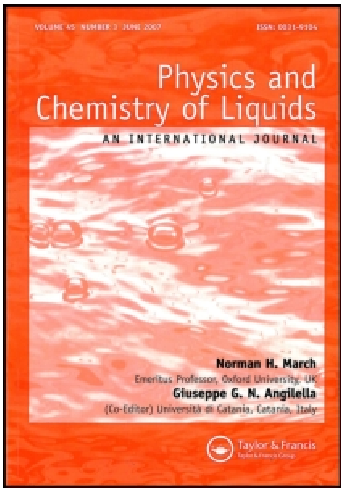

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Excess Molar Volumes of *n*-Pentanol Cumene, *n*-Pentanol 1,4-Dioxane and Cumene 1,4-Dioxane at Different Temperatures

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EXCESS MOLAR VOLUMES OF *n*-PENTANOL + CUMENE, *n*-PENTANOL + 1,4-DIOXANE AND CUMENE + 1,4-DIOXANE AT DIFFERENT TEMPERATURES

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Molar excess volumes (V^E) and partial molar excess volumes ($\bar{V}^E$) are reported for non-electrolyte binary mixtures of *n*-pentanol + cumene, *n*-pentanol + 1,4-dioxane and cumene + 1,4-dioxane at four temperatures and over the whole concentration range. In these systems, the *n*-pentanol is a highly polar molecule with association in its pure state, while the others two show little polarity without association in their pure states. The results of V^E are discussed in terms of the interactions between components. The Prigogine–Flory–Patterson model of solution thermodynamics has been used to predict V^E. This work shows the importance of the three contributions ΔV_{int}, ΔV_{P*} and ΔV_F to V^E.

KEY WORDS: Excess molar volumes, densities, *n*-pentanol + cumene, *n*-pentanol + 1,4-dioxane, cumene + 1,4-dioxane, Prigogine–Flory–Patterson theory.

1 INTRODUCTION

Molar excess volumes of binary mixtures have been extensively studied from both theoretical and experimental points of view[1,2].

This work reports the molar excess volumes (V^E) and partial molar excess volumes ($\bar{V}^E$) of three binary mixtures at 293.15 K, 298.15 K, 303.15 K and 308.15 K. These systems are *n*-pentanol + cumene; *n*-pentanol + 1,4-dioxane and cumene + 1,4-dioxane, in which *n*-pentanol is a polar molecule associated in its pure state by hydrogen bonds, and cumene and 1,4-dioxane are weak polar molecules.

Information could be obtained concerning the interactions between the mixed chemical species. The V^E data were analyzed in terms of the Prigogine–Flory–Patterson model. The analysis showed the importance of the three contributions ΔV_{int}, ΔV_{P*} and ΔV_F to V^E.

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2 EXPERIMENTAL SECTION

The methods used in our laboratory have been described previously[1,2]. Densities were determined with a digital densimeter AP, DMA 45 model. A thermostatically controlled bath (constant to ±0.01°C) was used. Calibration was carried out with air and doubly distilled water, with an error of $\pm 0.1\,\mathrm{kg\,m^{-3}}$. All weighings were made on a Mettler H315 balance. Temperatures were read from calibrated thermometers.

n-Pentanol (P) (Merck puriss.) was distilled over calcium oxide and the middle fraction were collected. Cumene (C) and 1,4-dioxane (D) (Merck, puriss.) were distilled over sodium at reduced pressure and also the middle colorless fraction were collected.

Mixtures were prepared by mixing weighted amounts of the pure liquids. Caution was taken to prevent evaporation.

3 RESULTS

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

Tables 2, 3 and 4 show the experimental values of densities of the three systems at four different temperatures.

The excess molar volumes were calculated with the following equation:

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

where x_1 and x_2 are the mole fractions of the components, M_1 and M_2 are the molecular weights of the components 1 and 2, and ρ, ρ_1 and ρ_2 are the densities of the solutions and of the pure components.

Each set of results were fitted with a Redlich–Kister equation of the type:

$$V^E = x_1(1 - x_1)\sum_{j=1}^{n} a_j(1 - 2x_1)^{j-1} \tag{2}$$

where a_j are the parameters obtained by a linear squares fitting procedure. In each case, the optimum number of coefficients was ascertained from an examination of

Table 1 Densities of the pure components.

