalool + 1-propanol due to higher viscosity values of linalool, particularly at lower temperatures in the interval, such as 288.15 and 293.15 K.

The experimental data were used to calculate derived thermodynamics properties. Excess molar volume (V^E) was calculated using Equation (4):

$$V^{\mathrm{E}} = \frac{x_1M_1 + x_2M_2}{\rho} - \left(\frac{x_1M_1}{\rho_1} + \frac{x_2M_2}{\rho_2} \right) \tag{4}$$

where ρ represents density of the binary mixture, ρ_1 and ρ_2 are densities of pure components, while M_1 and M_2 as well as x_1 and x_2 represent molar masses and mole fractions of components, respectively.

The viscosity deviation ($\Delta\eta$) was calculated by using the experimentally determined viscosity of the binary mixture, η, and viscosities of pure components, η_1 and η_2, Equation (5):

$$\Delta\eta = \eta - \sum_{i=1}^{2} x_i\eta_i \tag{5}$$

Isobaric thermal expansion describes the increase in a liquid's volume as its temperature rises, while the pressure remains constant. Coefficients of thermal expansion measure the extent to which a material expands in response to a change in temperature. The calculated thermal expansion coefficients for the three investigated mixtures are shown in Table S1 (Supplementary material).

Eq. (6) shows the temperature dependence of density in the mixtures using a polynomial expression; Equation (6):

$$\rho = a + bT + cT^2 \tag{6}$$

The isobaric thermal expansion coefficient (α) is obtained from a density value by the following equation:

$$\alpha = -\frac{1}{\rho}\left(\frac{\partial\rho}{\partial T} \right)_p \tag{7}$$

Table S1 (Supplementary material) indicates that α values are increasing as the temperature is increased.

Calculated values of the described quantities were correlated by using the Redlich-Kister [29] polynomial Equation (8):

$$Y = x_i x_j \sum_{p=0}^{k} A_p \left(2x_i - 1 \right)^p \tag{8}$$

A_p are the adjustable parameters in the equation of the related property Y (V^E, $\Delta\eta$) and the corresponding standard deviations are calculated by Equation (2). The Redlich-Kister parameters are shown in Table 4.

Figure 3 represents experimental and correlated values of the excess molar volume, calculated by the Redlich-Kister polynomial as a function of molar fraction x_1 for the investigated binary systems at different temperatures.

Table 4. *Redlich-Kister parameters for predictions of the excess molar volume, and viscosity deviation, with the corresponding root-mean-square deviations*

