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Experimental and Predicted Excess Molar Volumes of Ternary Mixtures (1-chlorobutane or 2-methyl, 2-chloro propane) + n-heptane + 2-pentanone at T=298,15 K

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Abstract
Densities, ρ , at 298.15 K and atmospheric pressure have been measured over the entire composition range for the ternary systems (2-methyl, 2-chloro propane or 1-chlorobutane) + n-heptane + 2-pentanone and for five corresponding binary systems. Excess molar volumes, V^E, were evaluated for the binary and ternary systems. The V^E results were correlated and fitted using the Redlich-Kister equation for the binary mixtures and the Nagata - Tamura equation for the ternary mixtures, as a function of mole fraction. Several predictive empirical relations were applied to predict the excess volumes of ternary mixtures from the binary mixing data and analyzed to gain insight about liquid mixture interactions. The excess molar volumes for the two ternary systems are positive over the entire range of composition for three fixed composition $f_m = x_1 / x_2$

Keywords:
Excess molar volumes; Chloroalkanes; n-heptane; 2-pentanone; Molecular interactions, Correlation.

1.INTRODUCTION

This paper is a part of thermodynamic study of chloalkanes, ketones and alkanes that was carried out in our laboratory. In this work, we present the excess molar volumes of the ternary systems (1-chlorobutane or 2-methyl, 2-chloro propane) +n-heptane + 2-pentanone and the five corresponding binary systems at T=298.15 K and atmospheric pressure. Excess molar volumes were determined from the densities of the pure liquids and mixtures, measured using an Anton Paar DMA 5000 densimeter. The binary experimental data were fitted to Redlich-Kister [1] equation .The Nagata and Tamura equation [2] has been used in order to correlate adequately the experimental values of ternary mixtures. The experimental values were also used to test different symmetric [1,3,4] and asymmetric [5-7] empirical expressions. These methods predict excess ternary properties from involved binary systems.

2.Experimental

The chemical substances, 1-chlorobutane (>99%), 2-methyl,2-chloro propane (>99%), n-heptane (>99%),2-pentanone (>99%), obtained from Fluka AG. The purity of theses compounds was checked by comparing the measured densities with those reported in the literature [8-10] ,and also by chromatography (GC).

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Table 1 comparison between experimental and literature densities at T=298.15K

substances	ρ / g. cm-3	
	This work	literature
1-chlorobutane	0.880682	0.88069[a]
2-methyl, 2-chloro propane	0.836994	0.83567[a]
n-heptane	0.680114	0.67969[b]
2-pentanone	0.801821	0.80163[c]

[a] [8] , [b] [9] , [c] [10]

Densities of pure components and mixtures were measured at T=298.15 K using Anton Paar vibrating-tube densimeter DMA 5000 with an estimating uncertainly of $\pm 5.10^{-5}$g.cm^{-3}. The temperature inside the vibrating-tube cell was regulated to better than ±0.01K using a Haake G thermostat. Before each series of measurements, the apparatus was calibrated periodically with double distilled water and dry air. The excess molar volumes were calculated from the densities of the pure liquids and their mixtures. Mixtures were prepared by weight with a probable error in the mole fraction lower 10^{-4}.

3.Results and discussion

Molar volumes of the mixtures were calculated from the equation:

$$V = \sum_{i=1}^{n} (x_i M_i) / \rho \quad (1)$$

Where xi and M_i are the molar fraction and molar mass of component I , and _ the measured density of the solution .

