Thermodynamics of binary liquid organic mixtures[a]

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Abstract Recent studies on the thermodynamic properties of binary organic liquid mixtures are reviewed. Emphasis is placed on structure-property correlations and pseudo-lattice group contribution models. The examples of application cover low-pressure phase diagrams, excess enthalpies and excess heat capacities for several classes of polar or nonpolar systems containing alkanes, cyclohexane, benzene, ethers, alkanones, chloroalkanes, or alkanols.

INTRODUCTION

In order to relate the nature of a given system to its thermodynamic properties, it is necessary to postulate a "molecular model" for the system, i.e., to define the structure of the molecules and the molecular interactions. The thermodynamic properties are then derived from the molecular model either by computer simulation or by means of a theoretical model, based on statistical thermodynamics (Fig. 1).

Computer simulation studies on mixtures are relatively scarce and deal mainly with simply-shaped rigid molecules (spheres, dumbbells, etc.). Mixtures formed by "hard molecules", i.e., molecules without attractive forces, have a merely theoretical interest. Mixtures of simple diatomic molecules possessing electrostatic charges (dipoles or quadrupoles) have been studied quite recently by Gubbins and coworkers (Refs. 1-3). Depending on the distribution of charges, different types of molecular clustering effects have been shown with significant consequences on the thermodynamic properties.
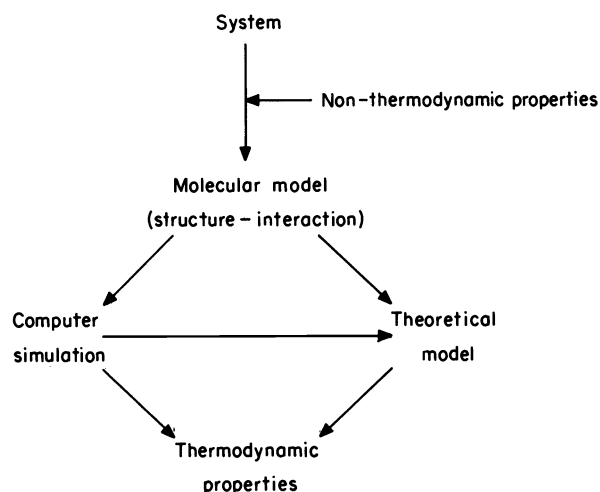

Fig. 1. Theoretical methods of investigating the thermodynamic properties of systems

In this paper we are concerned with dense (liquid) mixtures of simple organic molecules, i.e., members of homologous series of basic classes of organic compounds such as alkanes, ethers, alkanones, etc. Organic molecules, with a few exceptions, are polyatomic and flexible and their interaction forces are fairly complex. For physically obvious reasons, one may expect that the force field of a given segment or group in an organic molecule which belongs to a homologous series will depend less on the nature of the molecule, than on the nature of the group itself. The most general definition, or basic assumption, of the group contribution method is that, with conveniently defined groups, the interaction energy of the system is given by the sum of group interaction energies. This definition refers to the molecular model only, not

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a) Plenary lecture in honor of Dr. G.C. Benson

to the procedure followed to derive the thermodynamic properties, which may be computer simulation or a more or less rigorous theoretical model (Fig. 1).

Computer time is probably at present the main limitation in simulating organic mixtures in terms of group contributions. Another limitation results from our inadequate knowledge of the interaction forces between groups. For these reasons, at least, the development and use of theoretical models are necessary.

Perturbation theories are regarded as the most convenient compromise between rigor and ease of calculation of thermodynamic properties (Ref. 3). Like the computer simulation studies, perturbation theories have been applied mostly to spherical or to simple nonspherical molecules. Winkelmann (Ref. 4) has taken into account electrostatic interactions for a model of polarizable dipolar hard spheres. There have been significant advances in recent years in treating larger anisotropic molecules as multi-center-Lennard-Jones molecules (Refs. 5,6). Svejda and Kohler (Ref. 7) have presented a group contribution approach for pure nonpolar compounds with possible extension to mixtures.

PSEUDO-LATTICE GROUP CONTRIBUTION MODELS

The most widely applicable statistical group contribution methods are still based on rigid or free-volume pseudo-lattice models (Ref. 8). The use of such models is justified by their ability to correlate and predict low-pressure phase equilibria and related properties in terms of characteristic group interaction parameters. Moreover, the comparison of the model predictions with experimental data, taken within the limits of validity of the model, enables certain intra- and intermolecular effects to be highlighted which are relevant in any other, more empirical or more fundamental, group contribution approach.

Fischer (Refs. 9, 10) has recently tested the pseudo-lattice theory of Guggenheim (Ref. 11) for spherical molecules of equal size by using perturbation theory and has shown that the free energy predictions are qualitatively correct. The differences between the excess quantities at constant pressure and at constant volume are usually large, but this may have little effect in terms of group contributions if the intergroup distances at constant pressure are nearly the same for the different members of homologous series.

The random-mixing model. Guggenheim's rigid-lattice model in the random mixing approximation (Ref. 11) is the simplest group-contribution model founded on statistical thermodynamics. According to this model, in the group-surface interaction version (Refs. 12, 13), the configurational energy, U^C, is given by

$$U^C = \frac{A}{2} \left(\sum_s \alpha_s^2 \epsilon_{ss} + 1/2 \sum_s \sum_t \alpha_s \alpha_t \epsilon_{st} \right) \tag{1}$$

where A is the total intermolecular contact surface, α_s is the s-type surface fraction, and ϵ_{st} is the interaction energy per surface unit between s- and t-surfaces. The residual molar excess Gibbs energy, $G^E_{res,m}$, of a multicomponent system is of the form

$$G^E_{res,m} = 1/2 \left(\sum_i q_i x_i \right) \sum_i \sum_j \xi_i \xi_j g_{ij,m} \tag{2}$$

where

$$g_{ij,m} = 1/2 \sum_s \sum_t (\alpha_{si} - \alpha_{sj})(\alpha_{ti} - \alpha_{tj}) g_{st,m} \tag{3}$$

$g_{st,m}$ is the interchange Gibbs energy of contact (s,t), α_{si} is the value of α_s on molecule i, q_i is the total surface of molecule i, and x_i and ξ_i are, respectively, the mole fraction and the surface fraction of component i.

Equations (1)-(3) are applicable to nonpolar systems only, the quantities of $g_{st,m}$ representing "dispersive" interchange Gibbs energies. These are usually temperature-dependent (see Ref. 8). The temperature dependence can be expressed by a 3-constant equation (Ref. 14).

$$g_{st,m}(T)/RT = C_{st,1} + C_{st,2} \left((T°/T) - 1 \right) + C_{st,3} \left(\ln(T°/T) - (T°/T) + 1 \right) \tag{4}$$

where T = 298.15 K is the scaling temperature. The enthalpy of interchange, $h_{st,m}$, and the heat capacity of interchange, $c_{p,st,m}$, are then given by

$$h_{st,m}(T)/RT = C_{st,2}\frac{T°}{T} - C_{st,3} \left(\frac{T°}{T} - 1 \right) \tag{5}$$

and

$$c_{p,st,m}/R = C_{st,3} \tag{6}$$

the latter being assumed independent of T. $C_{st,i}$ are dimensionless quantities termed "interchange coefficients". The molar excess enthalpy, H^E_m, and the molar excess heat capacity, $C^E_{p,m}$, are given by equations similar to equations (2) and (3).

