

Excess molar volumes and excess viscosities of the 2,2,4-trimethylpentane (1)+3-methyl-1-butanol (2) and propan-2-ol (3) ternary system at 298.15 K

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Abstract

This paper reports experimental densities and viscosities of the ternary system 2-2-4-trimethylpentane+3-methyl-1-butanol+propan-2-ol and the binary systems 2-2-4-trimethylpentane (isooctane)+3-methyl-1-butanol (isoamyl alcohol), 2-2-4-trimethylpentane (isooctane)+propan-2-ol (isopropyl alcohol), and 3-methyl-1-butanol+propan-2-ol, over the entire range of composition at 298.15 K. Excess molar volume, excess viscosity and the excess energy of activation for viscous flow were evaluated from the experimental data obtained. These derived properties for binary and ternary systems were fitted to Redlich-Kister's and Cibulka's equations, respectively. Flory's statistical theory has been applied to predict excess molar volumes for ternary system. For viscosities we applied Grunberg and Nissan, Katti and Chaudhri, Bloomfield and Dewan and Wu equations and finally the GC-UNIMOD model.

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1. Introduction

There is an increasing interest in the thermodynamic behavior of liquid mixtures. In this way, a considerable amount of work has been carried out on the experimental determination of density and viscosity of the liquid mixtures and the corresponding excess molar volumes and viscosity deviations.

The thermodynamics of ternary mixtures of non-electrolytes has not received as much attention as the thermodynamics of binary mixtures. It is therefore interesting to estimate excess molar volumes and excess viscosities with more than two components.

The literature on ternary systems suggests the availability of some empirical correlations used to calculate the excess molar volumes and transport properties of ternary mixtures. Assuming that interactions in ternary mixtures are closely dependent on the interactions in binary systems, we considered the

application of geometrical solution prediction, correlation with fitting parameters and group contributions method. We also applied some theories of liquids to predict excess molar volumes.

In this paper, we report the experimental densities and viscosities of the ternary mixtures (2,2,4-trimethylpentane (isooctane) (1)+3-methyl-1-butanol (isoamyl alcohol) (2) and propan-2-ol (isopropanol) (3)) and the corresponding binary mixtures (2-2-4-methylpentane (1)+3-methyl-1-butanol (2), 3-methyl-1-butanol (2)+2-propanol (3), and 2-2-4-methylpentane (1)+2-propanol (3)) at 298.15 K. Molar excess volumes, excess viscosity and the excess energy of activation for viscous flow have been calculated from the experimental data. As far as we know, the only previous volumetric measurements on these mixtures are those of Blanco et al. [1] for 2,2,4-trimethylpentane+propan-2-ol, Neau et al. [2] at 298.15 K and of Yadav et al. [3], at 40 °C for 2,2,4-trimethylpentane+propan-2-ol and 2,2,4-trimethylpentane+3-methyl-1-butanol systems.

Isopropanol is a solvent which has several applications in industry [4]. It is interesting to know the interaction between alcohols which have hydrogen bonding with acyclic components as isooctane.

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2. Experimental

The methods used in our laboratory have been described previously [5]. Densities of 2,2,4-trimethylpentane (Merck, 99.5%), propan-2-ol (Merck, 99.5%) and 3-methyl-1-butanol (UCB, Belgium) were determined with a digital densimeter AP, model DMA 45. Calibration was done with air and doubly distilled water with a precision of $\pm 10^{-4}$ g cm⁻³.

Viscosities of the pure liquids and of the mixtures were determined with a viscosimeter Schott-Gerate, Model AVS 400, with a thermostat CT 1450, using Ubbelohde viscosimeters. A thermostatically controlled bath (constant to ± 0.01 K) was used. The Hagenbach correction was applied for the Ubbelohde viscosimeters. Time measurements were converted to a digital electrical signal to start the internal crystal-controlled clock with read out display. The electronic timer could measure time to ± 0.01 s. The estimated error in the viscosity was ± 0.005 mPa s.

