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Estimation of excess enthalpy for binary systems

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Abstract

Based on the author's molecular thermodynamic model for solution structure, a new equation with three parameters for correlating the excess enthalpy of binary solutions is proposed. We make use of the group statistical theory, Lagrange undetermined multiplier method and a pseudo-chemical reaction mechanism. Tested by 6059 experimental data in 282 kinds of binary systems, the new model shows the characteristics of convenience and wide applicability. The accuracy of the new equation has an advantage over the Redlich–Kister equation [J. Chem. Ind. Eng. (China) 49 (1998) 103] and the Shen–Liu equation proposed recently [J. Chem. Ind. Eng. (China) 51 (2000) 181], both of which have three parameters too. As for the SSF equation with four parameters, the accuracy of it and the new equation is equivallent, some times the latter is more accurate. The new equation is still tenable in the limiting condition of $x \to 0$ and 1. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

Excess enthalpy is an important basic datum used in chemical engineering designs, solution theory and molecular thermodynamics. The measurement, correlation and theoretical research on excess enthalpy are the subject of very active research. For simple solutions with minute molecules, it can be predicted by means of computer simulation, Perturbation theory and state equations [1,2]. However, for many non-ideal solutions that are valuable in practical application, there are few reliable theoretical predicting models. Some modified UNIFAC models have been widely researched [3–9], but the predicted results are not satisfying. Empirical or semi-empirical correlation models are better in accuracy. At present the Redlich–Kister (RK) equation

$$H^{\mathrm{E}} = x(1-x)\sum_{i=1}^{k} A_i(2x-1)^i \tag{1}$$

and the SSF equation [10]

$$H^{\mathrm{E}} = \sum_{i=1}^{k}\left\{\frac{A_i x(1-x)}{[(x/B_i)+B_i(1-x)]^2}\right\} \tag{2}$$

are most widely used, but both of them are multinomial with undetermined parameters. The number of parameters needs to be determined by means of empirical trials. The Shen–Liu (SL) equation with three parameters [11,12] has a fixed form

$$H^{\mathrm{E}} = \frac{V_0\phi_1\phi_2 A_{12}}{\phi_1+\phi_2\zeta_{12}} + \alpha(V_0^{-h} - V_{\mathrm{m}}^{-h}) \tag{3}$$

$$h = \frac{x_1V_1 + x_2V_2\zeta_{12}}{V_{\mathrm{m}}} \tag{4}$$

$$V_0 = x_1V_1 + x_2V_2 \tag{5}$$

Besides three undetermined parameters, the SL equation demands molar volumes of the solution and the pure components to be known. The errors of correlation can be significant. Therefore, it is necessary to develop new correlation models.

In this paper, on the basis of the molecular thermodynamic model for solution structure suggested by the authors [13–18], a new equation for correlating the excess enthalpy of binary solution is obtained. The new equation is tested by numerous experimental data and compared with the traditional RK equation, SSF equation and the recent SL equation.

2. Derivation of the new equation

According to the molecular thermodynamic model for solution structure raised by authors [13–17], the properties of a solution are determined by the mutual connection and

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Nomenclature

a, b	model parameters
A, B	model parameters
A_{12}	model parameter
g	model parameter
h	Hildebrand parameter
H^{E}	excess enthalpy
K_{ij}	interaction energy between molecules
n	number of the fitting parameters
n_i	number of subcluster centers in ith subcluster
n_j	number of aggregative molecules in jth subcluster
$\bar{n}_1$	most probable group degree of subcluster centers in subcluster
$\bar{n}_2$	most probable group degree of aggregative molecules in subcluster
N	number of the experimental data points
P_i	probability of subcluster occurring with n_i subcluster centers
P_j	probability of subcluster occurring with n_j aggregative molecules
v	volume with which aggregative molecules occupy in subcluster
v_{m}	volume with which aggregative molecules occupy in subcluster when molecular membrane aggregates
V	mole volume
x	friction of mole

Greek symbols

α	model parameter
ϕ	friction of volume
ξ_{12}	model parameter

Subscripts

m	real liquid mixture
1, 2	component 1 and 2
0	supposed liquid mixture

restriction among all the molecules in the solution. This mutualism is a complex synergetic conduct, rather than the simple addition of the interaction of each molecule in the solution. Compared with pure liquid, the particularity of the composition and properties of solution lies in the molecular aggregates and the special interaction. Binary solutions may be regarded as an aggregate of many "subclusters". Each subcluster in turn is made up of several subcluster centers and the aggregative molecules. Subclusters are the basic structural units of solution with their composition and aggregating degree reflecting the macro-properties of the solution.

