

Interactions in Alkane Systems by Depolarized Rayleigh Scattering and Calorimetry

Part 1.—Orientational Order and Condensation Effects
in n-Hexadecane + Hexane and Nonane Isomers

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Molecular optical anisotropies (γ^2) have been obtained from depolarized Rayleigh scattering experiments on the 5 hexane isomers and 15 nonane isomers of widely varying degrees of branching. Values of γ^2 have also been obtained for these molecules at high dilution in carbon tetrachloride. The latter values reflect the anisotropies of the molecular shapes of the isomers while the pure state values also contain a contribution due to correlation of the orientations of neighbouring molecules. Thus, for highly branched, isotropic isomers, the pure and dilute solution γ^2 values are the same and are small. With increasing molecular anisotropy, the pure state value increases more rapidly than the dilute, the divergence reflecting the increasing correlation of molecular orientations. Values of γ^2 have been found for n-hexadecane at high dilution in the hexanes and nonanes. They increase with the anisotropy of the solvent molecules and yield increasing values of the J_{12} parameter, which characterizes the correlation of orientations of the n-hexadecane and solvent molecules. The J_{12} values are given approximately by the geometric mean, $(J_{11}J_{22})^{1/2}$, of the order parameters of the pure liquids, indicating that the mixing of two liquids results in a net destruction of orientational order, *i.e.*, $\Delta J_{12} = \frac{1}{2}(J_{11} + J_{22}) - J_{12}$ is positive. This change explains the variation in the heats of mixing of n-C₁₆ + hexane systems. Molar heats of mixing have been measured at 25°C through the concentration range for n-C₁₆ with 21 nonane isomers. With increasing nonane branching, Δh_M increases proportionally to ΔJ_{12} . However, when nonane isomers have high degrees of steric hindrance, *e.g.*, 3,3-diethylpentane or 2,3,3,4-tetramethylpentane, a new and large negative contribution is encountered in Δh_M . For example, Δh_M for n-C₁₆ + 3,3-diethylpentane is S-shaped and negative at high nonane concentrations. Values of Δv_M and Δs_M also contain negative contributions for the few systems studied. The effect resembles a "condensation" of the less hindered alkane onto the large sterically hindered nonane, similar to the condensation effect found in cholesterol + lipid systems.

Three effects contribute to the change in enthalpy and entropy during the mixing of two liquids whose molecules are quasi-spheres: (i) the energetic weakness of (1-2) contacts relative to the pure component (1-1) and (2-2) contacts which occur when the (1-1) and (2-2) contacts are of different strengths ($\epsilon_{11}^* \neq \epsilon_{22}^*$), (ii) the changes of volume which take place during the mixing of two components which differ in free volume, and (iii) the usual combinatorial, ideal entropy of mixing. Systems containing molecules of anisotropic shape, *e.g.*, n-alkanes, show another effect¹ associated with the presence of short range orientational order, or correlation of molecular orientations in one or both of the components. A net decrease in order

accompanies the mixing of components of different molecular anisotropy and hence different degrees of orientational order. The decrease in order manifests itself in positive contributions to Δh_M and Δs_M . The heats of mixing of a large variety of systems have now been interpreted in terms of orientational order. They involve normal and branched alkanes,^{1a, b} cyclohexane,^{1a, b} linear and cyclic dimethylsiloxanes,^{1c} tetra-alkyltin compounds,^{1d} etc.

The most interesting feature of the thermodynamic work has been the consistent correlation between the magnitude of the heat of mixing of a system and the difference in orientational order parameters of the two components as derived from depolarized Rayleigh scattering.² This technique obtains molecular optical anisotropy values, γ^2 , for anisotropic molecules, *e.g.* an n-alkane, in the pure state and also in dilute solution amongst molecules of spherical shape, *e.g.* CCl₄. For short n-alkanes, $n < 7$, the pure liquid and dilute solution values are similar, but as the n-alkane chains become longer, there is a rapidly increasing difference.^{2a} The lower, dilute solution value could be interpreted in terms of the conformations of the n-alkane chain, but not the higher pure n-alkane value. Bothorel^{2b} and Nagai³ suggested that the value of γ^2 is enhanced by orientational order in the pure liquid, *i.e.*, a correlation of the molecular orientations (CMO) between neighbouring long n-alkane chains. More recent work by Bothorel^{2c} and collaborators has shown that the CMO is absent or greatly reduced for highly branched alkanes, as expected from their globular molecular shape. A study^{2d} was also made of n-C₁₆ as solute in substituted cycloalkane solvents of increasing molecular anisotropy and, as expected, the CMO between solute and solvent was found to increase.

Kielich⁴ and Bothorel have introduced a semi-empirical parameter, J_{ij} , characterizing the correlation of orientations of neighbouring molecules i and j . The thermodynamic results¹ suggested that the contact energy required to break an ij contact should contain an orientational order contribution dependent on J_{ij} . Thus the interchange energy Δw_{12} , or in terms of more recent theory,^{1c} the parameter X_{12}/s_1 was considered to contain a contribution of the form:

$$(X_{12}/s_1) \text{ (orientational order)} = \text{constant} \times \Delta J_{12}. \quad (1)$$

Here

$$\Delta J_{12} = \frac{1}{2}(J_{11} + J_{22}) - J_{12} \quad (2)$$

and represents the net decrease during mixing of orientational order between segments. Making the tentative approximation that^{1a}

$$J_{12} \simeq (J_{11}J_{22})^{\frac{1}{2}} \quad (3)$$

ΔJ_{12} is seen to be a positive quantity related to the difference between the J parameters of the two liquids being mixed, *i.e.*

$$\Delta J_{12} = \frac{1}{2}(J_{11}^{\frac{1}{2}} - J_{22}^{\frac{1}{2}})^2. \quad (4)$$

Thus from eqn (1), X_{12}/s_1 and ΔH_M also contain positive contributions reflecting the difference in degree of orientational order between the two components.

