The Effect of Pressure on Order Destruction and Order Creation in Linear or Branched Alkane Mixtures

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The pressure dependence of the excess enthalpy H^E, dH^E/dP, has been calculated from experimental excess volumes V^E and dV^E/dT using $dH^E/dP = V^E - TdV^E/dT$. dH^E/dP at zero pressure are reported at 25°C and equimolar concentration for the mixtures: cyclohexane with the series of normal alkanes (n-C_n, where $n = 6,8,10,12,14$ and 16) and with the series of highly branched alkanes (br-C_n, where $n = 6,8,12$ and 16), benzene, toluene and p-xylene + n-C_n and 1-chloronaphthalene + n-C_n and br-C_n. Experimental and Flory theory dH^E/dP values are in good agreement for the whole cyclohexane + br-C_n series. For the n-C_n series, dH^E/dP becomes increasingly positive deviating from the Flory predictions. This discrepancy is due to the presence of short-range orientational order in the higher n-C_n pure liquids which makes dH/dP more negative and which, upon mixing, is destroyed producing a positive contribution to dH^E/dP not accounted for by the theory. The discrepancy between theoretical and experimental dH^E/dP is large for benzene, but progressively smaller for toluene, p-xylene and 1-chloronaphthalene. These results are consistent with creation of order between the aromatic plate-like molecule and the long n-C_n in solution. For 1-chloronaphthalene + n-C_n, this order creation process produces a negative contribution to dH^E/dP which balances the positive order-destruction contribution originated by the rupture, upon mixing, of short-range orientational order in pure n-C_n.

KEY WORDS: Short-range orientational order; excess enthalpy; excess volume; excess expansivity; pressure; normal alkanes; branched alkanes, cyclohexane, benzene, toluene, *p*-xylene, 1-chloronaphthalene.

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1. INTRODUCTION

In recent years, a new contribution to the thermodynamic mixing functions has been shown to be of general importance. This contribution is associated with the effect of structure or order which may be decreased or enhanced in passing from the pure to the solution state.[1] Order-destruction and order-creation processes in solution have been studied through the measurement of second-order thermodynamic excess or mixing quantities, *viz.* dV^E/dT, $(\kappa_T V)^E$, $\Delta(\gamma VT)$, C_p^E, ΔC_v and $\Delta(\alpha\gamma VT)$; here, α, κ_T and γ are the thermal expansion, isothermal compressibility and thermal pressure coefficients, respectively. These quantities have been determined for a variety of systems: cyclohexane (c-C_6) mixed with the normal alkanes (n-C_n) and their highly branched isomers (br-C_n),[2] benzene,[3,4] toluene[4,5] and p-xylene[4,6] + n-C_n, and 1-chloronaphthalene + n-C_n and br-C_n.[7] The picture that emerges from these data is the following: i) there is short-range orientational order between long-chain n-C_n molecules in the pure state; when a long n-alkane is mixed with c-C_6, n-C_n/n-C_n order is destroyed so that mixing involves a net destruction of order, ii) when the br-C_n series is used, order effects are not present; this is attributed to the absence of orientational order in these globular-shaped alkanes, iii) when the n-C_n series is mixed with benzene, toluene and p-xylene, it is found that benzene has an order breaking ability comparable to that of c-C_6, but toluene and p-xylene showed a progressively lesser effect, the data for p-xylene being consistent with an ordering in solution between the plate-like p-xylene and the n-C_n molecules and iv) the order-breaking process observed for p-xylene + n-C_n is found to be more pronounced for 1-chloronaphthalene + n-C_n where the destruction of order in pure n-C_n appears to be counterbalanced by compensatory order formed between 1-chloronaphthalene and n-C_n.

The experimental determination of the second-order quantities mentioned above has allowed the thermodynamic analysis of the effect of order in the equation of state, *e.g.*, through the mixing function $\Delta(\gamma VT)$.[1a,2b,4a,7a] Contributions of order effects to the temperature dependence of excess functions such as the excess energy U^E (equal to H^E at P = 0) through the measurement of $dH^E/dT = C_p^E$ or the excess volume V^E *via* the determination of dV^E/dT have also been discussed in detail.[1a,2a,4a,7a] Order contributions to the pressure dependence of the excess functions have been studied *via* $(\kappa_T V)^E = -\,dV^E/dP$; it was found[2a,4a,7a] that the effect of order on $-\,dV^E/dP$ is insufficient to show up against the background of the other effects in this quantity. Another quantity where the influence of pressure on order can be studied is the

Table I. dH^E/dP at Zero Pressure, 25°C and Equimolar Concentration for Mixtures Containing Linear and Branched Alkanes[a]

