

Thermodynamic Excess Functions of Binary Liquid Mixtures with Chain Association of One Component* Part I: The Excess Gibbs Free Energy G^E/RT

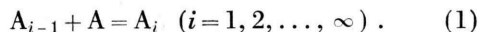
F. Becker, M. Kiefer, P. Rhensius, and H. D. Schäfer

Institut für Physikalische Chemie der Universität Frankfurt a. M.

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In this paper equilibrium models for the calculation of the excess Gibbs free energy of binary liquid mixtures are developed, the component A of which undergoes chain-forming self-association whilst the component B acts as an 'inert' solvent. It is shown that the extension of the well-known chain-association model of Mecke and Kemper, in which the probability of chain prolongation is assumed to be independent of chain length, is unable to establish satisfactory results because it does not exhibit sufficient unsymmetry. Reduction of the probability of chain growth with increasing chain length leads to an improved model with the geometric series replaced by the exponential series. This model, in which only two parameters are used, i. e. the equilibrium constants K for mutual solvation of A and B, and ϱ for self-association of A, allows fitting of isothermal experimental G^E/RT literature data on cycloalkanol-cycloalkane, alkanol-alkane, and NMF- CCl_4 systems within the limits of experimental error. Compared with the two-parameter Wilson equation which gives equally small standard deviations, our equilibrium model has the advantage of allowing passage from G^E to H^E data and of being applicable to liquid-liquid equilibria.

This paper is concerned with the application of the equilibrium models which we have developed previously¹⁻³ to the calculation of the thermodynamic excess properties of binary liquid mixtures the component A of which undergoes chain-forming self-association whilst the component B acts as an 'inert' solvent. Lassetre⁴, and Mecke and Kemper⁵ were the first to derive a relation between the concentration of the monomeric species A, c_A , and its analytical concentration, c_A^0 , by applying the ideal law of mass action to the equilibrium



The mathematical treatment is greatly simplified by the assumption that the equilibrium constant for chain prolongation, ϱ , is independent of the actual chain length, i , and that there is no limitation of i . By applying the formula for the sum of an infinite geometric series, the concentrations of all species A_i , except monomeric A, can be eliminated, yielding a simple relation between c_A , c_A^0 , and ϱ . Several authors have used this model, with some success, to interpret the observed dependence on concentration of specified physical properties of self-

associating solutes, like alcohols or phenols, in dilute solutions in inert solvents^{6,7}. The same model has been applied by Redlich and Kister⁸ to calculate the activity coefficients of alcohols in hydrocarbon solvents using Scatchard's equation for the excess Gibbs free energy⁹.

1. Contribution to G^E/RT of the Change of the Number of Associative A—A* Bonds, Caused by Dilution of Pure Liquid A with B

Our own attempts to extend the range of applicability of the above model to binary liquid mixtures have been based on the fact that only the change of the number of associative bonds A—A*,

$$N_A^0 \cdot \Delta = f(N_A^0) \quad (\leq 0),$$

caused by dilution of A with B to result in one mole of mixture, as compared with the same quantity of pure liquid A, contributes to the thermodynamic excess functions. This quantity $N_A^0 \Delta$ is defined by

$$N_A^0 \Delta = \sum_i (i-1) N_{A_i} - N_A^0 \sum_i (i-1) N_{A_i}^r \quad (i = 1, 2, \dots, \infty), \quad (2)$$

with N_{A_i} , $N_{A_i}^r$ and N_A^0 being the mole fractions of the species A_i in the mixture, in pure liquid A, and the analytical mole fraction of A, respectively. By stoichiometry, the relations

$$\sum_i i N_{A_i} = N_A^0 \quad \text{and} \quad \sum_i i N_{A_i}^r = 1 \quad (3)$$

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Reprint requests to Prof. Dr. F. Becker, Institut für Physikalische Chemie der Universität, Robert-Mayer-Str. 11, D-6000 Frankfurt a. M.

must hold. Insertion into Eq. (2) leads to

$$N_A^0 \Delta = N_A^0 \sum_i N_{A_i}^r - \sum_i N_{A_i}. \quad (4)$$

If ϱ designates the equilibrium constant for the formation of one A–A* bond by the reaction (1), the molar Gibbs free energy of formation of such a bond is $-RT \ln \varrho$, and the contribution of self-association of A to G^E/RT becomes

$$G_{\text{ass}}^E/RT = -N_A^0 \Delta \ln \varrho. \quad (5)$$

Application of the ideal law of mass action to Eq. (1) yields

$$N_A^0 \Delta = [1 - (1 + 4 \varrho N_A^0 (1 - N_A^0))^{1/2}] / [2(1 + \varrho)],$$

which is symmetric in N_A^0 . This result is at variance with the experimental findings that the thermodynamic excess functions of binary systems with an associating component A are unsymmetric, having the greater positive, or resp., the smaller negative initial slope of G^E/RT at $N_A^0 = 0$, i. e. when A is infinitely diluted by B. This fault is caused by the fact that competition between self-association of A and mutual solvation of A and B has not been accounted for.

a) Model 1 ('Geometric series')

We therefore replace the 'chemical' equilibrium (1) by an exchange equilibrium between 'contact sites'. Each molecule A is assumed to have one 'specific' and $(z-1)$ 'non-specific' contact sites. For simplicity, we further assume that B has z non-specific contact sites so that the total number of contact sites does not depend on the mole fraction. In an ideal mixture, the mole fraction N_{A_i} of the species A_i is proportional to the probability of simultaneously meeting the specific contact sites of i monomeric molecules A, i. e.

