

EXCESS MOLAR VOLUMES AND EXCESS VISCOSITIES OF THE 1-CLOROBUTANE + PENTANE + DIMETHOXYETHANE TERNARY SYSTEM AT 298.15 K.

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ABSTRACT

Excess molar volume and excess viscosity data of the 1-chlorobutane (1) + pentane (2) + dimethoxyethane (3) system and those of the corresponding binary systems have been determined at 298.15 K. Different expressions were used to calculate these excess properties from binary data, such as those of Radojkovic et al., Jacob-Fitzner, Kohler, Cibulka and Singh. The correlation of Cibulka is the best in this system for excess volume and viscosity.

The behavior of the experimental data of the ternary system can be represented by the Flory's equation with a MD = 0.16 for the excess molar volume. For viscosities we applied Grunberg-Nissan, Katti-Chaudhri, Bloomfield-Dewan, Wu and GC-UNIMOD equations, where the best for our system is Wu's equation with a MD = 0.019.

RESUMEN

Se determinaron datos del exceso volumen molar y de la viscosidad para el sistema ternario 1-clorobutano (1) + pentano (2) + dimetoxietano (3) a 298.15 K. A partir de los datos experimentales de los sistemas binarios, pueden calcularse las propiedades de exceso de los sistemas ternarios usando expresiones como la de Radojkovic, Jacob-Fitzner, Kohler, Cibulka, Singh, siendo la que mejor se adapta a los resultados experimentales la de Radojkovic y col.

El comportamiento de los datos experimentales del sistema ternario puede ser representado por la ecuación de Flory con una MD = 0.16 para el exceso de volumen molar. Para viscosidades se han aplicado las ecuaciones de Grunberg-Nissan, Katti-Chaudhri, Bloomfield-Dewan, Wu y GC-UNIMOD ecuaciones, siendo la de Wu, la que mejor se adapta a nuestro sistema, con una DM = 0.019.

INTRODUCTION

The knowledge of the densities and viscosities of new fluids and fluid mixtures is important to understand and to develop new theoretical models of molecular interactions and also in engineering applications of absorption heat pumps and heat transformers.

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.

We found in the literature viscosities of ternary mixture using alcohols and chlorobutane [1]. A search of the literature of ternary systems indicates that several empirical correlations are available to calculate the excess molar volumes and transport properties of liquid mixtures. In this paper, we report

the density and viscosity data of the 1-chlorobutane (CIBU) (1) + pentane (P) (2) + dimethoxyethane (DME) (3) ternary system at 298.15 K. From these data, excess volume and excess viscosity data were calculated.

EXPERIMENTAL

The methods used in our laboratory have been described previously [2]. Densities were determined with a digital densimeter AP, model DMA 45 for measurements at 298.15 K \pm 0.01 K (0.01 K). Densimeter calibration was made 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, and using Ubbelodhe viscosimeter. We employed the following equation:

$$\eta/\rho = K (t-\theta) \quad [I]$$

where K is the constant of the viscosimeter and θ the Hagenbach correction. Time measurements were converted to a digital electrical signal to start the internal crystal-controlled clock with readout display. The electronic timer could measure time to ± 0.01 s. The estimated error in the kinematic viscosity was ± 0.005 mPa.s.

1-Chlorobutane (Mallinckrodt, puriss.) pentane (Riedel de Haen puriss.) and dimethoxyethane (Merck, puriss.) were used without purification. Mixtures were prepared by mixing weighed amounts of the pure liquids. Caution was taken to prevent evaporation.

RESULTS AND DISCUSSION

The experimental results for the pure liquids are reported in Table 1, together with literature values for comparison:

TABLE 1. Properties characterizing the pure components at 298.15 K

Component	$\rho \times 10^3 (\text{kg m}^{-3})$		$\eta (\text{mPa s})$	
	Exp.	Lit.	Exp.	Lit.
1-Chlorobutane	0.8810	0.88095 ^a	0.426	0.426 ^a
n-Pentane	0.6215	0.62139 ^a	0.225	0.225 ^a
1,2-Dimethoxyethane	0.8637	0.86370 ^a	0.455	0.455 ^a

^aRef.[3].

The excess function of a binary system can be represented by a Redlich Kister form of the type:

$$X^E = x_i' x_j' \sum_{k=0}^n a_k (x_i' - x_j')^k \quad [II]$$

where X^E represents V^E or η^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 was used to determine the values of the coefficients a_k . In

each case, the optimum number of coefficients was ascertained from an examination of the standard deviation of the estimate with n , which is the number of parameters.

