

## New versions of quasichemical models for fluids with orientation effects

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**Abstract** - During the last two decades quasichemical approximation has been used in new applications in modelling fluids with orientation effects and association. Quasichemical group-contribution models for liquid solutions, hole versions describing both liquid and gas phases, models for the surface region of solutions etc. were worked out. The main features of the models and some calculated results for pure and mixed fluids are discussed.

### INTRODUCTION

Though progress in the statistical thermodynamics of fluids is mainly due to integral equations for correlation functions, to the perturbation theory and computer simulations (ref. 1,2), partly empirical approaches are still the most valuable in practical calculations. For the correlation and prediction of thermodynamic properties of such complicated systems as associated fluids, polymer solutions, liquid crystals, various multicomponent mixtures etc. lattice models appeared to be rather helpful. They propose the simplest way to take into account strong interactions (repulsive and specific) and to reflect properties due mostly to local structure. In physico-chemical studies the quasichemical (or Bethe-Guggenheim) approximation (QA) is widely used for local ordering estimations.

This approximation was formulated firstly for binary lattice systems formed by similarly sized molecules interacting via central forces such as a strict regular solution (ref. 3), the Ising model etc. It can be written as

$$\hat{N}_{12}^2 / \hat{N}_{11} \hat{N}_{22} = 4 \exp(-w_{12}/kT), \quad (1)$$

where  $\hat{N}_{ij}$  is the number of pairs of the nearest neighbours  $i$  and  $j$  ( $i, j=1, 2$ );  $w_{12}$  is the interchange energy, that is the difference  $u_{12} - (u_{11} + u_{22})/2$  (here,  $u_{ij}$  is the interaction energy for the  $i$ - $j$  pair);  $T$  is the absolute temperature,  $k$  is the Boltzman constant. Later, QA was applied to systems where molecules differ in sizes and orientation effects take place. A rather general model taking into account both these factors was formulated by Barker (ref. 4,5). New versions of quasichemical models for mixtures and pure fluids with orientation effects appeared in the seventies and eighties. Among these, there are group-contribution versions of the Barker model for the excess functions of liquid solutions (ref. 6-10) and a quasichemical hole group-contribution model which is valid both for liquid and gas phases giving the equation of state EOS and the wide range of thermodynamic quantities (ref. 11). The free volume factor was taken into account in the group-contribution model by Nitta et al. (ref. 12). There are special applications of QA to the surface region of solutions with polar components (ref. 13) and to liquid crystals (ref. 14). In this paper mainly the results obtained in our studies are considered.

### QUASICHEMICAL APPROXIMATION AND THE LAW OF MASS ACTION

In quasichemical models the description is made in terms of pairs of the nearest neighbours and equation (1) or several equations of the type are used to find the numbers of various pairs. They can be pairs between different contact points of molecular surface, which in a general case is considered energetically inhomogeneous. The idea was presented in the Barker lattice theory for solutions with orientation effects and association (ref. 4,5). Contact points of a molecule equivalent with respect to their energies of interaction with neighbouring molecules are considered as belonging to the same type. For example, an alcohol molecule is usually allotted three types of contact points: contact points of a hydrocarbon part (type I), hydrogen (H) and oxygen (O) of a hydroxyl group. Thus even for a pure alcohol several types of mixed pairs (H-O, H-I, O-I) should be taken into account, the H-O pair corresponding to the hydrogen bond. For each type of mixed contacts we can write a quasichemical equation similar to (1). Hole theories introduce vacancies as an extra component, and this results in additional quasichemical equations. In this part expressions for excess thermo-

dynamic functions of the k-component lattice system without vacancies will be given. Let n be the number of contact point types in the system,  $N_{ij}$  is the number of pairs (contacts) of different types. For the sake of convenience, we'll distinguish the pairs i-j and j-i when  $i \neq j$ . In a homogeneous fluid  $N_{ij} = N_{ji} = \hat{N}_{ij}/2$ ,  $\hat{N}_{ij}$  being the total number of pairs between i and j contact points. Instead of (1), we have

$$N_{ij} N_{ji} / (N_{ii} N_{jj}) = \exp(-2w_{ij}/kT), \quad (2)$$

where  $w_{ij} = u_{ij} - (u_{ii} + u_{jj})/2$ ;  $i, j=1, \dots, n$ . The overall number of equations (2) for the system is  $n(n-1)/2$ .

