HEATS OF MIXING PREDICTION OF BINARY SOLUTIONS OF HOMOLOGUES BASED ON THE SOLUTION OF GROUPS CONCEPT

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Received February 26th, 1979

A relation has been derived, on the basis of the solution of groups concept, for predicting partial molar excess enthalpies or activity coefficients of a system A + B′ from experimental data for a related system A + B, requiring no knowledge or adjustement of group contributions. The method suggested has been employed for predicting h^E of systems formed by compounds of the same homologous series. For these systems a relation has been derived between constants of the Redlich–Kister polynomial of the basal and predicted systems which makes it possible to obtain directly an easy estimate of these constants for the predicted system. The method has been tested with 20 mixtures of n-alcohols and 25 mixtures of 2-ketones. In the case that the component B′ lies in the homologous series between the components A and B the method makes possible the prediction of h^E with sufficient accuracy (on the average better than 8%). In the opposite case, providing that the numerical stability of the calculation is ensured, the method provides reliable results only for a slight extrapolation outside the range of components A and B.

A number of works in the literature have dealt with the excess thermodynamic properties of solutions of homologous compounds. Their theoretical basis has altogether been the principle of congruence in different versions or modifications[1–6]. A possibility offers, however, to employ the solution of groups concept, too. The methods of group contributions based on this concept have proved their utility for the interpretation and especially prediction of excess quantities of liquid solutions of non-electrolytes. In this respect, the best-known examples are the ASOG (ref.[7]) and UNIFAC (ref.[8]) methods. In this work which is thematically a continuation of our previous works[9,10], we formulate a simple predicting method for systems of homologous compounds which rests upon the same basis. The advantage of the method proposed is above all the fact that it does not require adjusting the group interaction parameters.

THEORETICAL

The solution of groups concept can be summarized into the following general equations

$$\overline{h_i^E} = \sum_{i \in I} \nu_i (H_i - H_i^{I1}) , \tag{1}$$

$$\ln \gamma_I = \ln \gamma_I^{res} + \ln \gamma_I^{comb} = \sum_{i \in I} \nu_i (\ln \Gamma_i - \ln \Gamma_i^{I1}) + \ln \gamma_I^{comb} , \tag{2}$$

where ν_i denotes the number of groups of the type i in a given molecule. The partial molar excess enthalpy H_i of the group i and the activity coefficient Γ_i of the group i are functions of temperature and concentrations of all groups in solution $Z_1, Z_2, \ldots$ $\ldots, Z_n$:

$$H_i = H_i(T, Z_1, Z_2, \ldots, Z_n) , \tag{3}$$

$$\ln \Gamma_i = \ln \Gamma_i(T, Z_1, Z_2, \ldots, Z_n) , \tag{4}$$

$$Z_i = \Big(\sum_{I=A,B} \nu_i x_I \Big) / \Big(\sum_{I=A,B} \sum_{k \in I} \nu_k x_I \Big) . \tag{5}$$

The index $I1$ denotes again the values for pure component.

Let us consider two related systems (primed and unprimed) with one common component A at a constant temperature. If we find the composition of the basal system $\boldsymbol{x}$ to that of the predicted system $\boldsymbol{x}'$ so that $\boldsymbol{Z}' = \boldsymbol{Z}$ holds, it follows from Eqs (*1*) and (*2*)

$$\overline{h^E}(\boldsymbol{x}') = \overline{h^E}(\boldsymbol{x}) , \tag{6}$$

$$\ln \gamma_A'^{res}(\boldsymbol{x}') = \ln \gamma_A^{res}(\boldsymbol{x}) . \tag{7}$$

The same relations can be also derived on the basis of the Barker quasi-lattice theory.

The outlined predicting possibilities have been employed for binary systems of homologous compounds. For the reason of agreement with our previous works we have used the number of contacts of individual types Q_i instead of the number of single groups ν_i to characterize the group structure of molecule. For the type of systems treated in this work, the resulting difference is, however, only formal, owing to the choice of Q_i (ref.[9]), because the numerical results are identical for both cases.