Substance	$\rho \times 10^{-3}/\mathrm{kg\,m^{-3}}$							
	293.15 K		*298.15 K*		*303.15 K*		*308.15 K*	
	Exp.	*Lit.*	*Exp.*	*Lit.*	*Exp.*	*Lit.*	*Exp.*	*Lit.*
n-pentanol	0.8156	0.81445[a]	0.8121	0.81115[b]	0.8084	0.8073[b]	0.8047	0.8039[b]
cumene	0.8621	0.86168[a]	0.8580	0.85743[a]	0.8539	0.85323[c]	0.8497	—
1,4-dioxane	1.0346	1.03322[d]	1.0292	1.02693[d]	1.0236	1.02262[d]	1.0180	1.01635[d]

[a] Ref. (3), [b] Ref. (4), [c] Ref. (5), [d] Ref. (6).

Table 2 Experimental densities for *n*-pentanol(1) + cumene-(2) system.

x_1	$\rho \times 10^{-3}/kg\ m^{-3}$			
	293.15 K	*298.15 K*	*303.15 K*	*308.15 K*
0.1032	0.8579	0.8538	0.8496	0.8453
0.2030	0.8538	0.8497	0.8455	0.8413
0.3661	0.8468	0.8428	0.8388	0.8346
0.3993	0.8454	0.8414	0.8373	0.8332
0.4995	0.8409	0.8369	0.8329	0.8289
0.6030	0.8360	0.8321	0.8281	0.8242
0.6973	0.8314	0.8276	0.8237	0.8197
0.8010	0.8262	0.8225	0.8186	0.8147
0.8953	0.8213	0.8177	0.8139	0.8100

Table 3 Experimental densities for *n*-pentanol(1) + 1,4-dioxane(2) system.

x_1	$\rho \times 10^{-3}/kg\ m^{-3}$			
	293.15 K	*298.15 K*	*303.15 K*	*308.15 K*
0.0994	1.0061	1.0009	0.9955	0.9899
0.1985	0.9795	0.9745	0.9692	0.9639
0.2909	0.9564	0.9516	0.9466	0.9415
0.3943	0.9321	0.9275	0.9227	0.9179
0.4941	0.9101	0.9057	0.9011	0.8965
0.5906	0.8901	0.8859	0.8814	0.8770
0.6889	0.8708	0.8667	0.8624	0.8582
0.7617	0.8571	0.8531	0.8489	0.8448
0.8989	0.8325	0.8288	0.8249	0.8210

Table 4 Experimental densities for cumene (1) + 1,4-dioxane(2) system.

x_1	$\rho \times 10^{-3}/kg\ m^{-3}$			
	293.15 K	*298.15 K*	*303.15 K*	*308.15 K*
0.1003	1.0076	1.0024	0.9970	0.9916
0.2529	0.9724	0.9674	0.9624	0.9573
0.2987	0.9630	0.9581	0.9531	0.9481
0.3882	0.9460	0.9412	0.9363	0.9314
0.4505	0.9350	0.9303	0.9255	0.9207
0.6013	0.9112	0.9067	0.9021	0.8975
0.7519	0.8906	0.8862	0.8848	0.8773
0.8119	0.8831	0.8788	0.8745	0.8702
0.8952	0.8734	0.8692	0.8650	0.8607

Table 5 Coefficients of Eq. (2) and standard deviation determined by the method of least squares.

System		a_1	a_2	a_3	a_4	a_5	a_6	σ
$P(1) + C(2)$	293.15	0.573	0.037	0.14	−0.25	−0.12	0.47	0.002
	298.15	0.649	−0.001	0.158	0.152	−0.18	—	0.001
	303.15	0.690	0.010	0.32	0.30	—	—	0.005
	308.15	0.737	0.083	0.76	−0.59	−0.91	2.04	0.003
$P(1) + D(2)$	293.15	1.384	0.331	−0.18	0.23	0.39	−0.79	0.003
	298.15	1.430	0.374	0.114	−0.35	—	—	0.004
	303.15	1.499	0.320	0.19	−0.26	—	—	0.006
	308.15	1.547	0.383	0.36	−0.20	—	—	0.005
$C(1) + D(2)$	293.15	0.358	0.010	0.020	—	—	—	0.001
	298.15	0.384	0.040	0.148	−0.016	−0.22	—	0.001
	303.15	0.417	0.019	0.103	−0.23	−0.11	0.33	0.001
	308.15	0.446	0.036	0.142	−0.44	−0.152	0.63	0.007