According to the group statistical theory, within unit volume of solution, using the Lagrange undetermined multiplier method, the most probable degree of grouping of the subcluster centers and aggregative molecules in subcluster are obtained as follows:

$$\bar{n}_1 = \sum n_i P_i = \sum n_i P_1^{n_i-1}(1 - P_1) \qquad (6)$$

$$\bar{n}_2 = \sum n_j P_j = \sum n_j P_2^{n_j-1}(1 - P_2) \qquad (7)$$

Rearranging Eqs. (6) and (7) gives

$$\bar{n}_1 = \frac{1}{1 - P_1} \qquad (8)$$

$$\bar{n}_2 = \frac{1}{1 - P_2} \qquad (9)$$

According to a pseudo-chemical reaction process, P_1 and P_2 can be expressed as

$$P_1 = \frac{K_{11}}{K_{11} + K_{12}x} \qquad (10)$$

$$P_2 = \frac{K_{22}x}{K_{22}x + K_{21}} \qquad (11)$$

Therefore, from Eqs. (8)–(11), we have

$$\bar{n}_1 = \frac{K_{12}x + k_{11}}{K_{12}x} \qquad (12)$$

$$\bar{n}_2 = \frac{K_{21} + k_{22}x}{K_{21}} \qquad (13)$$

If the effective volume of aggregative molecules is v_0, the general volume of aggregative molecules in a subcluster should be

$$v = \sum n_{2i} v_0 \qquad (14)$$

When the monomolecular membrane aggregates, it should correspondingly hold that

$$v_{\mathrm{m}} = \sum n_{1i} v_0 \qquad (15)$$

When the system reaches equilibrium, both n_1 and n_2 have the most probable distribution value $(\bar{n}_1, \bar{n}_2)$. Then Eqs. (12)–(15) gives

$$v = \frac{v_{\mathrm{m}} K_{12}x(K_{21} + K_{22}x)}{K_{21}(K_{12}x + K_{11})} \qquad (16)$$

From above-mentioned derivation, the symbol v is the volume that the aggregative molecules (i.e. solute molecules) occupy in the subcluster of the unit volume solution. Then v should be a function of solution composition and is defined by

$$v = f(x) \qquad (17)$$

Excess enthalpy is the difference between the enthalpy change when pure components form real mixtures and the enthalpy change when ideal mixtures are formed in the same conditions of temperature, pressure and composition. When ideal mixtures are formed, the enthalpy change is zero. Thus

$$H^{\mathrm{E}} = H - \sum x_i H_i \qquad (18)$$

For binary systems at constant temperature and pressure, the differential of Eq. (18) is

$$x\frac{\mathrm{d}H^{\mathrm{E}}}{\mathrm{d}x}=x\frac{\mathrm{d}H}{\mathrm{d}x}+(H_2-H_1)x \tag{19}$$

or generally

$$x\frac{\mathrm{d}H^{\mathrm{E}}}{\mathrm{d}x}=f'(x) \tag{20}$$

Eqs. (17) and (20) show that both v and $x(\mathrm{d}H^{\mathrm{E}}/\mathrm{d}x)$ are the functions of x, then $x(\mathrm{d}H^{\mathrm{E}}/\mathrm{d}x)$ is correspondingly related to v. Let

$$x\frac{\mathrm{d}H^{\mathrm{E}}}{\mathrm{d}x}=jv \tag{21}$$

Substituting Eq. (16) into Eq. (21) and integrating at constant temperature and pressure yields

$$H^{\mathrm{E}}=\frac{jv_{\mathrm{m}}K_{22}x}{K_{21}}+\frac{jv_{\mathrm{m}}}{K_{21}}\left(K_{21}-\frac{K_{11}K_{22}}{K_{12}}\right)\ln\left(1+\frac{K_{12}x}{K_{11}}\right) \tag{22}$$

For given systems, at constant temperature and pressure, the parameters of the new equation are defined as

$$a=\frac{jv_{\mathrm{m}}K_{22}}{K_{21}} \tag{23}$$

$$b=jv_{\mathrm{m}}\left(1-\frac{K_{11}K_{22}}{K_{21}K_{12}}\right) \tag{24}$$

$$g=\frac{K_{12}}{K_{11}} \tag{25}$$

Finally the new equation for calculating the excess enthalpy of binary systems is obtained

$$H^{\mathrm{E}}=ax+b\ln(1+gx) \tag{26}$$

3. Testing

Using a progressive approach, the optimal values of these parameters *a*, *b* and *g* in Eq. (26) were determined with the aid of experimental data.

As seen from Eqs. (23)–(25), and since v_{m} is the function of temperature, the parameters *a* and *b* are significantly affected by temperature, whereas *g* is insensitive to temperature. Thus, we can conveniently fit the parameters of this solution at another temperature with the optimal value at a given temperature. The parameters of partial systems can be seen in Table 1. For these binary systems composed of a certain constituent, the other one being a homologue, such as the systems numbered 18–22 in Table 1, it can be seen that the parameters *a*, *b*, *g* change follow the structure of the homologous chains regularly. This phenomenon provides a clue for predicting the parameters from an in-depth study.

