January, 1982] © *1982 The Chemical Society of Japan* *Bull. Chem. Soc. Jpn.*, ***55***, *23—27 (1982)* 23

Analysis of the Excess Gibbs Energies of Binary Mixtures Using Non-randomness Factors Determined from Excess Volume Data

Masanao Kato
Department of Chemistry, Faculty of Science, Tohoku University, Sendai 980

(Received March 28, 1981)

An analytical equation for the excess Gibbs energies of mixtures was derived on the basis of the non-random two-liquid model, which was applied to the derivation of an analytical equation for excess volumes proposed by the present author. The derived equation involves new adjustable parameters of intermolecular interaction. The validity of the equation was examined for 13 binary mixtures by using the non-randomness factors determined from the excess volume data, and it was shown that the calculated excess Gibbs energies were in good agreement with the observed values. The sequence of the values of the interaction parameters seems to be reasonable.

Recently, the present author found that the excess volumes of multi-component mixtures could be analyzed by an equation containing non-randomness factors as adjustable parameters, and showed that sufficient agreements were obtained between the calculated and the observed values of the excess volumes of binary and ternary mixtures.[1,2] The non randomness factors can be considered to represent the nonideality of the molecular rearrangement of the component molecules in the vicinity of a given molecule. On the other hand, the excess Gibbs energies of multicomponent mixtures have also been analyzed by an equation containing the parameters analogous to the non-randomness factor.[3–6] These parameters have been assessed to be very useful in representing the excess Gibbs energies of mixtures and widely utilized in chemical engineering. As the parameter in the equation for excess Gibbs energy is considered to have physical meanings similar to that for the excess volume, it is expected that the non-randomness factors determined from the excess-volume data can be applied to represent the excess Gibbs energies of the mixtures.

From the considerations above, the purpose of this study is to examine the applicability of the non-randomness factors in the excess-volume equation to the representation of excess Gibbs energies. The non-randomness factors at 298.15 K were determined from the excess-volume data previously reported.[1,2] On the other hand, the data for the excess Gibbs energies at the same temperature are not utilized. As the temperature dependence of the non-randomness factors was not entirely well-defined, the excess Gibbs energies at 298.15 K were measured from the vapor pressures of the mixtures.

Experimental

All the materials were guaranteed reagents of commercial origin and were purified by the distillation of 80 theoretical plates. The middle portions were collected and provided for measurements. The observed values of density, vapor pressure, and refractive index of the purified reagents were in good agreement with the literature values.[7,8]

The vapor-pressure measurements were carried out at 298.15±0.001 K by means of an apparatus constructed at our laboratory.[9,10]

The compositions of the liquid and the vapor phases were individually determined from refractive indexes measured by means of an Abbe refractometer for the methanol+benzene, ethanol+*m*-xylene, ethanol+benzene, ethanol+cyclohexane, acetone+cyclohexane, and benzene+cyclohexane mixtures. The compositions of the 1,2-dichloroethane+benzene and 1,2-dichloroethane+cyclohexane mixtures were determined from density measurements made by means of a pycnometer, while those of ethanol+acetone mixtures were determined from their ultra-violet spectra. The accuracy was ±0.02 for the mole fractions determined from the refractive-index and density measurements, and ±0.05 for those from spectrometry.

Results and Discussion

The excess Gibbs energies, g^{E}/RT, were calculated from Eq. 1:

$$g^{E}/RT = \sum_{i} x_i \ln \gamma_i, \tag{1}$$

while the activity coefficient, γ_i, of the *i*-th component was determined from Eq. 2:

$$\ln \gamma_i = \ln \frac{p y_i}{x_i p_i^*} + \frac{(B_{ii} - v_i^*)(p - p_i^*)}{RT} + \frac{(1 - y_i) p \delta}{RT}, \tag{2}$$

where

$$\delta = 2B_{ij} - B_{ii} - B_{ij}. \tag{3}$$

In Eqs. 1 to 3, x_i denotes the mole fraction of the liquid phase; R, the gas constant; T, the temperature; p, the total pressure; y_i, the mole fraction of the vapor phase; p_i^*, the vapor pressure of the pure i component; B_{ii}, the virial coefficient of the i component; B_{ij}, the cross-virial coefficient between the i and j components, and v_i^*, the molar volume of the pure i component. The virial coefficients were calculated from the empirical equation reported by O'Connell and Prausnitz.[11]