Mixtures were prepared by mixing weighed amounts of the pure liquids using a Mettler H20T balance. The error in the mole fractions was estimated in $\pm 4 \cdot 10^{-4}$. Caution was taken to prevent evaporation. The physical properties were measured experimentally for each pure component and the results are shown together with literature values in Table 1.

3. Results and discussion

The excess molar volumes, the excess viscosity, and excess Gibbs energy of activation for viscous flow of binary and ternary mixtures were computed applying Eqs. (1)–(3). The values obtained are shown in Tables 2 and 3, respectively.

$$V^E = \sum_{i=1}^N x_i M_i (\rho^{-1} - \rho_i^{-1}) \quad (1)$$

$$\eta^E = \eta - \exp\left(\sum_{i=1}^N x_i \ln \eta_i\right) \quad (2)$$

$$\Delta G^{*E} = RT \left(\ln \eta V - \sum_{i=1}^N x_i \ln \eta_i V_i \right) \quad (3)$$

where ρ , η , and V are density, dynamic viscosity and molar volumes of the mixture, M_i , ρ_i , η_i , and V_i are the

Table 1
Properties characterizing the pure components at 298.15 K

Component	ρ (g cm ⁻³)		η (mPa s)		n_D	
	Exp.	Lit.	Exp.	Lit.	Exp.	Lit.
2,2,4-Trimethylpentane	0.6878	0.68781 ^a	0.477	0.475 ^a	1.38950	1.38898 ^a
		0.68730 ^b		0.478 ^c		
		0.6877 ^c				
3-Methyl-1-butanol	0.8070	0.8071 ^a	3.740	3.738 ^a	1.40518	1.4052 ^a
Propan-2-ol	0.7813	0.78126 ^a	2.044	2.044 ^a	1.37525	1.3752 ^a
		0.77950 ^b		2.068 ^d		
		0.7812 ^d				

^a Ref. [6].

^b Ref. [1].

^c Ref. [8].

^d Ref. [7].

Table 2

Densities, viscosities, excess molar volumes, excess viscosities and excess Gibbs energy of activation for viscous flow for binary systems at 298.15 K

	ρ (g cm ⁻³)	η (mPa s)	V^E (cm ³ mol ⁻¹)	η^E (mPa s)	ΔG^{*E} (J mol ⁻¹)
x'_1	2,2,4-trimethylpentane (1)+3-methyl-1-butanol(2)				
0.0685	0.7952	3.063	-0.027	-0.185	-130
0.1409	0.7835	2.428	-0.044	-0.370	-323
0.2215	0.7712	1.908	-0.031	-0.462	-498
0.3110	0.7585	1.471	-0.002	-0.500	-677
0.3520	0.7529	1.326	0.031	-0.486	-721
0.4038	0.7460	1.175	0.093	-0.453	-754
0.4505	0.7400	1.051	0.157	-0.428	-790
0.4937	0.7347	0.967	0.208	-0.386	-775
0.6132	0.7214	0.772	0.270	-0.286	-727
0.6488	0.7178	0.723	0.264	-0.260	-710
0.7255	0.7105	0.642	0.223	-0.197	-621
0.7820	0.7053	0.595	0.211	-0.152	-527
0.8570	0.6989	0.544	0.155	-0.096	-378
0.9105	0.6946	0.512	0.102	-0.062	-264
0.9545	0.6912	0.494	0.053	-0.030	-136
x'_1	2,2,4-trimethylpentane(1)+propan-2-ol(3)				
0.0513	0.7701	1.722	0.151	-0.175	-190
0.1045	0.7602	1.470	0.259	-0.286	-349
0.1511	0.7524	1.300	0.353	-0.341	-455
0.2394	0.7400	1.066	0.460	-0.377	-588
0.2822	0.7343	0.947	0.566	-0.409	-712
0.4108	0.7207	0.751	0.696	-0.373	-803
0.5195	0.7114	0.640	0.769	-0.320	-812
0.6545	0.7021	0.562	0.784	-0.227	-675
0.8094	0.6938	0.505	0.686	-0.124	-439
0.9505	0.6887	0.490	0.306	-0.023	-80
x'_2	3-methyl-1-butanol (2)+propan-2-ol (3)				
0.0950	0.7844	2.195	0.024	0.030	50
0.1475	0.7861	2.277	0.028	0.042	68
0.2352	0.7891	2.411	0.001	0.055	86
0.3228	0.7918	2.562	-0.014	0.078	111
0.4092	0.7943	2.707	-0.029	0.090	120
0.5069	0.7970	2.896	-0.052	0.120	141
0.6126	0.7996	3.093	-0.063	0.133	143
0.7326	0.8024	3.271	-0.070	0.089	95
0.8525	0.8047	3.477	-0.064	0.056	56
0.9466	0.8064	3.651	-0.051	0.030	26

