Thermochimica Acta, 120 (1987) 161–181 161
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

ORDER DESTRUCTION AND ORDER CREATION IN BINARY MIXTURES OF NON-ELECTROLYTES *

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(Received 16 March 1987)

ABSTRACT

Order-destruction and order-creation during mixing are discussed for binary mixtures of various liquids (component 1) with the n-alkane series (component 2). When component 1 is a spherical molecule liquid, e.g. cyclohexane, anomalous positive contributions occur in H^E and S^E, but negative ones occur in C_p^E, ΔC_v, dV^E/dT and other second-order quantities. The Flory theory is used as a first approximation to the prediction of these quantities. Thermodynamic effects, not included in the theory, are attributed to a net decrease in structure during mixing because of a destruction of short-range correlations of molecular orientations (CMO) in pure n-C_n. When component 1 is a plate-like molecule, e.g. 1-chloronaphthalene, these effects are decreased and reversed in sign. This has been ascribed to a net increase in structure because of a hindrance to molecular motion or a change in molecular conformation. When component 1 is a linear or branched alcohol, the n-C_n are relatively inert while component 1 is associated in both the pure and solution states leading to positive or negative effects in C_p^E depending whether the solution or pure component 1 is more structured. The Treszczanowicz–Kehiaian model for self-associated liquids + inert solvents explains these results and also provides a general framework for the discussion of both the process of order-creation and the process of order-destruction in solution.

INTRODUCTION

Mixtures of non-electrolytes can be divided into two broad groups depending on whether the constituent molecules form or do not form hydrogen bonds. Current theories of non-hydrogen-bonded liquid mixtures interpret the excess and mixing quantities as the sum of three contributions: (1) a

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* Presented in part at the 41st Annual Calorimetry Conference, August 1986, Somerset, New Jersey, U.S.A.

combinatorial or positional entropy of mixing, whose value is not affected by the chemical nature of the components but only by their relative sizes, (2) an interactional contribution due to an energetic weakness of 1–2 contacts relative to 1–1 and 2–2 contacts; this is attributed to a dissimilarity of chemical nature between the two component molecules which are thus surrounded by force fields of different strength and (3) a contribution from volume changes during the mixing process when the pure components are of different free volumes. However, in recent years, a new contribution to the thermodynamic mixing functions has been shown to be of general importance. This contribution is associated with the effect of structure or order which may be decreased or enhanced in passing from the pure to the solution state. However, structural effects in hydrogen-bonded systems have long been recognized and, in general, are interpreted by various treatments based on association–dissociation equilibria.

Order-destruction and order-creation upon mixing give rise to contributions of opposite sign in the thermodynamic mixing functions. The signs of these contributions however are independent of whether the system under study is a hydrogen-bonded or a non-hydrogen-bonded mixture. Only the magnitudes of the contributions depend on the nature of the system. The present work traces the theme of order-destruction/order-creation running through the thermodynamics of a variety of systems and summarizes recent research.

NON-HYDROGEN-BONDED LIQUID MIXTURES

Destruction of pure liquid order

Both thermodynamic and depolarized Rayleigh scattering measurements [1–4] indicate that when components 1 and 2 are both *n*-alkanes, the contact energies for the 1–1, 2–2 and 1–2 pairs are all affected by correlations of molecuar orientations (CMO). A simpler situation occurs if component 1 is a spherical molecule liquid such as cyclohexane (*c*-C_6) or 2,2-dimethylbutane while component 2 is an *n*-alkane such as *n*-C_{16}. Both the 1–1 and 1–2 pairs are uncorrelated allowing the order associated with the 2–2 contacts in pure component 2 to be manifested when it is destroyed during mixing. While this orientational order or CMO is short-range in character, it affects the thermodynamic properties which depend on nearest neighbour interactions. Changes in the thermodynamic functions X due to the presence of CMO are small and difficult to isolate in the pure liquids, but they manifest themselves in the mixing (ΔX) or excess (X^E) functions. Since order only appears in *n*-C_n of large n, one expects the order contributions to ΔX or X^E to increase rapidly with n. Furthermore, for any n one can select alkane isomers with increasing degrees of chain-branching which reduce the

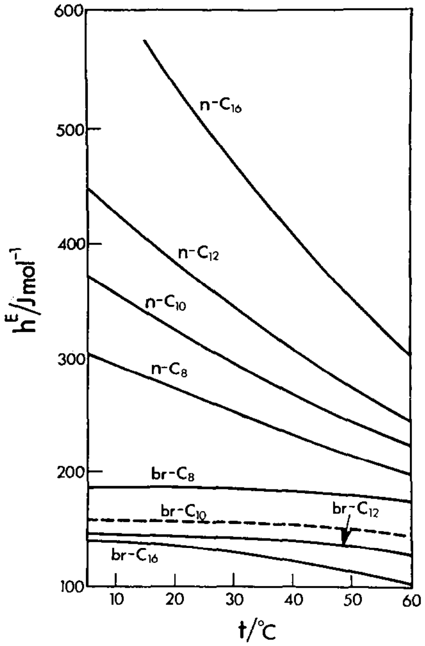

Fig. 1. Temperature dependence of the equimolar excess enthalpy for cyclohexane with *n*-alkanes and branched alkanes. The *br*-C_{10} curve was obtained by interpolation between *br*-C_8 and *br*-C_{12}. Figure taken from ref. 5.

ability of the alkane to order either in the pure or solution states, essentially eliminating the order contribution for a highly branched isomer (*br*-C_n). The *br*-C_n series has usually been taken to be: 2,2-dimethylbutane (*br*-C_6), 2,2,4-trimethylpentane (*br*-C_8), 2,2,4,6,6-pentamethylheptane (*br*-C_{12}) and 2,2,4,4,6,8,8-heptamethylnonane (*br*-C_{16}). In what follows, the existence of CMO in long-chain pure alkanes is discussed in terms of the contributions to ΔX and X^E that the destruction of the CMO brings about when the *n*-alkane is mixed with a spherical-molecule liquid.

CMO in the pure *n*-C_n appears to be equivalent to a molecular cohesion which lowers the energy U (equal to H at $P \approx 0$) and entropy S of the liquid. For systems of the type *n*-C_n + A where A is, for example, *c*-C_6, mixing will cause a net disruption of order and hence contributions to ΔX or X^E which are opposite in sign to the order contributions in the pure alkane quantities X; the order contributions are therefore positive in H^E and S^E. Figure 1 shows H^E for the series of linear and branched alkanes mixed with *c*-C_6 as a function of the temperature and at equimolar concentration [5]. For the branched series the H^E are small and practially temperature independent. In contrast, for the linear series H^E becomes substantial for higher n at 25 °C and decreases rapidly with increase in T. The different H^E behaviour of branched and linear alkanes cannot [1] be accounted for by a