In order to examine the wide applicability of the new equation proposed in this paper, it was tested by the experimental excess enthalpy data for 178 binary organic systems, 55 kinds of alcohol–hydrocarbon systems, 14 kinds of alcohol–water systems, 23 kinds of ketone–hydrocarbon systems and 12 kinds of alcohol–ketone systems. Partial results can be seen in Tables 2 and 3.

The standard deviation (S.D.) and the average relative deviation (ARD) between the calculated values by the new equation and the experimental data for the binary systems No. 1–31, which are numbered in Table 1, are shown in Table 2. In Table 2, there are also the corresponding deviations calculated by the RK equation with three parameters ($k = 3$), the SSF equation with four parameters ($k = 2$) and the SL equation with three parameters. The S.D. and ARD are respectively computed as follows:

$$\mathrm{S.D.}=\left[\sum_{i=1}^{N}\frac{(H^{\mathrm{E}}_{\mathrm{exp}}-H^{\mathrm{E}}_{\mathrm{cal}})^2_i}{N-n}\right]^{1/2} \tag{27}$$

$$\mathrm{ARD}=\frac{100}{N}\sum_{i=1}^{N}\frac{|H^{\mathrm{E}}_{\mathrm{exp}}-H^{\mathrm{E}}_{\mathrm{cal}}|}{H^{\mathrm{E}}_{\mathrm{exp}}} \tag{28}$$

For the systems No. 32–112 in Table 1, the ARD and S.D. of the experimental data and the results calculated by the new equation, the RK equation and the SSF equation are also listed in Table 2. From Table 2, it is clear that the new equation is better than the three-parameter RK equation and the SL equation. As to the comparison between the four-parameter SSF equation and the new equation, their accuracy is equivalent, and sometimes the latter is slightly more accurate. Of course, the RK equation and SSF equation can improve their correlating precision by adding to the number of parameters.

For alcohol–hydrocarbon, alcohol–ketone, alcohol–water, ketone–hydrocarbon and other binary organic systems, the experimental data and the values calculated by the new model were compared and the results are shown in Table 3. The overall ARD for 6059 data points of 282 kinds of systems is 2.01%. And the overall S.D. is 8.41 J mol^{-1}. Referring to the method of Tong et al. [19–21], the ternary systems can be treated with as pseudobinary system. The results of preliminary study are listed from No. 111 to 112 in Tables 1 and 2. Further extensive research will be carried out later.

4. Testing in the limiting condition

According to the definition of excess enthalpy, in the limiting condition of $x \to 0$ or 1, we have

$$\lim_{x\to 0} H^{\mathrm{E}}=0 \tag{29}$$

$$\lim_{x\to 1} H^{\mathrm{E}}=0 \tag{30}$$

Table 1
Parameters of the new model and the tested results in the limiting condition of $x \to 1$ for partial binary systems[a]