properties of the pure components of the mixtures, x_i is the mole fraction and N stands for the number of components. R is the gas constant and T is the Kelvin temperature.

The value of the excess molar volumes, the excess viscosity, and excess Gibbs energy of activation for viscous flow were fitted by Redlich-Kister equation for every binary mixture, according to the equation

$$\Delta X_i = x'_i x'_j \sum_{k=0}^n a_k (x'_i - x'_j)^k \quad (4)$$

where ΔX_i represents V^E , η^E , or ΔG^{*E} , x'_i , x'_j are the mole fractions of components i , j , and a_k are the polynomial coefficients.

The method of least squares has been used to determine the values of the coefficients. In each case, the optimum number of

Table 3 (continued)

x_1	x_2	ρ (g cm ⁻³)	V^E (cm ³ mol ⁻¹)	η (mPa s)	η^E (mPa s)
$x_2/x_3 = 0.7220$					
1.0000	0.0000	0.6878	0.000	0.477	0.000
0.7343	0.1114	0.7032	0.443	0.570	-0.181
0.5313	0.1965	0.7202	0.393	0.728	-0.335
0.3425	0.2757	0.7408	0.227	1.040	-0.427
0.2087	0.3318	0.7588	0.107	1.431	-0.413
0.0985	0.3780	0.7764	0.015	1.999	-0.226
0.0000	0.4193	0.7946	-0.033	2.736	0.103
$x_2/x_3 = 1.1516$					
1.0000	0.0000	0.6878	0.000	0.477	0.000
0.7400	0.1392	0.7043	0.353	0.579	-0.179
0.5445	0.2438	0.7213	0.318	0.740	-0.333
0.3556	0.3449	0.7421	0.190	1.066	-0.435
0.2247	0.4149	0.7597	0.078	1.473	-0.421
0.1147	0.4738	0.7770	-0.014	2.004	-0.299
0.0000	0.5352	0.7977	-0.053	2.948	0.124
$x_2/x_3 = 1.7685$					
1.0000	0.0000	0.6878	0.000	0.477	0.000
0.7507	0.1592	0.7045	0.330	0.579	-0.176
0.5474	0.2891	0.7229	0.276	0.760	-0.337
0.3705	0.4022	0.7429	0.131	1.077	-0.443
0.2374	0.4872	0.7607	0.035	1.494	-0.448
0.1091	0.5691	0.7807	-0.044	2.187	-0.273
0.0000	0.6388	0.8002	-0.063	3.125	0.118
$x_2/x_3 = 3.6576$					
1.0000	0.0000	0.6878	0.000	0.477	0.000
0.7559	0.1917	0.7055	0.296	0.591	-0.173
0.5568	0.3480	0.7243	0.256	0.786	-0.335
0.3691	0.4955	0.7462	0.102	1.153	-0.459
0.2359	0.6000	0.7644	0.005	1.629	-0.455
0.1173	0.6932	0.7827	-0.037	2.309	-0.311
0.0000	0.7853	0.8034	-0.070	3.365	0.080

coefficients was ascertained from an examination of the standard deviation of the estimate with n .

$$\sigma = \left[\frac{\sum (\Delta X_{\text{exp}} - \Delta X_{\text{cal}})^2}{(n_{\text{exp}} - n)} \right]^{1/2} \quad (5)$$

The values adopted for the coefficients and standard deviations of estimates associated with the use of Eq. (5) are summarized in Table 4.

