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Structure and the thermodynamics of non-electrolyte mixtures[1]

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Abstract

A review is given of the Prigogine-Flory theory and its prediction of the first and second order excess thermodynamic quantities of non-electrolyte mixtures. Effects outside the scope of this theory occur when the mixing process: (1) destroys structure existing in the pure components (orientational order between n-alkane chains, dipolar and quadrupolar order) or (2) creates order in the solution (concentration fluctuations, alcohol multimers, hydrophobic hydration, micelles). These thermodynamic effects are most apparent in the second order quantities. A qualitative interpretation can be given.

Keywords: Prigogine-Flory theory; Thermodynamics; Non-electrolyte mixtures

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1. Introduction

In the last 20 years, the scope of the thermodynamics of non-electrolyte mixtures has been extended from G^E, H^E and V^E to second-order excess quantities, e.g. $C_P{}^E$, $(\partial V^E/\partial T)_P$ and $-(\partial V^E/\partial P)_T$. Experimentally, this development was fostered by the availability of the Picker flow microcalorimeter [1] (Sodev, Sherbrooke, QC, Canada) which made accurate C_P measurements both convenient and rapid. Theoretically, the regular solution theory [2] of the 1940s, based on a rigid lattice model, could only deal with S^E and H^E. It was extended to take account of the equation of state of the mixture i.e. of the "free volume" surrounding the molecules in these liquids. Thus, the Prigogine-Flory [3,4] (PF) theory can also predict V^E and the second-order excess quantities mentioned above. It gives a simple, intuitively satisfying picture of various factors affecting all the excess quantities.

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Nevertheless, the predictions are poor for a number of important classes of systems. This appears to be due to the presence of "structure" which is not taken into account by PF. Mixing may destroy "structure" existing in pure components such as in normal alkanes (orientational order) or aromatics (quadrupolar order). Mixing may also create "structure" in the solution which ranges from concentration fluctuations to the more dramatic micelles and reverse micelles, i.e. organized solutions [5], and the water structure around a hydrophobic solute. In all these cases, the excess thermodynamic quantities, particularly C_P^E, are sensitive indicators of structure.

2. Experimental quantities

The molar mixing quantities, ΔY_M, are the changes of thermodynamic functions, Y, which take place on mixing two liquids and are expressed per mole of resulting mixture. The molar excess quantities, Y^E, are then defined by subtracting the value of ΔY_M for ideal mixing, i.e. $Y^E = \Delta Y_M - \Delta Y_M$ (ideal). G^E and S^E are useful quantities since usually ΔS_M is close to its large ideal value. It has become customary to use exclusively Y^E instead of ΔY_M. For many quantities ΔY_M (ideal) = 0 and $Y^E = \Delta Y_M$. This is the case for H and V and the second-order quantities C_P, $(\partial V/\partial T)_P = \alpha V$, $-(\partial V/\partial P)_S = \kappa_S V$ and $-(\partial V/\partial P)_T = \kappa_T V$. Here, α, κ_S and κ_T are respectively the thermal expansion coefficient at constant pressure, and the compressibilities at constant entropy and pressure. However, for a few quantities, e.g. C_V, κ_S and κ_T, ΔY_M (ideal) must be calculated following a complicated procedure [6]. In these cases, it seems acceptable, and certainly simpler, to retain ΔY_M instead of Y^E. Furthermore, when there is a large difference in molecular size between components as in polymer-solvent or polymer-polymer systems, the ideal solution is no longer a convenient reference state and is replaced by the athermal [2] system. Shinoda [5] has emphasized that the ideal solution is again inappropriate for organized solutions such as micellar systems and should be replaced by an "ideal organized system".

The last 20 years have seen many measurements of the excess second order quantities where the importance of C_P is being increasingly recognized. The vibrating-cell densitometer [7] has facilitated measurements of V^E and $\partial V^E/\partial T$. Jolicoeur and collaborators [8] have published a method using the Picker flow microcalorimeter to obtain α directly at a single temperature. Such a method should establish $\partial V^E/\partial T$ as a quantity of equal interest to C_P^E. The quantity $(\partial V^E/\partial P)_S$ is obtained simply from speed of sound measurements but is not predicted by theory. However, combined with C_P and α measurements it gives $-(\partial V^E/\partial P)_T$ which is predicted by the Prigogine-Flory Theory.

