



*Dedicated to the memory of
Dr. Henry V. Kehiaian (1929–2009)*

THE DISQUAC MODEL **

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The DISQUAC group contribution model for correlating and predicting the thermodynamic properties of liquid mixture (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 molecules, mono- or poly-functional compounds.

A fairly good description of the thermodynamic properties of mixing is obtained when the model is used with group-structure-dependent interaction parameters. These relationships are also of practical importance, since they allow the evaluation of experimental data and estimation of interaction parameters for certain molecules, e.g. in the presence of proximity effects, whereas other methods need additional measurements.

INTRODUCTION

This paper reviews the work carried out by two research groups in Italy (Bruno Marongiu and Silvia Porcedda, University of Cagliari, and Maria Rosaria Tiné, Luciano Lepori, and Enrico Matteoli, University of Pisa, CNR Pisa) on the determination of the phase equilibrium and thermal and volumetric properties of organic mixtures and on their interpretation in terms of DISQUAC, an extended quasi-chemical group contribution model proposed by Henry V. Kehiaian in 1978¹ and then revised in 1983² and 1985.³ The majority of the research work here reviewed is published in papers co-authored by H.V. Kehiaian. The remaining papers have been inspired by him and with him fruitfully discussed. For this reason, some of the authors (B.M., S.P., and M.R.T.) intend to dedicate this paper to Henry's memory.

The application of DISQUAC to several classes of substances is here considered and namely: tertiary amines and dialkylamines + n-alkanes and benzene;⁴⁻⁶ alkanals + alkane and cyclohexane;⁷⁻¹⁰ chloroalkane + n-alkane, benzene and tetrachloromethane;¹¹⁻¹³ alkanones + alkanes or cyclohexane;¹⁴ ketoamines + n-alkane;¹⁴ oxalkane + n-alkane or cyclohexane;¹⁶⁻¹⁸ nitroalkanes + alkanes;¹⁹ alkenes or cyclic alkenes + alkanes, benzene or CCl₄;^{20,21} thiaalkanes + alkane, cyclohexane;²² alkanenitriles + alkanes, alkanones, or chloroalkanes;²³⁻²⁵ alkanones + benzene, CCl₄;²⁶ alkylbenzenes + alkanes, cyclohexane;²⁷ alkylalkanoates + cyclohexane;²⁸ bromoalkanes + oxalkanes;²⁹ alkynes + alkanes, cyclohexane;³⁰ dimethylsulfoxide + alkanes, cyclohexane, benzene, CCl₄;³¹ chlorobenzenes + alkane, cyclohexane;³² aromatic ether, aromatic ketones + alkane;³³ perfluoroalkanes + alkanes;³⁴ oxalkanes + benzene and CCl₄;^{35,36} nitroalkanes + benzene

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** This paper is a tribute to the memory of Henry V. Kehiaian from prof. Bruno Marongiu, Maria Rosaria Tiné and co-workers

and CCl_4 .³⁷ The focus of this article is on the dependence of the DISQUAC parameters on the chemical structure of the compounds in the mixture. In fact, it has been demonstrated that interchange DISQUAC parameters are influenced by intra-molecular effects like the steric and inductive effect, the proximity of two or more functional groups in the same molecule, and the insertion of a functional group in a cycle. The use of structure dependent interaction parameters may appear as a lessening of the classical group contribution rules. However, it reflects the physical reality of the intra-molecular environment. Moreover, it has been observed that DISQUAC parameters regularly change with molecular structure and that the rules governing the structure dependence of the parameters are quite similar for several classes of substances. This result, is of paramount importance, from a practical point of view, and make DISQUAC a powerful tool among predictive methods, since it allows for useful prediction on the basis of a limited number of experimental data.

DISCUSSION

The DISQUAC model

The study of molecular interactions in liquid mixtures is of fundamental importance for the understanding and prediction of physico-chemical properties of the systems. Thermodynamic properties, in particular equations of state, equilibrium and thermal quantities, play a crucial role because they allow to characterize the state of a system and predict its evolution.

Calorimetry is undoubtedly one of the most powerful and sensitive techniques for the study of molecular interactions. In fact, any change in the state of a system is generally accompanied by a corresponding gain or loss of energy, whose precise and accurate measurement is a primary source of information on the structure of compounds and their molecular interactions. However, calorimetric data provide only an overall picture, a kind of average, of the processes occurring, at the molecular level, in the macroscopic system. To distinguish and characterize the nature of the different terms contributing to the measured global calorimetric effect, besides to draw further information from different investigation techniques, it is essential to rely on theoretical models describing the systems.

Among them, statistical models based on group contributions have been extensively and successfully used.

In the group contribution approach, the evaluation of the group parameters of a "key" single binary system containing a specific pair of structural groups, allows to describe and predict the thermodynamic properties of any other binary or multi-component system containing the same groups.