Function	T/K	A_0	A_1	A_2	A_3	A_4	σ
α-pinene (1) + 1-propanol (2)							
Excess molar volume	288.15	0.3514	0.1649	-0.0993	1.5115	-2.2787	0.0092
	293.15	0.4633	0.2873	0.0616	1.4390	-2.4316	0.0115
	298.15	0.5643	0.2688	0.0336	1.5310	-2.1820	0.0097
	303.15	0.2914	0.0664	0.2003	0.4380	-3.9064	0.0090
	308.15	0.7651	0.2642	0.5456	1.7332	-3.0780	0.0103
	313.15	0.9204	0.3711	0.3794	1.5923	-2.7362	0.0095
	318.15	1.0190	0.4336	0.6423	1.6913	-0.3112	0.0105
	323.15	1.1662	0.4888	0.7789	1.6904	-3.1645	0.0077
Viscosity deviation	288.15	-1.0541	-0.0013	-0.3747	0.2663	0.7841	0.0073
	293.15	-0.8530	0.0179	-0.4772	0.3109	0.7655	0.0048
	298.15	-0.7685	0.1266	-0.3965	0.1544	0.5694	0.0029
	303.15	-0.6549	0.1794	-0.4484	0.0384	0.7388	0.0037
	308.15	-0.5589	0.2024	-0.4120	0.0153	0.6524	0.0040
	313.15	-0.4762	0.1829	-0.3074	0.0726	0.4430	0.0039
	318.15	-0.4002	0.1908	-0.1772	-0.0122	0.2436	0.0024
	323.15	-0.3434	0.1787	-0.1714	-0.0048	0.2029	0.0020
p-cymene (1) + 1-propanol (2)							
Excess molar volume	288.15	0.1126	0.4746	-0.0580	1.0743	-1.6749	0.0069
	293.15	0.2174	0.5217	0.1833	1.1024	-1.9386	0.0076
	298.15	0.3383	0.5593	0.0955	1.1302	-1.7796	0.0068
	303.15	0.4600	0.5845	-0.2671	1.1817	-1.1274	0.0076
	308.15	0.5545	0.6738	-0.1092	1.1402	-1.2112	0.0064
	313.15	0.6908	0.7023	0.0955	1.2594	-1.4969	0.0051
	318.15	0.8332	0.8380	0.1991	1.0873	-1.6091	0.0042
	323.15	0.9386	0.8852	0.2250	1.2758	-1.2538	0.0051
Viscosity deviation	288.15	-2.1400	0.8394	-0.3645	0.2124	-	0.0039
	293.15	-1.7979	0.8023	-0.4156	0.1208	0.2068	0.0016
	298.15	-1.5895	0.6446	-0.2307	0.1924	-	0.0021
	303.15	-1.3717	0.5685	-0.2091	0.1955	-	0.0017
	308.15	-1.1864	0.4955	-0.1784	0.1895	-	0.0014
	313.15	-1.0264	0.4468	-0.1977	0.2959	-	0.0020
	318.15	-0.8843	0.3784	-0.1255	0.1984	-	0.0011
	323.15	-0.7733	0.3291	-0.1134	0.1773	-	0.0011
linalool (1) + 1-propanol (2)							
Excess molar volume	288.15	-2.1111	1.0005	-0.9016	-0.4801	0.7521	0.0095
	293.15	-2.1709	0.9625	-0.6558	-0.5210	-	0.0118
	298.15	-2.1571	1.0177	-0.9836	-0.5711	0.5421	0.0085
	303.15	-2.1963	1.0367	-0.7559	-0.4565	-	0.0096
	308.15	-2.2018	0.9465	-1.3225	-0.2499	0.8333	0.0073
	313.15	-2.2090	1.0129	-1.2869	-0.4501	0.8753	0.0022
	318.15	-2.2122	1.0029	-1.3522	-0.3603	0.8720	0.0042
	323.15	-2.2626	0.9727	-1.3729	-0.5575	0.7871	0.0052
Viscosity deviation	288.15	2.9352	-2.9218	-0.2324	2.6085	-	0.0094
	293.15	2.4852	-2.5063	0.0756	1.9475	-	0.0083
	298.15	2.0260	-1.8998	0.2083	1.3468	-	0.0067
	303.15	1.6506	-1.4524	0.3658	0.9980	-	0.0064
	308.15	1.3849	-1.0783	0.4062	0.6542	-	0.0047
	313.15	1.1008	-0.8123	0.3007	0.5216	-	0.0041
	318.15	0.9265	-0.6554	0.3534	0.3188	-	0.0029
	323.15	0.7608	-0.5028	0.3332	0.2282	-	0.0032

