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APPLICATION OF THE DISQUAC GROUP CONTRIBUTION MODEL TO BINARY LIQUID ORGANIC MIXTURES.

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SUMMARY

The DISQUAC group contribution method for correlating and predicting the thermodynamic properties of liquid mixtures (phase diagrams and related excess functions, Gibbs energy and enthalpy) is reviewed. Examples are given of its application to recently investigated mixtures, including linear or cyclic ketones, mono- or polychloroalkanes, cycloalkanes and n-alkanes.

INTRODUCTION

For separation design calculations it is essential to have analytical relations between the thermodynamic functions and the composition of multicomponent liquid mixtures. Several well-known empirical relations can be used for this purpose. They contain a number of adjustable parameters to describe the activity coefficients in binary systems. These parameters are derived from experimental measurements performed using the given binary system.

The group contribution method provides a basis for estimating properties of systems outside the set of investigated binaries. A single binary containing a specific pair of structural groups suffices to determine the corresponding group parameters. These parameters can be employed to estimate the properties of any other binary or multicomponent system containing the same structural groups. When applicable, this approach results in a considerable saving of experimental measurements, since the number of structural groups is much smaller than the number of molecular species.

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The group contribution method is based on a general assumption relative to the properties of the molecules and on more specific assumptions relative to the solution model adopted to describe the liquid mixture.

The general assumption may be formulated as follows (ref. 1): the molecules under consideration consist of given "groups" of atoms, each group being situated in a well-defined intramolecular environment which allows the internal degrees of freedom ofthe group and the external force field around it to be independent of the particular kind of molecule.

Violation of this general assumption is a cause of trivial disagreement between experimental and estimated values.

According to the solution of groups concept, the interactional Gibbs energy G_{int} is entirely determined by the numbers, n_s of the given constituent groups s. Obviously, G_{int} must be a extensive function with respect to n_s' s. Hence

$$G_{int} = \sum_s n_s G_s \qquad (1)$$

where $G_s = \partial G_{int} / \partial n_s \qquad (2)$

is the chemical potential of group s in the system. We may define a group activity coefficient Γ_s as

$$G_s = G_s^{\circ} + RT \ln \Gamma_s \qquad (3)$$

where G_s° is the chemical potential of pure group s. If ν_{si} is the number of groups of type s in a molecule of type i and n_i the number of moles of component i, we have

$$n_s = \sum_i \nu_{si} n_i \qquad (4)$$

$$G_{int} = \sum_i n_i \left(\sum_s \nu_{si} G_s\right) = \sum_i n_i \mu_{i,int} \qquad (5)$$

$$\mu_{i,int} = \sum_s \nu_{si} G_s^{\circ} + \sum_s \nu_{si} \ln \Gamma_s \qquad (6)$$

where $\mu_{i,int}$ is the interactional chemical potential of component i. For pure component i

$$\mu_{i,int}^{\circ} = \sum_s \nu_{si} G_s^{\circ} + \sum_s \nu_{si} \ln \quad {}_s \qquad (7)$$

Hence, we obtain a general equation for the excess chemical potential of component i

$$\mu_i^E = \mu_{i,comb}^E + \sum_s \nu_{si} (\ln \Gamma_s - \ln \Gamma_s^{(i)}) \qquad (8)$$

where $\mu_{i,comb}^E$ is the combinatorial excess chemical potential.

Depending on the model used to express Γ_s, we may distinguish empirical or more or less founded theoretical group contribution methods.

EMPIRICAL GROUP CONTRIBUTION METHODS.

ASOG and UNIFAC are at present the best worked out empirical group contribution methods.

The Wilson equation is the basis of the Analytical Solution of Groups (ASOG) method, proposed by Derr and Deal (ref. 2). The group coefficients are given by

$$\ln \Gamma_s = 1 - \ln(\Sigma_t X_t \Psi_{ts}) - \frac{X_t \Psi_{st}}{\Sigma_u X_u \Psi_{tu}} \tag{9}$$

where X_t represents group mole fractions and $\Psi_{ts} \neq \Psi_{st}$ represents two parameters adjusted for each pair of groups (s,t).

The UNIQUAC (Universal Quasichemical) equation of Abrams and Prausnitz (ref. 3) represents a significant improvement over the Wilson equation.

The corresponding group contribution method is called UNIFAC (UNIQUAC Functional-Group Activity Coefficients) (ref. 4) :

$$\ln \Gamma_s = q_s \left[1 - \ln (\Sigma_t \alpha_t \Psi_{ts}) - {}_t \frac{\Sigma_t \Psi_{st}}{\Sigma_u \alpha_u \Psi_{tu}} \right] \tag{10}$$

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. 5).