The configurational partition function of the system is given as

$$Z_c = Z_{fv} Z_{lat} \quad (3)$$

with  $Z_{fv}$  denoting the free volume factor and  $Z_{lat}$  being the lattice partition function;

$$Z_{lat} \approx g_o(N_1, \dots, N_k) \left[ \prod_{i,j} N_{ij}^* / N_{ij}! \right] \exp(-\sum_{i,j} N_{ij} u_{ij} / kT); \quad (4)$$

here,  $g_o$  is the overall number of different configurations for the system,  $N_{ij}$  and  $N_{ij}^*$  are the numbers of i-j pairs given by equations (2) and found in the random approximation respectively. When the free volume part is not taken into account, thermodynamic functions are written as a sum of combinatorial and residual parts. Thus, for the activity coefficients  $\gamma_i$  we have

$$\ln \gamma_i = \ln \gamma_i^{comb} + \ln \gamma_i^{res}. \quad (5)$$

In the Barker theory Guggenheim combinatorial formula for mixtures of chain molecules was used:

$$\ln \gamma_i^{comb} = \ln(\phi_i/x_i) + zq_i \ln(\theta_i/\phi_i)/2, \quad (6)$$

where z is the coordination number,  $zq_i$  is the number of contact points of molecule i, that is the number of lattice sites which are its nearest neighbours ( $zq_i$  is a measure of molecular surface);  $x_i$  is the mole fraction of component i,  $\phi_i$  and  $\theta_i$  are its volume and surface fractions:

$$\phi_i = r_i x_i / \sum_{j=1}^k r_j x_j; \quad \theta_i = q_i x_i / \sum_{j=1}^k q_j x_j,$$

$r_i$  being the number of lattice sites occupied by molecule i. Other approximations can be used instead of (6) to take into account the influence of molecular sizes.

The residual part will be written in a form suitable both for the original Barker model and for its group-contribution version. The following quantities are introduced:

$q_{si} z$  - the number of s-type contact points for molecule i;

$\alpha_{si} = q_{si}/q_i$  - the fraction of s-type contact points in the molecule i;

$\alpha_s = \sum_{i=1}^k q_{si} x_i / \sum_{j=1}^k q_j x_j$  - the surface fraction of s-type contact points in the mixture;

$X_s$  - solutions of the following set of equations (Note a)

$$X_s \sum_{t=1}^n \alpha_t X_t \eta_{st} = 1 \quad (7)$$

where  $\eta_{st} = \exp(-w_{st}/kT)$ ,  $s=1, \dots, n$ ;  $X_{si}$  - solutions of the corresponding set of equations for pure component i. Through  $X_s$  the most probable numbers of pairs in the system are obtained,  $\alpha_s \alpha_t X_s X_t \eta_{st}$  being the fraction of s-t pairs. We have

$$\ln \gamma_i^{res} = zq_i \sum_{s=1}^n \alpha_{si} \ln(X_s/X_{si}). \quad (8)$$

The excess enthalpy is given by

$$H^E = Nz \left( \sum_{j=1}^k q_j x_j / 2 \right) \sum_{s,t} (\alpha_s \alpha_t X_s X_t - \sum_i \theta_i \alpha_{si} \alpha_{ti} X_s X_t) \eta_{st} h_{st}, \quad (9)$$

where  $h_{st} = \partial(w_{st}/T)/\partial(1/T)$  is the interchange enthalpy.

An attractive feature of the model is the uniformity of its formulation. With the equations written above it is possible, in principle, to take into account both nonspecific and specific interactions, to describe different types of association. That is one of the advantages

Note a: Equations (7) follow from quasi-chemical equations (2) and from stoichiometric relations.

of the quasichemical approach in comparison with the theories of association equilibria where equations expressing the law of mass action should be written individually for each type of association. The difference between the two approaches is due to the fact that in the quasichemical approach we deal with the numbers of pairs of different types and in the theories of association equilibria, with the numbers of molecular species (monomers, dimers, etc). It was shown (ref. 15) that for the same interaction model both approaches give similar results and the relations were found between the parameters (association constants and interchange energy for strong bonds). But, in general, the two approaches differ in their capability to describe different types of association. The most serious restriction of contact points models is their inability to describe the dependence of interaction parameters on the structure of associates (thus, the energy of the O-H bond is supposed to be the same for associates AB and AB<sub>2</sub>, for A<sub>2</sub>, A<sub>3</sub>, ..., A<sub>i</sub> in the case of consecutive association). Some types of association patterns (e.g. formation of only trimers or only tetramers) cannot be described by contact points models. At the same time theories of association equilibria do not have any difficulties in this respect. But there exist also situations when contact points models work well whereas the approach using the law of mass action can be hardly realized (e.g. systems where a network of strong bonds is formed). The law of mass action is very widely used for associated systems when equations for excess functions or EOS are derived (ref. 16). Our attention will be focussed only on the quasichemical approach.

