

EFFECTS OF MOLECULAR SIZE AND SHAPE IN SOLUTION THERMODYNAMICS

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Abstract—The one-fluid corresponding states theory is used to predict excess thermodynamic quantities of a mixture of spherical molecules of different ϵ and σ . Two prescriptions of 'van der Waals type', and a third used by Flory, give the parameters ϵ_m and σ_m of the solution. Comparison of the results is made with Monte Carlo calculations of Singer and Singer and the Snider-Herrington theory, and also with experimental features of simple and polyatomic spherical molecule mixtures. For each prescription an intuitive discussion is given of contributions to the excess quantities arising from (a) the energetic weakness of (1-2) contacts relative to (1-1) and (2-2) and (b) dissimilarity of free volume between the components. Two free volume contributions are distinguished. One depends on the second derivative with respect to T of the energy, volume, etc. of the reference liquid. The other occurs only in V^E where it is of major importance and depends on dV/dT and a dissimilarity of molecular energy/volume parameters of the components. Recent experiments indicate two effects outside current theory. For systems containing anisotropic molecules, there is a third contribution to excess quantities (c), due to short-range orientational order or correlations of molecular orientations in one or both components. Mixing liquids of differing degrees of order usually brings about a net decrease of order, and hence positive contributions in ΔH_M and ΔS_M . The effect is illustrated by ΔH_M values of branched and normal alkane mixtures at 25°, the temperature dependence of ΔH_M for such systems, and the widely different ΔH_M of *cis* and *trans* dimethylcyclohexanes mixed with the orientationally ordered *n*-C₁₆. The properties of systems containing a nematic liquid crystal (MBBA) and an alkane are sensitive to the alkane shape and indicate that MBBA molecules correlate their orientations with normal, but not with highly branched alkanes. The fourth contribution (d) is seen in systems involving alkanes of the same molecular shape but different degrees of steric hindrance of torsional oscillations. Heats of mixing point to a thermodynamic effect associated with a coupling of the molecular motions of the components.

INTRODUCTION

The corresponding states theory developed by Prigogine and collaborators¹ and by Scott² and Brown³ was the dominant influence in solution thermodynamics during the 1960's. The starting point of the corresponding states theory was the strictly regular solution theory¹ of Guggenheim, extended in addition to polymer solutions by Flory, Huggins and others. However, these earlier theories were mainly concerned with the combinatorial entropy of mixing and so were based on a rigid lattice model for the liquid state. As a consequence they could not predict the volume of mixing, or the effect on the excess heat and entropy due to the volume changes undergone by the components during the mixing process. The missing factor was the equation of state, and this was introduced for spherical molecule mixtures, first in a cell model,⁴ and then in the corresponding states theory. Through the use of an equation of state for polymeric liquids, the theory was extended from spherical molecule mixtures to polymer solutions.^{5,6} For both of these classes of mixtures the theory has had notable successes in interpreting experiment and in predicting new effects.

Recently, theoretical interest has turned to the rapidly evolving molecular distribution function theories and computer calculations of the excess thermodynamic quantities. These developments,^{7,8} together with experiment, have shown that one element of the usual corresponding states approach, namely the average potential or random mixture prescription (see below), over-estimates effects of size difference between the component molecules. A major improvement is obtained through a different prescription of 'van der Waals' type, suggested by Leland, Rowlinson and Sather,⁹ and in fact several improved prescriptions are available, each leading to a form of the corresponding states theory with its prediction of the excess thermodynamic quantities. The first objective of this article is to assess the physical signifi-

cance of the prescriptions, and to compare the predictions with the results of Monte Carlo calculations in the literature¹⁰ and also with predictions of the Snider-Herrington theory¹¹ which is based on a simple distribution function approach. The corresponding states theory gives good results and may be used to lend physical insight into the origin of the excess functions for spheres of different size. However, a new effect not treated by current theory arises when dealing with mixtures of molecules of different shape. This effect is due to the presence of short-range orientational order in a liquid composed of highly anisotropic molecules such as the normal alkanes. Two liquids of different molecular shape, e.g. a branched and a normal alkane or two *n*-C_{*n*} of different *n*, will have different degrees of orientational order. When they are mixed there is a net decrease of order and corresponding positive contributions in ΔH_M and ΔS_M . These contributions are also of importance in the thermodynamics of systems containing liquid crystals or lipids. Another effect is revealed by studying systems where one component is taken from a series of alkane isomers of the same molecular shape but differing degrees of steric hindrance to internal motion. It appears that a thermodynamic contribution arises from a coupling between the motions of interacting molecules.

The present article is restricted in scope, but there are several excellent general reviews of the current situation in simple mixtures, e.g. by Scott and Fenby,¹² particularly for the corresponding states theory, and by Henderson and Leonard⁷ and by McDonald,⁸ especially for the distribution function theories and machine calculations.

MIXTURES OF SPHERES OF UNEQUAL SIZE

The review by Scott and Fenby emphasizes that a corresponding states theory consists of three steps:

(a) the establishment of the *equation of state* of the pure liquids in a corresponding states, i.e. reduced form,

giving the dependence of the thermodynamic quantities on V and T . This may be done using experimental data for the pure liquids, or results of a machine calculation with an assumed intermolecular potential, or through a theoretical model. This last can be the cell model which, perhaps surprisingly, is still very useful in work on mixtures, as indicated by the success of the Flory theory.⁶

(b) *combining rules* for passing from the parameters characterizing the potentials for interactions between like molecules in the pure liquids to the corresponding parameters for unlike molecules. The Lorentz–Berthelot rules have been generally used:

$$\sigma_{12} = \frac{1}{2}(\sigma_{11} + \sigma_{22}) \quad (1)$$

$$\epsilon_{12} = (\epsilon_{11} \cdot \epsilon_{22})^{1/2} \quad (2)$$

where the σ_{ij} and ϵ_{ij} are respectively the intermolecular distance at which the potential is zero, and the depth of the potential well. Theoretical and experimental evidence exists for deviations from the Berthelot geometric mean rule in the direction of lower cohesion of the (1-2) pair, i.e.

$$\epsilon_{12} = (1 - k_{12})(\epsilon_{11} \cdot \epsilon_{22})^{1/2}, \quad k_{12} > 0. \quad (3)$$

(c) a *prescription* for the extension of the equation of state and the thermodynamic properties from the pure components to the mixture. The simplest prescription is the one-fluid model where the mixture is taken to be equivalent to a single fluid with molecular parameters σ_m and ϵ_m . More complex two- and three-fluid models are available, but it is probable¹⁰ that they give no better results than the one-fluid. According to the one-fluid scheme, the excess thermodynamic quantities are given by:

$$V^E/N = \sigma_m^3 \tilde{V}(\tilde{T}_m) - x_1 \sigma_{11}^3 \tilde{V}(\tilde{T}_1) - x_2 \sigma_{22}^3 \tilde{V}(\tilde{T}_2) \quad (4)$$

and at zero pressure,

$$H^E/N = U^E/N = \epsilon_m \tilde{U}(\tilde{T}_m) - x_1 \epsilon_{11} \tilde{U}(\tilde{T}_1) - x_2 \epsilon_{22} \tilde{U}(\tilde{T}_2) \quad (5)$$

with the reduced temperatures given by equations of form:

$$\tilde{T} = kT/\epsilon. \quad (6)$$

The σ_m and ϵ_m are averages of the molecular parameters of the pure liquids, and it is in the averaging prescriptions that the differences appear between various theories with corresponding differences in the calculated excess properties.