The random-mixing model. The Guggenheim rigid-lattice model in the random mixing approximation (ref. 6) is the simplest group contribution model founded on statistical thermodynamics. According to this model, in the group-surface-interaction version (refs. 1-7), the configurational Gibbs energy $G^{c,dis}$ is given by:

$$G^{c,dis} = \frac{A}{2} \left(\Sigma_s \alpha_s g_{ss}^{dis} + \frac{1}{2} \Sigma_s \Sigma_t \alpha_s \alpha_t g_{st}^{dis} \right) \tag{11}$$

where A is the total intermolecular surface, α_s is the s-type surface fraction, and g_{st}^{dis} is the interaction energy per surface unit between s- and t-surfaces. Equation (11) is applicable to nonpolar systems only, the quantities of g_{st}^{dis} representing "dispersive" interchange Gibbs energies.

Quasichemical models. Weak orientational effects in mixtures can be accounted for by means of Guggenheim's quasichemical approach (ref. 1).

The configurational Gibbs energy $G^{c,quac}$ is given by an equation similar to equation(11)

$$G^{c,quac} = \frac{A}{2}\left(\sum_s X_s g_{ss}^{quac} + \frac{1}{2}\sum_s\sum_t X_s X_t g_{st}^{quac}\right) \qquad (12)$$

the random contact surfaces α_s being replaced by the quasichemical quantities X_s. The latter are obtained by solving the system of quasichemical equations in which the main parameters are the Boltzmann factors $\exp -g_{st}^{quac}/zkT$.

In the classic theory, molecules are forced to occupy the sites of a particular lattice.

However, the assignment of contact points is arbitrary and meaningless and can be avoided by using the group-surface-interaction version of the theory (ref.1) The coordination number z is a very crude representation of non-randomness.

The random-mixing equations are obtained for $z = \infty$.

The major shortcomings of the classic quasichemical approach are:

a) the entire interchange energy of any given contact is assumed to generate non-randomness to the extent expressed by z;

b) z is assumed to be the same for all the contacts.

A physically more realistic approach should take into account a dispersive, random, contribution for every contact, possibly supplemented by an electrostatic, non-random contribution. A simple extension of the quasichemical theory is DISQUAC, the "quasichemical" model (ref. 5).

<u>The DISQUAC model.</u> In DISQUAC, the same type of dispersive contribution supplements the quasichemical expressions. The configurational Gibbs energy G^c of the system is the sum of the two terms given by equations (11) and (12):

$$G^c = \frac{A}{2}\left(\sum_s \alpha_s^2 g_{ss}^{dis} + \frac{1}{2}\sum_s\sum_t \alpha_s \alpha_t g_{st}^{dis} + \right.$$

$$\left. + \sum_s X_s g_{ss}^{quac} + \frac{1}{2}\sum_s\sum_t X_s X_t g_{st}^{quac}\right) \qquad (13)$$

The surface fractions being constant, at a given composition x_i , the quasichemical contact surfaces X_s obtained by maximizing the configurational partition function (ref. 1) are the same as in the classical theory. Each contact(s,t), either polar or non polar, is thus characterized by a set of dispersive interchange coefficients, $C_{st,l}^{dis}$, and the polar contacts by an additional set of a quasichemical interchange coefficients, $C_{st,l}^{quac}$ and the coordination number z. The excess functions, molar excess Gibbs energy, G^E, and molar excess enthalpy, H^E, each contain a dispersive and a quasichemical term which are calculated independently and then simply added together:

$$G^E = G^E_{comb} + G^{E,dis}_{int} + G^{E,quac}_{int} \tag{14}$$

$$H^E = H^{E,dis} + H^{E,quac} \tag{15}$$

For a binary system, $G^E_{comb}/RT = x_1 \ln(\varphi_1/x_1) + x_2 \ln(\varphi_2/x_2)$ is the Flory-Huggins combinatorial term, $\varphi_i = r_i x_i/(r_1 x_1 + r_2 x_2)$ is the volume fraction, x_i is the mole fraction and r_i is the total relative molecular volume of component i(i=1,2)

The $G^{E,dis}_{int}$ and $H^{E,dis}$ terms are given by

$$G^{E,dis}_{int} = (q_1 x_1 + q_2 x_2)\xi_1 \xi_2 g^{dis}_{12} \tag{16}$$

and

$$H^{E,dis} = (q_1 x_1 + q_2 x_2)\xi_1 \xi_2 h^{dis}_{12} \tag{17}$$

where

$$g^{dis}_{12} = -\frac{1}{2}\sum_s \sum_t (\alpha_{s1} - \alpha_{s2})(\alpha_{t1} - \alpha_{t2})\, g^{dis}_{st} \tag{18}$$

and

$$h^{dis}_{12} = -\frac{1}{2}\sum_s \sum_t (\alpha_{s1} - \alpha_{s2})(\alpha_{t1} - \alpha_{t2})\, h^{dis}_{st} \tag{19}$$

α_{si} is the molecular surface fraction of surface type s on a molecule of type i, q_i, is the total relative molecular area of a molecule of type i and $\xi_i = q_i x_i/(q_1 x_1 + q_2 x_2)$ is the surface fraction of component i in the mixture (i=1,2).