3. The Prigogine-Flory theory

3.1. Background

The interplay between experiment and simple theory is probably the most attractive feature of the thermodynamics of non-electrolyte mixtures. Early well-known theories are the solubility parameter theory, still of interest in industry, and the regular solution theory [2]. The latter was developed mainly by Guggenheim assuming a rigid quasilattice for mixtures of small molecules. The thermodynamics reflected two contributions: (1) the combinatorial entropy of mixing which, for a random mixture, was predicted to have the ideal value so that $S^E = 0$ and, (2) a non-ideal H^E term associated with the new (1–2) contacts in the mixture which replace (1–1) and (2–2) contacts m the pure components. This requires an interchange energy, ΔW, which for van der Waals forces, is positive, with a magnitude dependent on the difference in energies of the (i–i) contacts. This simple theory, using solubility parameters for ΔW gives predictions of H^E and G^E, but not of V^E, which often has surprising values, i.e. it can be negative even when H^E and G^E are both positive and large, the system being close to phase separation. Furthermore, S^E usually has positive values, rather than zero. These experimental findings were the stimulus for the Prigogine-Flory theory [3,4] based on a deformable lattice, incorporating the equation of state of the liquids. Meanwhile, however, the regular solution theory had been extended to give the Flory-Huggins theory [9] of polymer systems by: (1) regarding the interchange energy as being between chain-segments rather than between whole molecules and, (2) replacing the ideal combinatorial entropy of mixing by the Flory-Huggins result for mixtures of molecules of different size. The Flory-Huggins theory is still a useful approach to the thermodynamics of polymer-solvent and polymer-polymer systems, and ternary systems [10] containing two polymers or a polymer and a surfactant dispersed in a solvent [11].

3.2. Theory

A brief presentation of the basic concepts of the PF theory seems warranted. The equation of state, and the free volume of the liquids are introduced through the dimensionless reduced volume, $\tilde{V} = V/V^*$ where the reduction parameter V^* is the molar volume of the liquid at 0 K. V^*, also called the core volume, is a temperature-independent parameter having dimensions of volume. Throughout the theory, tilde quantities are reduced and starred quantities are reduction parameters. $\tilde{V}$ for all liquids, including polymers and their mixtures, is postulated, and found [12] to be a single function, $\tilde{V}(\tilde{T})$, of a dimensionless reduced temperature, $\tilde{T}$, given by

$$\begin{aligned}\tilde{T} &= \frac{\text{external thermal energy at } T}{\text{cohesive energy at 0 K}} \\ &= 3ckT/U^* = T/T^*\end{aligned} \tag{1}$$

Here the denominator U^* is the cohesive energy or intermolecular contact energy at 0 K. It acts to compress the liquid. The ratio U^*/V^* gives the "characteristic pressure", P^*, corresponding to the cohesive energy of the liquid at 0 K. The numerator of Eq. (1), i.e. the external thermal energy, acts to expand the liquid. It is proportional to kT and to the number, $3c$, of external degrees of freedom, i.e. those which are of large amplitude, thus promoting expansion of the liquid. For small molecules, $3c$ will mainly refer to the degrees of freedom which corresponded to translation and rotation in the gas state and which in the liquid state become low frequency oscillations. For longer chains, $3c$ mainly reflects chain-flexibility. The quantity $S^* = 3ck$ constitutes the reduction parameter for quantities having dimensions of entropy. Thus $T^* = U^*/S^*$. Apart from combinatorial entropy any thermodynamic property Y of any liquid can be treated like V. A mixture is considered as a single liquid with values of $\tilde{T}$ and reduction parameters lying between those for the components. Thus,

$$Y(T) = Y^* \tilde{Y}(\tilde{T}) \tag{2}$$

where Y^* is a suitable combination of V^*, U^* and T^* having dimensions of Y. The mixing quantity is then given by a corresponding states approach

$$\Delta Y_M = Y^* \tilde{Y}(\tilde{T}) - [x_1 Y_1^* \tilde{Y}(\tilde{T}_1) - x_2 Y_2^* \tilde{Y}(\tilde{T}_2)] \tag{3}$$