Chemical association models. One may readily incorporate chemical association equilibria in the rigid pseudo-lattice group contribution model described above (Ref. 15). All the contacts (s,t) are characterized by "physical" (dispersive) interchange energies. In addition, certain contacts or "bonds" are assumed to be chemically active yielding "associates" $A_iB_j(i,j = 0,1,2,...)$, A and B being the monomeric species. Each associate A_iB_j is characterized by its association energies, Gibbs energy $\Delta G_{ij,m}^{CHEM}$ and enthalphy $\Delta H_{ij,m}^{CHEM}$, which may be expressed as a sum of bond energies. This is the so-called "non-athermal associated" solution model. Assuming that all the deviation from ideal behavior is due to the chemical equilibria, i.e., neglecting the dispersive interchange energies, we obtain the "athermal associated" model (Ref. 16).

If we also neglect the differences in size between the monomers and the associates we obtain the well-known model of ideal association.

Quasi-chemical models. Weak orientational effects in mixtures can be accounted for by means of Guggenheim's quasi-chemical approach (Ref. 11). The configurational energy, U^C, is given by an equation similar to equation (1)

$$U^C = \frac{A}{2} \left(\sum_s x_s^2 \epsilon_{ss} + 1/2 \sum_s \sum_t x_s x_t \epsilon_{st} \right)$$

(7)

the random contact surfaces α_s being replaced by the quasi-chemical quantities x_s. The latter are obtained by solving the system of quasi-chemical equations in which the main parameters are the Boltzmann factors $\exp\{-g_{st,m}/zkT\}$.

In the classical theory, molecules are forced to occupy the sites of a particular lattice. However, the assignment of contact points is arbitrary and irrelevant and can be avoided by using the group-surface-interaction version of the theory (Ref. 13). Moreover, we regard the coordination number z as a non-randomness factor. Since no explicit relation is given between z and the anisotropy of the intergroup potentials, z is a very crude representation of non-randomness. The random-mixing equations are obtained for z = ∞.

The major shortcomings of the classical quasi-chemical approach are the folowing: a) the entire interchange energy of any given contact is assumed to generate non-randomness to the extent expressed by the coordination number z; b) z is assumed to be the same for all the contacts.

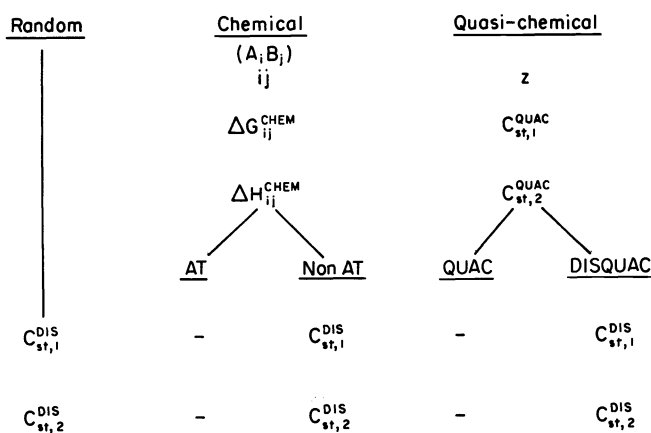| Random	Chemical		Quasi-chemical	
	(A_iB_j)			
	ij		z	
	ΔG_{ij}^{CHEM}		$C_{st,1}^{QUAC}$	
	ΔH_{ij}^{CHEM}		$C_{st,2}^{QUAC}$	
	AT	Non AT	QUAC	DISQUAC
$C_{st,1}^{DIS}$	–	$C_{st,1}^{DIS}$	–	$C_{st,1}^{DIS}$
$C_{st,2}^{DIS}$	–	$C_{st,2}^{DIS}$	–	$C_{st,2}^{DIS}$

Fig. 2. Pseudo-lattice models: AT, athermal associated; QUAC, classical quasi-chemical; DISQUAC, dispersive & quasi-chemical

A physically more realistic approach should take into account a dispersive, random, contribution for every contact, eventually supplemented by an electrostatic, non-random contribution. A simple extension of the quasi-chemical theory is DISQUAC, the "dispersive-quasi-chemical" model (Ref. 8). It resembles the theory of non-athermal associated mixtures (Fig. 2). In the latter, the chemical contribution is supplemented by the dispersive physical contribution. In DISQUAC the same type of dispersive

contribution supplements the quasi-chemical expressions. The configurational energy, U^C, of the system is the sum of the two terms given by equations (1) and (7)

$$U^C = \frac{A}{2} \left(\sum_s \alpha_s^2 \, \epsilon_{ss}^{DIS} + 1/2 \sum_s \sum_t \alpha_s \alpha_t \epsilon_{st}^{DIS} + \right.$$

$$\left. + \sum_s x_s^2 \, \epsilon_{ss}^{QUAC} + 1/2 \sum_s \sum_t x_s x_t \, \epsilon_{st}^{QUAC} \right)$$

(8)

The surface fractions α_s being constant, at a given composition x_j, the quasi-chemical contact surfaces x_s, obtained by maximizing the configurational partition function (see Ref. 13), are the same as in the classical theory. Each contact (s,t), either polar or nonpolar, is thus characterized by a set of dispersive interchange coefficients, $C_{st,i}^{DIS}$, and the polar contacts by an additional set of quasi-chemical interchange coefficients, $C_{st,i}^{QUAC}$, and the coordination number z. The excess functions each contain a dispersive and a quasi-chemical term which are calculated independently and then simply additioned.

For chemical association models, the consideration of a "physical", dispersive, contribution is necessary in order to predict partial liquid-liquid miscibility. The quasi-chemical model, even in its classical version, predicts partial miscibility. The superiority of DISQUAC appears clearly when we consider the concentration dependence of the molar excess functions for systems such as (alkanols + alkanes). G_m^E being a less sensitive quantity, we have represented in Fig. 3 H_m^E of (ethanol + heptane), the experimental points and the curves calculated with the classical quasi-chemical model using different values of z. The interchange coefficients $C_{ah,i}$, where h represents the OH group and a the CH$_2$ or CH$_3$ groups, were adjusted to fit the experimental G_m^E and H_m^E values for $x_1 = 0.5$.
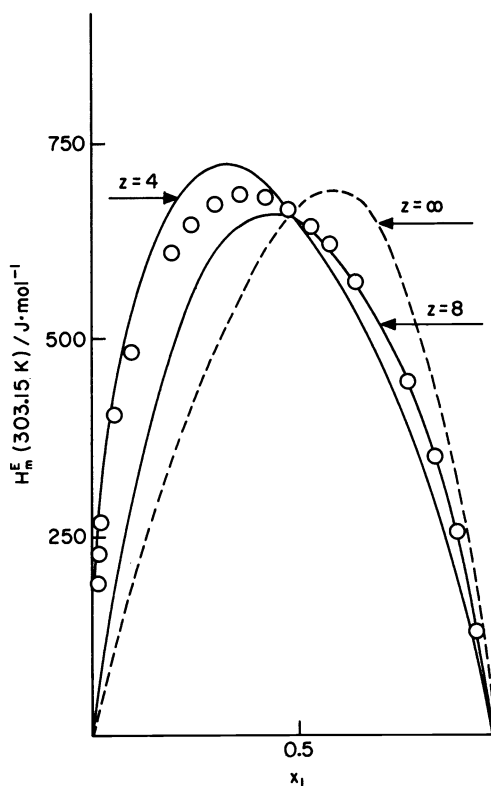

Fig. 3.   Molar excess enthalpy H_m^E of (ethanol + heptane) against x (ethanol). Points, experimental values (Ref. 17). Curves, quasi-chemical calculations for z = 4 or z = 8 with interchange coefficients fitted at $x_1 = 0.5$. Dashed curve, calculated in the random-mixing approximation.