The dispersive excess molar chemical potential of component i is

$$^{E,dis}_{int,i} = q_i (1 - \xi_i)^2 g^{dis}_{12} \tag{20}$$

$G^{E,quac}_{int}$ and $H^{E,quac}$ are given by the known quasichemical equations

$$G^{E,quac}_{int} = x_1 \mu^{E,quac}_{int,1} + x_2 \mu^{E,quac}_{int,2} \tag{21}$$

where

$$\mu^{E,quac}_{int,i} = z\, q_i \sum_s \alpha_{si} \ln(X_s \alpha_{si}/X_{si} \alpha_s)\ ;\ i = 1,2 \tag{22}$$

is the quasichemical excess molar chemical potential of component i, and

$$H^{E,quac} = \frac{1}{2}(q_1 x_1 + q_2 x_2)\sum_s \sum_t \left[X_s X_t - (\xi_1 X_{s1} X_{t1} + \xi_2 X_{s2} X_{t2})\right]\eta_{st} h^{quac}_{st} \tag{23}$$

$$\eta_{st} = \exp\left[-g^{quac}_{st}/zRT\right]$$

The quantities X_s and X_t are obtained by solving the system of λ equation (λ is the number of contact surfaces):

$$X_s \ (X_s + \sum_t X_t \ \ _{st}) = \alpha_s \tag{24}$$

X_s and X_{ti} (i=1,2) are the solution of the system of eqns.(24) for x_i = 1 (pure component i). The temperature dependence of the dispersive or quasichemical g_{st} parameters has been expressed by a three - constant equation of the type:

$$g_{st} \ (T)/RT = C_{st,1} + C_{st,2} \left[(T^{\circ}/T)\right] - 1 + C_{st,3} \left[\ln(T^{\circ}/T) - (T^{\circ}/T) + 1\right] \tag{25}$$

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

$$h_{st} \ (T)/RT = C_{st,2} (T^{\circ}/T) - C_{st,3} \left[(T^{\circ}/T) - 1\right] \tag{26}$$

and

$$C_{p,st} \ /R = C_{st,3} \tag{27}$$

the latter being assumed to be independent of T. $C_{st,i}$ are dimensionless quantities termed "interchange coefficients".

The interchange coefficients are not constant for the first members of a homologous series.

A correlating equation of the type:

$$C_{st,l} = C^{\circ}_{st,l} \ (\ 1 + n^{e} \sigma^{e}_{st,l} + n^{p} \sigma^{p}_{st,l} + \dots \ ) \quad (l = 1,2) \tag{28}$$

has been used quite frequently for open-chain molecules.

In eqn (28), $C^{\circ}_{st,l}$ are the coefficients of the base compound, $\sigma^{R}_{st,l}$, are alkyl-group increments and n represent the number of carbon atoms in the different "levels" around the functional group: e, denoting ethyl, p, propyl and so on (see Fig.1 for a bivalent group, such as carbonyl, CO).

One of the advantages of DISQUAC is the use of a single coordination number z in calculating the quasichemical term. This permits application of the model to mixtures containing groups of different polarities.

The degree of non-randomness is expressed by the relative amount of quasichemical to dispersive terms. If both groups (s and t) are non polar, then the contact (s,t) is characterized by the dispersive coefficients $C^{dis}_{st,l}$ only, all $C^{quac}_{st,l}$ =0.

The "reference" value chosen for the coordination number is z = 4, the same as in our previous applications of DISQUAC (refs. 8-9).

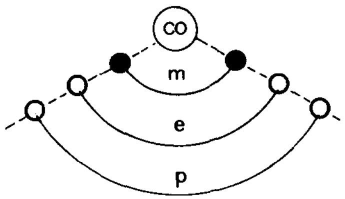

Fig. 1. Schematic representation of n-alkanone molecules. In 2-propanone, there are only two C atoms which occupy "level" m, and levels e and p are empty (n^e = n^p = 0). In 2-butanone, n^e = 1, n^p = 0; in 3-heptanone, n^e = n^p = 2; etc.