No.	Systems	Temperature (K)	*a*	*b*	*g*	Δ[b] (%)
1	2-Ethoxyethanol + 1,4-dioxane	298.15	−12169	26432	0.58443	−0.03
2	2-Ethoxyethanol + 1,2-dimethoxyethane	298.15	−3351.7	4022.0	1.3007	−0.02
3	Ethyl acetate + *n*-nonane	298.15	94089	671175	−0.13078	0.02
4	Ethyl acetate + *n*-undecane	298.15	55569	214789	−0.22785	0.05
5	Ethyl acetate + *n*-pentadecane	298.15	26038	40345	−0.47528	0.07
6	Ethyl pentanoate + *n*-pentane	298.15	−2971.5	2179.9	2.9767	1.26
7	Ethyl pentanoate + *n*-tridecane	298.15	47697	255729	−0.17010	0.03
8	Ethyl hexanoate + *n*-pentane	298.15	−2529.7	1802.1	3.0588	−0.21
9	Ethyl hexanoate + *n*-pentadecane	298.15	41394	198206	−0.18845	0.02
10	Ethyl heptanoate + *n*-undecane	298.15	−23009	87598	0.29999	−0.12
11	Methyl butyrate + *n*-dodecane	298.15	33426	94002	−0.29914	0.04
12	Methyl hexanoate + *n*-dodecane	298.15	173725	3541188	−4.7870E−2	0.01
13	Methyl heptanoate + *n*-dodecane	298.15	−45100	264992	0.18563	0.05
14	Quinoline + benzene	303.15	−1865.3	5638.9	0.38944	−0.57
15	Dimethylsulphoxide + 1-heptyne	298.15	1350.9	855.61	−0.77249	6.20
16	Methyl hexanoate + *n*-hexane	298.15	−10830	18435	0.79981	0.04
17	Methyl heptanoate + *n*-hexane	298.15	−8271.8	12286	0.96118	0.04
18	Methyl acetate + *n*-hexadecane	298.15	30203	47434	−0.47029	0.21
19	Methyl propionate + *n*- hexadecane	298.15	25631	41071	−0.46304	0.36
20	Methyl butyrate + *n*- hexadecane	298.15	21356	34336	−0.46250	0.18
21	Methyl hexanoate + *n*- hexadecane	298.15	25555	65684	−0.32227	0.01
22	Methyl heptanoate + *n*- hexadecane	298.15	71334	578932	−0.11589	0.03
23	Methyl propionate + *n*-octane	298.15	170212	2367394	−6.9369E-2	0.01
24	1-Butanol + isobutyl vinyl ether	298.15	−3781.6	1572.2	10.397	1.16
25	Isobutanol + isobutyl vinyl ether	298.15	−5795.4	3194.6	5.1963	0.54
26	1-Heptyne + sulfolane	303.15	10233	36029	−0.24809	0.40
27	1-Octyne + sulfolane	303.15	−2363.5	2404.3	1.7566	3.15
28	Methyl propionate + *n*-decane	298.15	49415	183168	−0.23628	0.09
29	Methyl butyrate + *n*-decane	298.15	70244	452280	−0.14383	0.02
30	Methyl hexanoate + *n*-decane	298.15	−35935	165245	0.24302	0.04
31	*n*-Methyl-2-pyrrolidinone + benzene	298.15	−75783	−1219195	−6.0339E-2	0.13
32	1-Octene+cyclohexane	298.15	−1717.1	1429.4	2.3441	0.49
33	*cis*-2-Hexene + cyclohexane	298.15	−2239.5	2954.3	1.1142	−1.20
34	*trans*-3-Hexene + cyclohexane	298.15	−1587.4	1723.9	1.4845	−1.18
35	1,5-Dichloropentane + 2-butanone	298.15	438.02	−319.57	2.8763	1.15
36	1,6-Dichloropentane + 2-pentanone	298.15	1074.7	−1372.6	1.1733	0.87
37	1,6-Dichlorohexane + acetone	298.15	−2682.9	3405.0	1.1963	−0.15
38	1,6-Dichlorohexane + 2-heptanone	298.15	400.54	−259.56	3.5703	0.01
39	Methyl valerate + *n*-decane	298.15	−390184	1.6848E+7	2.3429E-2	0.00
40	Methyl pentanoate + *n*-octane	298.15	−38305	180397	0.23660	0.01
41	Cyclohexane + *n*-decane	298.15	2340.1	2041.1	−0.68231	−0.02
42	Isopropylbenzene + toluene	298.15	−1118.1	1463.4	1.1521	0.31
43	Isopropylbenzene + toluene	308.15	−1016.9	1334.1	1.1521	0.55
44	Isopropylbenzene + toluene	318.15	−946.78	1239.2	1.1521	0.32
45	Isopropylbenzene + benzene	298.15	−1058.7	1326.4	1.2300	0.48
46	Isopropylbenzene + benzene	308.15	−968.61	1215.4	1.2300	0.63
47	Isopropylbenzene + benzene	318.15	−883.29	1109.2	1.2300	0.71
48	Tetrahydropyran + *n*-hexane	298.15	35432	280803	−0.11852	0.02
49	Tetrahydropyran + *n*-heptane	298.15	16248	54512	−0.25770	0.02
50	Tetrahydropyran + *n*-octane	298.15	13125	33189	−0.32656	0.03
51	Tetrahydropyran + *n*-nonane	298.15	8935.8	14313	−0.46470	−0.01
52	Cyclohexanone + benzene	298.15	−9886.5	−42677	−0.20670	−0.04
53	Cyclohexanone + isopropylbenzene	298.15	−2924.3	−20216	−0.13470	0.02
54	Cyclohexanone + *m*-dimethylbenzene	298.15	−427.36	371.48	2.2563	2.62
55	Cyclohexanone + bromobenzene	298.15	11153	−31594	0.42230	0.21
56	Cyclohexanone + chlorobenzene	298.15	13304	−42913	0.36330	0.03
57	2-Pyrrolidinone + ethanol	303.15	−2528.5	1518.6	4.3990	1.27
58	2-Pyrrolidinone + 1-propanol	303.15	−5707.7	4326.3	2.6881	−1.07
59	2-Pyrrolidinone + 1-butanol	303.15	−6682.5	5683.6	2.2545	0.36
60	Methanol + isopropanol	298.15	−1333.5	−977.40	−0.77265	8.57
61	Ethanol + isopropanol	298.15	−4291.9	−18847	−0.20373	0.39
62	1-Propanol + isopropanol	298.15	−205738	−7.6448E+7	−2.6876E−3	0.00
63	1−Butanol + isopropanol	308.15	−940.44	−5391.3	−0.16010	0.02