One-fluid prescriptions for σ_m and ϵ_m

Van der Waals prescriptions. It is now agreed^{7,8} that the most successful prescriptions are those of ‘van der Waals’ type,⁹ actually proposed by van der Waals¹³ in 1890 for passing from the constants $a \propto \sigma^3$ and $b \propto \sigma^3$ of pure fluids to equivalent parameters for the mixture. Thus, we have

$$a \propto \epsilon_m \sigma_m^3 = \sum_{ij} x_i x_j \epsilon_{ij} \sigma_{ij}^3. \quad (7)$$

Van der Waals proposed two prescriptions for b . The first was a *linear* combination of the co-volumes of the

components, so that

$$b \propto \sigma_m^3 = \sum_i x_i \sigma_{ii}^3 \quad (8)$$

and hence in eqn (7),

$$\epsilon_m = \frac{\sum_{ij} x_i x_j \epsilon_{ij} \sigma_{ij}^3}{\sum_i x_i \sigma_{ii}^3}. \quad (9)$$

This ‘linear’ van der Waals prescription has been used by Scott and van Konynenburg¹⁴ for alkane mixtures.

The second prescription for b comes from a *quadratic* averaging of the distances between centres of contacting molecules,

$$b \propto \sigma_m^3 = \sum_{ij} x_i x_j \sigma_{ij}^3 \quad (10)$$

leading to

$$\epsilon_m = \frac{\sum_{ij} x_i x_j \epsilon_{ij} \sigma_{ij}^3}{\sum_{ij} x_i x_j \sigma_{ij}^3}. \quad (11)$$

The quadratic van der Waals prescription is the usual vdW-I prescription of Leland, Rowlinson and Sather⁹ and widely used for comparison^{7,8} with experiments on simple mixtures and with Monte Carlo calculations. It is clear that both formulae for ϵ_m correspond to molecular volume fraction averages of the ϵ_{ij} , but the two prescriptions give rather different results for the excess thermodynamic quantities. It is therefore convenient to discuss immediately the two prescriptions in terms of parameters expressing the differences between the quantities σ_{ij} and ϵ_{ij} . These difference parameters may directly compare σ and ϵ of the pure components, as do for instance ρ and δ in the work of Prigogine and collaborators. However, in their Monte Carlo calculations, Singer and Singer compare one of the components, 1, with an intermediate reference liquid characterized by σ_{12} and ϵ_{12}^0 as given by the Lorentz–Berthelot rules, i.e. they introduce

$$\eta = \frac{\sigma_{11}}{0.5(\sigma_{11} + \sigma_{22})} - 1 = \frac{\sigma_{11}}{\sigma_{12}} - 1$$

$$\delta = \left(\frac{\epsilon_{11}}{\epsilon_{22}}\right)^{1/2} - 1 = \frac{\epsilon_{11}}{\epsilon_{12}^0} - 1. \quad (12)$$

We shall be concerned below with expansions of excess quantities in powers of difference parameters, and the above choice gives a more rapid convergence than do the more usual parameters.

We now determine for each prescription a molecular volume change on mixing,

$$\Delta \sigma^3 = \sigma_m^3 - x_1 \sigma_{11}^3 - x_2 \sigma_{22}^3 \quad (13)$$

and the corresponding change of molecular cohesion,

$$\Delta \epsilon = \epsilon_m - x_1 \epsilon_{11} - x_2 \epsilon_{22}. \quad (14)$$

It may be seen in eqns (4) and (5) that these quantities would give V^E and H^E if the reduced temperatures of the liquids were all the same, i.e. if one were to ignore effects associated with their free volume. It is of interest to note

that in the strictly regular solution theory where effects of size differences and free volumes are omitted,

$$\Delta\sigma^3 = 0$$

$$\Delta\epsilon/\epsilon_{12}^0 x_1 x_2 = -\delta^2 - 2k_{12}. \quad (15)$$

Here only the second order of δ is kept, and the first order of the very small k_{12} parameter. The normalizing factor ϵ_{12}^0 in the denominator of the left-hand side can to this approximation be any ϵ_{ij} , or ϵ_m itself. In eqn (15), $\Delta\epsilon$ is negative corresponding to a decrease in molecular cohesion during mixing. The negative sign comes first from a term $-\delta^2$ which is associated with the dissimilarity of the 'contact energies' ϵ_{11} and ϵ_{22} arising from the difference in chemical nature of the two components. Secondly, there is an obvious extra contribution $-2k_{12}$ from any deviation from the Berthelot rule. The heat of mixing is positive. Introducing for comparison the lattice coordination number and interchange energy of the strictly regular solution theory,

$$H^E/N = -\Delta\epsilon = z\Delta w_{12} x_1 x_2. \quad (16)$$

Table 1 gives $\Delta\sigma^3/\sigma_{12} x_1 x_2$ and $\Delta\epsilon/\epsilon_{12}^0 x_1 x_2$ for the various prescriptions under discussion. For the linear v dW, $\Delta\sigma^3 = 0$ and, as in the strictly regular solution theory, $\Delta\epsilon$ indicates a decrease of cohesion during mixing. However, the important dissimilarity is no longer between contact energies as such, but between contact energies per unit molecular volume, i.e. ϵ/σ^3 , entering the prescription through $[(\epsilon_{11}/\sigma_{11}^3)^{1/2} - (\epsilon_{22}/\sigma_{22}^3)^{1/2}]^2$ and resulting in the factor $-(\sigma - 3\eta)^2$. It is of interest to note that the well-known solubility parameter theory also stresses this difference in cohesive energy densities of the components. The linear v dW corresponding states theory and the solubility parameter theory are remarkably similar and differ from the strictly regular solution theory in having an η -dependence of $\Delta\epsilon$. This is intuitively reasonable. Given two spherical molecules of identical chemical nature, but very different σ , such as two highly branched alkanes, then the ϵ 's will also be very different, and both δ and η will be large. However, due to the chemical similarity of the components, we would expect $\Delta\epsilon$ and H^E to be small instead of large as predicted by strictly regular solution theory. The statement that $\Delta\epsilon$ depends on a dissimilarity of ϵ/σ^n , where $n = 3$, or $n = 2$ as in the Flory theory (below), is thus an advance over putting $n = 0$ as in the strictly regular solution theory.