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

Tables 2, 3, and 4 show the density and viscosity values for different mole fractions of the binary systems CIBU(1) + P(2), CIBU(1) + DME(3) and P(2) + DME(3).

TABLE 2. Densities, viscosities, excess molar volumes and excess viscosities for the 1-chlorobutane (1) + pentane (2) at 298.15 K.

x_j	$\rho \times 10^3 (\text{kg m}^{-3})$	$\eta (\text{mPa s})$	$V^E \times 10^6 (\text{m}^3 \text{mol}^{-1})$	$\eta^E (\text{mPa s})$
0.0000	0.6215	0.225	—	—
0.0184	0.6363	0.226	0.248	-0.009
0.1384	0.6527	0.231	0.305	-0.015
0.1935	0.6667	0.234	0.188	-0.021
0.3391	0.7051	0.249	-0.208	-0.030
0.4497	0.7337	0.268	-0.283	-0.032
0.5503	0.7599	0.288	-0.294	-0.032
0.6738	0.7922	0.317	-0.224	-0.029
0.7847	0.8219	0.350	-0.166	-0.021
0.8890	0.8496	0.385	-0.007	-0.012
0.9380	0.8637	0.405	-0.007	-0.005
1.0000	0.8810	0.426	—	—

TABLE 3. Densities, viscosities, excess molar volumes and excess viscosities for the 1-chlorobutane (1) + dimethoxyethane (3) at 298.15 K.

x_j	$\rho \times 10^3 (\text{kg m}^{-3})$	$\eta (\text{mPa s})$	$V^E \times 10^6 (\text{m}^3 \text{mol}^{-1})$	$\eta^E (\text{mPa s})$
0.0000	0.8637	0.455	—	—
0.1058	0.8642	0.414	0.270	-0.035
0.3022	0.8661	0.413	0.344	-0.033
0.3993	0.8675	0.413	0.328	-0.030
0.50 45	0.8692	0.416	0.392	-0.024
0.6032	0.8710	0.418	0.381	-0.019
0.6981	0.8730	0.423	0.377	-0.012
0.7996	0.8754	0.427	0.258	-0.005
0.8948	0.8777	0.433	0.178	-0.004
1.0000	0.8810	0.426	—	—

TABLE 4. Densities, viscosities, excess molar volumes and excess viscosities for the pentane (2) + dimethoxyethane (3) at 298.15 K.

x_j	$\rho \times 10^3 (\text{kg m}^{-3})$	$\eta (\text{mPa s})$	$V^E \times 10^6 (\text{m}^3 \text{mol}^{-1})$	$\eta^E (\text{mPa s})$
0.0000	0.8637	0.455	—	—
0.0834	0.8395	0.402	0.243	-0.027
0.1807	0.8125	0.366	0.456	-0.035
0.2854	0.7847	0.334	0.616	-0.038
0.3757	0.7615	0.309	0.724	-0.040
0.4754	0.7369	0.287	0.776	-0.039
0.5858	0.7167	0.231	0.769	-0.035
0.6699	0.6915	0.256	0.705	-0.028
0.7737	0.6688	0.243	0.529	-0.021
0.8154	0.6598	0.238	0.458	-0.018
0.9105	0.6398	0.236	0.245	-0.009
1.0000	0.6215	0.225	—	—

The values of the coefficients and estimated standard deviation associated with the use of equation III are summarized in Table 5.

TABLE 5. Coefficients a_k for equation I and standard deviation for the binary systems at 298.15 K

CIBU (1) + P (2)		CIBU(1) + DME (3)		P (2) + DME (3)	
V^E	η^E	V^E	η^E	V^E	η^E
$a_0 = -1.1490$	-0.1300	1.5337	-0.0922	3.1283	-0.1603
$a_1 = -0.1353$	-0.0006	0.2827	0.1564	0.2037	0.0894
$a_2 = 0.3921$	-0.0167	0.4534	-0.1370	-0.1742	—
$a_3 = -1.4002$	0.0216	-0.5106	—	-0.5381	—
$a_4 = 7.9370$	0.0486	—	—	—	—
$a_5 = -5.2694$	—	—	—	—	—
$\sigma = 0.024$	0.0006	3×10^{-4}	9×10^{-6}	3×10^5	8×10^{-6}

Figures 1 and 2 show the experimental values of V^E and η^E for the three systems.