Table 1 (*Continued*)

No.	Systems	Temperature (K)	a	b	g	Δ^{b} (%)
64	1-Pentanol + isopropanol	313.15	762.98	1846.3	−0.33855	−0.02
65	1-Hexanol + isopropanol	298.15	1192.0	1945.7	−0.45832	−0.08
66	1-Propanol + 1-heptanol	298.15	1932.5	4466.2	−0.35140	−0.06
67	1-Chloronaphthalene + dichloromethane	298.15	−2299.7	2145.7	1.9243	0.12
68	1-Chloronaphthalene + 1,10-dichlorodecane	298.15	−13392	−26389	−0.39825	0.08
69	*N*,*n*-Dimethylformamide + toluene	303.15	2205.1	3195.5	−0.49066	2.23
70	Methyl *tert*-butyl ether + 2,3-dimethylbutane	298.15	−23418	222001	0.11125	−0.01
71	Methyl *tert*-butylether + 2,2,4-trimethylpentane	298.15	10824	47002	−0.20571	−0.01
72	Nitromethane + 1-hexanol	298.15	119983	686976	−0.15970	0.38
73	Bromochloromethane + tetrachloromethane	298.15	−61201	782900	0.081358	0.06
74	Bromochlorobutane + tetrachloromethane	298.15	−947.65	485.89	5.9523	−0.58
75	1-Chlorooctane + 1-pentanol	298.15	6681.6	5908.6	−0.65176	6.72
76	1-Chlorooctane + 1-hexanol	298.15	5961.8	4590.5	−0.70293	6.54
77	1-Chlorooctane + 1-heptanol	298.15	5499.3	3983.5	−0.72200	7.27
78	1-Chlorooctane + 1-octanol	298.15	5469.2	3942.8	−0.72598	6.67
79	2-Butanol + trichloromethane	298.15	−4924.7	2800.5	4.5500	−2.54
80	*tert*-Butanol + trichloromethane	298.15	−5779.3	3944.1	3.3000	0.45
81	Isobutane + 2-methylpropene	298.15	−19708	488030	4.1211E−2	0.00
82	Isobutane + 2-methylpropene	323.5	67068	6176170	−1.0800E−2	0.00
83	Tetrahydropyran + tetrachloroethane	300.05	−14730	−16279	−0.60500	2.65
84	*n*-Propyl acetate + *n*-undecane	298.15	56669	273836	−0.18697	−0.02
85	*n*-Propyl acetate + *n*-heptadecane	298.15	30303	61214	−0.39000	0.15
86	*n*-Propyl propionate + *n*-undecane	298.15	88987	887948	−9.5351E−2	0.01
87	*n*-Propyl propionate + *n*-heptadecane	298.15	27053	62511	−0.35086	0.15
88	*n*-Propyl butyrate + *n*-heptadecane	298.15	25342	61624	−0.33704	0.05
89	Ethanediol + water	323.15	3502.9	−1950.2	4.8950	1.23
90	1,2-Propanediol + water	338.15	2004.2	−726.00	14.598	0.48
91	Benzene + isopropanol	283.15	6813.0	6266.2	−0.65371	2.46
92	Cyclohexane + isopropanol	288.15	9621.9	19257	−0.39000	1.07
93	Cyclohexane + 1-butanol	298.15	3312.5	2226.7	−0.76250	3.37
94	Methyl hexanoate + *n*-pentadecane	298.15	30274	94249	−0.27459	0.06
95	Methyl heptanoate + *n*-pentadecane	298.15	43206	212491	−0.18396	0.01
96	Methyl decanoate + *n*-pentadecane	298.15	−39106	231201	0.18434	0.02
97	Methyl dodecanoate + *n*-pentadecane	298.15	−20849	76719	0.31222	−0.01
98	Methyl pentadecanoate + pentadecane	298.15	−8793.3	17093	0.67288	0.02
99	Ethyldiethanolamine + water	298.15	8336.6	−3751.2	8.2000	0.14
100	1-Heptene + methyl *tert*-butyl ether	308.15	−5760.9	25455	0.25326	−0.25
101	1-Hexene + methyl *tert*-amyl ether	308.15	1358.4	3494.2	−0.32285	−0.28
102	2,2,4-Trimethylpentane + methyl *tert*-butyl ether	308.15	−5409.4	12919	0.51982	−0.03
103	Water + acetonitrile	293.15	−4856.4	3037.0	3.8201	−1.64
104	Water + *n*-butylamine	303.15	−4709.4	6140.8	1.1502	−0.18
105	Water + methanol	315.15	−2373.0	−934.18	−0.92951	4.41
106	Water + phenol	333.15	9095.2	12759	−0.50879	0.27
107	Water + 1,3-propanediol	298.15	−2784.2	−1131.5	−0.91510	0.23
108	Water + triethylamine	283.15	−12114	−7497.2	−0.79010	−3.38
109	Water + hexamethyltriamidephosphoric acid	298.15	−10873	−3824.0	−0.94020	−0.94
110	Methyl *tert*-butyl ether + diisopropyl ether	298.15	1210.7	7658.4	−0.14632	−0.07
111	Decane(1) + methyl *tert*-butyl ether(2) + diisopropyl ether(3) (at $x_2/x_3 = 1.0179$)	298.15	−89582	24573	0.44000	0.02
112	Decane(1) + methyl *tert*-butyl ether(2) + diisopropyl ether(3) (at $x_2/x_3 = 3.0209$)	298.15	−90455	22721	0.48904	0.00

