REPRESENTATION OF BINARY EXCESS ENTHALPY DATA

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An extensive test of five correlation relations for the concentration dependence of excess enthalpy of non-electrolyte solutions was carried out. The Redlich–Kister, root and reciprocal expansions, the SSF and Wilson equations were used to represent experimental data of 54 systems of different character. For the representation of data of symmetric and slightly asymmetric systems, we recommend the Redlich–Kister polynomial, more asymmetric systems are described excellently by the SSF equation.

Heat of mixing pertains today to the most accurately and also most often measured excess quantities for it provides very valuable indirect information on the structure of solutions and intermolecular interactions. Although at the present time the theoretical description does not reach the possibilities of experiment, it is suitable that the data for processing by models with a deeper theoretical basis should be compiled and stored as the already smoothed concentration and temperature dependences which would represent the experimental data with an accuracy comparable to the experimental error. However, the excess enthalpy is not unfrequently so complicated function of composition that even a great number of adjustable parameters of correlation relation is not a guarantee of excellent representation of experimental data.

The presented work deals in this part with testing some correlation relations for the concentration dependence of excess enthalpy of binary systems. In the subsequent part, the prediction and correlation relations for the concentration dependence of excess enthalpy in ternary systems are then tested.

Survey of Correlation Relations Used

The most often used relations are expansions of the Redlich–Kister polynomial[1] type

$$H^E = x_1 x_2 \sum_{i=0}^{p-1} A_i (x_1 - x_2)^i , \qquad (1)$$

where the symbol H^E stands for the dimensionless quantity $H^E \equiv h^E/RT$, x_1, x_2 are the mole fractions and A_i adjustable constants. Also the function which was proposed

by Missen[2] is of analogous type

$$H^E = x_1 x_2 \sum_{i=0}^{p-1} A_i x_i^{i/2} \qquad (2)$$

and was applied successfully to the system of the type cycloalcohol–cycloalkane[3]. Mrazek and Van Ness[4] proposed the following form of expansion

$$H^E = x_1 x_2 \sum_{i=0}^{p-1} A_i x_1^{-i} . \qquad (3)$$

Here, however, it is at once necessary to draw attention to the fact that expansion (3) has, on using three and more parameters, an infinite limit at the point $x_1 = 0$, which is contrary to the physical reality. Therefore it cannot be used for extrapolation and also other applications will be probably rather questionable.

The given expansions fail completely in case of very unsymmetric systems with a complicated course of concentration dependence of excess enthalpy, *e.g.* in case of systems alcohol–hydrocarbon[4,5].

Rogalski and Malanowski[6] have recently proposed for these systems a so-called SSF equation (Sum of Symmetrical Functions)

$$H^E = x_1 x_2 \sum_{i=1}^{p/2} A_i \left(\frac{x_1}{a_i} + a_i x_2 \right)^{-2} \qquad (4)$$

and obtained very satisfactory results. The symbols A_i, a_i in Eq. (4) denote adjustable constants.

To correlate excess enthalpy, it is possible to employ also the equations[7,8] which follow from the local composition concept. It has been proved that the best results of this group of relations are yielded apparently by the Wilson equation

$$H^E = \frac{x_1 x_2}{T} \left(\frac{a_{12} \Lambda_{12}}{x_1 + \Lambda_{12} x_2} + \frac{a_{21} \Lambda_{21}}{x_2 + \Lambda_{21} x_1} \right) . \qquad (5)$$

where

$$\Lambda_{12} = \exp \left[- \left(\frac{a_{12}}{T} + b_{12} \right) \right],$$

$$\Lambda_{21} = \exp \left[- \left(\frac{a_{21}}{T} + b_{21} \right) \right],$$

a_{ij}, b_{ij} being adjustable parameters. Unlike the form reported in the literature[7], the unsubstantial temperature dependence of molar volume ratio has been neglected

in Eq. (5) and this ratio has then been implicitly included into the arguments of exponential functions.