$$N_{A_i}^{\text{id}} \sim (N_A^0/z)^i.$$

The analogous expression for a non-ideal mixture is obtained by weighting each specific contact site of A by the factor $\varrho^{1/2}$, and each non-specific contact site of B by the factor $K^{1/2}$, viz.

$$N_{A_i} \sim (N_A^0 \varrho^{1/2}/z^*)^i \equiv z^i \quad (z < 1). \quad (6)$$

z^* has the meaning of an 'effective total number of contact sites':

$$z^* \equiv N_A^0 (\varrho^{1/2} + z - 1) + z K^{1/2} (1 - N_A^0), \quad (7)$$

the first term of which on the right-hand side is the contribution of A, the second term that of B. The

proportionality factor q [Eq. (6)] is determined by using the stoichiometric relations (3),

$$\begin{aligned} \sum_i i N_{A_i} &= q z \sum_i i z^{i-1} = q z \frac{d}{dz} \left(\sum_i z^i \right) \\ &= q z / (1 - z)^2 = N_A^0, \end{aligned} \quad (8)$$

giving

$$N_{A_i} = N_A^0 (1 - z)^2 z^{i-1} \quad \text{and} \quad \sum_i N_{A_i} = N_A^0 (1 - z). \quad (9)$$

The change of the number of associative bonds, $N_A^0 \Delta$, becomes now

$$N_A^0 \Delta = N_A^0 (z - z_r) = -z N_A^0 (1 - N_A^0) \cdot K^{1/2} \varrho^{1/2} / [z^* (\varrho^{1/2} + z - 1)]. \quad \text{'Model 1'} \quad (10)$$

It can easily be seen that the quantity $N_A^0 \Delta$ fulfils the following requirements: (1) It vanishes at $N_A^0 = 0$ and at $N_A^0 = 1$; (2) its limiting values at $\varrho \rightarrow 0$ and at $\varrho \rightarrow \infty$ are zero because no association takes place at the lower limit and no dissociation at the upper limit; (3) $N_A^0 \Delta$ is proportional to the weighted numbers both of the specific contact sites of A, $N_A^0 \varrho^{1/2}$, and of the competing contact sites of B, $z K^{1/2} (1 - N_A^0)$.

The contribution of self-association of A to the slope of G^E/RT is

$$\begin{aligned} (1/RT) (dG_{\text{ass}}^E/dN_A^0) \\ = -[\Delta + N_A^0 (d\Delta/dN_A^0)] \ln \varrho. \end{aligned} \quad (11)$$

By inserting (10) into (11) one obtains the following contribution of self-association to the unsymmetry of the limiting slopes of G^E/RT :

$$\begin{aligned} [(dG_{\text{ass}}^E/dN_A^0)_{(0)} + (dG_{\text{ass}}^E/dN_A^0)_{(1)}] / RT \\ = -[\Delta_{(0)} + (d\Delta/dN_A^0)_{(1)}] \ln \varrho \\ = [\varrho^{1/2} \ln \varrho (\varrho^{1/2} + z - 1 - z K^{1/2})] / [(\varrho^{1/2} + z - 1)^2]. \end{aligned} \quad (12)$$

If $\varrho > 1$ and $(\varrho^{1/2} + z - 1) > z K^{1/2}$, the right-hand side of (12) will be positive, i. e. G^E/RT has the greater positive, or, resp., the smaller negative initial slope at $N_A^0 = 0$, which is in qualitative accordance with experimental data on mixtures in which self-association of A is the main reason for unsymmetry. When dividing Eq. (12) by (G_{ass}^E/RT) one obtains a quantity which we name 'relative unsymmetry' of G^E/RT (=RUS):

$$\begin{aligned} \text{RUS} = -[(dG^E/dN_A^0)_{(0)} \\ + (dG^E/dN_A^0)_{(1)}] / [(N_A^0 \Delta)_{(1/2)} \cdot RT \ln \varrho]. \end{aligned} \quad (13)$$

Using Eqs. (10) and (12) one obtains

$$\begin{aligned} \text{RUS} = 2[(\varrho^{1/2} + z - 1)/z K^{1/2} \\ - z K^{1/2} (\varrho^{1/2} + z - 1)]. \quad \text{'Model 1'} \end{aligned} \quad (14)$$

Another informative quantity is the ‘mean degree of association of A’ which is defined by

$$\bar{i} = \frac{\sum_i i N_{A_i}}{\sum_i N_{A_i}} = N_A^0 / \sum_i N_{A_i}. \quad (15)$$

Insertion of (9) into (15) yields

$$\bar{i} = 1/(1-z) = 1 + N_A^0 \varrho^{1/2} / [N_A^0(z-1) + zK^{1/2}(1-N_A^0)]. \quad (16)$$

‘Model 1’

The limiting value of \bar{i} in pure liquid A, \bar{i}_r , is

$$\bar{i}_r = 1 + \varrho^{1/2}/(z-1) \quad (17)$$

which approaches infinity when $\varrho \rightarrow \infty$. In Figs. 1 and 2, examples of the functions $N_A^0 \Delta = f(N_A^0)$ and $\bar{i} = f(N_A^0)$ as calculated by Eqs. (10) and (16) are reproduced.

b) Model 2 (‘Exponential series’)

In the preceding section we have shown that an extension of the chain-association model of Mecke and Kempter⁵ to binary liquid mixtures is possible by applying it to exchange equilibria between pairs of contact sites. As will be seen from Table 1 and from the examples discussed later, model 1, however, does not exhibit sufficient unsymmetry. Of course, the rather drastic simplifications which this model implies must be responsible for this deficiency. The most serious simplification seems to be the use of a single association constant ϱ for all values of i , i. e. the assumption that the probability of chain prolongation is independent from the actual chain length. Several authors^{10, 11} have tried to improve the original model for dilute solutions by using two different association constants for the formation of dimers, and for all following chain prolongation steps. With regard to a reliable determination of the model parameters from experimental data we avoid to increase the number of independent equilibrium constants beyond two, i. e. K for mutual solvation of A and B, and ϱ for self-association of A.