[a] The pressure is 5 MPa in the system 81, 10 MPa in the system 82, and 0.1 MPa in other systems.
[b] $\Delta = ([a + b\ln(1+g)]/a) \times 100\%$.

As seen from Eq. (26), in the limiting condition of $x \to 0$, Eq. (29) is tenable. In the limiting condition of $x \to 1$, according to chemical engineering thermodynamics, the differential of Eq. (26) is

$$\overline{H}_i^{\mathrm{E}} = \left[\frac{\partial (nH^{\mathrm{E}})}{\partial n_i}\right]_{T,P,n_j} \tag{31}$$

yielding

$$\overline{H}_i^{\mathrm{E}} = a + b\ln(1 + gx_i) + \frac{bg(1 - x_i)}{1 + gx_i} \tag{32}$$

For pure component

$$\lim_{x\to 1} \overline{H}_1^{\mathrm{E}} = \lim_{x\to 1} H_1^{\mathrm{E}} = 0 = a + b\ln(1+g) \tag{33}$$

Table 2
Calculated results of excess enthalpy for partial systems by new equation and the comparison with other equations

No.	ARD (%)				S.D. (J mol^{-1})				Experimental data	
	New equation	RK equation	SSF equation	SL equation	New equation	RK equation	SSF equation	SL equation	Data sets	Reference
1	2.34	2.78	2.53	2.79	6.60	6.28	5.98	6.88	21	[22]
2	1.16	1.27	1.25	1.25	1.63	1.54	1.60	1.62	21	[22]
3	0.61	0.85	0.56	0.80	7.58	8.68	7.63	8.37	19	[23]
4	0.96	1.41	0.88	1.46	12.2	14.5	12.1	14.6	19	[23]
5	1.53	2.02	1.40	2.01	23.6	24.3	23.5	24.6	19	[23]
6	1.07	1.84	1.64	3.99	4.34	6.11	5.41	12.4	17	[23]
7	0.80	1.26	0.79	1.46	7.90	8.61	8.11	9.54	16	[23]
8	1.36	3.34	1.64	1.64	4.42	7.27	4.42	4.47	18	[23]
9	0.90	1.19	1.19	1.14	8.32	8.43	8.75	8.48	17	[23]
10	0.70	1.92	0.64	2.19	3.98	6.64	3.98	8.15	17	[23]
11	0.96	1.22	0.91	1.21	9.33	10.2	9.31	10.1	19	[24]
12	1.93	1.93	1.95	2.47	23.4	23.4	23.7	23.9	20	[24]
13	1.22	0.95	1.03	1.64	6.01	5.90	6.44	8.83	20	[24]
14	5.90	5.92	5.39	9.96	3.64	3.86	3.79	4.71	9	[25]
15	1.92	4.94	1.38	3.06	6.13	16.0	5.14	10.7	10	[26]
16	1.51	1.56	1.01	1.56	8.38	7.93	6.07	8.79	20	[27]
17	1.23	1.34	0.81	1.36	5.72	6.05	4.12	6.06	20	[27]
18	1.84	3.16	3.04	3.27	32.6	36.0	35.7	37.2	20	[28]