This paper deals with isomers of hexane and nonane and their mixtures with n-C₁₆. Values of the thermodynamic quantities ΔH_M ,⁵ ΔS_M ⁶ and ΔG_M ⁶ are known for mixtures of n-C₁₆ (component 2) with the five hexane isomers (components 1) n-C₆, 2- and 3-methylpentane and 2,2- and 2,3-dimethylbutane. Excess functions are not available in the literature for nonane + n-hexadecane systems, and values of H^E have been obtained here through the concentration range using the Picker dynamic microcalorimeter. A three part programme was undertaken: (i) As values of J_{22} for pure n-C₁₆ are known,^{2c} we wished to obtain J_{11} values for the pure hexane

isomers and to correlate those values with the molecular shapes of the isomers. The expected trend would be decreasing J_{11} values with increasing branching. (ii) By studying the depolarized Rayleigh scattering of $n\text{-C}_{16}$ in the isomers, values of J_{12} may be obtained. These values should also be interpretable in terms of isomer shape, *i.e.*, J_{12} should decrease with increasing isomer branching. (iii) Finally, the excess thermodynamic quantities should be interpretable in terms of ΔJ_{12} corresponding to the change in orientational order during mixing.

Mathot's study⁷ of 3,3-diethylpentane + $n\text{-C}_8$ revealed a surprising negative excess heat at 50°C, -84 J mol^{-1} at equimolar concentration, together with a negative molar excess entropy, $Ts^E = -130 \text{ J mol}^{-1}$. Both h^E and s^E should be positive in view of the orientational order present in the $n\text{-C}_8$, but absent from the spherical molecule in liquid 3,3-diethylpentane. Any energetic weakness of the methyl-methylene contact would also lead to a positive sign for h^E in the 3,3-diethylpentane + $n\text{-C}_8$ system. Although the free volume contributions to h^E and Ts^E are negative, the magnitude of the effect is much too small to explain the experimental values, which thus appear to indicate a new thermodynamic effect. Mathot suggested a change in the internal degrees of freedom of one or both of the molecules owing to their interaction. Similar anomalous values of h^E should be found for 3,3-diethylpentane + $n\text{-C}_{16}$ and for $n\text{-C}_{16}$ with other compact, sterically hindered nonane isomers such as 2,3,3,4-tetramethylpentane. This was found to be so, and anomalous negative contributions to H^E also occur when other normal alkanes are mixed with such sterically hindered molecules. An important negative contribution to H^E occurs when a large sterically hindered molecule such as 3,3-diethylpentane or 2,3,3,4-tetramethylpentane comes into contact with a molecule of freer thermal motion, *e.g.*, $n\text{-C}_8$ or $n\text{-C}_{16}$. Similar negative contributions occur in V^E and S^E , and the effect appears as a "condensation" of the freer component onto the sterically hindered alkane.

DEPOLARIZED RAYLEIGH SCATTERING RELATIONS

The depolarized intensity i_{jj}^\oplus scattered from a volume V of pure liquid, j , is related to the apparent molecular optical anisotropy γ_{jj}^2 through^{2a}

$$i_{jj}^\oplus = K(n_j^{\oplus 2} + 2)^2 \rho_j^\oplus \gamma_{jj}^2 \quad (5)$$

with

$$K = \frac{16\pi^4 E^2 N V}{135\lambda^4}.$$

Here the pure liquid j may be a hexane or nonane, components 1 in a thermodynamic system, or $n\text{-hexadecane}$, termed component 2. ρ_j^\oplus is the number of moles per unit volume, n_j^\oplus , the refractive index of the liquid j at wavelength λ , N is Avogadro's number and E the incident photometric illumination. The intensity has at least two origins, the anisotropic form of the molecules and the correlation of orientations of neighbouring molecules. Hence, following Kielich and Bothorel, γ_{jj}^2 may be decomposed into two parts, γ_{j0}^2 , mainly due to the anisotropic form of the j molecule, and a correlational part $\gamma_{jj}^2 J_{jj}$, or

$$\gamma_{jj}^2 = \gamma_{j0}^2 (1 + J_{jj}). \quad (6)$$

We shall see below that γ_{j0}^2 corresponds to the optical anisotropy of molecules j at infinite dilution in component 0 whose molecules are of such a spherical shape as to preclude CMO. Recent work⁸ indicates that γ_{j0}^2 may in part be owing to molecular collisions or other "parasitic" effects. At present only the correlational contribution

to γ^2 and not the make-up of γ_{j0}^2 is of concern. If the "collisional" contribution to the total γ^2 value is the same in the pure j liquid as at infinite dilution in the solvent, then the difference $\gamma_{jj}^2 - \gamma_{j0}^2 = \gamma_{j0}^2 J_{jj}$ will remain purely correlational in origin.

Consider a mixture of molecules j and k , *e.g.*, $n\text{-C}_6 + n\text{-C}_{16}$, both of which are capable of CMO, there will be a total scattered intensity i of form ⁴

$$i = K(n^2 + 2)\rho\Gamma^2. \quad (7)$$

Here n is the refractive index of the solution, $\rho = \rho_j + \rho_k$ is the total number density, and Γ is an effective average anisotropy for the mixture. It is related to the mole fraction, x_j and x_k and the intrinsic anisotropies of the components, and also to the correlations between the mutual orientations of pairs of molecules of (j - j), (j - k) and (k - k) types. Kielich ⁴ writes

$$\Gamma^2 = x_j\gamma_{j0}^2 + x_k\gamma_{k0}^2 + x_j^2\gamma_{j0}^2J_{jj} + 2x_jx_k\gamma_{j0}\gamma_{k0}J_{jk} + x_k^2\gamma_{k0}^2J_{kk}. \quad (8)$$

anisotropic form + \longleftrightarrow correlational \longrightarrow
"collisional"

If $x_k = 0$, we recover eqn (6) for γ_{jj}^2 . An apparent molecular optical anisotropy γ_{jk}^2 may be obtained for the component j as a solute in component k . The formula used previously ^{2a} is analogous to formulae for other apparent molar properties of components in solution, *e.g.*, molar volume, and is given by

$$i = K(n^2 + 2)^2(\rho_j\gamma_{jk}^2 + \rho_k\gamma_{kk}^2). \quad (9)$$

Here γ_{kk}^2 may be found from i_k of the pure liquid k through relation (5). Thus the apparent γ_{jk}^2 is found from the total intensity i by subtracting the intensity contributed by the k component molecules which are considered to have their pure state anisotropy γ_{kk}^2 . Both j and k molecules are acted on by the solution internal field, bringing in the term $(n^2 + 2)^2$. Equating relations (7) and (9) using (8), we find for γ_{jk}^2 at infinite dilution of j in k ,

$$\gamma_{jk}^2 = \gamma_{j0}^2 - \gamma_{k0}^2 J_{kk} + 2\gamma_{j0}\gamma_{k0}J_{jk}. \quad (10)$$