Our model 2 takes account of the decreasing probability of chain growth with increasing chain length in the following way: The probability of reaction (1) is reduced by a factor which equals the ratio of the total numbers of contact sites of monomeric A, and of the species A_i ,

$$z/[(i-1)z-2(i-2)] = z/[(i-1)(z-2)+2], \quad (18)$$

the denominator of (18) being equal to the total number of contact sites of A_{i-1} minus the contacts

which have become inaccessible by the formation of $(i-2)$ A–A* bonds. To simplify calculation, we neglect the term +2 compared with $(i-1)(z-2)$ in the denominator of (18). Introduction of one factor (18) for each prolongation step into (6) yields

$$N_{A_i} \sim \kappa^i [z/(z-2)]^{i-1} / (i-1)! \quad (i=1, 2, \dots, \infty). \quad (19)$$

If we further assume that each molecule A has one specific ‘acceptor’ and one specific ‘donator’ contact site, formation of an associative A–A* bond will require pairing among complementary contact sites. As chain prolongation can equally proceed from both chain ends, a factor 2 for each prolongation step, i. e. 2^{i-1} for A_i , is introduced by this assumption, now reading:

$$N_{A_i} \sim \kappa^i [2z/(z-2)]^{i-1} / (i-1)! \quad (i=1, 2, \dots, \infty). \quad (20)$$

Chain associates A_i may also be formed from shorter fragments by

$$A_{i-k} + A_k = A_i \quad (k=1, 2, \dots, i-1), \quad (21)$$

the number of different possibilities being proportional to $(i-1)$. Introduction of a factor $(i-1)$ into (19) leads back to model 1 which displays insufficient unsymmetry. We therefore do not make further use of Equation (21).

Again, the proportionality factor q of Eq. (19) is calculated from the stoichiometric relations (3),

$$\begin{aligned} \sum_i i N_{A_i} &= q \kappa \sum_i i [z \kappa / (z-2)]^{i-1} / (i-1)! \\ &= q \kappa [1 + z \kappa / (z-2)] \exp \{z \kappa / (z-2)\} = N_A^0, \end{aligned} \quad (22)$$

leading to

$$N_{A_i} = N_A^0 \frac{\exp \{-z \kappa / (z-2)\} \cdot [z \kappa / (z-2)]^{i-1}}{[1 + z \kappa / (z-2)] \cdot (i-1)!} \quad (23)$$

and

$$\sum_i N_{A_i} = N_A^0 / [1 + z \kappa / (z-2)]. \quad \text{‘Model 2 a’} \quad (24)$$

The main difference between models 1 and 2 is that the sum of the geometric series in the former model has been replaced by the exponential function in the latter model. The change of the number of associative bonds, according to Eq. (4), is now given by

$$N_A^0 \Delta = N_A^0 (z-2) [1/(z-2+z\kappa) - 1/(z-2+z\kappa)],$$

$$N_A^0 \Delta = \frac{-z^2(z-2)N_A^0(1-N_A^0)K^{1/2}\varrho^{1/2}}{[(z-2)(\varrho^{1/2}+z-1)+z\varrho^{1/2}][(z-2)z^*+z\varrho^{1/2}N_A^0]} \quad \text{'Model 2 a'} \quad (25)$$

The contribution of self-association to the unsymmetry of G^E/RT , cf. Eq. (12), reads

$$\begin{aligned} & (1/RT) [(dG_{\text{ass}}^E/dN_A^0)_{(0)} + (dG_{\text{ass}}^E/dN_A^0)_{(1)}] \quad \text{'Model 2 a'} \\ &= \frac{z\varrho^{1/2}[(z-2)(\varrho^{1/2}+z-1-zK^{1/2})+z\varrho^{1/2}]}{[(z-2)(\varrho^{1/2}+z-1)+z\varrho^{1/2}]^2} \ln \varrho. \end{aligned} \quad (26)$$

The relative unsymmetry of G^E/RT , as defined by Eq. (13), is

$$\text{RUS} = \left\{ \frac{\varrho^{1/2}+z-1+z\varrho^{1/2}/(z-2)}{zK^{1/2}} - \frac{zK^{1/2}}{\varrho^{1/2}+z-1+z\varrho^{1/2}/(z-2)} \right\}. \quad (27)$$

The mean degree of association of A, \bar{i} , according to Eq. (15), is

$$\bar{i} = 1 + \frac{zN_A^0\varrho^{1/2}/(z-2)}{N_A^0(\varrho^{1/2}+z-1)+zK^{1/2}(1-N_A^0)} \quad \text{'Model 2 a'} \quad (28)$$

The use of Eq. (20) (= Model 2 b) instead of Eq. (19) (= Model 2 a) means that $z\varrho^{1/2}$ in Eqs. (22) to (27) has to be replaced by $2z\varrho^{1/2}$. Putting $z=4$, the quantities $N_A^0 \Delta$ read

$$N_A^0 \Delta = \frac{-16N_A^0(1-N_A^0)K^{1/2}\varrho^{1/2}}{[N_A^0(5\varrho^{1/2}+3)+4K^{1/2}(1-N_A^0)](5\varrho^{1/2}+3)} \quad \text{'Model 2 b'} (z=4) \quad (29)$$

$$N_A^0 \Delta = \frac{-8N_A^0(1-N_A^0)K^{1/2}\varrho^{1/2}}{[3N_A^0(\varrho^{1/2}+1)+4K^{1/2}(1-N_A^0)]3(\varrho^{1/2}+1)} \quad \text{'Model 2 a'} (z=4) \quad (30)$$

The differences between these two variants of model 2 are not very important. Introducing the factor 2 ('Model 2 b') enhances unsymmetry and causes more steepness of the function $N_A^0 \Delta = f(N_A^0)$ at $N_A^0=0$ and at $N_A^0=1$ and less curvature in the center. A comparison of RUS for both models is given in Table 1. Dropping the factor 2 is a means of making allowance of imperfect chain character of association as found in systems of aliphatic alcohols with alkanes, for instance. It must, however, be remembered that distinction between such minor variants of models requires very precise experimental G^E/RT data with small steps

on the N_A^0 axis which are available in very few cases only.