The experimental values of the density and viscosity of the ternary system were obtained by adding component 1 to a constant relation of components 2 and 3. Similar by component 2 to a constant relation of components 1 and 3, and component 3 to a constant relation of components 1 and 2 were added. Molar excess volume was calculated with the equation:

$$V_{123}^E = x_1 M_1 (\rho^{-1} - \rho_1^{-1}) + x_2 M_2 (\rho^{-1} - \rho_2^{-1}) + x_3 M_3 (\rho^{-1} - \rho_3^{-1}) \quad \text{[IV]}$$

where M_1 , M_2 and M_3 are the molecular weights of the components, ρ_1 , ρ_2 and ρ_3 are the densities of the pure components and ρ the density of the mixture. The excess viscosity of the mixture is defined by the equation:

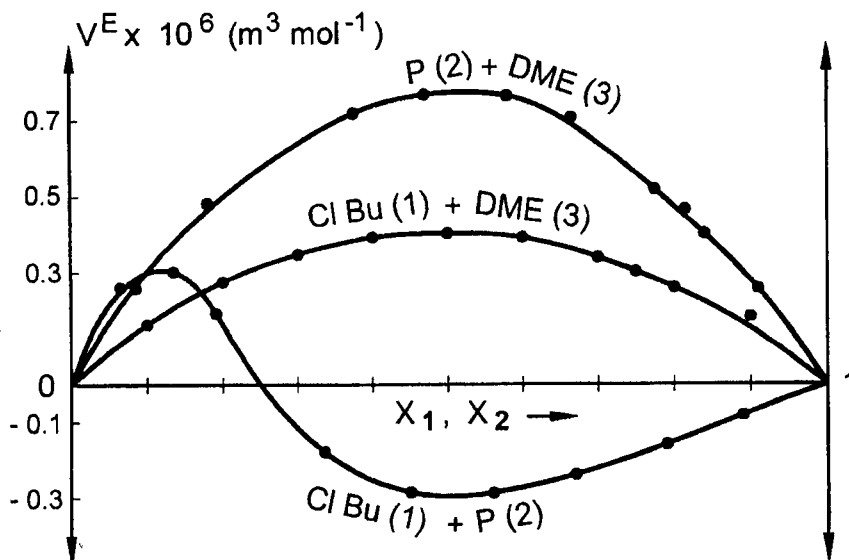


FIGURE 1. Excess molar volumes for the binary systems at 298.15 K. Continuous curves were calculated with equation I

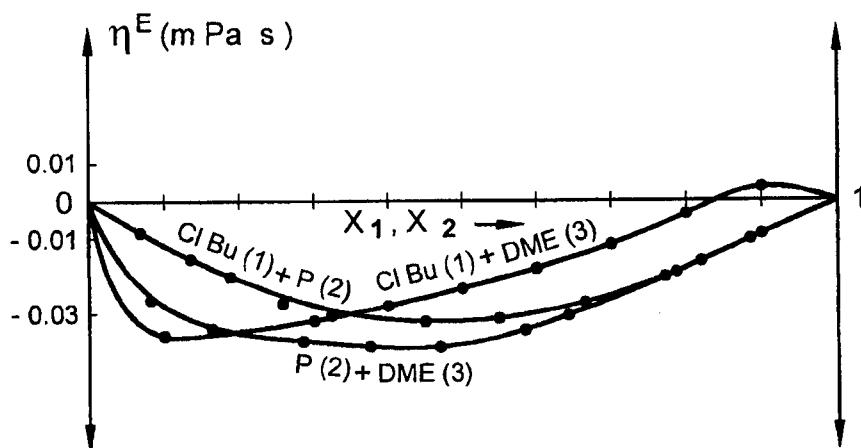


FIGURE 2. Excess viscosities for the binary systems at 298.15 K. Continuous curves were calculated with equation I.

$$\eta_{123}^E = \eta - \exp(x_1 \ln x_1 + x_2 \ln x_2 + x_3 \ln x_3) \quad [V]$$

where η_1 , η_2 and η_3 are the viscosities of the components and η the viscosity of the mixture. Table 6 shows the experimental density, excess molar volume and excess viscosity values for the ternary system at 298.15 K.

Figures 3 and 4 show the lines of constant V^E and η^E . These lines were obtained by plotting excess molar volumes and excess viscosities with respect to x_1 , x_2 or x_3 respectively.