From eqn (10) we see that the correlation parameter J_{jk} is given by

$$J_{jk} = \frac{(\gamma_{jk}^2 - \gamma_{j0}^2) + (\gamma_{kk}^2 - \gamma_{k0}^2)}{2(\gamma_{j0}^2\gamma_{k0}^2)^{\frac{1}{2}}}. \quad (11)$$

The quantities γ_{j0}^2 and γ_{k0}^2 are experimentally accessible as seen if one considers the case where solvent k is of particular type 0, such as CCl_4 , composed of spherical molecules unable to enter into correlations. In this case, eqn (10) may be used to obtain γ_{j0}^2 , the molecular anisotropy of solute j in the 0 solvent. Putting J_{00} and $J_{j0} = 0$, we recover the significance of γ_{j0}^2 as the optical anisotropy of j at infinite dilution in the spherical molecule solvent 0.

Flory and Patterson ^{8a} replace eqn (9) by another relation to obtain γ_{j0}^2 from the measured intensity of the solution. The relation, only applicable when the solvent is composed of spherical molecules, symbolized here by 0, is

$$i = K[(n^2 + 2)^2\rho_j\gamma_{j0}^2 + (n_0^{\oplus 2} + 2)^2\rho_0^{\oplus}\gamma_{00}^2]. \quad (12)$$

Here, γ_{j0}^2 is obtained from part of the total intensity found by subtracting the intensity scattered from a volume of pure liquid 0 equal to that of the whole solution. If $n_0^{\oplus} \simeq n_j^{\oplus}$, then

$$\gamma_{j0}^2[\text{eqn (12)}] = \gamma_{j0}^2[\text{eqn (9)}] - \gamma_{00}^2(V_1/V_0). \quad (13)$$

Eqn (12) represents an attempt to eliminate the "collisional" part of γ_{j0}^2 and this is

assumed equal to γ_{00}^2 for liquid 0, multiplied by the ratio of the molar volumes. The difference on the right hand side of eqn (13) is considered by Flory and Patterson to correspond to only the anisotropic form of the molecule. Further discussion of eqn (9) and (12) and their application is given in ref. (8b).

EXPERIMENTAL

MATERIALS

The normal and branched alkanes used here were from the Chemical Samples (Columbus, Ohio). Their stated purity was 99 % [except in the case of 2,2,3,4-trimethylpentane (98 %)] and tests by g.l.c. showed that purity was >99 %. The CCl_4 , cyclohexane and n-hexane used for light scattering experiments were from Prolabo (Paris) and of u.v. spectrometry grade. For the calorimetry, all solvents were filtered three times through a sintered glass funnel and degassed to obviate difficulties with the small teflon capillaries of the Picker microcalorimeter. For the light scattering measurements, all liquids were filtered over activated carbon (ACTIC 2S, S.C.C.A., Paris) to eliminate any fluorescent impurities. Fluorescence spectra were taken on some of the solutions at a wavelength of 5461 Å and verified the absence of fluorescence.

MOLECULAR OPTICAL ANISOTROPIES

The depolarized intensities scattered from the solutions or the pure liquids were measured with a "gamma-diffusometer", (Electronique appliquée, 33-Gradignan, France). A description of the instrument and its performance has been published previously.⁹ The source is a mercury arc (OSRAM HBO 200) and a filter was used to isolate the 5461 Å line. The measurements were made at $25 \pm 0.5^\circ\text{C}$. The solutions were prepared directly in the scattering cells. The two liquid components, purified as described above, were filtered through a sintered glass filter with a mean pore diameter of 1 μm . Four solutions in a range from 2 to 8 % composition were prepared for each system. The refractive index of the solution was taken to be the mole fraction average of the pure component values. The error made in such a way is still negligible in the final value of γ^2 when compared with the error made in the scattered intensities. Each solution was placed in the light path of an intense electric arc to verify that no dust was present. The precision on γ^2 is estimated to be from 3 to 5 %.

HEATS OF MIXING

The heats of mixing were obtained using the Picker dynamic microcalorimeter¹⁰ (Technurop, Montreal). The temperature was stabilized to $25 \pm 0.002^\circ\text{C}$ and the vacuum in the calorimeter chamber was held at 10^{-4} Torr with the help of a diffusion pump. The performance of the microcalorimeter was checked by measuring heats of mixing for the standard system cyclohexane+n-hexane at 25°C through the concentration range. The results compare to within 1 % with those of McGlashan and Stoeckli¹¹ as well as with our own values.

The reduction parameters V^* , T^* and P^* and the molecular surface/volume ratio, s are required for the application of the Prigogine-Flory theory¹² to the heats of mixing. The density data for the calculation of V^* and T^* were taken from the compilation by Dreisbach.¹³ The P^* and s parameters for n- C_6 , 2,2-dimethylbutane and n- C_{16} were taken from ref. (1a), while the P^* value for n- C_9 was interpolated between the values for other n- C_n and found to be 440 J cm^{-3} . The s parameter for that alkane was calculated in the usual way^{1a} to be 0.97 Å^{-1} . For the remaining branched alkanes, the P^* and s quantities were estimated to be (first entry, $P^*/\text{J cm}^{-3}$; second entry, $s/\text{Å}^{-1}$): 2-methylpentane (401; 0.96); 3-methylpentane (401; 0.96); 2,3-dimethylbutane (379; 0.88); the methyloctanes (400; 0.90); the dimethylheptanes (390; 0.85); the trimethylhexanes (380; 0.80); the substituted pentanes (380; 0.79). The X_{12}/s_1 parameter, calculated from the heat of mixing data using the Prigogine-Flory theory, is only slightly dependent on the choice of P^* and s values. One can show that the results which follow in the next section will be changed little, and the qualitative conclusions not at all, by different choices for these parameters.