Table 2 experimental densities, ρ , excess molar volumes, V^E , for binary systems at T=298.15 K

x	$\rho/(g.cm^{-3})$	$V^E(cm^3.mol^{-1})$	x	$\rho/(g.cm^{-3})$	$V^E(cm^3.mol^{-1})$	x	$\rho/(g.cm^{-3})$	$V^E(cm^3.mol^{-1})$
				x 1-chlorobutane + (1-x) n-heptane				
0.0407	0.685745	0.0589	0.2999	0.725604	0.2702	0.7138	0.806887	0.2366
0.0779	0.691044	0.1025	0.3630	0.736530	0.2787	0.8009	0.827492	0.1863
0.1497	0.701628	0.1740	0.4023	0.743557	0.2844	0.8875	0.849500	0.1192
0.2169	0.712072	0.2200	0.5052	0.762932	0.2819	0.9476	0.865780	0.0588
0.2565	0.718368	0.2583	0.5987	0.781747	0.2772			
				x 2-methyl, 2-chloro propane +(1-x) n-heptane				
0.0500	0.685812	0.1260	0.2961	0.718828	0.5127	0.8037	0.799991	0.3666
0.1026	0.692476	0.2509	0.4037	0.734646	0.5555	0.8522	0.808828	0.2887
0.1502	0.698717	0.3384	0.5014	0.749577	0.5660	0.9036	0.818385	0.2001
0.1965	0.704903	0.4146	0.5974	0.764905	0.5348	0.9501	0.827261	0.1072
0.2500	0.712337	0.4679	0.7042	0.782637	0.4725			
				x 1-chlorobutane + (1-x) 2-pentanone				
0.0725	0.807205	0.0290	0.4369	0,835120	0.0936	0.8055	0.864543	0.0648
0.1054	0.809681	0.0386	0.4930	0,839512	0.0958	0.8359	0.867072	0.0522
0.1321	0.811676	0.0478	0.5816	0,846526	0.0931	0.8866	0.871259	0.0372
0.2299	0.819100	0.0710	0.6518	0,852128	0.0873	0.9145	0.873619	0.0223
0.2994	0.824408	0.0864	0.6948	0,855567	0.0839			
0.3515	0.828446	0.0902	0.7490	0,859943	0.0762			
				x 2-methyl, 2-chloro propane + (1-x) 2-pentanone				
0.0996	0.805757	-0.0455	0.3502	0.815418	-0.1392	0.7501	0.829376	-0.1300
0.1502	0.807743	-0.0677	0.4032	0.817398	-0.1527	0.8052	0.831105	-0.1064
0.1923	0.809388	-0.0858	0.5004	0.820898	-0.1622	0.9032	0.834118	-0.0583
0.2502	0.811626	-0.1082	0.5980	0.824315	-0.1612	0.9502	0.835530	-0.0317
0.2953	0.813373	-0.1268	0.6875	0.827305	-0.1437			
				x n-heptane + (1-x) 2-pentanone				
0.0562	0.791973	0.0911	0.3664	0.744756	0.5296	0.7526	0.700987	0.5211
0.1047	0.783758	0.1765	0.4233	0.737310	0.5822	0.8233	0.694371	0.4466
0.1946	0.769368	0.3233	0.4921	0.728924	0.6013	0.8918	0.688404	0.3325
0.2463	0.761565	0.3986	0.5566	0.721442	0.6090	0.9500	0.683794	0.1737
0.3006	0.753741	0.4662	0.6001	0.716609	0.6053			
0.3120	0.752117	0.4833	0.7003	0.706120	0.5633			

Table 3 values of parameters , A_i , of equation(3) and standard deviations, σ , for binary systems at T=298.15 K

Systeme	A_1	A_2	A_3	A_4	A_5	$\sigma(V^E)$ $(cm^3.mol^{-1})$
x 1-chlorobutane + (1-x) n-heptane	1.15768	-0.14745	0.26599	---	---	0.0048
x 2-methyl, 2-chloro propane +(1-x) n-heptane	2.24752	-0.21492	0.78229	-0.06334	-0.60626	0.0029
x 1-chlorobutane +(1-x) 2-pentanone	0.39250	-0.01636	---	---	---	0,0028
x 2-methyl, 2-chloro propane + (1-x)2-pentanone	-0.65403	-0.10080	0.09677	---	---	0.0013
x n-heptane +(1-x) 2-pentanone	2.41027	0.43555	0.33407	0.87121	---	0.0039

The excess molar volumes V^E for the five binary systems and the corresponding ternary system were evaluated using the following equation :

$$V^E = V - \sum_{i=1}^{n} (x_i M_i / \rho_i) \quad (2)$$

_i: density of pure component.