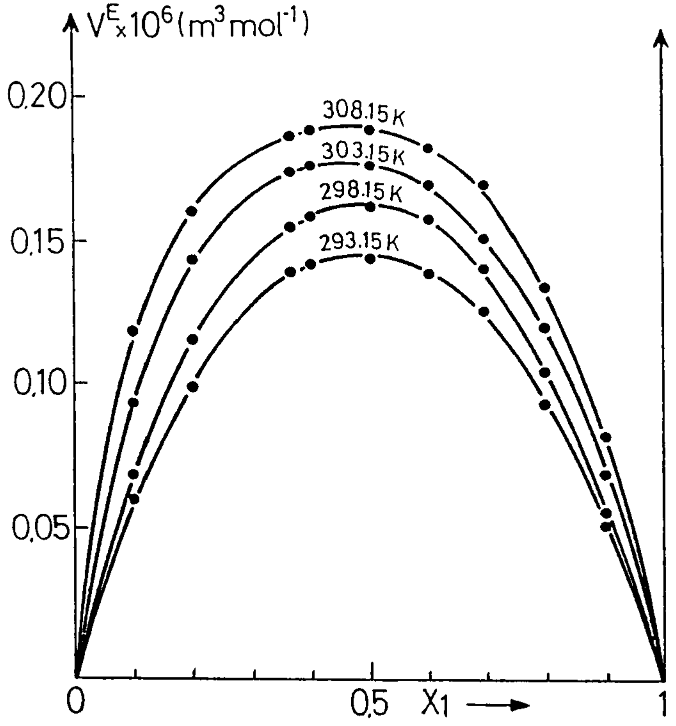

Figure 1 Excess molar volumes for *n*-pentanol (1) + cumene (2) system. Continuous curves were calculated from Eq. (2).

the variation of the standard error estimate with n, (calculated with a VAX 11/780 computer).

$$\sigma = \left[\sum (V^E_{\mathrm{obs}} - V^E_{\mathrm{cal}})^2/(n_{\mathrm{obs}} - n)\right]^{1/2} \tag{3}$$

The values adopted for the coefficients a_j and the standard error of estimates associated with the use of Eq. (3) are summarized in Table 5.

Figures 1, 2 and 3 show the experimental values of V^E as a function of the mole fraction of component 1. The continuous curves were calculated from Eq. (2) using the adopted values for the coefficients.

4 DISCUSSION

The three systems show positive values over the whole concentration range. Several effects may contribute to the values of V^E, such as the breaking of liquid order on mixing, unfavorable interactions between groups, differences in molecular volumes and differences in free volumes between liquid components[7].

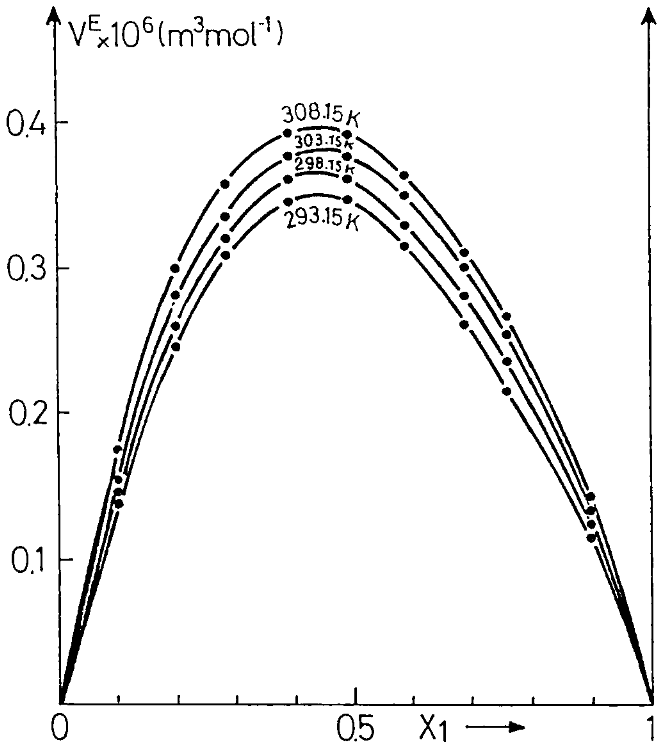

Figure 2 Excess molar volumes for *n*-pentanol (1) + 1,4-dioxane (2) system. Continuous curves were calculated from Eq. (2).

