

NEW POSSIBILITIES OF APPLICATIONS
OF THE BARKER QUASI-LATTICE THEORY.
PREDICTION OF g^E AND h^E OF BINARY SYSTEMS
WHOSE ONE COMPONENT IS FORMED BY *n*-ALKANES

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For binary systems of the type an arbitrary component + *n*-alkane we derived relations, on the basis of the Barker theory and on the basis of the group contribution concept, for predicting g^E and h^E from one system to another when the *n*-alkane length is changed. To carry out the prediction it is not necessary to evaluate any adjustable parameters. The developed method was tested using a large number of different systems covering alcohols, amines, ketones, esters, chlorinated derivatives of hydrocarbons, aromatic hydrocarbons and *n*-alkanes from *n*-pentane to *n*-hexadecane. The results of predictions are in very good agreement with experimental data in the cases, when the *n*-alkanes involved are not longer than *n*-decane. Systematic regular deviations in h^E in the cases, when at least one of *n*-alkanes involved is longer, can be explained by the presence of orientation effects in the pure longer *n*-alkanes. The correction suggested by us for these effects improves considerably results obtained. The developed method appears to be suitable for the systematic prediction of excess quantities of systems of the given type and represents an effective test of the Barker theory.

In the recent development of thermodynamics of non-electrolyte liquid mixtures, strong tendencies have appeared aiming at the effective exploitation of existing experimental information to predict properties of other systems. A typical example is the conceptually comprehensive UNIFAC method¹ for predicting activity coefficients.

With respect to its contribution approach and theoretical basis, the Barker quasi-lattice theory² hides considerable predicting possibilities. A number of new possibilities of its practical application follow from our analyses and calculations. One of them is brought in this work.

Binary solutions of *n*-alkanes especially with strongly polar and associating substances have already been a traditional subject of interest of the non-electrolyte solution thermodynamics. The behaviour of the systems mentioned is on the one hand to a considerable extent typical and extreme but on the other hand the chain monotonous molecule of *n*-alkane represents indisputable simplification of their theoretical description. The inert behaviour of *n*-alkanes as solvents allows to focus our attention to the behaviour of the second component, which is strongly utilized *e.g.*

in various association models for solutions of alcohols³⁻⁵ and amines⁶ in n-alkanes. The theory due to Brown, Fock and Smith^{7,10} applied to the interpretation of behaviour of systems of n-alcohols with n-alkanes employs on the contrary the chemical similarity of aliphatic chain of n-alcohols and that of n-alkanes. Interest in these systems results also from the fact that the interaction of methyl or methylene groups is practically the most frequent type of interaction in solutions of non-electrolytes.

In this work we deal with binary systems whose one component is arbitrary and the second is formed by n-alkanes of changing length. For systems of this type we obtained, on the basis of either the Barker quasi-lattice theory or the group contribution concept, the relations valid directly among their excess functions.

THEORETICAL

The Barker quasi-lattice theory^{2,8-10} considers a molecule of each component I as a chain of r_1 segments with overall number of zq_1 surface contact points. Each segment occupies one site on a z-coordinated lattice. It is assumed that the individual contact points of a molecule are not generally identical but that they belong to several different types. The contact points contained in molecules of different components are reckoned in different types. If we denote the number of contact points of the type i in a molecule I by Q_i it must hold

$$\sum_{i \in I} Q_i = zq_1. \quad (1)$$

The overall number of segments and overall number of surface contact points are usually bound by the simple relation

$$zq_1 = r_1 z - 2r_1 + 2. \quad (2)$$

The interactions of molecules in a solution are modelled by binary interactions of their contact points. Energetically these interactions of surface points are characterized by interchange free enthalpies g_{ij} and interchange enthalpies h_{ij} .

On the basis of these model conceptions it is possible to construct the partition function and, from it by a standard way, to derive thermodynamic functions^{2,8-10} characterizing the solution

$$h^E/RT = 2 \left[\sum_{I=A,B} \sum_{\substack{i \in I \\ i > j}} \sum_{j \in I} (X_i X_j - x_i X_i^{II} X_j^{II}) \eta_{ij} h_{ij} / RT + \sum_{i \in A} \sum_{j \in B} X_i X_j \eta_{ij} h_{ij} / RT \right], \quad (3)$$

$$g^E/RT = \sum_{I=A,B} x_I \ln \gamma_I, \quad (4)$$

$$\ln \gamma_1 = \sum_{i \in I} Q_i \ln \frac{X_i/X_i^*}{X_i^{II}/X_i^{II*}} + \ln \gamma_1^{\text{comb}}, \quad (5)$$

where x_1 is the mole fraction of component I in solution and η_{ij} denote the Boltzmann factors, $\eta_{ij} = \exp(-g_{ij}/RT)$. The activity coefficient γ_1 consists of two parts – the purely combinatorial contribution which is independent of temperature and the residual term. The concrete form of the dependence of $\ln \gamma_1^{\text{comb}}$ on composition is determined by the chosen relation for the athermal combinatorial factor g^* . In its original version the Barker theory contains the Guggenheim relation for g^* which leads to the following relation for the combinatorial contribution to the activity coefficient in binary solution

$$\ln \gamma_1^{\text{comb}} = \left(\frac{1}{2}zq_1 - 1\right) \ln \left(x_1 + \frac{r_1}{r_1} x_2\right) - \frac{1}{2}zq_1 \ln \left(x_1 + \frac{q_1}{q_1} x_2\right). \quad (6)$$