The excess molar volumes, V^E, are accurate to ±0.0001cm^{3}mol^{-1}. V^E for the binary systems were fitted by the least squares method to the Redlich-Kister[1] equation:

$$V^E = x(1-x)\sum_{i=1}^{n} A_i (2x-1)^{i-1} \quad (3)$$

Experimental excess volumes for the ternary mixtures were correlated using the equation:

$$V_{123}^E = V_{12}^E + V_{13}^E + V_{23}^E + x_1 x_2 x_3 \Delta_{123} \quad (4)$$

$x_3 = 1 - x_1 - x_2$,and $x_1 x_2 x_3 \Delta_{123}$ is ternary contribution whIch was correlated using the Nagata and Tamura equation [2].

$$\Delta_{123} = B_0 + B_1 x_1 + B_2 x_2 + B_3 x_1^2 + B_4 x_2^2 \quad (5)$$

A_i and B_i used in equation (3) and (5) for each mixtures are adjustable parameters .

Experimental values of densities, ρ , and excess molar volumes for the binary and ternary mixtures, are listed in tables 2 and 4 respectively.

Where A_i are fitting parameters

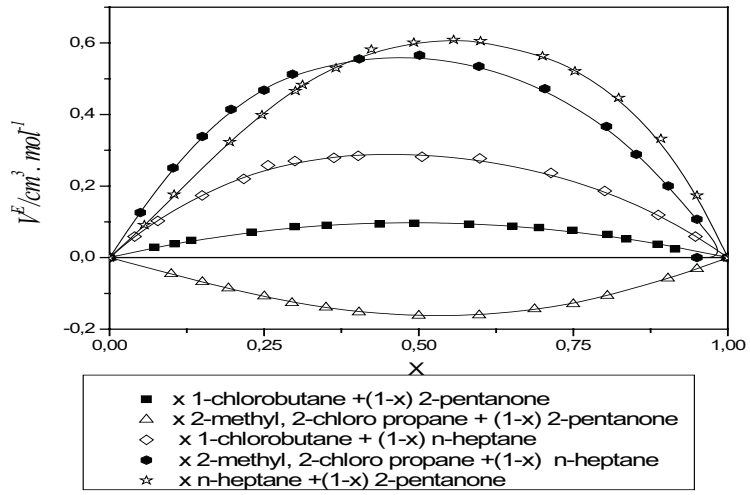

Figure 1 excess molar volumes of the binary mixtures at T=298.15K and atmospheric pressure.