Several group contributions methods have been proposed until now, depending on the underlying statistical model and on the equations used. For example UNIFAC³⁸ method uses two parameters, adjusted on a pair of groups, for describing the excess Gibbs energy of mixture, G^E . In this model the "combinatorial entropy" is evaluated by the Flory-Huggins equation while UNIQUAC equation is used to estimate the contribution due to molecular interactions. However, the Wilson's concept of local composition, at the base of UNIFAC, has been criticized by several authors¹² and UNIFAC is now considered more or less as an empirical method for estimating liquid-vapour equilibrium in complex systems. It is noteworthy to observe that group contributions methods are based on a "general assumption", concerning the properties of molecules, and on a "more specific assumption" concerning the solution model adopted to describe the liquid mixture. Molecules are considered consisting of groups of atoms each group being located in a well-defined intra-molecular environment which allows both the internal degrees of freedom of the group and the external force field, to be independent of the type of molecule in which the group is located. Violations of this assumption cause the disagreement between calculated and experimental values. In fact, an accurate study on organic mixtures reveals that the group parameters, while nearly constants for simple mono-functional molecules, undergo significant changes upon altering the molecular environment of the functional group. The vicinity of branched alkyl chains, the inclusion of a functional group in a cycle and the proximity of two functional groups, are among the main causes of apparent failure of the group contribution approach. This evidence suggests the need for more sophisticated group contribution models.

The Guggenheim-Barker reticular model,³⁹ modified by considering contact surfaces instead of points of contact, is characterized by two interaction parameters for contacts between the structural groups s and t : the Gibbs energy

interchange parameter, g_{st} , and the enthalpy interchange parameter, h_{st} .³⁴ In the zero approximation, where $z = \infty$, z being the lattice coordination number, the symmetry of the curves G^E/x_1 and H^E/x_1 is determined exclusively by the geometrical parameters, r_i (molecular volume) and q_i (molecular surface). This model has been successfully applied to the description and prediction of the excess thermodynamic properties and phase equilibrium of mixtures of non-polar liquids which include groups that do not interact preferentially. Later in this paper we will show the application of this model to liquid mixtures containing tertiary amines + alkanes,⁴ + benzene⁵ and diamines + alkanes.⁶

The limit of Guggenheim-Barker lattice model, which restricts its practical importance, is that it is not applicable to polar molecules. Weak orientational effects in the mixtures can be taken into account through the quasi-chemical Guggenheim approach. Many studies have shown that the quasi-chemical approach cannot describe strongly associated systems, as alcohols are, while it successfully applies to weakly associated systems, as aldehydes, ketones, or ethers. It is noteworthy that the discrepancies observed between experimental values and theoretical predictions are systematic and increase with increasing the complexity of the electronic structure of the groups. Typically, experimental curves representing the excess functions of complex mixtures of polar molecules in an inert solvent, are flatter and wider than those calculated and it is not possible to reproduce the correct form of the curves by adjusting the value of z . This behaviour reflects, probably, one of the biggest limitations of the quasi-chemical model. In fact, in the classical Guggenheim-Barker model, the total exchange energy is assumed to arise in a non-random way, while randomness is expressed by the lattice coordination number z . Moreover, the same value of z is assigned to all contacts. As the model requires the same value of z for all contacts, its applications to mixtures containing more than two types of contacts (s , t), individually characterized by different values of z , obliges to adopt an average z value.

Several alternative approaches^{40,41} have been proposed to simulate changes in the lattice coordination number in different molecular environments. They mainly involve the values of geometric parameters or of contact areas between groups or molecules. In fact, the increase of the

surface of the polar group of a molecule in a mixture with a non-polar solvent, *e.g.* the -OH group in alcohol + alkanes mixtures, causes in the form of the excess function curve an effect similar to that obtained with a lower coordination number. Although in principle it is not necessary to consider unalterable the Bondi group increments,⁴² we believe that major changes should be avoided. It is also important to be sure that the geometric parameters adopted for a given group are independent of the nature of the other groups in the molecule.

A simple extension of the classical Guggenheim-Barker model is the Dispersive Quasi-Chemical model DISQUAC,¹² which provides a physically more realistic approach to the description of group interactions. In this model, for each contact, a dispersive random contribution is added to an electrostatic non-random one. In this model the non randomness degree is given by a conventionally chosen constant lattice coordination number, z , and by a corresponding appropriate value of the dispersive/quasi-chemical contributions ratio. In mixtures containing non-polar groups the excess functions can be described only by the dispersive term, using reasonable geometric parameters, as has been demonstrated for mixtures containing CCl₄, cyclohexane, n-alkanes or other non-polar components. In mixtures of molecules containing both polar and non polar groups, each contact, is characterized by a set of dispersive interchange coefficients, C_{st} , and polar contacts by an additional set of quasi-chemical interchange coefficients, C_{st} , and by a constant value of the coordination lattice number, z . Every excess function contains both a dispersive and a quasi-chemical term, which are independently calculated and then simply added up. The final choice of z , common to all pairs of groups, will be made only when several systems will be investigated.

Of course, the smaller the value of z , the larger the range of applicability of DISQUAC to molecules containing groups with very different polarity. In any case, we cannot expect that this version of the DISQUAC model will provide satisfactory results for strongly interacting groups at least for two reasons: a) the approximation of the quasi-chemical approach; b) the assumed additivity of the dispersive and quasi-chemical contributions. Actually we have always to keep in mind the simplifications of the quasi-chemical model where the real distances among groups and the intermolecular potential, dependent on the contact angle, are roughly represented by a few

quantities: the isotropic exchange group parameters, the molecular surface fractions, by which we simulate the force field anisotropy, and the lattice coordination number accounting, by the Boltzmann factor, for the probability of contacts.