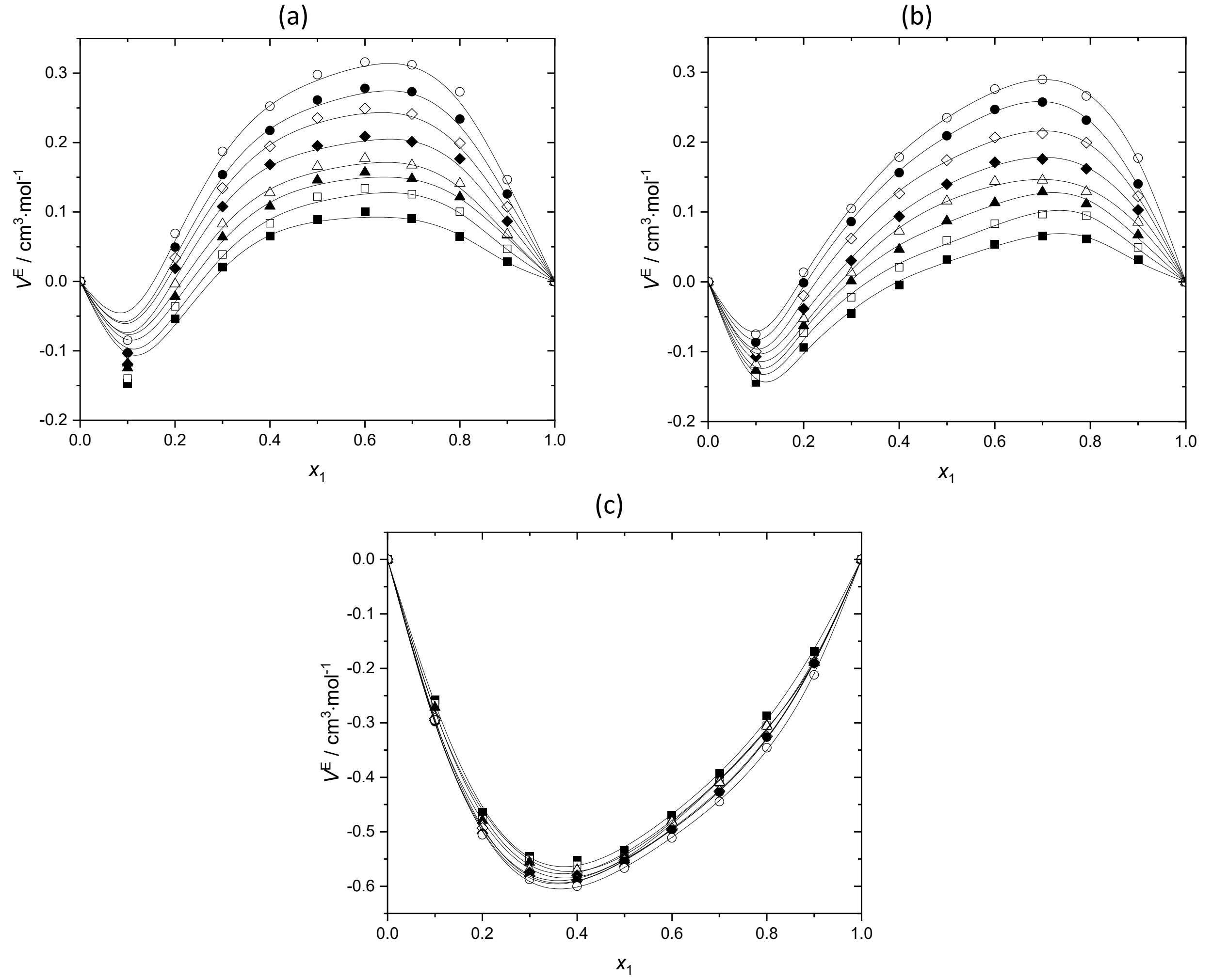

Figure 3. *Experimental values of excess molar volume* V^E *as a function of molar fraction* x_1 *for the binary systems: (a) α-pinene (1) + 1-propanol (2); (b) p-cymene (1) + 1-propanol (2); (c) linalool (1) + 1-propanol (2); at following temperatures:* ■ *- 288.15 K,* □ *- 293.15 K,* ▲ *- 298.15 K,* Δ*- 303.15 K,* ♦ *- 308.15 K,* ◊ *- 313.15 K,* ● *- 318.15 K,* ○ *323.15 K; —- predictions by the RK equation*

The excess molar volumes show S-shape curves for binary mixtures containing *α*-pinene and *p*-cymene, while the mixtures with linalool show negative deviation from the ideal behavior over the entire composition range. The non-ideality or positive/negative V^E is the result of physical, chemical and structural characteristics of the selected mixtures. For the lower concentrations of *α*-pinene in the *α*-pinene + 1-propanol mixture apparently attractive intermolecular forces dominate causing shrinkage of volume during the mixing process. As the concentration of *α*-pinene rises above $x_1 = 0.1$, V^E grows positive with the maximum at $x_1 = 0.6$, causing the expansion in volume. The same trend occurs in the system *p*-cymene + 1-propanol. Binary mixtures containing linalool and 1-propanol show negative values for V^E with the minimum at $x_1 = 0.4$. In these binary mixtures attractive intermolecular forces dominate, forming hydrogen bonds between OH groups, causing negative values of V^E through the entire composition range.

Comparison of the three investigated systems shows that the temperature has the same influence, i.e the deviation from ideal behavior increases with the temperature increase.

The systems *α*-pinene + 1-propanol as well as *p*-cymene + 1-propanol show negative values for deviations in viscosities ($\Delta\eta$) in the entire composition range (Figs 4a and 4b). Those negative values indicate that the mixtures are more viscous than the pure substances, which is more prominent for the system with *p*-cymene. Deviations grow less negative with the increase in the temperature. On the other hand, the system linalool + 1-propanol expresses asymmetrical $\Delta\eta$-x_1 function with a positive maximum at around x_1=0.4, with a lower temperature influence on $\Delta\eta$ for higher concentrations of linalool in the binary mixture.