Mixture	dH^E/dP J-bar^{-1}-mol^{-1}	Mixture	dH^E/dP J-bar^{-1}mol^{-1}
Cyclohexane +		Toluene +	
n-C$_6$	0.087(0.086)[b]	n-C$_6$	0.059
n-C$_8$	0.078	n-C$_8$	0.026
n-C$_{10}$	0.104	n-C$_{10}$	0.021
n-C$_{12}$	0.148	n-C$_{12}$	0.037
n-C$_{14}$	0.194	n-C$_{14}$	0.052
n-C$_{16}$	0.255	n-C$_{16}$	0.082
br-C$_6$	0.052		
br-C$_8$	-0.012	p-Xylene +	
br-C$_{12}$	-0.013	n-C$_6$	0.076
br-C$_{16}$	0.004	n-C$_{16}$	0.027
Benzene +		1-Chloronaphthalene +	
n-C$_6$	0.058	n-C$_6$	0.250
n-C$_8$	0.054	n-C$_8$	0.115
n-C$_{10}$	0.051	n-C$_{10}$	0.038
n-C$_{12}$	0.082	n-C$_{12}$	0.011
n-C$_{14}$	0.132	n-C$_{14}$	-0.010
n-C$_{16}$	0.165	n-C$_{16}$	-0.008
		br-C$_6$	0.406
		br-C$_8$	0.203
		br-C$_{12}$	0.101
		br-C$_{16}$	0.042

[a] Calculated using Eq. (1) with experimental V^E and dV^E/dT values taken from: cyclohexane, Ref. 2a; benzene, toluene and p-xylene, Ref. 4a; 1-chloronaphthalene, Ref. 7a. [b] Direct measurement, Ref. 9.

pressure dependence of the excess enthalpy, dH^E/dP. In order to asses such influence, the present work reports dH^E/dP at zero or ordinary atmospheric pressure for all the mixtures listed above. As in previous studies, these experimental results are compared with the theoretical predictions of the Flory theory[8] which ignores order effects both for the pure liquids and solutions and serves as a base line against which order contributions can be discerned.

2. RESULTS AND DISCUSSION

Values for dH^E/dP at zero pressure, 25°C and equimolar concentration for thirty four mixtures containing normal and branched alkanes are given in Table I. The br-C_n series is taken to be: 2,2-dimethylbutane (br-C_6), 2,2,4-trimethylpentane (br-C_8), 2,2,4,6,6-pentamethylheptane (br-C_{12}) and 2,2,4,4,6,8,8-heptamethylnonane (br-C_{16}). Values in Table I have been obtained through the thermodynamic relation,

$$(dH^E/dP)_T = V^E - T(dV^E/dT)_P \qquad (1)$$

where experimental V^E and dV^E/dT were taken from the references indicated in Table I. Considering that the accuracies[2a,4a,7a] for V^E and dV^E/dT are ± 0.002 cm^3-mol^{-1} and ± 0.0003 cm^3-K^{-1}-mol^{-1}, respectively, we estimate the error on $dH^E dP$ at zero pressure to be less than - 0.009 J-bar^{-1}-mol^{-1}, this error being mainly a reflection of the second term in Eq. (1). Of all the mixtures listed in Table I, dH^E/dP has been measured directly only for c-C_6 + n-C_6 at moderate[9] pressures; from these measurements, dH^E/dP was evaluated to be 0.086 ± 0.007 J-bar^{-1}-mol^{-1} which, as indicated in Table I, is in excellent agreement with the value obtained indirectly using Eq. (1). Both the calorimetric determination and the evaluation through Eq. (1) have similar absolute errors. Equation (1) has also been used for c-C_6 + n-C_6 by Goates et $al.$[10] with their own measured V^E and dV^E/dT values. They obtained for dH^E/dP at zero pressure a value of 0.091 J-bar^{-1}-mol^{-1} which is within experimental error, in agreement with both the value obtained here and the direct measurement. Heintz and Lichtenthaler have measured H^E as a function or pressure (atmospheric, 161 and 291 bar) at 25°C for c-C_6 + n-C_n (n = 7,8,10 and 12) and + br-C_8.[11] The use of these data to evaluate dH^E/dP at zero pressure is complicated by two factors: i) there are only three $H^E(P)$ experimental points and ii) the lowest, non- zero, pressure used was 161 bar. As a result, the evaluation of the slope at $P = 0$ using an adjusted H^E vs P curve is not reliable and produced larger errors than those obtained using Eq. (1).