Again in Table 1, one notices that for the quadratic v dW prescription $\Delta\sigma^3$ is no longer zero, but negative. Dissimilarity of molecular size causes the solution to be more compact than the pure components. This effect has

Table 1. Parameters for the corresponding states expansions (19-21)

	$\frac{\Delta\epsilon}{\epsilon_{12}^0 x_1 x_2}$	$\frac{\Delta\sigma^3}{\sigma_{12} x_1 x_2}$	B
Strictly regular	$-\delta^2$	$-2k_{12}$	0
Linear v dW	$-(\delta - 3\eta)^2$	$-2k_{12}$	0
Quadratic v dW	$-(\delta - 3\eta)^2 + 9\eta^2$	$-2k_{12}$	$-9\eta^2$
Flory	$-\delta(\delta - 6\eta)$	$-2k_{12}$	0
Average potential model	$-(\delta - 2\eta)^2$	$-2k_{12}$	0
	$-(\delta^2 + 72\eta^2)$	$-2k_{12}$	$13\eta^2 + 2\delta\eta 57\eta^2 + 6\delta\eta$

been compared with the contraction observed during the mixing of small and large ball bearings,¹⁵ the small spheres tending to enter the voids between the large. (However, the quadratic v dW prescription applied to ball bearings of widely different diameter predicts effects considerably larger than found experimentally, and there is even evidence that a small size-difference brings about an expansion on mixing.¹⁶) In $\Delta\epsilon$ we again see the $-(\delta - 3\eta)^2$ term due to contact energy dissimilarity giving decreased cohesion in the mixture, but there is a new term $+9\eta^2$ of opposite sign. This is the counterpart of the contraction just mentioned. It becomes dominant for molecules which are similar in molecular energy/volume ratios, so that $\Delta\epsilon$ is then positive and the predicted H^E is negative.

The Flory prescription. The Flory theory,¹⁷ which may be regarded as a corresponding states theory, also uses the linear prescription for σ_m^3 , so that $\Delta\sigma^3 = 0$. The theory makes the assumption that interaction takes place between the surfaces of molecules, a view taken in several approaches.^{18,19} Thus, the Berthelot geometric mean should be applied to contact energies between surfaces of molecules rather than the molecules themselves. Following the review of Henderson and Leonard,⁷ one can write the Flory prescription in a form similar to eqn (9) for the linear v dW prescription:

$$\sigma_m = \sum_i x_i \sigma_{ii}^3 \quad (17)$$

$$\epsilon_m = \frac{\sum_{ij} x_i x_j \epsilon_{ij} \sigma_{ij}^2}{\sum_i x_i \sigma_{ii}^2} \quad (18)$$

Here, to reproduce the Flory prescription exactly, we must use a geometric mean rule for $\sigma_{12} = (\sigma_{11} \cdot \sigma_{22})^{1/2}$. However, in calculations there is little difference in using the Lorentz eqn (1), and so either could be put in the Flory prescription. It is clear that this prescription corresponds to a surface fraction averaging of the ϵ_{ij} to obtain ϵ_m . Thus the weight accorded the sphere diameter in the averaging procedure is less than in the v dW scheme, but more than in the strictly regular solution theory where it was zero. In Table 1, $\Delta\sigma^3$ and $\Delta\epsilon$ are the same as with the linear v dW but with $(\delta - 2\eta)^2$ replacing $(\delta - 3\eta)^2$, indicating that the decrease of molecular cohesion in mixing now reflects the dissimilarity of the components in molecular energy/surface, i.e. ϵ/σ^2 or P^*/s in the Flory-type terminology. The linear v dW and Flory prescriptions give almost identical predictions of excess quantities as seen below.

Average potential prescription. The oldest prescription^{1,20} is the random mixing or average potential (crude model). Bellemans, Mathot and Simon²⁰ have reviewed the application to simple mixtures of the refined or two-fluid form of the prescription. Table 1 shows that the prescription gives great weight to the effect of size difference, but it is now^{7,8} agreed that this constitutes an over-estimate.

Corresponding states equations for the excess thermodynamic quantities

The excess quantities are given by eqns (4) and (5), but expansions in terms of ρ and δ have also been made by Prigogine¹ and by Rowlinson and collaborators.⁹ Similar expansions of the Monte Carlo excess quantities have been given by Singer and Singer.¹⁰ All of these are useful

in calculating the excess quantities, but of course not completely accurate. However, the original purpose of the expansions was instead to facilitate qualitative discussion, and for this they are indispensable. (The discussion below is analogous to that made in refs. 1 and 9b.) The expansions to squares of the difference parameters can be put in the form:

$$\begin{array}{l} \text{Contact energy} \\ \text{dissimilarity} \end{array} \quad \begin{array}{l} \text{Free volume dissimilarity} \\ \end{array} \\ \frac{H^E}{x_1x_2} = \left(\frac{-\Delta\epsilon}{x_1x_2\epsilon_{12}^0} \right) (-U + TC_p) - 2\delta^2 \left(T^2 \frac{dC_p}{dT} \right) \quad (19) \\ (12.54RT) \quad (1.14RT) \end{array}$$

$$\frac{G^E}{x_1x_2} = -BRT + \left(\frac{-\Delta\epsilon}{x_1x_2\epsilon_{12}^0} \right) (-U) + 2\delta^2(TC_p) \quad (20) \\ (11.09RT) \quad (1.45RT)$$

$$\frac{V^E}{x_1x_2} = \frac{\Delta\sigma^3}{\sigma_{12}^3x_1x_2} V + \left(\frac{-\Delta\epsilon}{x_1x_2\epsilon_{12}^0} \right) \left(T \frac{dV}{dT} \right) \\ (33.41 \text{ cm}^3) \quad (13.43 \text{ cm}^3) \\ -4\delta(\delta - 3\eta) T \frac{dV}{dT} - 2\delta^2 \left(T^2 \frac{d^2V}{dT^2} \right). \quad (21) \\ (19.58 \text{ cm}^3)$$

Here the quantities $\Delta\sigma^3$ and $\Delta\epsilon$ are as given by the different prescriptions in Table 1, and the U , C_p , V , etc. are the reference thermodynamic functions which may be taken from theory or a pure component, but which we take below as generated¹⁰ for an argon-like liquid by the Monte Carlo method. The relative magnitudes of the terms may be sensed from the values of these reference functions at 91°K, as indicated in eqns (19–21).

Effects of $\Delta\sigma^3$ and $\Delta\epsilon$

The different prescriptions affect the excess properties only through the changes of compactness and cohesion, $\Delta\sigma^3$ and $\Delta\epsilon$. These lead firstly to contributions in H^E , G^E and V^E which are directly proportional to, respectively, U , G and V of the reference liquid. (The term $-U$ in the expression for G^E may be replaced by $-G + T(\partial G/\partial T)_p$.) These contributions arise because $\Delta\sigma^3$ and $\Delta\epsilon$ represent net changes in the reduction parameters which appear in eqns (4) and (5). However, in addition, the usual negative $\Delta\epsilon$ or decrease of cohesion in mixing leads to a relatively higher value of \tilde{T} for the mixture than for the components, and hence $\Delta\epsilon$ causes supplementary contributions in G^E , H^E and V^E . As seen in the equations, these extra terms are proportional to the temperature derivatives of the corresponding functions of the reference liquid, i.e. C_p , $(\partial G/\partial T)_p$ and dV/dT .

