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A New Expression for Excess Volumes of Binary Mixtures

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A new expression for excess volumes of binary mixtures is derived. This equation contains four adjustable but physically-meaningful parameters: two non-randomness factors and two partial molar volumes at infinite dilution. The applicability of this equation is tested against data in the literature for several non-ideal mixtures, and it is found that this equation successfully expresses the experimental curves of excess volume, V^E, over the entire concentration range. Furthermore, it is demonstrated that the non-randomness factors used in the excess volume expression can be used to estimate the excess Gibbs energy, G^E, of binary mixtures based on the Wilson equation.

The excess volume is one of the fundamental thermodynamic quantities of liquid mixtures and an enormous amount of data has been obtained for this quantity.[1,2] Systematic attempts to describe quantitatively the properties of liquid mixtures have been based on current solution theories, *i.e.*, the Flory theory,[3] the cell model of Prigogine and co-workers,[4] regular solution theory,[5] the corresponding state theory,[6] *etc.*[7,8] These theories are almost successful in expressing the excess thermodynamic functions of non-polar binary mixtures, but only quantitative agreement has been obtained for polar binary mixtures.

Recently, Wilson and Scatchard[9] proposed an expression for G^E, H^E, and S^E, which is in excellent agreement with experimental results. Following Wilson, Prausnitz and his collaborators[10–12] introduced some equations for G^E based on the idea of a local mole or segment fraction. Unfortunately, these equations do not include terms involving pressure as a variable, so that they cannot be used to express V^E.

In this study, a new equation for V^E is derived by introducing the idea of non-random mixing. This new expression contains two measurable and two adjustable, but physically-meaningful, parameters, *i.e.*, two partial molar volumes at infinite dilution and two non-randomness factors. The applicability of the equation will be examined for several binary mixtures in the literature.

Derivation of the New Equation

As the general model of a binary mixture, we take into account non-random mixing of two components as introduced into two liquid models proposed by Scott[6] and extended by Renon and Prausnitz.[10] We assume that the probability of finding molecules of one type (i molecules) in the vicinity of a central molecule (j molecule) can be represented by the local mole fraction in a solvation sphere. Furthermore, we assume that the excess functions are determined by the local mole fraction of the first solvation sphere. We denote the local mole fraction of the component i adjacent to the central molecule j by x_{ij}, which is equal to $1-x_{jj}$.

When $x_{11}=1$, the volume occupied by one mole of the first component is equal to its molar volume in the pure state, $V_1{}^*$. For the state for which $x_{21}=1$, the volume occupied by one mole of the first component is denoted by V_{21}. Accordingly, the volume occupied by one mole of the first component in a mixture is $(V_1{}^*x_{11}+V_{21}x_{21})$. Similarly, the volume occupied by the second component can be represented by $(V_2{}^*x_{22}+V_{12}x_{12})$ in a mixture. Consequently, the molar volume of the liquid mixture can be represented by

$$V_{\text{mix}} = x_1(V_1{}^*x_{11}+V_{21}x_{21}) + x_2(V_2{}^*x_{22}+V_{12}x_{12}), \tag{1}$$

where x_1 and x_2 are the mole fractions of the first and second components, respectively. Therefore, the excess volume of the binary mixture is

$$\begin{aligned} V^E &= V_{\text{mix}} - V_{\text{ideal}} \\ &= x_1x_{21}(V_{21}-V_1{}^*) + x_2x_{12}(V_{12}-V_2{}^*). \end{aligned} \tag{2}$$

Now, we introduce the non-randomness factor, Λ_{ij}, which relates the local mole fraction to the overall mole fraction by

$$\frac{x_{ij}}{x_{jj}} = \Lambda_{ij}\frac{x_i}{x_j} \quad (x_{ij}+x_{jj}=1). \tag{3}$$