In fact, QA can be interpreted in a rather general manner only as a means to estimate local ordering without an obligatory connection with lattice models and one can assume that lattice models themselves can be considered just as a manner of enumerating the most significant configurations. The quality of QA was checked by comparison with strict Onsager's results for the plane lattice, with very accurate expansions (ref. 17) and with the results of computer simulations (ref. 18,19). It has appeared to be rather satisfactory excluding the critical region. Several attempts were made to improve QA (ref. 2), but as a rule its classical form is used, and this is done throughout the paper.

### QUASICHEMICAL GROUP-CONTRIBUTION MODELS FOR LIQUID SOLUTIONS

The models under consideration were first dealt with in a study of Kehiaian et al. (ref. 6), and later several versions differing in some details were proposed (ref. 7-10). The models exploit the general idea of a group-contribution approach, i.e. the additivity of the contributions of groups to thermodynamic properties represented as a sum of combinatorial and residual parts. In comparison with UNIFAC and ASOG, their specific feature is the use of QA for the calculation of the numbers of pairs between neighbouring groups. The models are in fact some extensions of the Barker-Guggenheim model and relate to the quasilattices without vacancies (therefore, volume changes on mixing are not considered). Not only linear, but also bulky molecules are now included. Molecular volumes  $r_i$  and surfaces  $q_i$  estimated according to Bondi's tables (ref. 20), and the Flory-Huggins (ref. 6) or Guggenheim-Staverman (ref. 8-10) combinatorial term is introduced. The version used in our work (ref. 8,9) differs from the Kehiaian model in the following: (1) in using the Guggenheim-Staverman expression for the combinatorial term, (2) in the manner of subdivision some heteroatomic polar groups into different contact parts, (3) in form (7) of quasichemical equations convenient for calculations in the whole concentration range, including infinite dilution. The residual contribution to the chemical potential is represented by expression (8), the excess enthalpy is given by (9),  $s$  and  $t$  denoting different groups. The interchange free energy  $w_{st}$  is considered as temperature dependent according to the formula used by Kehiaian et al. (ref. 6):

$$w_{st}(T)/T = w_{st}^0/T_0 + h_{st}^0(T_0 - T)/(T_0 T) + C_{pst} [\ln(T/T_0) - (T_0 - T)/T] \quad (10)$$

Three parameters are introduced for each pair of different groups  $s$  and  $t$ :  $w_{st}^0 = w_{st}(T_0)$  and  $h_{st}^0 = h_{st}(T_0)$  - interchange free energy and interchange enthalpy at some reference temperature  $T_0$ ;  $C_{pst}$  - interchange heat capacity. For the calculations in a small temperature range, the  $h_{st}$  parameter may be considered temperature independent, and the last term in the expression (10) disappears. The model was applied to systems formed by alkanes, alkanols, perfluoroalkanes (ref. 8,9,21,22), to mixtures of alkanes and alkanols with cellosolves (ref. 2), alkenes and alkynes (ref. 23). As an illustration, systems composed of alkanes, alkanols, and perfluoroalkanes are considered in more detail. The division of the molecules into groups and subgroups was made bearing in mind that in one group structural units with identical interaction energies are included. The subgroups of the same group differ only in their geometrical characteristics (the volume, the surface area). Thus, alkane molecules are assumed to consist of "CH<sub>2</sub>" groups, with CH<sub>2</sub> and CH<sub>3</sub> subgroups, molecules of perfluoroalkane are composed of "CF<sub>2</sub>" groups, with CF<sub>2</sub> and CF<sub>3</sub> subgroups. Alcohol molecules are considered to be formed of groups of three types - "CH<sub>2</sub>" (the hydrocarbon radical), H and O of the hydroxyl group. It seems that with the subdivision of the hydroxyl into two parts (groups), H and O, we have better possibilities to take into account orientation effects than with the models considering the OH group as a whole (ref. 10). The representation of heteroatomic polar groups as composed of different contact parts (different "groups") influences significantly the calculated results, helping to reproduce the asymmetry of excess function curves for strongly associated systems. Calculations for alkanol-alkane systems with  $z=10$  and  $z=4$  have shown