Abbott and Van Ness[9,10] have used the six-parameter relations

$$\frac{H^E}{x_1 x_2} = A_{21} x_1 + A_{12} x_2 - (B_{21} x_1 + B_{12} x_2) x_1 x_2 + (C_{21} x_1 + C_{12} x_2) x_1^2 x_2^2 \quad (6)$$

and

$$\frac{H^E}{x_1 x_2} = A_{21} x_1 + A_{12} x_2 - \frac{x_1 x_2 B_{12} B_{21}}{B_{21} x_1 + B_{12} x_2 + (C_{21} x_1 + C_{12} x_2) x_1 x_2} . \quad (7)$$

Testing the Correlation Relations

In this work, five correlation relations describing the concentration dependence of excess enthalpy of binary systems are tested, *viz.* three polynomial expansions $(1)-(3)$, the SSF equation (4) and the Wilson equation (5).

The optimum values of parameters of correlation equations were determined by the least-squares method. In case of the equations requiring non-linear optimization (the SSF and Wilson equations), we used the Newton–Raphson or Marquardt algorithm. The system of normal equations was solved by the Gauss method. With expansions $(1)-(4)$, double precission arithmetics was used for solving. The number of parameters in individual correlation relations was established on the basis of the statistical criterion of significance of difference of two variances (F-test). The maximum number of adjustable parameters, however, was limited — to eight for the polynomial expansions, to six for the SSF equation and to four for the Wilson equation.

The testing set has been formed by 54 binary systems containing different organic liquids. We have included only such systems for which a sufficient number of experimental points distributed uniformly over the entire concentration range was measured with a good accuracy. The selection of the systems was carried out so that the single combinations of classes of the Ewell classification of liquids[11] should be represented as uniform as possible. The excess enthalpies of the systems selected have kept within two orders of magnitude, they have been positive, negative and even showed an S-shaped dependence on concentration.

The quality of representation was judged by the standard deviation

$$\sigma = \left(\frac{S_p}{n - p} \right)^{1/2} , \quad (8)$$

where S_p is the residual sum of squares of deviations when using the p-parameter relation and n is the number of experimental data. For a more easy judgement of suc-

cess of the individual correlation relation, we introduced further a quantity ω, called location. It was defined by normalizing the mean standard deviation $\bar{\sigma}$ for a group of systems by the relation

$$\omega = C\bar{\sigma}/\sum \sigma \qquad (9)$$

TABLE I

Survey of mean standard deviations of correlation $\bar{\sigma} \cdot 10^4$ and location ω. Dividing the test set according to the Ewell classification

Type	Number of systems	Relation				
		(1)	*(2)*	*(3)*	*(4)*	*(5)*
I + I	3	37[a]	36	51	43	61
		2·4[b]	2·4	3·4	2·8	4·0
I + II	5	101	137	203	125	137
		2·2	2·9	4·3	2·7	2·9
I + III	3	327	315	552	288	312
		2·7	2·6	4·6	2·4	2·6
II + II	5	105	108	132	133	148
		2·5	2·6	3·2	3·2	3·6
II + III	2	141	156	296	152	188
		2·3	2·5	4·8	2·5	3·0
II + IV	3	43	80	115	67	66
		1·7	3·2	4·7	2·7	2·7
II + V	8	108	76	103	25	49
		4·5	3·2	4·3	1·1	2·0
III + III	3	12	11	12	14	16
		2·8	2·5	2·7	3·3	3·8
III + IV	4	122	106	138	128	277
		2·4	2·1	2·7	2·5	5·4
III + V	7	86	59	96	90	68
		3·3	2·2	3·6	3·4	2·6
IV + IV	1	1	0·9	0·9	0·9	1
		3·2	2·9	2·9	2·9	3·2
IV + V	4	49	52	54	51	51
		2·9	3·0	3·2	3·0	3·0
V + V	6	34	36	47	46	91
		2·0	2·1	2·8	2·7	5·4

[a] Mean standard deviation for the given group of systems and the given correlation relation; [b] location ω.

so that the sum of locations should yield the value

$$C = 1 + 2 + 3 + \ldots + (k - 1) + k = k(k + 1)/2 , \qquad (10)$$

where k is the number of correlation relations. The summation in Eq. (9) extends over all the correlation relations. The location ω makes it possible to compare the quality of representation also between groups of systems in which the average standard deviations differ considerably.

The results of the test performed are summarized in Table I and II. In Table I, the test set is divided according to Ewell classification. In each group of systems, the mean value of standard deviation $\bar{\sigma}$ and the value of location ω for the given correlation equation are given.