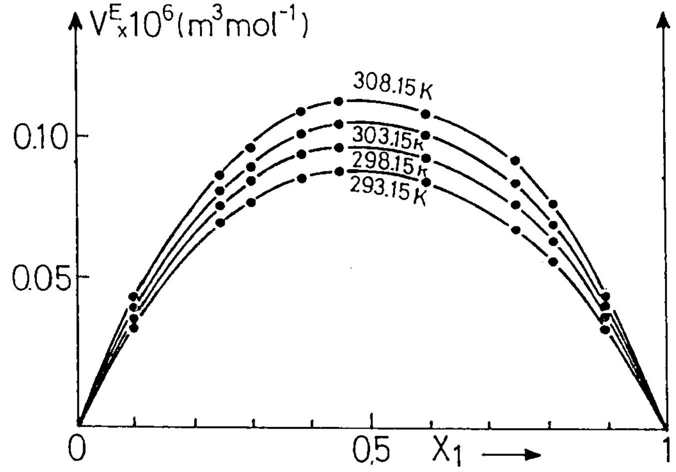

Figure 3 Excess molar volumes for cumene (1) + 1,4-dioxane (2) system. Continuous curves were calculated from Eq. (2).

The first two effects produce a positive V^E. Negative values of V^E indicate the presence of strong specific interactions between the components. *n*-Pentanol is an hydrogen-bonded associated liquid. The addition of cumene or 1,4-dioxane produces the disruption of the hydrogen bonded structure and gives rise to a positive contribution to V^E. We conclude that the primary contribution to the mixture effect for the systems reported here is the breakdown of the alcohol structure and consequently dispersion forces become dominant[8].

In the $P + D$ system, V^E is greater than in the $P + C$ system (Figures 1 and 2). For $x_1 = 0.5$ approximately, $V^E = 0.36 \times 10^{-6} m^3 mol^{-1}$ for the $P(1) + D(2)$ system and $V^E = 0.16 \times 10^{-3} m^3 mol^{-1}$ for $P(1) + C(2)$ system. This can be explained because 1,4-dioxane presents strong interaction 0–0 and has a dipole moment greater than that of cumene; then, its interactions with P molecules produces a volume expansion. In the $C(1) + D(2)$ system for $x_1 = 0.5$, the $V^E = 0.094 \times 10^{-3} m^3 mol^{-1}$ showing that the interactions between these two components are weak, due fundamentally to their different sizes and shapes.

The variation in the magnitude of V^E with increasing temperature is found to be small.

Rao and Reddy[9] showed negative V^E values for systems of ketones and 1,4-dioxane, indicating strong specific interactions and complex formation.

From a theoretical standpoint, examination of the partial derivative excess properties at infinite dilution appears to be of particular interest. At the limit of infinite dilution, solute-solute interactions disappear, thus, the values of the infinite dilution partial molar excess properties provide insight into the relationships between solute-solvent interactions and the respective thermodynamic properties, independent of composition effects.

The partial molar excess volume of a component in a binary mixtures can be determined from excess volume data, as follows:

$$\bar{V}^E = V^E + (1 - x_i)\left(\frac{\partial V^E}{\partial x_i}\right) \tag{4}$$

At the limit of infinite dilution, V^E and x_i become zero, then:

$$\bar{V}_i^{E,\infty} = \left(\frac{\partial V^E}{\partial x_i}\right)_{x_i = 0} \tag{5}$$

or the infinite dilution partial molar excess volume is the slope of the excess volume vs. mole fraction curve at infinite dilution. Thus, $\bar{V}_i^E$ can be obtained by fitting V^E vs. composition data to a curve, and obtaining the slope of the curve at $x_i = 0$.

Typically, five or six data points at mole fractions ranging from approximately 0.005 to 0.05 were used to determined $\bar{V}_i^E$. The curves obtained are linear and from the slope we obtain $\bar{V}_i^{E,\infty}$ showed in Table 6.

Figure 4 shows $\bar{V}_i^E$ at 298.15 K for the three systems. The maximum uncertainties in $\bar{V}^E$ were estimated as $\pm 0.1 \times 10^{-6}\,\mathrm{m^3\,mol^{-1}}$.

