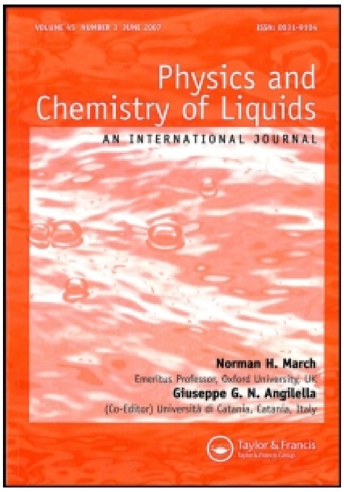

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THERMODYNAMICS OF THE BINARY MIXTURES OF 2-HEPTANONE WITH AN *n*-ALKANOL AT 298.15 K

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Excess molar enthalpies H_m^E at 298.15 K and atmospheric pressure for the five binary mixtures of 2-heptanone with *n*-propanol, *n*-pentanol, *n*-hexanol, *n*-heptanol and *n*-octanol have been obtained over the whole mole fraction range using a Calvet microcalorimeter. In addition, a vibrating-tube digital densimeter was used to determine the excess molar volumes V_m^E at the same temperature and pressure for the four different binary mixtures of 2-heptanone with *n*-propanol, *n*-hexanol, *n*-heptanol and *n*-octanol. The results show that all the systems are endothermic; H_m^E values increase with the number of carbons of the alkanol. The excess molar volumes are sigmoid for *n*-propanol and increasingly positive for the large alkanols. Two methods of correlating the results with a variable-degree polynomial are examined. The experimental results are compared with the predictions of Prigogine– Flory–Patterson theory.

KEY WORDS: Excess molar enthalpies and molar volumes, Calvet microcalorimeter, Prigogine–Flory–Patterson theory.

INTRODUCTION

We have recently reported a study[1] on the excess properties of binary mixtures of 2-pentanone with *n*-alkanols. We compared the experimental results with the predictions of the Nitta–Chao group-contribution model[2,4] finding a 15 per cent discrepancy between predicted and experimental H_m^E values. Quantitative interpretation of the observed excess volumes was not possible.

As a continuation of our research[1,5] in this type of mixtures and as part of our effort to explain the results in terms of the contribution of the interaction and in order to establish a basis for the evaluation of liquid models, we have microcalorimetricaly measured the excess molar enthalpies of 2-heptanone and *n*-propanol, *n*-pentanol, *n*-hexanol, *n*-heptanol and *n*-octanol at 298.15 K and atmospheric pressure and in the same conditions, by densitometry, the excess molar volumes of 2-heptanone with *n*-propanol, *n*-hexanol, *n*-heptanol and *n*-octanol.

To allow a comprehensive study of the behaviour of this type of mixtures our results have been supplemented with those other researchers.[6–16]

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The Prigogine–Flory–Patterson theory of liquid mixtures has been applied to mixtures that were studied experimentaly. The theory was initially derived in order to explain the thermodymamic properties of normal parafin hydrocarbon mixtures[17] and was subsequently extended to encompass systems of non-polar molecules differing in size and shape[18]. Recently, it has been applied to the study of alkanols mixtures[19]. The theory is based in the work by Flory and coworkers[17–21] who developed a model which relates thermodynamic excess properties of liquid mixtures to measurable macroscopic properties of the pure components. An improvement to this theory, the Prigogine–Flory theory, considers the excess thermodynamic properties of binary mixtures to be the sum of three contributions[22–24]: a combinatorial term, an interactional term arising from the difference in chemical nature of the two components, and a free volume contribution. The approximate equations given by Patterson and his coworkers[22–24] led to the separation of these contributions. The excess molar volume can be expressed as: an interactional term, proportional to the Flory χ_{12} parameter, a curvature term, originating from a difference in the two components and a free volume contribution, arising from the differences in the internal pressures and reduced volumes of components. The approximate form of their excess molar enthalpy equation is divided into a free volume and an interactional contribution.