The Ewell classification of liquids:

Group I: Liquids able to form a three-dimensional lattice of hydrogen bonds
Group II: Liquids whose molecules have an active hydrogen as well as electron donor
Group III: Liquids whose molecules contain an electron donor but not an active hydrogen
Group IV: Liquid that have an active hydrogen in the molecule but not an electron donor
Group V: Liquids incapable of forming hydrogen bonds.

In Table II, the systems are divided according to the position of extreme value of excess enthalpy on the concentration axis. The value of location ω is always given for each correlation relation in each group of systems.

Considering the tabulated results, it is possible to draw the following conclusions:

1) The Redlich–Kister polynomial yields in most cases very good results. The quality of representation of experimental data by this relation decreases, however, with increasing asymmetry of concentration dependence of excess enthalpy. For considerably unsymmetric systems, this expansion fails completely regardless of the

TABLE II

Survey of location ω. Dividing the test set according to the position of extreme of excess enthalpy

Extreme position $x_{ext} \in$	Number of systems	Relation				
		(1)	*(2)*	*(3)*	*(4)*	*(5)*
(0·45; 0·55)	19	2·4	2·5	3·5	3·0	3·6
(0·40; 0·45) (0·55; 0·60)	12	2·9	2·6	2·9	2·7	3·9
(0·35; 0·40) (0·60; 0·65)	9	3·8	2·5	4·1	2·4	2·2
(0·30; 0·35) (0·65; 0·70)	3	4·4	3·5	3·0	1·2	3·0
(0·25; 0·30) (0·70; 0·75)	1	7·1	3·9	1·3	0·5	2·2
S-shaped dependence	8	1·2	2·7	6·8	2·7	1·7

number of adjustable parameters. The Redlich–Kister expansion is especially inconvenient for the description of systems of the type II + V of the Ewell classification. It is, however, interesting that the systems with an S-shaped dependence of excess enthalpy on composition are described by this expansion, on the contrary, very well.

2) The correlation relation (2) yields similar results as the Redlich–Kister polynomial. The effect of asymmetry of concentration dependence of H^E on the quality of representation is not here so evident as in the foregoing case, nevertheless the description of considerably asymmetric systems by relation (2) is unsatisfactory.

3) Expansion (3) is least suitable for representation of excess enthalpy. The infinite limit which shows this expansion for $x_1 \to 0$ in case of a higher number of constants than two is naturally undesirable and causes among others the complete failure of this expansion in systems with an S-shaped course of $H^E(x)$.

4) The SSF equation describes well asymmetric dependences of $H^E(x)$ including the systems of the II + V type. It is, however, remarkable that nearly symmetric systems are represented altogether better by the Redlich–Kister polynomial than by this equation. The SSF equation therefore complements suitably the Redlich–Kister expansion.

5) The Wilson equation, unlike the foregoing relations, contains lower number of adjustable parameters — two or four. Nevertheless it represents the concentration dependence of excess enthalpy comparatively satisfactorily for most systems. It fails conspicuously only in case of the systems with strong specific interaction between components involved (type III + V). However, it is evident that it allows to describe heat of mixing only seldom with experimental accuracy.

REFERENCES

1. Redlich O., Kister A. T.: Ind. Chem. *40*, 341 (1948).
2. Brandreth O., O'Neill S. P., Missen R. W.: Trans. Faraday Soc. *62*, 2355 (1966).
3. Jones D. E. G., Weeks I. A., Anand S. C., Wetmore R. W., Benson G. C.: J. Chem. Eng. Data *17*, 501 (1972).
4. Mrazek R. V., Van Ness H. C.: AIChE J. 7, 190 (1961).
5. Ramalho R. S., Ruel M.: Can. J. Chem. Eng. *46*, 456 (1968).
6. Rogalski M., Malanovski S.: Fluid Phase Equil. *1*, 137 (1977).
7. Nagata I., Yamada T.: Ind. Eng. Chem., Process Des. Develop. *11*, 574 (1972).
8. Dohnal V., Vinš J., Holub R.: This Journal *44*, 808 (1979).
9. Morris J. W., Mulvey P. J., Abbott M. M., Van Ness H. C.: J. Chem. Eng. Data *20*, 403 (1975).
10. Shates J. P., Abbott M. M., Van Ness H. C.: J. Chem. Eng. Data *20*, 406 (1975).
11. Ewell R. H., Harrison J. M., Berg. L.: Ind. Eng. Chem. *36*, 871 (1944).

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