Whilst the qualitative properties of $N_A^0 \Delta$ and RUS, as calculated by models 1 and 2, are the same, there are considerable quantitative differences. This can clearly be seen from Fig. 1 in which the curves $N_A^0 \Delta = f(N_A^0)$, with $K^{1/2}=0.9$ and $\varrho^{1/2}=4.5$, are reproduced. The enhanced unsymmetry of model 2 results from the fact that the contributions of longer chains A_i are strongly reduced by the factor (18). In Fig. 2 a comparison of $\bar{i} = f(N_A^0)$ for both models is given. The curvatures of the function have opposite signs: Model 2 predicts a steeper increase of \bar{i} at

Table 1. Relative unsymmetry (RUS) of G_{ass}^E/RT , calculated for models 1, 2 a, and 2 b, by Eqs. (14) and (27), with $z=4$.

$K^{1/2}$	$\varrho^{1/2}$	RUS			$K^{1/2}$	$\varrho^{1/2}$	RUS		
		1	Model no. 2 a	2 b			1 a	Model no. 2 a	2 b
0.6	5.0	6.07	14.73	23.16	0.8	2	1.84	4.91	7.63
0.7	5.0	5.01	12.54	19.80	0.8	3	2.68	6.97	10.89
0.8	5.0	4.20	10.89	17.27	0.8	4	3.46	8.95	14.10
0.9	5.0	3.54	9.60	15.30	0.8	5	4.20	10.89	17.27
1.0	5.0	3.00	8.55	13.71	0.8	6	4.91	12.82	20.43
1.1	5.0	2.54	7.69	12.41	0.8	7	5.61	14.73	23.58
1.2	5.0	2.13	7.03	11.32	0.8	8	6.29	16.63	26.73

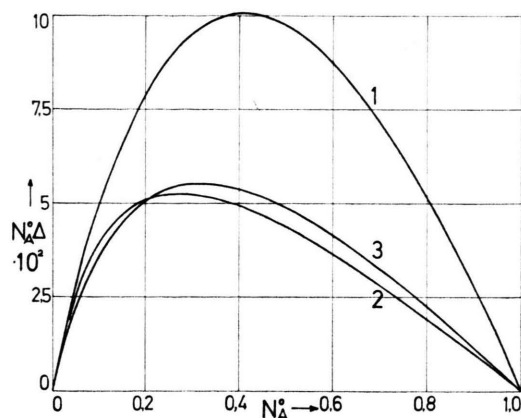


Fig. 1. Change on mixing of the number of associative A-A* bonds, $N_A^0 \Delta = f(N_A^0)$, calculated with $K^{1/2}=0.9$ and $\rho^{1/2}=4.5$. Curve 1 = model 1, curve 2 = model 2 b, curve 3 = model 2 a.

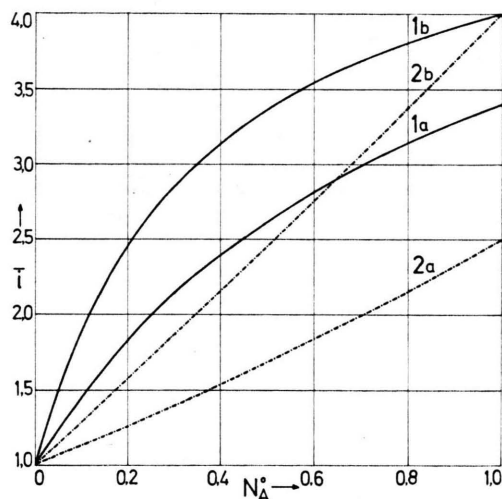


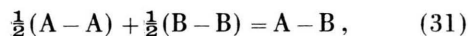
Fig. 2. Mean degree of association of A, $\bar{i} = f(N_A^0)$. Solid curves: Model 2 b; broken curves: Model 1. Calculated with $K^{1/2}=0.9$, $\rho^{1/2}=4.5$ (curves 1 a and 2 a), and with $K^{1/2}=0.8$, $\rho^{1/2}=9.0$ (curves 1 b and 2 b).

low N_A^0 and an asymptotic approach to a limiting value at high N_A^0 , which is in better accordance with experimental data.

Table 1 contains some calculated RUS values of models 1, 2 a, and 2 b, taking $z=4$. In all cases, RUS increases with increasing $\rho^{1/2}$, and with decreasing $K^{1/2}$, the ratio of the absolute values approximately being 1 : 2.5 : 4. RUS also depends on the coordination number z ; it rises when z decreases, and vice versa.

