PREDICTION AND REPRESENTATION
OF TERNARY EXCESS ENTHALPY DATA

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A survey of relations making it possible to predict ternary H^E's from binary data and of relations for representation of the concentration dependence of ternary H^E's is presented in this part. Altogether 13 prediction and 26 correlation relations (including some proposed recently) were tested using a thoroughly selected set of nine ternary systems. Relevant recommendations are given on the basis of the results obtained.

With regard to the laboriousness of experimental determination of properties of multicomponent mixtures, the methods are required enabling their reliable and accurate estimation from already determined properties of constituent binary mixtures. Complexity of the concentration dependence of excess enthalpy causes that the development of such a method for this quantity is rather problematic. For the same reason, just only the problem of representing the ternary H^E data with sufficient accuracy is difficult in a number of cases. In this part* we test altogether 13 prediction and 26 correlation relations for the concentration dependence of excess enthalpy in ternary systems.

Survey of the Relations for Predicting the Ternary Excess Enthalpies from Binary Data

The method of binary contributions is well-known and in general use:

$$H^E_{123} = \sum_{i<j} \sum_j H^E_{ij}(x_i, x_j), \qquad (1)$$

where $H^E_{ij}(x_i, x_j)$ is the value which is obtained on inserting mole fractions of the ternary mixture into the correlation equation for the binary system $i - j$. In comparison with further methods, relation (1) often yields unsatisfactory results. It is as well unsuitable that the result of prediction is considerably dependent on the correlation equations used for binary systems.

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The group of several next methods can be covered by the following formula

$$H_{123} = \sum_{i<j} \sum_j t_{ij} H_{ij}(x_i^{ij}, x_j^{ij}), \tag{2}$$

where

$$x_i^{ij} + x_j^{ij} = 1. \tag{3}$$

If Eq. (3) holds, we can, for the sake of clarity of the record, use hereafter the designation

$$H_{ij}(x_i^{ij}, x_j^{ij}) \equiv H_{ij}(x_i^{ij}). \tag{4}$$

Individual methods of this group differ in the functional dependence of weight factors t_{ij} and binary compositions x_i^{ij} on the composition of ternary mixture. One of the most often used relations of this group is the equation proposed by Scatchard[1] in the form

$$H_{123}^E = \sum_{i<j} \sum_j \frac{x_i x_j}{x_i^{ij} x_j^{ij}} H_{ij}^E(x_i^{ij}) \tag{5}$$

then a modified version due to the same author for one polar component

$$H_{123}^E = \frac{x_2}{1-x_1} H_{12}^E(x_1) + \frac{x_3}{1-x_1} H_{13}^E(x_1) + \frac{x_2 x_3}{x_2^{23} x_3^{23}} H_{23}^E(x_2^{23}). \tag{6}$$

For Eqs (5) and (6) holds

$$x_i^{ij} = (1 + x_i - x_j)/2. \tag{7}$$

Tsao[2] proposed an equation with different third term in the form

$$H_{123}^E = \frac{x_2}{1-x_1} H_{12}^E(x_1) + \frac{x_3}{1-x_1} H_{13}^E(x_1) + (1-x_1) H_{23}^E(x_2^{23}), \tag{8}$$

where, however,

$$x_2^{23} = x_2/(x_2 + x_3). \tag{9}$$

Knobeloch and Schwartz[3] modified Eq. (8) by inserting the exponent $a = 0.5$ at the weight of the third term, and, by a cyclic permutation of single components, obtained three analogous prescriptions. The arithmetic mean of the values obtained from single equations is then considered to be the resulting value of enthalpy of mixing of ternary mixture.