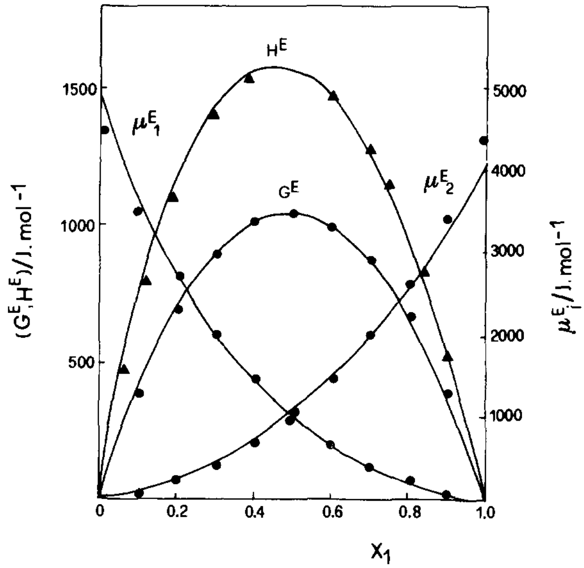

Fig. 2. Comparison of theory with experiment for the molar excess Gibbs energy G^E and the partial molar excess Gibbs energies μ_i^E at 323.15 K, and the molar excess enthalpy H^E at 298.15 K of 2-propanone (1) + cyclohexane (2) versus x_1, the mole fraction of 2-propanone. Full lines, predicted values; points, experimental results, ●, G^E and μ_i^E (ref. 20); ▲, H^E (ref. 19).

RECENT ORIGINAL WORK

The need to use DISQUAC clearly appeared for the first time during a preliminary study of mixtures containing alcohols (refs. 10-12).
A careful study of n-alkanone + n-alkane mixtures (ref. 13) showed that DISQUAC gives a much better representation of the experimental data by the classic method using $z = 10$ (refs. 14-15). The CO/CH_2 or CH_3 contact were characterized bytwo sets of interchange coefficients, quasichemical and dispersive (see below).

The importance of DISQUAC is especially evident in mixtures containing three or more types of groups of different polarities. For example, n-alkanal+cyclohexane systems (ref. 8) were regarded as possessing three types of surface: (i) type a, aliphatic (CH_3- or -CH_2- groups, which are assumed to exert the same force field); type f, formyl (-CHO); and (iii) type c, cyclohexane (C_6H_{12})).

These surfaces generate three pairs of contacts: (a,f),(c,f) and (a,c). The interchange parameters for the (a,f)- contact have been adjusted previously (refs. 16-17) using the experimental G^E and H^E values of n-alkanals + n-alkanes. It was necessary to apply the quasichemical approximation of the theory, with a coordination number $z_{af} = 4$ in order to reproduce the shape of the G^E and H^E curves.

We expected that the (c,f)- contact could also require a quasichemical treatment with $z_{cf} = 4$. Cyclohexane + n-alkane mixtures were treated in the zero approximation of the theoretical model as non-polar systems ($z_{ac} = \infty$). In the classic Guggenheim-Barker quasilattice model z is assumed to be the same for all the contacts. This is, of course, not the case for systems such as n-alkanals + cyclohexane, which consists of one polar group, f, and two non polar groups, a and c. To overcome the difficulty one should determine the interchange parameters of the non-polar (a,c)-contact quasichemically, using $z_{ac} = 4$, as for the polar contacts (a,f) and (c,f). The classic model could then be applied, but $z_{ac} = 4$ for cyclohexane + n-alkane would be unjustified.

We applied DISQUAC (ref. 8), considering the (a,f)- and (c,f)- contacts as entirely quasichemical and the (a,c)-contact as entirely dispersive. A similar treatment was used to describe 1-chloroalkane + cyclohexane systems (ref. 9) .

Below we report briefly on very recent, yet unpublished, applications of DISQUAC to several polar (alkanones or chloroalkanes) + n-alkane or + cycloalkane systems.

n-alkanone systems

The n-alkanone + n-alkane mixtures were regarded as possessing two types of surfaces: (i) type a, aliphatic (CH_3- or -CH_2- groups); (ii) type k, carbonyl (CO group); the n-alkanone + cyclohexane systems were regarded as possessing three types of surfaces: (i) type a; (ii) type k and (iii) type b, cyclohexane (C_6H_{12}). The DISQUAC coefficients $C^{dis}_{ak,1}$ and $C^{quac}_{ak,1}$ have been determined for n-alkanone + n-alkane systems by Kechavarz et al.(ref. 18) and represented by eqn. (28), the base compound being 2-propanone:

$$C^{dis}_{ak,1} = 3.044\ (\ 1 + 0.12\ n^e + 0.06\ n^p\ )$$

$$C^{dis}_{ak,2} = 4.065\ (\ 1 + 0.24\ n^e + 0.12\ n^p\ )$$

$$C^{quac}_{ak,1} = 5.934\ (\ 1 - 0.12\ n^e - 0.03\ n^p\ )$$

$$C^{quac}_{ak,2} = 9.029\ (\ 1 - 0.22\ n^e - 0.07\ n^p\ )$$

We extended the treatment to n-alkanone + cyclohexane mixtures. G^E and H^E data were available in the literature for 2-propanone and 2-butanone only.