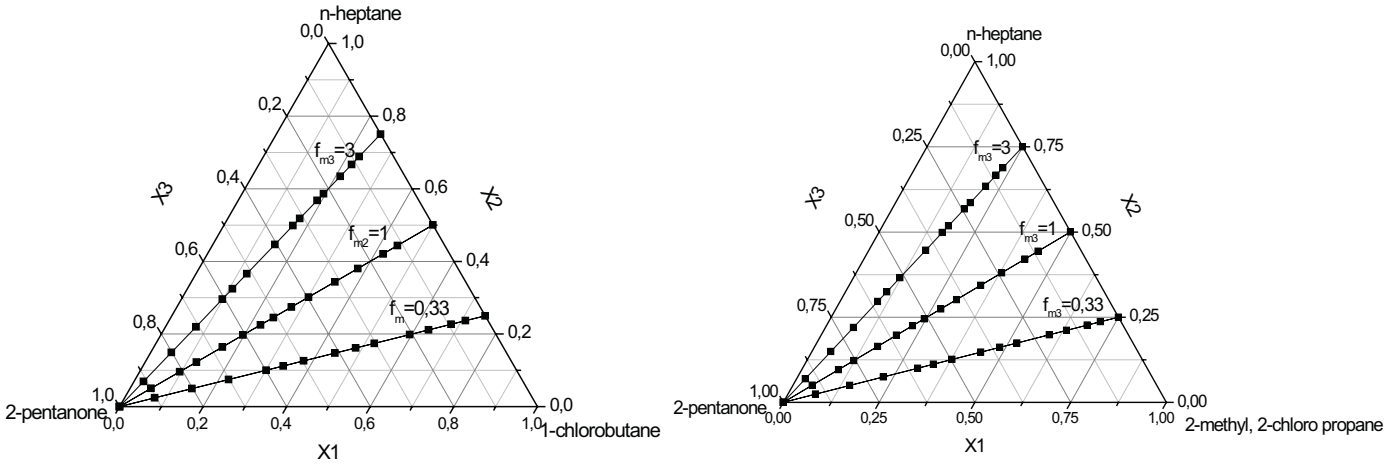

Figure 2 Experimental compositions for the ternary systems at T=298.15 K (1-chlorobutane or 2-methyl, 2-chloro propane + n-heptane + 2-pentanone)

Tables 3 and 5 present the parameters A_i and B_i of equation (3)and (5) respectively and the corresponding standard deviations for all mixtures. Figure 1 shows the experimental values of V^E, as well as the corresponding fitting curves.

The (V^E, x_3) for the two ternary mixtures at three fixed compositions ($f_m = x_1 / x_2$) have been plotted in fig 3. The Isolines of V^E_{123} have been plotted in fig 4. Although prediction of the physical properties of mulicomponent mixtures from those of their pure components is generally unreliable because of mixing effets, numerous schemes have been put forward for predictions based on the properties binary systems formed by pairs of components of the multicomponent system. In this work, we applied the following models.

Redlich-Kister [1] model

$$V^E_{ijk} = \sum_{j \succ i} V^E_{ij}\left(x'_i, x'_j\right) \qquad (6)$$

$$x'_i = x_i \qquad x'_j = x_j$$

Kohler [3] model

$$V^E_{ijk} = \sum_{j \succ i} \left(x_i + x_j\right)^2 V^E_{ij}\left(x'_i, x'_j\right) \qquad (7)$$

$$x'_i = \frac{x_i}{(x_i + x_j)} \qquad x'_j = 1 - x'_i$$

Colinet [4] model

$$V^E_{ijk} = \frac{1}{2}\sum_{i \prec j}\left[\frac{x_j}{(1-x_i)} V^E_{ij}(x'_i, x'_j) + \frac{x_i}{(1-x_j)} V^E_{ij}(x''_i, x''_j)\right] \qquad (8)$$

$$x'_i = x_i = 1 - x'_j \qquad x''_j = x_j = 1 - x''_i$$

Table 4 Excess molar volumes , V^E_{123}, and densities, ρ , at 298.15 K for the ternary mixtures.