The superiority of DISQUAC with respect to other group contribution models, appears clearly when we consider the composition dependence of the excess functions in mixtures containing strongly polar substances, such as alcohols + n-alkanes mixtures.³ If we consider the dependence of H^E on the composition of the mixture in the ethanol + n-heptane system, and we compare the experimental curve with that one calculated by the classic quasi-chemical model using different values of z , we observe that the maximum in the H^E experimental curves (Exp.) is found at a molar fraction of ethanol much lower than that calculated by the random-mixing approximation. This behaviour is common to all polar + non-polar mixtures. For $z = \infty$ the agreement is satisfactory for $x_1 > 0.5$ but not for $x_1 < 0.5$; vice versa for $z = 8$ and 4, the agreement is good for $x_1 < 0.5$ but not for $x_1 > 0.5$. We observe a similar behaviour for G^E curves. Therefore we cannot find a value of z able to represent H^E over the whole concentration range, since the experimental curves are wider and flatter than those calculated. Assuming, as in DISQUAC, that H^E is calculated by the sum of dispersive and quasi-chemical contributions, taken in appropriate proportions, we can reproduce much better the shape of the experimental H^E curves.

Because of experimental errors and the presence of intra-molecular effects, it is often difficult to assign unambiguously the dispersive and quasi-chemical interchange coefficients. For a particular contact (s, t), the ratio between the contributions *dis* and *quac* may vary within certain limits, without significantly affecting the agreement with experimental values. However, considering a large number of systems, we can identify a series of rules that are reasonable from the general point of view of physics and that can be applied consistently to determine the values of the interchange coefficients.

The interactional terms of the thermodynamic properties under consideration, G^E and H^E , are given by the DISQUAC model as the sum of the

and

$$H^{E, \text{quac}} = \frac{1}{2} (q_1 x_1 + q_2 x_2) \sum_s \sum_t [X_s X_t - (\xi_1 X_{s1} X_{t1} + \xi_2 X_{s2} X_{t2})] \eta_{st} h_{st}^{\text{quac}} \quad (9)$$

where

dispersive contribution, $G_{\text{int}}^{E, \text{dis}}$ or $H^{E, \text{dis}}$, and the quasi-chemical contribution, $G_{\text{int}}^{E, \text{quac}}$ or $H^{E, \text{quac}}$, thus

$$G^{E, \text{quac}} = G_{\text{comb}}^E + G_{\text{int}}^{E, \text{dis}} + G_{\text{int}}^{E, \text{quac}} \quad (1)$$

$$H^E = H^{E, \text{dis}} + H^{E, \text{quac}} \quad (2)$$

where, for a binary system, $G_{\text{comb}}^E / RT = x_1 \ln(\phi_1 / x_1) + x_2 \ln(\phi_2 / x_2)$, is the Flory-Huggins combinatorial term, $\phi_i = r_i x_i / (r_1 x_1 + r_2 x_2)$ 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 $G_{\text{int}}^{E, \text{dis}}$ and $H^{E, \text{dis}}$ terms are given by

$$G_{\text{int}}^{E, \text{dis}} = (q_1 x_1 + q_2 x_2) \xi_1 \xi_2 g_{12}^{\text{dis}} \quad (3)$$

and

$$H^{E, \text{dis}} = (q_1 x_1 + q_2 x_2) \xi_1 \xi_2 h_{12}^{\text{dis}} \quad (4)$$

where

$$g_{12}^{\text{dis}} = -\frac{1}{2} \sum_s \sum_t (\alpha_{s1} - \alpha_{s2}) (\alpha_{t1} - \alpha_{t2}) g_{st}^{\text{dis}} \quad (5)$$

and

$$h_{12}^{\text{dis}} = -\frac{1}{2} \sum_s \sum_t (\alpha_{s1} - \alpha_{s2}) (\alpha_{t1} - \alpha_{t2}) h_{st}^{\text{dis}} \quad (6)$$

g_{12}^{dis} and h_{12}^{dis} are respectively the dispersive Gibbs energy and enthalpy interchange parameters, of the (s,t)-contact, 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 ($i = 1, 2$). For a binary system, $G_{\text{int}}^{E, \text{quac}}$ and $H_{\text{int}}^{E, \text{quac}}$ are given by the known quasi-chemical equations

$$G_{\text{int}}^{E, \text{quac}} = x_1 \mu_{\text{int},1}^{E, \text{quac}} + x_2 \mu_{\text{int},2}^{E, \text{quac}} \quad (7)$$

where

$$\mu_{\text{int},i}^{E, \text{quac}} = z q_i \sum_s \alpha_{si} \ln(X_s \alpha_{si} / X_{si} \alpha_s), \quad i = 1, 2 \quad (8)$$

$$\eta_{st} = \exp(-g_{st}^{\text{quac}} / zRT)$$

g_{st}^{quac} and h_{st}^{quac} are the quasi-chemical interchange parameters, Gibbs energy and enthalpy respectively, of the (s,t)-contact and z is the 'lattice coordination number'.

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

$$X_s (X_s + \sum_t X_t \eta_{st}) = \alpha_s, \quad (10)$$

$$g_{st}(T) / RT = C_{st,1} + C_{st,2} [(T^0 / T) - 1] + C_{st,3} [\ln(T_0 / T) - (T_0 / T) + 1] \quad (11)$$

where $T^0 = 298.15$ K is the scaling temperature. Accordingly,

$$h_{st} / RT = C_{st,2} (T^0 / T) - C_{st,3} [(T^0 / T) - 1] \quad (12)$$

$C_{st,1} = g_{st}(T^0) / RT^0$, $C_{st,2} = h_{st}(T^0) / RT^0$ and $C_{st,3}$ are termed interchange energy coefficients.