Effect of free volume dissimilarity between components

Apart from the entropic term $-BRT$ in G^E , the remaining terms in eqns (19–21) are associated with the dissimilarity of the component liquids in free volume. They do not involve $\Delta\sigma^3$ and $\Delta\epsilon$ and are independent of the particular one-fluid prescription.

In each of H^E , G^E and V^E there occurs a term containing the second derivative with respect to temperature of U , G or V of the reference liquid. The factor δ^2 corresponds to the difference in ϵ between the components and hence to the difference in reduced temperatures ($\tilde{T} = kT/\epsilon$) and free volumes of the two liquids. This term is more important in V^E than in H^E or G^E . In particular,

the temperature dependence of V^E is sensitive to the equation of state assumed for the reference liquid since it involves the third derivative of V . This free volume term is well-known in polymer solution thermodynamics where it leads typically to negative V^E for these systems and a considerable negative H^E contribution. However, according to eqn (20), the contribution to G^E is positive and, at sufficiently high temperature, phase separation occurs at the lower critical solution temperature which is a general feature of polymer solutions.²¹

Equation (21) shows a second free volume contribution to V^E , in $-4\delta(\delta - 3\eta)$ which is of major importance. Its origin may be found by returning to eqn (4) for V^E :

$$\frac{V^E}{N\sigma_m^3} = \tilde{V}(\tilde{T}_m) - \left[\frac{x_1\sigma_{11}^3}{\sigma_m^3} \tilde{V}(\tilde{T}_1) + \frac{x_2\sigma_{22}^3}{\sigma_m^3} \tilde{V}(\tilde{T}_2) \right]. \quad (22)$$

This equation compares the \tilde{V} function at the reduced temperature of the solution, \tilde{T}_m , with an average of the \tilde{V} values at \tilde{T}_1 and \tilde{T}_2 for the pure components. This latter average may be approximated by \tilde{V} evaluated at a 'pure component' \tilde{T}_{1+2} intermediate between \tilde{T}_1 and \tilde{T}_2 , corresponding to a 'molecular volume fraction average' of \tilde{T}_1 and \tilde{T}_2 :

$$\tilde{T}_{1+2} = \frac{x_1\sigma_{11}^3\tilde{T}_1 + x_2\sigma_{22}^3\tilde{T}_2}{\sigma_m^3}. \quad (23)$$

However, \tilde{T}_m of the mixture corresponds to a different, 'contact energy fraction average' of \tilde{T}_1 and \tilde{T}_2 ,

$$\tilde{T}_m = \frac{kT}{\epsilon_m} = \frac{x_1\epsilon_{11}\tilde{T}_1 + x_2\epsilon_{22}\tilde{T}_2}{\epsilon_m}. \quad (24)$$

The effect on V^E due to the difference between the \tilde{T} will be

$$\frac{V^E}{N\sigma_m^3} = (\tilde{T}_m - \tilde{T}_{1+2}) \frac{d\tilde{V}}{d\tilde{T}}. \quad (25)$$

It is clear that $\tilde{T}_m - \tilde{T}_{1+2}$ requires: (a) inequality of \tilde{T}_1 and \tilde{T}_2 and (b) a difference between the molecular volume fraction and contact energy fractions, i.e. $\epsilon_{11}/\sigma_{11}^3 \neq \epsilon_{22}/\sigma_{22}^3$ or in the Prigogine-Flory nomenclature, $P_1^* \neq P_2^*$. In eqn (21) for V^E the term $\delta(\delta - 3\eta)$ factors into δ corresponding to requirement (a) and $(\delta - 3\eta)$ corresponding to (b).

Comparison of the corresponding states predictions with Monte Carlo and Snider-Herrington results

Figures 1 and 2 compare the corresponding states predictions with Monte Carlo results of Singer and Singer.¹⁰ These are for mixtures of Lennard-Jones 12-6 spheres obeying the Lorentz-Berthelot combining rules and with $\sigma_{12} = 3.596 \text{ \AA}$ and $\epsilon_{12}^0/k = 133.5^\circ\text{K}$. These parameters were chosen to be in the middle of the range for simple fluids, e.g. Ar, Kr, Xe, N₂, O₂, CO, CCl₄ and CF₄. Differences of sizes and potential depths lie in the range $0 \leq \eta \leq 0.12$ and $-0.190 \leq \delta \leq 0.235$. The largest size difference for a simple system where H^E , V^E and G^E are known corresponds to $\eta = 0.047$ for Ar + CH₄. Most simple mixtures have much smaller size differences, even though the force field differences can be large as in Ar + Kr where $\delta = 0.18$. All of the prescriptions become the same for component molecules of the same size. Thus, real simple mixtures are not as useful as the Monte Carlo calculations for differentiating between the prescriptions, or alternatively, all the prescriptions should give reason-

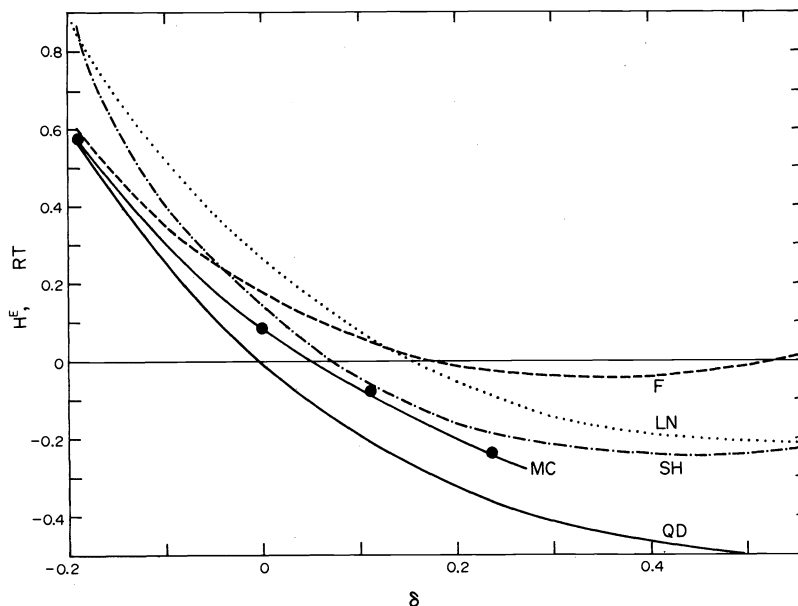


Fig. 1. The molar excess heat at 97°K of a mixture of spherical Lorentz-Berthelot molecules with $\sigma_{11}/\sigma_{12} = 1.12$ as a function of $\delta = \epsilon_{11}/\epsilon_{12} - 1$. Monte Carlo results of Singer and Singer (MC). Corresponding states theory prescriptions: Flory, eqns (17, 18), (F); linear van der Waals, eqns (8, 9), (LN); quadratic van der Waals, eqns (10, 11), (QD). Snider-Herrington theory (SH).