The auxiliary quantities X_i characterizing the frequencies of contacts among corresponding contact points are defined by the relations

$$N_{ij} = 2X_i X_j \eta_{ij} N, \quad N_{ii} = (X_i)^2 N, \quad (7, 8)$$

in terms of number of contacts N_{ij} between contact points of the type i and j in a solution with overall number of N molecules. The superscript II denotes values of these quantities for pure component I; the asterisk is related to a random arrangement (all $\eta_{ij} = 1$). The values of quantities X_i and X_i^{II} can be obtained by solving numerically the system of n non-linear equations⁹

$$\mathbf{LTX} = \mathbf{b}, \quad (9)$$

where

$$\mathbf{L} \equiv \begin{vmatrix} X_1 & & & \\ & X_2 & & \\ & & \dots & \\ & & & X_n \end{vmatrix} \quad (10)$$

is the diagonal matrix, $\mathbf{T} \equiv [\eta_{ij}]$ is the symmetrical matrix of Boltzmann's factors whose diagonal elements are unit.

The columns vectors \mathbf{X} and \mathbf{b} are defined as follows

$$\mathbf{X} \equiv \begin{vmatrix} X_1 \\ X_2 \\ \vdots \\ X_n \end{vmatrix} \quad \mathbf{b} \equiv \begin{vmatrix} Q_1 x_A / 2 \\ Q_2 x_A / 2 \\ \vdots \\ Q_n x_B / 2 \end{vmatrix} \quad (11, 12)$$

The quantities X_i^* and X_i^{11*} corresponding to a random arrangement can be obtained easily by solving the system of Eqs (9) in an explicit form.

Regardless of a number of relatively rough simplifications inherent in the model accepted, in a concrete application as main disadvantages come to the fore above all to a considerable extent arbitrary choice of types and number of surface contact points and with this connected large number of adjustable energy parameters. If more parameters are adjusted from the data of one system their values lose the predicting ability to related systems owing to the strong mutual compensation. For this reason and with respect to the relatively considerable complexity of practical calculation the number of types of the surface contact points is often reduced which always entails the danger of oversimplification of the model. A partial solution of this situation is successive evaluation of energy parameters from a number of systems of increasing complexity, as it is used by some authors⁹⁻¹¹. Since in molecules of organic substances a mutual intramolecular influencing of groups (especially if strongly polar groups are present) takes place naturally, the constancy of energy parameters assumed in this procedure when passing from a simpler system to a more complex one, is rather problematic. However, the constancy of energy parameters, on the contrary, can be assumed most justifiably in the case when the chemical nature of molecules does not change, *i.e.* for instance in the case that members of the same homologous series are included. Therefore we consider as the most hopeful the prediction of thermodynamic functions in terms of the Barker theory if both the predicted and basal systems contain the components of identical chemical nature and which, in addition to it, are not too remote in homologous series. The problem how to evaluate the adjustable parameters needed, however, remains.

Realizing the above-mentioned situation, we investigated whether it would not be possible to dispense with the evaluation of the energy parameters and to find relations directly among thermodynamic functions of closely related systems at least for some cases. This requirement corresponds to finding a relation between the solution \mathbf{X} of the system of Eqs (9) with the vector of right-hand sides \mathbf{b} (basal system) and the solution \mathbf{X}' of the system of Eqs (9) with the vector of right-hand sides \mathbf{b}' (predicted system) if the matrix $\mathbf{T} \equiv \mathbf{T}'$.

The trivial case $\mathbf{b}' = \mathbf{b}$ implicating $\mathbf{X}' = \mathbf{X}$ makes sense, however, only sometimes meets with practical application. The case is more general when the vector \mathbf{b}' is a multiple of the vector \mathbf{b} :

$$\mathbf{b}' = c\mathbf{b}, \quad (13)$$

from which follows

$$\mathbf{X}' = \sqrt{c}\mathbf{X}. \quad (14)$$

Practical application of the relations offers especially for systems of the type arbitrary component A + n-alkane B, where n-alkane changes or for systems of two

members of the same homologous series (e.g. mixture of two n-alcohols), where one of components changes within the range of a homologous series. Other possibilities can be expected for predicting the behaviour of multicomponent mixtures on the basis of binary data. In this paper we will only deal with the former possibility the latter will be the subject of some next work.