Application of the DISQUAC model

In this chapter we illustrate the advantages of applying the DISQUAC model, with structure dependent interaction parameters. This choice may seem a violation of the concept of group contribution, however, it reflects a physical reality, since there is a priori no reason for the force field of an atom or of a group of atoms should be completely independent from the intra-molecular environment. Moreover, the observed regular variation of the parameters with the molecular structure is of considerable importance from a practical point of view, because it allows good predictions based on a relatively small number of experimental data. Indeed, we found that the rules that govern the dependence of the structure parameters are very similar for many classes investigated.

We will consider mixtures of hydrocarbons and hetero-organic compounds, shortly: -X compounds, where X = N, O, S, F, Cl, Br, I, CN, NO₂, ... The organic compounds taken into account are:

(A) C-X compounds in which a functional X group is bonded to a carbon atom by a σ bond (e.g. ethers, ..);

(B) compounds where X is contained in a heterocyclic ring (e.g. pyridine)

(C) compounds in which X is attached to a C carbon atom (or to an heteroatom) by multiple or coordinated bonds (ketones, nitroalkanes, ...);

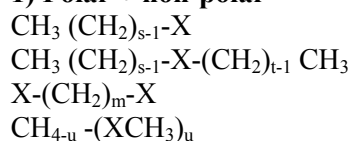
Moreover, the mixtures are classified, according to their physical properties such as polarity, polarizability, etc, as:

X_{si} and X_{ti} ($i = 1, 2$) are the solutions of eqn. (10) for $x_i = 1$ (pure component i). Equations (3) and (4) are obtained from the quasi-chemical eqns. (7) and (9) when $z \rightarrow \infty$, and represent the so-called random mixing (or zero) approximation of the model.

The temperature dependence of the dispersive or quasi-chemical g_{st} parameters has been expressed by a three-constant equation of the type

- 1) polar + non-polar
- 2) cyclic polar + non-polar
- 3) polar + polarizable
- 4) polar + polar
- 5) non-polar + non-polar

1) Polar + non-polar



Steric effect

The main factor influencing the interchange parameters in these systems seems to be the **steric effect** exerted by the alkyl groups adjacent to the functional group X. This is the most important and "specific" effect. It is less pronounced in weakly polar molecules and more pronounced where strong interactions, as hydrogen bonds, are present. As a consequence the steric effect causes a decrease of quasi-chemical coefficients of polar (x)/non-polar (s) contacts with increasing the aliphatic surface fraction, α_a . In open-chain molecules we observe a marked decrease of the quasi-chemical parameters for the first two or three terms of homologous series, which vanishes with increasing the alkylic chain length. We found this trend in mixtures of hydrocarbons with alkanals (R-CHO),^{8,10} nitroalkanes (R-NO₂),²⁰ alkanenitriles (R-CN),²³ primary and secondary amines (R-NH₂, R₂-NH),⁴³ alkanones (R-CO-R),¹⁴ ethers (ROR),¹⁷

anhydrides (R-COOCO-R)⁴⁴ and carbonates (R-OCOO-R).⁴⁵ The size of the functional group X, relative to the size of the groups CH₃ and CH₂, plays an important role, being the small groups more effectively shielded by the large alkyl groups. In molecules in which the functional X group have about the same size of alkyl groups this steric effect is attenuated and interchange quasi-chemical parameters result almost constant as was found in the classes of aloalkanes (R-Cl, R-Br, R-I)^{12, 46,47} and tioalkanes (R-S-R).²⁴

The interpretation of the molecular steric effect is possible by correlating the evolution of the quasi-chemical coefficients with the dipole moment of molecules, μ , or the solubility parameter, δ , related to the cohesive-energy, for homologous series.

The interchange quasi-chemical coefficients are independent of the type of alkane and assume the same value no matter the apolar component is acyclic or cyclic: *s* = *a* (aliphatic), *c* (cyclohexane).

Inductive effect

The dispersive interchange coefficients remain almost constant as increasing the number of alkyl groups adjacent to the functional group X or increase for the first terms of homologous series especially when the functional group contains π electrons, because the inductive effect exerted by the alkyl groups. For example, in the carbonyl compounds, R-CO-R, replacing R = H (alkanals) with R = CH₃ (alkanones) or higher alkyl, induces, in terms of DISQUAC, an increase in the dispersive contribution, while the classical approach (quac) requires a small coordination number for R = H ($z = 4$) and a larger ($z = 10$) for R = CH₃ or higher alkyls. In carbonates RO-COO-R the alkyl groups do not exert any inductive effect on dispersive parameters while it exerts a small steric effect on quasi-chemical ones, in contrast to what happens in aldehydes and ketones. This is probably due to the fact that alkyl groups are not directly attached to the carbonyl group. The esters (R-COO-R) show an intermediate behaviour.

The presence of an inductive effect is not detectable in the case of tertiary amines and ethers, because this effect is probably very weak and the steric effect prevail. Moreover, the deviation from ideality are very small in these systems.

In oxaalkanes the substitution of one or more CH₂ groups in the alkane skeleton by O atoms influences the intermolecular forces as result of

two effects: one weakens, owing to the smaller dispersive forces exerted by the atoms O compared with those of the CH₂ group, while the other strengthens, owing to electrostatic interactions between the C-O dipoles. The steric effect of branched-alkyl groups, adjacent to the O atom, probably affects the dispersive forces less than the electrostatic ones. This explains the constancy of the dispersive coefficients in oxaalkanes. On the contrary, the short-range electrostatic interactions are significantly weakened by alkyl groups attached to the O atom.

The interchange dispersive coefficients depend also on the class of the alkane (non-polar component), being larger for cyclohexane than for acyclic alkanes. Moreover they increase with increasing the number of alkyl groups in the chain.