RESULTS AND DISCUSSION

DEPOLARIZED RAYLEIGH SCATTERING

Column 1 of table 1 lists the thermodynamic systems studied, component 2 being n-hexadecane and component 1 a hexane or a nonane. Column 2 gives values of γ_{11}^2 for the pure hexanes and nonanes, as obtained from the scattered intensities through the use of eqn (5). The corresponding value for the pure n-C₁₆, *i.e.*, γ_{22}^2 , is 26.1 Å⁶. Column 3 of table 1 gives values of γ_{10}^2 for the nonanes and hexanes, these molecules being at high dilution in CCl₄. Here eqn (9) was used to obtain the molecular property from the scattered intensity. The corresponding value for n-C₁₆, *i.e.*, γ_{20}^2 , is 11.2 Å⁶. The value of γ_{j0}^2 was found to be independent of concentration between 3 and 8 % solute concentration. This effect, also found in previous work,^{2e} presumably indicates the requirement of a certain solute concentration before solute-solute correlation sets in.

For each set of isomers, as one ascends the table, the degree of branching decreases, *i.e.*, the molecules become less compact and, generally, more anisotropic. Accordingly, both γ_{11}^2 and γ_{10}^2 increase, the change being greater for the nonanes than for the hexanes. It is desirable to have quantities characteristic of the shapes of the isomers, *e.g.*, the three principal orthogonal components of the radius of gyration along the principal axes of inertia. These have been calculated by Solc^{14a} using random flight statistics for various categories of branched molecules, which however do not include all the present isomers. We have consequently taken the square of the radius of gyration, \overline{R}^2 , of the molecule as a rough measure of its shape, *i.e.*, the larger \overline{R}^2 the less compact the molecule and, usually, the more anisotropic. Values of this parameter have been calculated by Altenburg^{14b} using an assumption of free rotation around carbon-carbon bonds and neglecting the hydrogens. In spite of the simple assumptions, \overline{R}^2 is useful in comparing the shapes of the isomers. Fig. 1 shows γ_{11}^2 and γ_{10}^2 for the nonanes plotted against \overline{R}^2 . Similar curves are found for the hexanes. Fig. 1 and table 1 show that γ_{10}^2 increases with increasing anisotropy of the nonane shape. The γ_{11}^2 quantity starts by being equal to γ_{10}^2 for very isotropic molecules, but then diverges upwards. This corresponds to increasing orientational order in the nonane liquids. The J_{11} parameter characterizes CMO in the liquids and is related by eqn (6) to the $\gamma_{11}^2 - \gamma_{10}^2$ difference. Values are not listed in table 1, but it is clear that they start from zero and increase with the anisotropy of molecular shape.

We calculated the contribution to γ_{10}^2 using the Flory-Patterson assumption, *i.e.*, that γ_{10}^2 (collisional) = $\gamma_{00}^2 (V_1/V_0)$, as given by eqn (13). For CCl₄ we found $\gamma_{00}^2 = 1.53$ Å⁶. Since V_1 is similar for the hexane and nonane isomers, the collisional contributions to γ_{10}^2 are respectively 2.1 and 2.8 Å⁶ for the hexanes and the nonanes. Subtracting these values from the γ_{10}^2 in table 1 should leave the contribution due to the anisotropic form of the molecule. This is negative for 2,2- and 2,3-dimethylbutane and 3,3-diethylpentane, presumably indicating that the estimate for the "collisional" contribution is too large. A similar experience was encountered in ref. (8b) where the application of the Flory-Patterson equation led to a negative value of γ_{10}^2 for n-pentane.

Values of γ_{21}^2 are given in column 4 for n-C₁₆ at high dilution in the nonanes and hexanes, again obtained using eqn (9). The values are plotted in fig. 1 against \overline{R}^2 of the solvent nonane. Again, as the isomer becomes more anisotropic, *i.e.*, ascending the table or with increasing \overline{R}^2 , the values of γ_{21}^2 increase, indicating higher CMO between the n-C₁₆ molecules and those of the isomer.