The observed vapor pressures of mixtures and the excess Gibbs energies are summarized in Table 1 as a function of the liquid-phase composition. The excess Gibbs energy for each mixtures was fitted with Eq. 4 according to the ordinary method:

$$g^{E}/RT = x_1 x_2 \sum_{r=0}^{4} A_r (x_1 - x_2)^r, \tag{4}$$

where x_1 and x_2 are the mole fractions of the first and second components respectively. The values of the A_r coefficients, as determined by the least-squares procedure, are summarized in Table 2, along with the values of σ_g, the standard deviation between the experimental and calculated values of g^{E}/RT.

TABLE 1. OBSERVED EXCESS GIBBS ENERGIES AT 298.15 K

x_1	y_1	$\frac{p}{\text{mmHg}^{a)}}$	g^E/RT
Methanol(1)+benzene(2)			
0.063	0.334	170.74	0.352
0.223	0.371	181.00	0.529
0.415	0.399	182.48	0.538
0.527	0.419	181.79	0.476
0.608	0.443	179.60	0.410
0.678	0.467	176.59	0.338
0.787	0.525	168.84	0.206
0.837	0.581	161.92	0.146
0.882	0.645	154.22	0.090
0.958	0.818	138.39	0.017
Ethanol(1)+acetone(2)			
0.128	0.047	211.76	0.033
0.234	0.082	202.45	0.081
0.360	0.134	188.35	0.125
0.527	0.176	169.00	0.090
0.558	0.203	159.59	0.088
0.595	0.217	157.76	0.097
0.663	0.268	139.39	0.061
0.800	0.381	118.94	0.061
0.925	0.650	83.73	0.039
Ethanol(1)+*m*-xylene(2)			
0.033	0.731	31.98	0.146
0.133	0.821	45.87	0.320
0.260	0.849	50.30	0.421
0.277	0.859	50.77	0.398
0.362	0.862	52.25	0.466
0.562	0.877	54.01	0.465
0.630	0.886	54.67	0.430
0.652	0.891	54.94	0.412
0.778	0.910	56.70	0.319
0.842	0.916	57.49	0.258
Ethanol(1)+benzene(2)			
0.090	0.253	120.41	0.195
0.208	0.291	124.36	0.352
0.324	0.305	124.40	0.424
0.461	0.326	123.37	0.443
0.545	0.340	122.52	0.427
0.660	0.375	117.50	0.362
0.750	0.409	112.92	0.292
0.917	0.632	85.60	0.117
0.959	0.766	73.38	0.058
Ethanol(1)+cyclohexane(2)			
0.068	0.293	134.71	0.196
0.188	0.332	139.06	0.395
0.248	0.332	139.23	0.461
0.315	0.332	139.35	0.512
0.330	0.336	139.30	0.520
0.461	0.340	138.64	0.550
0.584	0.350	137.66	0.523
0.653	0.357	136.21	0.481
0.737	0.378	133.36	0.417
0.784	0.385	129.78	0.347
0.842	0.421	122.78	0.257
0.897	0.475	111.17	0.180
Acetone(1)+cyclohexane(2)			
0.120	0.543	192.52	0.175
0.204	0.654	228.22	0.242
0.366	0.682	248.29	0.402
0.501	0.703	255.06	0.434
0.660	0.730	259.77	0.396
0.703	0.719	259.53	0.370
0.899	0.829	255.30	0.165
0.949	0.882	247.82	0.087
Benzene(1)+cyclohexane(2)			
0.098	0.141	102.17	0.040
0.227	0.276	106.29	0.086
0.322	0.362	108.04	0.107
0.439	0.462	109.12	0.123
0.528	0.519	109.26	0.128
0.613	0.579	108.72	0.123
0.773	0.714	105.92	0.095
0.828	0.763	104.07	0.076
0.930	0.887	99.55	0.037
1,2-Dichloroethane(1)+benzene(2)			
0.107	0.096	92.29	-0.006_6
0.267	0.226	90.45	-0.000_9
0.348	0.305	89.25	0.001_4
0.455	0.422	87.86	0.007_8
0.573	0.527	85.94	0.006_0
0.654	0.609	84.92	0.009_2
0.765	0.730	82.74	0.005_5
0.841	0.807	81.52	0.004_3
0.914	0.890	80.40	0.005_1
1,2-Dichloroethane(1)+cyclohexane(2)			
0.123	0.220	111.19	0.125
0.199	0.297	115.51	0.185
0.304	0.366	118.58	0.250
0.382	0.405	119.33	0.281
0.501	0.454	119.32	0.303
0.634	0.511	116.74	0.284
0.716	0.562	113.16	0.251
0.850	0.645	105.89	0.160
0.870	0.689	101.34	0.136
0.946	0.807	91.47	0.059