Voňka and coworkers[4] have proposed in their work to use, for developing the weight functions, the condition of the solution regularity conservation and have got

$$t_{ij} = x_i x_j / (x_i^{ij} x_j^{ij}) . \qquad (10)$$

The relation between the composition of ternary mixture and that of constituent binary systems x_i^{ij} is determined on the basis of geometric view in three different ways. In the first case (Fig. 1a) holds

$$x_i^{ij} = (1 + x_i - x_j)/2 . \qquad (11)$$

On combining Eqs (10), (11) and (2)

$$H_{123}^E = \sum_{i<j} \sum_j \frac{4 x_i x_j}{1 - (x_i - x_j)^2} H_{ij}^E(x_i^{ij}) . \qquad (12)$$

In the second case (Fig. 1b), it is assumed

$$x_i^{ij} = x_i / (x_i + x_j) \qquad (13)$$

which, on inserting into Eq. (2), yields

$$H_{123}^E = \sum_{i<j} \sum_j (x_i + x_j)^2 H_{ij}^E(x_i^{ij}) . \qquad (14)$$

In the third case, two compositions are considered in each binary system (Fig. 1c)

$$x_i^{ij,1} = x_i , \quad x_i^{ij,2} = 1 - x_j , \qquad (15)$$

and the resulting value of H_{123}^E is a mean of the values yielded by Eq. (2)

$$H_{123}^E = \frac{1}{2} \sum_{i<j} \sum_j \left[\frac{x_j}{1 - x_i} H_{ij}^E(x_i) + \frac{x_i}{1 - x_j} H_{ij}^E(1 - x_j) \right] . \qquad (16)$$

It is possible to show that the Scatchard equation (5) and Eq. (12) are equivalent. The modified Scatchard equation follows from Eqs (2) and (10) when choosing the binary composition in terms of Fig. 1d, and is substantially a combination of Eqs (12) and (16). As well some special cases of the method of binary contributions correspond to the above-mentioned approach. For instance, if all the binary systems are described by the Redlich–Kister polynomial, then the method of binary contributions (1) corresponds to Eq. (12); if they are described by a root expansion (Eq. (2) in foregoing paper), Eq. (1) corresponds to the first term in Eq. (16).

In the Voňka-and-coworkers approach, the composition of single binary mixtures is determined on the basis of geometric representation. Instead of it, it is possible to introduce another condition laid down to the position of single binary points, *e.g.* the requirement of validity of material balance on forming the ternary solution. Then it must obviously hold

$$x_1 = t_{12}x_1^{12} + t_{13}x_1^{13},$$
$$x_2 = t_{12}x_2^{12} + t_{23}x_2^{23}, \qquad (17)$$
$$x_1 + x_2 + x_3 = 1.$$

The systems of equations (17) and (10) are simultaneously satisfied by three physical solutions

1) $$x_1^{12} = x_1/(x_1 + x_2), \quad x_1^{13} = x_2^{23} = 0 \qquad (18)$$

2) $$x_1^{12} = 0, \quad x_1^{13} = x_1/(x_1 + x_3), \quad x_2^{23} = 0 \qquad (19)$$

3) $$x_1^{12} = x_1^{13} = 0, \quad x_2^{23} = x_2/(x_2 + x_3). \qquad (20)$$

It is evident that the ternary mixture of a required composition is always formed by mixing a binary mixture and the remaining pure component. Inserting Eq. (18)
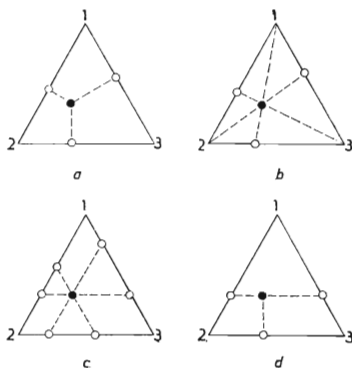
into (2) and (10) we have

$$H_{123}^E = (x_1 + x_2)^2 H_{12}^E(x_1^{12}) + x_1 x_3 \lim_{x_1^{13} \to 0} \frac{H_{13}^E(x_1^{13})}{x_1^{13} x_3^{13}} + x_2 x_3 \lim_{x_2^{23} \to 0} \frac{H^E(x_2^{23})}{x_2^{23} x_3^{23}} . \qquad (21)$$

In the limits in Eq. (21), it is possible to identify the partial molar enthalpy of mixing at infinite dilution. Their values can be determined in principle from the knowledge of the analytical function which describes the concentration dependence of excess enthalpy of the corresponding binary solution. Further, two relations analogous to Eq. (21) can be derived on using the remaining two solutions of Eq. (19) or (20).

