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Measurements, Correlations, and Predictions of Viscosities for the Ternary Mixture (2-Butanol + Hexane + 1-Chlorobutane) at 298.15 K and 313.15 K

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Viscosities of the ternary mixture (2-butanol + hexane + 1-chlorobutane) at 298.15 K and 313.15 K have been measured at atmospheric pressure. Viscosity deviations for the ternary system were fitted to Cibulka's equation. To correlate experimental data of the ternary system, extended Nissan−Grunberg and McAllister equations have been used and their parameters have been calculated. The "viscosity−thermodynamic" model (UNIMOD) has been applied first to correlate experimental data for the binary mixtures and then to predict the viscosity for the ternary system. The group-contribution thermodynamic viscosity model (GC−UNIMOD) and the group contribution method proposed by Wu have been applied to predict the viscosity for the binary and ternary systems.

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1. Introduction

Experimental viscosity data and methods for the estimation of viscosities of multicomponent mixtures are not only of theoretical but also of great practical interest. Although a number of predictive equations[1] are available for estimating thermodynamic excess properties (excess volume, excess enthalpy, and excess free energy) of multicomponent systems, such methods are rarely used for viscosity. However, many empirical or semiempirical equations can correlate viscosity data of binary mixtures using several adjustable parameters.[2] The literature of correlations of flow properties for ternary and multicomponent liquid mixtures is rather limited. Recently, some empirical and semiempirical equations for binary mixtures were extended to ternary mixtures by introducing a ternary parameter,[3] also new models have been developed for the prediction of viscosities of mixtures. Some of them are based on a molecular approach,[4,5] whereas others are based on the group contribution concept.[6,7] The first type of models require binary interaction parameters for each binary system present in the multicomponent mixture, but no ternary (or higher) constants are generally needed.

In this work, viscosities of the ternary mixture (2-butanol + hexane + 1-chlorobutane) at 298.15 K and 313.15 K have been measured. The viscosity data have been used to calculate the viscosity deviations ($\Delta\eta$). The correlation equations of Nissan−Grunberg[8] and McAllister[9] extended to multicomponent mixtures[3] were applied to the viscosity data of the ternary system using binary parameters obtained from the correlation of the binary systems. The UNIMOD model[5] has been employed to correlate the viscosity of the binary systems and then to predict the viscosity of the ternary mixture without additional parameters. The GC−UNIMOD model[7] and the group contribution method proposed by Wu[6] have been used to predict the viscosity of binary and ternary mixtures.

Table 1. Properties of the Pure Components

	$T = 298.15$ K				$T = 313.15$ K	
	η		ρ		η	ρ
	mPa·s		g·cm^{-3}		mPa·s	g·cm^{-3}
component	expt	lit.[a]	expt	lit.[a]	expt	expt
2-butanol	3.0804	2.998	0.80239	0.80241	1.7942	0.78939
hexane	0.2944	0.294	0.65493	0.65484	0.2537	0.64108
1-chlorobutane	0.4273	0.426	0.88085	0.88095	0.3645	0.86384

[a] Reference 23.

Previously, we reported density and speed of sound measurements for this system as a function of mole fraction and discussed their behavior in terms of molecular interactions.[10]

2. Experimental Section

The compounds used, namely, 2-butanol (purity better than 99.0 mol %), hexane (purity better than 99.0 mol %), and 1-chlorobutane (purity better than 99.0 mol %), were obtained from Aldrich. The butanol was dried with activated molecular sieve type 0.3 nm from Merck. The purities of the chemicals were verified not only by comparing the measured densities and viscosities with those reported in the literature but also by gas chromatography using a semicapillary methyl silicone column (o.d. 530 μm) and a flame-ionization detector. The absence of other significant compounds was confirmed, so no further purification was considered necessary. The pure component properties compared with those found in the literature, are gathered in Table 1.