It may be seen that the maximum of the experimental H_m^E curve is situated at much lower concentrations of ethanol than that calculated in the random-mixing approximation. This is quite characteristic for all (polar + nonpolar) systems. For z = 8, the agreement is satisfactory for $x_1 > 0.5$, but not for $x_1 < 0.5$. At low ethanol concentrations, we should take z ~ 4, but in this case no $C_{ah,1}$ can fit the experimental G_m^E (Fig. 4).   As a matter of fact, no value of z can represent H_m^E over the entire concentration range, the

experimental curve being broader and flatter than any of the calculated ones. This behavior is quite general for (polar+ nonpolar) mixtures (see next Section).
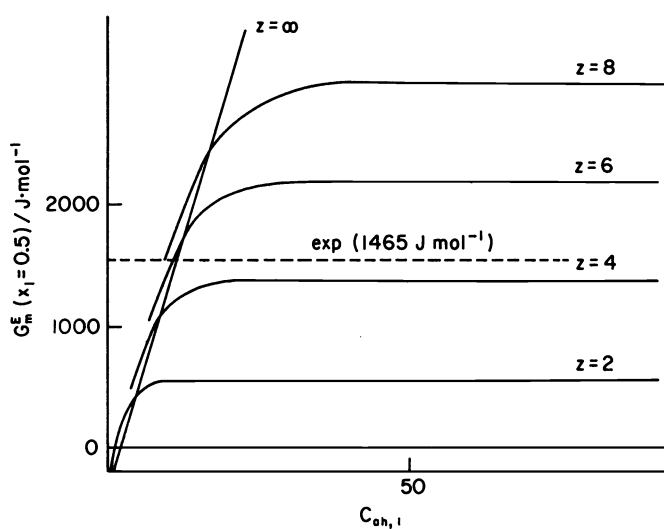

Fig. 4. Equimolar excess Gibbs energy $G_m^E(x_1 = 0.5)$ of (ethanol + heptane) at 303.15 K. Dashed line, experimental value (Ref. 18). Curves, model calculations for different values of z against the interchange Gibbs energy coefficient, $C_{ah,1}$ (Ref. 19).

Assuming, as in DISQUAC, that the calculated H_m^E is the sum of two contributions, dispersive and quasi-chemical, taken in adequate proportions, with the maxima situated at different values of x_1, we can reproduce much better the shape of the experimental H_m^E (Fig. 5).
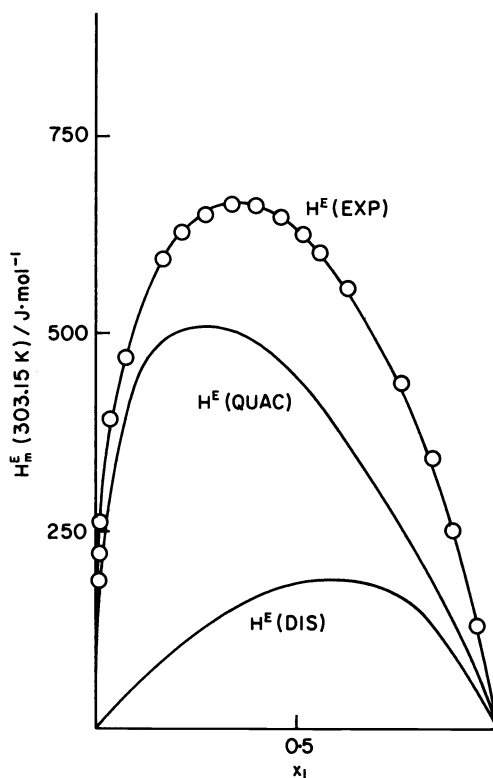

Fig. 5. Molar excess enthalpy H_m^E of (ethanol + heptane) against x(ethanol) represented schematically by DISQUAC (Ref. 19). Points, experimental values (Ref. 17).

APPLICATION TO BINARY SYSTEMS

The examples of application in this paper were selected among the systems which have already been investigated quite carefully in terms of the classical pseudo-lattice group contribution model. All these systems contain a nonpolar or polar component + an alkane. These studies revealed, in addition to the above-mentioned systematic deviations between the predicted and the experimental concentration dependence of H_m^E, an anomalous variation of the interchange coefficients with temperature and the structure of the alkane. The very accurate $C_{p,m}^E$ measurements performed recently on these systems appear to be of considerable value for a better understanding of their behavior.

(Benzene + alkanes). G_m^E and H_m^E of (benzene + n-alkane) are correlated quite well in the random-mixing approximation using the coefficients $C_{ab,1} = 0.2598$ and $C_{ab,2} = 0.5623$ (Ref. 13). The experimental H_m^E values for the higher n-alkanes (ten or more carbon atoms) are somewhat larger than the corresponding calculated results. This additional H_m^E has been attributed to conformational and/or short-range orientational changes when n-alkanes are mixed with globular molecules. This effect, which we termed "Patterson effect", has been extensively investigated by Patterson and collaborators (Refs. 20,21).

An analysis of $C_{p,m}^E$ of (benzene + n-alkane) (Ref. 22) revealed that the compositional dependence is fairly well represented by the random-mixing model, but the interchange coefficient $C_{ab,3}$ depends strongly on the size of the n-alkane (Fig. 6).
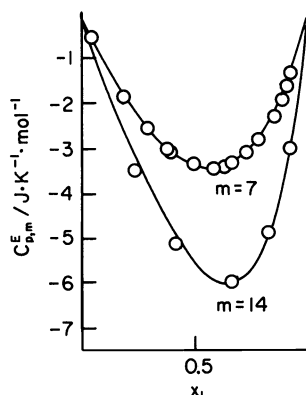

Fig. 6.   Molar excess heat capacities, $C_{p,m}^E$, at 298.15 K, of (benzene + heptane) (m=7) or + tetradecane (m=14) against x(benzene). Points, experimental values (Ref. 22). Curves calculated according to the random-mixing approximation with $C_{ab,3} = -0.600$ (m=7) or $C_{ab,3} = -0.828$ (m=14).

In Fig. 7 we have represented $C_{ab,i}$ of (benzene + n-alkanes), adjusted to the equimolar, experimental, G_m^E, H_m^E, and $C_{p,m}^E$ data, as a function of m, the number of carbon atoms in the n-alkane. We note the relative constancy of $C_{ab,1}$ (enthalpy-entropy compensation, Ref. 20), the slight increase of $C_{ab,2}$, and the strong decrease of $C_{ab,3}$, with increasing m.