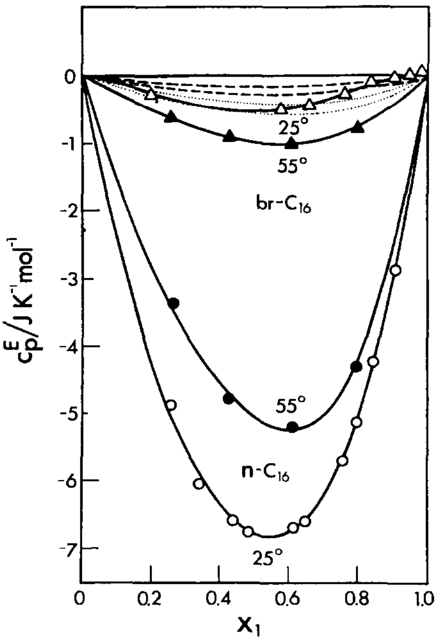

Fig. 2. Molar excess heat capacity as a function of cyclohexane mole fraction for c-C_6 + n-C_{16} and c-C_6 + 2,2,4,4,6,8,8-heptamethylnonane (br-C_{16}) at 25 °C and 55 °C. Flory theory predictions: broken curves for c-C_6 + n-C_{16} at 25 °C (upper curve) and 55 °C (lower curve); dotted curves for c-C_6 + br-C_{16} at 25 °C (upper curve) and 55 °C (lower curve). Figure taken from ref. 5.

difference in force fields surrounding methyl and methylene groups comprising the two sets of isomers. The explanation lies in the presence of CMO in pure n-C_n which upon mixing is destroyed giving a positive contribution to H^E. For the n-C_n series Flory theory [6] gives H^E curves whch decrease slightly with T, similar to those for the br-C_n series, i.e. predictions from this theory are good for the branched alkanes but fail for the linear alkanes since this theory does not take into account the presence of CMO. The decrease in H^E with T seen in Fig. 1 for long n-alkanes corresponds to a rapid decrease in CMO in the pure n-C_n as T increases. The excess heat capacity $C_p^E = \mathrm{d}H^E/\mathrm{d}T$ must then be abnormally negative for long n-alkanes. Thus, the presence of order in the pure alkane increases the heat capacity C_p of the pure liquid and, upon mixing with c-C_6, gives a negative contribution to C_p^E. This is illustrated in Fig. 2 which shows C_p^E for c-C_6 + n-C_{16} and + br-C_{16} at 25 °C and 55 °C [5]; while C_p^E for br-C_{16} is small and negative in accordance with Flory theory, for n-C_{16}, C_p^E is large and negative. As the temperature is increased C_p^E becomes less negative indicating again the rapid decrease of CMO in the pure n-alkane as T increases.

The ability of a long n-alkane to form CMO has been tested through the introduction of a methyl group at various positions on the linear chain [7].

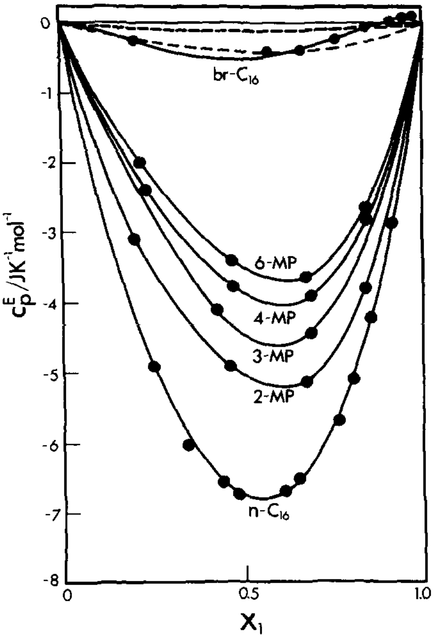

Fig. 3. Molar excess heat capacity at 25 °C as a function of c-C$_6$ mole fraction for c-C$_6$ mixed with the series of hexadecane isomers from 2,2,4,4,6,8,8-heptamethylnonane (br-C$_{16}$) through the methylpentadecanes (MP) to n-C$_{16}$. Broken curves predicted for c-C$_6$ + br-C$_{16}$ (lower curve) and c-C$_6$ + n-C$_{16}$ (upper curve), using Flory theory which ignores CMO. Other systems give intermediate curves. Figure taken from ref. 7.

Figure 3 shows C_p^E for a series of C_{16} isomers and it can be seen that as the methyl group is moved from an end of a 15 carbon chain to the center of the chain, C_p^E becomes less negative indicating weaker CMO for the latter than for the former. It seems then that disruption of chain linearity by a methyl group lessens the ability of the alkane to form CMO.

The effect of order in the equation of state has also been studied. Figure 4 shows experimental and predicted values of dV^E/dT for c-C$_6$ + n-C$_n$ and + br-C$_n$ [9]. In the case of the br-C$_n$ the Flory theory predicts dV^E/dT very well. However, for n-C$_n$ similar dV^E/dT are predicted whereas experiment yields quite different results as seen in Fig. 4. These may be attributed to the presence of temperature-dependent order in the pure long n-alkane which decreases V, enhances dV/dT and hence because of the destruction of order upon mixing, gives a negative contribution to dV^E/dT. Since order must be enhanced by pressure, making dV/dP more negative, one would expect a positive contribution to dV^E/dP. However, both the n-C$_n$ and br-C$_n$ series mixtures with c-C$_6$ give similar dV^E/dP results [10] and the Flory theory predicts both sets reasonably well [10,11]. A simple argument can in fact show that order effects in dV^E/dP are relatively small [10].

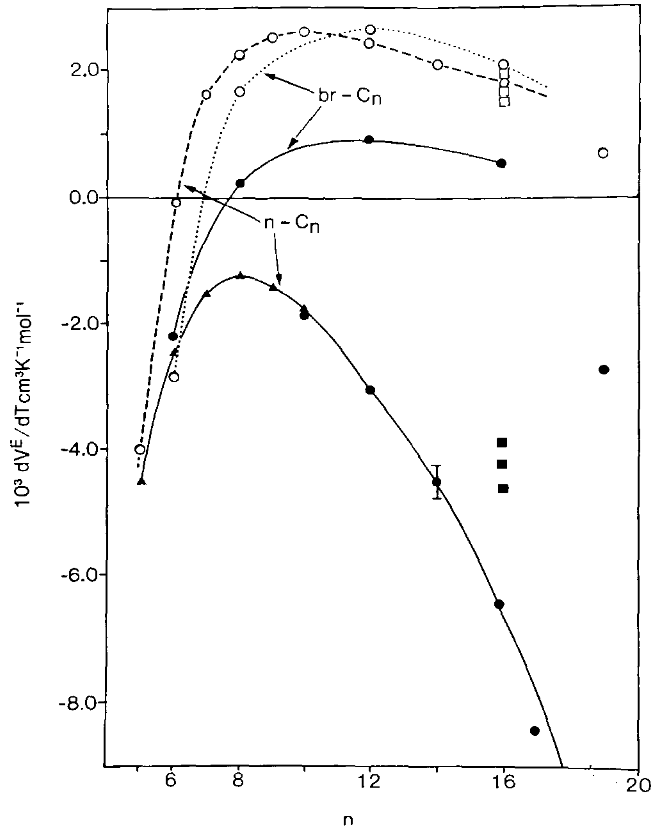

Fig. 4. Equimolar dV^E/dT against n for the n-alkane and branched alkane series. (— — —) and (······), Flory theory predictions; (———), experiment; ▲, data from ref. 8; ●, data from ref. 9. ■ and □ experimental and theoretical points for, in descending order 2-, 4- and 6-methylpentadecane. At $n = 19$: ● and ○, experimental and theoretical points for 2,6,10,14-tetramethylpentadecane. Figure taken from ref. 9.

