Volumetric Study of the Binary Mixtures Containing a Branched Hexane and an Isomeric Chlorobutane

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Abstract: This paper reports densities at atmospheric pressure and at three temperatures T = (283.15, 298.15, and 313.15) K of eight binary mixtures involving a branched hexane (3-methylpentane or 2,2-dimethylbutane) and each one of the isomeric chlorobutanes (1-chlorobutane, 2-chlorobutane, 1-chloro-2-methylpropane or 2-chloro-2-methylpropane). Excess volumes were calculated from experimental densities and correlated with the Redlich-Kister equation. Moreover, the excess volumes were analysed using the Prigogine-Flory-Patterson theory.

Keywords: Branched hexane, Isomeric chlorobutane, Prigogine-Flory-Patterson theory, Volumetric behaviour.

1. INTRODUCTION

In previous papers we have studied the volumetric behaviour of the systems formed by a linear alkane (n-hexane or n-heptane) and a chloroalkane (1-chloropropane or isomeric chlorobutanes) at several temperatures and at atmospheric pressure or at high pressures [1-3]. In order to study the influence of the ramification of the alkane on the excess volumes we present here the densities and the corresponding excess volumes at atmospheric pressure and at three temperatures T = (283.15, 298.15, and 313.15) K of eight binary systems formed by a branched isomer of hexane (3-methylpentane or 2,2-dimethylbutane) and each one of the isomers of chlorobutane (1-chlorobutane, 2-chlorobutane, 1-chloro-2-methylpropane or 2-chloro-2-methylpropane).

Finally the Prigogine-Flory-Patterson theory [4, 5] was employed at T = 298.15 K to obtain the different contributions to excess volume.

A perusal of the literature shows that there are practically no studies on volumetric properties of these kinds of mixtures.

2. EXPERIMENTAL

The liquids used were: 3-methylpentane, 2,2-dimethylbutane, 1-chlorobutane, 2-chlorobutane and 2-chloro-2-methylpropane, (>99%) provided by Aldrich as well as 1-chloro-2-methylpropane (>99%) obtained from Fluka. The purities of these compounds were checked by chromatographic methods and no further purification was needed.

Densities, ρ, of both pure compounds and their mixtures, were determined using a vibrating tube densimeter Anton Paar DMA-5000, the temperature was controlled automatically within ± 0.001 K. The uncertainty of the density measurements after proper calibration of the densimeter is 5×10^{-6} g·cm^{-3}. The mixtures were prepared by mass using a Sartorius CP225D balance, the estimated uncertainty in the mole fraction is 10^{-4}.

The densities of the pure compounds at work temperatures properties together with density literature values at T = 298.15 K are collected in Table **1** [6-10].

3. RESULTS AND DISCUSSION

Excess volumes, V^E, were calculated from the density of the mixture, ρ, densities, ρ_i, and molar masses, M_i, of the pure compounds, and the corresponding molar fractions, x_i, by using the equation:

$$V^E = x_1 \left(\frac{M_1}{\rho} - \frac{M_1}{\rho_1} \right) + x_2 \left(\frac{M_2}{\rho} - \frac{M_2}{\rho_2} \right) \tag{1}$$

The experimental densities along with the calculated excess volumes can be found in the supplementary material. On the other hand, excess volumes are graphically represented in Figures **1-6**.

The excess volumes, V^E, were correlated with a Redlich-Kister polynomial expansion [11]:

$$Y^E = x_1 x_2 \sum_i A_i (x_1 - x_2)^i \tag{2}$$

being A_i adjustable parameters and x_i the mole fraction of component i; the number of parameters for each system has been chose in order to minimize the standard deviation. The values of these parameters

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Table 1:   Densities of the Pure Compounds at Work Temperatures and Comparison with Literature Data at $T = 298.15$ K