2. Contribution to G^E/RT of the Mutual Unspecific Solvation of A and B

In order to obtain the complete expression of G^E/RT , the contribution of mutual unspecific solvation of A and B, G_{solv}^E/RT , must be added to G_{ass}^E/RT . We first consider the simplest case that G_{solv}^E/RT is symmetric in N_A^0 . As we have shown previously¹, formation of a binary mixture with both components having the coordination number $z=1$, according to the exchange equilibrium



gives rise to an excess Gibbs free energy of

$$G_{\text{solv}}^E/RT = - \left[\frac{1}{2} N_{AB} + N_A^0 (1 - N_A^0) \right] \ln K \quad (32)$$

with

$$N_{AB} = K(K-s)/(K^2-1) \quad \text{and} \\ s = [K^2 + 4N_A^0(1-N_A^0)(1-K^2)]^{1/2}. \quad (33)$$

As we have established in the preceding papers¹⁻³, coupling of a 'chemical' and a 'statistical' equilibrium in Eq. (32) is required in order to obtain correct behaviour in liquid-liquid equilibria. Formation of a statistical mixture of A and B by proceeding from a less probable to a more probable state, and formation of nearest-neighbour pairs of molecules due to chemical interactions with decrease of Gibbs free energy, are two phenomena with independent causes. They only proceed in such a way that both, statistical order and Gibbs free energy of A-B pairing, are monotonously decreasing functions. As these two phenomena independently lead to the same equilibrium state, both contributions must be incorporated into G^E/RT .

Addition of Eq. (32), multiplied by z , to Eq. (5) leads to

$$G^E/RT = -z \left[\frac{1}{2} N_{AB} + N_A^0 (1 - N_A^0) \right] \ln K \\ - N_A^0 \Delta \ln \rho. \quad (34)$$

Simple addition of G_{solv}^E/RT and G_{ass}^E/RT in Eq. (34) means that solvation and self-association are assumed to be fully independent. This may be approximately true if no preferential solvation of the functional groups of A being responsible for self-association takes place. In other words, monomeric A and the associated species A_i are nearly equally well solvated by B. Such a behaviour is indicated in systems in which intensive cooling does not cause liquid-liquid phase separation. As a counterpart, we must consider the case that the functional groups of A

are specifically solvated by B, which means that there is strong competition between self-association and solvation, only non-associated A being specifically solvated by B. This can be accounted for by using an 'effective' equilibrium constant K^* , given by

$$K^* = K/\sqrt{1+\varrho}, \quad (35)$$

in G_{solv}^E/RT . Even in systems which exhibit liquid-liquid phase separation on cooling it is not very realistic to assume such a strong competition. An alternative, more flexible way which allows reducing competition to one (or two, resp.) contact sites of A is to express K^* by

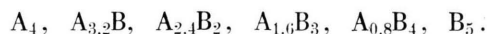
$$K^* = K \exp \{ -\varrho^{1/2} \ln \varrho/z(1+\varrho^{1/2}) \}; \quad (36)$$

K^* equals K if $\varrho \neq 0$ and if $\varrho = 1$, and corresponds to a molar Gibbs free energy of formation of one A-B pair of

$$\Delta G_{\text{AB}}/RT = -[\ln K - \varrho^{1/2} \ln \varrho/z(1+\varrho^{1/2})]. \quad (37)$$

Usually, the excess functions of binary liquid mixtures in which only unspecific mutual solvation occurs are endothermic and more or less unsymmetric. An important reason for this unsymmetry is the difference of the molar volumes, or molar contact surfaces, resp., of A and B. Numerous examples of experimental G^E and H^E data reveal that these functions are more endothermic if the component with the smaller contact surface is in excess, i.e. if 'endothermic solvation' of the component with the greater number of contact sites is more complete ('endothermic solvation' means that the energy parameters of pair interaction show a positive deviation from the arithmetic mean, i.e. $w = w_{\text{AB}} - (w_{\text{AA}} + w_{\text{BB}})/2 > 0$).

To make allowance for this effect, formation of nearest-neighbour complexes $A_i B_j$ with higher coordination numbers must be considered in G^E/RT . Retaining K as single equilibrium constant of A-B pairing, differences between the molar contact surfaces can be accounted for by attributing different coordination numbers, z_A and z_B , to both components, and assuming linear variation of z with the mole fraction of the mixture. As an example, we consider the case that $z_A = 3$ and $z_B = 4$, and that 6 different nearest-neighbour complexes will be formed:



As can be seen from the maximum ratio of the components in the 'mixed' complexes, being 5 : 1 for B : A, but only 3.2 : 1 for A : B, it is B which

has the smaller contact surface. If A and B had equal contact surfaces, the numbers of pair interactions in $A_{3.2}B$, $A_{2.4}B_2$, $A_{1.6}B_3$, and $A_{0.8}B_4$ would be 3.2 - 4.8 - 4.8 - 3.2, resp. As covering of the contact surface of A becomes more complete with increasing ratio B : A, we must change these figures in such a way that the resulting deviation from the 'symmetric' figures above falls linearly with N_B^0 , e.g. 1.6 - 3.0 - 3.6 - 2.8. These assumptions lead to the following expression for G_{solv}^E/RT :

$$G_{\text{solv}}^E/RT = -[0.8 N_{A_{3.2}B} + 1.5 N_{A_{2.4}B_2} + 1.8 N_{A_{1.6}B_3} + 1.4 N_{A_{0.8}B_4} + N_A^0(1 - N_A^0)] \ln K. \quad (38)$$

The contribution to the unsymmetry of G^E/RT of Eq. (38) is:

$$\begin{aligned} (1/RT) [(dG_{\text{solv}}^E/dN_A^0)_{(0)} + (dG_{\text{solv}}^E/dN_A^0)_{(1)}] \\ = [0.8(dN_{A_{3.2}B}/dN_A^0)_{(1)} - 1.4(dN_{A_{0.8}B_4}/dN_A^0)_{(0)}] \ln K. \end{aligned} \quad (39)$$

The right-hand side of (39) is positive, i.e. G_{solv}^E/RT has the greater positive, or, resp., the smaller negative limiting slope at $N_A^0 = 0$, if $K < 1$, which corresponds to an 'endothermic solvation'.