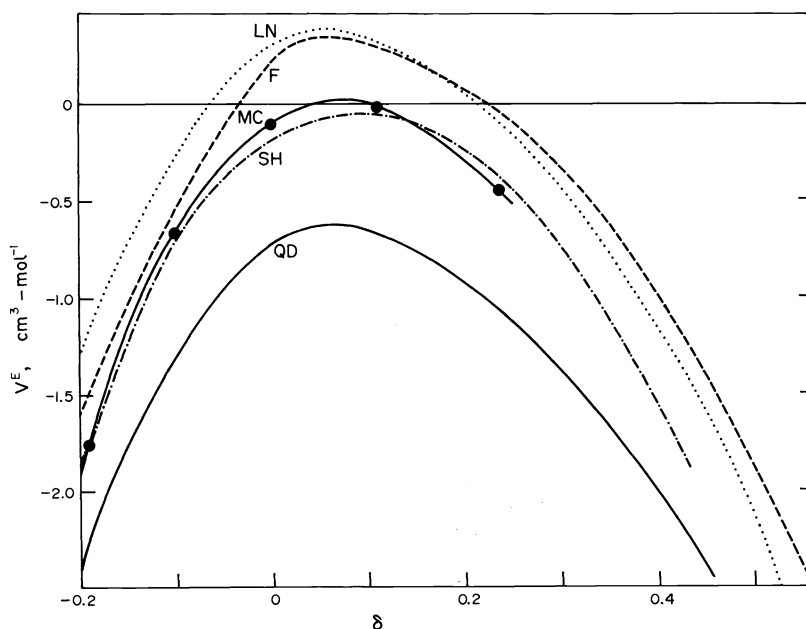


Fig. 2. The molar excess volume at 97°K of a mixture of spherical Lorentz-Berthelot molecules with $\sigma_{11}/\sigma_{12} = 1.12$ as a function of $\delta = \epsilon_{11}/\epsilon_{12} - 1$. Monte Carlo results of Singer and Singer (MC). Corresponding states theory prescriptions: Flory, eqns (17, 18), (F); linear van der Waals, eqns (8, 9), (LN); quadratic van der Waals, eqns (10, 11), (QD). Snider-Herrington theory (SH).

able results for simple mixtures. In Figs. 1 and 2 attention is confined to the maximum value of η , viz. 0.12, and equimolar values¹⁰ of V^E and H^E/RT at 97°K are plotted as functions of δ . The Monte Carlo results follow a corresponding states principle so that those in Figs. 1 and 2 will also apply to polyatomic systems with higher ϵ_{12} at higher T but the same value of \bar{T} . The easiest way to 'scale up' is through critical data. Using a simple Lennard-Jones approach, the reference liquid with $\epsilon/k = 133.5^\circ\text{K}$ and $\sigma = 3.596$ should have $T_c = 171^\circ\text{K}$ and $V_c =$

$79.4 \text{ cm}^3/\text{mol}$, and at 97°K, $\bar{T} = 0.727$. This value of the reduced temperature would be found for cyclohexane, with $T_c = 554^\circ\text{K}$, at 40°C. The corresponding values of H^E/RT at 40°C may be obtained directly from the ordinate of Fig. 2, but to obtain V^E one must multiply up the ordinate in Fig. 1 by $V_c(\text{cyclohexane})/V_c(\text{reference}) = 3.9$.

Figures 1 and 2 also show the excess thermodynamic functions from the linear and quadratic v dW and Flory prescriptions and the Snider-Herrington theory. For the

corresponding states calculations we have used eqns (4) and (5). The reduced thermodynamic properties of the reference liquid are as given by the Monte Carlo calculations,¹⁰ and they furnish the energy volume, and free energy of the mixture and the two components once the σ and ϵ are specified by the prescription. The expansions, eqns (19–21) may also be used to give accurate predictions, indicating that terms containing cubes of η and δ are not important in this range of size differences. In the case of the Snider–Herrington theory the equation of state is of course already present in the theory, and was merely fitted to the present values of σ_{12} and ϵ_{12}^0 to make the predictions in Figs. 1 and 2. The dependence of G^E on δ has also been calculated analogously to H^E and V^E . The results show much the same qualitative effects as H^E and hence are not given.

The main result of the comparison is that the corresponding predictions and the Snider–Herrington theory are all close to the Monte Carlo results and differ only in detail. Thus the corresponding states expansions may be used to assess the origin of the main trends of H^E and V^E . Figure 1, for instance, shows how H^E may be interpreted as the sum of contributions arising from dissimilarity of the components in contact energy and in free volume. A parabolic dependence of H^E/NkT against δ comes from the *contact energy dissimilarity contribution* in the linear v dW and Flory prescriptions proportional to respectively $(\delta - 3\eta)^2$ and $(\delta - 2\eta)^2$. With $\eta = 0.12$, the minima of the parabolas would occur at $\delta = 0.36$ and 0.24 respectively. However, the small negative *free volume contribution* increases in magnitude as δ increases and hence displaces the minima of the curves to higher δ . The quadratic v dW prescription repeats the linear v dW curve but it is translated to lower H^E since $\Delta\epsilon$ includes the extra $9\eta^2$ term. From $\Delta\epsilon$ in Table 1 it is clear that H^E should change sign with δ , and this behaviour is seen in Fig. 1. The difference between the prescriptions is apparent only at higher δ where the quadratic v dW seems in better agreement with the Monte Carlo calculations than the other prescriptions. On the other hand, the Snider–Herrington theory for positive δ is in very good agreement with the Monte Carlo results, and at very high values of δ where there are no Monte Carlo results, this theory is in better agreement with the linear than the quadratic v dW.

Figure 2 for V^E against δ shows that the shape of V^E is also parabolic but, contrary to intuition, is almost the *negative* of H^E . This occurs because H^E is dominated by the contact energy effect and V^E by free volume effects. A positive parabolic contribution again occurs proportional to $(\delta - 3\eta)^2$ and $(\delta - 2\eta)^2$ for the linear v dW and Flory prescriptions. However, for V^E this positive contribution is overcome by two free volume terms. First, for $\delta < 0$ the molecular energy/volume effect in $-\delta(\delta - 3\eta)$ gives a large negative V^E contribution leading to increasingly negative V^E values in Fig. 2 as δ becomes more negative. This is just the region in Fig. 1 where H^E is becoming increasingly positive. This interesting prediction of negative V^E and positive H^E was originally made by Prigogine and collaborators, and this behaviour is in fact common particularly for polymer solutions. For $\delta < 0$, the energy/volume effect is positive but becomes zero at $\delta = 3\eta$ and eventually the negative free volume term in d^2V/dT^2 becomes dominant giving increasingly negative V^E as δ increases. The quadratic v dW prescription gives values of V^E which are the same as the linear v dW but translated downwards due to the negative

$\Delta\sigma^3$ term proportional to V of the reference liquid. Comparing V^E from this prescription with the Monte Carlo results, it seems that V^E is too negative and experimental systems confirm this.