Compound	$T = 283.15$ K	$T = 298.15$ K		$T = 313.15$ K
	ρ^{exp} / g·cm^{-3}	ρ^{exp} / g·cm^{-3}	ρ^{lit} / g·cm^{-3}	ρ^{exp} / g·cm^{-3}
3-Methylpentane	0.673277	0.659654	0.65967 [6]	0.645693
2,2-Dimethylbutane	0.658465	0.644407	0.64450 [7]	0.629991
1-Chlorobutane	0.897339	0.880785	0.88075 [8]	0.863882
2-Chlorobutane	0.884340	0.867474	0.86752 [9]	0.850266
1-Chloro-2-methylpropane	0.888845	0.871533	0.8719 [10]	0.853902
2-Chloro-2-methylpropane	0.855249	0.837096	0.83711 [9]	0.818536

together with the standard deviations $\sigma(V^E)$ are given in Table **2**.
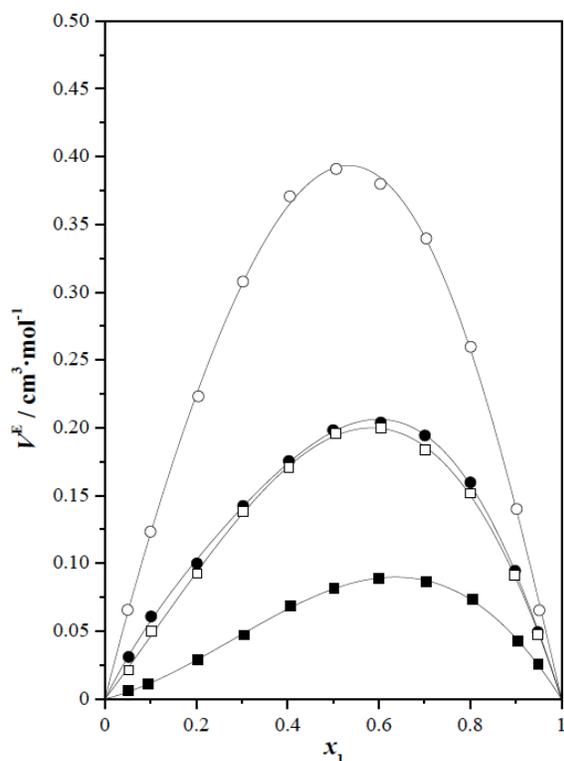
Figure 1: Excess volume, V^E, for 3-methylpentane (1) + isomeric chlorobutane (2) at $T = 283.15$ K as a function of mole fraction, x_1: 1-chlorobutane (■), 2-chlorobutane (●), 1-chloro-2-methylpropane (□), 2-chloro-2-methylpropane (○).

The mixtures containing 3-methylpentane show positive excess volumes through the complete range of compositions at the three temperatures. For a given temperature the excess volumes increase following the sequence: 1-chlorobutane < 1-chloro-2-methylpropane < 2-chlorobutane < 2-chloro-2-methylpropane, although the V^E values for 1-methyl-2-chloropropane and 2-chlorobutane are quite similar specially at $T = 283.15$ K. For the system 3-methylpentane + 2-chloro-2-