The experimental values in Table I are displayed in Fig. 1 together with the theoretical predictions of the Flory theory. Parameters required by the theory, $i.e.$, P^*, α, ρ and s for the pure components and values for the solution parameter χ_{12}, obtained by fitting to experimental H^E values at equimolar concentration, were taken from the references indicated in Table I. In that calculation Eq. (15) in Ref. (12) was used
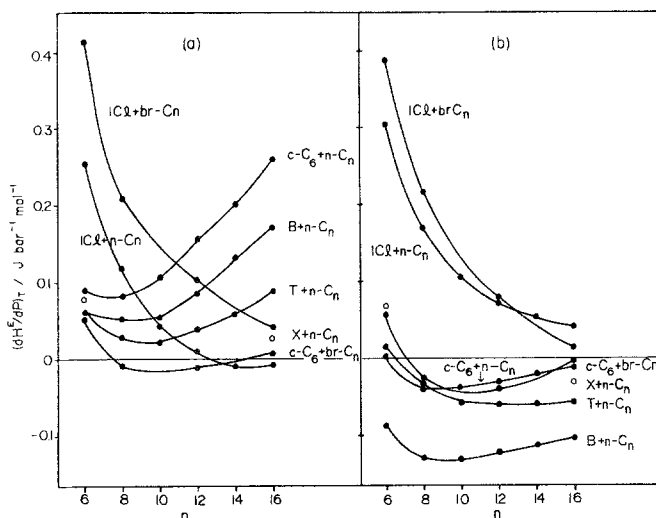
Fig. 1. Experimental (a) and theoretical (b) values of dH^E/dP at zero pressure, 25°C and equimolar concentration of cyclohexane (c-C_6) and 1-chloronaphthalene (1Cl) + the linear (n-C_n) and branched (br-C_n) series of alkanes and for benzene (B), toluene (T) and p-xylene (X) + n-C_n.

for V^E and Eq. (6) in Ref. (2a) for dV^E/dT.[4]

In Fig. 1, experimental and theoretical dH^E/dP values are in good agreement for the whole c-C_6 + br-C_n series; on the other hand, experimental values for the n-C_n start in reasonable agreement with the theoretical values for n-C_6 and n-C_8, but as n increases dH^E/dP becomes increasingly positive deviating from the theoretical results. The different dH^E/dP behavior of branched and linear alkanes cannot[13] be accounted for by a difference in force fields surrounding methyl and methylene groups comprising the two sets of isomers. The explanation lies in the presence of short range orientational order between long-chain n-C_n molecules in the pure state. This orientational order corresponds to a molecular cohesion which lowers the energy U (equal to H at $P = 0$) and the entropy of the liquid. An increase of pressure enhances this cohesion and hence, for an ordered liquid, as the pressure is increased the energy U is expected to decrease more rapidly than for a non-ordered liquid, making dU/dP or dH/dP more negative and producing a positive contribution to dH^E/dP. This is not accounted for by the

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[4]In Ref. 12, the second term in Eq. (15) is in error; the correct term is $(14/9)\tilde{V}^{-1/3}- 1$.
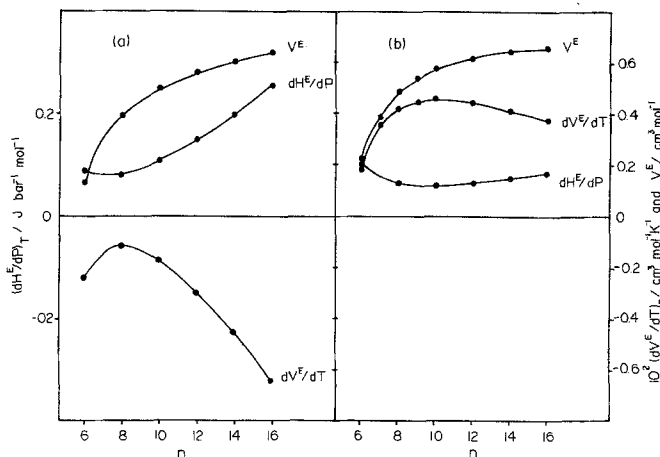
Fig. 2. Experimental (a) and theoretical (b) values for dH^E/dP, V^E and dV^E/dT at 25°C and equimolar concentrations of cylohexane mixed with the n-alkane series.

Flory theory with a pressure independent χ_{12} parameter. Heintz and Lichtenthaler have shown[11] that good results for dH^E/dP are obtained by the Flory theory provided the theory is amended by addition of a pressure-dependent χ_{12} solution parameter. This correction has, however, the inconvenience that the order effects seen in Fig. 1 are then hidden in the parametrization $\chi_{12}(P)$. The use of the original Flory theory sacrifices quantitative agreement but allows the order effects to be discerned.