Kinematic viscosities, ν, of pure components and the ternary mixture were determined using an Ubbelohde viscosimeter (inner diameter = 0.63 mm, capillary length

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Table 2. Experimental Kinematic Viscosities, ν, and Densities, ρ, and Calculated Viscosity Deviations, $\Delta\eta$, of the Ternary Mixture 2-Butanol (1) + Hexane (2) + 1-Chlorobutane (3) at 298.15 K and 313.15 K

		T = 298.15 K			T = 313.15 K		
		ν	ρ	$\Delta\eta$	ν	ρ	$\Delta\eta$
x_1	x_2	$mm^2 \cdot s^{-1}$	$g \cdot cm^{-3}$	mPa·s	$mm^2 \cdot s^{-1}$	$g \cdot cm^{-3}$	mPa·s
0.0501	0.0519	0.4862	0.86159	−0.1344	0.4225	0.84470	−0.0736
0.0497	0.1033	0.4820	0.84752	−0.1369	0.4201	0.83083	−0.0752
0.0504	0.8480	0.4572	0.67825	−0.1382	0.3989	0.66398	−0.0777
0.0512	0.8989	0.4580	0.66860	−0.1374	0.3997	0.65445	−0.0765
0.0999	0.0503	0.5009	0.85768	−0.2560	0.4329	0.84081	−0.1379
0.1028	0.0990	0.5037	0.84403	−0.2617	0.4361	0.82736	−0.1398
0.1037	0.1985	0.4907	0.81758	−0.2749	0.4246	0.80128	−0.1506
0.1020	0.2978	0.4842	0.79267	−0.2745	0.4194	0.77671	−0.1517
0.1031	0.3972	0.4797	0.76869	−0.2793	0.4156	0.75306	−0.1550
0.1105	0.5333	0.4759	0.73719	−0.2988	0.4127	0.72202	−0.1654
0.1021	0.5963	0.4732	0.72431	−0.2762	0.4107	0.70933	−0.1531
0.1043	0.6952	0.4726	0.70356	−0.2791	0.4106	0.68890	−0.1537
0.1034	0.7964	0.4724	0.68353	−0.2729	0.4108	0.66916	−0.1492
0.1025	0.8465	0.4727	0.67397	−0.2681	0.4111	0.65972	−0.1460
0.2036	0.0993	0.5413	0.83560	−0.5020	0.4615	0.81914	−0.2666
0.2049	0.1983	0.5332	0.80917	−0.5131	0.4555	0.79307	−0.2743
0.2049	0.2981	0.5257	0.78394	−0.5192	0.4502	0.76818	−0.2786
0.2053	0.3961	0.5201	0.76034	−0.5239	0.4465	0.74491	−0.2816
0.2053	0.4966	0.5158	0.73736	−0.5256	0.4433	0.72226	−0.2828
0.2024	0.5994	0.5116	0.71524	−0.5187	0.4408	0.70048	−0.2787
0.2026	0.6979	0.5107	0.69479	−0.5172	0.4408	0.68035	−0.2769
0.3023	0.0991	0.6004	0.82786	−0.7191	0.5031	0.81169	−0.3774
0.3039	0.1990	0.5909	0.80108	−0.7338	0.4959	0.78528	−0.3876
0.2994	0.2990	0.5789	0.77611	−0.7326	0.4876	0.76062	−0.3886
0.2970	0.4005	0.5706	0.75190	−0.7330	0.4834	0.73674	−0.3886
0.2966	0.5030	0.5652	0.72854	−0.7356	0.4793	0.71374	−0.3907
0.2969	0.5999	0.5625	0.70746	−0.7373	0.4773	0.69301	−0.3917
0.3954	0.0997	0.6756	0.82051	−0.9087	0.5551	0.80467	−0.4722
0.3936	0.2060	0.6607	0.79229	−0.9207	0.5449	0.77681	−0.4812
0.3990	0.3010	0.6562	0.76782	−0.9420	0.5411	0.75268	−0.4944
0.3959	0.4013	0.6453	0.74391	−0.9443	0.5341	0.72911	−0.4967
0.3974	0.5016	0.6415	0.72084	−0.9525	0.5319	0.70640	−0.5014
0.4930	0.1037	0.7864	0.81197	−1.0829	0.6291	0.79652	−0.5568
0.4942	0.2066	0.7724	0.78442	−1.1051	0.6199	0.76935	−0.5713
0.4974	0.3004	0.7664	0.76037	−1.1243	0.6159	0.74564	−0.5831
0.4981	0.4006	0.7604	0.73610	−1.1358	0.6108	0.72171	−0.5914
0.5954	0.1029	0.9566	0.80444	−1.2237	0.7386	0.78943	−0.6213
0.5925	0.2058	0.9354	0.77715	−1.2449	0.7239	0.76253	−0.6368
0.5967	0.3019	0.9447	0.75235	−1.2595	0.7256	0.73809	−0.6486
0.6955	0.1016	1.216	0.79722	−1.2896	0.8974	0.78272	−0.6452
0.6921	0.2066	1.193	0.76932	−1.3182	0.8793	0.75524	−0.6670
0.7941	0.1033	1.600	0.78920	−1.2577	1.133	0.77532	−0.6099
0.8457	0.0521	1.957	0.79953	−1.0994	1.326	0.78570	−0.5260
0.8488	0.0996	1.973	0.78594	−1.1153	1.324	0.77241	−0.5443
0.8991	0.0493	2.410	0.79613	−0.8875	1.571	0.78268	−0.4149
0.8981	0.0511	2.402	0.79569	−0.8920	1.549	0.78225	−0.4312