The weight functions t_{ij} in foregoing relations have always been determined from the condition of the regularity conservation (10). We can also proceed in another way: To determine the composition of single binary systems according to some alternative of Fig. 1, and to calculate t_{ij} from the balance equations (17). In such a way derived relations fulfil then material balance but do not satisfy the condition of regularity conservation.

The last group of relations for predicting the ternary H^E from binary data involves the prescriptions which are specific for a given binary correlation equation.

Rogalski and Malanowski[5] have proposed for the SSF equation

$$H_{123}^E = \sum_{i<j} \sum_j (x_i + x_j) H_{ij}^E(x_i, x_j) , \qquad (22)$$

where $H_{ij}(x_i, x_j)$ is expressed by Eq. (4) in foregoing paper. By a logical extension of the Wilson equation to the ternary system, we get[6,7]

$$H_{123}^E = \sum_i x_i \sum_j x_j \Lambda_{ij} a_{ij} / \sum_j x_j \Lambda_{ij} . \qquad (23)$$

Relations for Representation of Excess Enthalpies of Ternary System

The following expression is most often used as a correlation relation

$$H_{123}^E = \sum_{i<j} \sum_j H_{ij}^E(x_i, x_j) + H_T^E , \qquad (24)$$

where the sum corresponds to the method of binary contributions and H_T^E is a so-called ternary term given usually in the form

$$H_T^E = x_1 x_2 x_3 (A + B x_1 + C x_2) . \qquad (25)$$

In this work, the ternary term

$$H_T^E = x_1 x_2 x_3 (A + B x_1^{0.5} + C x_2^{0.5} + D x_3^{0.5}) \qquad (26)$$

is tested as well. The symbols A, B, C, D in Eq. (25) and/or (26) denote the parameters adjustable to the ternary data. However, a situation often occurs when the value of the ternary term is too high, and amounts to frequently more than 40% of the total value of heat of mixing. This is already evidently contrary to the physical reality for the ternary term is usually interpreted as a contribution involving the effect of ternary interactions. In these cases, the ternary terms with small number of parameters do not suffice. For instance, Van Ness and coworkers[8,9] have proposed for such cases a ternary term with ten parameters

$$H^E = x_1 x_2 x_3 (C_0 - C_1 x_1 - C_2 x_2 - C_3 x_1^2 - C_4 x_2^2 - C_5 x_1 x_2 -$$
$$- C_6 x_1^3 - C_7 x_2^3 - C_8 x_1^2 x_2 - C_9 x_1 x_2^2). \qquad (27)$$

In this work, any prediction expression supplemented by a ternary term (*e.g.* Eq. (25) or (26)) is considerred as a correlation relation.

Testing the Prediction and Correlation Relations

The single prediction and correlation relations have been applied to nine testing ternary systems with the aim to judge the quality of these methods and to select the best procedures. To ensure mutual consistence of binary and ternary experimental data, it was required when selecting them that the experimental data on enthalpy of mixing of the ternary and all the constituent binary systems should be measured by the same author in the same experimental apparatus. On combining the experimental data from different laboratories, the probability of introducing a systematic deviation is considerable, and the information ability of the test carried out can be easily endangered.

The systems of the testing set are presented clearly in Table I. Using this set, altogether 13 prediction and 26 correlation relations were tested. The results of predictions and correlations are summarized in Tables II and III. As it has been shown in our foregoing paper, it is not possible to describe satisfactorily different types of binary systems by one relation. Therefore the principle was kept in this work to represent binary system by the relation which brings out best the concentration dependence of its excess enthalpy. An exception naturally are the ternary extensions of the SSF and Wilson equations which require that the constituent systems should be described by relations of the same type.

The tested correlation relations consist of one of prediction methods complemented by the ternary term on the one hand in the form of Eq. (25) and on the other hand in the form of Eq. (26). The number of ternary adjustable parameters was controlled by a statistical criterion (F-test).