x_1	x_2	$\rho/(g.cm^{-3})$	$V^E(cm^3.mol^{-1})$	x_1	x_2	$\rho/(g.cm^{-3})$	$V^E(cm^3.mol^{-1})$
x_1 1-chlorobutane + x_2 n-heptane + x_3 2-pentanone							
0.2497	0.7504	0.717263	0.2528	0.2963	0.2974	0.774686	0.4416
0.2317	0.6964	0.721314	0.3817	0.2809	0.2799	0.776184	0.4296
0.2208	0.6635	0.723947	0.4428	0.2351	0.2342	0.779865	0.3853
0.2055	0.6177	0.727801	0.5063	0.1810	0.1804	0.784472	0.3158
0.1945	0.5846	0.730704	0.5423	0.1610	0.1604	0.786239	0.2870
0.1809	0.5437	0.734522	0.5616	0.1108	0.1104	0.790736	0.2217
0.1725	0.5186	0.736908	0.5733	0.0680	0.0678	0.794776	0.1552
0.1498	0.4502	0.743809	0.5682	0.0490	0.0488	0.796686	0.1155
0.1301	0.3911	0.750218	0.5320	0.7497	0.2503	0.815243	0.2117
0.1094	0.3287	0.757259	0.4923	0.7074	0.2362	0.814231	0.2434
0.0959	0.2883	0.762058	0.4534	0.6704	0.2239	0.813424	0.2593
0.0697	0.2096	0.771807	0.3756	0.6490	0.2167	0.812946	0.2693
0.0558	0.1678	0.777418	0.3024	0.5900	0.1970	0.811673	0.2902
0.0395	0.1188	0.783992	0.2495	0.5473	0.1827	0.810777	0.3000
0.0206	0.0622	0.792278	0.1326	0.4754	0.1587	0.809439	0.2913
0.5009	0.4991	0.762047	0.2905	0.4640	0.1549	0.809226	0.2900
0.4675	0.4658	0.763763	0.3633	0.3853	0.1287	0.807840	0.2655
0.4477	0.4461	0.764863	0.3946	0.3125	0.1044	0.806570	0.2388
0.4430	0.4414	0.765139	0.4001	0.2671	0.0892	0.805858	0.2099
0.4261	0.4245	0.766151	0.4186	0.2181	0.0728	0.805104	0.1759
0.4144	0.4129	0.766894	0.4235	0.1858	0.0620	0.804530	0.1629
0.4007	0.3993	0.767739	0.4362	0.1384	0.0462	0.803786	0.1300
0.3628	0.3615	0.770255	0.4482	0.1025	0.0342	0.803242	0.1023
0.3361	0.3349	0.772081	0.4567	0.0619	0.0207	0.802684	0.0612
0.3293	0.3281	0.772543	0.4538	0.0358	0.0120	0.802303	0.0379
x_1 2-methyl, 2-chloro propane + x_2 n-heptane + x_3 2-pentanone							
0.2497	0.7503	0.708738	0.4473	0.2453	0.2454	0.769845	0.4499
0.2291	0.6884	0.713940	0.5986	0.2250	0.2251	0.772297	0.4111
0.2219	0.6666	0.715739	0.6665	0.1969	0.1970	0.775756	0.3575
0.2111	0.6343	0.718870	0.6870	0.1640	0.1640	0.780040	0.2718
0.1951	0.5863	0.723699	0.7026	0.1226	0.1227	0.785392	0.1900
0.1889	0.5676	0.725613	0.7100	0.0959	0.096	0.788892	0.1423
0.1724	0.5181	0.730973	0.6924	0.0502	0.0502	0.794973	0.0711
0.1659	0.4984	0.733176	0.6816	0.7500	0.2501	0.785669	0.4399
0.1487	0.4467	0.739054	0.6563	0.7095	0.2366	0.786451	0.4190
0.1218	0.3660	0.748924	0.5641	0.6801	0.2268	0.787050	0.3999
0.1079	0.3243	0.754138	0.5300	0.6340	0.2114	0.787965	0.3746
0.0984	0.2958	0.757914	0.4861	0.5951	0.1984	0.788830	0.3406
0.0731	0.2198	0.768096	0.4041	0.5228	0.1743	0.790289	0.3025
0.0497	0.1492	0.778344	0.2787	0.4843	0.1615	0.791088	0.2803
0.0230	0.0691	0.790719	0.1182	0.4417	0.1473	0.792104	0.2380
0.4999	0.5001	0.738799	0.5616	0.3775	0.1259	0.793521	0.1936
0.4433	0.4435	0.748664	0.6352	0.3357	0.1119	0.794478	0.1613
0.4205	0.4206	0.750875	0.6300	0.3005	0.1002	0.795307	0.1318
0.3803	0.3804	0.754827	0.6247	0.2238	0.0746	0.796980	0.0906
0.3436	0.3437	0.758609	0.6054	0.1484	0.0495	0.798642	0.0516
0.3013	0.3014	0.763205	0.5594	0.0719	0.0240	0.800291	0.0215
0.2743	0.2744	0.766311	0.5185				

Table 5 values of parameters, B_i, of equation (5) and standard deviations, σ, for ternary systems at T=298.15 K.