The entire value of $C_{ab,1}$ and almost the entire value of $C_{ab,2}$ may be attributed to differences in interaction energies between benzene and CH_2 or CH_3 groups. $C_{p,m}^E$ of (benzene + 2,3-dimethylbutane), a branched alkane, being negative and fairly large (Ref. 23), we infer that the interactional part in $C_{ab,2}$ is temperature-dependent and contributes significantly to the value of $C_{ab,3}$. The slight increase of $C_{ab,2}$ with m is due to the Patterson effect. The latter being very sensitive to temperature causes $C_{ab,3}$ to decrease rapidly with increasing m. Additional $C_{p,m}^E$ measurements for (benzene + higher branched alkanes) are needed to confirm these remarks.

(Cyclohexane + alkanes). The differences in interaction energies between cyclohexane and alkanes are much smaller than between benzene and alkanes. The interaction contribution to G_m^E in (cyclohexane + n-alkanes) is very small, $C_{ac,1} = 0.0512$ (Ref. 13). Comparing H_m^E and $C_{p,m}^E$ of (cyclohexane + n-alkanes)
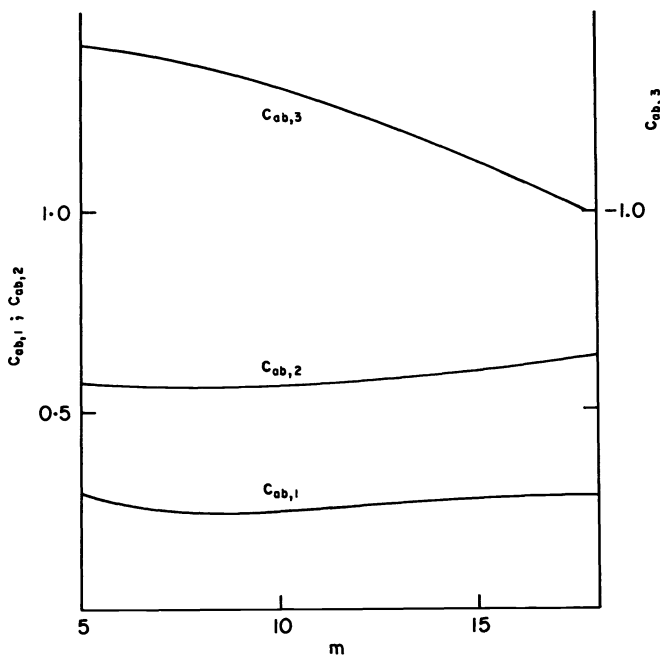
Fig. 7.   Interchange coefficients $C_{ab,i}$ of (benzene + n-alkanes) against m, the
number of carbon atoms in the n-alkane (Ref. 23).

with H_m^E and $C_{p,m}^E$ of (cyclohexane + branched alkanes) (Refs. 24–26), we see that the Patterson effect contributes largely to H_m^E of (cyclohexane + n-alkanes) and that it represents almost the entire source of $C_{p,m}^E$. Formally we can describe H_m^E and $C_{p,m}^E$ by means of $C_{ab,2}$ and $C_{ab,3}$ coefficients, but these depend very strongly on the chain length of the n-alkane. The shape of the calculated excess quantities is also less satisfactory than, e.g., for (benzene + n-alkanes), where the interaction contribution is predominant.

Branched alkanes behave similarly to cyclohexane as shown recently by Benson and collaborators (Ref. 27).

(n-Ethers + n-alkanes). The previously reported (Ref. 13) interchange coefficients for O/CH_2 or O/CH_3 in (n-ether + n-alkane), in the random-mixing approximation, are: $C_{ae,1} = 15.73$ and $C_{ae,2} = 29.04$. The availability of recent, very accurate, G_m^E, H_m^E and $C_{p,m}^E$ measurements permit a check to be made of both the model and the values of the coefficients. The G_m^E of (dibutyl ether + hexane), calculated by Marsh and Ott (Refs. 28,29) from LVE measurements, agree to better than $3 \, J \cdot mol^{-1}$ (1 per cent) with the predictions. The partial molar excess Gibbs energies at infinite dilution, $G_{i,m}^{E;\infty}$, are reproduced to within 2.5 per cent. As already noted (Ref. 30), the experimental H_m^E data fall about $50 \, J \cdot mol^{-1}$ (30 per cent in the central range of concentration (Ref. 30)) below the predicted curve, due to the strong steric effect of the two butyl groups. In dipropyl ether the steric effect is smaller and the recent experimental H_m^E results of Kimura et al. (Ref. 31) fall about $25 \, J \cdot mol^{-1}$ (10 per cent in the central range of concentration) below the predicted curve. The predicted H_m^E curve of (2,5,8-trioxanonane + heptane) agrees much better with the recent measurements (Ref. 32) which fall about $100 \, J \cdot mol^{-1}$ (less than 6 per cent in the central range of concentration) below the predicted curve. These measurements require therefore a readjustment of the enthalpic interchange coefficient, $C_{ae,2}$, and appropriate consideration of the steric effect. It should be remembered that similar steric effects, always stronger for H_m^E than G_m^E, have been observed for many other classes of compounds of the type RX, e.g., alkanals (Refs. 33,34), R_2X, e.g., alkanones (Refs. 35,36) or alkanoates (Ref. 37), and R_3X, e.g., tertiary amines (Refs. 38,39). Nonetheless, the random-mixing

model seems to be in satisfactory agreement with the experimental G_m^E and H_m^E results for (n-ether + n-alkane).
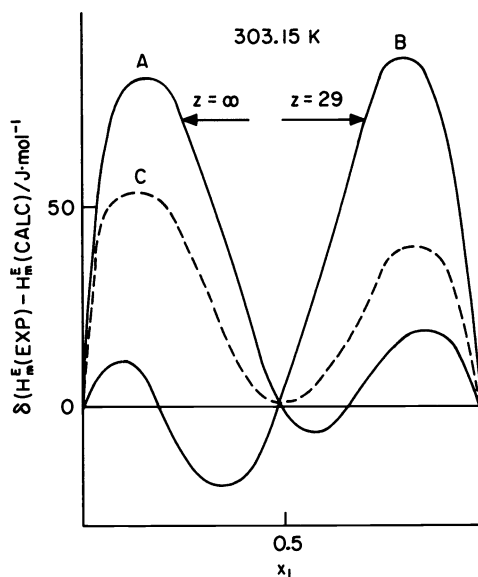

Fig. 8.   Deviation plot of the measured, H_m^E(EXP) (Ref. 32), and the calculated, H_m^E(CALC), molar excess enthalpies for (2,5,8-trioxanonane + heptane). Curve A, random-mixing calculation with $C_{ae,2}$ = 27.35; Curve B, quasi-chemical calculation with $C_{ae,1}$ = 12.62 and $C_{ae,2}$ = 18.51 (z=29); Curve C, DISQUAC calculation with $C_{ae,1}^{DIS}$ = 13.00, $C_{ae,2}^{DIS}$ = 23.00, $C_{ae,1}^{QUAC}$ = 1.861, $C_{ae,2}^{QUAC}$ = 22.447 (z=2).