The problem remains of finding $\tilde{Y}(\tilde{T})$ and the starred quantities for the components and the mixture. $\tilde{Y}(\tilde{T})$ has been obtained through two approaches: (1) by use of experimental data or (2) by prediction through a theoretical model. Flory [4] has emphasized the simple Hirschfelder-Eyring cell model. This is of the "smoothed-potential" type where $\tilde{C}_v$ is set to zero. Thus, κ_S and ΔC_v, cannot be predicted. Using the model for $\tilde{Y}(\tilde{T})$ and the experimental quantities V, α and κ_T the three reduction parameters V^*, T^* and U^* (or P^*) are calculated for the pure components. For the mixture, Flory simplified Prigogine's work and put

$$V^* = x_1 V_1^* + x_2 V_2^* \tag{4}$$

Thus, in the mixture there is no net "loosening" or "tightening" of the molecular packing at 0 K. This formula has been amazingly successful in predicting V^E. Both Prigogine and Flory use

$$S^* = x_1 S_1^* + x_2 V_2^* \tag{5}$$

so that the external degrees of freedom of the molecules in the mixture do not interfere with one another. Alternatives to (4) and (5) have been explored [13,14] but have not met general acceptance. U^* cannot be obtained from a similar equation since it must reflect the new (1–2) contacts in the mixture, i.e. ΔW of the regular solution theory. The analogue of this parameter is X_{12}, and Prigogine and Flory put

$$U^* = x_1 U_1^* + x_2 U_2^* - X_{12} (f(x_1, x_2) \tag{6}$$

The effect of unfavorable (1–2) contacts and positive X_{12}, is to lower the cohesion of the solution and hence to raise its values of $\tilde{T}$ and $\tilde{V}$, affecting all the thermodynamic functions. In the regular solution theory, ΔW affected only H^E and G^E. Its analogue X_{12} now appears as a positive contribution in all the first- and second-order excess quantities.

A difference in free volume between components affects all of the mixing quantities even when $X_{12} \simeq 0$, e.g. in mixtures of chain-molecules composed of identical segments such as alkanes. The positive curvature of $\tilde{V}(\tilde{T})$ leads to a $\tilde{V}$ value for the mixture which is lower than a simple average of the V_i. The free volume contribution is then negative in H^E, S^E and $C_P{}^E$ but positive in G^E. As emphasized by Prigogine, these signs are connected with the positive upward curvature of $\tilde{Y}$ against $\tilde{T}$ for the first three quantities and negative downward for $\tilde{G}$ against $\tilde{T}$. For most small-molecule systems the effect of the free volume difference in H^E, S^E and G^E is less than that of X_{12}, while for $C_P{}^E$, it is usually greater, so that $C_P{}^E$ is predicted to be small and negative. It is with polymer solutions that the free volume effect becomes important, first in explaining the LCST [15], the phase separation on increasing T which occurs as a general phenomenon in polymer solutions. The difference in $\tilde{V}$ between polymer and solvent increases greatly with increase of T towards the critical temperature of the solvent. The rapidly increasing positive G^E leads to the LCST. Furthermore, application of pressure [15] to a system will decrease the free volume difference between polymer and solvent, thus enhancing polymer solubility as particularly seen when supercritical fluids are used as solvents. While the difference of free volume leads to a single contribution in H^E, G^E and $C_P{}^E$, two free volume contributions can be distinguished [16] in V^E. One reflects the positive curvature of $\tilde{V}$ against $\tilde{T}$, and is always negative. However, the other termed the P^* contribution is proportional to $(P_1^* - P_2^*)(\tilde{V}_1 - \tilde{V}_2)$, which can be of either sign. In a typical example [16], component 1 can be an aromatic or polar liquid and component 2 is drawn from the series of n-alkanes. Here $(P_1^* - P_2^*)$ is an almost constant positive quantity. With increase