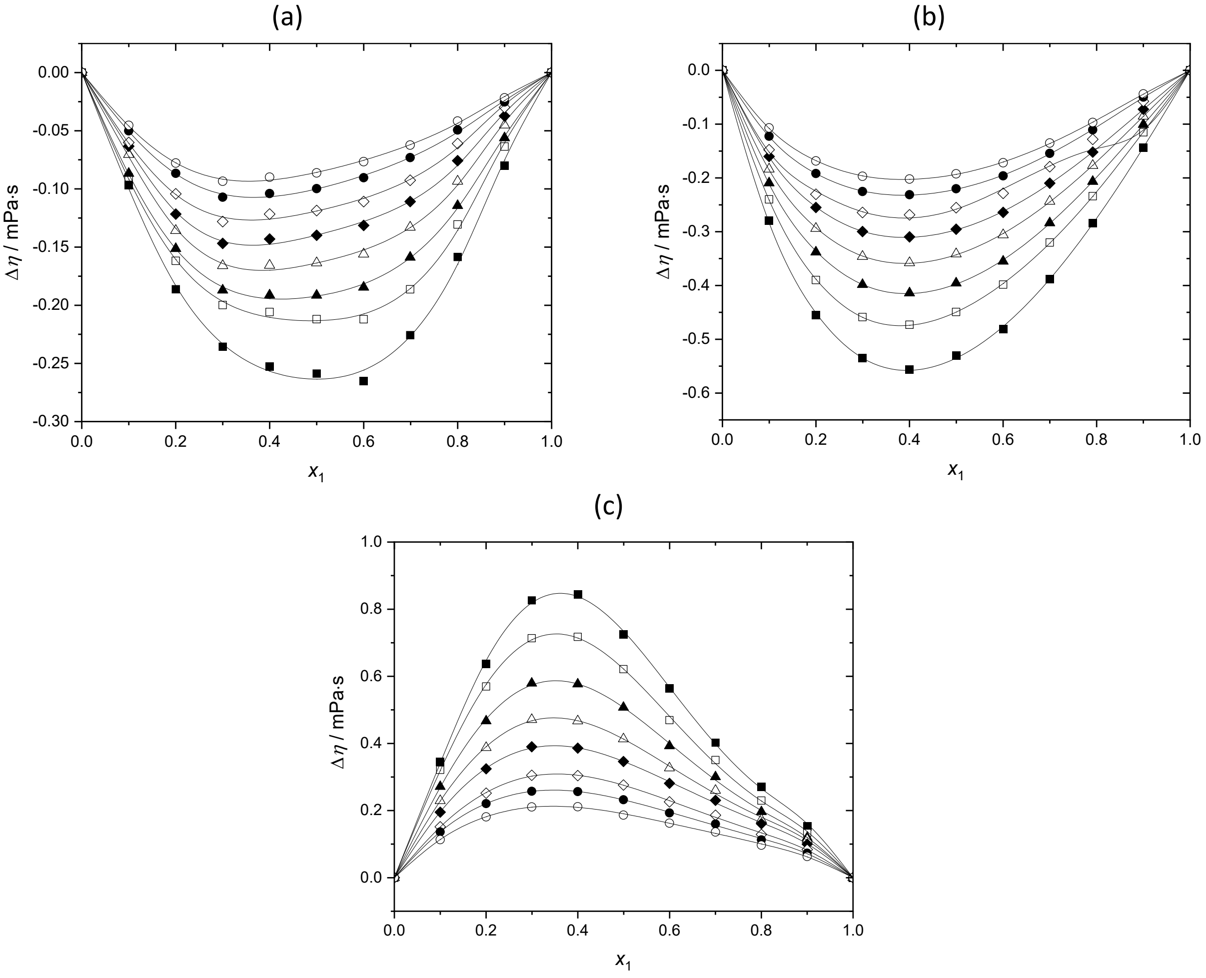

Figure 4. *Experimental values of deviations in viscosities Δη as a function of molar fraction x_1 for the binary systems: (a) α-pinene (1) + 1-propanol (2); (b) p-cymene (1) + 1-propanol (2); (c) linalool (1) + 1-propanol (2); at following temperatures: ■ - 288.15 K, □ - 293.15 K, ▲ - 298.15 K, Δ - 303.15 K, ♦ - 308.15 K, ◊ - 313.15 K, ● - 318.15 K, ○ - 323.15 K; —- predictions by the RK equation*