Another equation of state quantity that appears to be a sensitive order indicator is the dependence of energy on relative compression [10] dV/V, i.e. $V(\partial U/\partial V)_T = \gamma VT$. Here γ is the thermal pressure coefficient given by α/κ_T where α is the thermal expansion coefficient and κ_T the isothermal compressibility, and the term $-PV$ which normally appears on the right-hand side is neglected for experiments at atmospheric pressure. For an ordered liquid, as the volume is decreased the energy U is expected to decrease more rapidly than for a non-ordered liquid, increasing $V(\partial U/\partial V)_T$ and producing a negative contribution to $\Delta(\gamma VT)$ (or positive to $-\Delta(\gamma VT)$). The mixing quantity $-\Delta(\gamma VT)$ is not only of interest where order is concerned but is of general importance since any theory based on the concept of van der Waals liquids (as the Flory theory) where $U \propto -1/V$ predicts $-\Delta(\gamma VT) = H^E$. Deviations from this equality indicate a corre-

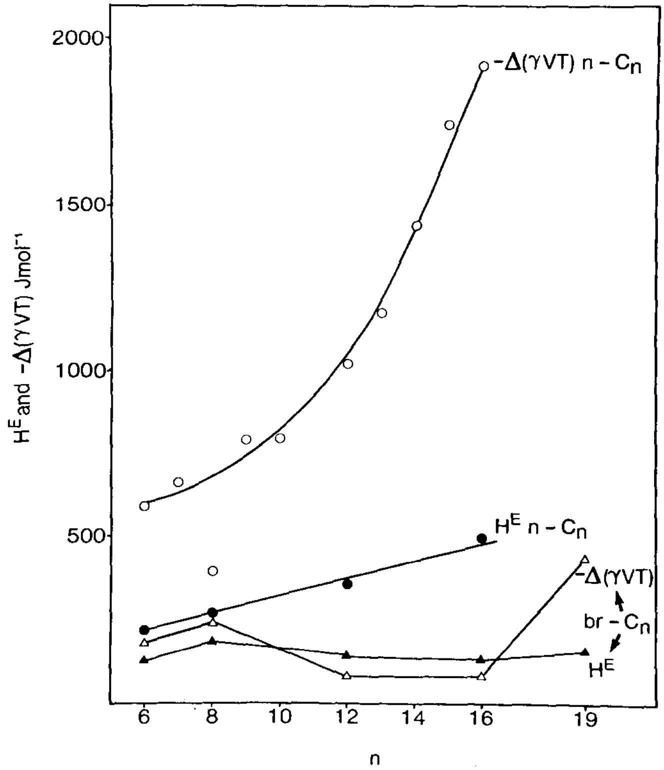

Fig. 5. Equimolar values of $-\Delta(\gamma VT)$ and H^E for c-C_6 mixed with the linear and branched series of alkanes at 25 °C. Lines through H^E and $-\Delta(\gamma VT)$ are only to aid visualization. Figure taken from ref. 10.

sponding departure from van der Waals behaviour. In general, for systems where there is a net destruction of order during mixing one expects $-\Delta(\gamma VT) > H^E$. Figure 5 shows that for c-C_6 mixed with the br-C_n series, $-\Delta(\gamma VT)$ is practically independent of n and very close to the corresponding H^E values, i.e. van der Waals type behaviour appears to occur. In striking contrast, for the n-C_n series $-\Delta(\gamma VT) > H^E$ and the discrepancy between these two quantities increases rapidly as n increases. Figure 5 indicates then that $-\Delta(\gamma VT)$ constitutes another useful and sensitive indicator of CMO. The measurement of γ also allowed the determination of the two contributions to $C_p^E = \Delta C_v + \Delta(\alpha\gamma VT)$; ΔC_v corresponds to the effect of thermal motion on U (or H at $P \approx 0$) and $\Delta(\alpha\gamma VT)$ to the effect on U or H of the increase of volume with temperature at constant pressure. In the case of the n-C_n + c-C_6 systems, it was found that both these quantities are negative, $\Delta(\alpha\gamma VT)$ being the largest contribution to C_p^E. This, in turn, indicates that the decrease of CMO with T in the pure n-C_n is mainly due to expansion of the liquid which brings about a loosening of the packing between chain segments, rather than being due to increased thermal agitation. Theoretical models of CMO have been presented by Bendler [12] and Costas [13] using liquid crystal and lattice model approaches. An excellent review [14] of CMO phenomena also exist dealing with spectroscopic and light scattering as well as thermodynamic aspects.

Creation of order in the mixtures

A large body of data indicating an ordering in solution has been recently reported by Grolier and collaborators [15,16]. They have measured V^E, H^E and C_p^E for systems A + n-C$_n$ where A is a plate-like, usually polar, molecule: chlorobenzene, dichlorobenzenes, 1,2,4-trichlorobenzene, 1-chloronaphthalene etc. In almost all cases H^E decreases as n increases; this is opposite to the trend found for spherical molecules mixed with n-C$_n$. Furthermore, the excess heat capacity can be positive, as in the very interesting 1-chloronaphthalene + n-C$_n$ systems. The anomalous behaviour of the excess quantities, i.e. $H^E(n)$ decreasing with increasing n and $C_p^E > 0$, suggest that order of some sort is being created in these mixtures. Since $\Delta(\gamma VT)$ proved to be a sensitive structural indicator, it appeared interesting

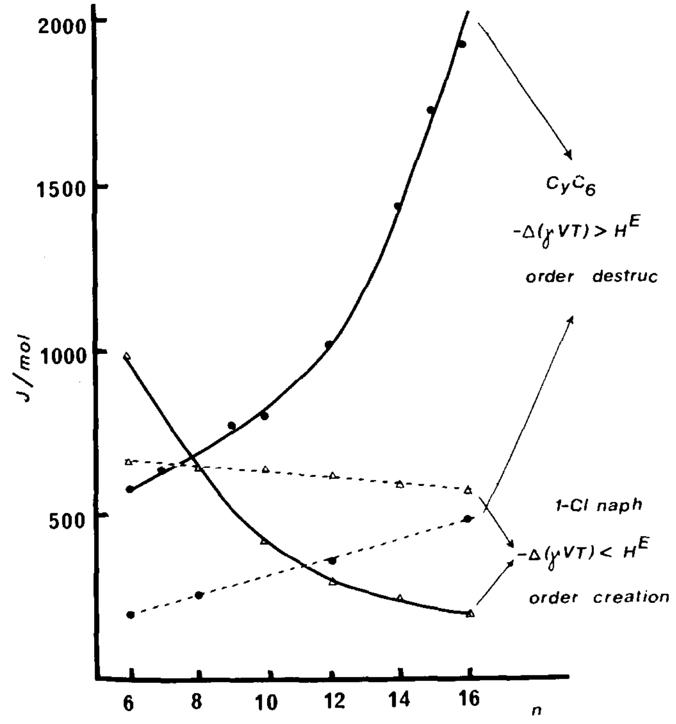

Fig. 6. Equimolar values of $-\Delta(\gamma VT)$, full lines, and H^E, dotted lines, for cyclohexane and 1-chloronaphthalene mixed with the n-C$_n$ series at 25 °C.