19	1.34	2.80	1.03	2.63	18.1	32.4	15.7	31.4	20	[28]
20	0.92	1.92	0.82	1.82	11.5	16.7	9.38	15.8	20	[28]
21	0.49	0.53	0.52	0.54	6.69	6.73	6.98	6.74	16	[28]
22	1.10	1.70	0.94	1.71	7.69	10.3	7.48	10.4	18	[28]
23	0.92	1.13	0.85	1.29	9.96	10.1	8.11	10.4	20	[29]
24	2.52	6.60	0.42	4.33	23.8	57.5	3.17	39.1	12	[30]
25	2.27	3.73	1.53	5.15	27.8	41.7	8.18	39.6	11	[30]
26	2.51	2.78	2.41	3.95	8.58	9.23	8.78	10.7	21	[31]
27	2.58	2.58	2.41	3.59	9.10	11.6	9.08	10.9	15	[31]
28	1.44	1.88	0.93	2.11	13.9	17.9	12.3	19.6	20	[32]
29	0.65	1.08	0.63	1.07	7.39	8.15	7.46	8.14	18	[32]
30	0.59	0.79	0.46	1.08	3.78	4.34	3.65	5.56	20	[32]
31	0.51	0.99	0.45	1.50	2.83	5.48	2.84	8.25	12	[33]
32	0.42	0.55	0.36		1.26	1.44	1.36		9	[34]
33	0.27	0.44	0.26		0.69	1.04	0.72		6	[34]
34	0.59	1.36	0.49		1.10	2.33	1.18		6	[34]
35	3.54	3.55	3.57		1.53	1.56	1.56		15	[35]
36	3.90	5.76	5.75		2.58	2.63	2.76		14	[35]
37	2.95	3.68	3.49		4.81	5.03	5.02		18	[35]
38	4.86	7.54	7.64		2.01	2.05	2.05		14	[35]
39	0.43	0.81	0.41		3.93	4.93	4.01		18	[32]
40	0.64	0.74	0.75		4.79	4.86	4.96		17	[29]
41	1.18	1.72	1.18		2.15	2.78	2.08		22	[36]
42	0.62	0.57	0.54		0.67	0.66	0.67		9	[37]
43	0.74	0.69	0.70		0.76	0.68	0.64		10	[37]
44	0.45	0.48	0.42		0.42	0.42	0.42		10	[37]
45	0.52	0.98	1.03		0.29	0.30	0.33		11	[37]
46	0.75	1.04	0.97		0.27	0.28	0.28		10	[37]
47	0.94	1.14	1.13		0.26	0.29	0.30		11	[37]
48	0.86	0.91	0.83		4.56	4.61	4.71		16	[38]
49	1.14	1.18	1.19		6.39	6.46	6.77		13	[38]
50	1.01	1.04	0.98		4.61	4.75	4.75		15	[38]
51	0.89	0.92	1.01		5.62	5.80	5.91		15	[38]
52	2.12	2.22	2.22		5.32	5.51	5.87		12	[39]
53	5.01	5.41	5.76		2.01	2.08	2.15		14	[39]
54	4.65	5.51	4.63		2.84	3.14	2.96		14	[39]
55	2.46	3.01	2.96		9.98	11.6	12.1		16	[39]
56	1.20	1.34	1.32		5.59	5.70	5.90		16	[39]
57	3.41	4.27	3.57		14.9	17.3	4.56		11	[40]
58	0.60	0.96	0.39		4.86	6.76	3.15		10	[40]
59	0.88	1.26	0.91		9.53	11.7	8.27		11	[40]
60	1.77	3.27	0.63		2.34	4.86	1.48		9	[41]
61	0.72	0.67	0.63		0.53	0.46	0.47		11	[41]