We measured H^E of cyclohexane + 2-pentanone, + 3-pentanone, + 2-hexanone and + 3-hexanone (ref. 19). The G^E values reported by Crespo Colin et al.(ref. 20) were selected for calculating the dispersive energy coefficients, $C^{dis}_{bk,1} = 3.182$ and $C^{dis}_{bk,2} = 4.294$, of 2-propanone assuming that $C^{quac,\circ}_{bk,1} = C^{quac,\circ}_{ak,1}$.

DISQUAC reproduces G^E and H^E of 2-propanone + cyclohexane quite well over the whole concentration range (fig. 2). Using the same parameters, the model a fairly good prediction of the solid-liquid equilibrium phase diagram (ref. 21) and a metastable liquid-liquid miscibility gap (fig. 3).

Assuming that the alkyl-group increments for cyclohexane are the same as for n-alkane, $\sigma^R_{bk,1} = \sigma^R_{ak,1}$, we calculated G^E and H^E for higher n-alkanones + cyclohexane.

In fig. 4 we have represented the equimolar values of $G^E$and H^E of 2-alkanones + cyclohexane as a function of the number n of C atoms in the alkanone. The agreement is quite satisfactory and shows that the properties of n-alkanone + cyclohexane systems can be calculated with the coefficients of n-alkane systems by slightly increasing the dispersive coefficients of the base compound.

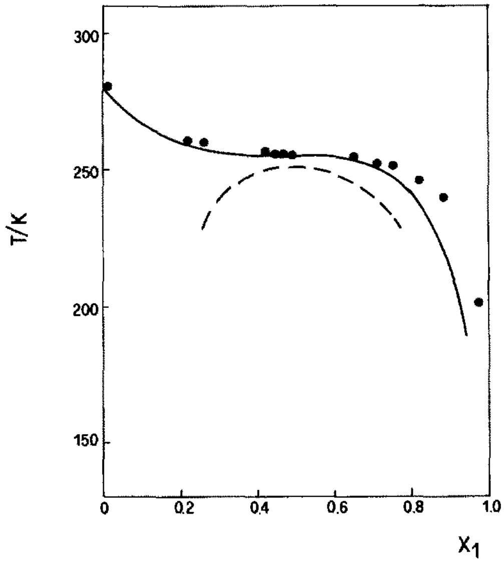

Fig. 3. Solid-liquid and metastable liquid-liquid phase diagram of 2-propanone + cyclohexane. Lines, predicted curves; points, experimental results (ref.21).

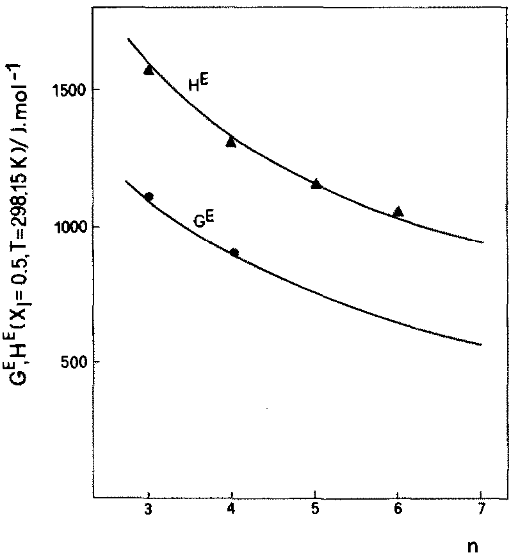

Fig. 4. Comparison of theory with experiment for the molar excess Gibbs energies G^E and molar excess enthalpies H^E at 298.15 K and x_1 = 0.5 of 2-alkanone (1) + cyclohexane (2) mixtures versus <u>n</u> , the number of C atoms in the 2-alkanone. Full lines, predicted values; points, experimental results, ●, G^E (refs 20,32), ▲, H^E (ref. 24).

TABLE I

Enthalpies of solution at infinite dilution, H_1^{∞}, and 298.15 K of 2-alkanones in cyclohexane: comparison of direct experimental results(exp) (ref. 23) with values calculated (calc) using the DISQUAC model.