Fig. 1 shows the obtained values of V^E for the three binary systems.

The (1)+(2) system shows a sigmoid curve in V^E with negative values over the region rich in alcohol and positive

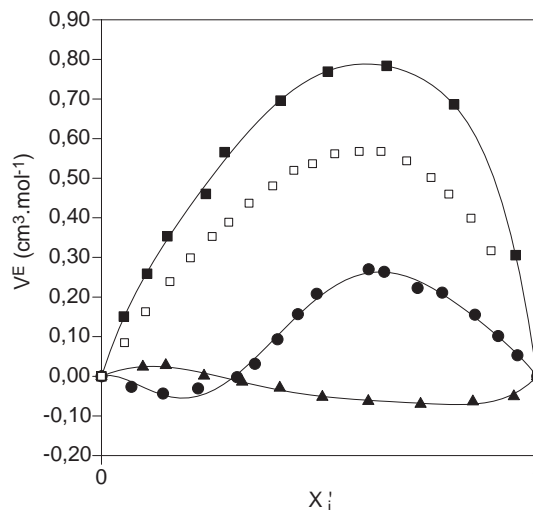


Fig. 1. Excess molar volumes for the three binary systems at 298.15 K. (●) 1+2 system; (■) 1+3 system; (▲) 2+3 system. Continuous curves were calculated from Eq. (4). (□) V^E values of 1+3 system taken from Ref. [1].

values in the region rich in component (1). The (1)+(3) system is positive, and the (2)+(3) system is sigmoid too and with smaller values of V^E . The negative values of excess volumes may be due to the predominant structural effects which arise from interstitial accommodation and changes of free volume. The positive V^E change may be explained in terms of the predominant intermolecular hydrogen bond stretching of associated alcohol molecules in the presence of isooctane. The V^E values of Blanco et al. [1] and Neau et al. [2] for the (1)+(3) system at 298.15 K differ at 0.5 of molar fraction with our values by $0.21 \text{ cm}^3 \text{ mol}^{-1}$. In Fig. 1 we have included V^E values of Blanco et al. [1] for this system at 298.15 K together with our V^E experimental values; difference in the values could be explained by origin of the reagents.

Fig. 2 shows the values of η^E for the three systems.

The excess viscosities are negative for systems (1–2) and (1–3) and positive and small for the system (2–3). A similar behavior is observed for the ΔG^{*E} values for these systems.

Table 3 shows the experimental values of density and viscosity together with the V^E and η^E values for the ternary systems. If interaction in a ternary system $i+j+k$, is assumed to be closely dependent on the interactions of the constituents $i+j$, $j+k$ and $i+k$ mixtures, it should be possible to evaluate excess properties of ternary mixtures of non-electrolytes from the

Table 4
Coefficients a_k for Eq. (4) and standard deviations for the binary systems at 298.15 K^a

	2,2,4-Trimethylpentane (1)+3-methyl-1-butanol (2)			2,2,4-Trimethylpentane (1)+propan-2-ol (3)			3-Methyl-1-butanol (2) + propan-2-ol (3)		
	V^E	η^E	ΔG^{*E}	V^E	η^E	ΔG^{*E}	V^E	η^E	ΔG^{*E}
a_0	0.8036	-1.5293	-3131	3.0489	-1.3198	-3245	-0.2002	0.3993	565
a_1	1.7169	1.7522	209	1.0093	1.0651	347	-0.2572	0.1176	122
a_2	-1.6020	-1.2395	64	0.5607	-0.5464	399	0.1965	-0.0963	-476
a_3	-1.1628	-0.4955	-1125	1.1311	0.7147	744	-0.5460	-0.0346	-353
a_4	1.6355	1.0599	842	1.9507	-0.4654	-37	-0.3372	0.2111	645
σ	0.010	0.005	7	0.010	0.003	18	0.004	0.002	5

^a Units: V^E , cm³ mol⁻¹; η^E , mPa s; ΔG^{*E} , J mol⁻¹.