3. Comparison between Predicted and Experimental G^E/RT Data

In Figs. 3 and 4, some G^E/RT model curves are shown, as calculated by Eqs. (34), (10), or (29), taking $z = 4$ and $\varrho^{1/2} = 4.5$:

$$\begin{aligned} \frac{G^E}{RT} = -2 \left\{ \frac{K(K-s)}{K^2-1} + 2 N_A^0(1-N_A^0) \right\} \ln K \\ + \frac{4 N_A^0(1-N_A^0) K^{1/2} \varrho^{1/2} \ln \varrho}{[N_A^0(\varrho^{1/2}+3) + 4 K^{1/2}(1-N_A^0)](\varrho^{1/2}+3)}, \end{aligned} \quad (40)$$

$$\begin{aligned} \frac{G^E}{RT} = -2 \left\{ \frac{K(K-s)}{K^2-1} + 2 N_A^0(1-N_A^0) \right\} \ln K \\ + \frac{16 N_A^0(1-N_A^0) K^{1/2} \varrho^{1/2} \ln \varrho}{[N_A^0(5\varrho^{1/2}+3) + 4 K^{1/2}(1-N_A^0)](5\varrho^{1/2}+3)} \end{aligned} \quad (41)$$

(Model 1 = Eq. (40); Model 2 b = Equation (41)).

Change of sign, with positive values of G^E/RT at lower N_A^0 , and negative values at higher N_A^0 , occurs if $K > \text{ca. } 1.15$ (Model 1), and if $K > \text{ca. } 1.05$ (Model 2 b). The ordinate scale of model 1 is shifted by 0.15 to more positive G^E/RT values, as compared with model 2 b, and it is obvious that the former model exhibits less unsymmetry.

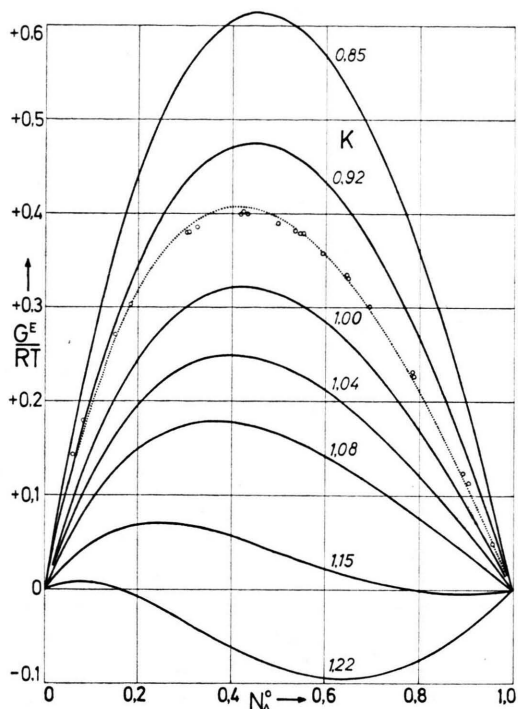


Fig. 3. $G^E/RT = f(N_A^0)$, according to model 1, with $z=4$ [Eq. (40)], calculated with $\rho^{1/2}=4.5$ and $K=0.85-0.92-1.00-1.04-1.08-1.15-1.22$ (solid curves). \circ Experimental values of G. C. Benson et al.¹² for cyclohexanol (A) - cyclohexane (B) at 25°C. Dotted curve: Least-squares fit with $K=0.98$ and $\rho^{1/2}=5.65$ (see Table 2).

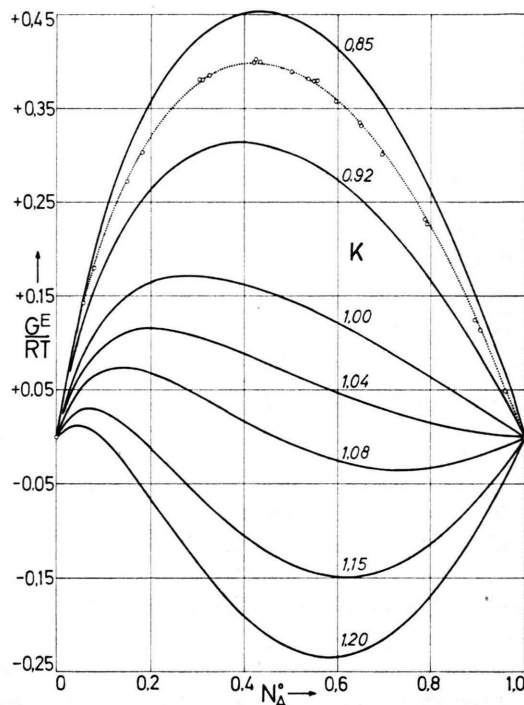


Fig. 4. $G^E/RT = f(N_A^0)$, according to model 2 b, with $z=4$ [Eq. (41)], calculated with $\rho^{1/2}=4.5$ and $K^{1/2}=0.85-0.92-1.00-1.04-1.08-1.15-1.20$ (solid curves). \circ Experimental values of Benson et al.¹² for cyclohexanol (A) - cyclohexane (B) at 25°C. Dotted curve: Least-squares fit with $K=0.877$ and $\rho^{1/2}=4.49$ (see Table 2).