2-Alkanone	$H^{\infty}_{1,calc}$ 10^3 mol^{-1}	$H^{\infty}_{1,exp}$ 10^3 mol^{-1}
2-propanone	11.01	9.74 ± 0.10
2-butanone	8.58	8.20 ± 0.12
2-pentanone	7.48	7.11 ± 0.09
2-hexanone	7.24	6.75 ± 0.10
2-heptanone	6.98	6.80 ± 0.09

As an additional and very sensitive test, we compared DISQUAC predictions for properties at infinite dilution with the available experimental data. There is only one measurement of activity coefficients at infinite dilution for this class of systems, viz of 2-butanone in cyclohexane $\ln \gamma_{1,exp} = 1.305$ at 350.8 K, obtained by differential ebulliometry (ref. 22). The calculated value is $\ln \gamma_{1,calc} = 1.308$. Fortunately, the accurate data on the enthalpies of solution at 298.15 K of 2-alkanones in cyclohexane determined by Della Gatta et al.(ref. 23) are available. In Table 1, we compare the experimental data with our calculations. The agreement is better than expected, the model using only parameters fitted to represent the properties of mixtures.

Cycloalkanone systems.

The calculated G^E, and H^E curves for cycloalkanones (cyclopentanone, cyclohexanone, cycloheptanone or cyclooctanone) + cycloalkane (cyclopentane or cyclohexane) or + n-alkanes (C_6 - C_{16}), mixtures, show that agreement with the experimental data (refs. 24-26) is excellent over the entire concentration range (fig. 5) when the values in Table 2 are used for the dispersive and quasichemical parameters. The quasichemical interchange energy coefficients $C^{dis}_{bk,l}$ for the cycloalkane/carbonyl contact are the same for mixtures of cycloalkanones with cyclopentane and cyclohexane, assuming for dispersive interchange energy coefficients $C^{dis}_{bk,l}$ constant values for the four cycloalkanones investigated. The cyclohexane coefficients differ slightly from, whereas the cyclopentane coefficients are much smaller than, the n-alkane

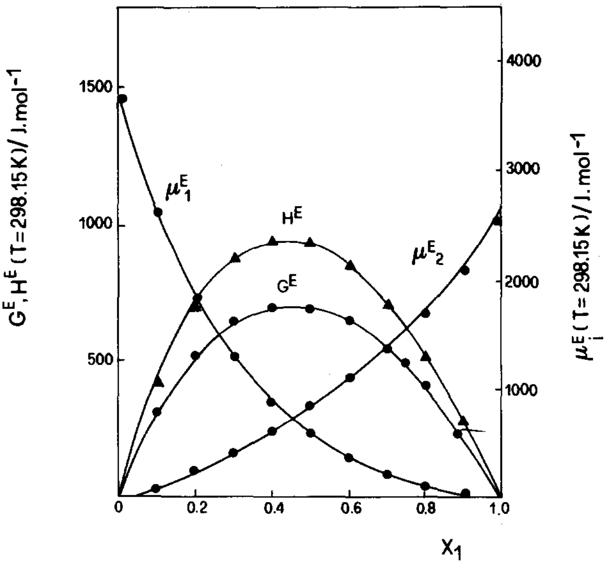

Fig. 5. Comparison of theory with experiment for the molar excess Gibbs energy G^E, the partial molar excess Gibbs energies μ_i^E, and the molar excess enthalpy H^E at 298.15 K of cyclohexanone (1) + cyclohexane (2) versus x_1, the mole fraction of cyclohexanone. Full lines, predicted values; ●, G^E and μ_i^E (ref. 25); ▲, H^E (ref. 24).

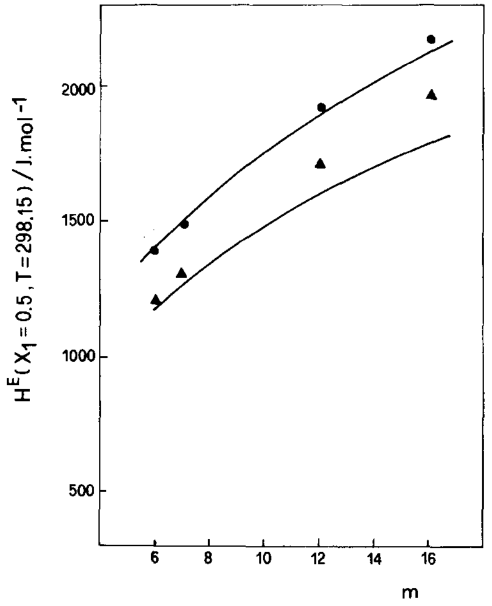

Fig. 6. Comparison of theory with experiment for the molar excess Gibbs energies G^E and molar excess enthalpies H^E at 298.15 K and x_1 = 0.5 of cycloalkanone (1) + n-alkane (2) mixtures versus m, the number of C atoms in n-alkane. Full lines, predicted values; points, experimental results (ref. 24): ●, cyclopentanone; ▲, cyclohexanone.

coefficients. Other compounds behave similarly (ref. 27).