TABLE 1.—DEPOLARIZED RAYLEIGH SCATTERING AND CALORIMETRIC DATA FOR ALKANE SYSTEMS

| | $\gamma_{11}^2/\text{\AA}^6$ | $\gamma_{10}^2/\text{\AA}^6$ | $\gamma_{21}^2/\text{\AA}^6$ | J_{12} | $c_0/\text{J mol}^{-1}$ | $c_1/\text{J mol}^{-1}$ | $c_2/\text{J mol}^{-1}$ | $c_3/\text{J mol}^{-1}$ | $(\chi_{12}^{(s)})/10^{-8} \text{ J cm}^{-2}$ |
|------------------------------------|------------------------------|------------------------------|------------------------------|----------|-------------------------|-------------------------|-------------------------|-------------------------|---|
| n-C ₉ (component 2) + | | | | | | | | | |
| n-C ₉ (component 1) | 7.9 | 4.6 | 21.2 | 0.93 | 242.25 | 10.40 | 12.98 | -6.62 | 1.55 |
| 2-methyl-C ₈ | 6.7 | 4.6 | 20.0 | 0.75 | 414.16 | -2.28 | 57.86 | -1.43 | 2.83 |
| 3-methyl-C ₈ | 5.7 | 4.0 | 18.3 | 0.66 | 448.03 | -9.89 | 75.79 | 1.30 | 3.00 |
| 4-methyl C ₈ | 5.4 | 3.9 | 18.2 | 0.64 | — | — | — | — | — |
| 3-ethyl C ₇ | — | — | — | — | 598.56 | -0.129 | 73.17 | 9.80 | 4.06 |
| 4-ethyl-C ₇ | — | — | — | — | 591.10 | -8.94 | 66.37 | 32.08 | 4.00 |
| 2,2-dimethyl C ₇ | 4.5 | 3.8 | 18.1 | 0.60 | 745.75 | 102.89 | 167.03 | 31.83 | 5.35 |
| 2,3-dimethyl C ₇ | 4.6 | 3.7 | 17.1 | 0.53 | 594.73 | -8.55 | 111.50 | 29.17 | 4.00 |
| 2,4-dimethyl C ₇ | 4.4* | 3.9* | 16.7* | 0.45* | 738.20 | -15.59 | 126.19 | 46.54 | 5.00 |
| 2,5-dimethyl C ₇ | 4.7* | 4.0* | 17.0* | 0.48* | 806.25 | 8.51 | 121.56 | 6.86 | 5.44 |
| 2,6-dimethyl C ₇ | 5.2 | 4.4 | 17.7 | 0.53 | 692.67 | -6.32 | 123.92 | 41.95 | 4.72 |
| 3,4-dimethyl C ₇ | 4.0 | 3.4 | 15.7 | 0.41 | 628.20 | -35.66 | 136.37 | -56.38 | 4.22 |
| 3,5-dimethyl C ₇ | 4.2 | 3.5 | 16.3* | 0.45* | 773.24 | 68.12 | 144.24 | -41.41 | 5.21 |
| 4,4-dimethyl C ₇ | 3.8* | 3.5* | 15.6* | 0.37* | 732.87 | -21.59 | 125.91 | -3.09 | 4.94 |
| 2,2,4-trimethyl C ₆ | 3.5 | 3.3 | 14.7 | 0.31 | 774.96 | 11.17 | 150.41 | 21.00 | 4.69 |
| 2,2,5-trimethyl C ₆ | 3.8 | 3.5 | 15.4 | 0.36 | 1266.35 | 49.52 | 214.36 | 115.29 | 7.65 |
| 2,3,4-trimethyl C ₆ | 3.8 | 3.3 | 15.1 | 0.35 | 533.60 | -4.40 | 45.93 | 23.80 | 3.26 |
| 2,2,3,3-tetramethyl C ₅ | 2.8* | 2.8* | 13.9* | 0.24* | 529.82 | 5.58 | 32.67 | 44.37 | 3.65 |
| 2,2,3,4-tetramethyl C ₅ | 3.0* | 3.0* | 14.3* | 0.26* | 602.75 | 33.59 | 174.91 | 136.05 | 4.17 |
| 2,2,4,4-tetramethyl C ₅ | 2.9 | 2.9 | 14.5* | 0.29* | 940.63 | 121.80 | 334.44 | 147.05 | 6.54 |
| 2,3,3,4-tetramethyl C ₅ | 3.0 | 3.0 | 15.0 | 0.26 | 314.10 | -63.00 | -0.146 | 11.12 | 1.54 |
| 3,3-diethyl C ₅ | 2.5 | 2.5 | 14.0 | 0.26 | 73.30 | -102.34 | -35.86 | -77.62 | 0.51 |
| n-C ₆ | 3.4 | 2.9 | 18.9 | 0.71 | 454.24 | -18.83 | 49.94 | — | 4.66 |
| 2-methyl C ₅ | 2.6 | 2.6* | 17.1 | 0.54 | 736.57 | -12.52 | -16.76 | — | 7.08 |
| 3-methyl-C ₅ | 2.3 | 2.3* | 16.6 | 0.52 | 678.16 | 8.69 | 63.41 | — | 6.56 |
| 2,2-dimethyl C ₄ | 1.5 | 1.5* | 14.9 | 0.44 | 927.42 | 118.75 | 153.95 | — | 9.26 |
| 2,3-dimethyl-C ₄ | 2.0 | 2.0* | 16.0 | 0.51 | 751.55 | 19.62 | -30.81 | — | 7.50 |

* Values obtained by interpolation of the experimental data of fig. 1.

Table 1 also shows that γ_{21}^2 increases from n-C₆ to n-C₉, indicating the greater CMO of n-C₁₆ with longer alkane solvent chains. We obtained a γ_{21}^2 value of 25.0 Å⁶ for n-C₁₆ in n-C₁₂. The value of γ_{22}^2 for pure n-C₁₆, *i.e.*, γ_{21}^2 for n-C₁₆ in n-C₁₆, is again higher, 26.1 Å⁶. Thus, γ_{21}^2 of n-C₁₆ with n-alkane solvents increases monotonically between n-C₆ and n-C₁₆, but the rate of increase probably falls off towards n-C₁₆.

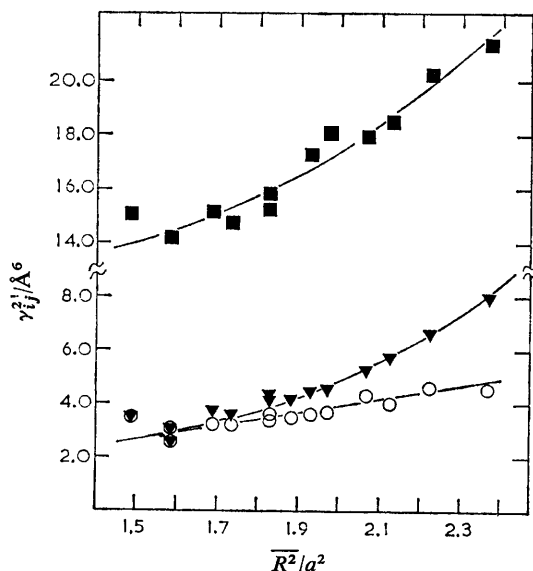


FIG. 1.—Molecular optical anisotropy data for nonane isomers against the (radius of gyration/carbon bond length)²: O, γ_{10}^2 , the values for the isomers at high dilution in CCl₄; ▼, γ_{11}^2 , for the pure nonanes; ■, γ_{21}^2 , for n-C₁₆ at high dilution in the nonane isomers.

A direct measure of the CMO between n-C₁₆ and the nonane and hexane isomers is afforded by the J_{21} parameter (or J_{12} since it must be symmetrical). Table 1 lists values calculated for the 1-2 pairs using eqn (11). With increasing anisotropy of the isomers there are increasing J_{12} values and hence increasing CMO with the n-C₁₆. Values of J_{12} for n-C₁₆ in highly spherical nonane and hexane isomers are low, but not zero, apparently indicating some CMO between n-C₁₆ and these molecules. This would seem unlikely, and we find that the non-zero values depend on the selection of CCl₄ as the "spherical molecule" solvent. The use of 2,2-dimethylbutane or 3,3-diethylpentane would reduce these values to essentially zero. A further possibility is that the Kielich relation (11) gives values of J_{12} which are too large. However, our qualitative conclusions are independent of whether there is a zero, or only a low, degree of ordering between n-C₁₆ and the spherical nonanes and hexanes.