However, careful examination of the shape of the H_m^E curves and, especially, of the recently determined $C_{p,m}^E$ curves reveals serious discrepancies between the experimental and the predicted curves. This is best illustrated by H_m^E and $C_{p,m}^E$ of (2,5,8-trioxanonane + heptane). Figure 8 represents the deviation plot $\delta H_m^E = H_m^E$(EXP) - H_m^E(CALC). In the random-mixing approximation (Fig. 8, Curve A), δH_m^E is relatively large (may exceed 80 J·mol^{-1}) for x_1 < 0.5, the agreement being better at x_1 > 0.5 (δH_m^E < 20 J·mol^{-1}). This indicates that ethers are slightly oriented and, indeed, if H_m^E(CALC) is calculated in the quasi-chemical approximation, with z=29 (Fig. 8, Curve B), then the agreement improves for x_1 < 0.5 (δH_m^E < 20 J·mol^{-1}), but worsens for x_1 > 0.5. Thus we find the same behavior as for (ethanol + heptane) (Fig. 3), though with much less pronounced deviations. DISQUAC gives a somewhat better agreement. Thus, for curve C in Fig. 8, δH_m^E is positive and less than 60 J·mol^{-1} over the whole concentration range. We did not attempt to find the best set of parameters and, apparently, none would exactly fit the H_m^E curve over the whole concentration range. For this purpose, it is necessary to consider an additional positive H_m^E contribution. The latter may be ascribed to "conformational" changes, similar to those noted in (benzene or cyclohexane + n-alkanes). It is difficult, if not impossible, to quantify the different contributions from the H_m^E values alone. The curves H_m^E(DIS), H_m^E(QUAC) and H_m^E(CONF) in Fig. 9 are an estimate of the dispersive, quasi-chemical, and "conformational" contributions respectively.

The complexity of the mixture can be better shown by considering the experimental $C_{p,m}^E$ curve (Fig. 10), Curve EXP) and comparing it with curves calculated in terms of contact interactions only. As a first approximation, the interchange enthalpies, $C_{ae,2}$, are assumed independent of the temperature, i.e., all $C_{ae,3}$ = 0. In the random-mixing approximation, $C_{p,m}^E$ = 0 in the whole concentration range (Fig. 10, Curve A). The quasi-chemical curve B in Fig. 10 corresponds to curve B in Fig. 8. Both curves A
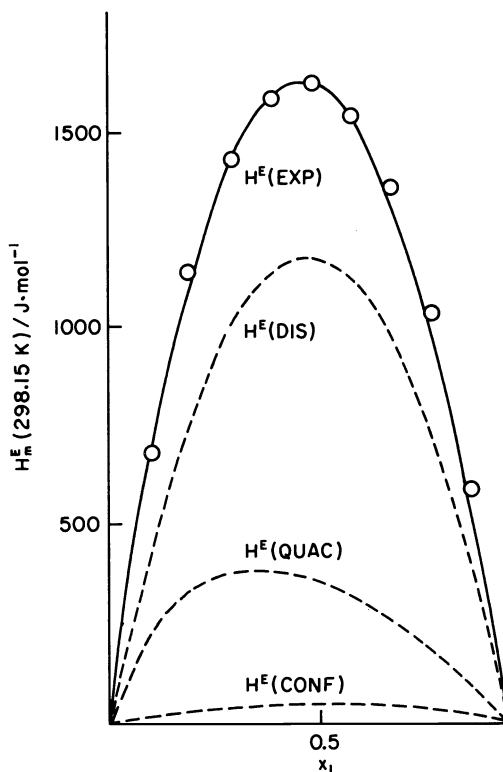
Fig. 9. Molar excess enthalpy H_m^E for (2,5,8-trioxanonane + heptane) against x(2,5,8-trioxanonane), represented schematically by DISQUAC + H_m^E(CONF). DISQUAC parameters as for curve C in Fig. 8. Points, experimental values (Ref. 32)

and B differ considerably from the experimental curve. Curves C, D, and E in Fig. 10 were calculated with different sets of parameters using the DISQUAC approach. S-shaped curves are predicted for this system with DISQUAC, but not the double-minimum experimental curve. The latter may be obtained by adding to the quasi-chemical $C_{p,m}^E$ (Curve QUAC in Fig. 11) and/or by assuming that $C_{ae,2}^{DIS}$ is temperature dependent.

(Di-n-propyl ether + n-heptane) is another (n-ether + n-alkane) system for which accurate $C_{p,m}^E$ data are available. The experimental $C_{p,m}^E$ is negative over the whole concentration range and has a single minimum (see Fig. 2 in Ref. 33). Using the set of parameters listed in Fig. 11, we obtain, indeed, a single minimum negative $C_{p,m}^E$, but not exactly the experimental curve. It should be stressed that all these calculations are very preliminary and are reported here only because the results seem quite promising.

(Cyclic ethers + alkanes). Experimental G_m^E and H_m^E data are available for two cyclic ethers, oxane and 1,4-dioxane. Due to the more exposed position of the oxygen atom(s), there is less steric hindrance in cyclic ethers than in n-ethers and the molecules seem more oriented. A satisfactory description is obtained in the quasi-chemical approximation with z=24 (Ref. 40). However, as shown in Fig. 12, the H_m^E curves of (oxane + heptane) (Curve C7) or + tetradecane (Curve C14) are slightly broader than calculated, indicating the presence of at least two contributions, quasi-chemical and dispersive. The effect is even stronger with 1,4-dioxane (Fig. 13). Quasi-chemical calculations of solid-liquid equilibrium diagrams (Ref. 40) for (oxane + n-alkanes) are in relatively good agreement (Fig. 14) with experiment, the deviations being much larger in the case of (1,4-dioxane + n-alkanes) (Fig. 15).
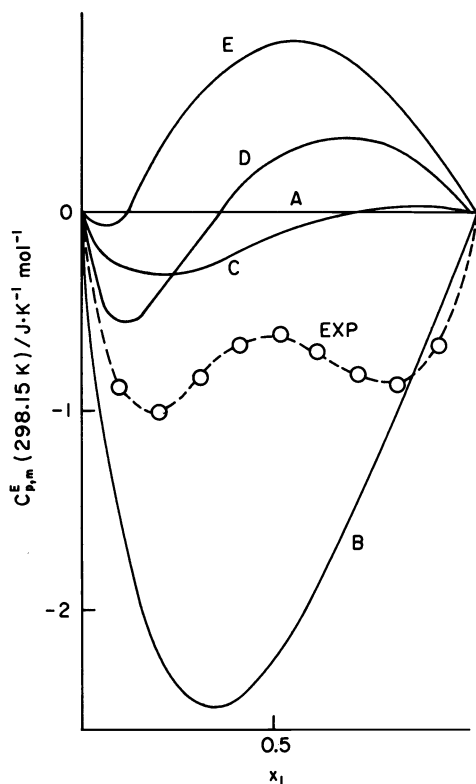
Fig. 10.   Molar excess heat capacity $C_{p,m}^{E}$ for (2,5,8-trioxanonane + heptane) against x(2,5,8-trioxanonane).   Points, experimental values (Ref. 32).   Curve A, random-mixing calculation;   Curve B, quasi-chemical calculation with coefficients given in Fig. 8;   Curves C, D, and E, DISQUAC calculations.
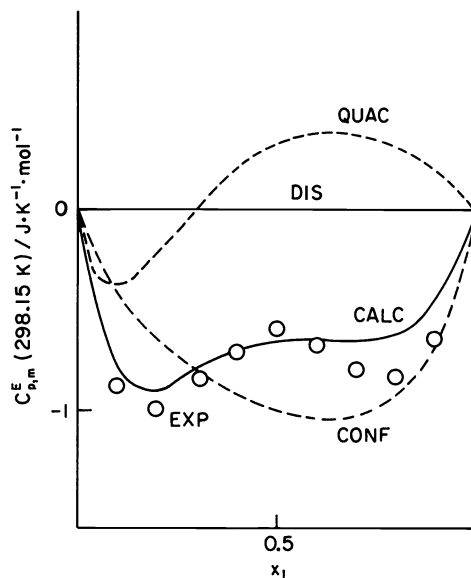
Fig. 11.   Molar excess heat capacity $C_{p,m}^{E}$ for (2,5,8-trioxanonane + heptane) against x(2,5,8-trioxanonane).   Points, experimental values (Ref. 32).   Curve DIS and QUAC calculated with $C_{ae,1}^{DIS}$ = 12.00, $C_{ae,2}^{DIS}$ = 22.00, $C_{ae,3}^{DIS}$ = 0, $C_{ae,1}^{QUAC}$ = 2.425, $C_{ae,2}^{QUAC}$ = 2.556, $C_{ae,3}^{QUAC}$ = 0, (z=2). Curve CONF is an estimate of the "conformational" contribution to $C_{p,m}^{E}$, Curve CALC is the sum of curves DISQUAC + CONF.