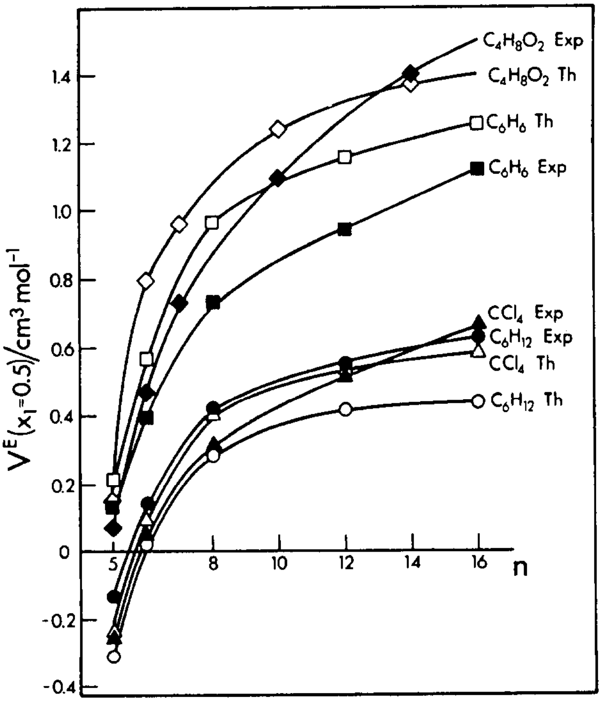

Fig. 1. Experimental and theoretical values of the molar V^E at equimolar composition and 25°C for cyclohexane, carbon tetrachloride, benzene, and *p*-dioxane mixed with n-alkane series (from Ref. [16]).

of carbon number, however, $\tilde{V}_2$ decreases so that typically $(\tilde{V}_1 - \tilde{V}_2)$, changes from negative to positive giving the same change of sign in V^E. Meanwhile, H^E and G^E, dominated by X_{12}, are positive for every system. This is illustrated in Fig. 1 showing the comparison between predicted and experimental values of V^E for a number of liquids mixed with the normal alkane series. We conclude that the PF theory predicts a richness and complexity in the excess quantities and it also provides an intuitive interpretation of the various effects.

4. Destruction of order

4.1. Alkane systems

In spite of the success of the PF theory there are notable shortcomings, leaving the predictions as a base line or reference line against which new effects may be distinguished. These effects appear to be due to structure, either created or destroyed by the mixing process. The presence of structure in a liquid effectively changes the $Y(T)$ relation from that followed by an ordinary liquid. Schematically we expect that the first order quantities H, S and V will be lowered by the presence of structure and increasingly so at low T (see Fig. 2). The temperature derivatives, i.e. C_P and $\mathrm{d}V/\mathrm{d}T$ should thus show positive contributions, particularly at low T, as seen in Fig. 2. If order is destroyed during mixing to make the solution an "ordinary" liquid, it is clear that there will be positive contributions to H^E, S^E and V^E, and negative in $C_P{}^E$ and $\mathrm{d}V^E/\mathrm{d}T$. On the other hand, if order is created in the solution, all of these signs should be reversed.

Figs. 3–5 show equimolar values of H^E, $C_P{}^E$ and $\mathrm{d}V^E/\mathrm{d}T$ for cyclohexane mixed with two series of alkanes: the normal alkanes (n-C_n) and a series of highly branched isomers (br-C_n): 2,2-dimethylbutane, 2,2,4-trimethylpentane, 2,2,4,6,6-pentamethylheptane and 2,2,4,4,6,8,8-heptamethylnonane. Depolarized Rayleigh scattering demonstrates [17] that

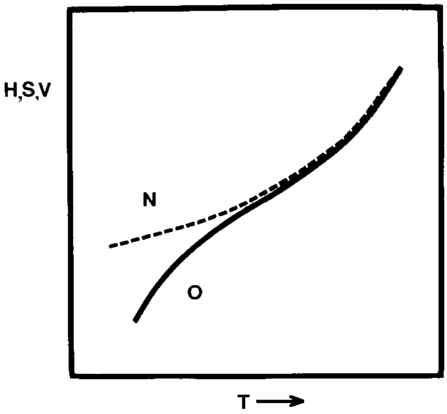

Fig. 2. Schematic representation of the temperature dependence of enthalpy, entropy or volume of a liquid capable of ordering (O) compared with a normal (N), "ordinary" liquid.