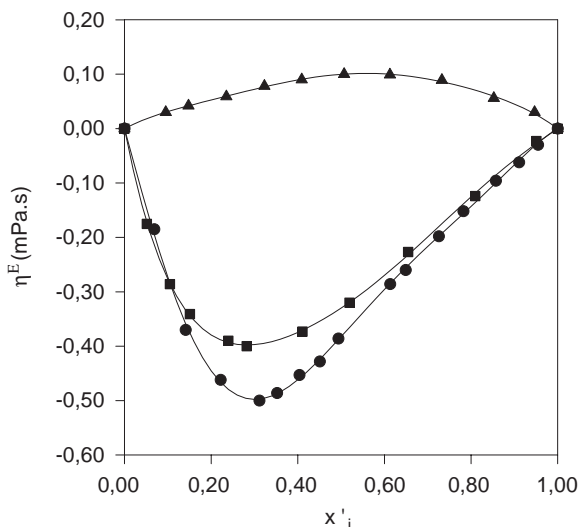


Fig. 2. Excess viscosities for the three binary systems at 298.15 K. (●) 1+2 system; (■) 1+3 system; (▲) 2+3 system. Continuous curves were calculated from Eq. (4).

corresponding function for the binary $i+j$, $j+k$ and $i+k$ mixtures.

Different expressions can be used by calculating excess molar volumes for the ternary system from the excess volume values of the binary systems which can be compared with the experimental values of the ternary systems. We applied the Radojkovic et al. [9] equation, which considered an expression proposed by Redlich-Kister. For excess molar volumes:

$$V_{123}^E = V_{12}^E + V_{13}^E + V_{23}^E \quad (6)$$

where V_{12}^E , V_{13}^E and V_{23}^E represent the excess molar volumes with x_1 , x_2 and x_3 mole fractions in the ternary system.

Jacob and Fitzner [10] suggested an equation for estimating the properties of a ternary system based on the binary data at compositions nearest the ternary composition by using the following equation for the excess molar volume:

$$V_{123}^E = \frac{x_1 x_2 V_{12}^E}{\left(x_1 + \frac{x_3}{2}\right)\left(x_2 + \frac{x_3}{2}\right)} + \frac{x_1 x_3 V_{13}^E}{\left(x_1 + \frac{x_2}{2}\right)\left(x_2 + \frac{x_2}{2}\right)} + \frac{x_2 x_3 V_{23}^E}{\left(x_2 + \frac{x_1}{2}\right)\left(x_3 + \frac{x_1}{2}\right)} \quad (7)$$

so that, for binary systems at compositions x'_i and x'_j $x_i - x_j = x'_i - x'_j$

Kohler [11] proposed an equation for a ternary system of the form

$$V_{123}^E = (x_1 + x_2)^2 V_{12}^E + (x_1 + x_3)^2 V_{13}^E + (x_2 + x_3)^2 V_{23}^E \quad (8)$$

Kohler's equation is symmetrical in that all three binary systems are treated identically. In this equation, V_{ij}^E refers to the excess volumes of x'_i and x'_j in the binary mixtures using $x'_i = 1 - x'_j = x_i / (x_i + x_j)$

These equations can calculate V^E and η^E for the ternary system from experimental data of the binary systems which can

be compared with the experimental values of the ternary systems. Table 5 shows the mean deviation (MD) defined by the following equation:

$$MD = \left[\frac{\sum (\Delta M_{\text{exp}} - \Delta M_{\text{calc}})^2}{n} \right]^{1/2} \quad (9)$$

where ΔM represents V_{123}^E ($\text{cm}^3 \text{mol}^{-1}$), η_{123}^E (mPa s) or ΔG_{123}^{*E} (J mol^{-1}).

The ternary excess volumes and excess viscosities were correlated using Cibulka's and Singh's equations. Cibulka [12] proposed the following expression

$$V_{123}^E = V_{12}^E + V_{13}^E + V_{23}^E + x_1 x_2 x_3 (A + Bx_1 + Cx_2) \quad (10)$$

where A , B and C are parameters calculated from experimental data.