The $C_{p,m}^{E}$ values of (cyclic ethers + alkanes) reveal the same type of complexity as found in (n-ethers + n-alkanes). In (oxane + cyclohexane) (Fig. 2 in Ref. 46), $C_{p,m}^{E}$ has a single minimum very similar to (di-n-propyl ether + n-heptane). On the contrary, (1,4-dioxane + cyclohexane) (Fig. 2 in Ref. 46) has a double minimum, similar to (2,5,8-trioxanonane + n-heptane). In (1,4-dioxane + n-alkanes) the $C_{p,m}^{E}$ curves also have a double minimum separated by a maximum (see Fig. 1 in Ref. 47). The minimum at low concentrations decreases and the maximum increases with increasing chain length of the n-alkane. Model calculation with DISQUAC, using the parameters for (2,5,8-trioxanonane + heptane) (Fig. 11), yields S-shaped $C_{p,m}^{E}$ curves changing with the chain length of the n-alkane in qualitative agreement with the observations. The second minimum at high ether concentrations and the rapid decrease of the $C_{p,m}^{E}$ with increasing chain length of the n-alkane should be attributed in part to "conformational" effects and in part to the temperature dependence of $C_{ae,2}^{DIS}$. The latter may also explain the double minimum of the $C_{p,m}^{E}$ of (1,4-dioxane + cyclohexane).   Additional $C_{p,m}^{E}$ measurements are needed for (cyclic ethers + branched alkanes).
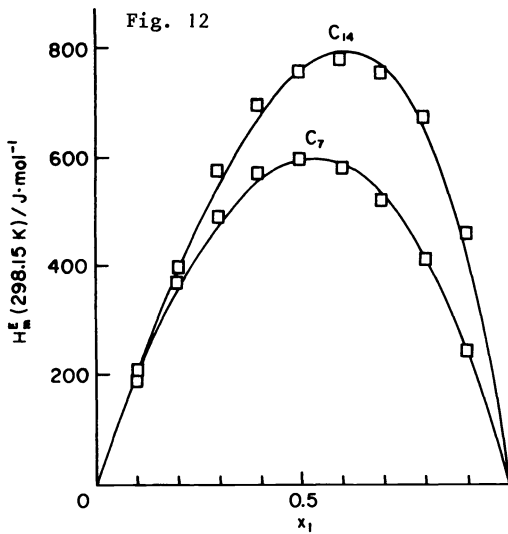
Fig. 12. Molar excess enthalpy, H_m^E, of (oxane + heptane) (Curve C_7) or + tetradecane (Curve C_{14}) against x(oxane). Points, experimental data (Refs. 41,42). Curves calculated with the quasi-chemical model (z=24) using the coefficients $C_{ae,1} = 15.74$ and $C_{ae,2} = 18.07$ (C_7) or 17.50 (C_{14}) (Ref. 40).
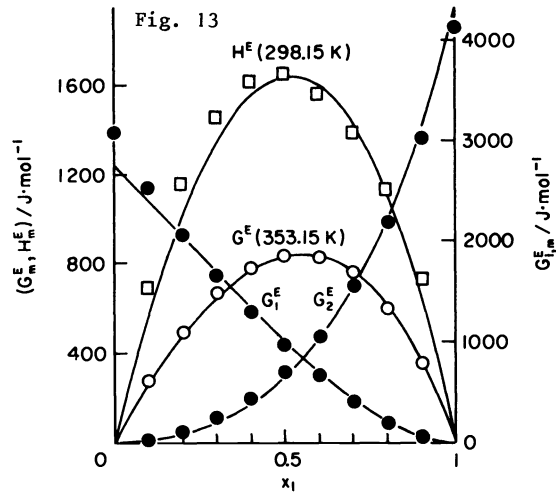
Fig. 13. Molar excess Gibbs energy, G_m^E, and enthalpy H_m^E, of (1,4-dioxane + heptane) against x(1,4-dioxane). Points, experimental data, G_m^E, (Refs. 43,44), and H_m^E, (Refs. 41,42). Curves calculated with the quasi-chemical model (z=24) using the coefficients $C_{ae,1} = 14.06$ and $C_{ae,2} = 19.97$ (Ref. 40).
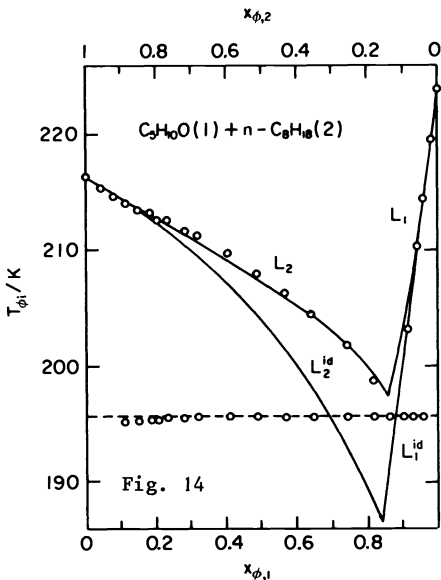

Fig. 14. Solid-liquid phase diagram of (oxane + octane). Points, experimental temperature, $T\phi i$, against x(oxane) (Ref. 45). Curves L_1 and L_2 calculated with the quasi-chemical model (z=24) using the coefficients $C_{ae,1} = 15.74$ and $C_{ae,2} = 17.97$. L_i^{id} are the ideal solubility curves (Ref. 40).
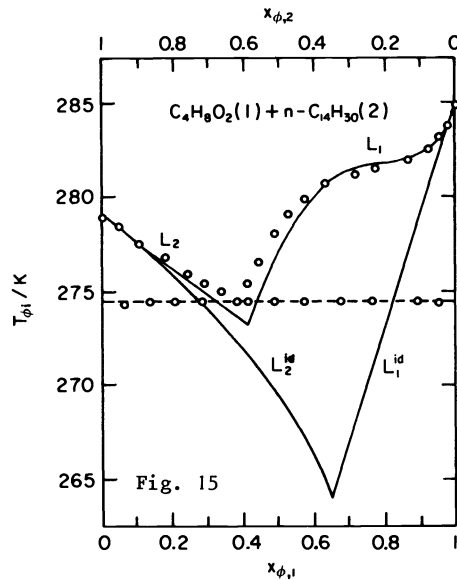
Fig. 15. Solid-liquid phase diagram of (1,4-dioxane + tetradecane). Points, experimental temperature, $T\phi i$, against x(1,4-dioxane) (Ref. 45). Curves L_1 and L_2 calculated with the quasi-chemical model (z=24) using the coefficients $C_{ae,1} = 13.72$ and $C_{ae,2} = 18.34$. L_i^{id} are the ideal solubility curves (Ref. 40).