Let us assume that molecules of n-alkanes are, from the point of view interactions with their environment, uniform molecules with monotonic surface, it means the surface contact points of n-alkanes are just of an only type and do not change their properties with prolongation of n-alkane. This assumption is strongly supported by recent research of Patterson and coworkers¹² who found the interaction energy between methyl and methylene group in alkanes to be very low and not to be able to explain the heats of mixing of alkane solutions. Let us denote the number of surface contact points of n-alkane in predicted system by Q'_n and in the basal system by Q_n . The second component of the binary solution is an arbitrary molecule A containing $n-1$ types of contact points, where n is the overall number of types of contact points in the mixture. The surface of molecule A contains altogether $\sum_{i=1}^{n-1} Q_i$ of surface contact points. The vectors \mathbf{b}' and \mathbf{b} take then the forms

$$\mathbf{b}' = \begin{vmatrix} Q_1 x'_A / 2 \\ Q_2 x'_A / 2 \\ \vdots \\ Q_{n-1} x'_A / 2 \\ Q'_n (1 - x'_A) / 2 \end{vmatrix} \quad \mathbf{b} = \begin{vmatrix} Q_1 x_A / 2 \\ Q_2 x_A / 2 \\ \vdots \\ Q_{n-1} x_A / 2 \\ Q_n (1 - x_A) / 2 \end{vmatrix} \quad (15, 16)$$

If the vector \mathbf{b}' is to be a multiple of the vector \mathbf{b} it must hold for the corresponding compositions of the predicted and basal systems

$$c = x'_A / x_A = Q'_n (1 - x'_A) / [Q_n (1 - x_A)], \quad (17)$$

or

$$x_A = x'_A / [Q'_n / Q_n + x'_A (1 - Q'_n / Q_n)]. \quad (18)$$

The relation (18) represents a transformation relation which mutually uniquely attaches a certain composition of the basal system to every chosen composition of predicted system so that the relations (13) and (14) may be fulfilled. Now if we write the relations for activity coefficient and heat of mixing for the predicted system at a composition x'_A and for the basal system at a composition x_A considering the relations (13) or (14), respectively, and (17) we easily attain the following relations

$$\frac{h^{E'}(x'_A)}{RT} = \frac{x'_A}{x_A} \frac{h^E(x_A)}{RT}, \quad (19)$$

$$\ln \gamma'_A(x'_A) = \ln \gamma_A(x_A) - \ln \gamma_A^{\text{comb}}(x_A) + \ln \gamma_A^{\text{comb}'}(x'_A), \quad (20)$$

$$\ln \gamma'_B(x'_A) = \frac{Q'_B}{Q_B} \ln \gamma_B(x_A) - \frac{Q'_B}{Q_B} \ln \gamma_B^{\text{comb}}(x_A) + \ln \gamma_B^{\text{comb}'}(x'_A). \quad (21)$$

Eqs (19)–(21) make possible simple conversion of excess free enthalpy and heat of mixing of the systems A + B and A + B', where A is the arbitrary component and B, B' are two different n-alkanes.

We derived analogous relations in terms of the group contribution concept. The group contribution concept can be summarized into the following general equations (e.g.^{13,14})

$$\ln \gamma_i = \sum_{i \in A} v_i (\ln \Gamma_i - \ln \Gamma_i^{I1}) + \ln \gamma_i^{\text{comb}}, \quad (22)$$

$$\frac{h^E}{RT} = \frac{1}{RT} \sum_{i=A,B} x_i \sum_{i \in I} v_i (H_i - H_i^{I1}), \quad (23)$$

where v_i denotes the number of groups of the type i in a given molecule. The activity coefficient of the group i , Γ_i , and the partial enthalpy of the group i , H_i , are functions of temperature T and concentrations of all groups in the solution, Z_1, \dots, Z_n :

$$\ln \Gamma_i = \ln \Gamma_i(T, Z_1, \dots, Z_n), \quad (24)$$

$$H_i = H_i(T, Z_1, \dots, Z_n), \quad (25)$$

$$Z_i = \left(\sum_{i=A,B} v_i x_i \right) / \left(\sum_{i=A,B} \sum_{k \in I} v_k x_i \right). \quad (26)$$

Superscript I1 again denotes the values for pure component.

If, at constant temperature, the concentrations of all groups present do not change nor do the group contributions $\ln \Gamma_i$ and H_i . If we return to our type of system an arbitrary component A + n-alkanes the condition $\mathbf{Z}' = \mathbf{Z}$ leads to the transformation equation of composition similar to the relation (18):

$$x_A = x'_A / [v'_n/v_n + x'_A(1 - v'_n/v_n)], \quad (27)$$

where v'_n and v_n are the numbers of carbon atoms of n-alkane in the predicted and basal system, respectively. The equations for conversion of thermodynamic functions are an analogy to Eqs (19)–(20) in the same sense.

The similarity of the results obtained on the basis of the Barker theory and the group contribution concept is in harmony with the fact that the Barker relations for thermodynamic functions can be rewritten into the form of Eqs (22) and (23) as it has been shown recently by Kehiaian¹⁰ for activity coefficients.