Comparison with experiment

Simple mixtures. Some nine simple mixtures of Ar, Kr, methane, CO, etc. have been intensively studied and used by Henderson and Leonard⁷ to test predictions of the quadratic v dW and average potential model prescriptions, as well as the Barker–Henderson perturbation theory and the 2-fluid v dW prescription. The reference liquid was argon whose thermodynamic properties are given in ref. 20, rather than the present Monte Carlo thermodynamic properties. However, the predictions are not very sensitive to the exact equation of state of the reference liquid, and similar results are obtained using the Monte Carlo results. The theories were fitted to G^E through adjustment of k_{12} , and H^E and V^E were calculated. The average potential model predictions are excellent, but call for $k_{12} < 0$ and hence must be considered unsatisfactory. The quadratic v dW predictions are good but usually H^E and V^E are predicted too low. Repeating the procedure with the linear v dW and Flory prescriptions we find identical predictions which are marginally better for H^E but improved for V^E . By fitting k_{12} to G^E , $\Delta\epsilon$ becomes an adjustable parameter. In eqn (2) for G^E the term $-BRT$ is small and varies little between the prescriptions. Thus, $\Delta\epsilon$ is adjusted to essentially the same value in all prescriptions, leading to H^E values which are only marginally higher in the linear v dW and Flory prescriptions than in the quadratic v dW. On the other hand, the quadratic v dW with a significant negative value of $\Delta\sigma^3$ in V^E gives V^E predictions which are more negative than those of the other prescriptions, which it appears are closer to experiment. Liu and Miller^{22a} have measured V^E of the Ar + CH₄ system between 97 and 120°K, finding that it changes sign from positive to negative. If the Snider–Herrington theory is fitted to V^E at 97°K through adjustment of k_{12} the temperature variation of V^E is satisfactorily predicted. On the other hand, if the quadratic v dW theory is similarly fitted at 97°K the temperature dependence is found incorrectly to be extremely positive. This result is consistent with the $-9\eta^2 V$ term in the quadratic v dW prescription being incorrect, but compensated by the highly temperature dependent $+k_{12}T dV/dT$ term. But the superiority of the Snider–Herrington theory may only reflect an equation of state which is better than the empirical representation of argon data given in ref. 20, and which was used in the v dW prediction. The temperature dependence of V^E is in fact sensitive not only to the second derivative of V against T , but also to the third which is missing from the empirical equation of state. Perhaps an improved equation of state is the reason for the greater success of the quadratic v dW in light hydrocarbon systems.^{22b,c} However, the difficulty of choosing between the prescriptions points to the need for data on systems where η rather than δ is large.

Polyatomic mixtures. Two main groups of spherical molecule mixtures have been studied: (a) mixtures of cyclopentane, benzene, and CCl₄ with octamethylcyclotetrasiloxane (OMCTS),²³ (b) systems containing branched globular alkanes, cyclic alkanes and tetraalkyltin compounds. One should note in particular the very extensive series of papers by Ewing and Marsh²⁴ on mixtures of cyclic alkanes with other cyclic alkanes or with branched alkanes; the authors will use these results

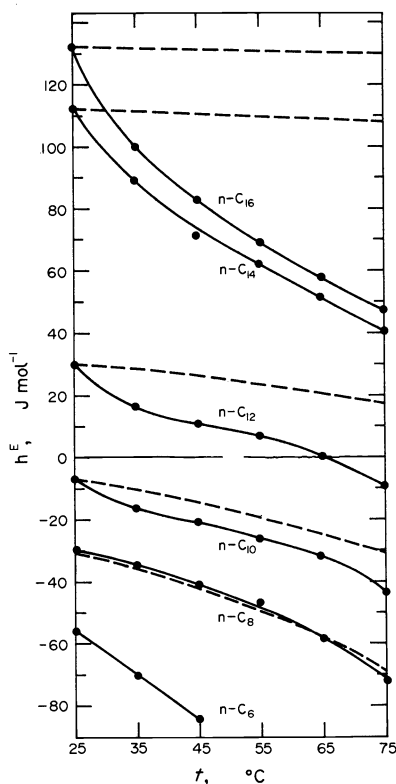


Fig. 3. The temperature dependence of the molar h^E of squalane + n -alkane systems. The squalane mole fractions, segment fractions are respectively as follows: n -C₁₆, 0.587, 0.720; n -C₁₄, 0.558, 0.723; n -C₁₂, 0.531, 0.728; n -C₁₀, 0.493, 0.731; n -C₈, 0.548, 0.804; n -C₆, 0.491, 0.808. The dashed lines give theoretical Δh_M using the Flory theory with X_{12} parameters fitted to the experimental values at 25°C. (For squalane + n -C₆ the theoretical curve coincided with the experimental and is not shown.)

to test the theories. Also interesting are mixtures of branched alkanes amongst themselves or with tetra-alkyltin compounds.²⁵ Here typical systems would be 2,2-dimethylbutane + Sn(C₄H₁₀)₄ or heptamethylnonane. The value of η can be very large for such systems. The parameter δ , as found empirically from the critical temperatures or thermal expansion coefficients of the components, is almost always of the same sign as η but considerably smaller. In Fig. 1, this would correspond to δ lying between zero and 0.1. The excess heats of these systems will be dominated by the contact energy dissimilarity term in eqn (19). For the Flory or linear v dW prescriptions, H^E will be positive and large due to the factor $(\delta - 2\eta)^2$ or $(\delta - 3\eta)^2$. On the other hand, the quadratic v dW prescription bringing in $\delta(\delta - 3\eta)$ predicts strongly negative H^E . In practice the heats are usually small and often negative. This would seem to indicate the superiority of the quadratic v dW prescription, since any deviation from the Berthelot rule will furnish a positive contribution to H^E . However, the quadratic v dW prescription again gives values of V^E which are usually much too negative, as seen in ref. 23. The conclusion to be drawn is, we believe, that these polyatomic molecules cannot be treated as spheres with only three degrees-of-freedom. One must take into account other external degrees arising from rotations and torsional oscillations within the molecule, making a total

of $3c$ external degrees-of-freedom. This is the approach taken by the Prigogine-Flory theory^{5,6} which has been applied to polymer solutions, and Marsh has shown²³ it to be successful with the OMCTS solutions. However, in polyatomic systems it now appears that other effects connected with molecular shape are of importance, and it is to these that we now turn.

EFFECTS OF MOLECULAR SHAPE IN SOLUTION THERMODYNAMICS

Two thermodynamic effects have been indicated so far, associated with dissimilarities between the contact energies and free volumes of the spherical molecule components. In the case of molecules of anisotropic shape, such as the normal alkanes there is now thermodynamic evidence for another contribution associated with the presence of orientational order, or a correlation of molecular orientations, in one or both of the components. In the cases investigated, having a *dissimilarity in orientational order* between components, there is a net destruction of order during mixing, with positive contributions in ΔH_M and ΔS_M . Work has been mainly on mixtures of alkanes of different size and shape,^{25,26} and mixtures of these alkanes with tetra-alkyltin compounds and also with a nematic liquid crystal,²⁷ *p*-methoxybenzylidene-*p*-*n*-butylalnine, (MBBA) where long-range order undoubtedly exists.