Figure 2 shows the two contributions to dH^E/dP indicated by Eq. (1) for c-C_6 mixed with the n-C_n series. The experimental results indicate that the dH^E/dP curve appears to be the mirror image of the dV^E/dT curve, *i.e.*, the variation of dH^E/dP with carbon number n is mainly given by the change of dV^E/dT with n. The theoretical results, as indicated also in Fig. 2, show that while the Flory theory fails to predict both dH^E/dP and dV^E/dT, the variation of V^E with n is well reproduced. Similar $V^E(n)$ dependences for the n-C_n series mixed with liquids of different internal pressures, *e.g.*, cyclopentane, carbon tetrachloride, p-dioxane, benzene, toluene, p-xylene and 1-chloronaphthalene, have been previously discussed and interpreted using the Flory theory.[14] The success of the Flory theory in reproducing $V^E(n)$ dependences implies that V^E is not a direct indicator of order like other second-order excess quantities such as dV^E/dT and dH^E/dP. The differences between the Flory theory and the experimental data for dV^E/dT seen in Fig. 2 are then a consequence of the presence of orientational order for long n-C_n: order
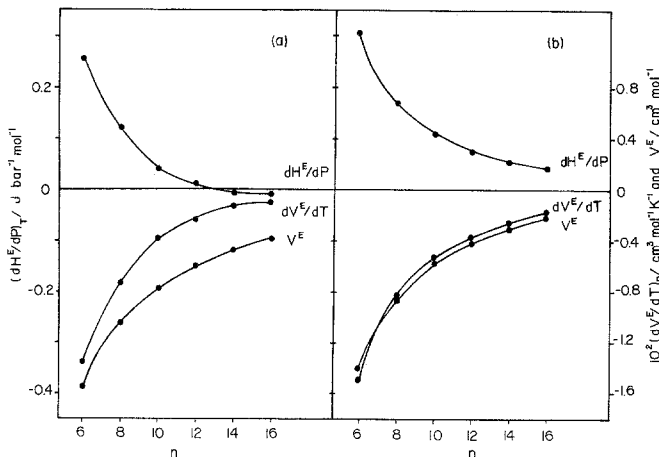
Fig. 3. Experimental (a) and theoretical (b) values for dH^E/dP, V^E and dV^E/dT at 25°C and equimolar concentrations of 1-chloronaphthalene mixed with the n-alkane series.

decreases V for a pure n-C_n liquid, enhances dV/dT and hence because of the destruction of order upon mixing, gives a negative contribution to dV^E/dT.[2a] Since the rupture of n-C_n order is not reflected in V^E, Eq. (1) indicates that the opposite sign order-breaking contributions to dV^E/dT and dH^E/dP are equivalent.

The results for benzene + n-C_n, shown in Fig. 1, also indicate substantial differences between experimental and theoretical dH^E/dP values. Benzene has then an order-breaking ability comparable to that of cyclohexane. The discrepancy between theory and experiment shown in Fig. 1 is reduced on going from benzene through toluene to p-xylene. For p-xylene, the Flory theory predictions are in fair agreement with the experimental values. This suggest that the positive order-breaking contribution to dH^E/dP has been balanced by a negative contribution which would correspond to the creation of order between the aromatic and n-C_n molecules in solution. The data shown in Fig. 1 indicate that this compensation between order destruction and order creation in solution is even more pronounced for 1-chloronaphthalene + n-C_n. Here, in contrast with the results for c-C_6, both the br-C_n and n-C_n series display similar dH^E/dP behavior. The success of the theory to predict dH^E/dP is, of course, also reflected in its results for dV^E/dT as indicated in Fig. 3 where theory and experiment are compared for both these quantities and also for V^E. The net balance between the order-destruction and creation effects, observed by comparison between the experimental results and

the base line given by the Flory theory was, however, visible with $-\Delta(\gamma VT)$ and C_p^E where it was found[1a,7a] that $C_p^E > 0$ and $-\Delta(\gamma VT) < H^E$ both clear indications of order creation. It appears then that the agreement between calculated and experimental dH^E/dP (and hence dV^E/dT) values for the $n\text{-}C_n$ series shown in Fig. 3 can be considered as fortuitous. The nature of the aromatic $n\text{-}C_n$ order in mixtures such as p-xylene or 1-chloronaphthalene + a long n-alkane is not yet clearly understood: it might be an intermolecular ordering due to a restriction of the n-alkane segmental rotational motion by molecules of flat, plate-like shape as suggested by de St. Romain et al.,[15] or it might be an intramolecular order associated with a change in the *trans-gauche* population of the n-alkane as suggested by Grolier and coworkers.[7b,16]. Since conformational and rotational order are not very different mechanisms, it is possible that order creation is the resultant of both processes.

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