Singh et al. [13] proposed an equation of the following form

$$V_{123}^E = V_{12}^E + V_{13}^E + V_{23}^E + x_1 x_2 x_3 \left(A + Bx_1(x_2 - x_3) + Cx_1^2(x_2 - x_3)^2 \right) \quad (11)$$

Cibulka's equation shows the best agreement with experimental data for this system, for V^E and η^E . Singh's equation does not differ very much from Cibulka's equation. The mean deviation MD and parameters A , B , and C are given in Table 5. Obviously, the models using ternary parameters are superior to the calculated ones (not containing ternary parameters). The facts that so many equations have been developed suggest that no simple equation can describe all types of available systems.

Table 5

Mean deviations (MD) of the experimental results from the calculated results for different equations of excess molar volume and excess viscosities for ternary system at 298.15 K

Equation	MD of V_{123}^E (cm ³ mol ⁻¹)	Parameter	MD of η_{123}^E (mPa s)	Parameter
Radojkovic	0.124		0.105	
Jacob–Fitzner	0.124		0.105	
Kohler	0.129		0.090	
Cibulka	0.036	$A = -6.9273$ $B = -3.8556$ $C = 5.8758$	0.032	$A = -8.8772$ $B = 11.0796$ $C = -1.0553$
Singh	0.024	$A = -5.9851$ $B = 7.3192$ $C = -28.4332$	0.061	$A = -5.4211$ $B = 0.3099$ $C = 69.0782$
Flory	0.160	$X_{12} = 4.54 \text{ J cm}^{-3}$ $X_{13} = 26.21 \text{ J cm}^{-3}$ $X_{23} = -2.57 \text{ J cm}^{-3}$		
Grunberg and Nissan			0.109	$\delta = -9.6376$
Katti and Chaudhri			0.096	$W_{\text{vis}} = -19534$
Bloomfield–Dewan			0.072	$\alpha = 1$ $\beta = 1$
Wu			0.225	$A = 1$
GC-UNIMOD			0.106	

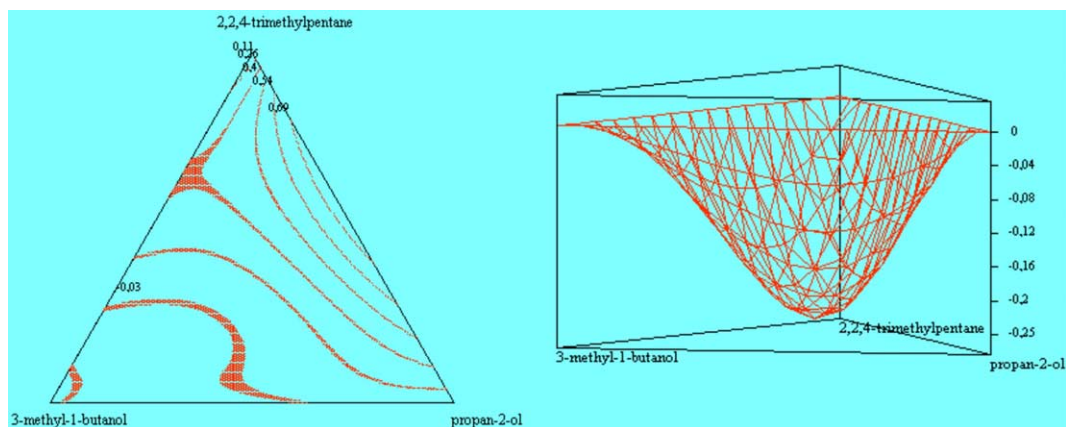


Fig. 3. Lines of constant excess molar volumes for the 2,2,4-trimethylpentane (1)+3-methyl-1-butanol (2)+propan-2-ol (3) ternary system at 298.15 K (left). In the three-dimensional representation of the ternary contribution for excess molar volumes, full line reticulate represents the surface generated by Cibulka fitting (right).

Figs. 3 and 4 (on the left) show the lines of constant V^E and η^E obtained from Cibulka's equation for the ternary system. The ternary contributions to the excess volume and viscosity deviation are plotted in Figs. 3 and 4 (on the right), respectively.