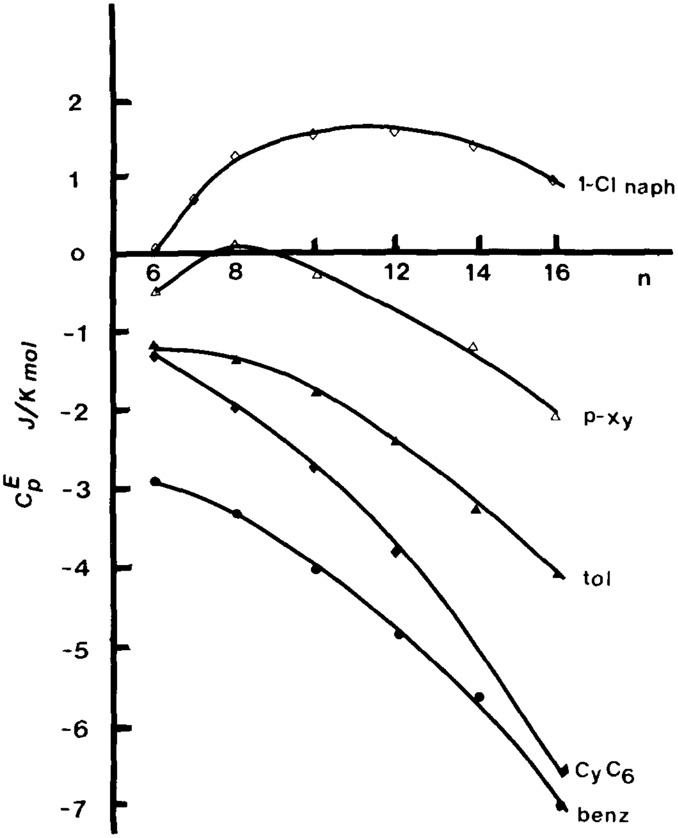

Fig. 7. Molar excess heat capacity at 25 ° C and equimolar concentration for the n-C_n series mixed with: cyclohexane, benzene, toluene, p-xylene and 1-chloronaphthalene. Data for n-C_n + c-C_6, + benzene, + toluene and p-xylene + n-C_6 and n-C_{16} from ref. 18; data for n-C_n + 1-chloronaphthalene and p-xylene + n-C_8, n-C_{10} and n-C_{14} from refs. 17 and 15.

to measure this quantity for 1-chloronaphthalene + n-C_n [17]. Order-creation in solution implies that $-\Delta(\gamma VT) < H^E$ and in Fig. 6 it can be seen that this is precisely the case for long n-alkanes mixed with 1-chloronaphthalene; this figure contrasts, through the differences between $-\Delta(\gamma VT)$ and H^E, the situation for a mixture where there is order-destruction (c-C_6 + n-C_n for large n) with the situation for a mixture where there is order-creation (1-chloronaphthalene + n-C_n for large n). It is to be noted that $-\Delta(\gamma VT) > H^E$ for 1-chloronaphthalene + n-C_6, apparently indicating order-destruction in this system. No satisfactory explanation of this result has yet been given.

Figure 7 shows that for systems n-C_n + A it is possible, through changing A, to move from a system (e.g. n-C_{16} + c-C_6 or + benzene) where C_p^E is negative and large indicating order is being destroyed to a system (e.g. n-C_{16} + 1-chloronaphthalene) where C_p^E is positive apparently indicating that order is being created in solution. In Fig. 7, C_p^E values for cyclohexane and benzene indicate that these two molecules have good CMO-breaking ability, toluene has a lesser effect and *p*-xylene already shows some order-formation in solution [18,19] which becomes more pronounced for the case of 1-chloronaphthalene. Although, at first glance, the order-creating effects shown in Figs. 6 and 7 seem small, it must be kept in mind that in addition to this structural effect the destruction of pure n-C_n CMO is still present. In this way, the positive C_p^E in Fig. 7 and $-\Delta(\gamma VT) > H^\mathrm{E}$ in Fig. 6 are really the result of two opposing effects: the destruction of CMO in pure n-C_n which makes $C_\mathrm{p}^\mathrm{E} < 0$ and $-\Delta(\gamma VT) > H^\mathrm{E}$ and the creation of order in solution which overcomes these effects and finally produces $C_\mathrm{p}^\mathrm{E} > 0$ and $-\Delta(\gamma VT) < H^\mathrm{E}$. The fact that for 1-chloronaphthalene + n-C_{16} in Fig. 7 C_p^E is less positive than for shorter alkanes is in line with the above, since there is more CMO in pure n-C_n as n increases.

The nature of the order being created in solution is, at this stage, still speculative. Two hypotheses have been advanced: (i) order is created by the A molecules through hindering of rotational motion of segments of the flexible *n*-alkane chain [20] and (ii) order created in solution is essentially intramolecular associated with a change in the *trans-gauche* population of the *n*-alkane [15,16] produced by a favourable interaction between the *trans* conformers and the flat A molecule. However, since rotational and conformational order are not very different mechanisms it is possible that order-creation is the result of both processes. In any event, more thermodynamic and spectroscopic work is needed to establish the nature of the order created in these solutions.

HYDROGEN-BONDED LIQUID MIXTURES

Many results have been obtained for A + n-C_n where A is an associated liquid such as an alcohol. In these mixtures structure is imposed in solution through the existence of hydrogen bonds; here the alkane may be taken to be inert and it is the alcohol which is structured. The literature indicates that both H^E and C_p^E are strongly positive; positive H^E reveals a net breaking of hydrogen bonds on mixing, but positive C_p^E indicates more structure in the solution, so the fewer hydrogen bonds in solution correspond to bringing together alcohol molecules over longer distances than in the pure alcohol. A simple association model [21] due to Treszczanowicz and Kehiaian (TK) can predict the C_p^E behaviour throughout the concentration range starting from

$$C_\mathrm{p}^\mathrm{E} = x_\mathrm{OH}\left(\phi_\mathrm{C} - C_\mathrm{p}^0\right) \tag{1}$$

with ϕ_C being the apparent heat capacity of the alcohol in solution and C_p^0 the value for the pure state. In using this equation we need only be concerned with that part of the heat capacity which is due to association

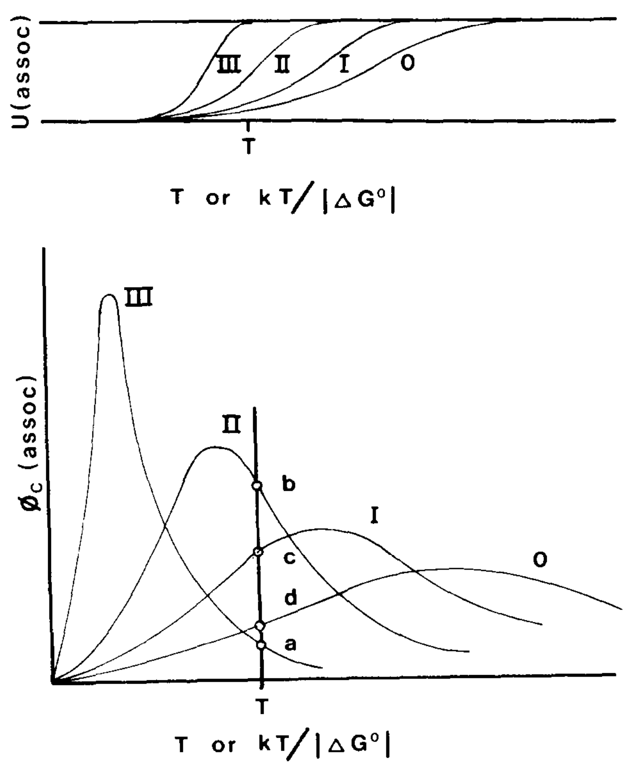

Fig. 8. Schematic representation of energy (upper diagram) and heat capacity (lower diagram) against T or $kT/|\Delta G^0|$ for an alcohol in the pure state (O) and at increasing dilution in an inert solvent (I, II, III). T' represents the experimental temperature.