RESULTS AND DISCUSSION

The quality of predicting ability of relations (19)–(21) was tested by using seventy binary systems which contained as the component A substances of the most different chemical types as alcohols, amines, ketones, chlorinated derivatives of hydrocarbons, aromatic hydrocarbons, esters of fatty and aromatic acids and as the second component B or B' n-alkanes from n-pentane to n-hexadecane.

For the combinatorial contribution to activity coefficient, the relation (6) was chosen which corresponds to the Guggenheim equation for g^* . The concrete calculation requires further a choice of the lattice coordination number and a choice of the size (number of segments r_A , r_B and r'_B) of molecules involved. Preliminary test calculations showed that the results of predictions are very slightly sensitive to the value of coordination number z as far as it lies within physically reasonable limits, *i.e.* z is in the range 4–12. For our calculations we chose $z = 6$; this choice showed to be best in preliminary calculations. The number of segments of the alkane molecule was determined according to the relation

$$r_B = 1 + n_c/2, \quad (28)$$

where n_c is the number of carbon atoms in molecule, which means that the CH_3 group occupies one lattice site and the CH_2 group only one half. This choice corresponds to the dependence of molar volume of n-alkanes on the number of carbon atoms¹⁵. The number of segments r_A of molecule A was determined by means of the following rules: 1) Only non-hydrogen atoms contribute to the value of r_A . 2) Middle atoms of a molecule contribute with the value $r_m = 1/2$, end atoms with the value $r_e = 1$. 3) In case that the middle atom is sterically very strongly hindered it does not contribute to the value of r_A . The choice of r_A according to the above-mentioned rules corresponds roughly in most cases to molar volumes.

The sources of the used experimental data on excess functions are given in Table I and II. Excess free enthalpy was calculated from direct data on vapour-liquid equilibrium by means of the technique described previously¹⁶ (the needed data on saturated vapor pressures¹⁷ and molar volumes¹⁸ of pure substances and the auxiliary quantities for estimating second virial coefficients by O'Connell and Prausnitz^{19,20} were taken over from the literature).

Considering that for our calculations it is suitable to use smoothed dependences of excess functions on composition the respective data were correlated by the Red-

TABLE I
Comparison of Experimental and Predicted Results for Excess Free Enthalpy g^E/RT

°C	System ^a	Ref.	σ_{cor}	σ_{pred}	σ_{integ}
80	<i>p</i> -dioxane + <i>n</i> -heptane	23	0.005	0.015	0.016
	<i>p</i> -dioxane + <i>n</i> -hexane	23	0.012	0.012	0.015
80	<i>p</i> -dioxane + <i>n</i> -nonane	23	0.012	0.008	0.007
	<i>p</i> -dioxane + <i>n</i> -heptane	23	0.005	0.007	0.006
80	<i>p</i> -dioxane + <i>n</i> -hexane	23	0.012	0.010	0.013
	<i>p</i> -dioxane + <i>n</i> -nonane	23	0.012	0.012	0.013
80	<i>p</i> -dioxane + <i>n</i> -octane	23	0.002	0.014	0.017
	<i>p</i> -dioxane + <i>n</i> -hexane	23	0.012	0.013	0.016
80	<i>p</i> -dioxane + <i>n</i> -nonane	23	0.012	0.007	0.007
	<i>p</i> -dioxane + <i>n</i> -octane	23	0.002	0.006	0.006
45	ethanol + <i>n</i> -hexane	24	0.013	0.009	0.008
	ethanol + <i>n</i> -octane	25	0.002	0.009	0.009
30	ethanol + <i>n</i> -heptane	28	0.003	0.018	0.021
	ethanol + <i>n</i> -hexane	24 ^c	(0.008)	—	0.020
40	ethanol + <i>n</i> -heptane	29	0.012	0.024	0.019
	ethanol + <i>n</i> -octane	25 ^c	(0.002)	—	0.019
25	<i>n</i> -propanol + <i>n</i> -decane	26 ^b	0.003	—	0.022
	<i>n</i> -propanol + <i>n</i> -hexane	26 ^b	0.004	—	0.016
30	<i>n</i> -pentanol + <i>n</i> -pentane	27 ^d	—	0.010	0.011
	<i>n</i> -pentanol + <i>n</i> -hexane	27 ^d	—	0.010	0.011
-20	methylamine + <i>n</i> -nonane	30 ^b	—	—	0.009
	methylamine + <i>n</i> -butane	30 ^b	—	—	0.010
-20	methylamine + <i>n</i> -butane	30 ^b	—	—	0.006
	methylamine + <i>n</i> -hexane	31 ^b	—	—	0.006
-20	methylamine + <i>n</i> -nonane	30 ^b	—	—	0.004
	methylamine + <i>n</i> -hexane	31 ^b	—	—	0.004
0	ethylamine + <i>n</i> -butane	30 ^b	—	—	0.011
	ethylamine + <i>n</i> -hexane	30 ^b	—	—	0.012
30	diethylamine + <i>n</i> -pentane	34 ^b	—	—	0.017
	diethylamine + <i>n</i> -heptane	33 ^{b,c}	(0.002)	—	0.019
30	diethylamine + <i>n</i> -pentane	34 ^b	—	—	0.009
	diethylamine + <i>n</i> -hexane	32 ^b	—	—	0.009
30	<i>n</i> -butylamine + <i>n</i> -pentane	32 ^b	—	—	0.018
	<i>n</i> -butylamine + <i>n</i> -heptane	33 ^{b,c}	(0.002)	—	0.019