TABLE 6. Densities, viscosities, excess molar volumes and excess viscosities of 1-chlorobutane(1) + pentane(2) + dimethoxyethane(3) system at 298.15 K.

x_1	x_2	$\rho \times 10^3$ (kg m^{-3})	$V^E \times 10^6$ ($\text{m}^3 \text{mol}^{-1}$)	η (mPa s)	η^E (mPa s)
$x_1 / x_2 = 0.2113$					
0.0300	0.1336	0.8260	0.355	0.380	-0.033
0.0601	0.2683	0.7900	0.623	0.338	-0.037
0.0863	0.3848	0.7610	0.683	0.305	-0.040
0.1198	0.5343	0.7270	0.450	0.277	-0.033
0.1481	0.6608	0.6988	0.285	0.254	-0.029
$x_1 / x_2 = 0.5432$					
0.0601	0.1107	0.8328	0.315	0.386	-0.033
0.1133	0.2086	0.8076	0.417	0.354	-0.036
0.1697	0.3142	0.7819	0.411	0.324	-0.037
0.2249	0.4140	0.7591	0.275	0.301	-0.034
0.2853	0.5252	0.7344	0.092	0.275	-0.033
$x_1 / x_2 = 1.0687$					
0.0840	0.0786	0.8417	0.300	0.395	-0.033
0.1693	0.1584	0.8216	0.402	0.369	-0.036
0.2548	0.2384	0.8031	0.329	0.341	-0.037
0.3361	0.3144	0.7863	0.193	0.330	-0.033
0.4265	0.3990	0.7688	-0.087	0.303	-0.031
$x_1 / x_2 = 2.1696$					
0.1255	0.0578	0.8480	0.292	0.400	-0.033
0.2141	0.0987	0.8385	0.335	0.387	-0.036
0.3437	0.1584	0.8253	0.310	0.365	-0.034
0.4089	0.1884	0.8193	0.226	0.359	-0.029
0.5655	0.2606	0.8059	-0.084	0.341	-0.023
$x_1 / x_2 = 5.7385$					
0.1524	0.0266	0.8565	0.280	0.408	-0.034
0.2809	0.0490	0.8526	0.352	0.396	-0.035
0.4197	0.0731	0.8487	0.321	0.392	-0.028
0.5688	0.0991	0.8455	0.201	0.391	-0.018
0.7100	0.1238	0.8431	0.000	0.382	-0.015
$x_1 / x_3 = 0.1965$					
0.0391	0.7620	0.6723	0.500	0.243	-0.022
0.0580	0.6468	0.6988	0.552	0.257	-0.030
0.0857	0.4777	0.7390	0.600	0.287	-0.036
0.1124	0.3151	0.7799	0.520	0.322	-0.040
0.1366	0.1678	0.8185	0.416	0.363	-0.038
$x_1 / x_3 = 0.5094$					
0.0594	0.8239	0.6595	0.378	0.236	-0.028
0.1192	0.6467	0.7008	0.403	0.256	-0.030
0.1765	0.4769	0.7426	0.326	0.289	-0.032
0.2189	0.3512	0.7742	0.317	0.315	-0.035
0.2856	0.1539	0.8252	0.348	0.366	-0.035

$x_1 / x_3 = 0.9368$

0.0903	0.8132	0.6626	0.327	0.235	-0.020
0.1735	0.6410	0.7040	0.251	0.256	-0.030
0.2536	0.4754	0.7455	0.147	0.288	-0.032
0.3315	0.3145	0.7862	0.200	0.324	-0.033
0.4056	0.1610	0.8261	0.261	0.363	-0.032

 $x_1 / x_3 = 1.9568$

0.1179	0.8219	0.6579	0.305	0.233	-0.020
0.2500	0.6223	0.7108	0.080	0.257	-0.032
0.3542	0.4647	0.7509	-0.010	0.288	-0.033
0.4580	0.3080	0.7915	-0.001	0.327	-0.028
0.5736	0.1334	0.8373	0.115	0.380	-0.019

 $x_1 / x_3 = 5.1425$

0.1554	0.8143	0.6639	0.250	0.234	-0.020
0.3068	0.6335	0.7103	-0.105	0.255	-0.030
0.4777	0.4294	0.7624	-0.150	0.298	-0.028
0.5906	0.2946	0.7980	-0.130	0.331	-0.025
0.7069	0.1556	0.8354	-0.080	0.374	-0.016