a) 1 mmHg ≈ 133.322 Pa.

Derivation of an Equation for the Excess Gibbs Energy. An equation for the excess Gibbs energy including the non-randomness factor is derived under two restrictions. The first restriction is to use the same model of mixture as that employed in the derivation of the equation for excess volumes,[1,2] that is, the non-random two-liquid (NRTL) model.[4] The second is that the equation for the excess volume must be obtained by the differentiation of the equation for the excess Gibbs energy with respect to the pressure.

The interaction free energy of the *i*-th component

Table 2. Coefficients for least-squares fit of data obtained by the use of Eq. 4

Mixture	A_0	A_1	A_2	A_3	A_4	$10^3\sigma_g$
Methanol + benzene	1.9803	0.9172	−0.1072	2.5855	2.3907	10.380
Ethanol + acetone	0.4170	0.4311	0.0129	−1.0139	−0.1766	8.033
Ethanol + *m*-xylene	1.9485	0.2379	−0.7455	0.4752	3.1598	9.835
Ethanol + benzene	1.7508	0.4637	0.1710	0.1096	0.1941	1.930
Ethanol + cyclohexane	2.1926	0.2416	0.3789	0.5267	0.0121	4.481
Acetone + cyclohexane	1.7666	−0.1813	−0.5875	0.0969	0.7584	8.568
Benzene + cyclohexane	0.5077	−0.0427	0.0190	−0.0228	−0.0347	1.015
1,2-Dichloroethane + benzene	0.0303	−0.0271	−0.0996	−0.0739	0.0565	1.367
1,2-Dichloroethane + cyclohexane	1.2076	−0.0796	0.0222	0.0626	−0.1099	1.721

Table 3. Interaction free-energy parameters, $g_{ij}-g_{jj}$, and non-randomness factors, Λ_{ij}, of binary mixtures at 298.15 K

Mixture	Λ_{21}	Λ_{12}	$\frac{g_{21}-g_{11}}{RT}$	$\frac{g_{12}-g_{22}}{RT}$	Data source
Water + 1-butoxyethanol	2.375	3.623	1.147	−0.071	Ref. 13
Methanol + 1-butanol	2.451	1.592	0.253	−0.194	Ref. 14
Methanol + benzene	0.225	0.161	5.606	−0.595	This work
Ethanol + acetone	2.653	2.942	0.094	0.166	This work
Ethanol + toluene	0.164	0.352	0.753	0.429	Ref. 15
Ethanol + *m*-xylene	0.199	0.799	1.876	1.392	This work
Ethanol + benzene	0.159	0.701	2.645	1.171	This work
Ethanol + cyclohexane	0.199	0.313	3.634	1.732	This work
Acetone + cyclohexane	0.141	0.825	−0.021	1.873	This work
Benzene + *m*-xylene	1.060	0.945	0.023	0.023	Ref. 16
Benzene + cyclohexane	3.754	2.450	0.157	0.169	This work
1,2-Dichloroethane + benzene	0.479	0.181	−0.022	0.088	This work
1,2-Dichloroethane + cyclohexane	6.345	2.028	0.239	0.555	This work