The CMO of the (1-2) pair relative to (1-1) and (2-2) pairs is of importance for the interpretation of the thermodynamics of the (1-2) mixtures. Therefore ΔJ_{12} as defined in eqn (2) was determined and found to be positive in every case, *i.e.*, there is a net decrease of CMO on mixing liquids of different degrees of CMO. Thus the contribution of orientational order to ΔH_M and ΔS_M should be positive. More quantitatively, one can compare experimental values of J_{12} with values obtained through the approximation that J_{12} is the geometric mean of the corresponding parameters in the pure liquids, given by eqn (3). Fig. 2 shows a plot of J_{12} against

$(J_{11}J_{22})^{\frac{1}{2}}$. The agreement is reasonable, and hence we conclude that eqn (1) for X_{12}/s_1 should give good results, as it has for many systems studied previously.

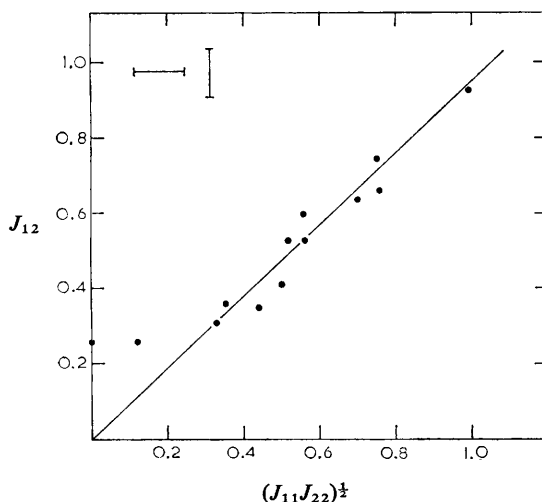


FIG. 2.—Values of the J_{12} parameter characterizing the correlation of molecular orientations between n-C₁₆ and the nonane isomers plotted against approximate values given by the geometric mean of the corresponding parameters of the pure components.

HEATS OF MIXING

The Redlich–Kister equation

$$\Delta h_M = x_1 x_2 \sum_{i=0} c_i (x_1 - x_2)^i \quad (14)$$

was fitted to the molar heats at the different concentrations, ~25 points being used. The standard deviation was calculated in each case, and ranged from 0.22 to 1.2 J mol⁻¹. Table 1 gives values of the c_i constants for the n-C₁₆ heats of mixing data obtained here, and also from the ΔH_M data published⁵ by Scott and coworkers for the hexane + n-C₁₆ systems. The equimolar Δh_M value is given by $c_0/4$, while the slope of $\Delta h_M/x_1 x_2$ against x_2 is $-2c_1$. Thus c_1 gives the dependence of the Δh_M curve on mole fraction. The table also gives values of the X_{12}/s_1 parameter, as calculated from the equimolar value of Δh_M , using the Prigogine–Flory theory.¹² This parameter is similar to the interchange energy between segments, but is obtained from the heat of mixing with the (negative) free volume contribution eliminated. The free volume contribution is small, however, and for any set of isomers is essentially constant. Thus the variation with the system of the equimolar Δh_M and X_{12}/s_1 should be similar.

THE HEXANE SYSTEMS AND ORIENTATIONAL ORDER EFFECT

Descending the list of hexane systems, the isomer becomes more spherical in shape. The γ_{21}^2 and J_{12} decrease accordingly while ΔJ_{12} increases, showing that there is an increasing destruction of order on mixing the isomers with n-C₁₆. In table 1, both $c_0/4$, i.e. the equimolar Δh_M , and X_{12}/s_1 increase in the expected manner. More quantitatively, one can plot Δh_M or X_{12}/s_1 against γ_{21}^2 , J_{12} or ΔJ_{12} . The error is greatest in ΔJ_{12} , but this is the quantity most closely related to the decrease of order during mixing. Values of the equimolar Δh_M of the five hexane + n-C₁₆ systems are

plotted against ΔJ_{12} in fig. 3. In spite of the inevitably low accuracy of ΔJ_{12} , the correlation is reasonable and indicates that the origin of Δh_M lies in the change of orientational order during the mixing process. Thus, the change is larger for 2,2-dimethylbutane than for $n\text{-C}_6$ corresponding to its more spherical shape. However, one would expect the line of Δh_M against ΔJ_{12} to pass through the origin, and the value of ΔJ_{12} for the $n\text{-C}_6$ system is presumably too low, reflecting values of J_{12} which are slightly too high. A more acceptable result would be obtained by changing the spherical molecule solvent 0 from CCl_4 to 2,2-dimethylbutane. However, as mentioned above, the elevated J_{12} values may be due to an inadequacy of eqn (11).

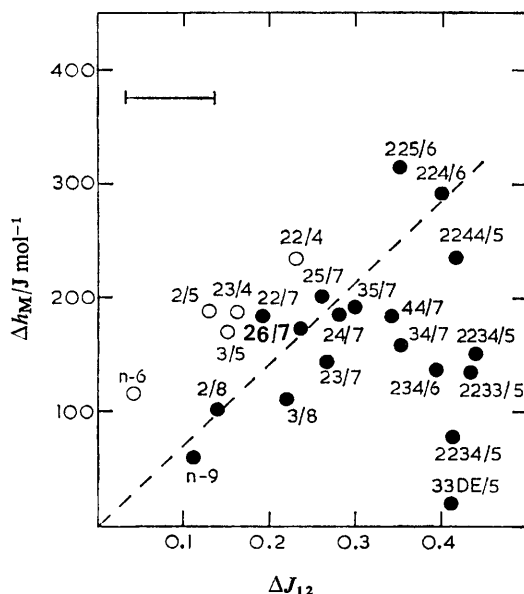


FIG. 3.—The equimolar values of the molar heat of mixing of hexane (○) and nonane isomers (●) with $n\text{-C}_{16}$ against the decrease of orientational order parameter ΔJ_{12} . The alkanes are identified by the positions of the methyl substituents/number of carbons in the main chain.