that the value of  $z$  does not influence the estimated results much. The results below relate to  $z=10$ . The volume and the surface area for standard segment are:  $v^* = 18.927 \text{ cm}^3/\text{mole}$  and  $a^* = 3.13 \times 10^{19} \text{ cm}^2/\text{mole}$ . There was some arbitrariness in the determination of geometrical characteristics for H and O groups, as only  $r_{OH} = (r_H + r_O)$  and  $q_{OH} = (q_H + q_O)$  are fixed by the Bondi tables. Particular  $r_H$  and  $r_O$  values are not significant, so it was assumed arbitrarily that  $r_O = r_{OH}$ ;  $r_H = 0$ . The values of  $q_H$  and  $q_O$  influencing the residual part were chosen taking into consideration that  $q_i z$  is proportional to the number of contacts in which this group takes part. The values  $q_{H_z}$  and  $q_{O_z}$  are to show the ability of the hydroxyl group to form one hydrogen bond through the hydrogen atom and two bonds through the oxygen atom. But these are effective parameters, and their values can differ from 1 and 2 (notice that for  $z=10$   $q_{OH_z} = 4.6$ ). The best agreement with the experiment was obtained for  $q_{H_z} = 1$ ;  $q_{O_z} = q_{OH_z} z^{-1}$ . The model parameters are given in Appendix. Satisfactory  $G^E$  and  $H^E$  values were predicted for alkane-alkanol solutions (ref. 21), for the limiting activity coefficients in binary and ternary alkanol-alkane-perfluoroalkane mixtures (ref. 22), for the mutual solubilities of perfluoroalkanes and alkanols or alkanes at temperatures far from the critical point of solubility. In general, the results for alkane-alkanol solutions are better than those obtained with a model close to ours, but considering the OH group as a whole, without subdivision to H and O contact parts (ref. 10). Hence, we point out once again the usefulness of such subdivision. For the calculations of the activity coefficients and phase equilibria in a wide temperature range as well as for the calculations of the excess enthalpies an approximation considering  $h_{st}$  as a temperature dependent parameter has evident advantages, in comparison with a cruder approximation  $h_{st} = \text{const}$ . But in some cases even with  $c_{pst} \neq 0$  the calculated  $H^E$  curves did not reproduce the asymmetry of experimental functions. This was observed for alkanol-alkane and alkanol-alkyne solutions, where experimental phase equilibria and  $H^E$  data used for the parameter estimation related to very different temperatures (ref. 23), the standard temperature  $T_0$ , corresponding to the phase equilibria data. It seems that for a better parameter estimation it is desirable to include  $H^E$  data near the standard temperature.

Certainly, the possibilities offered by the model under consideration should not be overestimated. There are general shortcomings of the group-contribution approach, and problems of the dependence of energy parameters on the position of the group in the molecule, on the presence of other groups etc. are very important. It seems that in comparison with UNIFAC and ASOG the quasichemical models have some advantages in the quality of a simultaneous  $G^E$  and  $H^E$  description and in the treatment of association. But at the same time they cannot compete with UNIFAC and ASOG in the simplicity, thoroughness of the parameter list and convenience of practical calculations.

Solutions with intramolecular hydrogen bond formation. The specificity of solutions where not only intermolecular but also intramolecular hydrogen bonds are formed cannot be reflected by the models discussed above. Not making any difference between the two types of bonds, the models prescribe that there are no specific contacts for associated component in nonpolar solvent at infinite dilution. But, in fact, if molecules A are capable of intramolecular hydrogen bond formation, such bonds will exist even at  $x_A \rightarrow 0$ , and this should influence the thermodynamic properties. A method to deal with such systems using the quasichemical group-contribution model was proposed and applied to cellosolve solutions (ref. 2). General conditions of chemical equilibria are written for the mixture composed of three molecular species:  $A_c$  - molecule A with an intramolecular hydrogen bond (cyclic form),  $A_1$  - molecule A without internal bonds (linear form) and molecule B:

$$\mu_{Ac} = \mu_{A_1} = \mu_A \cdot$$

To find the activity coefficients of the species, we can use equations (5) and (8) for a three-component mixture with known concentrations of cyclic and linear forms. The method was proposed for the determination of these concentrations using spectroscopic data related to high dilutions.