since the internal C_p of the alcohol is eliminated and other intermolecular contributions will be small. The associational ϕ_C and C_p^0, i.e. ϕ_C (assoc) and C_p^0 (assoc), are given satisfactorily by the TK model in which each molecule is capable of two energy levels corresponding to the associated state and the dissociated monomer as indicated by Fig. 8. For a pure alcohol, at very low temperature the energy U(assoc) will be low because all the alcohol molecules will be associated through hydrogen bonds; as the temperature is raised the energy will rise corresponding to dissociation of the hydrogen bonds. In Fig. 8, room temperature (T') will correspond to a temperature where most of the alcohol molecules will still be associated forming hydrogen bonds. For a highly concentrated mixture of an alcohol with an inert solvent (I in Fig. 8), it will be slightly easier to break up the hydrogen bonds; there is now a greater entropic driving force towards the randomly dispersed alcohol molecules. Going to lower alcohol concentrations in the inert solvent, the driving force towards dissociation becomes greater giving curves II and III in Fig. 8. Taking the slope of the energy curves, i.e. $\mathrm{d}U$ (assoc)/$\mathrm{d}T$, the associational heat capacity of the alcohol, ϕ_C(assoc), is obtained at the different concentrations, as a function of T; this is indicated in the lower part of Fig. 8 where the ϕ_C(assoc) curves have the form of "Schottky peaks" [22].

The Schottky peaks indicated in Fig. 8 can explain quite satisfactorily both the concentration and temperature dependences of ϕ_C(assoc) [23]. At $T' = 25\,^\circ C$, ϕ_C(assoc) is small for very low concentration (point a on curve III) because there is no structure in the solution, almost all the alcohol being dissociated; as the concentration increases (point b in curve II) ϕ_C(assoc) increases corresponding to the coming together of alcohol molecules into multimers over long distances. With further increase in concentration (point c in curve I) ϕ_C(assoc) decreases. Structure decreases since although almost all alcohol molecules are associated into multimers they have come together over smaller distances. According to Fig. 8 then ϕ_C(assoc) must go through a maximum when plotted against concentration at constant temperature; the experimental ϕ_C(assoc) values at 25 °C for 1-hexanol + n-dodecane shown in Fig. 9 corroborate this prediction. Here, the experimental $\phi_C(\text{assoc}) = \phi_C - \lim \phi_C(x_{OH} \rightarrow 0)$ where the infinite dilution apparent molar heat capacity represents the contribution to the heat capacity of the alcohol in the absence of any association, each alcohol molecule being isolated in an inert solvent. In accordance with this interpretation the lim $\phi_C(x_{OH} \rightarrow 0)$ has been found to be the same for a given alcohol in a series of inert solvents (n-C_n) [24]. Figure 8 also predicts that as T' is increased the maxima in ϕ_C(assoc) must decrease and occur at a higher alcohol concentration. These predictions are clearly supported by the experimental values of ϕ_C(assoc) shown in Fig. 9 for different temperatures.

The temperature dependence of C_p^E also follows from the Schottky peaks in Fig. 8 [23]. According to eqn. (1) C_p^E corresponds to the difference between two Schottky curves, one for the alcohol in solution and the other in the pure state. At very low alcohol concentration (curve III in Fig. 8) $\phi_C(\text{assoc}) < C_p^0(\text{assoc})$ and hence $C_p^E < 0$; furthermore, the difference between points a and d in Fig. 8 increases as T increases, C_p^E must become more negative as the temperature is raised. This is seen in the experimental results for 1-decanol + n-decane shown in Fig. 10, this behaviour being completely general for all alcohol + inert mixtures. The negative C_p^E corresponds to a net breaking of order or structure on passing from the pure alcohol to the solution which is so dilute as to contain only monomeric alcohol. As the alcohol concentration is increased, the solution Schottky peak moves to higher T (curve II in Fig. 8) and here, at T', $\phi_C(\text{assoc}) > C_p^0(\text{assoc})$ producing $C_p^E > 0$. Since the difference between points b and d decreases as T increases in this concentration region $\mathrm{d}C_p^E/\mathrm{d}T$ remains negative. This is seen with the experimental results for 1-decanol + n-decane shown in Fig. 11. The positive C_p^E indicates that the solution is extremely structured, corresponding to a localization of monomers into multimers, i.e. the process of order-creation in solution through the formation of hydrogen

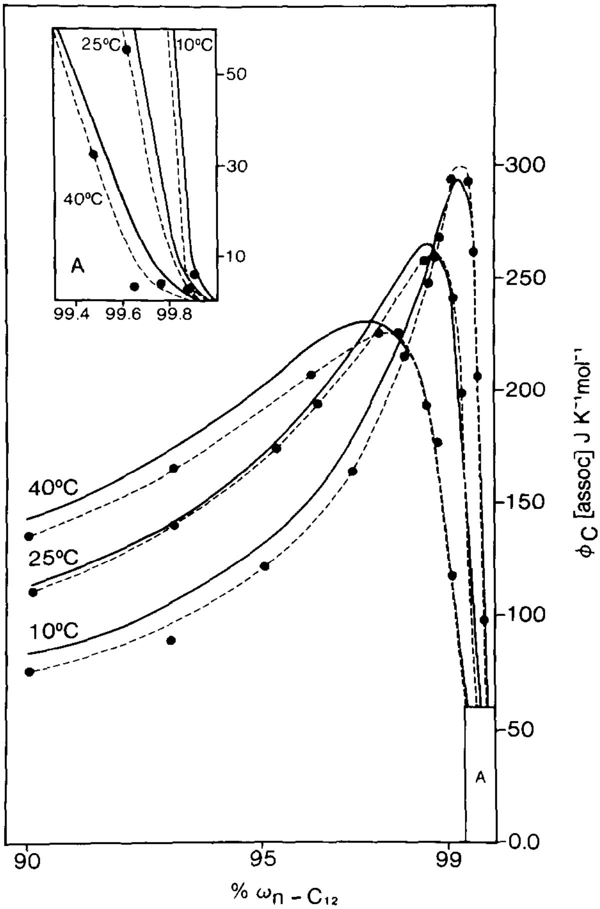

Fig. 9. Associational part of the apparent molar heat capacity for 1-hexanol + *n*-dodecane at 10, 25 and 40 °C (broken lines). Full lines are ϕ_C(assoc) calculated using the TK model. Figure taken from ref. 23.

bonds. Finally, at higher alcohol concentration (curve I in Fig. 8) $C_p^E > 0$ but now since the difference between points c and d increases as T increases dC_p^E/dT is positive as illustrated by experimental C_p^E values in Fig. 11. The above description of the C_p^E behaviour in the three concentration regions should be completely general for an alcohol mixed with an inert solvent. Note that regions III and II are confined to very low concentration and hence it is concentration region I which is familiar from published work on alcohol + inert-solvent systems.