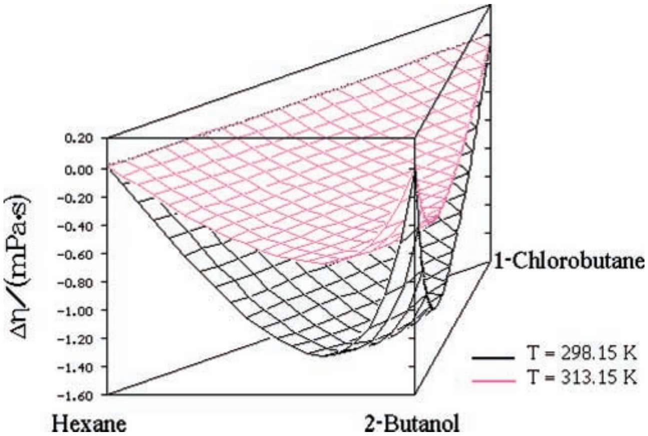

Figure 1. Three-dimensional surfaces of $\Delta\eta$/(mPa·s) for the ternary system 2-Butanol (1) + Hexane (2) + 1-Chlorobutane (3) correlated with the Cibulka's eq 2; (black lines) at T = 298.15 K; (pink lines) at T = 313.15 K.

= 893 mm) connected to a Schott-Geräte automatic measuring unit model AVS-440, for which the reproducibility of the flow time measurement is ±0.01 s. The correspond-

Table 3. Coefficients in (mPa·s) of the Redlich−Kister's Eq 4 and Cibulka's Eq 2, and the Corresponding Standard Deviations, σ, for the Binary and Ternary Mixtures at 298.15 and 313.15 K

T						σ ($\Delta\eta$)
K	A_0	A_1	A_2	A_3	A_4	mPa·s
		2-Butanol (1) + Hexane (2)[a]				
298.15	−4.5698	−3.1302	−1.9632	−2.1300	−1.6353	0.0049
313.15	−2.3666	−1.5650	−1.2544	−0.7922		0.0050
		2-Butanol (1) + 1-Chlorobutane[b]				
298.15	−4.2248	−3.0271	−2.5744	−1.4640		0.0062
313.15	−2.1686	−1.4162	−1.2615	−0.7721		0.0041
		Hexane (2) + 1-Chlorobutane (3)[c]				
298.15	−0.0755	0.0115	−0.0015	0.0093		0.0005
313.15	−0.0641	0.0084	−0.0017	0.0015		0.0007

T				σ ($\Delta\eta$)
K	B_1	B_2	B_3	mPa·s
		2-Butanol (1) + Hexane (2) + 1-Chlorobutane (3)		
298.15	0.7156	13.0871	0.3936	0.0139
313.15	0.4438	6.2769	−0.0204	0.0077

[a] Reference 12. [b] Reference 13. [c] Reference 14.