The hole group-contribution model. Unlike models without vacancies describing liquids, hole models are valid for both liquid and gas phases of the system. A hole model for pure and mixed fluids with arbitrary molecular sizes was suggested by Sanchez and Lacombe (ref. 25) under the assumption of complete randomness in the distribution of molecules and holes on the lattice. The model has further extensions (ref. 26-29), the group-contribution hole model was formulated in random approximation (ref. 30). Though in some models local ordering is considered, none of them takes into account orientational effects due to non-homogeneity of the molecular surface; this is why their possibilities to describe systems with polar components and association are restricted. The group-contribution approach for such systems could not be developed. A hole model which takes into account orientational effects, along with the influence of molecular size and shape, was proposed in our work with Viktorov (ref. 11). In fact, it was an extension of the model described in the preceding part for systems with vacancies. It is supposed that molecules of  $k$ -component mixture and vacancies (holes) are distributed on the lattice, each molecule of component  $i$  occupying  $r_i$  sites. Formally the holes are treated as a kind of species (component or group number zero) with  $r_0 = 1$ ,  $q_0 = 1$ . For them  $q_{s0} = 0$  if  $s \neq 0$ ,  $s$  denoting the group type,  $q_{00} = 1$ .

The volume of mixture containing  $N_i$  molecules of component  $i$  ( $i=1, \dots, k$ ) and  $N_0$  vacant sites are defined by

$$V = v'(N_0 + \sum_{i=1}^k r_i N_i), \quad (11)$$

$v'$  being the volume per site (the standard segment volume).

The lattice partition function can be represented by formula (4) written for a system with components  $i=0, 1, \dots, k$ . The numbers of contacts are found from equations (7), where  $s$  and  $t$  run from zero to  $n$ . The lattice partition function depends upon  $T$ ,  $N_1, \dots, N_k$  and on volume via  $N_0$  subject to relation (11). The derivation of thermodynamic quantities is straightforward. The equation of state is defined by

$$Pv^*/kT = -\ln(1-\tilde{\rho}) + \tilde{\rho} \sum_{i=1}^k x_i l_i / \sum_{i=1}^k x_i r_i + (z/2) \ln(1+Q) - z \ln X_0, \quad (12)$$

where  $P$  is the pressure,  $v^* = v'N_A$  is the molar standard segment volume ( $N_A$  - the Avogadro constant),  $\tilde{\rho} = v' \sum_{i=1}^k N_i r_i / V$  is the reduced density,  $l_i$  is the bulkiness factor for molecule  $i$ ,

$$Q = \tilde{\rho} \left( \sum_{i=1}^k x_i q_i / \sum_{i=1}^k x_i r_i - 1 \right),$$

and  $X_0$  is the solution of quasichemical equations for holes. If  $z \rightarrow 0$   $l_i = 0$  (linear molecules), from (12) we obtained EOS by Sanchez and Lacombe.