For comparison, isothermal experimental G^E/RT data at 25°C of the system cyclohexanol (A)-cyclohexane (B), due to Benson et al.¹² are reproduced in Figs. 3 and 4, together with the theoretical curves obtained by a least-squares fit of K and ρ , using Eqs. (40) and (41), resp. Undoubtedly, the self-association which cyclohexanol undergoes in cyclohexane solution is not precisely chain-forming, particularly in concentrated solutions. From the fact that model 2 allows fitting of the experimental data within the limits of experimental error it may be

argued that a good approximation of the concentration dependence of self-association has been found.

More detailed results of a least-squares fit of models 1 and 2 b to isothermal G^E/RT data at 25°C on 4 different cycloalkanol-cycloalkane systems^{12, 13} are presented in Table 2. The sum of the squared deviations between experimental and calculated G^E/RT values,

$$U(K, \rho) = \sum_n (G_{\text{exp}}^E/RT - G_{\text{calc}}^E/RT)_n^2, \quad (42)$$

Table 2. Least-squares fit of models 1 and 2 b [Eqs. (40) and (41)] to isothermal experimental G^E/RT data at 25°C on 4 cycloalkanol-cycloalkane systems from Benson et al.^{12, 13}.

System:		No. of exptl. values	Model 1 [Eq. (40)]				Model 2 b [Eq. (41)]			
A	B		K	$\rho^{1/2}$	$10^4 \cdot U_{\text{min}}$	$\sigma \%$	K	$\rho^{1/2}$	$10^4 \cdot U_{\text{min}}$	$\sigma \%$
cy-C ₅ H ₉ OH	cy-C ₅ H ₁₀	14	0.965	5.12	5.04	1.54	0.874	4.25	0.712	0.59
cy-C ₅ H ₉ OH	cy-C ₆ H ₁₂	20	0.924	5.18	28.39	2.61	0.865	4.34	2.919	0.92
cy-C ₆ H ₁₁ OH	cy-C ₅ H ₁₀	19	0.995	5.93	12.79	2.18	0.887	4.72	3.752	1.24
cy-C ₆ H ₁₁ OH	cy-C ₆ H ₁₂	23	0.980	5.65	13.65	1.96	0.877	4.49	2.799	0.90

Table 3. Least-squares fit of model 2 a [Eq. (30)] and of the Wilson equation [Eq. (44)] to isothermal G^E/RT data at 25° on 4 cycloalkanol-cycloalkane systems, from Benson *et al.* [l. c.].

System:		No. of exptl. values	Model 2 a [Eq. (30)]				Wilson equation [Eq. (44)]			
A	B		K	$\rho^{1/2}$	$10^4 \cdot U_{\min}$	$\sigma \%$	A	B	$10^4 \cdot U_{\min}$	$\sigma \%$
cy-C ₅ H ₉ OH	cy-C ₅ H ₁₀	14	0.882	5.37	0.321	0.39	0.0833	0.657	0.491	0.49
cy-C ₅ H ₉ OH	cy-C ₆ H ₁₂	20	0.873	5.70	4.807	1.18	0.0685	0.616	6.822	1.41
cy-C ₆ H ₁₁ OH	cy-C ₅ H ₁₀	19	0.896	6.31	2.441	0.95	0.0634	0.789	1.965	0.86
cy-C ₆ H ₁₁ OH	cy-C ₆ H ₁₂	23	0.886	5.96	1.880	0.73	0.0680	0.712	1.819	0.72

has been minimized with respect to K and ρ by a numerical gradient procedure:

$$\partial U / \partial K = 0 \quad \text{and} \quad \partial U / \partial \rho = 0 \quad (U = U_{\min}). \quad (43)$$

The values of K and $\rho^{1/2}$ which correspond to U_{\min} , together with U_{\min} , and the per cent standard deviation, $\sigma\%$ (= p.c. of the maximum value of G^E/RT), are incorporated in Table 2. Comparison of U and σ of both models makes evident that model 2 b is much superior to model 1. The rather large differences between the prediction of model 1 and the experiment are beyond experimental error, indicating that systematic deviations of curve shape exist.

Table 3 presents the results of the application of model 2 a, and of the two-parameter Wilson equation¹⁴,

$$G^E/RT = -N_A^0 \ln [N_A^0 + A(1 - N_A^0)] - (1 - N_A^0) \ln [1 - N_A^0 + B \cdot N_A^0], \quad (44)$$

to the same cycloalkanol-cycloalkane systems as in Table 2. The standard deviations from the experiment of model 2 a are just as small as those of the Wilson equation, and, in both cases, are within the limits of experimental error. In contrast to our equilibrium models however, the Wilson equation suffers from the serious disadvantage that it is unable to predict limited miscibility.

Recently published isothermal G^E/RT data of Sayegh and Ratcliff¹⁶ on some pentanol-hexane systems (interpolated values in steps of 0.1 N_A^0)

Table 4. Least-squares fit of model 2 b to isothermal G^E/RT data at 25° on mixtures of n-pentanol and isopentanol with isomeric hexanes, according to Sayegh and Ratcliff¹⁶.

System:		K	$\rho^{1/2}$	$10^4 \cdot U_{\min}$	$\sigma \%$
A	B				
n-pentanol	n-hexane	0.8640	4.796	0.975	0.82
n-pentanol	2-Me-pentane	0.8642	4.739	1.824	1.12
n-pentanol	3-Me-pentane	0.8678	4.771	1.798	1.14
n-pentanol	2,2-Di-Me-butane	0.8647	4.667	0.834	0.76
n-pentanol	2,3-Di-Me-butane	0.8666	4.513	0.730	0.72
isopentanol	n-hexane	0.8603	4.292	0.087	0.24

may serve as a further test of model 2 b (see Table 4). Chain-branching of the alkane component causes a minor decrease of $\rho^{1/2}$ whilst K remains virtually unchanged. By chain-branching of pentanol, however, $\rho^{1/2}$ is markedly reduced.