TABLE I
 Continued)

°C	System ^a	Ref.	σ_{cor}	σ_{pred}	σ_{integ}
50	chloroform + n-hexane	35 ^{b,c}	(0.002)	—	0.010
	chloroform + n-heptane	36 ^b	—	—	0.010
40	benzene + n-decane	37 ^b	—	—	0.008
	benzene + n-heptane	37 ^b	—	—	0.007
40	acetone + n-dodecane	38 ^b	—	—	0.009
	acetone + n-decane	38 ^b	—	—	0.008
40	acetone + tetradecane	38 ^b	—	—	0.034
	acetone + n-decane	38 ^b	—	—	0.025
60	acetone + n-hexadecane	38 ^b	—	—	0.011
	acetone + n-tetradecane	38 ^b	—	—	0.010
60	acetone + n-dodecane	38 ^b	—	—	0.029
	acetone + n-hexadecane	38 ^b	—	—	0.035
65	acetone + n-heptane	39	0.010	0.019	0.018
	acetone + n-hexane	24	—	—	0.017

^a Systems are arranged in couples — predicted and basal and *vice versa*. ^b Constants of Redlich–Kister polynomial were taken over from literature cited. ^c Temperature-extrapolated or -interpolated data. ^d Static data.

Redlich–Kister polynomial

$$Z^E = x_A x_B \sum_{i=0}^{p-1} A_i (x_A - x_B)^i, \quad (29)$$

where Z^E denotes g^E/RT or h^E/RT , respectively. The number of constants in the relation (29) was determined on the basis of the statistical criterion of significance (F-test). In the cases when authors do not give direct experimental data but constants of correlation relationships or in the cases when the method of data processing by authors agrees fully with our method we used for calculating the values of constants taken over (Table I and II).

The quality of representation of experimental data with the Redlich–Kister polynomial and the quality of predictions carried out was judged in terms of the standard deviations σ

$$\sigma_{\text{cor}}^2 = \sum_{i=1}^n (Z_{i,\text{exp}}^E - Z_{i,\text{cor}}^E)^2 / (n - p), \quad (30)$$

$$\sigma_{\text{pred}}^2 = \sum_{i=1}^n (Z_{i,\text{pred}}^E - Z_{i,\text{cor}}^E)^2/n, \quad (31)$$

$$\sigma_{\text{integ}}^2 = \int_0^1 (Z_{\text{pred}}^E - Z_{\text{cor}}^E)^2 dx_A, \quad (32)$$

where n is the number of experimental points and p the number of parameters in relation (29). The standard deviation σ_{integ} measures the distance of the predicted curve and the correlated one of Z^E over the entire concentration range. It can be shown easily that in case of a uniform distribution of experimental points along the concentration range $\sigma_{\text{pred}} \rightarrow \sigma_{\text{integ}}$ when $n \rightarrow \infty$. The values of standard deviations for correlation and prediction of a number of binary systems are given in Tables I and II. The results for several systems are illustrated in Figs 1 and 2.

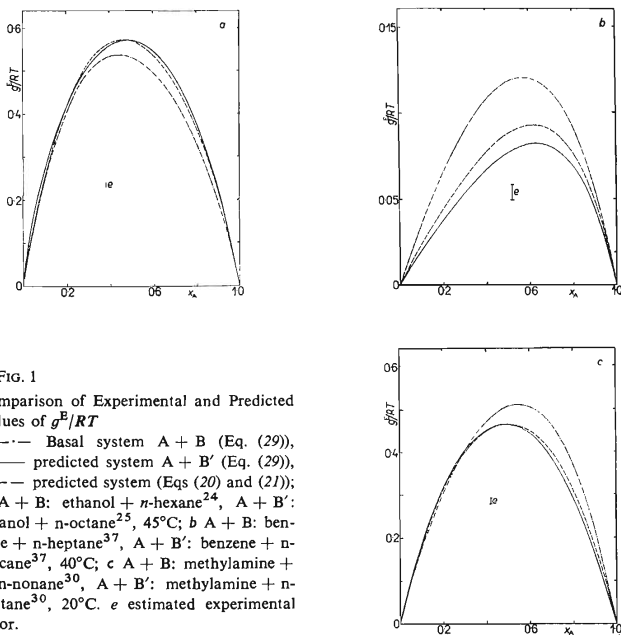


FIG. 1

Comparison of Experimental and Predicted Values of g^E/RT

— · — Basal system A + B (Eq. (29)),
 — predicted system A + B' (Eq. (29)),
 — · — predicted system (Eqs (20) and (21));
 a A + B: ethanol + *n*-hexane²⁴, A + B': ethanol + *n*-octane²⁵, 45°C; b A + B: benzene + *n*-heptane³⁷, A + B': benzene + *n*-decane³⁷, 40°C; c A + B: methylamine + *n*-nonane³⁰, A + B': methylamine + *n*-butane³⁰, 20°C. *e* estimated experimental error.