For the calculations to be made, we must possess the geometrical ( $r_s, q_s$ ) and energy ( $w_{st}, h_{st}, c_{st}$ ) parameters for the system under consideration. They, excluding  $q_s$ , were adjusted using some experimental data. The  $q_s$  parameters were calculated from the  $r_s$  values and from the prescribed values of the molecular bulkiness factor. The results of calculations presented in the publications (ref. 11) related to pure n-alkanes from butane to hexadecane, n-alkanols from ethanol to hexadecanol, acetic acid, hydrogen sulfide and water. Binary mixtures of n-alkanes with n-alkanes, alkanols, acetic acid, water and hydrogen sulfide, alkanol-alkanol mixtures about 80 systems on the whole) and some ternary systems were included. Now the list of substances under investigation includes also light alkanes  $C_1 - C_3$ ,  $CO_2$ ,  $N_2$ , 1-alkenes and 1-alkynes  $C_6 - C_{16}$ . Binary mixtures of n-alkanes  $C_1 - C_{16}$  with n-alkanes  $C_1 - C_{16}$ ,  $H_2S$ ,  $CO_2$ ,  $N_2$  are investigated, calculations are made for mixtures of alkenes and alkynes  $C_6 - C_{16}$  with alkanes  $C_4 - C_{16}$ . The majority of the systems are treated at several temperatures or pressures, and for some mixtures a high pressure region (up to 50MPa) is included. Among the mixtures under consideration are systems with a supercritical component (e.g., mixtures containing light alkanes,  $H_2S$ ,  $CO_2$ ,  $N_2$ ), systems with azeotropes (alkanol-alkane, alkyne-alkane etc.) and with miscibility gaps (alkane-water). For each of alkanes  $C_1 - C_3$ , for  $H_2O$ ,  $H_2S$ ,  $CO_2$ ,  $N_2$  parameters were estimated individually, n-Alkanes  $C_4 - C_{16}$ , n-alkanols  $C_2 - C_{16}$ , 1-alkenes and 1-alkynes  $C_6 - C_{16}$  were treated in the group-contribution manner. n-Alkane molecules (from butane and higher) were subdivided into  $CH_3$  and  $CH_2$  groups differing in their geometrical and energy characteristics. For alkanols, the hydroxyl group was added and subdivided into O and H contact parts, the O-H interaction representing the hydrogen bond. In acetic acid, water and hydrogen sulfide molecules the H contact parts were also distinguished. 1-Alkenes were considered as composed of  $CH_3$ ,  $CH_2$  and  $CH_2=CH$  groups, the specific group for 1-alkyne was  $CH \equiv C$ . The model parameters necessary for the description of the pure component properties were estimated from the saturated vapour pressure and liquid density data. If a group-contribution approach is implemented, then with these parameters one can predict the properties of those mixtures where no new types of contacts are present in comparison with the pure liquids (alkane  $C_4 - C_{16}$  - alkane  $C_4 - C_{16}$ , alkanol  $C_2 - C_{16}$  - alkane  $C_4 - C_{16}$ , alkanol - alkanol mixtures for example). To obtain a better description of excess functions, the parameters in some cases were corrected using  $G^E$  and  $H^E$  data for mixtures. Thus the  $CH_2$  and  $CH_3$  group-interaction parameters were corrected using data for decane-hexane mixture. Experimental data on alkane-alkanol and alkanol-alkanol solutions were not used for the parameter estimations. Binary mixing functions and vapour-liquid equilibrium data were necessary to find parameters of interaction between substances described individually and other compounds. The temperature range to which the parameters relate varies for different systems, but the 270 - 350 K interval is usually included. Calculations of thermodynamic quantities and phase equilibria carried out for many systems have shown that, in general, the model gives satisfactory results, both for pure nonpolar or polar compounds and for mixtures. Some experimental points along with theoretically calculated curves are given in Figs 1-3. The results on saturated vapour pressure of alkanes  $C_4 - C_{16}$  are much better than the hole group-contribution model of Ischizuka et al. (ref. 30) gives and are comparable with those following from the Sanchez and Lacombe theory with an individual description of each system (ref. 25). In comparison with Redlich-Kwong and Peng-Robinson equations of state, the present model gives usually more accurate results for fluids composed of long-chained and/or polar molecules, but in the case of short nonpolar molecules, such as light alkanes, it is in general less successful, especially near the critical point. The densities of liquid phase are usually better reproduced by the hole model and those of vapour phase by the cubic equations of state. The hole model under consideration ensures approximately the same accuracy of  $G^E$  and  $H^E$  prediction for liquid solutions with associating components as the quasichemical group-contribution approach described in the preceding

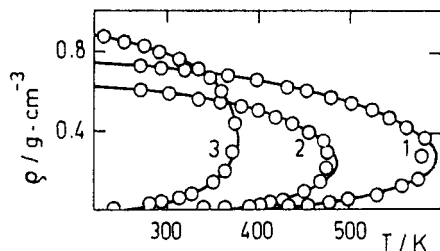


Fig. 1. Densities of coexisting pure vapour and liquid phases. 1 - n-octane, 2 - n-pentane, 3 - hydrogen sulphide (ref. 11).