The above qualitative arguments for ϕ_C(assoc) and C_p^E can be made quantitative through the use of the TK model [23]. Full lines in Figs. 9 and 10 are calculated from this model where its parameters, i.e. the enthalpy change for the formation of a hydrogen bond ΔH^0 and the volumetric equilibrium constants K_i^ϕ for each species i ($i = 2$, 3 and 4), were fitted to

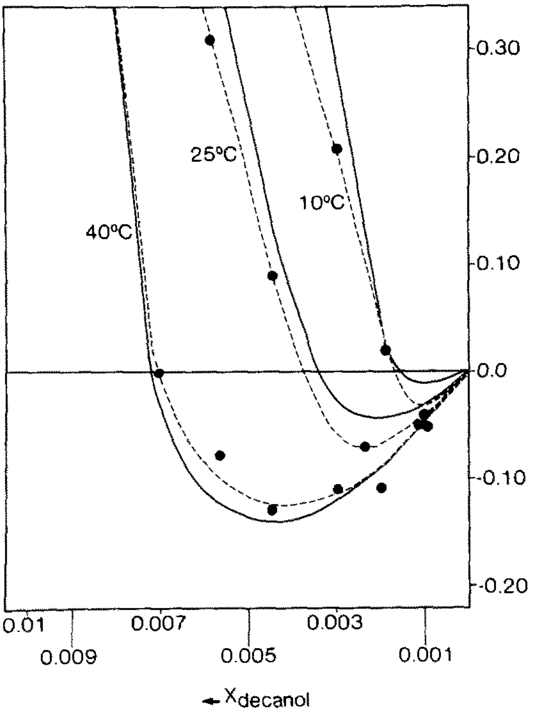

Fig. 10. Excess heat capacity at very low alcohol concentrations for 1-decanol + *n*-decane at 10, 25 and 40 °C as a function of the alcohol mole fraction (broken lines). Full lines are calculated C_p^E values using the TK model. Figure taken from ref. 23.

ϕ_C(assoc) at 25 °C; full lines in Figs. 9 and 10 at 40 °C and 10 °C were then predicted taking ΔH^0 to be temperature-independent. One of the most interesting results of applying the TK model to the experimental data is that tetramers turned out to be the predominant species, dimers being almost absent even at very low alcohol concentration. The volumetric equilibrium constants K_i^{ϕ} obtained from experiment can be transformed, with the aid of Flory lattice theory, into a single equilibrium constant K for the actual formation of the hydrogen bond [24]; this transformation indicated that the thermodynamic parameters for hydrogen bond formation in dilute solution in an inert solvent are independent on the chain length of the 1-alkanol; a similar result has been obtained from IR spectroscopy [25].

The Schottky peaks in Fig. 8 are not only useful in interpreting heat-capacity data for primary alcohols as described above but are also able to explain the experimental results for secondary and tertiary alcohols mixed with an inert solvent [26]. Secondary and tertiary alcohols form weaker hydrogen bonds in comparison with primary alcohols reflecting the fact that the hydroxyl group on the alcohol becomes increasingly hindered, effectively reducing the alcohol self-association capabilities. For secondary and tertiary alcohols the free energy of association ΔG^0 is less negative than for primary

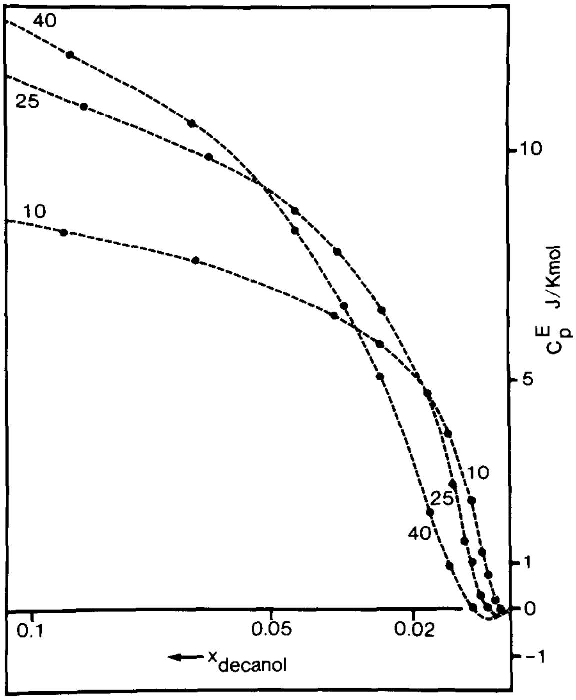

Fig. 11. Excess heat capacity for 1-decanol + n-decane at 10, 25 and 40 °C as a function of the alcohol mole fraction. At very low 1-decanol concentrations points have been omitted owing to crowding but are shown in Fig. 10. Figure taken from ref. 23.

alcohols. In Fig. 8, the abcissa is more properly taken to be $kT/|\Delta G^0|$ rather than T itself, representing the ratio of the thermal energy to the hydrogen bonding free energy. With this change, the experimental temperature T' for a secondary or tertiary alcohol will correspond to a higher value of the $kT/|\Delta G^0|$ ratio in Fig. 8 than for a primary alcohol, and will act like a primary alcohol at $T > T'$. Figure 8 predicts that for a secondary or tertiary alcohol ϕ_C(assoc) will have a lower maximum which will occur at higher alcohol concentration than for the corresponding isomeric primary alcohol. Figure 12 illustrates this situation through the experimental ϕ_C(assoc) at 25 °C for 1-decanol and three of its isomers [26]; another primary alcohol (3,7-dimethyloctanol), a secondary alcohol (5-decanol) and a tertiary one (4-propyl-4-heptanol). The introduction of two methyl groups along the hydrocarbon chain does not significantly affect the self-association ability of the primary alcohol. However, for the secondary and tertiary alcohols the maximum is progressively displaced towards lower values and occurs at higher alcohol concentrations, i.e. ϕ_C(assoc) for these two alcohols correspond to ϕ_C(assoc) for 1-decanol at $T > 25$ °C as shown in Fig. 9. The excess heat capacities for these mixtures are shown in Fig. 13; C_p^E is negative at low alcohol concentrations becoming positive at increasingly

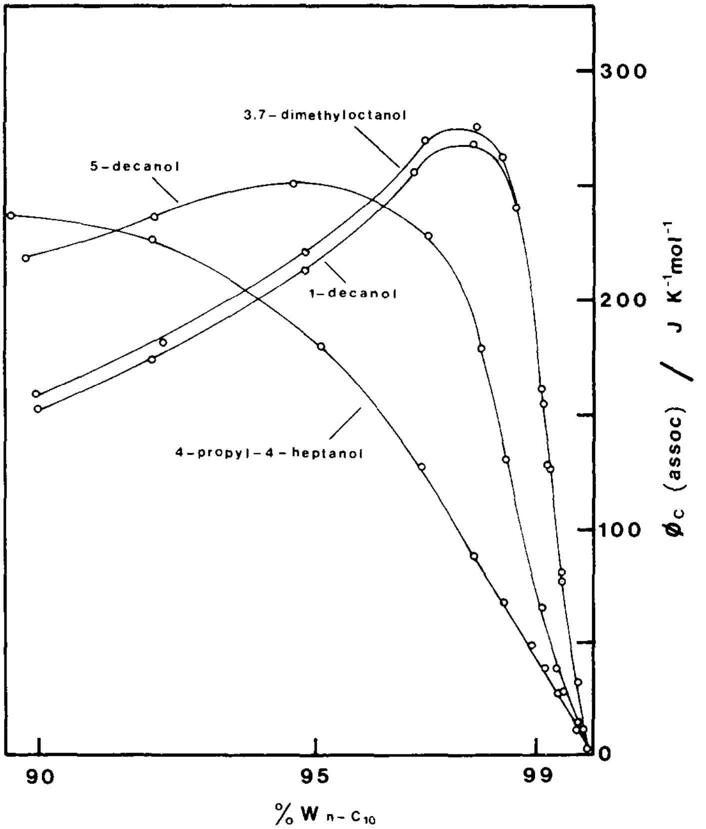

Fig. 12. Associational part of the apparent molar heat capacity for 1-decanol, 3,7-dimethyloctanol, 5-decanol and 4-propyl-4-heptanol + *n*-decane at 25 ° C.