Let us assume the uniformity of n-alkyl chain. From the condition of equality of group concentrations of the predicted (A + B′) and basal (A + B) system, the following transformation equations follow easily for the composition

$$x_A = [(Q_{1A} - Q'_{1B}) x'_A + Q'_{1B} - Q_{1B}] / (Q_{1A} - Q_{1B}) \tag{8}$$

or

$$x_B = (Q_{1A} - Q'_{1B}) x'_B / (Q_{1A} - Q_{1B}) , \tag{9}$$

where Q_{1A}, Q_{1B} and Q'_{1B} is the number of contacts of aliphatic chain of components A, B and B', respectively. If we require the prediction for the whole concentration range it is evident from Eq. (*8*) or (*9*) that $Q_{1A} > Q'_{1B} > Q_{1B}$ or $Q_{1A} < Q'_{1B} < Q_{1B}$ must hold, *i.e.* the component B' lies in homologous series between the components *A* and *B*. If this condition is not fulfilled the data of the basal system make it possible, when the possibility of extrapolation is not considered, just the prediction in the part of the concentration range of the system A + B'. On inserting the transformation

TABLE I

Results of Predicting h^E/RT for Binary Systems of 2-Ketones
Experimental data from ref.[5], temperature 25°C.

A[a]	B'[a]	B[a]	$\sigma_{cor} \cdot 10^4$	$\sigma_{pred} \cdot 10^4$	$\sigma_{integ} \cdot 10^4$	δ^b_{rel}
3	4	5	1	6	5	4·4
3	4	7	1	11	10	8·8
3	4	8	1	20	18	15·8
3	4	11	1	12	11	9·6
3	5	7	2	24	24	5·9
3	5	8	2	16	18	4·4
3	5	11	2	11	12	2·9
3	7	8	4	29	27	2·5
3	7	11	4	29	27	2·5
3	8	11	3	64	66	4·4
4	5	7	2	5	5	7·5
4	5	8	2	9	9	13·4
4	5	11	2	13	13	19·4
4	7	8	3	16	15	3·9
4	7	11	3	12	13	3·4
4	8	11	8	31	25	3·9
5	7	8	2	11	10	6·5
5	7	11	2	17	16	10·4
5	8	11	3	11	13	4·0
8	4	3	8	86	74	11·5
8	5	3	3	16	14	4·4
8	5	4	3	15	13	4·0
11	5	3	2	44	38	4·4
11	5	4	2	35	29	3·3
11	4	3	3	68	63	4·4

[a] Components are designated by the number of carbon atoms.

relation of composition (*8*) or (*9*) into the Guggenheim relation for $\ln \gamma_A^{comb}$ (ref.[9]) it is further possible to prove easily that for binary systems of homologous compounds it holds as well

$$\ln \gamma_A'^{comb}(x_A') = \ln \gamma_A^{comb}(x_A) \qquad (10)$$

and consequently also

$$\ln \gamma_A'(x_A') = \ln \gamma_A(x_A) . \qquad (11)$$

Relations (*6*) and (*11*) make it possible to predict partial molar quantities only for the component A; however, the prediction would be desirable to yield molar excess quantities. One of the possible ways leads through the numerical solution of the Gibbs–Duham equation. However, we suggest a more advantageous way.

TABLE II

Results of Predicting h^E/RT for Binary Systems of n-Alcohols at the Temperature of 25°C

A[a]	B'[a]	B[a]	Ref.	$\sigma_{cor} \cdot 10^4$	$\sigma_{pred} \cdot 10^4$	$\sigma^b_{integ} \cdot 10^4$	δ_{rel}
2	3	6	12	0	1	2	2·6
2	3	10	12	0	9	10	12·8
2	6	10	12	2	63	60	11·4
3	5	8	4	1	18	17	13·3
3	5	9	4, 11	1	19	16	12·5
3	5	10	4	1	45	42	32·8
3	5	11	4, 11	1	11	9	7·0
3	5	12	4, 11	1	21	18	14·1
3	8	9	4, 11	4	48	43	7·0
3	8	10	4	4	33	28	4·6
3	8	11	4, 11	4	17	15	2·4
3	8	12	4, 11	4	50	44	7·2
3	9	11	11	17	35	30	4·0
3	9	12	11	17	10	12	1·6
3	11	12	11	12	47	46	4·0
4	10	12	11	10	14	15	2·2
5	8	10	4	2	9	8	3·1
10	4	3	11, 12	10	36	27	3·9
10	6	4	12, 11	15	75	80	20·7
12	4	3	11	35	29	22	2·1

[a] Components are designated by the number of carbon atoms.