The dependence of both dispersive and quasi-chemical parameters from the number of alkyl groups adjacent to the functional group can be conveniently used for assessing, by extrapolation, the interchange parameters in special systems such as ammonia, NH₃, or water, H₂O.

If we treat NH₃ as a homogeneous group, with an isotropic force field and assign to it physically reasonable geometric parameters, we are not able to reproduce by a lattice model the concentration dependence of the excess functions of mixtures of NH₃ (1) + n-alkanes (2).⁴³ To do this we have to regard NH₃ as consisting of two types of contact surfaces, thus simulating the anisotropy of the force field. Since the three hydrogen atoms in the molecule are identical, the most reasonable approach seems to consider H atoms as a type of surface and N atom as the second one. Mixtures of NH₃ with n-alkanes, are regarded as possessing three types of contact surfaces (CH₃, CH₂, H, N). This requires, in the DISQUAC approach, the evaluation of 6 different interchange parameters, two for any contact, which is impossible without making additional assumptions. In order to reduce the number of contacts, we assigned to the parameters of the contacts *a*/*N* the same values obtained from the contacts *a*/*N* of the tertiary amines in n-alkanes and neglected the parameters of the contact *a*/*H*. This allowed us to determine the parameters corresponding to the contact *N*/*H*. We also used a different approach in order to correlate the *a*/*N* parameters of NH₃ to those determined for the alkylamines. To this purpose we considered NH₃ as composed by an amino group NH₂ and an alkanic group H, that is a primary amine without carbon atoms: H-(CH₂)_{*u*}-NH₂, *u* = 0.

Extrapolating for $u = 0$ the dispersive and quasi-chemical parameters of a/N contact in n-alkylamines we obtained parameters very close to those obtained by using the experimental critical temperature (T^C) and critical composition x^C of mixtures of ammonia with n-alkanes which are the only experimental data available in the literature.⁴³ This procedure could appear quite artificial, but it is certainly promising. In fact it allows us to simulate the anisotropy of the molecule by maintaining the same types of contact surfaces of primary amines and by obtaining parameters comparable with those directly derived from experimental data. Other hetero-atoms could be examined in the same way, e.g. considering water as an alcohol derived from $H-(CH_2)_u-OH$ and extrapolating the parameters for $u = 0$.

Several authors⁴⁸⁻⁵⁰ have used DISQUAC to describe the VLE, LLE and H^E data of mixtures of alcohols + n-alkanes. Unfortunately, the coefficients obtained vary irregularly with the length of the alkyl chain of 1-alkanols, and a different parameter is necessary for each alcohol, from methanol (C_1) to hexadecanol (C_{16}). Moreover, it is unclear whether the properties of very diluted solutions can be reproduced. We believe that interchange parameters so far obtained need to be verified and therefore cannot be used in order to make reliable extrapolations.

Proximity effect

In poly-functional molecules of type $X-(CH_2)_m-X$, containing two identical X groups, the number of CH_2 groups, m , influences the energy of the contacts (X/CH_2), (iso-proximity effect), while in asymmetric molecules of type $X-(CH_2)_m-Y$, containing two different functional groups, X and Y, m , affects at the same time the energies of the contacts (X/CH_2), (Y/CH_2) and (X/Y) (hetero-proximity effect). The proximity of two X groups in the same molecule (O—O, S—S, N—N, Cl—Cl,...) weakens the intermolecular interactions and has a strong influence both on the quasi-chemical and on the dispersive parameters: the parameters decrease with decreasing the distance X—X. The proximity effect increases with increasing the polarity or the polarisability of the C—X bond. Polarity has a short-range proximity effect, while polarisability acts to a longer range. We believe that this effect is strictly intramolecular effect and that a group contribution model, even though sophisticated, cannot improve

the agreement experimental/calculated without a regular variation in the interchange coefficients or a change in the values of the contact surfaces.

The study of asymmetrical molecules, containing two different groups X and Y, $X(CH_2)_nY$, is much more difficult, the variable n affecting the energies of three contacts simultaneously (X,CH_2), (Y,CH_2) and (X,Y). In mixture of chloroalkylbenzenes ($Y = Cl$),³² aromatic ethers ($Y=O$), or aromatic ketones ($Y = CO$)³³ + alkanes the dispersive coefficients of the (Y,CH_2) contact are constant ($Y = Cl, O$) or slightly increase ($Y = CO$) as n increases because of the inductive effect. The quasi-chemical coefficients of the (Y/CH_2) contact increase as n increases because of the steric effect ($Y = Cl, CO, O$). The dispersive coefficients of the (X/Y) contact ($X = C_6H_5-$; $Y = Cl, O, CO$) decrease as n increases and the quasi-chemical parameters are constant for ($Y = O$) or zero for $Y = CO, Cl$; i.e. they are not influenced by the reciprocal distance also when short molecules are involved. Finally for the (X/CH_2) contact the quasi-chemical parameters are zero while the dispersive are constant or slightly decrease as n increases.

As a general remark, we have to observe that the values of the interchange parameters are constant or only vary for the first three or four terms of the series. This allow us to predict the values of excess properties for compounds with three or more CH_2 groups.