 $x_2 / x_3 = 0.0960$

0.8474	0.0134	0.8739	0.105	0.418	-0.010
0.6696	0.0289	0.8656	0.236	0.409	-0.012
0.5000	0.0438	0.8581	0.305	0.402	-0.022
0.3497	0.0569	0.8518	0.339	0.395	-0.032
0.1703	0.0726	0.8447	0.315	0.392	-0.036

 $x_2 / x_3 = 0.6152$

0.8318	0.0641	0.8610	-0.044	0.405	-0.007
0.6620	0.1287	0.8405	0.055	0.382	-0.016
0.4850	0.1961	0.8193	0.143	0.361	-0.023
0.3292	0.2555	0.8181	0.235	0.340	-0.032
0.1921	0.3077	0.7842	0.365	0.325	-0.037

 $x_2 / x_3 = 1.3685$

0.8385	0.0933	0.8535	-0.055	0.397	-0.011
0.6715	0.1898	0.8257	-0.057	0.369	-0.020
0.5077	0.2844	0.7983	-0.010	0.339	-0.025
0.3481	0.3767	0.7716	0.107	0.312	-0.032
0.1950	0.4555	0.7483	0.300	0.295	-0.033

 $x_2 / x_3 = 4.5710$

0.8555	0.1186	0.8476	-0.085	0.391	-0.011
0.6784	0.2639	0.8075	-0.150	0.350	-0.022
0.5527	0.3670	0.7796	-0.185	0.310	-0.028
0.3565	0.5280	0.7357	-0.081	0.275	-0.032
0.1751	0.6768	0.6957	0.236	0.251	-0.028

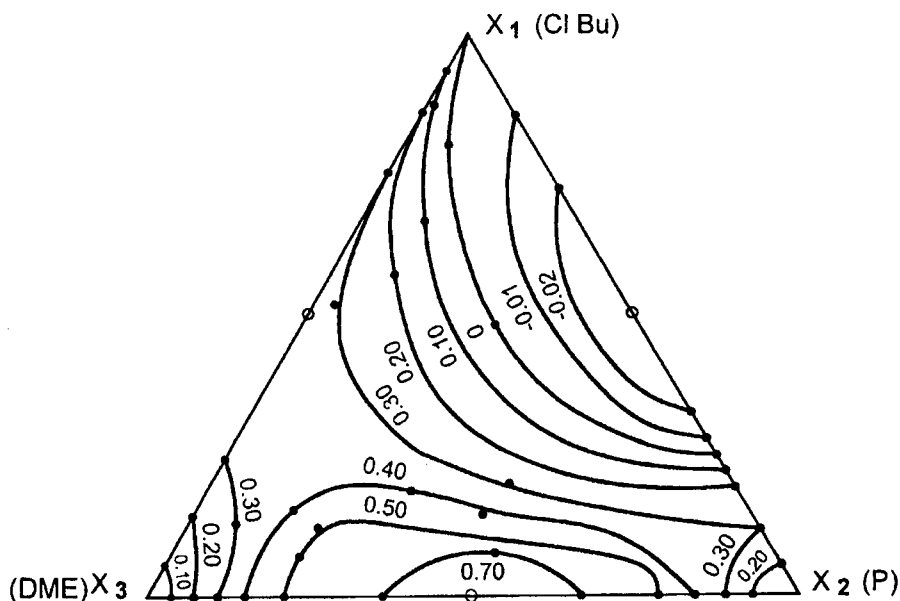


FIGURE 3. Lines of constant excess molar volumes for the 1-chlorobutane (1) + pentane (2) + dimethoxyethane (3) system at 298.15 K.

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 corresponding function for the binary $i + j$, $j + k$ and $i + k$ mixtures. The (1) + (2) system shows a sigmoid curve in V^E and positive for the other two systems, indicating that dispersion forces are dominant [4]. The excess viscosity for the three systems is negative and small, indicating that the interactions are very small. These deviations depend on the type of molecular interactions, as well as size and shape of molecules.