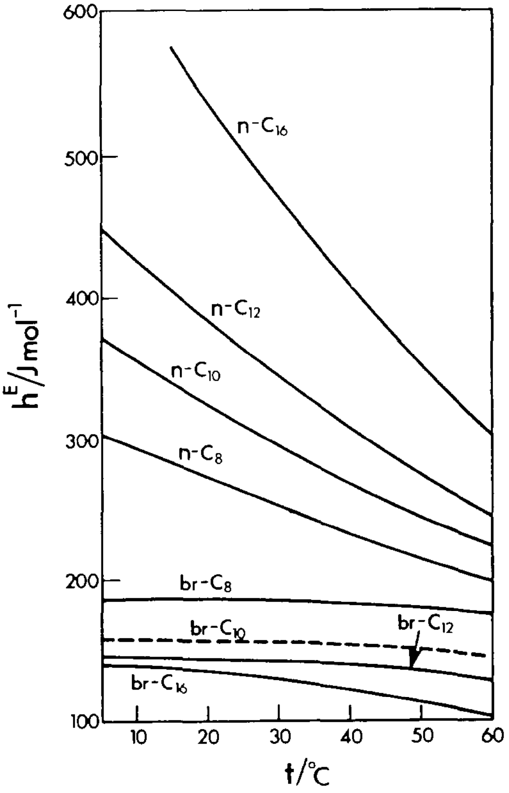

Fig. 3. Temperature dependence of the equimolar H^E for cyclohexane with normal and branched alkanes (The br-C_{10} curve was obtained by interpolation between br-C_8 and br-C_{10}) (from Ref. [19]).

orientational order exists between adjacent normal alkane chains, and this increases with increasing carbon number. The same technique shows that the br-C_n molecules cannot order because of their globular shape [18]. Cyclohexane, also globular in shape, acts as an order-destroyer when mixed with the n-C_n. Thus, H^E [19] for the n-C_n contains a positive contribution which is absent for the br-C_n series (Fig. 3). Since the orientational order falls off with increase of T, $dH^E/dT = C_P^E$ [19] is strongly negative for the n-C_n series (Figs. 3 and 4) and $dC_P^E/dT > 0$. The PF theory predicts (Fig. 4) small negative C_P^E and $dC_P^E/dT < 0$ for both series due to the free volume difference between components which increases with T. This behavior is correct for br-C_n but not for the n-C_n series. A similar situation prevails in Fig. 5 for dV^E/dT values [20] at 25°C for the two series plotted against carbon number. The PF theory predicts negative dV^E/dT changing to positive with increase of n, for both series. This is correct for the br-C_n but for the n-C_n, the experimental values deviate below the theoretical, becoming increasingly negative as n increases (Fig. 5). This reflects the negative order contribution to dV^E/dT increasing in magnitude with n, similar to the negative contribution in C_P^E.

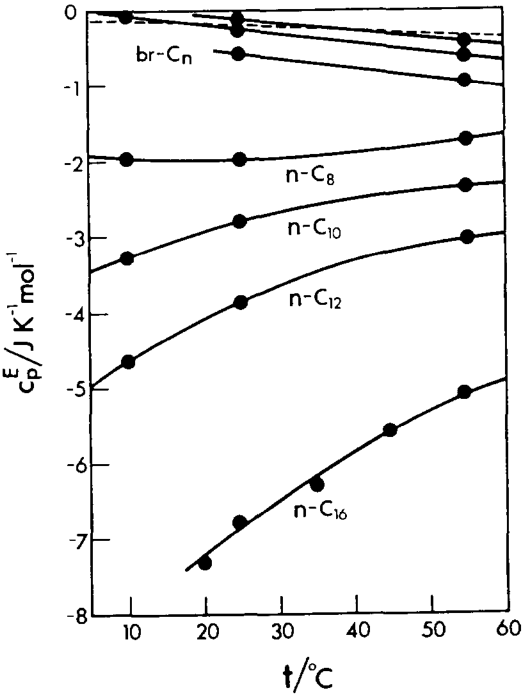

Fig. 4. Equimolar excess heat capacity values at different temperatures for cyclohexane with the normal alkanes (as indicated) and branched alkanes (full lines reading from top: br-C_8, br-C_{12}, and br-C_{10}. The Prigogine-Flory theoretical curve is shown for cyclohexane + n-C_{16} as a dashed line at the top of diagram. Similar curves are obtained for the other systems (from Ref. [19]).