EXPERIMENTAL

The sources and mole-fraction purities of the substances employed were: 2-heptanone (Aldrich, >98%), *n*-propanol (Aldrich, >99.9%), *n*-pentanol (Aldrich, >99%), *n*-hexanol (Fluka, >99.5%), *n*-heptanol (Fluka, >99.5%) and *n*-octanol (Fluka, >99.5%). Prior to measurements all the liquids were degassed and stored over 4A molecular sieves (Union Carbide) to remove any traces of water.

Mixtures were prepared by mass. The uncertainties in the mole fractions were estimated to be less than 1.10^{-4}. The conversion to molar quantities was based on the relative mass table of 1985 issued by IUPAC[25].

The experimental H_m^E determination was carried out using a Calvet microcalorimeter. Details of the experimental technique, auxiliary equipment, calibrations and the procedure for calculating the excess molar enthalpies have been described previously[26–27]. The precision in excess molar enthalpies is estimated to be better than $10^{-2} \cdot H_m^E$.

Excess molar volumes V_m^E were calculated from the densities of the pure liquids and mixtures with an Anton–Paar Model DMA 60/602 densimeter. The temperature of the fluid in the density cell was maintained constant to within ±0.01 K (Heto, type 04 PT 623 circulating thermostat) and was measured with a precision digital thermometer (Anton Paar DT 100-30). Before each series of measurements, the densimeter was calibrated with doubly distilled and degassed water[28] (0.9970429 g.cm^{-3} at 298.15 K) and air[29].

RESULTS

Experimental densities of the pure liquids at 298.15 K were: 2-heptanone (0.81096 g.cm^{-3}), *n*-propanol (0.79981 g.cm^{-3}), *n*-pentanol (0.81102 g.cm^{-3}), *n*-hexanol (0.81509 g.cm^{-3}), *n*-heptanol (0.81885 g.cm^{-3}) and *n*-octanol (0.82167 g.cm^{-3}) in agreement with the literature[30–32].

The experimental results are reported in Tables 1 and 2. A smoothing function of the form:

$$Y_m^E = x(1-x)\sum_{i=1}^{k} A_i(2x-1)^{i-1} \tag{1}$$

where x is the mole fraction of the 2-heptanone, and either $Y_m^E = H_m^E/(\mathrm{J.mol^{-1}})$ or $Y_m^E = V_m^E/(\mathrm{cm^3.mol^{-1}})$, was fitted to the results using the (unweighted) least squares method. The parameter A_1 and the standard deviations s of the fit are listed in Table 3. The number of parameters was determined in each case using an *F*-test[33].

Table 1 Experimental excess molar enthalpies H_m^E for the binary systems: x 2-heptanone + $(1-x)$ *n*-alkanol at 298.15 K

x	H_m^E/J·mol^{-1}	x	H_m^E/J·mol^{-1}	x	H_m^E/J·mol^{-1}	x	H_m^E/J·mol^{-1}
			x 2-heptanone + $(1-x)$ *n*-propanol				
0.0343	172	0.2012	818	0.5480	1262	0.7937	924
0.0638	310	0.2943	1043	0.5563	1259	0.8827	633
0.1099	506	0.3456	1119	0.6112	1230		
0.1532	649	0.4068	1210	0.7469	1028		
			x 2-heptanone + $(1-x)$ *n*-pentanol				
0.0466	256	0.3096	1111	0.5167	1343	0.7618	1031
0.1445	633	0.3796	1258	0.5550	1323	0.8415	791
0.2093	903	0.4312	1316	0.6247	1289	0.9199	450
0.2904	1130	0.4896	1317	0.6791	1216		
			x 2-heptanone + $(1-x)$ *n*-hexanol				
0.0950	505	0.4017	1315	0.7485	1104	0.9498	260
0.2004	904	0.4959	1386	0.7877	996		
0.2716	1107	0.5903	1358	0.8281	859		
0.3505	1267	0.6771	1258	0.8997	558		
			x 2-heptanone + $(1-x)$ *n*-heptanol				
0.1101	574	0.3788	1336	0.5252	1441	0.7188	1228
0.1900	898	0.4052	1371	0.5657	1426	0.7984	1014
0.2993	1162	0.4892	1406	0.6304	1371	0.8941	616
			x 2-heptanone + $(1-x)$ *n*-octanol				
0.0980	544	0.3844	1401	0.5333	1506	0.7014	1313
0.1856	909	0.4517	1478	0.5617	1477	0.8119	994
0.2809	1199	0.4877	1486	0.5852	1470	0.8944	637