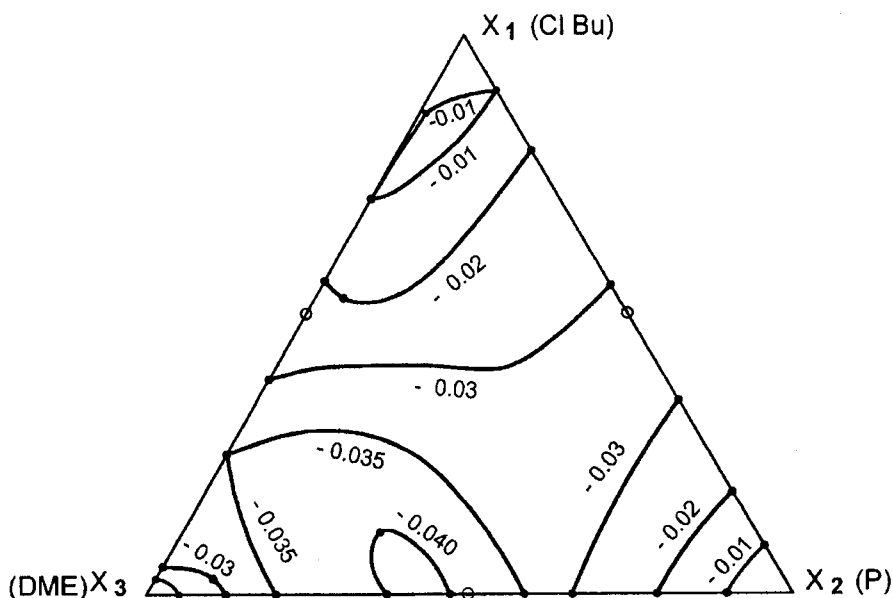


FIGURE 4. Lines of constant excess viscosities for the 1-chlorobutane (1) + Pentane (2) + dimethoxyethane (3) system at 298.15 K.

Vogel and Weiss [5] have considered that mixtures with strong molecular interactions present positive excess viscosity ($H^E < 0$), and mixtures with weak molecular interactions, the excess viscosity are negative ($H^E > 0$) where H^E is the excess enthalpy. In this case, the interactions are small, and dispersion forces are dominant. Among different expressions that have been reported in the literature, we chose Radojkovic *et al.* [V] equation for the excess molar volumes:

$$V_{123}^E = V_{12}^E + V_{13}^E + V_{23}^E \quad [VI]$$

where V_{12}^E , V_{13}^E and V_{23}^E represent the excess molar volumes with x_1 , x_2 and x_3 being the mole fractions in the ternary system. Jacob and Fitzner [7] have suggested an equation for estimating the properties of a ternary system based on the binary system data at compositions near to the ternary composition, using for the excess molar volume the expression:

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

thus for binary systems at compositions x_i' , x_j' , it is $x_i - x_j = x_i' - x_j'$. Kohler [8] have proposed an equation for a ternary system of the following form

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

Kohler's equation is symmetrical with respect to the fact that all three binary systems are treated identically. In this equation V_{ij}^E refers to the excess volumes of x_i' , x_j' in the binary mixtures using $x_i' = 1 - x_j' = x_i / (x_i + x_j)$. These equations allowed us to calculate V^E and η^E for the ternary system from experimental data of binary systems, which can be compared with the experimental values of the ternary systems. Table 7 shows the deviations using equation XI for V^E and η^E with Kohler's equation.

TABLE 7. Mean deviations (MD) for the 1-chlorobutane(1) + pentane (2) + dimethoxyethane (3) system at 298.15 K.

Equation	(V)	(VI)	(VII)	(VIII)	(IX)
MD [V_{123}^E ($\text{cm}^3 \text{mol}^{-1}$)]	0.146	0.146	0.179	0.043	0.050
MD [η_{123}^E (mPa s)]	0.008	0.008	0.009	0.008	0.008

There are other equations that introduce fitting parameters, such us Cibulka's equation [9]:

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

where A, B and C are parameters calculated from experimental data. The parameters obtained for the excess molar volumes are A = -1.5799; B = -9.7651; C = -4.9828, and for the excess viscosity A = 0.5864; B = -0.2431; C = -0.3865. Singh *et al* [10] have proposed an equation of the following form:

$$V_{123}^E = V_{12}^E + V_{13}^E + V_{23}^E + x_1 x_2 x_3 \left[A + B x_1 (x_2 - x_3) + C x_1^2 (x_2 - x_3)^2 \right] \quad [X]$$

In this case, the parameters obtained for the excess molar volume are A = -6.5764 ; B = -5.3903 ; C = 23.2655, and for the excess viscosity A = -6.5764; B = -5.3903 and C = 23.2655. These parameters were also evaluated by the method of least squares. Equations IX and X are modifications of Radojkovic's *et al.* equation VI. Table 7 shows the mean deviation defined by the following equation:

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

where M is either the excess molar volume or excess viscosity.