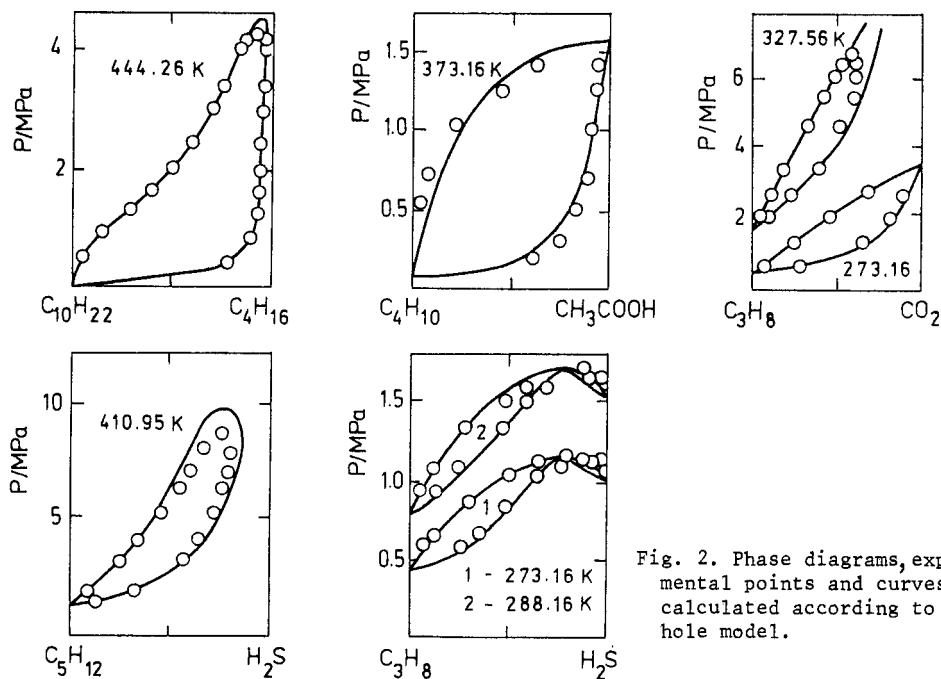


Fig. 2. Phase diagrams, experimental points and curves calculated according to the hole model.

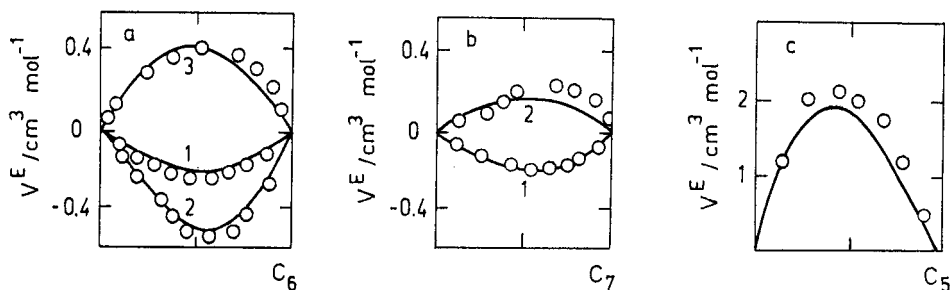


Fig. 3. Excess volumes for solutions of: (a) (at 298.16K) n-hexane + n-decane (1), + n-hexadecane (2), + n-decanol (3); (b) (at 298.16K) n-heptane + n-dodecane (1), + n-butanol (2); (c) (at 310.95K) n-pentane + hydrogen sulphide; (ref. 11).

part;  $V^E$  is obtained in addition. In comparison with UNIFAC, we obtain better excess enthalpies. In the case of n-alkane mixtures we obtained good results for  $G^E$  and  $V^E$  and only a qualitative prediction for  $H^E$ . The failure of the model in  $H^E$  prediction may be connected with its inability to take into account the short-range orientational order due to repulsive forces, which is very important for alkanes (ref. 31). A comparison with phase equilibria calculations using other hole models shows that, as a rule, our results are at least of the same quality, but for light components Kleintjens-Koningsveld EOS (ref. 27) is somewhat more

precise than ours. In general it should be accepted that the proposed model is far from being the most precise in the description of special classes of systems (*n*-alkanes for example), but its main advantage is the wide range of systems it can treat, including associated fluids and fluids composed of long-chained molecules. The application to such complicated systems the preferences of the model are revealed best. The second amendment is the possibility of a group-contribution treatment which significantly enlarges the predictive power of the model. Among the main shortcomings of the present model we should name its insufficient description of the temperature dependence of thermodynamic properties and a poor reproduction of the critical behaviour of pure components and mixtures.

It seems that the improvements of the model should be aimed predominantly at a better description of fluids formed by small nonpolar molecules as just here the model is inferior to the best modern approaches. We see several possibilities to make improvements. One of them is to change the combinatorial part of thermodynamic functions using a good EOS for fluids of hard bodies differing in size and shape. Rather inspiring results were obtained for nonpolar substances by combining the Carnahan-Starling or Boublik-Nezbeda EOS and an attractive part of the Van-der-Waals type (refs 24,31). It is reasonable to assume that with the equation of the type and with the residual part found in quasichemical approximation we'll succeed in describing both nonpolar and polar systems. Then there are possibilities to modify the classical QA itself.