Polarity effect

The quasi-chemical coefficients, C_{ax}^{quac} , in the series $CH_{4-u}(XCH_3)_u$ decrease regularly with increasing u , the number of X atoms directly linked to the same carbon atom. For $X = Cl$,¹² the quasi-chemical coefficients are obviously equal to zero in CCl_4 . Considering the dipole moments μ in the gas phase, we see that it decreases in the order: CH_3Cl (1.87 D) > CH_2Cl_2 (1.60 D) > $CHCl_3$ (1.01 D) > CCl_4 (0.00 D), that is the same order of the quasi-chemical coefficients. However, higher homologues have higher μ : CH_3CH_2Cl (2.05 D) \approx CH_3CHCl_2 (2.06 D) > CH_3CCl_3 (1.78 D) but smaller quasi-chemical coefficients. We believe that in this case the dipole orientations are sterically hindered.

We have to be careful when correlating the excess functions of liquid mixtures with dipolar moments. In fact, when $X = O$, S ^(17,22) the quasi-chemical parameters, C_{ax}^{quac} , extrapolated to $u = 4$,

$C(OCH_3)_4$ and $C(SCH_3)_4$, are different from zero. On the other hand these small molecules have a small dipole moment and this may explain the finite value of the quasi-chemical coefficients.

2) Cyclic polar + non-polar

$(c-CH_2)_m-X + (c-CH_2)_n$

The quasi-chemical coefficients are independent of the nature of the alkane and decrease with the size of the alkyl groups (steric effect). Moreover, they are greater than the corresponding coefficients for linear open chain molecules with the same number of carbon atoms. We can explain this behaviour by observing that the steric effect is lower in the cycle, where the polar group X is more exposed and less sterically hindered, *e.g.* amines, ethers, ketones.

On the contrary, the dispersive coefficients depend on the nature of the alkane, *e.g.* the coefficients of the contact O/CH₂ in cyclic ethers (e,c)¹⁷ are greater than the corresponding O/CH₂ in linear ethers (e,a) and increase with decreasing the number of carbon atoms in the ring for the strain ring effect. As it is known, the distortion of bond angles in small cyclic molecules gives to the molecules an ethylenic unsaturated character, because a fraction of σ electrons, more localized and less polarisable, that predominates in open chain molecules, is converted into π electrons, less localized and more polarisable as it can be deduced by the electric dipole moments: for cyclic molecules $(c-CH_2)_{m-1}-X$ ($m = 3$, $X = NH$, O , $\mu = 1.9$ D) while for the corresponding linear one we find $\mu = 0.9$ for $X = NH$ and $\mu = 1.3$ D for $X = O$.

Some polar cyclic molecules (cycloethers, trichlorobenzene) show in mixtures with n-alkanes an anomalous dependence of the excess enthalpy H^E on the length of the alkane. This exothermic effect was explained by Wilhelm⁵¹ in terms of conformational changes induced in alkanes (predominance of trans conformations).

3) Polar + polarisable

The excess functions of such mixtures generally have a S-shaped pattern which results from the balance of an endothermic contribution, due to a/b (a, aliphatic surface; b, benzene or tetrachloromethane) interactions, and an exothermic one, due to specific X/b interactions, such as charge transfer or dipole-dipole induced interactions, between the polar group of the solute and the polarisable molecules of the solvent, as it happens when the solvent is CCl₄ or unsaturated/conjugated hydrocarbons, as benzene. The interpretation of the

excess functions of these systems is very difficult because they are the sum of a dispersive positive and a quasi-chemical negative contribution. In this case, slight modifications of the interchange parameters related to structural effects involve large changes on the calculated functions. It was noted that polar-polarisable contacts are best described assuming that they are fully dispersive.

Since the model parameters represent interchange energy of pairs of groups, a relatively large ratio between the dispersive and the quasi-chemical term does not necessarily mean that both the groups should be non-polar. When the groups are both polar, or one of them is polar and the other polarisable, the degree of orientation of contact surfaces can only slightly change. Assuming that the ratio between the dispersive and quasi-chemical contribution is a measure of the degree of change of orientational order of the groups involved, we can explain the observed effect. The influence of inductive and steric effect of alkyl groups adjacent to the X group on the dispersive, C_{sx}^{dis} and quasi-chemical, C_{sx}^{quac} , parameters can be explained if we consider that the interchange energy $\Delta\epsilon_{sx}$ are related to the interaction energies trough:

$$\Delta\epsilon_{sx} = \frac{(|\epsilon_{ss}| + |\epsilon_{xx}|)}{2} - |\epsilon_{sx}| \quad (13)$$

being the ϵ negative.

In the polar + non-polar systems ($s = a, c$), where the interactions are mainly of type 1-1, the inductive effect exerted by the alkyl groups adjacent to the polar group X increases the dispersive interaction energies, ϵ_{xx} , and consequently increases $\Delta\epsilon_{sx}$ and C_{sx}^{dis} . In polar-polarisable systems, where the interactions of type 1-2 dominate, the inductive effect increases the interaction energies ϵ_{sx} thus decreasing $\Delta\epsilon_{sx}$ and C_{sx}^{dis} . The steric effect influences mainly the quasi-chemical parameters. In the polar-non-polar systems it decreases the dipole-dipole energy interaction ϵ_{xx} and consequently decreases $\Delta\epsilon_{sx}$ and C_{sx}^{quac} ($s = a, c$), while in polar-polarisable systems, dominated by the 1-2 interactions, it decreases the electrostatic interactions thus increasing $\Delta\epsilon_{sx}$ and the quasi-chemical interchange coefficients, C_{sx}^{quac} .