B_0	B_1	B_2	B_3	B_4	σ (V^E)/(cm3mol-1)
x_1 1-chlorobutane + x_2 n-heptane+ x_3 2-pentanone					
-0.341362	-0.709507	-0.024383	2.453130	5.237071	0.0085
x_1 2-methyl, 2-chloro propane + x_2 n-heptane+ x_3 2-pentanone					
1.126279	7.918206	4.050720	-10.980100	-0.542510	0.0127

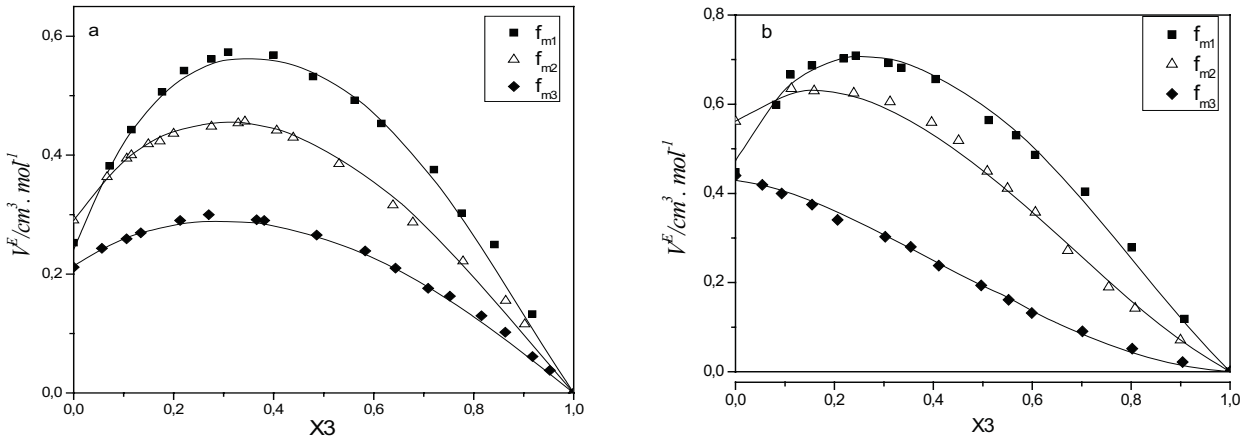

Figure 3 Excess molar volumes of the ternary mixtures at T=298.15 K

(a) x_1 1-chlorobutane + x_2 n-heptane + x_3 2-pentanone (f_{m1}=0.3327 , f_{m2}=1.0036, f_{m3}=2.9947)

(b) x_1 2-methyl, 2-chloro propane + x_2 n-heptane + x_3 2-pentanone (f_{m1}=0.3328 , f_{m2}=0.9982, f_{m3}=2.9992)