An error analysis indicates that $\bar{V}^E$ tends to be slightly less accurate for systems in which the solvent has a large molar volume or in which the densities of the two components differ greatly (such as pentanol + 1,4-dioxane). Conversely, greater accuracy in $\bar{V}^E$ is obtained when the solvent has a small molar volume and when the two components have similar densities[10].

The original Prigogine–Flory theory[11,12] includes three contributions in order to explain the thermodynamic behavior of liquid mixtures; an interactional contribution to V^E ($\Delta V^E_{\mathrm{int}}$) which is proportional to the interactional parameter X_{12}; the free volume contribution which arises from the dependence of the reduced volume upon the reduced temperature as a result of the differences between the degrees of expansion of the two components (ΔV_F), and the internal pressure contribution (ΔV_{P*}) which depends on both the differences of the characteristic pressures and the reduced volumes of the components.

Some new effects not treated by this theory have been discussed for the case of mixtures of molecules of different shapes[13,14].

Table 6 Partial molar excess volumes at infinite dilution at 298.15 K.

System	$\bar{V}_1^{E,\infty} \times 10^6$ $(m^3\,mol^{-1})$	$\bar{V}_2^{E,\infty} \times 10^6$ $(m^3\,mol^{-1})$
$P(1) + C(2)$	0.72	0.53
$P(1) + D(2)$	1.53	1.36
$C(1) + D(2)$	0.33	0.35

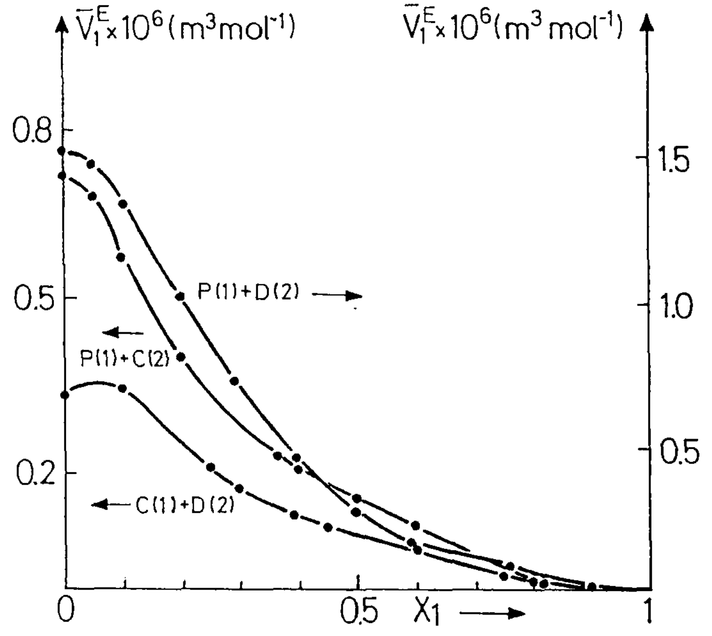

Figure 4 Partial molar excess volumes for component (1) at 298.15 K.

The equation is:

$$\frac{V^E}{x_1 V_1^* + x_2 V_2^*} = \frac{(\tilde{V}^{1/3} - 1)\tilde{V}^{2/3}}{\frac{4}{3}\tilde{V}^{-1/3} - 1}\,\psi_1\theta_2\,\frac{X_{12}}{P_1^*} - \frac{(\tilde{V}_1 - \tilde{V}_2)(\frac{14}{9}\tilde{V}^{-1/3} - 1)}{(\frac{4}{3}\tilde{V}^{-1/3} - 1)\tilde{V}}\,\psi_1\psi_2$$

$$+ \frac{(\tilde{V}_1 - \tilde{V}_2)(P_1^* - P_2^*)}{P_1^*\psi_2 - P_2^*\psi_1}\,\psi_1\psi_2 = \Delta V_{\text{int}} + \Delta V_F + \Delta V_{P*} \qquad (6)$$

The various parameters involved in Eq. (6) for the pure components (with subscript) and the mixture (without subscript) are obtained through the Flory's theory[15] and showed in Table 7.

Table 7 Values of thermal expansion coefficients, isothermal compressibilities, characteristics and reduces parameters for pure liquids at 298.15 K.