Table 2 Experimental excess molar volumes V_m^E for the binary systems: x 2-heptanone + $(1-x)$ *n*-alkanol at 298.15 K

x	V_m^E / $\mathrm{cm^3 \cdot mol^{-1}}$	x	V_m^E / $\mathrm{cm^3 \cdot mol^{-1}}$	x	V_m^E / $\mathrm{cm^3 \cdot mol^{-1}}$	x	V_m^E / $\mathrm{cm^3 \cdot mol^{-1}}$
			2-heptanone + $(1-x)$ *n*-propanol				
0.0553	−0.0027	0.3541	0.0122	0.6520	0.0319	0.9053	0.0217
0.1380	−0.0018	0.4266	0.0170	0.6992	0.0327		
0.2110	0.0014	0.5011	0.0230	0.7934	0.0298		
0.2816	0.0072	0.5678	0.0263	0.8276	0.0295		
			2-heptanone + $(1-x)$ *n*-hexanol				
0.0310	0.0010	0.2377	0.0150	0.5181	0.0149	0.7688	0.0105
0.0598	0.0038	0.3212	0.0155	0.5842	0.0136	0.8678	0.0074
0.1237	0.0101	0.3867	0.0158	0.6428	0.0128	0.9427	0.0021
0.1880	0.0138	0.4417	0.0157	0.6966	0.0124		
			2-heptanone + $(1-x)$ *n*-heptanol				
0.0488	0.0155	0.2818	0.0343	0.5504	0.0254	0.8280	0.0123
0.0714	0.0213	0.3477	0.0331	0.6217	0.0239	0.8952	0.0069
0.1424	0.0292	0.4212	0.0303	0.6846	0.0195	0.9616	0.0025
0.2046	0.0324	0.4736	0.0283	0.7561	0.0171		
			2-heptanone + $(1-x)$ *n*-octanol				
0.0289	0.0124	0.2724	0.0506	0.5522	0.0485	0.8286	0.0249
0.0782	0.0249	0.3661	0.0542	0.6246	0.0448	0.8959	0.0154
0.1497	0.0355	0.4225	0.0545	0.6868	0.0394	0.9628	0.0045
0.2251	0.0449	0.4842	0.0522	0.7649	0.0321		

Table 3 Parameters A_i and standard deviations s for least-squares fits of Equation 1 to $H_m^E/(\mathrm{J \cdot mol^{-1}})$ and $V_m^E/(\mathrm{cm^3 \cdot} mol^{-1})$ at 298.15 K

2-heptanone +	A_1	A_2	A_3	A_4	S
n-propanol					
H_m^E	5036	371	917	401	7
V_m^E	0.0913	0.1348	0.0241	0.0570	0.0008
n-pentanol					
H_m^E	5356	352	615		19
n-hexanol					
H_m^E	5556	244	659		15
V_m^E	0.0612	−0.0210	0.0236		0.0010
n-heptanol					
H_m^E	5710	462	828		13
V_m^E	0.1102	−0.675	0.1043	−0.0929	0.0007
n-octanol					
H_m^E	5977	397	737		6
V_m^E	0.2066	−0.0833	0.0495		0.0014

Table 4 Parameters C_{ij} and standard deviations s for correlation of $H^E_m/(\mathrm{J\cdot mol^{-1}})$ and $V^E_m/(\mathrm{cm^3\cdot mol^{-1}})$ at 298.15 K with Equation 2

	$\frac{H^E_m}{\mathrm{J\cdot mol^{-1}}}$	$\frac{V^E_m}{\mathrm{cm^3\cdot mol^{-1}}}$		$\frac{H^E_m}{\mathrm{J\cdot mol^{-1}}}$	$\frac{V^E_m}{\mathrm{cm^3\cdot mol^{-1}}}$
C_{11}	−4730.7	0.42888	C_{23}	−24.17	0.00722
C_{12}	−74.14	−0.16298	C_{31}	−1518.1	−0.02285
C_{13}	−10.01	0.01687	C_{32}	300.4	0.01599
C_{21}	−1124.8	0.47849	C_{33}	−26.30	−0.00056
C_{22}	279.0	−0.12936	s	14	0.0021