There appears to be no simple theory to quantify effects of orientational order. However, Siddiqi et al. [21] have achieved remarkable success in dealing with C_P^E for mixtures of molecules of different shape including cycloalkanes, methylcycloalkanes and the normal alkane decane.

4.2. Aromatic hydrocarbons

The benzene + cyclohexane system is apparently one of the simplest systems to treat since the two components, having the same value of α, have the same free volume. Furthermore, since their molecular sizes are almost the same, the combinatorial entropy will be ideal. There is, however, a large value of H^E and X_{12} and hence, according to the PF theory, positive values of S^E, G^E, C_P^E, and dV^E/dT. These values and the experimental values [22] are given in Table 1, where one sees that S^E is considerably larger than predicted, and there is a degree of enthalpy-entropy compensation which is unpredicted. Furthermore, C_P^E is large and negative while dV^E/dT is much smaller than predicted. All of these deviations from the PF prediction are manifestations of quadrupolar [23] ordering of the benzene molecules in the pure liquid [24] which is a remnant of that existing in

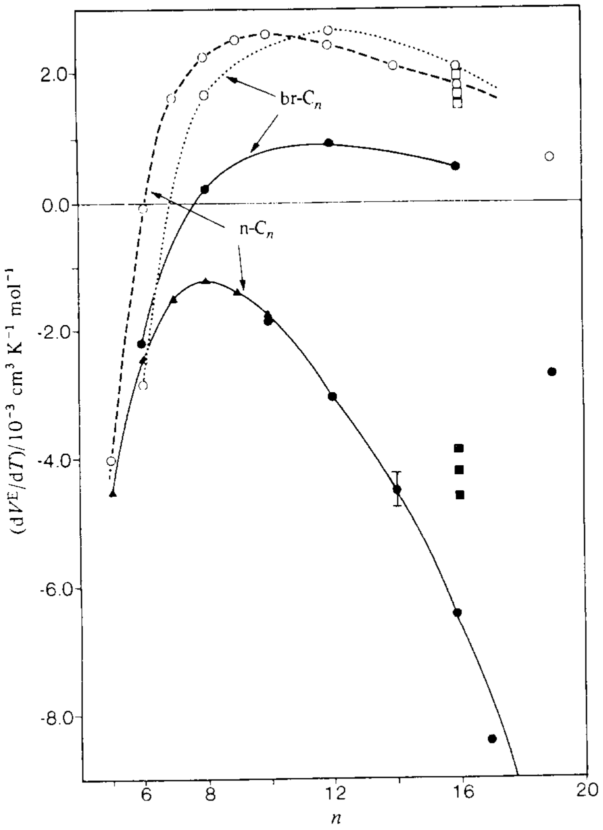

Fig. 5. Equimolar dV^E/dT (full curves, experiment; dashed or dotted curves, PF theory) for cyclohexane with normal and highly branched alkanes plotted against their carbon numbers. At $n = 16$: ■ and □, experimental and theoretical points for, in descending order, 2-, 4- and 6-methylpentadecane. At $n = 19$: ● and O, experimental and theoretical points for 2,6,10,14-tetramethylpentadecane (from Ref. [20]).

the solid. The order is broken by dispersing the benzene in cyclohexane which has a very small quadrupole moment. C_P^E is generally considerably more negative than predicted for mixtures [25] of cyclohexane and cyclopentane with aromatic hydrocarbons, e.g. toluene or xylene, or hydrocarbons with double bonds, e.g. tetralin or cyclododecatriene.