The predicted dependence of H^E at 298.15 K and $x_1 = 0.5$ on m, the number of C atoms in the n-alkane, is represented in fig. 6 and compared with experimental results (ref. 24). It appears that for mixtures of cyclopentanone or cyclohexanone the experimental H^E data for increasing values of m are higher than the calculated data. This extra-endothermic contribution may be attributed to destruction of the orientational order in n-alkanes during the process of mixing with more or less globular molecules (ref. 28).

TABLE II

Interchange energy coefficients, $C^{dis}_{sk,1}$, and $C^{quac}_{sk,1}$, for cycloalkanone + n-alkane or + cycloalkane mixtures s = 5 or 6 for cycloalkane contact (b) or a for contact (a); (b-5 means cyclopentane; b-6 means cyclohexane)

cycloalkanone	s	$C^{dis}_{sk,1}$	$C^{dis}_{sk,2}$	$C^{quac}_{sk,1}$	$C^{quac}_{sk,2}$
cyclopentanone	a	3.61	6.50	5.41	6.40
cyclohexanone	"	"	"	4.95	5.40
cyclopentanone	b-5	2.80	5.36	5.41	6.40
cyclohexanone	"	"	"	4.95	5.40
cycloheptanone	"	"	"	4.60	4.48
cyclooctanone	"	"	"	"	"
cyclopentanone	b-6	3.70	6.40	5.41	6.40
cyclohexanone	"	"	"	4.95	5.40
cycloheptanone	"	"	"	4.60	4.80
cyclooctanone	"	"	"	"	"

Polychloroalkane systems

The purpose of this study (ref. 29) was to examine in terms of DISQUAC the thermodynamic excess functions, G^E, and H^E, of binary mixtures of n-alkanes or cycloalkanes with the following classes of chloroalkanes:

A) 1- chloroalkanes, $CH_3(CH_2)_{m-2}CH_2Cl$

B) dichloromethane, H_2CCl_2

C) 1,1-dichloroalkanes, $CH_3(CH_2)_{m-2}CHCl_2$

D) trichloromethane, $HCCl_3$

E) 1,1,1- trichloroalkanes, $CH_3(CH_2)_{m-2}CCl_3$

F) tetrachloromethane, CCl_4

These systems were regarded as possessing three types of surface:(i), type a, aliphatic (CH_3 -or - CH_2 - groups), (ii), type b, cyclohexane, and (iii), type d, chlorine (-Cl group).

We first noted the relatively small deviations from ideality in CCl_4 + alkane mixtures. Therefore, it was tempting to use the dispersive interchange energies of the CCl_4 - alkane contact when calculating the dispersive contribution of the Cl atoms in polar chloroalkane mixtures.

In 1-chloroalkanes, the electrostatic part, due to the C-Cl bond dipole, predominates, the dispersive contribution being almost negligible (fig.7).

In 1,1 - dichloroalkanes and 1,1,1-trichloroalkanes the dispersive contribution is larger and the quasichemical interchange coefficients $C^{quac}_{ad,1}$ decrease as the number of Cl atoms increases. In CCl_4, the quasichemical coefficients are, of course, zero. This regular decrease in the interchange energy in coefficients (fig. 8) is the most interesting result of our study.

The molecular dipole moments of the components in the series H_3CCl (1.87 D)> H_2CCl_2(1.60 D)>$HCCl_3$(1.01 D)>CCl_4 (0.00 D) decrease in the same order as the $C^{quac}_{ad,1}$(fig. 8). Another result which deserves attention is the behavior of $HCCl_3$ as opposed to $H_3.CCl_3$.

The G^E and H^E curves indicate somewhat stronger orientation in $HCCl_3$, probably due to more favorable steric conditions, than in H_3CCl_3, but there is no evidence for specific C-H...Cl H-bond type interaction in $HCCl_3$(ref. 30), other wise the interchange energy coefficients would be quite different. The same conclusion applies to H_2CCl_2.

CONCLUSIONS

The present investigations prove that DISQUAC is superior in several respects to the classic quasichemical method.

1. It better reflects the nature of molecular interactions by taking specifically into account a dispersive term, always present, and an electrostatic term, present in polar systems.
2. It enables groups with different polarities to be handed by the model.
3. It reproduces the experimental data better, including liquid-liquid equilibria and properties of very dilute solutions.
4. The interchange coefficients have a better physical significance than in any