Cibulka's equation shows the best agreement values of V^E and η^E resulting from our system. Singh's *et al* equation does not differ very much from Cibulka's equation. Obviously, those models using parameters are superior to the calculated ones (not containing parameters). Following Shulka *et al.* [11] we applied Flory's theory to our ternary system. The values of reduced volume (\tilde{V}), reduced temperatures (\tilde{T}), characteristic pressures (P^*) and volumes characteristic (V^*) obtained for the pure components are shown in Table 8, using values of thermal expansion coefficient α and isothermal compressibility κ_T . The mean deviation defined by equation XI for the ternary system is 0.16.

TABLE 8. Paramaters of the pure components at 298.15 K.

Substance	$\alpha \times 10^3$ (K^{-1})	$\kappa_T \times 10^6$ (kPa^{-1})	$V^* \times 10^6$ ($m^3 \text{ mol}^{-1}$)	P^* ($J \text{ cm}^{-3}$)	T^* (K)	\tilde{V}	\tilde{T}
CIBU	0.8 ^a	1.187 ^b	87.2511	292	5957	1.2051	0.05005
P	1.61 ^a	2.180 ^a	85.3165	408	4158	1.3607	0.07171
DME	1.19 ^b	1.151 ^b	81.1764	509	4773	1.2854	0.06246

^aRef.[3] ; ^bRef.[22].

X_{12} , X_{13} and X_{23} are the exchange parameters calculated using the algorithm of Marquardt [12] assuming two body collisions, calculated for the binary systems. They are $X_{12} = -17.9504 \text{ J.cm}^{-3}$, $X_{13} = 1.5479 \text{ J.cm}^{-3}$ and $X_{23} = 32.8022 \text{ J.cm}^{-3}$. For viscosities, the empirical Grunberg and Nissan equation [13] extended to a ternary system, was found useful:

$$\ln \eta = x_1 \ln \eta_1 + x_2 \ln \eta_2 + x_3 \ln \eta_3 + x_1 x_2 x_3 \delta \quad [XII]$$

where δ is the parameter that reflects the system nonideality. This parameter has usually been regarded as an appropriate measure of the strength of the component interactions. For our system $\delta = 9.5213$, with a MD = 0.029. Katti and Chaudhri [14] have proposed that extended to a ternary system is:

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

where V is the molar volume of the solution, $V = \sum x_i M_i / \rho$ and W_{vis} is the interaction parameter, its value results in 15086 and a MD = 0.018. On the other hand, viscosity deviations from ideality can be quantitatively related to the thermodynamic properties of mixtures through the absolute rate and free volume theory for the viscosity of liquids. According to Bloomfield and Dewan [15] scheme, and following Celda *et al.* [16]; thus

$$\ln \frac{\eta}{\eta_{id}} = \alpha \ln \eta_{fv} + \beta \ln \eta_{ar} \quad [\text{XIV}]$$

where η_{fv} and η_{ar} are the deviation from the ideal mixture calculated by the free volume and the absolute rate reaction theory respectively, and α and β are weighting coefficients which usually made equal to 1. Thus departures from ideality are, respectively, given by:

$$\ln \eta_{fv} = \frac{1}{\tilde{V} - 1} - \frac{x_1}{\tilde{V}_1 - 1} - \frac{x_2}{\tilde{V}_2 - 1} - \frac{x_3}{\tilde{V}_3 - 1} \quad [\text{XV}]$$

and

$$\ln \eta_{ar} = -G^R / RT \quad [\text{XVI}]$$

where G^R is the residual energy of mixing calculated from the expression:

$$G^R = G^E + RT(x_1 \ln \frac{x_1}{\phi_1} + x_2 \ln \frac{x_2}{\phi_2} + x_3 \ln \frac{x_3}{\phi_3}) \quad [\text{XVII}]$$

Flory and co-workers [17] have proposed the relationships between η_{fv} , η_{ar} and the excess thermodynamic theory of liquid mixtures. To obtain G^E , it is necessary to know the activity coefficients obtained from the vapor-liquid equilibrium of our system. Then, it is possible to calculate G^E using Flory's theory, extended to a ternary system. In this case, MD = 0.047. We employed the following Eyring viscosity equation [18] for liquid mixture:

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

where h is the Planck's constant, N_A is the 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 universal gas constant and T is 298.15 K. Wu [19] has employed this equation. The free energy of mixing is obtained by Flory's theory different for each mole fraction and the standard deviation obtained was 0.019.