with the *j*-th component is denoted as g_{ij} (equals to g_{ji}). The local mole fraction of the *j*-th component in the vicinity of a given molecule of the *i*-th component is denoted as x_{ji}. Provided that the non-randomness factor, Λ_{ij}, is defined as a function of the local mole fractions, x_{ii} and x_{ji}, and the overall mole fractions of the mixture, x_i and x_j, as follows:

$$\frac{x_{ji}}{x_{ii}} = \Lambda_{ji}\frac{x_j}{x_i}. \tag{5}$$

We obtain the equation for the excess Gibbs energies of multi-component mixtures by means of a procedure similar to the derivation of the equation for the excess volume of multi-component mixtures:[2)]

$$g^{\mathrm{E}}/RT = \sum_{i=1}^{n} x_i \left[\frac{\sum_j (g_{ji}-g_{ii})x_j\Lambda_{ji}}{RT\sum_k x_k\Lambda_{ki}} \right], \tag{6}$$

$$(\Lambda_{ii}=\Lambda_{jj}=1)$$

where n denotes the number of components.

Equation 6 is in the same form as the NRTL equation well-known in chemical engineering.[4)] In the NRTL equation, the non-randomness factor is defined as a function of the interaction free energy. It should be noticed that the derivation descrived above leads to the same equation. It is considered that, in the NRTL equation, the number of parameters is reduced by regarding the non-randomness factor as a function of the interaction free energy. When the Boltzmann distribution is assumed to hold in the local composition, the local mole fraction should be represented as a function of the interaction potential between molecules, as has been described by Guggenheim in his text.[12)] Based on his description, the non-randomness factor is defined as follows:

$$\Lambda_{ij} = \exp\left(-\frac{w_{ij}-w_{jj}}{zRT}\right), \tag{7}$$

where w_{ij} is the interaction potential between the i and j components, and z, the coordination number of the pseudo-lattice of mixture. If both the interaction potential and the coordination number are assumed to be independent of the pressure and the temperature, the equation for the excess volume is obtained by differentiating Eq. 6 with respect to the pressure:[2)]

$$v^{\mathrm{E}} = \sum_{i=1}^{n} x_i \left[\frac{\sum_j (v_{ji}-v_{ii})x_j\Lambda_{ji}}{\sum_k x_k\Lambda_{ki}} \right]. \tag{8}$$

Comparison of the Calculated g^{E} Values with Those Observed. The values of the non-randomness factors were determined from the excess volume data,[1,2)] as the values of the non-randomness factors could be obtained more accurately. The $g_{ij}-g_{jj}$ values were determined from the excess-Gibbs-energy data by an algebraic calculation of Eq. 6. The values thus obtained are listed in Table 3. The observed and the