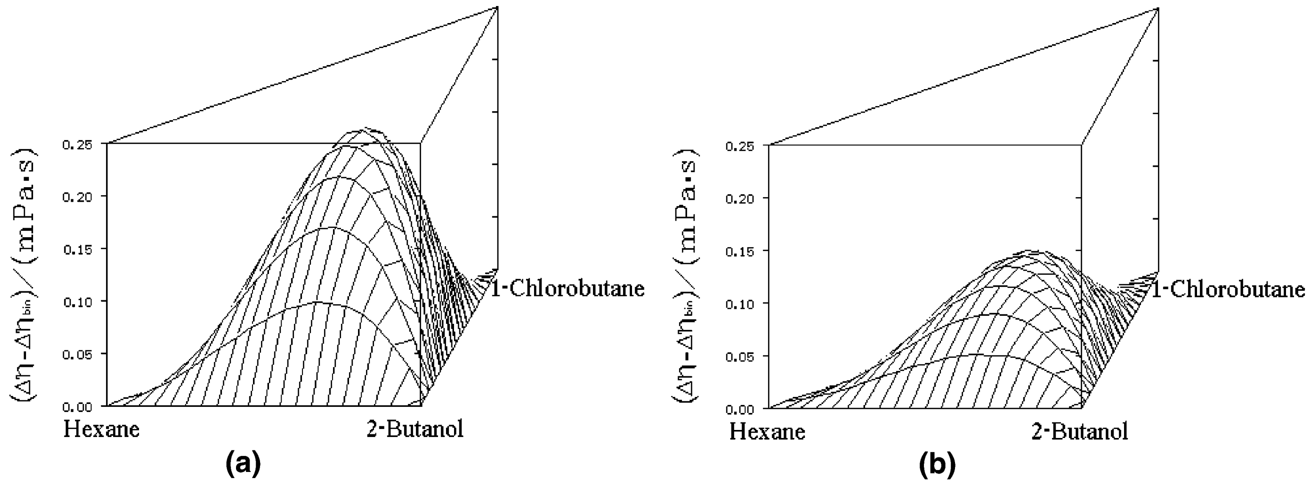

Figure 2. Three-dimensional surfaces of $(\Delta\eta - \Delta\eta_{\text{bin}})$/(mPa·s) for the ternary system 2-Butanol (1) + Hexane (2) + 1-Chlorobutane (3) correlated with the Cibulka's eq 2; (a) at $T = 298.15$ K; (b) at $T = 313.15$ K.