N -alkane mixtures have received much attention because of their apparent simplicity and also because they serve as models of polymer solutions. The heats of mixing are quite large and positive, e.g. for n -C₆ + n -C₁₆ at 25°C, the equimolar value of the molar $h^E = 111$ J mol⁻¹. The values of the h^E were explained by the older lattice theories, due to a weakness of contacts between supposedly dissimilar methyl chain-ends and methylene in-theories, as due to a weakness of contacts between supposedly requires the assumed contact energy contribution to be increased further to fit the experimental H^E , and in fact it appears unreal large when analysed^{25a} in terms of the methyl-methylene interaction. A new interpretation is required for the positive Δh_M of n -alkane systems.

Orientational order or correlation of molecular orientations

Bothorel and collaborators²⁸ have established depolarized Rayleigh scattering as a technique for studying the orientational order of liquids. They obtained apparent optical anisotropy values, γ^2 , for the n -alkanes^{28b} in the pure state and also in dilute solution amongst molecules of spherical shape, e.g. CCl₄, 2,2-dimethylbutane, cyclohexane, etc. For short n -alkanes, $n < 7$, the pure liquid and dilute solution γ^2 values are similar, but as the n -alkane chains become longer, there is a rapidly increasing difference. The lower dilute solution value could be interpreted in terms of the conformation of the n -alkane chains, but not the higher pure n -alkane value. Bothorel,^{28c} and independently Nagai,^{28c} suggested the value of γ^2 is enhanced due to orientational order in the pure liquids, i.e. a correlation of the molecular orientations (CMO) between neighbouring long n -C_{*n*} chains. This correlation should not occur between n -C_{*n*} and a spherical solvent molecule, so that the CMO in the pure liquid will correspond to the difference between the pure state and dilute solution values of γ^2 . Bothorel and collaborators propose a measure of orientational order in the pure state given by

$$J = \frac{\gamma^2(\text{pure})}{\gamma^2(\text{dil. soln. in spherical solvent})} - 1. \quad (26)$$

Alkane molecules with large n , but which are highly branched and hence globular in shape have^{28d} similar γ^2 values in the pure state and in dilute solution in CCl_4 or shorter n -alkanes. This indicates that the globular shape hinders the CMO of the molecules in the pure state and also in mixtures with n -alkanes.

From these experiments it appears that on mixing liquids of differing degrees of orientational order there is an overall decrease of order. Accompanying this there should be positive contributions to ΔH_M and ΔS_M . (An increase of order during mixing is possible but is probably not common.) Table 1 shows equimolar Δh_M at 25° for some systems made up of normal and branched C_6 and C_{16} isomers together with an estimate based on the Prigogine-Flory theory of the contribution to h^E from free volume dissimilarity of the components. Values of the orientational order parameters J of the pure component liquids are also listed as obtained through eqn (26), the spherical-molecule solvent being CCl_4 . Inspection shows the values cannot be interpreted by the free volume effect plus a conventional methyl-methylene interactional term. Instead, the results follow by assuming the interactional term to be negligible, the effect of branching being to change the molecular shape and thus the orientational order in the liquid. The system $n\text{-C}_6 + br\text{-C}_6$ gives essentially zero value of Δh_M , the free volume difference being ~ 0 , and neither liquid having significant orientational order. Both $n\text{-C}_6 + br\text{-C}_{16}$ and $br\text{-C}_6 + br\text{-C}_{16}$ have negative heats due to the free volume difference between the components. This contribution is outweighed for $n\text{-C}_6 + n\text{-C}_{16}$ and $br\text{-C}_6 + n\text{-C}_{16}$ by the endothermic destruction of orientational order in $n\text{-C}_{16}$. Finally, orientational order constitutes the only contribution in $br\text{-C}_{16} + n\text{-C}_{16}$.

Effect of temperature on orientational order

It is intuitively evident that the orientational order in a liquid should decrease with increase of temperature, bringing a corresponding decrease of that contribution in

Δh_M . Furthermore, one might expect the decrease to be rapid at low T , but to slow down at higher T . This effect can be seen in the heats of mixing²⁶ of squalane (a C_{24} with six methyl branches) with various n -alkanes shown in Fig. 2 as a function of T . In the case of squalane + $n\text{-C}_8$ there is little or no order in either of the components, but the free volume difference is large. The heat is thus negative, increasing in magnitude with T , and more rapidly the higher the temperature. On the other hand, the free volume difference between squalane and $n\text{-C}_{16}$ is small, and there is a large difference of orientational order. The heat is now positive, decreasing rapidly with temperature but more slowly at high T . The Δh_M of squalane + $n\text{-C}_{12}$ constitutes an intermediate case, the orientational order contribution prevailing at low T and the free volume contribution at high, so that an S-shaped curve results. In the case of squalane + $br\text{-C}_{16}$, (not shown in Fig. 3) the free volume contribution is small and the orientational order effect absent. Thus the heat is small, negative and independent of temperature. In each case, one can fit the X_{12} parameter of the Prigogine-Flory theory to the heat at 25°, and keeping it constant, predict $\Delta h_M(T)$. The prediction is good for squalane + $n\text{-C}_8$ and squalane + $br\text{-C}_{16}$, but fails for the other systems since it associates the temperature dependence of $\Delta h_M(T)$ with only the increasing dissimilarity of the free volumes of the components.

Molecular shape is clearly an important and sensitive parameter in determining the excess thermodynamic quantities. As an example, in Table 3, we give equimolar Δh_M values²⁹ at 25° for $n\text{-C}_6$ and $br\text{-C}_6$ mixed with C_{16} isomers including three methylpentadecanes and the globular 6-pentylundecane. It is clear that only one methyl branch on the long alkane chain greatly reduces Δh_M and the orientational order prevailing in the C_{16} liquid. Furthermore, as the methyl branch is moved toward the middle of the chain, there is a striking decrease of Δh_M . This indicates that 2-methylpentadecane with thirteen carbons between the methyl branch and the chain extremity is

Table 2. Contributions to h^E in alkane systems

	Equimolar h^E (J mol ⁻¹)	Free volume contribution (J mol ⁻¹)	$J(1)$	$J(2)$
$n\text{-C}_6 + 2,2\text{-dimethyl-}$ $\text{butane } (br\text{-C}_6)$	+7	-1	0.19	0
$n\text{-C}_6 + 2,2,4,4,6,8,8\text{-}$ heptamethylnonane $(br\text{-C}_{16})$	-67	-69	0.19	0.12
$br\text{-C}_6 + br\text{-C}_{16}$	-55	-85	0	0.12
$n\text{-C}_6 + n\text{-C}_{16}$	+110	-57	0.19	1.32
$br\text{-C}_6 + n\text{-C}_{16}$	+230	-71	0	1.32
$br\text{-C}_{16} + n\text{-C}_{16}$ (at $x_2 = 0.718$)	+238	-1	0.12	1.32

Table 3. Equimolar h^E (J mol⁻¹) with C_{16} isomers

	$n\text{-C}_6$	2,2-DMB	J^\dagger (C_{16})
$n\text{-C}_{16}$	110	230	1.32
2-methyl C_{15}	47	154	1.04
4-methyl C_{15}	25		0.85
6-methyl C_{15}	6	80	0.73
6-pentyl C_{11}	-42	-27	0.42
$br\text{-C}_{16}$	-67	-55	0.12

[†]Dilute solution measurement in CCl_4 ²⁹.

significantly more ordered than 6-methylpentadecane where the corresponding number of carbons is nine.