In view of the dependence of H^E_m and V^E_m on the length of the *n*-alkanol, we have also used another correlation method[34] to analyse the experimental results. Assuming quadratic dependence on N, the number of carbons atoms in the *n*-alkanol molecule, and assigning equal weights to all the experimental points, we fitted the results with the expression:

$$Y^E_m/(N) = x(1-x)\sum_{i=1}^{p}\sum_{j=1}^{3} C_{ij}N^{j-1}(2x-1)^{i-1} \tag{2}$$

The values of the parameters C_{ij} and the standard deviations s of the fit are listed in Table 4.

APPLICATION OF THE PRIGOGINE–FLORY–PATTERSON THEORY

Theoretical excess molar enthalpies were calculated from expression,

$$H^E_m = H^E_{\mathrm{int}} + H^E_{\mathrm{fv}} \tag{3}$$

where H^E_{int} is the interactional contribution and is expressed as,

$$H^E_{\mathrm{int}}/[x_1U^*_1 + x_2U^*_2] = [\chi_{12}\theta_2\psi_1/P^*_1][-\tilde{U}(\tilde{T}_U) + \tilde{T}_U\tilde{C}_P(\tilde{T}_U)] \tag{4}$$

and H^E_{fv} represents the free volume contribution,

$$H^E_{\mathrm{fv}}/[x_1U^*_1 + x_2U^*_2] = \tilde{C}_P(\tilde{T}_U)[\psi_1\tilde{T}_1 + \psi_2\tilde{T}_2 - \tilde{T}_U] \tag{5}$$

Here the quantities with tilde for the pure components and the solutions are the reduced configurational energy $\tilde{U}$, heat capacity $\tilde{C}_p$ and temperature $\tilde{T}$. They are related by the Flory model[35] to the reduced volume $\tilde{V}$ and the macroscopic thermal expansion coefficient α of the pure component or solution through:

$$\begin{aligned} \tilde{U} &= -\tilde{V}^{-1}; \qquad \tilde{C}_P^{-1} = \tfrac{4}{3}\tilde{V}^{-1/3} - 1 \\ \tilde{T} &= (\tilde{V}^{1/3} - 1)/\tilde{V}^{4/3}; \qquad \tilde{V}^{1/3} - 1 = \alpha T/3(1 + \alpha T) \end{aligned} \tag{6}$$

Table 5 Parameters for the pure components at 298.15 K of Equation 7

Liquid	$\frac{V}{\text{cm}^3\cdot\text{mol}^{-1}}$	$\frac{V^*}{\text{cm}^3\cdot\text{mol}^{-1}}$	$\frac{p^*}{\text{J}\cdot\text{cm}^{-3}}$
2-heptanone	140.83[a]	111.67[c]	528[d]
n-propanol	75.14[a]	60.18[b]	455[b]
n-pentanol	108.70[a]	88.52[b]	460[b]
n-hexanol	125.35[a]	102.57[b]	475[b]
n-heptanol	141.91[a]	116.45[e]	486[d]
n-octanol	158.50[a]	130.87[b]	473[b]

[a] from our experimental data.

[b] from α and K_t data found in the literature (Ref. 30).

[c] α was obtained by the authors by determining densities as a function of temperature.

[d] K_t was estimated by the Lydersen method (Ref. 36).

[e] α was obtained from the relationship between densities and temperature (Ref. 37).

The starred reduction parameters of the components or solutions are obtained through the relationships of the Flory model

$$P^* = (\alpha/K_t)T\tilde{V}^2; \qquad V^* = V\tilde{V}^{-1}; \qquad U^* = P^*V^* \tag{7}$$

where γ is the thermal pressure coefficient and V the molar volume. Values of these parameters and the methods used for its calculation for the pure liquids at 298.15 K are shown in Table 5.