methylpropane the maximum V^E values are centered while for the rest of the isomeric chlorobutanes the maximum is shifted to the zone rich in alkane. With respect to the temperature behaviour, the excess volumes increase for the four binary mixtures in a similar way. It can be outlined that the excess volumes of the mixtures 3-methylpentane + isomeric chlorobutane and n-hexane + isomeric chlorobutane is very similar, altough the V^E values for these last mixtures are higher.
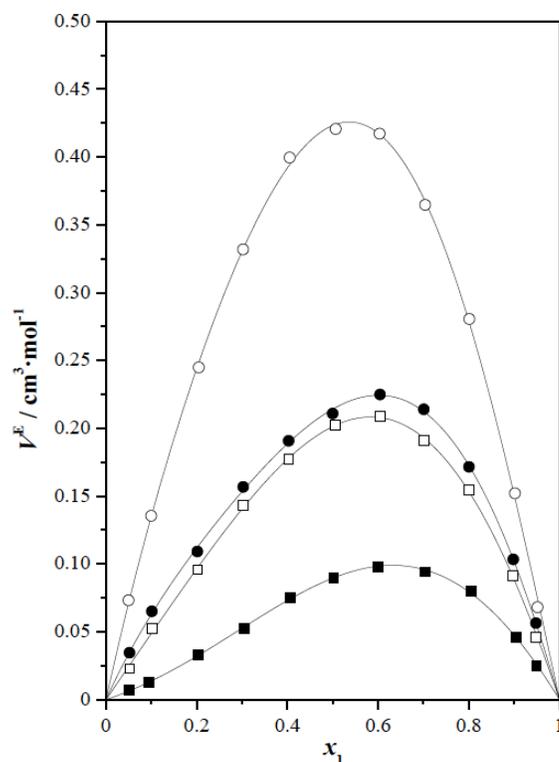
Figure 2: Excess volume, V^E, for 3-methylpentane (1) + isomeric chlorobutane (2) at $T = 298.15$ K as a function of mole fraction, x_1: 1-chlorobutane (■), 2-chlorobutane (●), 1-chloro-2-methylpropane (□), 2-chloro-2-methylpropane (○).
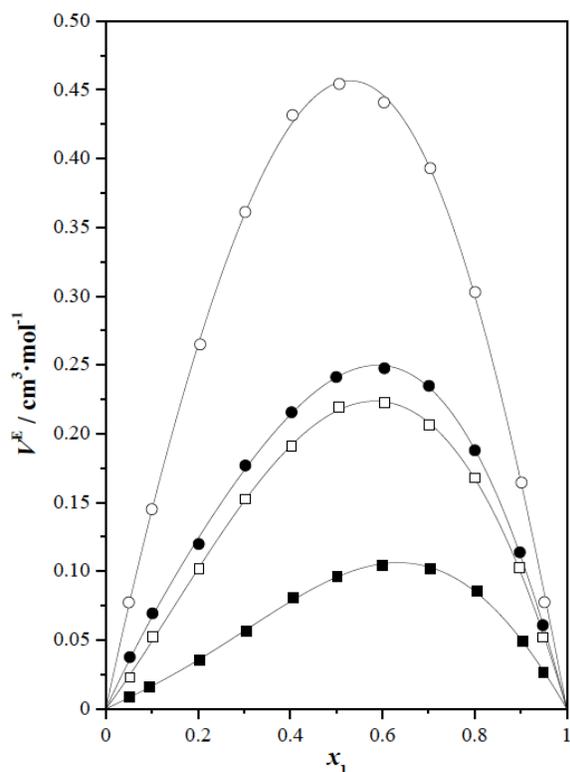
Figure 3: Excess volume, V^E, for 3-methylpentane (1) + isomeric chlorobutane (2) at T = 313.15 K as a function of mole fraction, x_1: 1-chlorobutane (■), 2-chlorobutane (●), 1-chloro-2-methylpropane (□), 2-chloro-2-methylpropane (○).
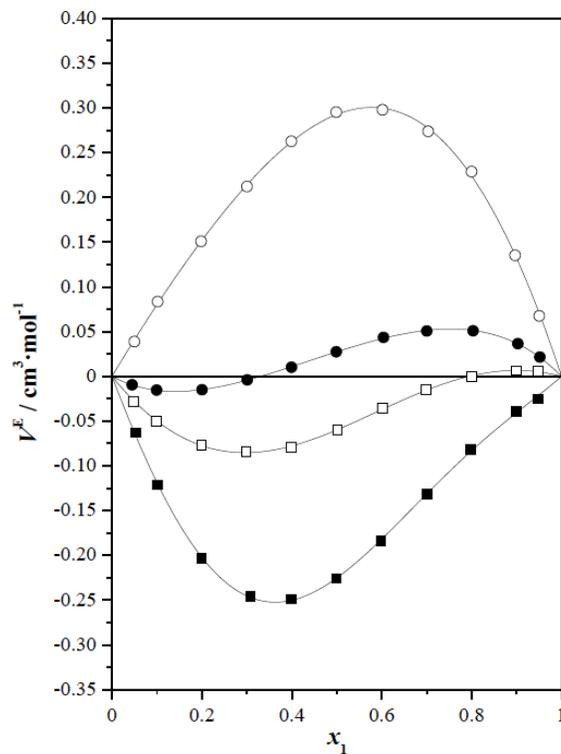
Figure 5: Excess volume, V^E, for 2,2-dimethylbutane (1) + isomeric chlorobutane (2) at T = 298.15 K as a function of mole fraction, x_1: 1-chlorobutane (■), 2-chlorobutane (●), 1-chloro-2-methylpropane (□), 2-chloro-2-methylpropane (○).
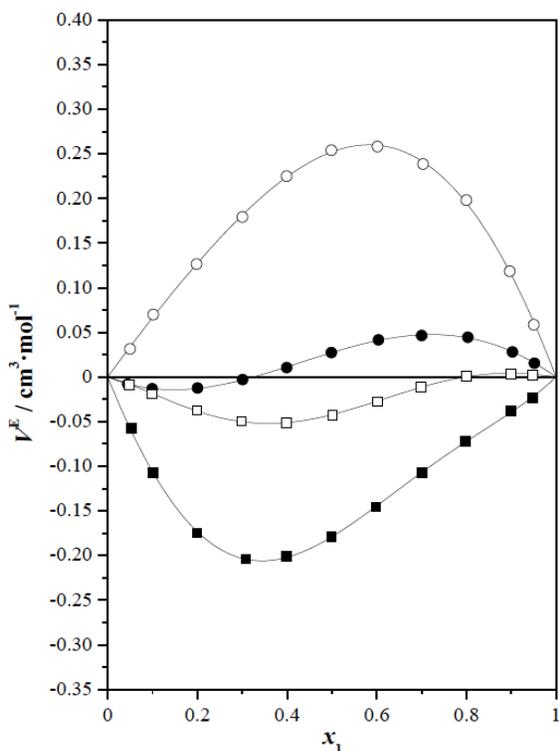
Figure 4: Excess volume, V^E, for 2,2-dimethylbutane (1) + isomeric chlorobutane (2) at T = 283.15 K as a function of mole fraction, x_1: 1-chlorobutane (■), 2-chlorobutane (●), 1-chloro-2-methylpropane (□), 2-chloro-2-methylpropane (○).
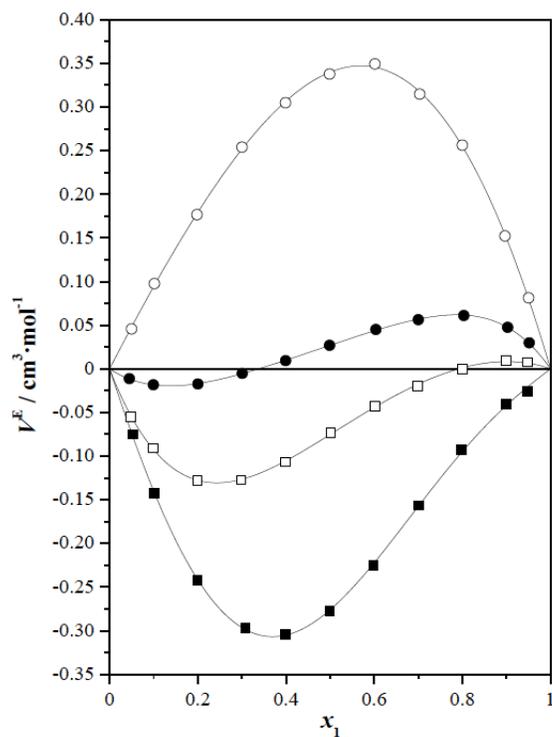
Figure 6: Excess volume, V^E, for 2,2-dimethylbutane (1) + isomeric chlorobutane (2) at T = 313.15 K as a function of mole fraction, x_1: 1-chlorobutane (■), 2-chlorobutane (●), 1-chloro-2-methylpropane (□), 2-chloro-2-methylpropane (○).