DISQUAC model takes into account the inductive and steric effects trying to establish general rules. In mixtures in which either dispersive random, and electrostatic, non-random

interactions are present, DISQUAC dispersive parameters, change with the structure influenced by the inductive effect while quasi-chemical parameters, vary because of the steric effect of alkyl groups. In mixtures where only dispersive interactions are present, the model considers only dispersive parameters, obviously influenced by both the inductive and steric effect exerted by the alkyl groups. In mixtures of polar substances $RX +$ an "active" polarisable solvent, b , (benzene, tetrachloromethane) specifically interacting with the polar group X we can observe some general rules are: ^{26, 30, 34-36} (1) The dispersive interchange coefficients decrease with increasing the length of the alkyl chain adjacent to the polar group X . This is true both if a perfect compensation takes place between the asymmetry of the polar and the polarisable group and if it doesn't. In the latter instance a quasi-chemical contribution needs to be introduced. In the case of mixtures of alkanes with CCl_4 , the dispersive parameters increase, probably because of the dominance of steric effects to the inductive ones, while in the case of mixtures of alkenes + benzene or + tetrachloromethane the dispersive parameters remain constant. Of particular importance are the negative values found for the parameters $>C=C</math> / CCl_4 indicating a specific π - σ interaction. In the case of mixtures of alkanes + CCl_4 we can observe the presence of an exothermic contribution, given by the specific interaction $alkane / CCl_4$, and an endothermic one R / CCl_4 (R, aliphatic surface). The latter is smaller than that of $R / benzene$ and this explains the relatively low increase of the excess enthalpies with increasing the chain. In mixtures with $X = O, CHO$, the asymmetry between the polar and the polarisable group does not perfectly compensate and it is then necessary to introduce a quasi-chemical contribution; (2) The quasi-chemical coefficients remain constant or increase with increasing chain length of alkyl groups adjacent to the polar group X . This is attributed to the steric effect that reduces the electrostatic interactions of type 1-2.$

4) Polar + polar

As polar-polarisable contacts do, also polar-polar contacts (ethers, aldehydes, nitroalkanes + chloroalkanes, ^{25,52,53} ethers + bromoalkanes, ²⁹ alkanes + alkanes, ⁵⁴ alkanenitriles + alkanones²⁴) are well described by dispersive interchange parameters slightly decreasing with increasing the length of the alkyl chain adjacent to polar groups X, Y . This may be ascribed to the

inductive effect on the 1-2 interactions. In some cases, some quasi-chemical contribution should be introduced for a non-perfect compensation between the two polar groups. In this case, quasi-chemical parameters slightly increase, with increasing the size of alkyl groups due to the steric effect.

In mixtures of chloroalkanes + chloroalkanes of the series $(CH_{4-u})Cl_u$ the dispersive parameters of polar-polar contacts (d/d') decreased regularly with the increase of the number of chlorine atoms due to the polarity effect.

5) Non-polar + non-polar

The mixtures where both the components are non-polar, such as perfluoroalkane + alkanes, ³⁴ alkylbenzene + alkane, ²⁷ alkanes + benzene, alkanes + cyclohexane, tetrachloromethane + alkanes, tertiary amines + alkanes or + cyclohexane, alkynes ($RC\equiv CR$) + alkanes or + cyclohexane and alkenes, ³⁰ $RCH=CHR$ + alkanes or + cyclohexane, the weak polarisability of N or $C=C$, with respect to that of CH_2 , is partially compensated by the small dipole moment of the $C-N$ bond or of the $C=C$ double bond. These mixtures are well described in the DISQUAC random-mixing approximation. The interchange coefficients of non-polar contacts s/t ($s, t = a, aliphatic; b, benzene, c, cyclohexane, d, tetrachloromethane, n, nitrogen$) generally remains constant, except in the case of tertiary amines, in which the predominant steric effect leads to a slight decrease of the parameters, and alkenes or alkynes, in which the inductive effect predominate implying a slight increase in parameters with increasing the size of the alkyl groups adjacent to the group $C=C$ or $C\equiv C$. A closer examination of these systems shows that, as in mixtures containing alkanes, the interchange coefficients are dependent on the length of the alkane (m). For instance, we can observe that in benzene + n -alkanes mixtures the experimental H^E curves of for higher alkanes ($m > 10$) are higher than those calculated by the model. This extra endothermic contribution to H^E was attributed to the so-called "Patterson effect"⁵⁵ that is conformational changes and / or short-range orientational effects arising when alkanes are mixed with globular molecules, and the orientational order in this long chain alkanes, is destroyed.

In mixtures containing molecules of different lengths, H^E is the result of two contributions: the first one of interactional origin and the second one is due to changes in orientational order in pure liquid. DISQUAC group contribution model is

particularly effective in this case, because it allows for calculating the interactional contribution, by considering molecules of similar shape and sizes and then to estimate the conformational contribution as the difference between the calculated and experimental values when molecules of different size are considered.

EXPERIMENTAL - CALCULATED COMPARISON

In this paragraph, first we will test the validity of the model on the main properties (G^E and H^E) related to the phase equilibrium and then we will examine the derived properties (partial molar quantities at infinite dilution and excess heat capacities) that usually are hardly predicted by theoretical models. The DISQUAC model, accurately predicts the excess Gibbs energies, G^E , by using structure dependent parameters. The differences between experimental and calculated values rarely exceed the limits of the experimental error. As expected, the largest deviations occur when the reduced temperature of one or both components is higher than 0.7. In these conditions the systems are obviously outside the range of applicability of the rigid lattice models.

The excess enthalpies, H^E , are very accurately predicted by the model except for mixtures containing long-chain alkanes in which experimental values are higher than those calculated.