Table 1

Excess thermodynamic quantities for equimolar mixtures of benzene–cyclohexane

	H^{Ea}	V^{Eb}	TS^{Ea}	G^{Ea}	C_p^{Ec}	C_v^{Ec}	dV^E/dT^d
Expt	800	0.651	490	310	−2.89	−1.63	0.64
PF theory	800	0.623	213	586	0.49	0	5.20

[a] J mol^{-1}; [b] cm^3 mol^{-1}; [c] J K^{-1}; [d] 10^{-3} mol^{-1} K^{-1}.

Surprising differences in the effects of dipolar and quadrupolar order on excess properties are predicted by Gubbins and Gray and co-workers [26]. A polar/non-polar mixture gives positive H^E and S^E for either dipoles or quadrupoles. But, the concentration dependences of these excess functions are predicted to be different; the maximum lies at a low mole fraction of the polar component for dipoles and a high concentration for quadrupoles. Even more remarkable is the prediction that for these systems ΔC_v is positive for dipoles and negative for quadrupoles. It is hard to see why both "order" effects should not have the same sign in ΔC_v, i.e. negative. The quadrupole prediction is correct for the benzene–cyclohexane system. Murakami and collaborators [27] are measuring second-order excess properties for dipolar/non-polar, dipolar/dipolar and complex-forming mixtures. A variety of order effects are revealed by these interesting results. There does not appear to he conclusive evidence for or against the qualitative predictions of Ref. [26].

5. Creation of order

5.1. Concentration fluctuations

The most evident "order" in solution is constituted by non-randomness or concentration fluctuations caused by "antipathy" between the two components.

The thermodynamic manifestation of this structure is the "W-shape" concentration dependence discovered and extensively studied by Grolier and collaborators [28]. Here, $C_P{}^E$ typically starts with a negative sign at the edges of the concentration range, but becomes positive, or passes through a maximum, in the middle of the range. The unexpected behavior in this region is due to the concentration fluctuations, equivalent to "structure" [29], and is of course unpredicted by PF. Rubio has suggested [29] that S_{cc}, the concentration–concentration correlation function, or structure factor, related simply to the free energy of the system should be a useful predictor of the non-randomness and hence of $C_P{}^E$. Work has been done on mixtures of series of chain-molecules and indeed $C_P{}^E$ and S_{cc} can be correlated [30]. At present, however, there is no direct relation between the quantities.

5.2. Association of alcohols in solution

The association, through hydrogen bonding, of alcohol molecules dispersed in an inert solvent is analogous to small-scale micellization, being cooperative in nature and typically involving several molecules. Here the most sensitive indicator of order again seems to be C_P, either as $C_P{}^E$ of the solution or as $C_{p,\phi}$, the apparent molar heat capacities of the alcohol solute in solution. $C_{p,\phi}$, shows a dramatic peak at low concentration associated with the formation of multimers, essentially tetramers [31]. Simple association models, in particular that due to Treszczanowicz and Kehialan, give remarkably good predictions [31] of $C_{p,\phi}$ for 17 1-alkanol + alkane mixtures showing that, for all these alkanols and alkanes, ΔH and ΔS for H-bond formation is the same and that tetramers are the dominant multimers. The TK approach is applicable to alcohol–proton acceptor mixtures [32], and to alcohol–alcohol mixtures [33].

5.3. Aqueous solutions and hydrophobicity

Probably the most important structure in solution, often called a clathrate or "iceberg", occurs in the water surrounding a hydrophobic solute or group. This structure enters the discussion of hydrophobicity and, particularly, its temperature-dependence. The aqueous solubility of hydrocarbons, a measure of hydrophobicity, has a remarkable behavior with increasing temperature: it decreases to an unexpected minimum before finally increasing [34]. (The minimum lies at about 50°C for n-alkanes and 15°C for aromatics.) The same behavior is found with surfactants, where, as T is raised, the CMC also passes through a minimum [35]. Similarly, aqueous solutions of organic molecules containing hydrophobic and hydrophilic groups phase separate [36], on raising T, at an LCST, but may become homogeneous again when T is above a UCST. The same minimum in hydrophobe solubility apparently exists in the temperature region corresponding to the native state of proteins. Proteins therefore can denature, exposing their hydrophobic groups to water, both at low (cold denaturation) and at high (heat denaturation) temperatures [37].