The concentration dependence of the heat of mixing might also be expected to reflect the orientational order origin of Δh_M . The regular solution theory for mixtures of equal sized molecules predicts symmetry of the molar heat in mole fraction. On the other hand, when there is a molecular size difference between the components, one expects symmetry of the heat/volume in the volume fraction or in the very similar segment fraction used by the Prigogine-Flory theory. If $\Delta h_m/(x_1 V_1 + x_2 V_2)$ is symmetrical in the volume fraction $\phi = x_1 V_1/(x_1 V_1 + x_2 V_2)$, then one finds from eqn (14) that

$$\frac{c_1}{c_0} = \frac{V_2 - V_1}{V_1 + V_2}. \quad (15)$$

In the case of the hexane + $n\text{-C}_{16}$ systems, eqn (15) gives a value of +0.381 for the c_1/c_0 ratio, while for the nonane + $n\text{-C}_{16}$ systems, the corresponding value is +0.242. Inspection of the c_0 and c_1 columns in the table shows that for all of the systems, c_1/c_0 is less than these values or negative, indicating that the heat of mixing/volume

curve is skewed toward the hexadecane side of the volume fraction range. This is typical behaviour for mixtures of *n*-alkanes at 25°C where the molar heats of mixing are symmetrical in mole fraction rather than volume fraction. Such a skewing of the curves toward the hexadecane side would be expected if the *n*-C₁₆ were ordered to some extent cooperatively, so that the perturbation due to adding another component would be relatively greater at high hexadecane concentration than at low.

More precisely, the Prigogine-Flory theory indicates that after elimination of the free volume contribution to Δh_M , the remaining "interactional" term should be symmetrical in the molecular surface fraction. (For components of similar molecular surface/volume ratio, the molecular surface fraction and the volume or segment fraction would be similar.) If the Prigogine-Flory theory is correct, then the X_{12} or X_{12}/s_1 parameter should be independent of the composition. Fig. 4 shows that X_{12} for the hexane + hexadecane systems varies considerably with the composition, being larger at high hexadecane concentration. A similar behaviour is found for the nonane + hexadecane systems, and is consistent with the orientational order origin of X_{12} . However, in the cyclohexane + *n*-C₁₆ and the squalane + *n*-C₁₆ systems,^{1a, b} the heats of mixing are highly symmetrical in volume fraction, yet they are only interpretable in terms of orientational order in the *n*-C₁₆. Our conclusion there was that the concentration dependence of Δh_M was not affected by orientational order which had to be considered as short range in character rather than long range and cooperative. Subsequently, heats of mixing symmetrical in volume fraction were observed^{1c} with dimethylsiloxane + *n*-C₁₆, but skewed curves were found^{1d} with tetra-alkyltin compounds + *n*-C₁₆. In view of this, we conclude that, whereas the magnitude of the heat of mixing is related simply to orientational order, its concentration dependence is not.

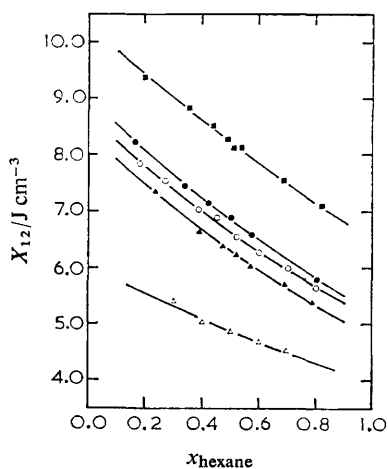


FIG. 4.—The heat of mixing parameter X_{12} for hexane isomer + *n*-C₁₆ systems as a function of hexane mole fraction. Alkanes identified as in fig. 3, from top to bottom: ■ 2, 2/4; ● 2/5; ○ 2, 3/4; ▲ 3/5; △ *n*-6.

THE NONANE SYSTEMS AND THE CONDENSATION EFFECT

The nonane + *n*-C₁₆ data in the table show that there is an increase in the equimolar Δh_M , i.e., $c_0/4$, and of the parameter X_{12}/s_1 in passing from *n*-C₉ to the two methyl-octanes, and another increase in the two parameters on going to the substituted heptanes. This corresponds to the behaviour found with the hexanes + *n*-C₁₆ and

is expected. However, for the group of trimethylhexanes, a further increase in equimolar Δh_M and X_{12}/s_1 does not occur, except for 2,2,5-trimethylhexane which, of all the nonanes, gives the highest values of Δh_M and X_{12}/s_1 . With the substituted pentanes the values of Δh_M and X_{12}/s_1 apparently become randomly scattered. In particular, 3,3-diethylpentane is the nonane of most spherical shape, and it would be expected most to disorder the n-C₁₆, giving the highest values of Δh_M or X_{12}/s_1 . Instead, the equimolar value of Δh_M is the lowest of the systems, the heat becoming negative at high nonane concentration. The equimolar value of X_{12}/s_1 is nearly zero, and the value at high nonane concentration is negative, whereas this parameter is expected to be positive in non-electrolyte systems. Similarly, the 2,3,3,4-tetramethylpentane system has the next lowest value of X_{12}/s_1 , yet the 2,2,4,4-tetramethylpentane system behaves normally and its X_{12}/s_1 value is the second highest of all the nonane values. This unexpected behaviour is emphasized by a plot of equimolar Δh_M against ΔJ_{12} similar to that for the hexane + n-C₁₆ systems. Fig. 3 for the nonanes shows that the correlation between Δh_M and ΔJ_{12} is only successful for the isomers with low degrees of branching. For high degrees of branching, *i.e.*, the substituted hexanes and pentanes, the heats generally fall far below the straight line dependence set up by the other nonanes. Inspection shows that low Δh_M values are associated with adjacent methyl groups on the alkane chain as in the substituted pentanes except for 2,2,4,4-tetramethylpentane, or where two ethyl groups are on the central carbon (3,3-diethylpentane). This corresponds to steric hindrance in the isomer. The differences can be made clear by building molecular models where 2,3,3,4-tetramethylpentane appears as a "hard sphere" with little internal motion, whereas in 2,2,4,4-tetramethylpentane the two isobutyl groups librate more freely. In the systems showing low Δh_M values, the ΔJ_{12} values are still large, indicating that the order of the n-C₁₆ is destroyed as expected from the spherical shape of the nonanes. However, the corresponding large positive contribution to Δh_M is counter-balanced by a hitherto unsuspected negative contribution which must be associated with steric hindrance in the nonane.