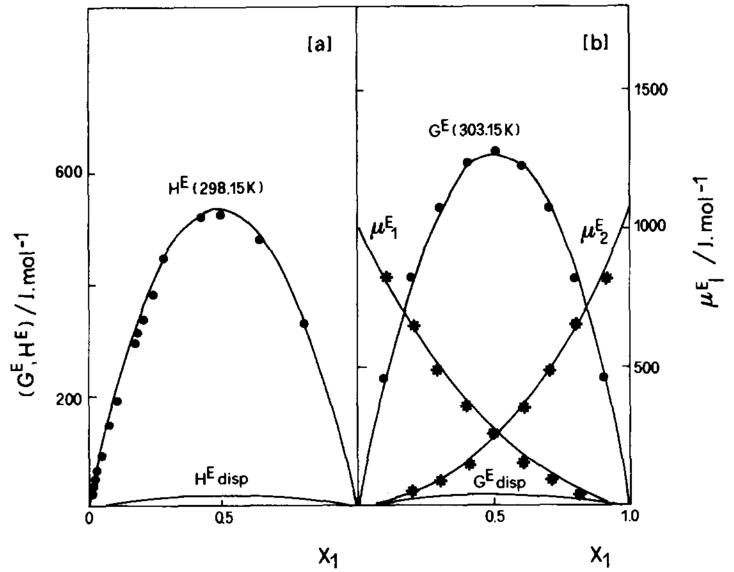

Fig. 7. Comparison of theory with experiment for the molar excess Gibbs energy G^E and partial molar excess Gibbs energies μ_i^E at 303.15 K (b) and molar excess enthalpy H^E at 298.15 K(a) of 1-chlorobutane (1) + n-heptane (2) versus x_1, the mole fraction of 1-chlorobutane. Full lines, predicted values; points, experimental results (refs. 33-34); G^E_{dis} and H^E_{dis}, calculated dispersive contribution.

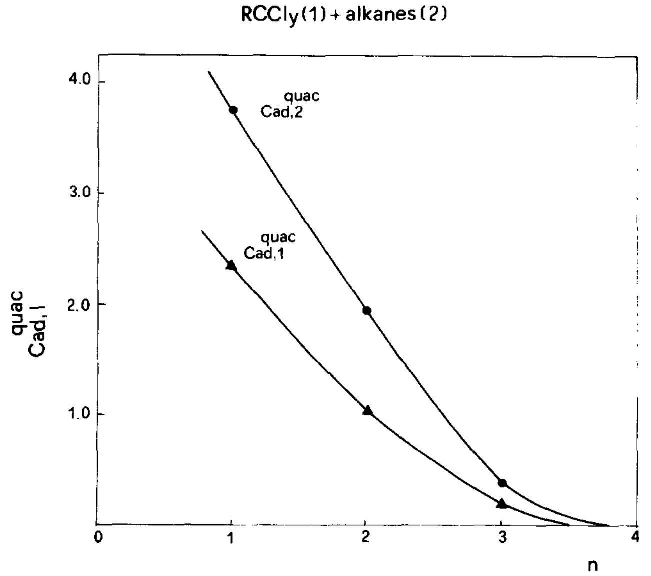

Fig. 8. Quasichemical interchange coefficients $C^{quac}_{ad,l}$ (l = 1,2) of polychloroalkane + n-alkane mixtures versus n, the number of Cl atoms in the CCl_n group ▲, $C^{quac}_{ad,1}$; ●, $C^{quac}_{ad,2}$

other group contribution method. This can be illustrated very well by comparing the dependence of the energy parameters of the $-CCl_n/CH_2$ groups on the number $\underline{n}$ of Cl atoms for DISQUAC and UNIFAC.

The UNIFAC parameters reported in the most recent collection (ref. 31) show no systematic trend with $\underline{n}$ (Table 3).

TABLE III

UNIFAC group interaction parameters, $a_{mn,k}$ for the chloroalkane/alkane contacts (ref. 31).

Group	$a_{12,1}$	$a_{12,2}$	$a_{21,1}$	$a_{21,2}$
CCl	246.3	0.2579	-67.33	-0.6791
CCl_2	101.2	-0.8471	12.87	0.2650
CCl_3	103.1	-0.1245	-35.46	-0.1233
CCl_4	-12.65	0.0452	27.88	-0.1656

TABLE IV

Interchange energy coefficients, $C^{dis}_{ad,l}$, and $C^{quac}_{ad,l}$ (l = 1,2) for contact (a,d) (a, aliphatic, d, chlorine) as function of the number $\underline{n}$ of Cl atoms in chloroalkane.

Group	$C^{dis}_{ad,1}$	$C^{dis}_{ad,2}$	$C^{quac}_{ad,1}$	$C^{quac}_{ad,2}$
CCl	0.093	0.180	2.342	3.752
CCl_2	"	"	1.040	1.960
CCl_3	"	"	0.203	0.413
CCl_4	"	"	0.000	0.000

DISQUAC uses the same number of coefficients per contact, but all the dispersive coefficients are constant, and the quasichemical coefficients decrease with decreasing polarity, being zero for the nonpolar CCl_4(Table 4 and fig. 8).

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