Following Shulka et al. [14] we applied Flory's theory to a ternary system. The values of reduced volumes, reduced temperatures and characteristic pressures for the pure components are obtained and Table 6 gives these parameters.

X_{12} , X_{13} and X_{23} are the interchange parameters calculated using the algorithm of Marquardt [15] assuming two body collisions [14]. The values of X_{ij} and the MD obtained are given in Table 5.

For viscosities, the empirical Grunberg and Nissan equation [16] has been found to be useful. Extended to a ternary system, it takes the following expression:

$$\ln \eta = x_1 \ln \eta_1 + x_2 \ln \eta_2 + x_3 \ln \eta_3 + x_1 x_2 x_3 \delta \quad (12)$$

where δ is the parameter which reflects the nonideality of the system. This parameter has usually been regarded as an appropriate measure of the strength of interaction between

components. The values of δ obtained for this system and the MD are given in Table 5.

Katti and Chaudhri [17] found an equation which introduced the molar volumes, which extended to a ternary system, as follows:

$$\ln \eta V = x_1 \ln \eta_1 V_1 + x_2 \ln \eta_2 V_2 + x_3 \ln \eta_3 V_3 + x_1 x_2 x_3 \frac{W_{\text{vis}}}{RT} \quad (13)$$

where V is the molar volume of the solution given by $\sum x_i M_i / \rho$ and W_{vis} is the interaction parameter. W_{vis} and MD are given in Table 5.

On the other hand, excess viscosity may be quantitatively related to the thermodynamic properties of mixtures through the two major semiempirical theories of liquid viscosity, namely the absolute rate and free volume theories.

According to the Bloomfield and Dewan [18] scheme, and following Celda et al. [19] we write

$$\ln \frac{\eta}{\eta_{\text{id}}} = \alpha \ln \eta_{\text{fv}} + \beta \ln \eta_{\text{ar}} \quad (14)$$

where η_{fv} and η_{ar} represent the deviation from ideal mixture calculated by the free volume and absolute rate reaction

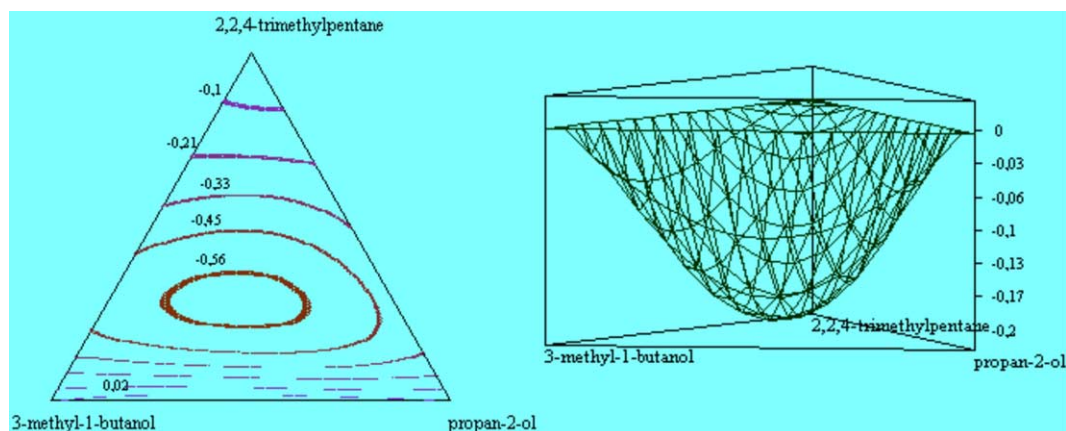


Fig. 4. Lines of constant excess viscosities for the 2,2,4-trimethylpentane (1)+3-methyl-1-butanol (2)+propan-2-ol (3) ternary system at 298.15 K (left). In the three-dimensional representation of the ternary contribution for viscosity deviation, full line reticulate represents the surface generated by Cibulka fitting (right).