The results processing was carried out analogously to the foregoing paper. Unlike the correlations, the quality of prediction is judged, however, by the mean absolute

deviation instead of standard deviation. The mean and standard deviations were in the end converted to the location ω (see foregoing paper) giving the success of the given method.

By analyzing the results of predictions summarized in Table I, it is possible to draw these conclusions:

1) Two conspicuous groups can be distinguished between the methods tested: The first one includes the Tsao method (Eq. (8)) and the modified Scatchard method (Eq. (6)) which give the best predictions. The second one is formed, on the contrary, by the methods yielding the predictions of the least quality — above all the method of binary contributions (1) and both the methods in which the condition of the regularity conservation (MB1, MB2) is abandoned. The remaining methods form nearly continuous transition between these two groups.

2) The methods based on the condition of regularity and the choice of binary compositions (12), (14) and (16) are very successful in case of the systems number 3 and 8, *i.e.* those which do not exhibit too complicated concentration dependence of enthalpy of mixing. Use of unsymmetric methods (6), (8) in case of "simple" ternary systems, *e.g.* hydrocarbon mixtures, cannot be even justified.

3) The SSF and Wilson equations, which differ somewhat from the other methods tested by their character, yield satisfactory results and are numbered among successful methods.

4) In agreement with the results by Ramalho and Ruel[10], it is shown lucidly that the use of exponent 0·5 in the Knobeloch method is not justified for the method employing the unity exponent gives conspicuously better results.

TABLE I

Testing set of ternary systems

No	System	Type by Ewell	Ref.
1	Diethylamine–ethanol–triethylamine	II + II + III	11
2	Water–1-propanol–1-butanol	I + II + II	12
3	Acetonitrile–benzene–tetrachloromethane	III + V + V	13
4	Benzene–ethanol–n-hexane	V + II + V	14
5	n-Tetradecane–1-propanol–1-decanol	V + II + II	10
6	n-Octane–ethanol–1-pentanol	V + II + II	10
7	1-Chlorobutane–1-octanol–n-hexane	V + II + V	15
8	Benzene–cyclohexane–n-heptane	V + V + V	16
9	Acetone–chloroform–benzene	III + IV + V	17

TABLE II
Results of predicting the excess enthalpies of ternary systems — values of mean absolute error $\delta \cdot 10^4$

No[a]	Representation of binary systems[b]	Method (relation)												
		(12)	(14)	(16)	(21)	MB1[c]	MB2[d]	(1)	(6)	(8)	K.5[e]	K1[f]	(22)	(23)
1	2 5 1	1 278	1 246	1 168	870	2 329	2 528	1 348	1 093	263	219	454	1 282	1 194
2	4 4 1	257	457	411	166	362	495	789	180	182	412	398	457	263
3	4 2 2	87	94	86	203	371	758	576	65	117	425	266	93	92
4	4 1 5	149	123	74	723	791	1 078	1 607	359	96	710	394	122	596
5	4 4 4	93	184	203	51	337	540	—	105	180	719	466	184	262
6	4 4 4	138	203	225	60	189	327	—	91	129	654	446	203	102
7	4 2 4	523	449	435	1 271	1 084	1 254	1 914	649	383	231	114	449	185
8	1 1 2	131	141	107	295	636	932	103	104	169	715	435	123	137
9	2 1 1	230	230	232	256	787	1 082	177	175	331	597	298	233	264
$\bar{\delta} =$		321	347	327	433	765	999	931	313	206	520	363	350	343
$\omega =$		4·7	5·1	4·8	6·3	11·2	14·6	13·6	4·6	3·0	7·6	5·3	5·1	5·0

[a] See Table I; [b] 1 Redlich–Kister expansion, 2 root expansion, 3 reciprocal expansion; 4 SSF equation, 5 Wilson equation; [c] material balance (17) and choice of binary compositions according to Fig. 1a; [d] material balance (17) and choice of binary compositions according to Fig. 1b; [e] Knobeloch method with exponent 0·5; [f] Knobeloch method with exponent 1.