4. CONCLUSION

Within this paper, densities and viscosities of three binary systems, *α*-pinene + 1-propanol, *p*-cymene + 1-propanol and linalool + 1-propanol were experimentally determined in the temperature range T = 288.15 to 323.15 K and at atmospheric pressure over the entire composition range. Based on the experimental results the excess molar volume and viscosity deviation were calculated and fitted to the Redlich-Kister equation. Two binary mixtures, α-pinene and p-cymene with 1-propanol, showed negative values for excess molar volume for the lower concentrations of terpene in the mixture, growing positive with increasing terpene molar fractions. The system linalool + 1-propanol is the only system with positive viscosity deviation, while *α*-pinene and *p*-cymene express negative viscosity deviations in mixtures with 1-propanol. The Heric-Brewer-Jouyban-Acree model was successfully used to correlate the experimental values of the density and viscosity. For density measurements the maximum average percent deviation of 0.06 % was obtained for all three mixtures, while for the viscosity the maximum average percent deviation of 0.65 % is obtained for the α-pinene and p-cymene with 1-propanol and around 2 % for the linalool with 1-propanol. Both models successfully correlated given properties what is approved with obtained deviations.

The presented study offers valuable insights into the thermodynamic and transport properties of binary mixtures involving α-pinene, p-cymene, linalool, and 1-propanol. These findings provide a robust foundation for better understanding intermolecular interactions in systems containing terpenes and alcohols, which is critical for tailoring such mixtures for industrial applications. From a practical perspective, the distinct behavior of linalool mixtures, especially the positive viscosity deviations, could be leveraged to optimize formulations in the pharmaceutical, cosmetic, and fragrance industries where viscosity and miscibility are essential parameters.

SUPPLEMENTARY MATERIAL

Additional data are available electronically at https://www.ache-pub.org.rs/index.php/HemInd/article/view/1134, or from the corresponding author on request.

CRediT authorship contribution statement: *Ivona A. Đorđević: experimental & writing, Nikola D. Grozdanić: modeling, Mirjana Lj. Kijevčanin: supervision, resources, Ivona R. Radović: conceptualization, writing - review & editing, supervision.*

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Termodinamička svojstva dvokomponentnih smeša terpena i 1-propanola u intervalu temperature od 288,15 do 323,15 K na atmosferskom pritisku

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(Naučni rad)

Izvod

Najzastupljenija klasa hemijskih jedinjenja prisutna u esencijalnim uljima jesu terpeni. Smatraju se zelenim rastvaračima, a potiču iz prirodnih izvora poput biljaka, citrusnog voća, ali i lišća drveća ili šišarki. Pronalaze veliku komercijalnu upotrebu u granama prehrambene industrije, kao prirodne arome i dodaci hrani, a pored toga su veoma zastupljeni i u farmaceutskoj i kozmetičkoj industriji. U cilju proučavanja termodinamičkih svojstava smeša terpena (α-pinen, p-cimen i linalool) sa 1-propanolom, eksperimentalno su određene gustine i viskoznosti za navedene smeše. Eksperimentalna merenja rađena su u opsegu temperatura od 288,15 do 323,15 K na atmosferskom pritisku, za ceo opseg udela. Na osnovu eksperimentalno dobijenih rezultata za gustine i viskoznosti izračunate su vrednosti dopunske molarne zapremine, kao i vrednosti promene viskoznosti pri mešanju. Izmerene veličine (gustina i viskoznost) korelisane su korišćenjem modela Herik-Bruer-Džuben-Eikrija (Heric-Brewer-Jouyban-Acree), dok je za korelisanje dopunskih veličina (dopunska molarna zapremina, promena viskoznosti i koeficijent termičke ekspanzije) korišćen Redlih-Kisterov (Redlich-Kister) polinom. Svi eksperimentalno dobijeni podaci i njihove izvedene veličine korišćene su za analizu neidealnog ponašanja odabranih smeša. Herik-Bruer-Džuben-Eikrijev model je uspešno korelisao eksperimentalne vrednosti za sva tri binarna sistema u celom temperaturnom opsegu i na atmosferskom pritisku, dok je Redlih-Kisterov polinom uspešno korelisao izvedene veličine.

Ključne reči: gustina; viskozitet, dopunske veličine, modelovanje