The composition variables, related to the mole fractions x, were

$$\begin{aligned} \psi_1 &= 1 - \psi_2 = x_1U_1^*/(x_1U_1^* + x_2U_2^*) \\ \theta_1 &= 1 - \theta_2 = x_1V_1^*s_1/(x_1V_1^*s_1 + x_2V_2^*s_2) \end{aligned} \tag{8}$$

The ratio s_1/s_2 of the surface contact sites per segment has been calculated following the approximation of Abe and Flory[20],

$$s_1/s_2 = (V_2^*/V_1^*)^{1/3} \tag{9}$$

Theoretical excess molar volumes were calculated from the expression,

$$V_m^E = V_{\text{int}}^E + V_{\text{cur}}^E + V_{\text{fv}}^E \tag{10}$$

where the interactional term, V_{int}^E, is expressed as,

$$V_{\text{int}}^E/(x_1V_1^* + x_2V_2^*) = (\tilde{V}^{1/3} - 1)\tilde{V}^{2/3}\psi_1\theta_2\chi_{12}/\tfrac{4}{3}\tilde{V}^{-1/3} - 1)P_1^* \tag{11}$$

the curvature term, V_{cur}^E, is expressed as,

$$V_{\text{cur}}^E/(x_1V_1^* + x_2V_2^*) = (\tilde{V}_1 - \tilde{V}_2)^2(\tfrac{14}{9}\tilde{V}^{-1/3} - 1)\psi_1\psi_2/(\tfrac{4}{3}\tilde{V}^{-1/3} - 1)\tilde{V} \tag{12}$$

Table 6 Predicted values of H_m^E and V_m^E at $x_1 = 0.5$ and 298.15 K determined with Prigogine–Flory–Patterson theory

System	X_{12}	H^E_{cal}	H^E_{int}	H^E_{fv}	V^E_{cal}	V^E_{int}	V^E_{cur}	V^E_{fv}
	J·cm^{-3}	J·mol^{-1}			cm^3·mol^{-1}			
2-heptanone +								
n-propanol	54.27	1259	1260	−1	1.034	1.003	−0.004	0.036
n-pentanol	50.17	1339	1345	−6	1.091	1.019	−0.040	0.112
n-hexanol	49.61	1389	1389	−9	1.072	1.022	−0.060	0.110
n-heptanol	49.00	1428	1440	−12	1.047	1.023	−0.077	0.100
n-octanol	49.62	1494	1511	−17	1.114	1.061	−0.113	0.166

and the free volume contribution as,

$$V^E_{\mathrm{fv}}/(x_1V_1^* + x_2V_2^*) = (\tilde{V}_1 - \tilde{V}_2)(P_1^* - P_2^*)\psi_1\psi_2/(P_2^*\psi_1 + P_1^*\psi_2) \tag{13}$$

The results obtained from the application of the model to H_m^E and V_m^E data is given in Table 6.