The analysis of a large number of activity coefficients data at infinite dilution, γ^∞ , by DISQUAC allows us to draw some general conclusions. In a graph where $\Delta \ln \gamma^\infty = \ln \gamma^\infty (\text{Exp}) - \ln \gamma^\infty (\text{Calc.})$ is reported as a function of $\omega = r_i/r_j$, the ratio of the molecular volumes of solute i and solvent j , we can clearly distinguish a ω -range, where $\Delta \ln \gamma^\infty$ is almost zero, and a ω -range where $\Delta \ln \gamma^\infty$ rapidly increases with increasing ω . In the first range the model correctly predicts the γ^∞ , while in the second range the higher values of $\Delta \ln \gamma^\infty$ derive, at least in part, by the Flory-Huggins equation that, as it is known, overestimates the combinatorial entropy term. However, being the combinatorial entropy independent of the temperature, DISQUAC correctly predict the values of partial molar enthalpies at infinite dilution $h^{E,\infty}$ ¹⁰.

The most severe test of validity of the model is the calculation of the liquid-liquid equilibrium curves, LLE, by using the same interchange parameters which predict vapour-liquid equilibrium, VLE, and excess enthalpy curves. Therefore, we consider a success the prediction of the miscibility gap. The critical point is predicted with small differences in temperature and composition³⁴, even though the experimental curves near the critical temperature are flatter than the calculated ones. Moreover, the model correctly predicts the liquid-solid equilibrium diagram.

CONCLUSIONS

This work demonstrates that the DISQUAC is an accurate predictive model for systems containing small molecules at low temperatures ($T_r < 0.7$). Deviations arising in the presence of

molecules containing more than 10 C atoms show a regular trend and can be predicted a priori and therefore corrected.

Relationships between the interaction parameters and the molecular structure suggest that the DISQUAC has a better physical basis than other models. These relationships have also a practical importance because they allow for the evaluation of unknown thermodynamic data without the need of additional measurements. In polar + non-polar systems the main contribution is the quasi-chemical one, and it is more important as more polar the functional group is. The dispersive contribution is relatively small for simple polar functional groups, as a halogen in haloalkanes, while it increases for -O- group. More complex functional groups (CO, CN, NO₂, ..) show higher dispersive contributions which adds to the quasi-chemical ones. The model of athermal non-associated solutions developed on a different basis than DISQUAC gives roughly the same numerical results when weakly associated systems are considered. In the absence of extra-thermodynamic evidence for the formation of specific forms of A_iB_j associated mixtures, DISQUAC model is preferable. In order to compare DISQUAC with the most popular predictive models, UNIFAC and ASOG, we will consider chloroalkanes mixtures because these models define the same chlorine groups, CCl, CCl₂, CCl₃ and CCl₄, defined in DISQUAC. However, only the MODIFIED UNIFAC version, which uses temperature-dependent parameters, is closely comparable with DISQUAC.

In the MODIFIED UNIFAC there is no correlation between the contact parameters and the structure of the chlorine groups that vary irregularly while the parameters DISQUAC decrease regularly with decreasing the polarity of the group. Moreover, also the ratio $C_{st,1}/C_{st,2}$ changes on a regular way. UNIFAC model does not take into account the proximity effect existing in mixtures of polychloroalkanes + polychloroalkanes and uses the parameters fitted on a single system, such as CCl₄ + CHCl₃, for all classes of haloalkanes. This causes a scarce exp/calc agreement especially when compared with that obtained through the structure dependent DISQUAC parameters. The activity coefficients at infinite dilution are intentionally calculated using the Flory-Huggins combinatorial entropy, and neglecting both the heat capacity coefficients, $C_{st,3}$, and the corrections for conformational effects. The

purpose was to highlight and identify the reasons causing differences between calculated and experimental values. Unfortunately, these differences depend on many simultaneous causes and are difficult to interpret.

To consider a different expression for the combinatorial entropy could obviously improve the prediction of γ° for systems containing long-chain molecules. In fact, it is very difficult to describe quantitatively the conformational order effects are very difficult in long chain molecules. The free-volume theory of Flory has been used to take into account the conformational effects by assuming that the interchange energy parameters, X_{12} , is dependent on both temperature and pressure. Unfortunately, this approach seems to be inconsistent with the equation of state. Costas⁵⁶ proposed an equation of state for pure n-alkanes able to simulate the correlation of molecular orientations in the frame of a lattice model. Some results obtained for cyclohexane + n-alkanes mixtures seem to be promising and suggest to improve the quasi-chemical lattice theories by including in an equation of state term,

We think that the present version DISQUAC may not give completely satisfactory results in the case of strongly interacting groups due to the approximations inherent in the quasi-chemical model and the assumed additivity of the dispersive and quasi-chemical contributions. In fact, we must always bear in mind the intrinsic simplifications of the quasi-chemical model where the real distance and the angle dependent intermolecular potentials are roughly represented by a few quantities: isotropic interchange parameters, fractions of molecular surface, which simulate the anisotropy of forces field and a lattice coordination number, which weighs, through the Boltzmann factor, the "probability" of contacts.

At present, the DISQUAC parameters table is limited to a little number of groups. We hope to expand it in the future. Anyway, the long-term strategy of DISQUAC is not to establish and disseminate a table of parameters such the UNIFAC.

We believe that doesn't exist a simple set of equations for calculating the thermodynamic properties within the limits of experimental errors and therefore that the DISQUAC group contribution method here presented is a realistic method and a physically valid approach to the study of liquid mixtures.

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