high alcohol concentrations as the steric hindrance on the hydroxyl group increases. C_p^E turns positive at $x_{OH} \approx 0.01$ (1.1 wt.%) for 5-decanol and at $x_{OH} \approx 0.03$ (3.3 wt.%) for 4-propyl-4-heptanol. Application of the TK model to the data in Figs. 12 and 13 indicates that while for 1-decanol tetramers are the predominant species, for the corresponding isomeric alcohols the concentration of tetramers is severely reduced and the lower species, i.e. trimers and dimers, are more important. For the highly hindered tertiary alcohol, monomers are the predominant species in the concentration range shown in Fig. 12, reflecting the decrease in the self-association ability imposed by steric hindrance of the OH group. For this alcohol, the order-creation process in solution is "delayed" to higher concentrations where finally enough structure, i.e. higher species like tetramers, has been created and C_p^E becomes positive.

The success of the TK model in explaining the heat-capacity data of mixtures of linear and branched alcohols + hydrocrabon-solvent prompted its extension to more complex mixtures. This model has been extended to

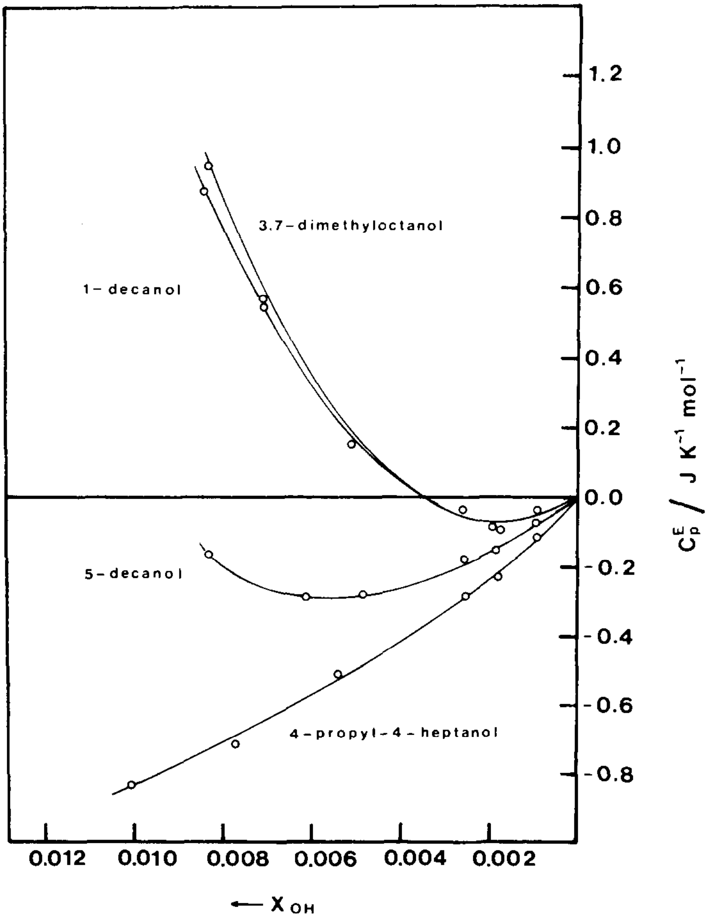

Fig. 13. Excess heat capacity for 1-decanol, 3,7-dimethyloctanol, 5-decanol and 4-propyl-4-heptanol + *n*-decane at 25 ° C.

and a proton-acceptor organic solvent. This extension allowed the interpretation of the thermodynamic behaviour of a variety of systems: (1) solutions of cholesterol mixed with triglycerides or phospholipids in an inert solvent [27], (2) water + organic-solvent mixtures where at the organic-rich region water was found to behave similarly to a lower alcohol mixed with a proton acceptor [28], (3) mixtures of linear and branched alcohols with acetates of different chain length [29] and (4) mixtures of alcohols [30].

A GENERAL FRAMEWORK FOR ORDER-CREATION AND ORDER-DESTRUCTION IN SOLUTION

One of the most attractive features of Fig. 8 is that it provides a general framework for consideration of both order-creation and order-destruction.

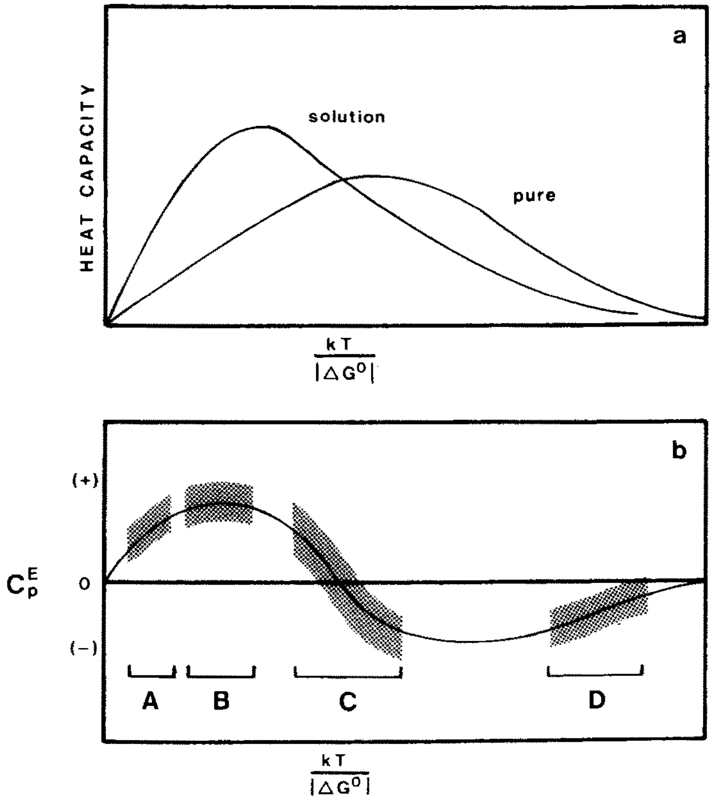

Fig. 14. (a) Schematic representation of the heat capacity for a pure associated liquid and a solution in an inert solvent against $kT/|\Delta G^0|$; (b) variation of the excess heat capacity C_p^E against $kT/|\Delta G^0|$; regions A, B, C and D represent decreasing magnitudes of ΔG^0, the free energy of association.