### LATTICE MODEL FOR SURFACE REGION OF SOLUTIONS WITH POLAR COMPONENTS

In the series of our publications (refs 13,32) the multilayer model was proposed for the description of surface properties of solutions containing polar and associated components. As in the models described previously, the idea of molecules having different types of contact parts was exploited and the numbers of contacts were estimated in QA. Mixtures of spherical or linear molecules are considered. It is supposed that above the solution there is a homogeneous phase S of a constant composition (it may be vacuum, a solid or some liquid phase immiscible with the solution), the surface of the solution being plane. The lattice is divided into layers of sites parallel to the surface. For each layer *p* we should find the numbers of pairs  $N_{ij}^{pq}$  between contact points *i* and *j* belonging to the same layer (*q=p*) or to the adjacent layers (*q=p-1, p+1*). Quasichemical equations have the form

$$N_{ij}^{pq} N_{ji}^{pq} / (N_{ii}^{pq} N_{jj}^{pq}) = \exp(-2w_{ij}/kT) . \quad (13)$$

From the grand partition function the equations were derived determining the concentration and orientation profiles of the solution, surface tension and adsorption. Using the model, the liquid-vacuum interface was investigated for many binary and several ternary systems (solutions of organic compounds, alloys). Hydrogen bond formation was taken into account for such solutions as acetone-chloroform, alkanol-alkane, cellosolve-alkane and cellosolve-alkanol. We could conclude that the model is rather promising for the investigation of adsorption from solutions of complicated chemical nature. The calculations help to understand in which way the nature of polar groups, association processes and the length of hydrocarbon radicals influence the surface properties of solutions. The model may be formulated in a hole version and then be applied to the vapour-liquid interface. It is not difficult to modify the model for the description of adsorption from solution on the nonuniform solid surface.

### CONCLUSIONS

Thus, various applications of QA were considered in the paper. A number of advantages of the approach were outlined: a reasonable description of local ordering while taking into account orientational effects and association, the possibility to carry out a group-contribution treatment, the generalized mathematical form of equations suitable for various types of systems. QA looks rather attractive for an estimation of the residual part of thermodynamic quantities. Using this approximation in combination with good equations for the combinatorial part seems a promising tool in fluid properties modelling.

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## APPENDIX

Parameters of the quasichemical group-contribution model for systems composed of alkanes, alkanoles, alkenes and perfluoroalkanes (refs 8,23).

$$\tilde{w}_{st}^0 = w_{st}(T_0)/kT_0, \quad \tilde{h}_{st}^0 = h_{st}(T_0)/kT_0, \quad \tilde{c}_{pst} = C_{pst}/k$$

## Geometrical parameters

Groups	"CH <sub>2</sub> "		H	O	"C=C"		"CF <sub>2</sub> "	
	CH <sub>3</sub>	CH <sub>2</sub>			CH <sub>2</sub> =CH	CH=CH	CF <sub>3</sub>	CF <sub>2</sub>
r <sub>s</sub>	0.7220	0.5406	0.0	0.4248	1.0785	0.8959	1.1271	0.8101
q <sub>s</sub>	0.6773	0.4313	0.1	0.3664	0.9393	0.6901	1.1025	0.7349

## Energetical parameters

s-t contact	H-CH <sub>2</sub> and O-CH <sub>2</sub>	O-H	CH <sub>2</sub> -CF <sub>2</sub>	CF <sub>2</sub> -O	CF <sub>2</sub> -H	O-H	H-CH <sub>2</sub> and O-CH <sub>2</sub>	CH <sub>2</sub> -C=C	O-C=C and H-C=C
$\tilde{w}_{st}^0$	0.497	-4.3650	0.0556	0.5155	0.7829	-2.9706	0.3218	0.00875	2.2386
$\tilde{h}_{st}^0$	0.327	-5.0822	0.0634	0.4407	0.4960	-4.6106	0.6300	0.02357	0.5402
$\tilde{c}_{pst}$	0	0	0	0	0	-21.08	2.119	-0.0367	-1.1664
T <sub>0</sub>	298.16	298.16	298.16	298.16	298.16	377.15	377.15	377.15	377.15