Hydrophobicity is characterized quantitatively by the transfer functions $\Delta_H{}^W Y$ for a hydrophobe, e.g. a hydrocarbon, moving from the pure liquid into water at infinite dilution. Experimentally, $\Delta_H{}^W Y$ is given by the solubility of the hydrocarbon, x_H in water:

$$\ln x_H = -\Delta_H{}^W G/RT \qquad (7)$$

Accurate measurement of x_H as a function of T using either traditional methods, or a new thermodynamic application of HPLC [38], gives the transfer functions seen in the top line of Table 2. The positive sign for $\Delta_H{}^W G$ is expected, but the negative or near-zero values of $\Delta_H{}^W H$, the negative sign for $\Delta_H{}^W S$ and positive for $\Delta_H{}^W C_P$ were surprising. The original interpretation of hydrophobicity explained [34] the negative sign of $\Delta_H{}^W S$ by the presence of "structured" water around the hydrophobe, the clathrates or "icebergs". This falls off rapidly on raising T so that $\Delta_H{}^W C_P$ is positive. However, identification of hydrophobicity solely with such structure apparently indicates a continuous decrease of hydrophobicity as T is raised, rather than the characteristic change of sign encountered with aqueous phenomena.

Shinoda [39] and Hvidt [40] have given other treatments. For the essentials, they may be considered as a single approach which immediately predicts the change of sign. For convenience the total transfer functions at 25°C are split into two parts (see Table 2) associated with two conceptual steps in the transfer process: (1) the breaking of H-bonds to form a cavity. This process is strongly endothermic, but $\Delta_H{}^W S(1)$ is small and in Table 2,

Table 2
Functions for hydrocarbon transfer into water

	$\Delta_H{}^W G$	$\Delta_H{}^W H$	$\Delta_H{}^W S$	$\Delta_H{}^W C_p$	dx_H/dT
Total	+	–, +	–	+	–, +
H-bond breaking (1)	+	+	≈ 0	0	+
Structured H-bond formation (2)	–	–	–	+	–

for simplicity, it is set approximately to zero; hence $\Delta_H{}^W G(1)$ is positive. The solute then enters the cavity with negligible thermodynamic effect. As T is raised, the ratio $\Delta_H{}^W G(1)/RT$ obviously decreases so that x_H increases continuously. At this point, water would be acting similarly to any solvent of much higher cohesive energy than the solute. However, the special nature of water allows a further step: (2) at low T, the water molecules reorient or structure, allowing them to re-form H-bonds around the cavity. A thermodynamic effect of this H-bonding is a negative $\Delta_H{}^W H(2)$ which essentially cancels $\Delta_H{}^W H(1)$ to leave a small total $\Delta_H{}^W H$ which may be negative or positive depending on whether T is lower or higher than the temperature where the minimum solubility occurs. A quite different situation prevails for S; due to the necessity of structuring, $\Delta_H{}^W S(2)$ is negative, giving a negative total $\Delta_H{}^W S$. Furthermore, $\Delta_H{}^W H(2)$ and $\Delta_H{}^W S(2)$ combine to give a negative value of $\Delta_H{}^W G(2)$, i.e. the water structuring in step 2 actually promotes solubility, the contrary of the effect of structure in the traditional view. On raising T, this structure decreases, so that $\Delta_H{}^W C_P(2)$ is positive and $\Delta_H{}^W G(2)/RT$ becomes less negative, causing x_H to decrease.

It is the structuring in step 2, of importance at low T, which brings about the decrease of x_H towards a minimum, to be followed by the normal increase of solubility given by step 1. The use of two steps does appear to be confusing. However, they are only a conceptual device and the same thermodynamics would result from a single, but complex step.

A quantitative treatment of the hydrophobic hydration process from the two-step point of view has been given by Privalov and Gill [37] and more recently by Costas et al. [41]. The latter authors have also reviewed [42] the application of these ideas to aqueous phenomena and their temperature dependence. Much more theoretical work could be mentioned, e.g. that by Karplus and associates [43] who found that solvent reorganization has no net effect on $\Delta_H{}^W G$. We believe that the test of each approach should be the T-dependence of the aqueous stability of hydrophobes.

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