TABLE II
Comparison of Experimental and Predicted Results for Heat of Mixing h^E/RT

°C	System ^a	Ref.	σ_{cor}	σ_{pred}	σ_{integ}	σ'_{integ}
25	ethanol + n-hexane	40	0.001	0.008	0.010	
	ethanol + n-octane	41	0.005	0.013	0.011	
25	ethanol + n-hexane	40	0.001	0.008	0.011	
	ethanol + n-heptane	41	0.015	0.012	0.012	
25	ethanol + n-heptane	41	0.015	0.008	0.009	
	ethanol + n-octane	41	0.005	0.009	0.009	
25	n-propanol + n-hexane	40	0.001	0.004	0.014	
	n-propanol + n-heptane	41	0.004	0.022	0.016	
25	n-propanol + n-hexane	40	0.001	0.004	0.013	
	n-propanol + n-octane	41	0.004	0.022	0.017	
25	n-propanol + n-octane	41	0.004	0.004	0.004	
	n-propanol + n-heptane	41	0.004	0.004	0.004	
45	ethanol + n-nonane	42	0.006	0.008	0.009	
	ethanol + n-hexane	42	0.007	0.006	0.008	
25	n-propanol + n-tetradecane	41	0.002	0.022	0.019	0.022
	n-propanol + n-heptane	41	0.004	0.020	0.018	0.016
25	n-propanol + n-tetradecane	41	0.002	0.018	0.015	
	n-propanol + n-octane	41	0.004	0.016	0.015	
45	n-butanol + n-heptane	42	0.005	0.040	0.023	
	n-butanol + n-hexane	40	0.001	0.010	0.020	
25	n-octanol + n-octane	41	0.012	0.010	0.012	
	n-octanol + n-heptane	41	0.017	0.010	0.012	
25	n-octanol + n-decane	44	0.005	0.010	0.010	
	n-octanol + n-octane	41	0.012	0.008	0.008	
25	n-octanol + n-decane	44	0.005	0.016	0.016	
	n-octanol + n-heptane	41	0.017	0.013	0.012	
25	n-octanol + n-tetradecane	41	0.006	0.029	0.029	0.020
	n-octanol + n-heptane	41	0.017	0.022	0.022	0.013
25	n-octanol + n-tetradecane	41	0.006	0.023	0.024	0.009
	n-octanol + n-decane	41	0.005	0.021	0.021	0.008
25	n-octanol + n-tetradecane	41	0.006	0.025	0.025	0.013
	n-octanol + n-octane	41	0.012	0.020	0.020	0.009
25	n-pentanol + n-tetradecane	41	0.003	0.027	0.028	0.014
	n-pentanol + n-octane	41	0.012	0.025	0.024	0.012
25	n-pentanol + n-tetradecane	41	0.003	0.033	0.034	0.019
	n-pentanol + n-heptane	41	0.009	0.030	0.028	0.015

TABLE II
(Continued)

°C	System ^a	Ref.	σ_{cor}	σ_{pred}	σ_{integ}	σ'_{integ}
25	n-pentanol + n-octane	41	0.012	0.008	0.009	
	n-pentanol + n-heptane	41	0.009	0.008	0.009	
25	acetone + n-decane	46	0.010	0.027	0.021	
	acetone + n-hexadecane	46 ^c	0.006	0.053	0.041	
0	acetone + n-pentane	45	0.001	0.002	0.003	
	acetone + n-hexane	45	0.002	0.003	0.003	
25	chloroform + n-heptane	47	0.001	0.003	0.002	
	chloroform + n-hexane	47	0.002	0.002	0.002	
25	dichloromethane + n-heptane	47	0.006	0.020	0.021	
	dichloromethane + n-hexane	47	0.005	0.018	0.019	
25	1-chlorobutane + n-decane	48	0.004	0.004	0.005	0.002
	1-chlorobutane + n-heptane	48	0.003	0.004	0.005	0.002
25	1-chlorobutane + n-hexadecane	48	0.004	0.036	0.037	0.006
	1-chlorobutane + n-heptane	48	0.003	0.023	0.027	0.005
25	1-chlorobutane + n-hexadecane	48	0.004	0.030	0.031	0.005
	1-chlorobutane + n-decane	48	0.004	0.023	0.026	0.004
25	cyclohexane + n-heptane	51	0.000	—	0.005	
	cyclohexane + n-hexane	50	0.001	—	0.005	
25	cyclohexane + n-hexadecane	53	0.002	—	0.050	0.020
	cyclohexane + n-octane	52	0.001	—	0.038	0.016
25	benzene + n-decane	37	0.003	0.011	0.012	
	benzene + n-heptane	37	0.003	0.010	0.010	
25	benzene + n-tetradecane	54	0.002	—	0.016	0.007
	benzene + n-hexadecane	54	0.003	—	0.017	0.008
25	benzene + n-hexadecane	54	0.003	—	0.038	0.009
	benzene + n-octane	54	0.001	—	0.030	0.009
25	benzene + n-pentane	54	0.001	—	0.010	
	benzene + n-octane	54	0.001	—	0.012	
25	methyl acetate + n-octane	49 ^b	0.005	—	0.007	
	methyl acetate + n-hexane	49 ^b	0.006	—	0.007	
25	methyl acetate + n-dodecane	49 ^b	0.008	—	0.022	0.015
	methyl acetate + n-octane	49 ^b	0.005	—	0.021	0.014
25	methyl acetate + n-hexane	49 ^b	0.006	—	0.021	0.015
	methyl acetate + n-dodecane	49 ^b	0.008	—	0.023	0.017
25	ethyl acetate + n-hexane	49 ^b	0.004	—	0.020	
	ethyl acetate + n-octane	49 ^b	0.005	—	0.021	