Table 6
Parameters of the pure components at 298.15 K

Substance	$\alpha \cdot 10^3$ (K ⁻¹)	$\kappa_T \cdot 10^6$ (kPa ⁻¹)	$V^* \cdot 10^6$ (m ³ mol ⁻¹)	$P^* \cdot 10^{-3}$ (kPa)	T^* (K)
2,2,4-Trimethylpentane	1.198 ^a	2.064 ^b	129.05	388	4758
3-Methyl-1-butanol	0.920 ^a	0.650 ^b	88.73	353	5483
Propan-2-ol	1.064 ^a	1.332 ^a	61.01	378	5058

^a Ref. [6].

^b Ref. [25].

theories, respectively, and α and β are weighting coefficients which are usually made equal to 1. Both contributions to the departure from ideality are, respectively, given by

$$\ln \eta_{fv} = \frac{1}{\tilde{V} - 1} - \frac{x_1}{\tilde{V}_1 - 1} - \frac{x_2}{\tilde{V}_2 - 1} - \frac{x_3}{\tilde{V}_3 - 1} \quad (15)$$

and

$$\ln \eta_{ar} = -G^R/RT \quad (16)$$

where G^R is the residual energy of mixing, calculated by the following expression:

$$G^R = G^E + RT \left(x_1 \ln \frac{x_1}{\Psi_1} + x_2 \ln \frac{x_2}{\Psi_2} + x_3 \ln \frac{x_3}{\Psi_3} \right) \quad (17)$$

with Ψ_i , the segment fraction of component i .

In the Bloomfield–Dewan scheme, the relationships between η_{fv} , η_{ar} , and the excess thermodynamic theory of liquid mixtures were proposed by Flory et al. [20].

To obtain G^E it is necessary to know the activity coefficients obtained by measuring vapor–liquid equilibria for this system. If these values are unknown, it is possible to calculate G^E using Flory's theory, which was extended to a ternary system. The MD obtained is given in Table 5.

Wu [21] use the following modified Eyring viscosity equation [22] to predict the viscosity of liquid mixtures

$$\eta = \frac{hN_A}{V_m} \exp \left[\frac{\left(\sum x_i G_i^* \right) - G^E/A}{RT} \right] \quad (18)$$

where h is Planck's constant, N_A is Avogadro's number, V_m is the molar volume of the liquid mixture, G_i^* is the Gibbs energy of activation for viscous flow of the pure liquid, G^E is the free energy of mixing, A is an empirical factor (in this case 1.0), R is the gas constant and T is 298.15 K. The free energy of mixing is obtained by Flory's theory and the MD obtained is given in Table 5.

The Group Contribution Thermodynamic-Viscosity Model (GC-UNIMOD) [23] is used as a predictive model. A liquid mixture is described as a solution of groups and a physical property of the mixture is the sum of contributions for all groups in the mixture. The assumptions of group contributions are shown as additive of molecular properties in terms of group properties and independence of a group in the solution from its molecule of origin.

The viscosity equation of GC-UNIMOD can be expressed as:

$$\ln \eta = \sum_{i=1}^n (\zeta_i^C + \zeta_i^R) \quad (19)$$

$$\zeta_i^C = \phi_i \ln \left(\eta_i \frac{V_i}{V_m} \right) + 2\phi_i \ln \left(\frac{x_i}{\phi_i} \right) \quad (20)$$

$$\zeta_i^R = \sum_{\text{all } k \text{ groups}} v_k^{(i)} [\Xi_{ki} - \Xi_{ki}^{(i)}] \quad (21)$$

where ϕ_i , is the average area fraction, $v_k^{(i)}$ is the number of k groups in the molecule, Ξ_{ki} and $\Xi_{ki}^{(i)}$ are the group residual viscosity of group k for the component i in the mixture, and the group residual viscosity of group k for the component i in the solution of groups of pure liquid i , respectively. Both the van der Waals properties of the different subgroups and the group interaction parameters have been obtained from Hansen et al. [24]. The MD for this system is given in Table 5.

From the different equations for viscosity, the Bloomfield–Dewan model is the best for our system.

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