(n-Alkanones + n-alkanes). The excess Gibbs energy, G_m^E, and enthalpy, H_m^E, of (2-propanone + n-alkanes) have been successfully correlated using the quasi-chemical approach with a coordination number $z=10$ and coefficients $C_{ak,1} = 8.514$ and $C_{ak,2} = 10.66$ (Ref. 35). Higher alkanones have been equally well correlated by making reasonable corrections for the steric effect of the alkyl groups (Ref. 36).

A careful examination of the H_m^E against x curves showed, however, that the experimental curves are always broader and flatter than the calculated ones, especially at lower temperatures (Fig. 16). Thus, the same behavior is observed with alkanones as with ethers.
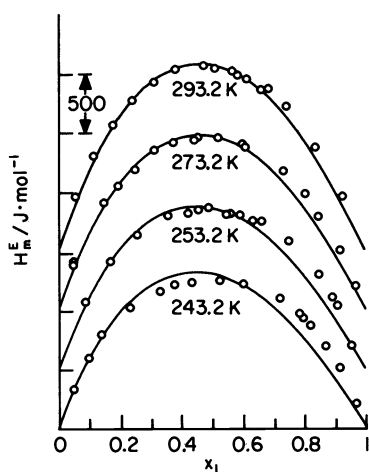

Fig. 16. Molar enthalpy H_m^E for (2-propanone + hexane) against x(2-propanone). Points, experimental values (Refs. 48,49). Curves calculated with the quasi-chemical model (z=10) using the coefficients $C_{ak,1} = 8.514$, $C_{ak,2} = 10.662$, and $C_{ak,3} = 8.133$ (Ref. 35).
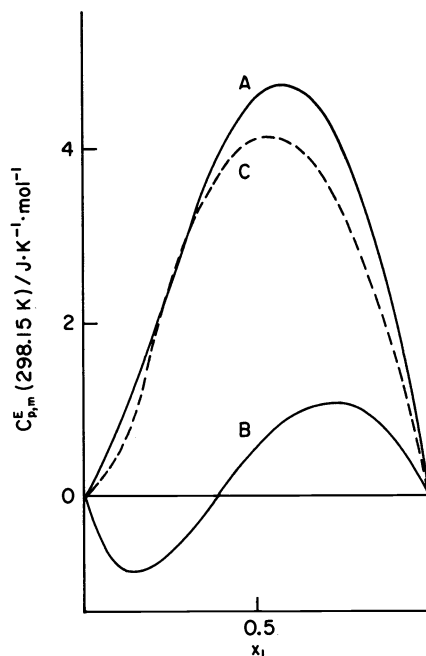
Fig. 17. Molar excess heat capacity $C_{p,m}^E$ for (2-propanone + hexane) against x(2-propanone). Curve A, quasi-chemical calculation with the coefficients of Fig. 16; Curve B, quasi-chemical calculation with the coefficients of Fig. 16 but $C_{ak,3} = 0$; Curve C, DISQUAC calculation with coefficients $C_{ak,1}^{DIS} = 3.044$, $C_{ak,2}^{DIS} = 4.065$, $C_{ak,1}^{QUAC} = 5.934$, $C_{ak,2}^{QUAC} = 9.029$ (z=4) and $C_{ak,3}^{DIS} = C_{ak,3}^{QUAC} = 0$,

Another anomaly is the large positive value of $C_{ak,3}$ required to account for the temperature dependence of H_m^E. No direct calorimetric $C_{p,m}^E$ values are available for (2-propanone + n-alkanes) but the measurements of Schäfer and Rohr (Refs. 48,49) indicate that $C_{p,m}^E \approx 4$ $J \cdot K^{-1} \cdot mol^{-1}$ at $x_2 = 0.5$. Assuming that $C_{ak,3} = 0$ the classical quasi-chemical model gives a rather small S-shaped $C_{p,m}^E$ curve (Fig. 17). DISQUAC, with the coefficients specified in Fig. 17, gives $C_{p,m}^E \sim 4$ $J \cdot K^{-1} \cdot mol^{-1}$ at $x_1 \approx 0.5$, the temperature dependence resulting simply from the Boltzmann factor.

Moreover, DISQUAC improves the shapes of the calculated H_m^E curves. The G_m^E curves also change but this has little effect on the calculated liquid-vapor equilibrium phase diagrams. The liquid-liquid equilibrium is a much more sensitive property and it appears that DISQUAC improves considerably the shapes of the calculated coexistence curves (Fig. 18, Ref. 50).
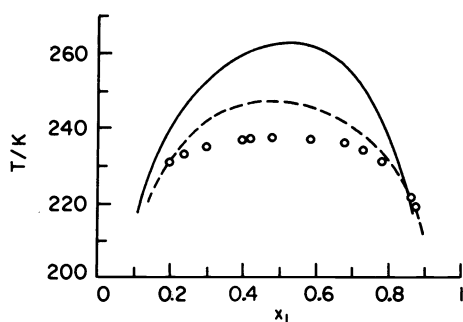

Fig. 18. Liquid-liquid phase diagram of (2-propanone + hexane). Points, experimental measurements (Ref. 51). Full curve calculated with the quasi-chemical model using the parameters of Fig. 16 (Ref. 35); dashed curve, DISQUAC calculation with the coefficients of Fig. 17 (Ref. 50).
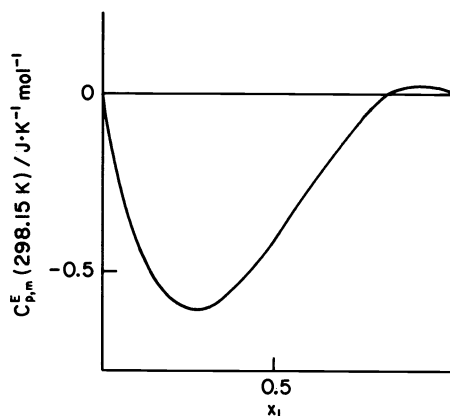
Fig. 19. Molar excess heat capacity $C_{p,m}^E$ for (1-chlorobutane + heptane) against x(1-chlorobutane). Curve calculated with the classical quasi-chemical model (z=4) using the parameters $C_{ad,1} = 2.455$, $C_{ad,2} = 3.850$ and $C_{ad,3} = 0$.