Substance	$\alpha \times 10^4$ (κ^{-1})	$\kappa_T \times 10^7$ (kPa^{-1})	$V \times 10^6$ $(m^3\ mol^{-1})$	$\tilde{V}_i$	$\tilde{T}_i$	$V_i^* \times 10^6$ $(m^3\ mol^{-1})$	$P_i^* \times 10^{-6}$ $(J\ m^{-3})$	T_i^* (K)
n-pentanol	9.05[a]	8.84[a]	108.075	1.2279	0.05387	88.016	460	5535
cumene	9.86[b]	8.93[a]	139.411	1.2449	0.05656	111.983	510	5271
1,4-dioxane	11.15[a]	7.38[a]	85.158	1.2708	0.06042	67.010	728	4935

[a] Ref. (3);

[b] Obtained from densities values.

Table 8 Experimental and theoretical molar excess volumes, Eq. (6) at 298.15 K.

System	X_{12} $(J\,m^{-3})$	ΔV_{int}	ΔV_F	ΔV_{P^*}	$V^E_{\text{exp}} \times 10^6$ $(m^3\,mol^{-1})$	$V^E_{\text{cal}} \times 10^6$ $(m^3\,mol^{-1})$
$P(1) + C(2)$	7.92	1.35×10^{-3}	1.05×10^{-4}	4.29×10^{-4}	0.161	0.168
$P(1) + D(2)$	3.06	4.92×10^{-4}	6.81×10^{-4}	4.89×10^{-3}	0.360	0.365
$C(1) + D(2)$	−5.19	-8.63×10^{-4}	2.44×10^{-4}	2.20×10^{-3}	0.094	0.097

The interactional contribution to V^E contains the interaction parameter X_{12}, which is usually calculated using experimental values of the excess enthalpy H^E. As there are no values for H^E for these systems, X_{12} values were derived by fitting the theory to experimental values of V^E of each one of the three systems at 298.15 K. Table 8 gives the calculated equimolecular values of the three contributions to V^E, according to Eq. (6) together with X_{12} values and the experimental and calculated V^E values.

An analysis of each of the three contributions to V^E shows that the interactional contributions are negative in the $C + D$ system and positive in the other two, increasing from $P + D$ to $P + C$. The internal pressure contribution V_{P^*} is positive and higher in the $P + D$ and $C + D$. The term which arises from the dependence of the reduced volume and the degrees of expansion is higher in the $P + D$ system. We

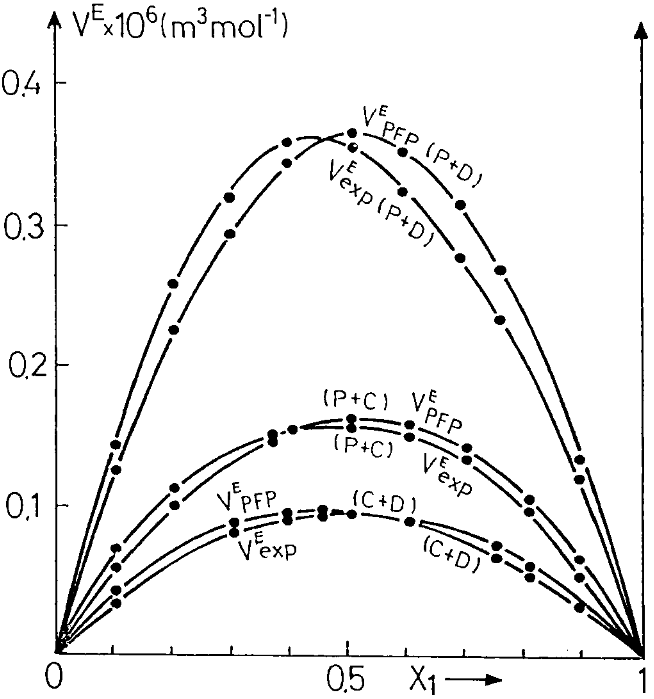

Figure 5 Experimental and theoretical excess molar volumes at 298.15 K.

conclude that when *D* substitute *C* in the mixture with *P*, the interactional term decreases but both other terms increase and they together produce an expansion in volume and a higher V^E.

The total theoretical V^E values for $x_1 = 0.5$ are found to be in excellent agreement with the experimental ones (Table 8).

Figure 5 shows at 298.15 K a comparison of theoretical and experimental V^E values throughout the composition range. It may be observed that the theory reproduces the main features of the experimental data, although quantitative agreement is not achieved in all mixtures. This is not surprising considering that the PFP theory does not take into account all the possible interactions which give values different to the observed ones.

The acontributions values are in general small, compared with for example ethylbenzene + hydrocarbons mixtures[16].

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