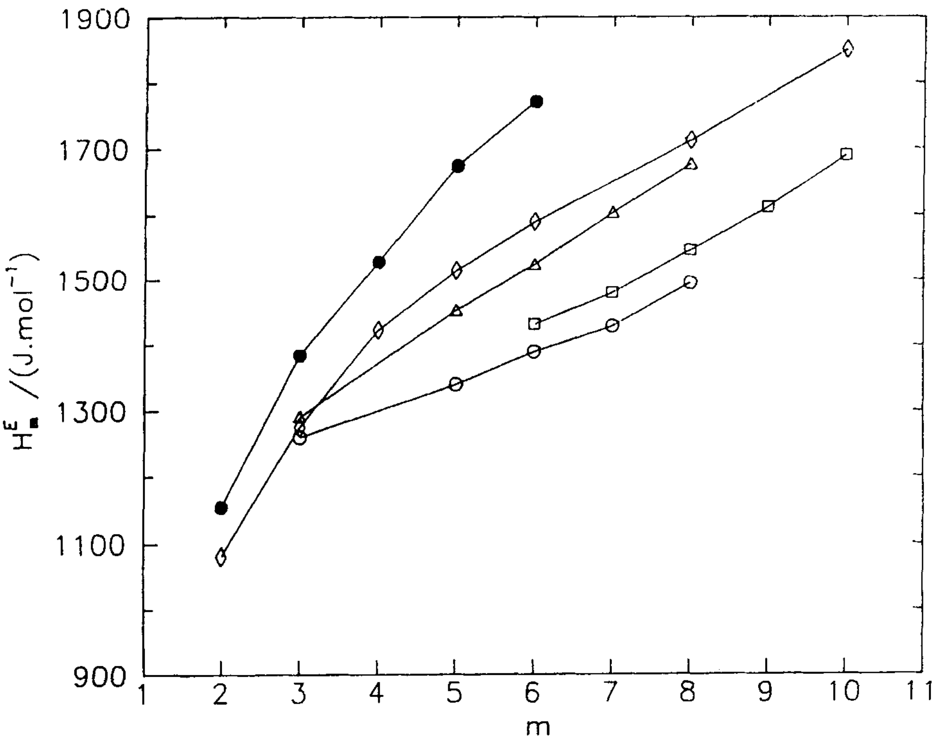

Figure 1 Excess molar enthalpies for 2-ketone + *n*-alkanols at 298.15 K and molar fraction $x = 0.5$ with respect to m, the number of carbons in the *n*-alkanol: (●) $m = 3$, (◇) $m = 4$, (△) $m = 5$, (□) $m = 6$, (○) $m = 7$.

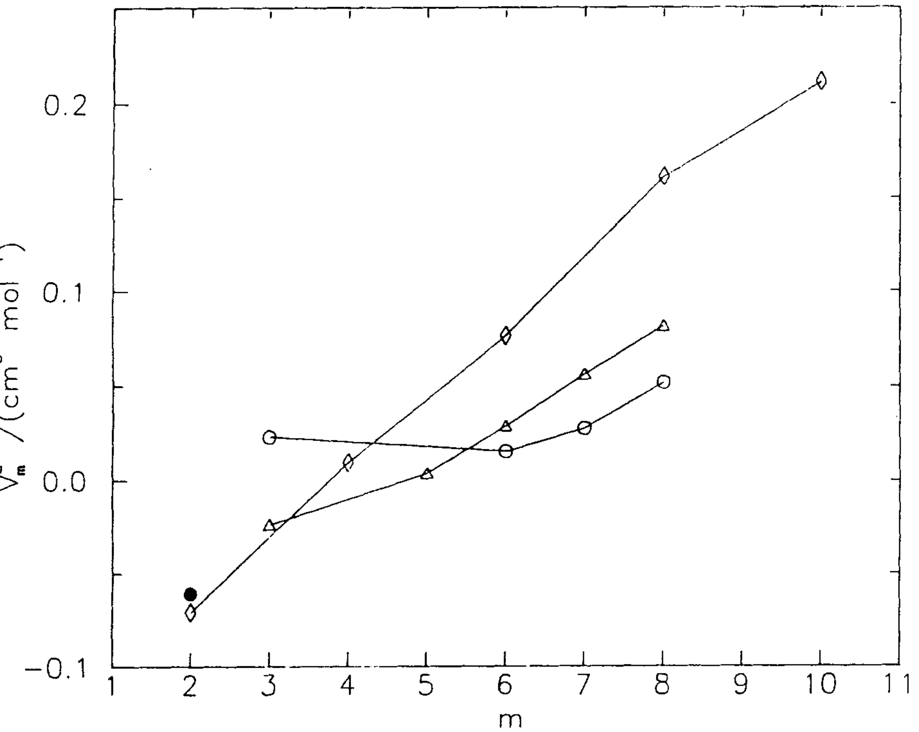

Figure 2 Excess molar volumes for 2-ketone + n-alkanols at 298.15 K and molar fractions $x = 0.5$ with respect to m, the number of carbons in the n-alkanol: (●) $m = 3$, (◇) $m = 4$, (△) $m = 5$, (○) $m = 7$.

DISCUSSION

The analysis of the experimental values of H_m^E leads to highlighting some facts: The excess molar enthalpies are positive over the entire composition range. Two opposite effects exist in this type of mixtures, a positive one due to the rupture of alkanol–alkanol hydrogen bonds and ketone–ketone dipole interactions and to physical interactions among equal molecules; and a negative one corresponding to the formation of $\mathrm{O{-}H \cdots O{=}C}$ hydrogen-bonded complexes. The net values show that the positive contribution must vastly outweigh the negative one.