The Group Contribution Thermodynamic-Viscosity Model [19] (GC-UNIMOD) is used as a predictive model. According to this model, a liquid mixture is described as a solution of groups and any physical property of the mixture is the sum of contribution from all groups in the mixture. The additivity of molecular properties in terms of group properties and independence of a group in the solution from its molecule of origin has been assumed. The GC-UNIMOD viscosity equation is:

$$\ln \eta = \sum_{i=1}^n \left(\xi_i^c + \xi_i^r \right) \quad [\text{XIX}]$$

$$\xi_i^c = \phi_i \ln \left(\eta_i \frac{V_i}{V_m} \right) + 2\phi_i \ln \left(\frac{x_i}{\phi_i} \right) \quad [\text{XX}]$$

$$\xi_i^r = \sum_{\text{all groups}} v_k^{(i)} \left[\Xi_{ki} - \Xi_{ki}^{(i)} \right] \quad [\text{XXI}]$$

where $v_k^{(i)}$ is the number of k groups in the molecule, Ξ_{ki} and $\Xi_{ki}^{(i)}$ are the 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 Hansel *et al* [20]. In this case $MD = 0.025$. From the different equations for the excess viscosity, it results in that the Wu's model is the best one for our system.

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REFERENCES

- [1] Dominguez, M.; Santafé, L.; López, M. C.; Royo, M. F. Urieta, J. S. *Fluid Phase Eq.* **1998**, *152*, 133.
- [2] Bardavid, S. M.; Pedrosa, G.C.; Katz, M.; Postigo, M. A.; García, P. J. *Sol. Chem.* **1996**, *25*, 1125.
- [3] Riddick, J. L.; Bunger, N. M.; Sakano, T. *Organic Solvents*, 4th Ed., J. Wiley & Sons, New York, **1986**.
- [4] Marcheselli, L.; Marchetti, A.; Tagliazuchi, M.; Tassi, L.; Tosi, G. *J. Chem. Soc. Faraday Trans.* **1992**, *88*, 3159.
- [5] Vogel, H.; Weiss, A. *Ber. Bunsenges. Phys. Chem.* **1982**, *86*, 193.
- [6] Radojkovic, N.; Tasic, A.; Grozdanic, D.; Djordevic, B.; Malic, H. *J. Chem. Thermodyn.* **1977**, *9*, 349.

- [7] Jacob, K. T.; Fitzner, D. *Thermochim. Acta.* **1977**, *18*, 192.
- [8] Kohler, F. *Monatsch. Chem.* **1960**, *91*, 738.
- [9] Cibulka, I. *Collec. Czech. Commun.* **1982**, *47*, 1414.
- [10] Singh, P.; Nigam, R. K.; Sharma, S. P.; Aggarwal, S. *Fluid Phase Eq.* **1984**, *18*, 333.
- [11] Shukla, R.S.; Shukla, A.K.; Raiod, R.D.; Pandey, J.D. *J. Phys. Chem.* **1989**, *93*, 4627.
- [12] Marquardt, D.V. *J. Soc. Appl. Mat.* **1963**, *2*, 431.
- [13] Grunberg, L.; Nissan, A.H. *Nature*, **1949**, *164*, 799.
- [14] Katti, P.; Chaudhri, M.M. *J. Chem. Eng. Data.* **1964**, *9*, 442.
- [15] Bloomfield, V.A.; Dewan, J. *J. Phys. Chem.* **1971**, *75*, 3113.
- [16] Celda, B.; Guevara, R.; Tejero, R.; Figueruelo, J.E. *J. Chem. Eng. Data.* **1987**, *32*, 31.
- [17] Flory, P.J.; Orwoll, R.A.; Vrij, A. *J. Am. Chem. Soc.* **1964**, *86*, 3507.
- [18] Eyring, H.; Powell, E.G.; Roseveare, W.E. *Ind. Eng. Chem.* **1941**, *33*, 430.
- [19] Wu, D.T. *Fluid Phase Eq.* **1986**, *30*, 149.
- [20] Cao, W.; Knudsen, K.; Fredenslund, A.; Rasmussen, P. *Ind. Eng. Chem. Res.* **1993**, *43*, 2088.
- [21] Hansen, H.K.; Rasmussen, P.; Fredenslund, A.; Schiller, A.; Gmehling, J. *Ind. Eng. Chem. Res.* **1991**, *30*, 2352.
- [22] Salas, J.A.; O'Donnell, B.; Scida, L.; Katz, M. *Anal. Asoc. Quím. Arg.* **1989**, *77*, 101.