Table 2: Parameters and Standard Deviations of the Redlich Kister Equation

T / K	A_0	A_1	A_2	A_3	$\sigma(V^E)$
3-methylpentane (1) + 1-chlorobutane (2)					
283.15	0.3242	0.2396	-0.0139	-0.0152	0.0010
298.15	0.3582	0.2657	-0.0277	-0.0492	0.0011
313.15	0.3825	0.2908	-0.0123	-0.0843	0.0012
3-methylpentane (1) + 2-chlorobutane (2)					
283.15	0.7885	0.3467	0.0709	-0.1586	0.0022
298.15	0.8567	0.3798	0.0905	-0.1717	0.0023
313.15	0.9640	0.3781	0.0363	-0.1118	0.0024
3-methylpentane (1) + 1-chloro-2-methylpropane (2)					
283.15	0.7737	0.2996	-0.0373	-0.0049	0.0021
298.15	0.8052	0.3259	-0.0678	-0.0789	0.0022
313.15	0.8657	0.3388	-0.0676	0.0103	0.0021
3-methylpentane (1) + 2-chloro-2-methylpropane (2)					
283.15	1.5656	0.2383	-0.1616	-0.1702	0.0042
298.15	1.6931	0.2781	-0.1609	-0.2642	0.0044
313.15	1.8191	0.2411	-0.1475	-0.1489	0.0044
2,2-dimethylbutane (1) + 1-chlorobutane (2)					
283.15	-0.7156	0.6091	-0.1435	-0.2293	0.0017
298.15	-0.9010	0.7230	0.0266	-0.2834	0.0025
313.15	-1.1043	0.8742	0.1473	-0.3035	0.0030
2,2-dimethylbutane (1) + 2-chlorobutane (2)					
283.15	0.1097	0.3047	-0.0323	-0.0221	0.0006
298.15	0.1100	0.3210	0.0141	0.0677	0.0006
313.15	0.1080	0.3418	0.0902	0.1897	0.0007
2,2-dimethylbutane (1) + 1-chloro-2-methylpropane (2)					
283.15	-0.1686	0.2553	0.1391	-0.1522	0.0008
298.15	-0.2393	0.4243	-0.0014	-0.0488	0.0009
313.15	-0.3010	0.6307	-0.2622	0.1110	0.0014
2,2-dimethylbutane (1) + 2-chloro-2-methylpropane (2)					
283.15	1.0086	0.3717	-0.0027	-0.0568	0.0026
298.15	1.1706	0.3928	0.0115	-0.0512	0.0031
313.15	1.3597	0.4067	-0.0072	-0.0341	0.0026