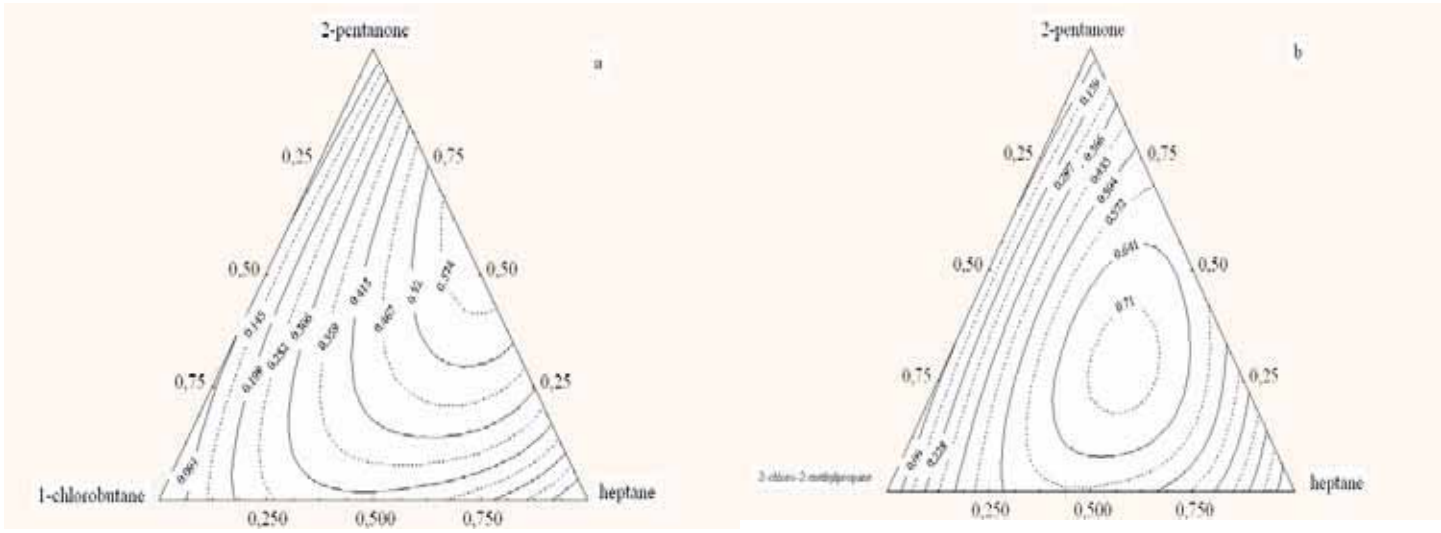

Figure 4 Isolines of V^E_{123} ($cm^3\ mol^{-1}$), for the ternary systems at T=298.15K, calculated with equation (4)

(a) x_1 1-chlorobutane + x_2 n-heptane + x_3 2-pentanone

(b) x_1 2-methyl, 2-chloro propane + x_2 n-heptane + x_3 2-pentanone

Tsao and Smith [5] model

$$V^E_{123}=\frac{1}{1-x_1}\left[x_2V^E_{12}\left(x_1',x_2'\right)+x_3V^E_{13}\left(x_1',x_3'\right)\right]+\left(1-x_1\right)V^E_{23}\left(x_2'',x_3''\right) \quad (9)$$

Component 1asymmetric $x_i'=x_1=1-x_j'$ for system 1,2 and 1,3 $x''_i = 1-x''_j = x_i/(x_i+x_j)$ for system2,3.

Toop [6] model

$$V^E_{123}=\frac{1}{1-x_1}\left[x_2V^E_{12}\left(x_1',x_2'\right)+x_3V^E_{13}\left(x_1',x_3'\right)\right]+\left(1-x_1\right)^2V^E_{23}\left(x_2'',x_3''\right) \quad (10)$$

Component 1asymmetric $x_i'=x_1=1-x_j'$ for system 1,2 and 1,3 $x''_i = 1-x''_j = x_i/(x_i+x_j)$ for system2,3.

Scatchard and al [7] model

$$V^E_{123}=\frac{1}{1-x_1}\left[x_2V^E_{12}\left(x_1',x_2'\right)+x_3V^E_{13}\left(x_1',x_3'\right)\right]+V^E_{23}\left(x_2'',x_3''\right) \quad (11)$$

Component 1asymmetric $x_i'=x_1=1-x_j'$ for system 1,2 and 1,3 $x''_i = x_2$ and $x''_j = x_3$ for system 2,3.

Standard deviations, σ, presented in table 3,5,6 , were determined by the following equation:

$$\sigma=\left[\frac{\sum_{i=1}^{N}\left(V^E_{(\exp)}-V^E_{(cal)}\right)^2}{N-p}\right]^{\frac{1}{2}} \quad (12)$$

p : the number of parameters , N : number of experimental data.