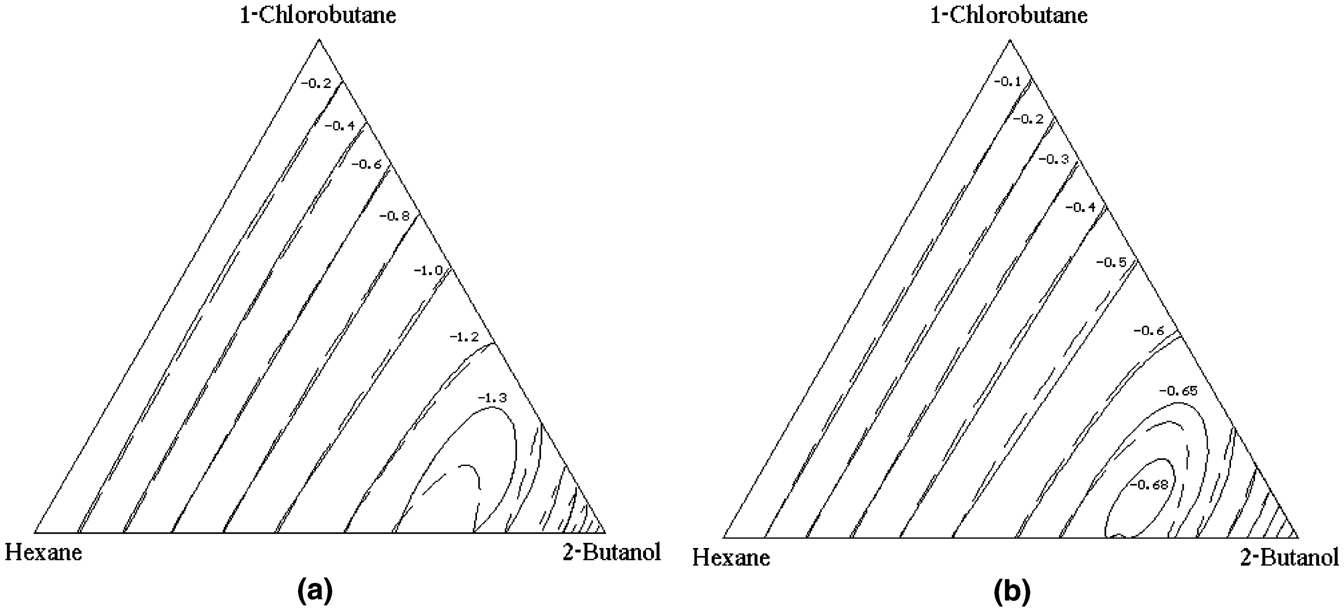

Figure 3. Isolines at constant $\Delta\eta$/(mPa·s) for the ternary system 2-Butanol (1) + Hexane (2) + 1-Chlorobutane (3): (—) correlated with Cibulka's eq 2; (— — —) predicted by UNIMOD model. (a) at $T = 298.15$ K; (b) at $T = 313.15$ K.

Table 4. Minimum Values of the Viscosity Deviations, $\Delta\eta$, and Maximum Values of the Ternary Contribution, $(\Delta\eta - \Delta\eta_{\text{bin}})$, to the Cibulka's Equation

T			$\Delta\eta$			$(\Delta\eta - \Delta\eta_{\text{bin}})$
K	x_1	x_2	mPa·s	x_1	x_2	mPa·s
298.15	0.711	0.185	−1.352	0.483	0.260	0.2304
313.15	0.695	0.230	−0.688	0.484	0.258	0.1120

ing uncertainty in the kinematic viscosity was $\pm 1 \times 10^{-4}$ $\text{mm}^2\cdot\text{s}^{-1}$. The temperature was controlled within ±0.01 K. Kinetic energy corrections were applied to the data. At least four measurements of flow time were performed for each composition and temperature, and the results were averaged. The viscosimeter was calibrated with deionized doubly distilled water. More details of calibration and procedure can be found in an earlier paper.[11]

Densities, ρ, required for obtaining absolute (or dynamic) viscosities from kinematic viscosities ones, $\eta = \nu\cdot\rho$, have been calculated for the corresponding mole fractions from a Cibulka's equation that fitted experimental density data.[10]

The mole fractions of binary and ternary mixtures were determined by mass using a Mettler H20T balance with a precision of ± 0.01 mg. The uncertainty of the mole fraction is estimated to be less than $\pm 1 \times 10^{-4}$. The mixtures were completely miscible over the whole composition range.

3. Results and Discussion

In previous papers, we reported the viscosities for the binary mixtures (2-butanol + hexane),[12] (2-butanol + 1-chlorobutane),[13] and (hexane + 1-chlorobutane)[14] as a function of mole fraction at 298.15 K and 313.15 K.

The experimental viscosities and densities for the ternary mixture (2-butanol + hexane + 1-chlorobutane) at 298.15 K and 313.15 K are shown in Table 2.

The viscosity deviations, $\Delta\eta$, for ternary mixture were determined through the following equation:

$$\Delta\eta = \eta - \sum_{i=1}^{n} x_i\eta_i \qquad (1)$$

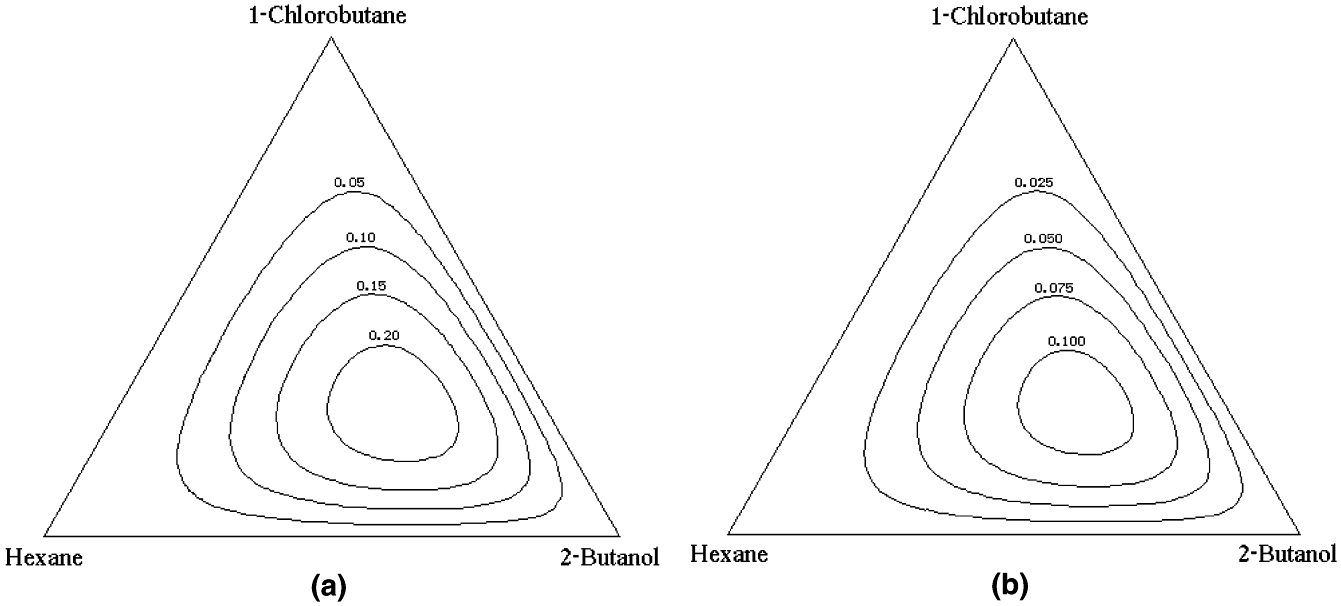

Figure 4. Isolines at constant $(\Delta\eta - \Delta\eta_{\mathrm{bin}})$/(mPa·s) for the ternary system 2-Butanol (1) + Hexane (2) + 1-Chlorobutane (3) correlated with Cibulka's eq 2; (a) at $T = 298.15$ K; (b) at $T = 313.15$ K.

Table 5. Adjustable Parameters and Standard Deviations of Nissan−Grunberg and McAllister Equations for the Viscosities of Binary and Ternary Mixtures

		binary parameters		
T/(K)	equation	A_{ij}	A_{ji}	$\sigma(\eta)$/(mPa·s)
		2-Butanol (1) + Hexane (2)[c]		
298.15	Nissan−Grunberg[a]	−2.4514		0.0336
	McAllister[b]	58.1791	45.2162	0.0092
313.15	Nissan−Grunberg[a]	−1.9858		0.0205
	McAllister[b]	46.4801	38.5137	0.0040
		2-Butanol (1) + 1-Chlorobutane (2)[d]		
298.15	Nissan−Grunberg[a]	−2.3638		0.0453
	McAllister[b]	59.9308	51.9464	0.0091
313.15	Nissan−Grunberg[a]	−1.9346		0.0306
	McAllister[b]	46.9767	43.6092	0.0106
		Hexane (1) + 1-Chlorobutane (2)[e]		
298.15	Nissan−Grunberg[a]	−0.1458		0.0003
	McAllister[b]	39.2790	40.9913	0.0002
313.15	Nissan−Grunberg[a]	−0.1475		0.0001
	McAllister[b]	34.2832	35.9258	0.0001

		ternary parameter	$\sigma(\eta)$/(mPa·s)	
T/(K)	equation	A_{ijk}	predicted from binary parameters	correlated with ternary parameter
		2-Butanol (1) + Hexane (2) + 1-Chlorobutane (3)		
298.15	Nissan−Grunberg[a]	1.8158	0.0337	0.0282
	McAllister[b]	44.8484	0.1884	0.0075
313.15	Nissan−Grunberg[a]	1.8423	0.0208	0.0140
	McAllister[b]	40.8874	0.1472	0.0052

[a] A_{ij}/Dimensionless. [b] A_{ij} 10^3/(kg·m^4·s^{-1}·mol^{-1}). [c] Reference 12. [d] Correlated from ref 13. [e] Correlated from ref 14.

where η is the absolute viscosity of the mixture, η_i is the absolute viscosity of pure component i, x_i is the mole fraction in component i, and n is the number of components in the mixture.