Table 2 (*Continued*)

No.	ARD (%)				S.D. (J mol^{-1})				Experimental data	
	New equation	RK equation	SSF equation	SL equation	New equation	RK equation	SSF equation	SL equation	Data sets	Reference
62	0.51	0.34	0.42		0.32	0.30	0.33		15	[41]
63	0.18	0.29	0.27		0.04	0.05	0.05		13	[41]
64	0.94	0.80	0.75		0.35	0.31	0.33		10	[41]
65	1.21	1.16	1.02		1.13	1.10	1.13		11	[41]
66	0.32	0.28	0.26		0.29	0.28	0.28		18	[42]
67	1.50	5.87	3.99		1.98	5.31	4.36		15	[43]
68	0.82	1.54	0.87		5.09	6.06	5.57		16	[43]
69	1.69	3.36	1.78		3.21	6.95	3.20		15	[44]
70	0.73	0.85	0.85		1.70	1.71	1.76		21	[45]
71	0.85	0.91	0.91		1.83	1.85	1.90		20	[45]
72	1.74	4.95	2.09		28.6	51.0	23.7		14	[46]
73	1.56	2.31	1.51		6.85	9.36	6.94		16	[47]
74	1.60	5.64	3.23		2.68	6.36	3.76		13	[47]
75	1.73	7.79	1.56		9.95	53.8	8.30		20	[48]
76	2.27	9.37	1.94		12.5	62.4	9.11		20	[48]
77	1.31	8.77	0.91		12.3	70.4	7.24		20	[48]
78	1.29	7.62	0.72		12.0	65.2	6.14		20	[48]
79	8.88	11.2	7.12		29.8	41.4	31.2		24	[49]
80	3.94	7.23	4.86		27.8	37.5	22.9		24	[49]
81	0.67	0.77	0.60		0.34	0.37	0.39		25	[50]
82	0.32	0.37	0.32		0.19	0.20	0.20		26	[50]
83	0.45	1.33	0.48		7.52	15.8	6.10		11	[51]
84	0.67	0.92	0.86		8.91	9.07	9.22		16	[52]
85	0.48	1.00	0.52		7.62	10.7	8.17		16	[52]
86	0.76	0.85	0.85		7.29	7.41	7.74		17	[52]
87	0.77	1.33	0.67		9.40	12.9	9.48		17	[52]
88	1.11	1.71	1.70		11.9	11.9	12.3		17	[52]
89	1.11	3.37	2.12		5.92	14.1	9.11		18	[53]
90	1.89	7.21	1.81		8.98	23.2	5.22		18	[53]
91	1.19	3.17	1.39		7.84	24.0	9.42		16	[54]
92	0.99	1.69	1.00		5.43	11.0	5.83		14	[54]
93	0.73	4.12	0.88		3.51	18.2	4.42		14	[54]
94	0.66	1.09	0.52		5.27	6.82	5.27		18	[55]
95	0.47	0.56	0.56		4.01	4.23	4.25		17	[55]
96	0.42	0.79	0.39		3.23	3.89	3.34		18	[55]
97	1.01	0.96	0.96		4.32	4.34	4.46		16	[55]
98	0.60	0.64	0.63		2.02	2.07	2.05		17	[55]
99	2.08	6.67	2.16		30.7	82.3	30.5		15	[56]
100	0.86	1.32	0.82		1.25	1.66	1.28		21	[57]
101	2.39	3.47	2.39		1.09	1.39	1.12		20	[57]
102	1.83	1.95	1.95		3.70	3.71	3.81		23	[57]
103	34.9	97.8	30.1		35.0	58.3	40.6		14	[58]
104	1.15	1.08	1.09		3.15	3.54	3.35		19	[58]
105	3.06	6.35	3.59		9.50	18.7	10.7		19	[58]
106	4.52	7.74	7.50		21.3	22.0	22.8		13	[58]
107	3.01	7.37	1.85		15.4	28.9	9.75		32	[58]
108	1.47	2.98	1.13		49.1	90.8	40.0		8	[58]
109	2.29	6.32	1.17		59.5	177	45.0		15	[58]
110	0.16	0.22	0.23		1.03	1.79	1.71		21	[19]
111	0.43	0.48	0.49		1.36	1.27	1.27		20	[19]
112	0.48	0.48	0.48		1.69	1.66	1.71		20	[19]

It is obvious that if this new model is tenable under the limiting condition of $x \to 1$, a necessary condition is needed as follows:

$$a = -b \ln(1+g) \tag{34}$$

As seen from Table 1, when $g > 0$, a and b are of opposite sign and Eq. (34) is possibly tenable. When $g < 0$, a and b have identical sign. Eq. (34) is still possibly tenable since $\ln(1+g) < 0$. This is only a qualitative discussion. In order to prove the rationality of Eq. (34) quantitatively, the values

Table 3
Overall results for a wide variety of systems with the new model

Class of systems	Number of systems	ARD (%)	S.D. ($\mathrm{J\,mol^{-1}}$)	Data sets	Reference
Alcohol + hydrocarbon	55	3.01	9.86	1654	[41,42,46,48,49,54,60–62]
Alcohol + ketone	12	2.02	8.14	233	[40,63,64]
Alcohol + ester	19	1.88	8.05	308	[22,30,65]
Alcohol + water	14	4.63	20.3	463	[53,56,58,66]
Ketone + hydrocarbon	23	2.83	4.05	371	[33,35,39,44,46,67,68]
Other oxyorganic + hydrocarbon	118	1.01	8.28	2149	[23,24,27–29,32,38,45,51,52,55,57,59,69–78]
Other binary organics	41	0.91	1.78	881	[25,26,31,34,36,37,43,44,47,50,60,79–83]
Total	282	2.01	8.41	6059	

of $b\ln(1+g)$ are obtained by use of the values of a, b and g for the systems in Table 1. and are compared with the values of a by

$$\Delta=\left\{\frac{[a+b\ln(1+g)]}{a}\right\}\times 100\% \tag{35}$$

The results of this comparison are listed in the last column of Table 1. The results are consistent with Eq. (34). Therefore, the limiting condition of $x \to 1$ for this new model is still tenable.

5. Conclusions

On the basis of the molecular thermodynamic model for solution structure, a new equation with three parameters for correlating the excess enthalpy of binary solution is proposed. This uses the group statistical theory, Lagrange undetermined multiplier method and a pseudo-chemical reaction mechanism.The new model was tested by the experimental data of 282 kinds of binary systems. The new equation is simple, convenient and has a wide applicability. For the tested data, the new equation is more accurate than the three-parameter RK equation and SL equation. As for the comparison with the four-parameter SSF equation, its accuracy is equivalent, and sometimes the new model is better.

This new model is still tenable in the limiting conditions of $x \to 0$ and 1.

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