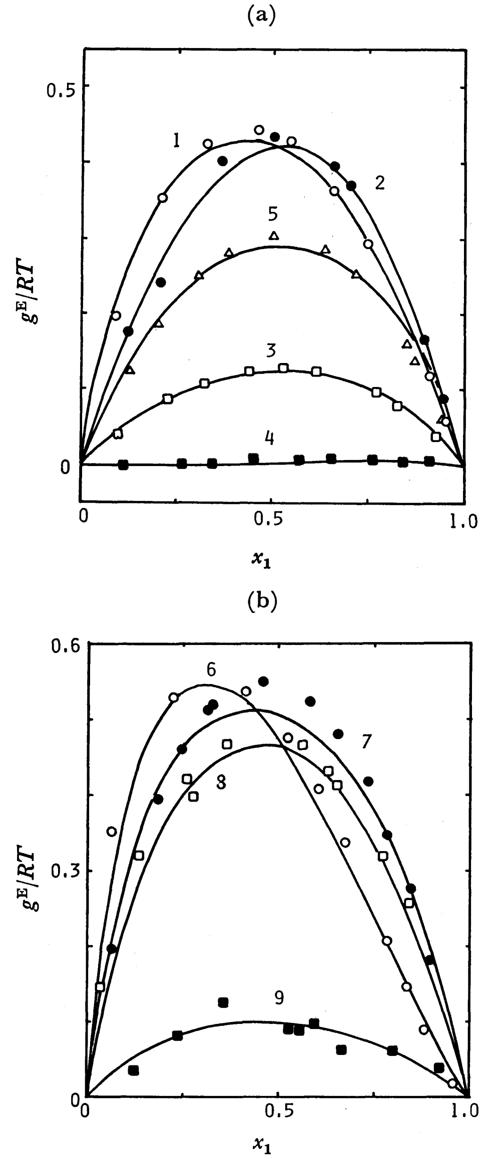

Fig. 1. Observed and calculated excess Gibbs energy of nine binary mixtures at 298.15 K. Solid lines indicate the values calculated from Eq. 6. a): 1 and ○ is ethanol(1)+benzene(2), 2 and ●, acetone (1)+cyclohexane(2), 3 and □, benzene(1)+cyclohexane(2), 4 and ■, 1,2-dichloroethane(1)+benzene (2), and 5 and △, 1,2-dichloroethane(1)+cyclohexane(2) mixtures. b): 6 and ○ is methanol(1)+benzene(2), 7 and ●, ethanol(1)+cyclohexane(2), 8 and □, ethanol(1)+*m*-xylene(2), and 9 and ■, ethanol(1)+acetone(2) mixtures.

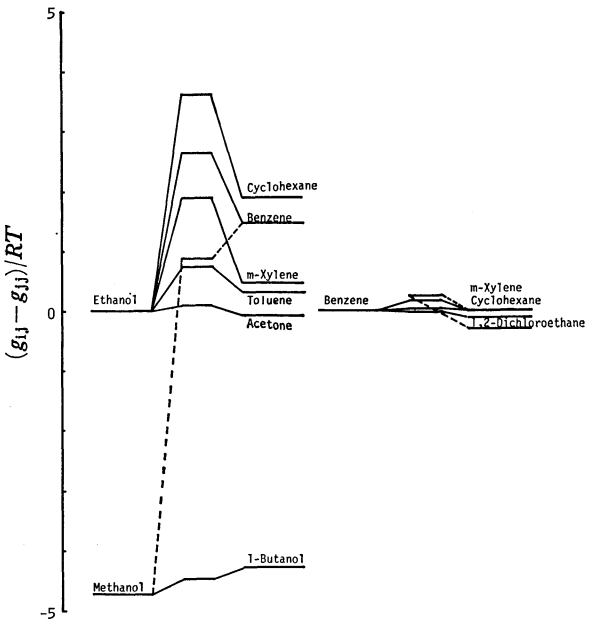

Fig. 2. The interaction free energy diagram in some binary mixtures at 298.15 K.

calculated excess Gibbs energies were in good agreement, as is shown in Fig. 1.

In Fig. 2, a qualitative diagram of the interaction free-energy parameters is shown. This diagram was constructed from the values of $g_{ij}-g_{jj}$ given in Table 3. The component on the left-hand side of the diagram was established as a standard component; next, the interaction free-energy level between unlike components was calculated from the $g_{ij}-g_{jj}$ values, and finally that for the pure state of the second component was calculated from the $g_{ji}-g_{ii}$ value, where g_{ji} equals g_{ij}. In the mixtures containing ethanol, the sequence of the interaction free-energy parameters was as follows: ethanol–acetone≈ethanol–ethanol<ethanol–toluene<ethanol–*m*-xylene<ethanol–benzene<ethanol–cyclohexane. It is likely that the hydrogen-bonding interaction or associative interaction between ethanol and acetone forms the lowest energy level among the mixtures selected. The negative values of the interaction potential parameters, $w_{ij}-w_{jj}$, of the ethanol+acetone mixture, which were calculated from the non-randomness factors by using Eq. 7, support the associative interaction. The interaction between ethanol and cyclohexane is the highest energy level, and the interaction is expected to be accompanied by the destruction of the hydrogen bond of ethanol. Ethanol is considered to interact with benzene through OH-π interaction. Toluene and *m*-xylene are expected interact slightly more strong with ethanol than benzene is, because they are slightly polar molecules (the dipole moment of toluene is 0.31 Debye, and that of *m*-xylene is 0.30 Debye, at 20 to 60 °C.[7]).