Grolier and Benson (Ref. 52) have recently measured $C_{p,m}^E$ for 2-butanone + or (3-pentanone + n-alkanes). The experimental curves are S-shaped for the lower n-alkanes, but a second minimum appears with the higher n-alkanes (see Fig. 2 in Ref. 52). Detailed calculations, as well as additional measurements of $C_{p,m}^E$ for (n-alkanone + branched alkane) are needed to explain the origin of the double minimum (Patterson effect and/or temperature dependence of the $C_{ak,2}^{DIS}$ coefficient).

It is interesting to note that the quasi-chemical contribution is relatively large (ca. 50 per cent) in the case of alkanones, due to the polarity of the carbonyl group. The oxygen atom and the double bond of the carbonyl group give rise to the dispersive contribution. In ethers, the oxygen atoms generate much less nonideality, of essentially dispersive nature, than in alkanones, the electrostatic part being relatively small (ca. 20 per cent).

(Chloroalkanes + alkanes). (1-chloroalkanes + n-alkanes) form a class of mixture in which the electrostatic part, due to the C-Cl bond dipole, seems to predominate, the difference between the dispersive forces of C_1 and CH_2 or CH_3 probably making only a small contribution. This follows from the relatively small nonideality in (tetrachloromethane (CCl_4) + n-alkanes), similar to (cyclohexane + n-alkanes). The random mixing model well describes G_m^E and H_m^E of (CCl_4 + n-alkanes) (Ref. 13), the H_m^E data indicating the occurrence of the Patterson effect. No direct $C_{p,m}^E$ values are available for (CCl_4 + branched alkanes), but $C_{p,m}^E$ of (CCl_4 + cyclohexane) (Ref. 53) as well as $H_m^E(T)$ of (CCl_4 + 2,2,4-trimethylpentane) (Ref. 54) indicate that most of the experimental $C_{p,m}^E$ (Refs. 55, 56) is "conformational". The H_m^E data for (1-chloroalkanes + n-alkanes) (Refs. 57,58) are well described by the

classical quasi-chemical model (z=4) with coefficients $C_{ad,1}$ = 2.455 and $C_{ad,2}$ = 3.850 (Refs. 57-59). Fig. 19 represents $C_{p,m}^E$ of (1-chlorobutane + heptane), calculated with the same coefficients, assuming that $C_{ad,3}$ = 0. No experimental values are available for comparison.

The proximity of two groups in a molecule may considerably alter the interchange coefficients, as has been shown for O-O groups in acetals (Ref. 60), S-S groups in disulfides (Ref. 61), N-N groups in diamines (Ref. 39), Cl-Cl groups in α,ω-dichloroalkanes (Ref. 57), etc. For example, the Cl/CH_2 or Cl/CH_3 interchange parameters for (1,2-dichloroethane + heptane) are $C_{ad,1}$ = 1.771 and $C_{ad,2}$ = 3.305 (z=4).

The predicted interactional $C_{p,m}^E \sim 1.6$ $J \cdot K^{-1} \cdot mol^{-1}$ at x_1 = 0.5 is much larger than the experimental $C_{p,m}^E$ values (Ref. 62) of (1,2-dichloroethane + cyclohexane) (-2.09 $J \cdot K^{-1} \cdot mol^{-1}$) or + methylcyclohexane (-1.03 $J \cdot K^{-1} \cdot mol^{-1}$). Systematic $C_{p,m}^E$ measurements for other α,ω-dichloroalkanes $Cl(CH_2)_m Cl$ (m=1, 2, 3, ...) + normal or branched alkanes are needed in order to identify the different contributions, in particular the effect of hindered rotation in 1,2-dichloroethane (Ref. 62).

DISCUSSION

The many systems investigated since 1978 (Ref. 13) prove that the pseudo-lattice group contribution approach, even in its crudest, "rigid" version, is fundamentally adaptable to the prediction of thermodynamic properties of dense (liquid) mixtures of organic molecules. At present, it is probably the only approach through which such systems become tractable.

For nonpolar molecules, the random-mixing approximation gives satisfactory results, the main discrepancies being due to "conformational" effects in mixtures containing long-chain molecules.

DISQUAC is a straightforward extension of the classical quasi-chemical model and appears to be more adequate than the latter for (polar + alkane) systems. The "quasi-chemical" contribution in such systems is the more important, the more polar the functional group. The "dispersive" contribution is relatively small for simple, polar functional groups, such as chlorine (e.g., in 1-chloroalkanes). It increases for oxygen (in ethers) and we expect it will be still larger for fluorine (e.g., in 1-fluoroalkanes). Larger dispersive contributions occur with more complex functional groups, such as carbonyl (e.g., in alkanones, alkanals and alkanoates). We expect to find a still larger dispersive contribution, in addition to the strong quasi-chemical one, with functional groups such as cyano (in nitriles), nitro (in nitroalkanes), and sulfonyl (in sulfones).

Previous applications of the classical quasi-chemical model have shown that the best z is not the same for different pairs of groups. For example, z=4 for Cl/CH_2 or Cl/CH_3 groups in (chloroalkane + alkane) (Ref. 57), z=10 for CO/CH_2 or CO/CH_3 groups in (alkanone + alkane) (Refs. 35,36), etc. Therefore, the application of the theory to systems containing more than two types of groups would raise serious difficulties. With DISQUAC we may, at least in principle, treat all the quasi-chemical contacts with a unique, rather small, value of z, adjusting adequately the corresponding dispersive contributions. Extensive calculations are needed in order to establish the limits of applicability of DISQUAC and the best common value if any, for z.

The non-athermal associated solution model, though developed on an essentially different basis than DISQUAC, gives nearly the same numerical results as the latter, for weakly associating substances. In the absence of any extra-thermodynamic evidence for the formation of specific kinds of associates A_iB_j, the DISQUAC model is to be preferred.

Recent very accurate $C_{p,m}^E$ measurements appear to be extremely useful for detecting "conformational" and/or orientational effects in mixtures and for assessing the quality of different theoretical models. The few examples considered in this paper seem to support the DISQUAC model.

The deviations from ideality in mixtures of polar molecules with nonpolar but polarizable molecules, e.g., benzene, or with polar molecules are in general much smaller than for the same (polar molecules + alkanes). These deviations are calculated as the difference between large quantities, so the predictions are usually made with a large relative error. Many systematic studies are needed in order to test DISQUAC for such systems and to establish the ratio of dispersive to quasi-chemical contributions for polar/polarizable or polar/polar contacts.

The first step in refining the rigid pseudo-lattice theories is to include equation-of-state terms. Since 1978 several "free volume" models have been proposed but the only one that has been more carefully tested is the older theory of Flory (Ref. 63). Although the equation-of-state of Flory is not strictly valid, not even for single-component non-polar systems, it has the merit of being able to demonstrate the significance of equation-of-state contributions. Recent studies have shown that the theory of associated solutions, extended by including Flory-type free volume effects, gives reasonable values for the excess volumes of (alkanol + alkane) (Refs. 64,65).

The Flory theory has also been extended to account for conformational effects by assuming that the interchange energy parameter x_{12} is temperature dependent (Ref. 66). However, this theory assumes that x_{12} is temperature (and/or pressure) dependent and this is inconsistent with the given equation-of-state. A satisfactory quantitative interpretation of "conformational" effects, as a function of molecular structure, temperature and concentration, is necessary for the accurate prediction of thermodynamic properties, especially of $C_{p,m}^E$. This can probably be achieved only by computer simulation studies.

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