The behaviour of excess volumes for the mixtures containing 2,2-dimethylbutane is a bit more complex. The system 2,2-dimethylbutane + 1-chlorobutane show negative V^E values at all temperatures studied while the mixture of 2,2-dimethylbutane with 2-methyl-2-chloropropane present positive V^E values at the three temperatures. Finally, the remaining systems show an intermediate behaviour, presenting the V^E plots a sigmoidal shape with slightly negative values a low mole fractions of 2,2-dimethylbutane and positive values in the richer alkane region. Considering a given temperature the excess volumes increase following the same sequence as in the mixtures with 3-methylpentane, that is: 1-chlorobutane < 1-chloro-2-methylpropane < 2-chlorobutane < 2-chloro-2-methylpropane, but the values are lower. On the other hand, when temperature increases the V^E values increase in absolute value, that is the positive excess volume become more positive and the negative ones become more negative.

In a general way the excess volumes are the result of different energetic and structural effects. The weakness of the dipole-dipole interactions between chloroalkane molecules when the alkane molecules are added leads to positive V^E values. On the other hand, the changes in the free volume in the mixing process and the interstitial acommodation of the components have a negative effect on excess volumes. This contribution is more notable in the case of mixtures involving 1-chlorobutane, its flexibility allows a better accommodation among the alkane molecules, while for 2-chloro-2-methylpropane the interstitial acommodation is worse and consequently the excess volumes are positive and moderately high.

4. PRIGOGINE-FLORY-PATTERSON THEORY

The Prigogine-Flory-Patterson theory considers the excess volume of a mixture as the sum of three contributions [5, 6]: the interactional contribution that is proportional to the Flory or interaction parameter, χ_{12}, the free volume contribution and the internal pressure contribution. The final expression for V^E is:

$$
\begin{aligned}
\frac{V^E}{x_1 V_1^* + x_2 V_2^*} &= \frac{\left(\tilde{V}^{1/3} - 1\right) \tilde{V}^{2/3}}{(4/3) \tilde{V}^{-1/3} - 1} \psi_1 \theta_2 \frac{\chi_{12}}{P_1^*} \\
&\quad - \frac{\left(\tilde{V}_1 - \tilde{V}_2\right)\left[(14/9)\,\tilde{V}^{-1/3} - 1\right]}{\left[(4/3)\,\tilde{V}^{-1/3} - 1\right] \tilde{V}} \psi_1 \psi_2 \\
&\quad + \frac{\left(\tilde{V}_1 - \tilde{V}_2\right)\left[(14/9)\,\tilde{V}^{-1/3} - 1\right]}{P_1^* \psi_2 + P_2^* \psi_1}\left(P_1^* - P_2^*\right)\psi_1 \psi_2
\end{aligned}
\tag{3}
$$

In this equation the reduced volume for the mixture, $\tilde{V}$, has been obtained from the reduced volumes of the pure compounds by using:

$$
\tilde{V} = \psi_1 \tilde{V}_1 + \psi_2 \tilde{V}_2 \tag{4}
$$

where the contact energy fraction, ψ_i, is defined as:

$$
\psi_1 = 1 - \psi_2 = \frac{x_1 P_1^* V_1^*}{x_1 P_1^* V_1^* + x_2 P_2^* V_2^*} \tag{5}
$$

The rest of the parameters can be obtained using Flory's theory [12, 13]. Physical properties of the pure compounds [14, 15] together with calculated Flory's parameters are given in Table **3**, the number of contact sites per segment of a molecule, s, has been calculated using the method proposed by Bondi [16].