TABLE II
 (Continued)

°C	System ^a	Ref.	σ_{cor}	σ_{pred}	σ_{integ}	σ'_{integ}
25	ethyl acetate + n-dodecane	49 ^b	0.009	—	0.016	0.008
	ethyl acetate + n-octane	49 ^b	0.005	—	0.013	0.006
25	ethyl acetate + n-hexane	49 ^b	0.004	—	0.030	0.023
	ethyl acetate + n-dodecane	49 ^b	0.009	—	0.036	0.026
25	ethyl benzoate + n-decane	49 ^b	0.004	—	0.015	
	ethyl benzoate + n-hexane	49 ^b	0.006	—	0.013	
25	ethyl benzoate + n-octane	49 ^b	0.005	—	0.007	
	ethyl benzoate + n-decane	49 ^b	0.004	—	0.007	
25	CCl ₄ + n-hexane	55	0.000	0.006	0.006	
	CCl ₄ + n-heptane	56	0.000	0.007	0.006	
25	CCl ₄ + n-hexane	55	0.000	0.015	0.014	
	CCl ₄ + n-decane	56	0.000	0.019	0.016	
25	CCl ₄ + n-hexane	55	0.000	0.021	0.020	
	CCl ₄ + dodecane	56	0.000	0.026	0.027	
25	CCl ₄ + n-dodecane	56	0.000	0.007	0.013	
	CCl ₄ + n-decane	56	0.000	0.009	0.012	

^a Systems are arranged in couples — predicted and basal and *vice versa*. ^b Constants of Redlich-Kister polynomial were taken over from the literature cited. ^c System with immiscibility.

The results of the developed method should be judged from two points of view — partly as an effective test of the Barker theory and of the group contribution concept, respectively, which is not complicated by secondary effects (numerical compensation of adjustable parameters) partly with respect to the applicability of the method proposed for systematic prediction of excess quantities of systems of the given type.

Our calculations predict, in agreement with experiment, the shift of the height and position of maximum of excess function with a change in size of n-alkanes practically for all systems investigated. This fact supports strongly the suitability of the accepted model. Let us remark, however, that for h^E according to Eqs (18) and (19) the value at maximum increases always with elongating the n-alkane chain. The Barker theory cannot consequently describe the systems exhibiting the opposite trend of this dependence (Wilhelm effect²²). Fortunately, as it seems, this phenomenon is anomalous and results probably from conformation or structural changes in system.

The calculated results are also in most cases very good in a quantitative way – for many systems the deviation in prediction is comparable with experimental error or correlation deviation. Generally it can be said that the results are best when both alkanes (from basal and predicted system) are not too long (let us say not longer than *n*-decane). It can be seen as well the direction of prediction from a longer to a shorter *n*-alkane is generally better. This finding can be employed to advantage for predicting h^E of rather volatile systems (containing *n*-pentane, *n*-butane, ...) that are at usual temperatures accessible to experiment only with difficulty.