Let the experimental data (*e.g.* on h^E/RT) of the basal system be represented by the Redlich–Kister equation

$$h^E/RT = x_A x_B \sum_{l=1}^{p} A_l (x_A - x_B)^{l-1} . \qquad (12)$$

Then it holds for partial molar quantity of component A

$$\overline{h_A^E}/RT = x_B^2 \sum_{l=1}^{p} A_l (x_A - x_B)^{l-2} (2l x_A - 1) =$$

$$= x_B^2 \left[A_1 + \sum_{l=2}^{p} A_l (2l - 1 - 2l x_B) \sum_{k=0}^{l-2} \binom{l-2}{k} (-2x_B)^k \right]. \qquad (13)$$

Polynomial (*13*) can be arranged according to powers of x_B:

$$\overline{h_A^E}/RT = \sum_{l=1}^{p} c_{l+1} x_B^{l+1} , \qquad (14)$$

where

$$c_{l+1} = \sum_{k=l+1}^{p} A_k (2k - 1) \binom{k-2}{l-1} (-2)^{l-1} +$$

$$- \sum_{k=1}^{p} A_k \, 2k \binom{k-2}{l-2} (-2)^{l-2} + \delta_{l+1,2} A_1 . \qquad (15)$$

($\delta_{l+1,2}$ denotes Kronecker delta).

TABLE III

Effect of the Value of α and of the Number of Constants p in Eq. (*12*) on the Reliability of Predicting h^E/RT for Binary Systems of Homologues ($\alpha > 1$)

System type	A[a]	B'[a]	B[a]	Ref.	α	p	$\sigma_{integ} \cdot 10^4$	δ_{rel}
[b]	4	11	5	5	7·00	2	1 561	109·0
[b]	5	11	8	5	2·00	3	816	93·5
[b]	5	8	7	5	1·50	2	62	19·3
[c]	3	10	8	4	1·40	5	1 042	100·4
[c]	4	12	10	11	1·33	2	81	7·9
[c]	5	10	8	4	1·66	2	43	7·2

[a] Components are designated by the number of carbon atoms, [b] 2-ketones, [c] n-alcohols.

If we use the transformation relation (*9*)

$$x_B = (Q_{1A} - Q'_{1B})\, x'_B/(Q_{1A} - Q_{1B}) = \alpha x'_B \tag{16}$$

and Eqs (*14*) and (*6*), then

$$\overline{h^E_A}/RT(x_B) = \sum_{l=1}^{p} c_{l+1}(\alpha x'_B)^{l+1} =$$

$$= \sum_{l=1}^{p} (c_{l+1}\alpha^{l+1})\, x_B'^{l+1} = \sum_{l=1}^{p} c'_{l+1} x_B'^{l+1} = \overline{h^E_A}/RT(x'_B)\,, \tag{17}$$

$$c'_{l+1} = c_{l+1}\alpha^{l+1} \quad l = 1, 2, \ldots, p\,. \tag{18}$$

From the above-mentioned we ascertain that

a) If the data of basal system are represented by a polynomial then the predicted system will be also described by a polynomial of the same order. *b*) Constants of this polynomial are to be determined on the basis of Eq. (*18*) from the constants of the polynomial describing the data of basal system.

However, let us rivet our attention to the determination of constants of the Redlich–Kister equation for predicted system. For this purpose we express the coefficients c_{l+1} and c'_{l+1} in the form

$$c_{l+1} = \sum_{k=1}^{p} q_{l+1,k} A_k\,, \tag{19}$$

$$c'_{l+1} = \sum_{k=1}^{p} q_{l+1,k} A'_k\,. \tag{20}$$

Since it follows from Eq. (*15*)

$$q_{l+1,k} = 0 \quad l = 1, 2, \ldots, p \qquad k = 1, 2, \ldots, l-1\,, \tag{21}$$

the matrix $\mathbf{Q} \equiv \{q_{l+1,k}\}$ $l = 1, 2, \ldots, p$ $k = 1, 2, \ldots, p$

is a triangular one. The system of Eqs (*18*) can consequently be solved easily by the back substitution. We will get

$$A'_l = \alpha^{l+1} A_1 + \sum_{k=l+1}^{p} \frac{q_{l+1,k}}{q_{l+1,l}} (A_k \alpha^{l+1} - A'_k)$$

$$l = p, p-1, \ldots, 1 , \qquad (22)$$

where

$$q_{2,k} = 2k - 1 \quad k \geqq 2$$

$$q_{l+1,k} = (2k-1)\binom{k-2}{l-1}(-2)^{l-1} - 2k\binom{k-2}{l-2}(-2)^{l-2} \quad \begin{matrix} l \geqq 2 \\ k \geqq l+1 \end{matrix} \qquad (23)$$

$$q_{l+1,l} = -2l(-2)^{l-2} .$$

Relations (*22*) and (*23*) make it possible to convert the constants of the Redlich–Kister equation from the basal to the predicted system.