Figures 1 and 2 show H_m^E and V_m^E values for different ketone–alkanol systems. For a given alkanol, the excess molar enthalpy decreases as the aliphatic chain length of the ketone increases. One possible explanation can be the effect of chain length on the polarity of the C=O group; dipole moments[38] show that, the longer the chain of the ketone, the weaker the polarity of C=O, and thus the weaker the corresponding dipole–dipole interaction. Moreover, increasing the ketone chain length reduces the concentration of C=O, which must likewise weaken their interactions (as evidenced by Meyer and Wagner's[39] results on the cohesion energy of ketones). Both effects make likely that the negative alkanol–ketone interactions become relatively more important as ketone chain length increases.

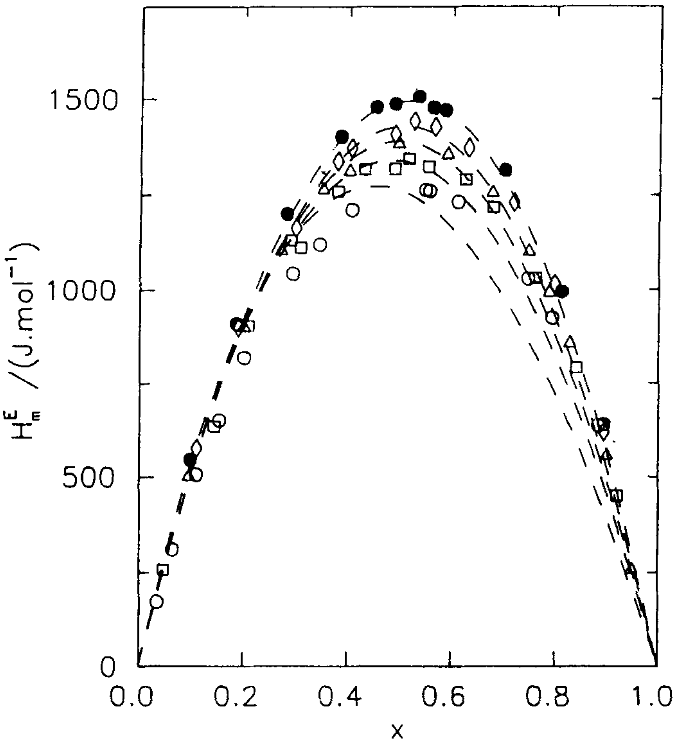

Figure 3 Excess molar enthalpies at 298.15 K of 2-heptanone + *n*-alkanols: (○) *n*-propanol, (□) *n*-pentanol, (△) *n*-hexanol, (◇) *n*-heptanol and (●) *n*-octanol; -----, predictions of the Progogine–Flory–Patterson theory.

For a given ketone H^E_m increase with the length of the alkanol chain. This implies that the breaking of the alkanol–alkanol bonds predominates over the formation of O—H···O=C bonds (though both effects decrease with increasing alkanol chain length).

The excess molar volumes are sigmoid for the *n*-propanol and increasingly positive for the larger alkanols. This can be explained in terms of the ease with which the alkanol chains fit into the volume left vacant by the ketone molecules: this ease of insertion increases as the length of the ketone chain increases, and decreases as the length of the alkanol chain increases. Published results[1,6–16] agree with this observation.

The predictions of H^E_m using the Prigogine–Flory–Patterson theory are excellent for the mixtures studied, as showed in Figure 3 (dashed lines). This can be seen by considering the results in Table 6. In all cases, the dominant term is the interactional term. The free volume contribution is negative in all mixtures in which the thermal expansion of coefficients of the components are similar.

With regards to V^E_m, for all the mixtures studied the interactional contributions were found to be positive, being the most important contribution. The magnitude and sign of both the free volume and the curvature terms are dependent on the relative magnitudes of thermal expansion coefficients of the component. No quantitative predictions of the observed excess volumes is possible with the theory, as can be seen in Table 6.

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