One of the best examples of a liquid in which chain-forming self-association takes place, is N-methyl formamide (NMF). Table 5 presents the results obtained by applying model 2 b (with $z = 4$) to isothermal G^E/RT data at 45° on the systems NMF-CCl₄, and NMF-C₆H₆¹⁷. The much greater standard deviations in Table 5 are caused by a marked scattering of the experimental values, and not by the inability of the models to fit the data. For the same reason probably, no differences between the use of K or K^* can be detected. The calculated parameters K and $\rho^{1/2}$ indicate that CCl₄ is the poorer solvent and enhances self-association of NMF. This is also supported by the fact that the system NMF-CCl₄ has an upper critical solution temperature at 39.5 °C¹⁷.

Table 5. Application of model 2 b, with K [Eq. (41)], and with K^* [Eq. (36)], to isothermal G^E/RT data at 45 °C on the systems NMF-CCl₄, and NMF-C₆H₆, according to Messow, Quitzsch *et al.*¹⁷.

System:			with K				with K^*			
A	B	No. of exptl. values	K	$\rho^{1/2}$	$10^2 \cdot U_{\min}$	$\sigma \%$	K	$\rho^{1/2}$	$10^2 \cdot U_{\min}$	$\sigma \%$
NMF	CCl ₄	23	0.809	3.75	1.106	4.04	0.824	3.74	1.143	4.11
NMF	C ₆ H ₆	30	0.842	2.78	1.107	4.10	0.850	2.75	1.098	4.10

The chain association model presented in this paper can also be applied to systems in which only dimers of A are formed. To use model 2 b for dimerization, the stoichiometric relation (3) must be replaced by

$$N_A + 2 N_{A_2} = N_A^0, \quad (45)$$

and the change of the number of associative A – A* bonds when mixing N_A^0 moles of A with $(1 - N_A^0)$ moles of B to obtain one mole of mixture, is

$$N_A^0 \Delta = N_{A_2} - N_A^0 \cdot N_{A_2}^r. \quad (46)$$

Using Eqs. (6) and (20), with $z = 4$, one obtains

$$N_A = \alpha; \quad N_{A_2} = 2 \alpha^2; \\ \text{with } \alpha = \frac{N_A^0 \rho^{1/2}}{N_A^0 (\rho^{1/2} + 3) + 4 K^{1/2} (1 - N_A^0)}. \quad (47)$$

Inserting (47) into (46) yields

$$N_A^0 \Delta = 2 N_A^0 [\alpha / (1 + 4 \alpha) - \alpha_r / (1 + 4 \alpha_r)], \\ N_A^0 \Delta = \frac{-8 N_A^0 (1 - N_A^0) K^{1/2} \rho^{1/2}}{[N_A^0 (5 \rho^{1/2} + 3) + 4 K^{1/2} (1 - N_A^0)] (5 \rho^{1/2} + 3)}, \quad (48)$$

which differs from model 2 b [Eq. (29)] by a factor $\frac{1}{2}$ only.

In Table 6, the results of the application of Eq. (48), together with Eq. (34), to isothermal G^E/RT data on the system acetic acid-carbon tetrachloride at 20° and 40°¹⁸, are reproduced. For comparison, the chain association model 2 b [Eq. (41)] was fitted to the same data. Selectivity of the dimerization model for systems in which dimerization is predominant issues from the fact that this model gives the best fit with significantly smaller standard deviations. The least-squares fit by the Wilson equation [Eq. (44)], the results of which

are also incorporated in Table 6, is inferior to that obtained by the dimerization model.

From the examples given in this chapter it is evident that equilibrium models can serve as a powerful means of describing the excess Gibbs free energy and related thermodynamic quantities of binary mixtures in which chain association or dimerization of one component takes place. To summarize, the main features by which equilibrium models are characterized and which, in our opinion, make them superior to other empirical models for liquid mixtures, are pointed out:

(1) Equilibrium constants of well-chosen exchange equilibria among nearest-neighbour complexes, or among pairs of contacts sites, resp., prove to be advantageous parameters of theoretical models for the equilibrium properties of liquid mixtures. Their use allows reduction of the number of parameters needed to a minimum.

(2) Equilibrium models can selectively be adapted to the various types of intermolecular interactions in liquid mixtures and therefore allow examination of the validity of the model assumptions.

(3) Equilibrium models are consistent with equilibrium thermodynamics and can be applied to all equilibrium phenomena in liquid mixtures, including partial miscibility.

Part II of this paper which will be published forthcoming, will be concerned with the application of the chain association models presented here to the excess free enthalpies of mixing, and to liquid-liquid phase equilibria.

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Table 6. Least-squares fit of the dimerization model [Eqs. (34) and (48)], of model 2 b [Eq. (41)], and of the Wilson equation [Eq. (44)] to isothermal G^E/RT data at 20 °C and 40 °C on the system acetic acid-carbon tetrachloride, according to Kohler *et al.*¹⁸. (11 values of G^E/RT in 0.1 steps of N_A^0 , additionally 0.05 and 0.95.)

Model	Temperature °C	K (A)	$\rho^{1/2}$ (B)	$10^4 \cdot U_{\min}$	σ %
dimerization	20	0.8385	5.80	0.791	0.70
	40	0.8425	5.06	1.133	0.86
chain association (model 2 b)	20	0.8600	2.49	3.576	1.50
	40	0.8585	2.19	3.752	1.56
Wilson Eq. (Parameters A and B)	20	0.094	0.661	26.55	4.07
	40	0.181	0.530	5.104	1.82

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