TABLE III
Results of correlating the excess enthalpies of ternary systems — standard deviation $\sigma \cdot 10^4$

No[a]	Representation of binary systems[b]	Method (relation)												
		(12)	(14)	(16)	(21)	MB1[c]	MB2[d]	(1)	(6)	(8)	K.S[f]	K1[f]	(22)	(25)
1	2 5 1	276	259	276	409	425	1 340	301	271/304	347	253	255	242	368
2	4 4 1	304	394/418	287/297	138/140	188	186/190	505/543	193	192	332/354	330/349	394/418	214
3	4 2 2	83/86[g]	83/87	86/88	116/119	125	338/82	314	86	89/91	116	92/95	83/88	84/86
4	4 1 5	80/70	145	94	479/384	208/216	493/477	861/715	96/79	112	230	142	145	219/196
5	4 4 4	56	165	106	30	96	299	—	56/36	65/37	254	164	165	62/36
6	4 4 4	33/31	155/70	66/36	68/55	70	231	—	22/14	24/16	197	140	155/70	44
7	4 2 4	232/155	137/97	176/120	596/365	349/210	525/552	1 300	263/177	188/203	105/109	118/127	137/97	83/87
8	1 1 2	113	125	108	137/116	211/224	421/453	104	112/118	108/106	74	94	100	101/98
9	2 1 1	226	229	225	243	407	962	211/221	215	222/227	358/225	243	222	317/335
$\sigma =$		156/146	188/177	158/150	246/207	231/218	533/510	513/500	153/144	158/157	213/201	175/179	183/172	166/163
$\omega =$		4·6/4 5	5·6/5·5	4·7/4·7	7·3/6·4	6·8/6·8	16/16	15/16	4·5/4·5	4·7/4·9	6·3/6·3	5·2/5·6	5·4/5·4	4·9/5·1

[a]–[f] See Table II; [g] the value before oblique stroke corresponds to ternary term (25), the value behind oblique stroke to ternary term (26); if only one number is given, both cases give identical value.

5) The recently proposed method (21) ranks among less successful with its location $\omega = 6 \cdot 3$. It is interesting that it gives very good results for several systems but fails in the others. Success of this method is considerably influenced by the way in which the corresponding partial molar excess enthalpies at infinite dilution are evaluated. In this work we have used the extrapolation in terms of an analytical relation which has described best the concentration dependence of the given binary system. It appears, however, that even the most successful relation is not still a guaranty of reliable extrapolation. Although only one most suitable version of method (21) was chosen from three possible ones — on the basis of comparison of analytical extrapolation with graphic extrapolation of experimental data in coordinates $H^E/x_1 x_2$ vs. x_1 — a satisfactory prediction was not reached in all cases. The reason of failure is apparently also the fact that the contributions of two binary systems to the ternary quantity are described by a simple symmetric relation $A_{ij}x_i x_j$, where the value A_{ij} is represented by a partial molar quantity at infinite dilution.

6) Only two methods (6) and (8) are unsymmetric towards the numbering of components in ternary system and therefore give results dependent on the way of numbering. It was found that the best results can be reached if, as the binary system $2-3$ is chosen this one which has the lowest value of enthalpy of mixing — considered at maximum. This finding is in full agreement with the recommendation by Ramalho and Ruel[10].

By analyzing Table II, analogous conclusions can be reached also for correlation. It appears that the method yielding a prediction of good quality is, after adding a ternary term, a good correlation method as well. The alternative ternary terms (25) and (26) do not give substantially differing results. Expression (26) is mildly better in the cases when more parameters than in Eq. (25) are used. With the same number of parameters, Eq. (25) is slightly more successful.

In conclusion it is then possible to recommend both unsymmetric relations (6) and (8) for predicting the enthalpy of mixing of ternary systems from binary data, and, in case of simpler ternary systems, also the relations based on the principle of regularity, i.e. Eqs (12), (14) and (16). It is not possible to recommend the method of binary contributions (1) and the methods MB1, MB2 utilizing only material balance. Relation (21) can be used sucessfully if it is possible to determine, with sufficient accuracy, the values of partial molar excess enthalpy at infinite dilution. For correlating, it is generally suitable to employ that method which yields first-quality results as a prediction method. Then it is on the whole indifferent whether expression (25) or (26) is used as the ternary term.

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