The interaction parameter χ_{12}, for each mixture has been estimated from experimental equimolar V^E values by fitting the Prigogine-Flory-Patterson theory. The χ_{12} values are reported in Table **4** along with the calculated contributions to excess volume.

The interactional contribution to V^E is positive for all the mixtures except for the system 2,2-dimethylbutane + 1-chlorobutane, showing the existence of specific interactions between the mixed compounds. This contribution is greater when the alkane is 3-methylpentane although for the system 2,2-dimethylbutane + 2-chloro-2-methylpropane this contribution is also significative. The free volume contribution that depends mainly on the differences between the reduced volumes of the components is negative for all the mixtures although for the systems containing 2-chloro-2-methylpropane this contribution is very small due to this compound present a reduced volume very similar to the reduced volume of the alkanes. The internal pressure contribution that depends on both the differences between the reduced volumes and the internal pressures of the components is negative for the mixtures studied here except for the system 2,2-dimethylbutane + 2-chloro-2-methylpropane that present slightly positive values because the reduced volume and internal pressure of 2-chloro-2-methylpropane are closer to the values for the alkanes, specially in the case of 2,2-dimethylbutane.

Table 3:   Physical Properties and Calculated Flory Parameters of the Pure Compounds at *T* = 298.15 K

Compound	α_p / kK^{-1}	κ_T / TPa^{-1}	P^* / J·cm^{-3}	$\tilde{V}$	s / Å^{-1}
3-Methylpentane	1.3972	1725.72	391.43	1.3381	1.411
2,2-Dimethylbutane	1.4781	2015.85	423.03	1.3238	1.441
1-Chlorobutane	1.2640	1232.68	516.20	1.2994	1.424
2-Chlorobutane	1.3087	1366.07	488.52	1.3078	1.410
1-Chloro-2-methylpropane	1.3123	1341.73	499.21	1.3084	1.422
2-Chloro-2-methylpropane	1.4614	1675.35	463.65	1.3352	1.446

Table 4: Interaction Parameter, χ_{12}, and PFP Excess Volume Contributions at Equimolar Composition and at T = 298.15 K

System	V^E_{PFP} /cm^3·mol^{-1}	χ_{12} / J·cm^{-3}	ΔV_{int} / cm^3·mol^{-1}	ΔV_{fv} / cm^3·mol^{-1}	ΔV_{P^*} / cm^3·mol^{-1}
3-Methylpentane +					
1-chlorobutane	0.0894	14.17	0.3768	-0.0490	-0.2384
2-chlorobutane	0.2140	14.10	0.3942	-0.0302	-0.1501
1-chloro-2-methylpropane	0.2011	14.10	0.3911	-0.0289	-0.1611
2-chloro-2-methylpropane	0.4231	13.87	0.4344	-0.0003	-0.0111
2,2-Dimethylbutane +					
1-chlorobutane	-0.2255	-3.83	-0.0957	-0.0199	-0.1099
2-chlorobutane	0.0273	3.36	0.0881	-0.0086	-0.0523
1-chloro-2-methylpropane	-0.0600	0.22	0.0057	-0.0079	-0.0578
2-chloro-2-methylpropane	0.2925	9.34	0.2729	-0.0044	0.0239

5. CONCLUSIONS

This work presents the experimental densities of the binary mixtures containing a branched alkane (3-methylpentane or 2,2-dimethylbutane) and an isomeric chlorobutane (1-chlorobutane, 2-chlorobutane, 1-chloro-2-methylpropane or 2-chloro-2-methylpropane) over the whole composition range at three temperatures (283.15, 298.15 and 313.15 K). From these experimental data excess volumes of the mixtures were calculated and correlated using a Redlich-Kister polynomial expansion.

The mixtures containing 3-methylpentane show positive excess volumes while the excess volumes of the mixtures formed by 2,2-dimethylbutane show more complexity. Presenting positive V^E values for 1-chlorobutane and negative V^E values for 2-methyl-2-chloropropane being the excess volume behavior of the rest of the mixtures containing 2,2-dimethylbutane intermediate between these two extremes.

Finally we have used the Prigogine-Flory-Patterson theory to analyze the results. The interactional and the internal pressure are the main contributions to V^E.

ACKNOWLEDGEMENTS

SUPPLEMENTAL MATERIALS

The supplemental materials can be downloaded from the journal website along with the article.

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