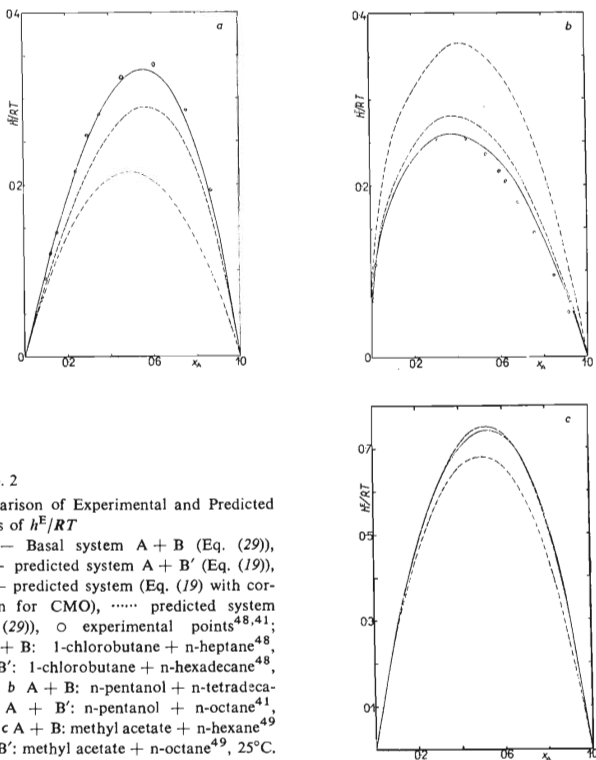


FIG. 2

Comparison of Experimental and Predicted Values of h^E/RT

— — Basal system A + B (Eq. (29)),
 - - - predicted system A + B' (Eq. (19)),
 ——— predicted system (Eq. (19) with correction for CMO), ····· predicted system (Eq. (29)), ○ experimental points^{48,41};
 a A + B: 1-chlorobutane + *n*-heptane⁴⁸, A + B': 1-chlorobutane + *n*-hexadecane⁴⁸, 25°C; b A + B: *n*-pentanol + *n*-tetradecane⁴¹, A + B': *n*-pentanol + *n*-octane⁴¹, 25°C; c A + B: methyl acetate + *n*-hexane⁴⁹ A + B': methyl acetate + *n*-octane⁴⁹, 25°C.

In the cases when at least one of the systems — predicted or basal — contains a longer n-alkane (let us say than n-decane) striking systematic deviations from experiment are to be observed when predicting heat of mixing. When predicting from a lower to a higher n-alkane, the predicted values of h^E are systematically lower than experiment and *vice versa* (Fig. 2a,b). The disagreement increases with increasing length of n-alkanes.

The phenomenon mentioned cannot be explained by increasing flexibility of long alkane chains as this should appear only in the athermal combinatorial factor g^* which does not enter the relation for heat of mixing. However, this phenomenon shows clearly to be a consequence of the so-called correlation of molecular orientations (CMO) described by Patterson and coworkers^{12,21}. According to it the molecules of higher n-alkanes in pure state are ordered in a certain way; the addition of another component results in destroying the structure and consequently brings a positive contribution to heat of mixing. With increasing length of n-alkane the degree of ordering increases and therefore the endothermic contribution on mixing increases, too.

With the aim to arrive at a better agreement of the prediction and experiment for systems with longer n-alkanes we tried to express quantitatively this contribution at the very cost of certain simplifications. Let us assume that the destruction of the structure in long n-alkanes depends above all on the size and shape of the molecule of component added. Further let us assume that heats of mixing of longer n-alkanes with other alkanes originate mostly just in destroying the structure of longer n-alkanes. Then it is possible to approximate roughly the so-called "CMO contribution" to heat of mixing of a mixture arbitrary component A + long n-alkane by the heat of mixing of the homomorph of component A with the respective n-alkane. The prediction from one system to another one is then carried out generally in three

TABLE III
Constants of Redlich-Kister Polynomial for h^E/RT of n-Alkanes¹²

n-Hexane +	A_0	A_1	A_2
n-Octane	0.0035	0.0021	—
n-Nonane ^a	0.009	—	—
n-Decane ^a	0.020	—	—
n-Dodecane	0.0595	-0.0082	-0.0067
n-Tetradecane ^a	0.112	—	—
n-Hexadecane	0.1789	-0.0086	-0.0434

^a Interpolated.

steps: 1) From h^E of the basal mixture A + B, h^E is subtracted of the mixture homomorph A + B. 2) The relation (19) is applied. 3) h^E of the mixture homomorph A + B' is added to the predicted h^E .

With respect to the lack of data on heats of mixing of n-alkanes we used for the description of "CMO contribution" only the heats of mixing of n-hexane with higher n-alkanes¹² (Table III). The improved version of prediction was applied to the systems with arbitrary component A in those cases when one of n-alkanes involved is higher than n-decane. (If both n-alkanes are lower then the corresponding correction for "CMO contribution" is low and often is covered by experimental errors.) The results are expressed by the deviation σ'_{integ} in Table II. In all cases (except the systems with n-propanol) great improvement occurred. The best results were obtained with the systems where n-hexane is, as to its size and shape, a relatively good approximation of the molecule A (n-pentanol, 1-chlorobutane). In these cases the deviations of predictions lie practically within the range of experimental errors. The results for the other systems prove that the correction for "CMO contribution" is suitable to take even in the cases when the molecule A is approximated very badly.

In conclusion it is possible to say that the proposed method for predicting excess quantities of systems of the given type was found very useful. Its accuracy (when using the correction for "CMO contribution") is in most cases comparable with the accuracy of experimental data of an average quality.

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