The viscosity deviations for the ternary mixture have been fitted to the Cibulka's equation:[15]

$$\Delta\eta = \Delta\eta_{\mathrm{bin}} + x_1x_2(1 - x_1 - x_2)[B_1 + B_2x_1 + B_3x_2] \quad (2)$$

where

$$\Delta\eta_{\mathrm{bin}} = \Delta\eta_{12} + \Delta\eta_{13} + \Delta\eta_{23} \quad (3)$$

and $\Delta\eta_{ij}$ is the contribution of the pair i, j to viscosity deviations. These contributions are given by the a Redlich−Kister type equation:[16]

$$\Delta\eta_{ij} = x_ix_j \sum_{p=0}^{p} A_p(x_i - x_j)^p \quad (4)$$

where x_i denotes the mole fraction of component i in the mixture and A_p are adjustable parameters. The coefficients A_p and B_p obtained by a least-squares method are listed in Table 3. In this table are also included the standard

Table 6. Adjustable Parameters ($U_{ji} - U_{ii}$) and Standard Deviations $\Sigma(\Delta\eta)$ of the UNIMOD Model for the Binary and Ternary Mixtures at 298.15 K and 313.15 K

T/(K)	U_{21}-U_{11}/(J·mol^{-1})	U_{12}-U_{22}/(J·mol^{-1})	$\sigma(\Delta\eta)$/(mPa·s)
	2-Butanol (1) + Hexane (2)[a]		
298.15	−205.2819	−2.2100	0.0056
313.15	−202.4603	17.9091	0.0020
	2-Butanol (1) + 1-Chlorobutane (2)[b]		
298.15	−308.6819	83.1090	0.0141
313.15	−343.2513	167.6242	0.0098
	Hexane (1) + 1-Chlorobutane (2)[c]		
298.15	−13.5663	13.3820	0.0003
313.15	−14.7673	14.5917	0.0005
	2-Butanol (1) + Hexane (2) + 1-Chlorobutane (3)		
298.15			0.0090
313.15			0.0037

[a] Reference 12. [b] Parameters obtained from data of ref 13. [c] Reference 14.

Table 7. Standard Deviations of GC−UNIMOD Model and Wu's Model for the Binary and Ternary Systems at 298.15 K and 313.15 K

	$\sigma(\eta)$/(mPa·s)				
		Wu			
		UNIFAC		ASOG	
T/(K)	GC−UNIMOD	$A = 1$	$A = 2.45$	$A = 1$	$A = 2.45$
	2-Butanol (1) + Hexane (2)[a]				
298.15	0.3353	0.1343	0.2880	0.1363	0.2883
313.15	0.1863	0.0520	0.1485	0.0529	0.1479
	2-Butanol (1) + 1-Chlorobutane (3)[b]				
298.15	0.4893	0.2197	0.3597	0.2358	0.3679
313.15	0.2766	0.1070	0.1967	0.1127	0.1997
	Hexane (2) + 1-Chlorobutane (3)[c]				
298.15	0.0067	0.0103	0.0005	0.0117	0.0004
313.15	0.0034	0.0068	0.0013	0.0100	0.0001
	2-Butanol (1) + Hexane (2) + 1-Chlorobutane (3)				
298.15	0.3087	0.0886	0.1915	0.1318	0.2448
313.15	0.1711	0.0697	0.0910	0.0535	0.1256

[a] Reference 12. [b] Parameters obtained from data of ref 13. [c] Reference 14.

deviations, σ, calculated through the expression

$$\sigma(\Delta\eta) = \left(\frac{\sum_{i=1}^{m} (\Delta\eta_{\text{exptl.}} - \Delta\eta_{\text{calc.}})^2}{m - p}\right)^{1/2} \tag{5}$$

with m being the number of experimental data and p being the number of adjustable parameters in eqs 2 and 4.

Three-dimensional surfaces of both viscosity deviations, $\Delta\eta$, and ternary contributions, $(\Delta\eta - \Delta\eta_{\text{bin}})$, calculated from Cibulka's equation at 298.15 K and 313.15 K have been plotted in Figures 1 and 2, respectively. The isolines at constant values of $\Delta\eta$ and $(\Delta\eta - \Delta\eta_{\text{bin}})$ have been drawn in Figures 3 and 4.

In Figure 1, it can be observed that ternary viscosity deviations are negative over the whole composition range and that the surfaces of $\Delta\eta$ have the same shape at both temperatures, and the increase of temperature considerably modifies the values of $\Delta\eta$ that become less negative. In Figure 2, it can be seen that the ternary contribution $(\Delta\eta - \Delta\eta_{bin})$ is positive for the entire range of ternary compositions and the increase of temperature makes smaller. Locations of minima for $\Delta\eta$ and maxima for $(\Delta\eta - \Delta\eta_{bin})$ are shown in Table 4.

