Effects of Orientational Order in Solution Thermodynamics: Mixtures Containing a Liquid Crystal

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Summary The thermodynamic properties, nematic order parameters and nematic–isotropic transition temperatures of *p*-methoxybenzylidene-*p*-n-butylaniline (MBBA)–alkane systems are highly sensitive to the alkane shape and indicate that MBBA molecules correlate their orientations with normal, but not with highly branched isomers.

Thermodynamic evidence has recently been given[1] for the presence of a short-range orientational order, or correlation of molecular orientations, in the liquid phase of long-chain n-alkanes. The existence of such a correlation of orientations is revealed by heat and entropy effects associated with the loss of order when the n-alkane is mixed with a second component composed of molecules of more isotropic shape, *e.g.* alkanes of different degrees of chain branching. The correlation of molecular orientation is analogous to, but much weaker than, the ordering in liquid crystals, and to extend our studies from short- to long-range ordering effects on solution thermodynamics, we have examined mixtures of normal and branched alkanes with the nematic liquid crystal *p*-methoxybenzylidine-*p*-n-butylaniline (MBBA).

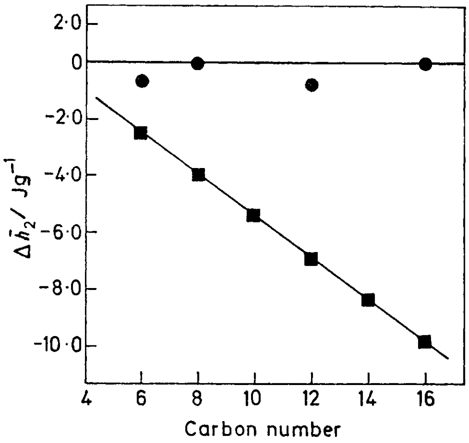

Figure 1. The heats of transfer for MBBA + alkane systems plotted against the alkane carbon number. (■) n-alkanes, (●) branched alkanes.

Heats of solution were obtained at 25 °C for mixtures of MBBA with normal alkanes C_nH_{2n+2} where n = 6, 8, 10, 12, 14 and 16 and with the following branched chain alkanes: 2,2-dimethylbutane, 2,2,4-trimethylpentane, 2,2,4,6,6-pentamethylheptane and 2,2,4,4,6,8,8-heptamethylnonane. A heat of transfer, $\Delta\bar{h}_2$,† can be obtained which corresponds to the enthalpy change for transferring MBBA molecules at essentially infinite dilution from a reference alkane into another alkane. The heptamethylnonane was selected as the reference alkane since this compound does not show any correlation of molecular orientation in its pure state.[1] The heats of transfer are shown in Figure 1 as a function of the carbon number. Values of $\Delta\bar{h}_2$ for the branched alkanes are virtually zero, thus the local environments in the branched alkanes are similar and little or no orientational ordering occurs. However, on transferring from heptamethylnonane to n-hexadecane a large negative $\Delta\bar{h}_2$ is obtained, showing that MBBA can correlate its molecular orientations with the long-chain alkane with a consequent lowering of the energy. $\Delta\bar{h}_2$ decreases with decreasing chain length of the n-alkane, as would be expected, since the correlation of orientations is less probable with shorter chains. This dependence of the molecular correlation upon chain length has also been observed in the pure n-alkanes using depolarised Rayleigh scattering methods.[2]

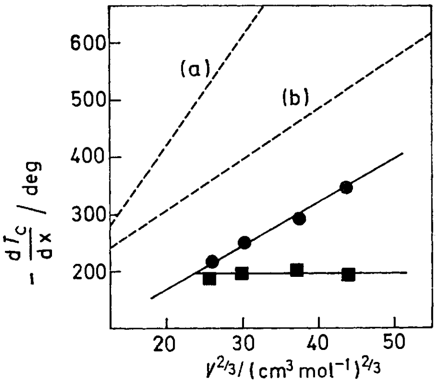

Figure 2. The depression of the transition temperature per alkane mole fraction plotted against the molar volume of the alkane to the 2/3 power. (a) Lattice model, (b) virial expansion. (■) n-alkanes, (●) branched alkanes.

The order parameter, S, has been obtained from wide-line n.m.r. measurements for pure MBBA and MBBA doped with small (5 mole %) quantities of alkane solute.[3] 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. This difference is enhanced with increase of the carbon number. Correspondingly, the heats of transfer of alkanes into MBBA from a reference solvent show that the value for the normal isomer is much less endothermic than for the branched isomer.[4] Both of these results are consistent with the idea of a correlation of orientations taking place between the long-chain n-alkane and the MBBA.

Figure 2 shows the dependence of the nematic–isotropic transition temperature as a function of the molar volume

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† $\Delta\bar{h}_2$ is defined as $\{\bar{h} - h^{\bullet}(n)\}_{\text{alkane}} - \{\bar{h}_2 - h^{\bullet}(n)\}_{\text{br-C}_{16}}$ where $\bar{h}_2 - h^{\bullet}(n)$ is the enthalpy change in taking MBBA from its pure nematic state, $h^{\bullet}(n)$, to one of essentially infinite dilution in the solvent, $\bar{h}_2$. This quantity is obtained from the measured heats of solution as a function of composition; h is used to denote molar enthalpy.

of the solute.‡ The striking difference between normal and branched alkanes is very apparent in the observation that the branched alkanes reduce the transition temperature, on a per mole basis, to a much greater degree than the corresponding linear alkanes. The branched alkanes do not correlate their molecular orientations, and therefore are more effective in destroying the long-range order of the nematic solvent. Theoretical predictions based both upon a lattice model of mixtures of hard rods and cubes[5] and a virial expansion of hard spheres and spherocylinders[6] are also shown in Figure 2. Both of these models involve repulsive forces only. Considering their simplicity, the agreement is encouraging for those molecules which do not correlate their orientations. The introduction of an anisotropic attractive potential could possibly lead to an improvement in the case of the linear chains.

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‡ The 2/3 power in the molar volume indicates the importance, for the transition, of the two-dimensional density of the aligned MBBA rods in a plane perpendicular to their long axes.

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