RESULTS AND DISCUSSION

Owing to the lack of reliable isothermal VLE data for systems of homologous compounds, the predicting method proposed has been tested using only the heats of mixing of binary systems of this type. We have used especially the plentiful data on heats of mixing of 2-ketones[5] and n-alcohols[4,11,12]. The corresponding data have been correlated by the Redlich–Kister polynomial (*12*). The number of constants in Eq. (*12*) has been assessed on the basis of the statistical criterion of significance (F-test). The quality of representation in terms of the Redlich–Kister polynomial and that of predictions carried out has been judged by means of the standard deviations σ:

$$\sigma^2_{cor} = \sum_{i=1}^{n} (H^E_{i,exp} - H^E_{i,cor})^2 / (n - p) , \qquad (24)$$

$$\sigma^2_{pred} = \sum_{i=1}^{n} (H^E_{i,pred} - H^E_{i,cor})^2 / n , \qquad (25)$$

$$\sigma^2_{integ} = \int_0^1 (H^E_{pred} - H^E_{cor})^2 \, dx_A , \qquad (26)$$

where $H^E \equiv h^E/RT$.

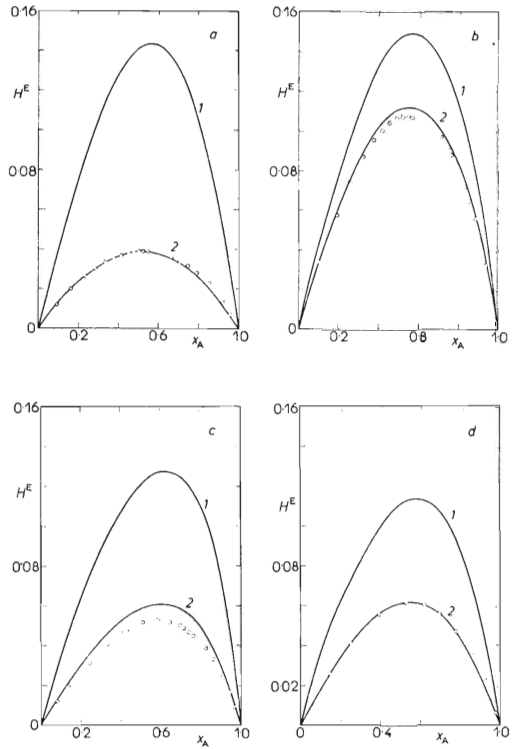

FIG. 1

Comparison of Experimental and Predicted Values of $H^E \equiv h^E/RT$

1 Basal system (A + B), *2* predicted system (A + B′), ○ experimental points; *a* A + B: 2-butanone + 2-undecanone[3], A + B′: 2-butanone + 2-heptanone[3]; *b* A + B: acetone + + 2-octanone[4], A + B′: acetone + 2-heptanone[4]; *c* A + B: ethanol + n-decanol[12], A + B′: ethanol + n-hexanol[12]; *d* A + B: n-propanol + n-undecanol[11], A + B′: n-propanol + n--octanol[4].

The results of predictions for $\alpha < 1$ (B′ lies in a homologous series between A and B) are arranged lucidly in Tables I (2-ketones) and II (n-alcohols) in the form of deviations just given above. Since the values of heats of mixing differ considerably for individual systems, the deviation δ_{rel} is added in tables which is defined by the relation

$$\delta_{rel} = 100\sigma_{integ}/H^{E}_{max} . \qquad (27)$$

Typical results are also shown in Fig. 1.

Systems with methanol have been excluded owing to their considerable systematic deviations. The agreement of predictions with experiments is otherwise more than satisfactory. The average deviation δ_{rel} for systems with 2-ketones amounts to 6·6% and for those with alcohols 8·5%. So it appears that the method proposed yields results at least as good as the principle of congruence does.

The estimation of constants of the Redlich–Kister equation provides theoretically the possibility to predict excess functions in the entire concentration range even in the cases when $\alpha > 1$. However, our computations show that the possibilities in this direction are rather limited. It is so especially because the extrapolation to other group concentrations, which is made possible by predicting the analytical expression itself of h^{E} of predicted system, is rather unreliable already for values $\alpha > 1{\cdot}5$. As another negative factor the numerical instability of Eq. (*22*) becomes evident for larger number of constants and greater values of α. The situation discussed is illustrated by several typical examples in Table III. It follows from our experimence that the prediction in terms of Eqs (*22*) and (*23*) is reliable only for α lower than approximately 1·5 and for number of constants in Eq. (*12*) not greater than three on the assumption that the constants of Eq. (*12*) are given to four decimal places.

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Translated by J. Linek.