Figure 14(a) shows Schottky peaks for a pure associated component and for a given concentration (say equimolar) in an inert solvent, while Fig. 14(b) shows C_p^E obtained through eqn. (1) by the subtraction of the two curves in Fig. 14(a). At constant temperature, it is possible to move from left to right along the horizontal axes in Figs. 14(a) or 14(b) by decreasing $|\Delta G^\circ|$, i.e. by making the association weaker and weaker. We wish to discuss four regions of Fig. 14(b), each of which corresponds to a class of systems where C_p^E has been studied: (A) where $|\Delta G^0|$ is large, $C_p^E > 0$ and $dC_p^E/dT > 0$, (B) where $|\Delta G^0|$ is lower, $C_p^E > 0$ and dC_p^E/dT changes from positive to negative, (C) where $|\Delta G^0|$ has been further decreased, C_p^E changes from positive to negative and $dC_p^E/dT < 0$ and (D) where $|\Delta G^0|$ is small, $C_p^E < 0$ and $dC_p^E/dT > 0$. Examples of mixtures in these four regions are shown in Fig. 15. Region (A) is illustrated with 1-decanol + *n*-decane; here the negative C_p^E at extremely low alcohol concentration (discussed earlier in the section on hydrogen bonded liquid mixtures) is not seen because of the scale

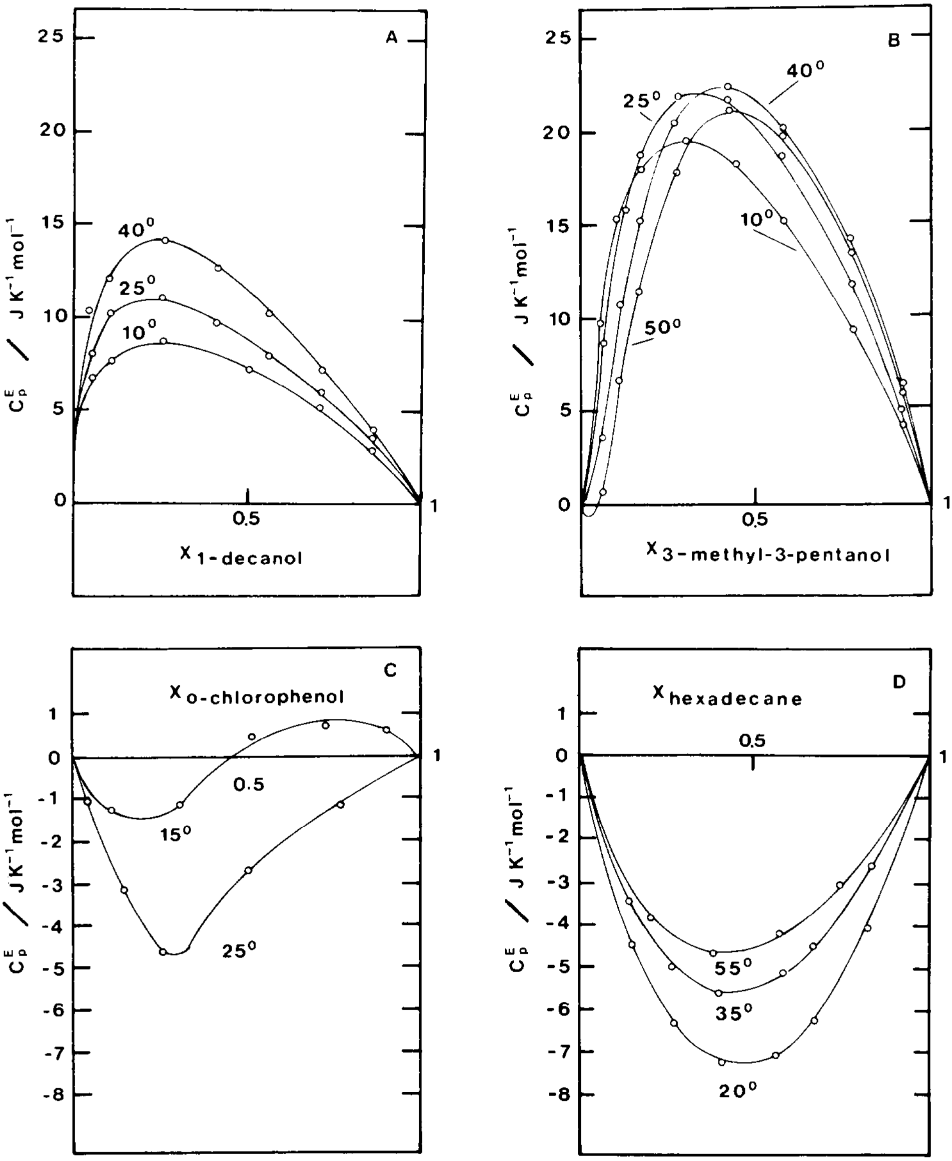

Fig. 15. Examples of mixtures of an associated-liquid + inert solvent corresponding to the four different regions indicated in Fig. 14. Region A: 1-decanol + *n*-decane at 10, 25 and 40 ° C; negative C_p^E values at extremely low alcohol concentrations are not seen due to the concentration scale used in the figure; region B: 3-methyl-3-pentanol + *n*-decane at 10, 25, 40 and 55 ° C; region C: *o*-chlorophenol + benzene at 15 and 25 ° C and region D: *n*-hexadecane + cyclohexane at 20, 35 and 50 ° C (from ref. 31).

of the figure. All 1-alkanols will belong to region (A) due to their large negative ΔG^0 [24,26]. The tertiary alcohol 3-methyl-3-pentanol + *n*-decane is an example for region (B); here $|\Delta G^0|$ has been reduced because of the steric hindrance of the OH group and hence the ratio $kT/|\Delta G^0|$ is increased for the usual temperature range. Correspondingly the branched alcohol displays different C_p^E behaviour from that of a linear alcohol when mixed with an inert solvent. C_p^E is considerably larger as seen in Fig. 15 region (B) and dC_p^E/dT now changes sign from positive to negative within the temperature range studied, 10–50 °C. The negative C_p^E region at low alcohol concentration is also visible. In short, the branched alcohol behaves like a linear alcohol at a higher temperature as suggested in Fig. 14.

Since a tertiary alcohol possesses the largest possible crowding on the OH group, in order to further reduce $|\Delta G^0|$ it is necessary to introduce another factor that effectively decreases the alcohol self-association capability. This can be accomplished through the introduction of the possibility of an intramolecular hydrogen bonding. An alcohol that fulfils this condition is *o*-chlorophenol which mixed with benzene exemplifies region (C); here C_p^E is positive and S-shaped at low T becoming negative as the temperature increases. Region (D), where $|\Delta G^0|$ must be very small, is represented by the normal alkanes + a spherical-molecule liquid discussed earlier. Normal alkanes are weakly associated through molecular orientation of the chains of neighbouring molecules (CMO). This association is, of course, extremely weak compared with that of systems in region (A): in terms of ΔH^0, the association between n-C_{16} molecules has been estimated [32] to be about 2 kJ mol^{-1} while for 1-alkanols it is about 25 kJ mol^{-1}. Of course, for *n*-alkane order the TK model can only be taken in a qualitative sense, and to obtain correct values of C_p^E, one would require a temperature-dependent and volume-dependent energy of association. From the general perspective provided by Fig. 14 the apparently very different C_p^E behaviours displayed in Fig. 15 regions (A)–(D) arises simply through the changing strength of association between molecules of the first component.

ACKNOWLEDGEMENTS

We thank the Journal of Physical Chemistry for permission to reprint Figs. 1 and 2, the Journal of Solution Chemistry for Fig. 3, and the Journal of the Chemical Society, Faraday Transactions 1, for Figs. 4, 5, 9, 10 and 11.

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