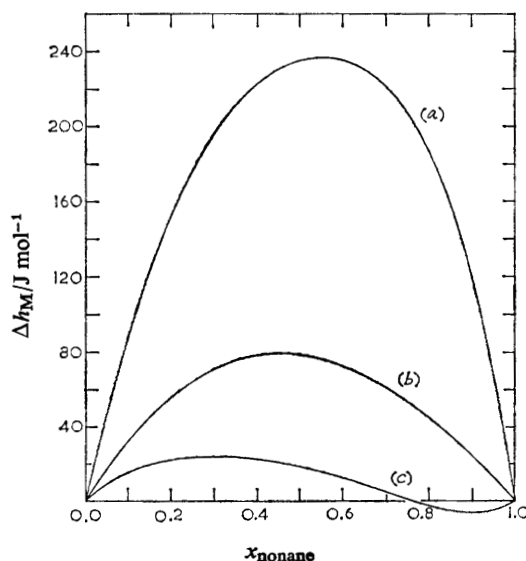


FIG. 5.—The molar heats of mixing for (a) 2,2,4,4- and (b) 2,3,3,4-tetramethylpentane and (c) 3,3-diethylpentane, spherical nonanes of different degrees of steric hindrance, mixed with n-C₁₆.

The conclusion that there is another, negative contribution to Δh_M is reinforced by a consideration of the concentration dependence of the heats shown in fig. 5, where the 2,2,4,4-tetramethylpentane + n-C₁₆ system appears to be normal, but as steric hindrance of the nonane increases there is a decrease in Δh_M , reaching an S-shaped concentration dependence for the 3,3-diethylpentane system. The negative contribution apparent there at high nonane concentration is not the usual free volume contribution which as calculated by the Prigogine-Flory theory is very small, *i.e.*, only -0.7 J mol^{-1} at a 3,3-diethylpentane mole fraction of 0.9.

Steric hindrance within the molecule has a marked effect on the macroscopic properties of the liquid, in particular the equation of state quantities such as the molar volume and thermal expansion coefficient. One expression of this is the conformational rule¹⁵ which states that the isomer which has the highest enthalpy also has the lowest molar volume, *i.e.*, steric hindrance lowers the stability of the molecule increasing the enthalpy, and it also decreases the molar volume. This,

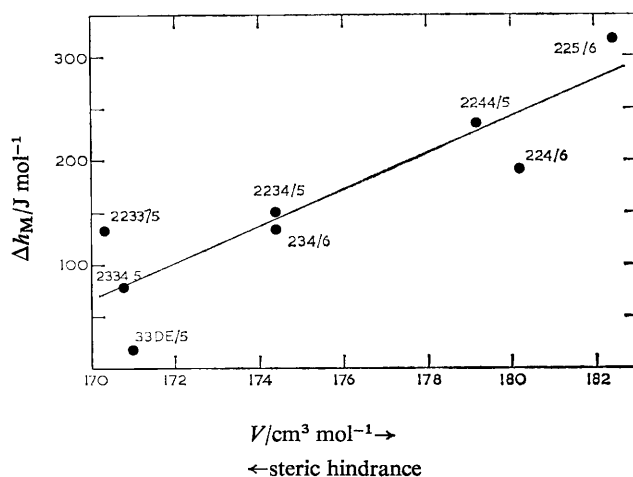


FIG. 6.—Equimolar heats of mixing for trimethylhexanes and tetramethylpentanes with n-C₁₆ against the nonane molar volume. Alkanes identified as in fig. 3.

together with arguments based on the Prigogine-Flory theory of the equation of state, suggests that the molar volume is indicative of the degree of steric hindrance in the isomer. We have accordingly plotted the equimolar Δh_M for n-C₁₆ with the substituted hexanes and pentanes against the molar volumes of these nonane isomers at 25°C (fig. 6). These systems all have similar values of ΔJ_{12} . Hence the orientational order in the n-C₁₆ is destroyed to a similar extent, producing the same endothermic effect. The correlation shown in fig. 6 indicates that the very different heats for these systems arise from negative contributions to Δh_M due to different degrees of steric hindrance in the nonane isomers.

Exothermic contributions are also present for mixtures of these nonanes with n-C₈.¹⁶ For instance, the equimolar Δh_M of 2,2,5-trimethylhexane + n-C₈ is $+95 \text{ J mol}^{-1}$ at 25°C while the corresponding value for 3,3-diethylpentane is -83 J mol^{-1} . At 50°C, Mathot found a very similar value, -84 J mol^{-1} . Other nonane + n-C₈ systems have been studied and a correlation again exists between Δh_M and the molar volume of the nonane.

Mathot⁷ found a negative value of Ts^E for the 3,3-diethylpentane + n-C₈ system

at 50°C. Equimolar values of V^E have been determined¹⁶ at 25°C for 2,2,5-trimethylhexane + n-C₈ (+0.058 cm³ mol⁻¹) and 3,3-diethylpentane + n-C₈ (-0.155 cm³ mol⁻¹). The negative values of H^E , S^E and V^E associated with the 3,3-diethylpentane + n-C₈ system suggest a "condensation" of the normal alkane with its relatively free internal motion onto the sterically hindered nonanes. The mechanism of this "condensation" is still not clear, but a coupling of the modes of the molecules of the two components, as originally suggested by Mathot and Prigogine, may be involved. We believe that the "condensation" interaction is of wide occurrence, and preliminary experiments indicate its existence in other systems where the sterically hindered molecule is a large cycloalkane or a rigid plate such as cholesterol. It is well known that a similar condensation interaction takes place between lipids and cholesterol¹⁷ or between lipids and the globular protein, rhodopsin.¹⁸

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