Small differences of shape connected with stereochemistry are important, as seen in the heats of mixing of C_{16} isomers with dimethylcyclohexanes³⁰ in Table 4. The equatorial-axial arrangement of the methyls leads to a greater disruption of the order in $n\text{-C}_{16}$ than does the equatorial-equatorial, an effect which is missing for mixtures containing the $br\text{-C}_{16}$. The heat of mixing 1, *trans* 4-dimethylcyclohexane with $n\text{-C}_{16}$ is *S*-shaped,

Table 4. Equimolar h^E ($J \text{ mol}^{-1}$) for dimethylcyclohexane isomers + C_{16} at 25°C

Dimethylcyclohexane isomer	Conformation of methyls	$h^E(n\text{-}C_{16})$ (J/mol)	$h^E(br\text{-}C_{16})$ (J/mol)
1, <i>cis</i> 2	ea	152	-30
1, <i>trans</i> 2	ee	54	-60
1, <i>cis</i> 3	ee	99	+14.5
1, <i>trans</i> 3	ea	235	+7.0
1, <i>cis</i> 4	ea	182	-6
1, <i>trans</i> 4	ee	+7	-51

being endothermic/exothermic at high/low $n\text{-}C_{16}$ concentration, thus indicating that a small amount of the dimethylcyclohexane is destroying a relatively large amount of order.

The excess heats of a large number of systems have been rationalized in terms of the contribution from orientational order, and more quantitatively, a correlation may be established between h^E and the difference of the J parameters for the two components.^{25a} So far there has not been much recent theory on mixtures of non-spherical molecules. Chambers and McDonald,³¹ however, have given a perturbation theory for polar fluids interacting through a Stockmayer potential, i.e. Lennard-Jones potential plus a point dipole term. A mixture of a polar with a non-polar component gives a positive contribution to G^E and a small positive effect in V^E . Qualitatively similar effects are to be found in the older theories of Cook and Rowlinson³² and Pople,³³ and are seen in the experimental data on mixtures of branched and normal alkanes.

Liquid crystals + solutes of different molecular size and shape²⁷

Thermodynamic data, nematic order parameters and the nematic-isotropic transition temperature all attest to the importance of molecular shape in influencing the interaction between nematogenic molecules and those of another component. Thus, heats may be obtained for the transfer of MBBA molecules from a reference solvent, 2,2,4,4,6,8,8-heptamethylnonane ($br\text{-}C_{16}$) into a second alkane. When the second alkane is another highly branched alkane or a normal alkane of low carbon number, the heat of transfer is zero, indicating all these alkanes are similar to the $br\text{-}C_{16}$ in not allowing correlation of molecular orientations with the MBBA. However, as the carbon number of the n -alkane is increased, the heat of transfer becomes increasingly negative due to the possibility of CMO between the MBBA and the n -alkane.

The order parameter, S , has been obtained from wide-line NMR measurements for pure MBBA and with MBBA containing small quantities (5%) of alkane solute. It has been found that for equal quantities of isomeric alkanes, the branched isomer decreases S to a greater extent than the corresponding normal isomer. In the same way, the nematic-isotropic transition temperature is depressed to a much greater degree by a highly-branched globular alkane than by the normal isomer. Again, the heats of transfer of normal alkane molecules from a reference solvent, toluene, into nematic MBBA are much less endothermic than for the branched isomers and for high n become exothermic. All of these results are consistent with the idea of a correlation of orientations taking place between long-chain normal alkanes and the MBBA.

Effects associated with coupling of torsional oscillations

The great variety of alkane isomers makes them convenient systems for investigating thermodynamic effects associated with molecular structure. Interesting differences occur between H^E values³⁴ of systems which contain branched alkanes of the same external molecular shape, but with different degrees of steric hindrance. Thus, Table 5 gives heats of mixing of $n\text{-}C_8$ and $n\text{-}C_{16}$ with $n\text{-}C_9$ and with five highly branched isomeric nonanes. Depolarized Rayleigh scattering studies³⁴ show the nonanes to be of essentially the same quasi-spherical shape, not to have any orientational order in the pure state, and also indicate that $n\text{-}C_8$ and $n\text{-}C_9$ molecules do not correlate their orientations with these highly branched nonanes, whereas there is a correlation of the orientations of these molecules with the normal C_9 . One would thus expect that the heats of mixing of $n\text{-}C_8$ or $n\text{-}C_{16}$ with the branched nonanes would all be similar and much larger than with normal nonane. Instead, a wide range of H^E values is found, depending on the degree of steric hindrance in the nonane. A consideration of molecular models shows that 2,3,3,4-tetramethylpentane, for instance, and 2,2,4,4-tetramethylpentane are both spheres. However, whereas the former nonane is essentially hindered and rigid, the latter allows a torsional oscillation of the two isobutyl hemispheres. This motion is reflected in the larger molar volume (and thermal expansion coefficient) of this alkane due to increased free volume, as seen in Table 4. The shape of the vibrational-rotational band³⁵ of a DCI solute in these nonanes varies in a completely analogous manner with the steric hindrance of the nonane and indicates a coupling of the DCI motion with the torsional modes of the nonanes. We believe that a similar coupling of motion between the two alkane components must be responsible for the variation of heats seen in Table 5, and suggest that negative heat, entropy and volume contributions occur when sterically-hindered molecules come into contact with molecules freer in motion, similar to a condensation of the latter onto the former.

Table 5. Equimolar h^E for $n\text{-}C_8$ and $n\text{-}C_{16}$ + quasi-spherical C_9 isomers

Nonane	$h^E(n\text{-}C_8)$ $J \text{ mol}^{-1}$	$h^E(n\text{-}C_{16})$ $J \text{ mol}^{-1}$	$V(25^\circ)$ $\text{cm}^3 \text{ mol}^{-1}$
$n\text{-}C_9$	0	60	
2,2,5-trimethylhexane	94	315	181.4
2,2,4,4-tetramethylpentane	38	237	178.3
2,2,3,4-tetramethylpentane	-3	150	173.6
2,3,3,4-tetramethylpentane	-57	72	169.9
3,3-diethylpentane	-83	16	170.2

It is most interesting that Mathot and Prigogine³⁶ in 1950 studied the $n\text{-C}_8 + 3,3\text{-diethylpentane}$ system in detail at 50°C, finding the equimolar h^E and Ts^E to be respectively -83 and -134 J mol^{-1} . The unexpected negative sign led the authors to suggest an effect involving the vibrational and rotational modes of interacting molecules which could be accessible to spectroscopic investigation.

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