For methanol mixtures, the interaction free-energy level of methanol with benzene is much higher than that with 1-butanol. The interaction of methanol with 1-butanol is a result of the hydrogen bonding, and that with benzene is the OH-π interaction.

In the benzene+*m*-xylene, benzene+cyclohexane, 1,2-dichloroethane+benzene, and 1,2-dichloroethane+cyclohexane mixtures, the interaction free-energy parameters are relatively smaller than in ethanol mixtures. The interaction in 1,2-dichloroethane+cyclohexane is indicated by a broken line on the right-hand side in Fig. 2. Particularly, the excess Gibbs energies of the benzene+*m*-xylene and 1,2-dichloroethane+benzene mixtures are nearly zero; that is, they are almost ideal mixtures. The interaction free-energy parameters of these benzene mixtures are very small. However, the excess-volume curves of these mixtures show appreciable positive deviations from ideal behavior. The v^E values of equimolar mixtures are 0.3 $cm^3 \, mol^{-1}$ for the benzene+*m*-xylene mixture and 0.2 $cm^3 \, mol^{-1}$ for the 1,2-dichloroethane+benzene mixture.[2] These results seem to suggest that the volumes of central molecules surrounded by different component molecules differ from those of molecules surrounded by the same component molecules, in spite of almost the same magnitude of interaction free-energy parameters between like and unlike molecular pairs.

Interaction free-energy diagrams of the non-polar or slightly polar mixtures show small free-energy gaps, as is shown in Fig. 2. When the ethanol-ethanol interaction is chosen as the standard energy level, however, a different feature appears. The interaction of ethanol molecules in pure ethanol differs remarkably from that in mixtures with non-polar or slightly polar molecules. As has been described above, the interaction of ethanol with a non-polar molecule is accompanied by a destruction of the hydrogen bonding. On the other hand, the interaction in mixtures of two non-polar substances, such as the benzene+*m*-xylene mixture, is considered not to differ essentially between pure and mixed states. It may be deduced from the above reason that the combination of the diagrams of the hydrogen bonding and the non-polar mixtures gives an inconsistent feature of interaction free energy. This fact may show the limitation of the applicability of Eq. 6.

References

1) M. Kato and N. Suzuki, *Bull. Chem. Soc. Jpn.*, **51**, 1020 (1978).

2) M. Kato, *Bull. Chem. Soc. Jpn.*, **53**, 1937 (1980).

3) G. M. Wilson and G. Scatchard, *J. Am. Chem. Soc.*, **86**, 127 (1964).

4) H. Renon and J. M. Prausnitz, *AIChE J.*, **14**, 135 (1968).

5) T. Tuboka and T. Katayama, *J. Chem. Eng. Jpn.*, **8**, 181 (1975).

6) D. S. Abrams and J. M. Prausnitz, *AIChE J.*, **21**, 116 (1975).

7) J. A. Riddick and W. B. Bunger, "Organic Solvents," 3rd ed, J. Wiley and Sons, New York (1970).

8) D. Radulescu and M. Alexa, *Bull. Soc. Chim. Romania*, **20A**, 89 (1938).

9) M. Inoue, K. Azumi, and N. Suzuki, *Ind. Eng. Chem., Fundam.*, **14**, 312 (1975).

10) M. Kato, *Ind. Eng. Chem., Fundam.*, **19**, 253 (1980).

11) J. P. O'Connell and J. M. Prausnitz, *Ind. Eng. Chem., Process Res. Dev.*, **6**, 245 (1967).

12) E. A. Guggenheim, "Mixtures," Oxford University Press (1952).

13) G. Scatchard and G. M. Wilson, *J. Am. Chem. Soc.*, **80**, 133 (1964).

14) J. Polák, S. Murakami, V. T. Lam, H. D. Pflug, and G. C. Benson, *Can. J. Chem.*, **48**, 2457 (1970).

15) S. C. P. Hwa and W. T. Ziegler, *J. Phys. Chem.*, **70**, 2572 (1966).

16) J. Singh, H. D. Pflug, and G. C. Benson, *J. Phys. Chem.*, **72**, 1939 (1968).