The negative values observed for $\Delta\eta$ of the ternary system under study point out the easier flow of the mixture when compared with the behavior of its pure components. This could be explained by the breaking of the hydrogen bonding of alcohols that makes the mixture flow more easily. The breaking of self-association is important enough to overcome other effects that would increase the viscosity, e.g. those of OH−Cl interactions present in this system. This is also in accordance with the conclusions of Fort and Moore[17] about the behavior of systems containing an associated component.

Comparing the values for the present ternary mixture with those reported for the system (1-butanol + hexane + 1-chlorobutane),[14] it can be seen that the $\Delta\eta$ values are more negative for the mixture containing 2-butanol. This agrees with the fact that hydrogen bonding in secondary butanol is not as strong as in primary butanol and its breaking is less difficult during the mixing process. The same behavior has been observed in the ternary mixtures (1-butanol + hexane + 1-butylamine)[18] and (2-butanol + hexane + 1-butylamine).[12]

The extensions to multicomponent mixtures of the correlation equations of Nissan−Grunberg and McAllister proposed by Canosa et al.[3] have been applied to the studied system:

Nissan−Grunberg:

$$\ln(\eta) = \sum_{i}^{n} x_i \ln(\eta_i) + \sum_{i}^{n} \sum_{j>i}^{n} x_i x_j A_{ij} + \sum_{i}^{n} \sum_{j>i}^{n} \sum_{k>j}^{n} x_i x_j x_k A_{ijk} \tag{6}$$

$$\ln(\eta V) = \sum_{i}^{n} x_i^3 \ln(\eta_i V_i) + 3 \sum_{i}^{n} \sum_{j \neq i}^{n} x_i^2 x_j ln(A_{ij}) + 6 \sum_{i}^{n} \sum_{j>i}^{n} \sum_{k>j}^{n} x_i x_j x_k \ln(A_{ijk}) \tag{7}$$

where, in each equation, x is the mole fraction, η and η_i are the dynamic viscosity of the mixture and of the pure components, respectively, V and V_i are the molar volume of the mixture and of the pure components, respectively, A_{ij} are the binary correlation parameters, and A_{ijk} is the ternary correlation parameter. The parameters A_{ij} are estimated by adjusting data of the binary mixtures with the nonextended equations. Then, these parameters are included in the extended equation, and A_{ijk} is determined by fitting the ternary mixture data. Correlation parameters and standard deviations for these equations are gathered in Table 5. The best correlation for all of the binary systems and also for the ternary one is obtained when using the McAllister equation.

The "viscosity−thermodynamic" model UNIMOD[5] is used for correlating the viscosities of binary mixtures. Then, the parameters obtained are employed to predict the viscosities of the multicomponent mixture. In this model, the adjustable parameters are ($U_{ji} - U_{ii}$) that denote the interaction potential energies. Their values, obtained using a Simplex method,[19] are shown in Table 6 along with the corresponding standard deviations. Figure 3, parts a and b, presents the isolines of constant $\Delta\eta$ predicted with UNIMOD model (dashed lines) and compared with the experimental values (continuous lines).

The group-contribution thermodynamic-viscosity model[7] (GC−UNIMOD) and the Wu's model[6] have been used as predictive models for both binary and ternary mixtures. The van der Waals properties for the different subgroups and the group interaction energy parameters used in the GC−UNIMOD model have been obtained from Hansen et al.[20] The free energy of mixing needed in Wu's model is obtained using the UNIFAC and ASOG parameters proposed by Gmehling et al.[21] and Tochigi et al.,[22] respectively. Table 7 shows the standard deviations for binary and ternary mixtures at both temperatures, 298.15 K and 313.15 K, obtained by application of GC−UNIMOD and Wu's model. Comparing these values with $\sigma(\eta)$ of the UNIMOD model for the ternary mixture, it can be seen that the last model yields a smaller deviation despite its simplicity. It is capable to predict the viscosity of the ternary mixture quite well without other additional parameters that those obtained from binary mixtures.

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