Experimental data and fit equations (3) for V^E for the five binary systems are represented in figure 1. Excess molar volumes for the binary systems formed by 1-chlorobutane with n-heptane or 2-pentanone , 2-methyl, 2-chloro propane with n-h-eptane and n-heptane with 2-pentanone, are positive. This would indicate that molecular interactions between different molecules are weaker than interactions between molecules in the same pure liquid and that repulsive forces dominate the behaviour of the solution. The negative values of the excess molar volumes for the binary system of 2-methyl, 2-chloro propane with 2-pentanone suggested the specific

intermolecular interactions between different molecules.

Table 6 Standard deviations, σ, of the experimental and predicted ternary excess molar volumes V^E at T = 298.15 K

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	σ (V^E)/ cm3mol-1)	
Empirical equation	x_1 1-chlorobutane + x_2 n-heptane + x_3 2-pentanone	x_1 2-methyl, 2-chlro propane + x_2 n-heptane+ x_3 2-pentanone
Redlich-Kister	0.0169	0.0733
Kohler	0.0131	0.0738
Colinet	0.0147	0.0711
Tsao-Smith [a]	0.0840	0.0317
Tsao-Smith [b]	0.0177	0.1100
Tsao-Smith [c]	0.0544	0.0449
Toop [a]	0.0118	0.0599
Toop [b]	0.0287	0.0942
Toop [c]	0.0147	0.0604
Scatchard [a]	0.0223	0.0792
Scatchard [b]	0.0284	0.0855
Scatchard [c]	0.0184	0.0535

[a] 1-chlorobutane or 2-methyl, 2-chlor propane is asymmetric component in equation.
[b] n-heptane is asymmetric component in equation.
[c] 2-pentanone is asymmetric component in equation.

Experimental data of V^E of the ternary system at three fixed compositions, fm , are shown in figure 3. The data included in table 4 , figure 3 and figure 4, show that the excess molar volumes for the ternary mixtures (1-chlorobutane or 2-methyl, 2-chloro propane) + n-heptane + 2-pentanone at T=298.15K are positive over the entire composition range. The positive values indicate that the interactions among (1-chlorobutane or 2-methyl, 2-chloropropane) , n-heptane , and 2-pentanone are obviously similar to those in binary ones.

The ternary mixtures with 1-chlorobutane shows maximum values at x_2=0.5566 , x_3=0.4434 , V^E_{123}=0.609 cm^3 mol^{-1}.The ternary mixtures with 2-methyl, 2-chloro propane shows maximum values at x1 =0.1889 , x_2=0.5676 , x_3=0.2435 , V^E_{123}=0.710 cm^3mol^{-1} .

Table 6 shows deviations between experimental data and predicted values. For the asymmetric equation, three different numberings of the component have been tested, in order to check the differences in the predicted values, and to find a rule to decide which ordering should be used in each case. 1-chlorobutane or 2-methyl, 2-chloro propane, n-heptane and 2-pentanone were respectively, named as 1,2,3. Then the rows a,b,c of table 6 fit to the (1-chlorobutane or 2-methyl, 2-chloro propane) + n-heptane + 2-pentanone as 123 , 231 and 312 respectively, ordered, being the first element considered in each case (1-chlorobutane or 2-methyl, 2-chlro propane) , n-heptane or 2-pentanone in order. It is worth from table 6 that best excess molar volume correlation for the three methods which use asymmetric criteria depend on the chosen asymmetric component. For the system 1-chlorobutane+ n-heptane + 2-pentanone , the toop's equation gives a better result when 1-chlorobutane is asymmetric component, but Tsao-Smith's methods gives lower deviation if 2-methyl, 2-chloro propane is the asymmetric component in the ternary system 2-methyl, 2-chloro propane + n-heptane + 2-pentanone. The best agreement with the experimental data was achieved by the symmetric equation suggested by Colinet for the ternary with 2-methyl,2-chloro propane, and by Kohler for the ternary with 1-chlorobutane.

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