The non-randomness factor has been independently defined by different authors as follows:

$$\Lambda_{ij} = \exp\frac{-\alpha_{ij}(g_{ij}-g_{jj})}{RT} \quad \text{(by Renon and Prausnitz)} \tag{4}$$

and

$$\Lambda_{ij} = \frac{V_i{}^*}{V_j{}^*}\exp\frac{-(\lambda_{ij}-\lambda_{jj})}{RT} \quad \text{(by Wilson)}, \tag{5}$$

where g_{ij} and λ_{ij} are the parameters corresponding to the interaction energy between the i and j molecules and α_{ij} is the parameter characteristic of the reciprocal of the coordination number of lattice. These two definitions for Λ have similar physical meanings. Wilson's definition includes the fixed volume term $V_i{}^*/V_j{}^*$, so that it cannot be applied to the calculation of V^E. The definition of the non-randomness factor used here is

$$\Lambda_{ij} = \exp\frac{-(\lambda_{ij}-\lambda_{jj})}{RT}, \tag{6}$$

since the local mole fraction is used. Recently, Huggins[13] pointed out that the parameters, g_{ij} and λ_{ij}, are of ambiguous units. So, the value of the non-randomness factors themselves were estimated, as Wilson did, although it is possible to express the non-randomness factors as a function of $(\lambda_{ij}-\lambda_{jj})/R$.

From Eq. 3, x_{ij} can be represented as

$$x_{ij} = \frac{x_i\Lambda_{ij}}{x_j+x_i\Lambda_{ij}}, \tag{7}$$

where $\Lambda_{jj}=\Lambda_{ii}=1$. By substitution of Eq. 7 into Eq. 2, the equation for a binary mixture is obtained, thus,

$$V^{\mathrm{E}} = x_1x_2\left\{\frac{\Lambda_{21}}{x_1+x_2\Lambda_{21}}(V_{21}-V_1{}^*)+\frac{\Lambda_{12}}{x_1\Lambda_{12}+x_2}(V_{12}-V_2{}^*)\right\}. \tag{8}$$

This equation can be partially differentiated with respect to x_1, according to the relations, $(\partial V^{\mathrm{E}}/\partial x_1)_{x_1=0}=(V_1{}^\infty-V_1{}^*)$ and $-(\partial V^{\mathrm{E}}/\partial x_1)_{x_1=1}=(V_2{}^\infty-V_2{}^*)$, where V^∞ is the partial molar volume at infinite dilution. From this procedure, we obtain

$$V^{\mathrm{E}} = x_1x_2\left\{\frac{x_2\Lambda_{21}(V_1{}^\infty-V_1{}^*)+x_1\Lambda_{12}(V_2{}^\infty-V_2{}^*)}{(x_1+x_2\Lambda_{21})(x_2+x_1\Lambda_{12})}\right\}. \tag{9}$$

Equation 9 shows that if the partial molar volumes at infinite dilution and, at least, two measured values of V^{E} are accurately obtained, the two non-randomness factors, Λ_{21} and Λ_{12}, can be calculated.

The advantage of this analysis is that the parameters in this expression are physically meaningful and the non-randomness factors thus obtained can be used to estimate the excess Gibbs energy by combination with the Wilson equation.[9] In this case, the Wilson equation must be transformed to

$$\frac{G^{\mathrm{E}}}{RT} = -x_1\ln\left(x_1+\frac{V_2{}^*}{V_1{}^*}\Lambda_{21}x_2\right)-x_2\ln\left(\frac{V_1{}^*}{V_2{}^*}\Lambda_{12}x_1+x_2\right). \tag{10}$$

Applicability of the New Equation

Figure 1 shows some typical examples of theoretical curves of V^{E}. For curves 1, 3, and 5, the non-randomness factors are assumed to be constant and equal to 1. When $V_1{}^\infty-V_1{}^*=V_2{}^\infty-V_2{}^*$, the curve is symmetrical, but when $V_1{}^\infty-V_1{}^*\neq V_2{}^\infty-V_2{}^*$, a skewed curve is obtained. Especially, when $V_1{}^\infty-V_1{}^*>0>V_2{}^\infty-V_2{}^*$, the curve has an S-shape. Curves 2, 4, 6, and 7 show cases of non-randomness factors of different magnitudes. Curve 2 differs in flatness from curve 1. For curve 4, the mole fraction corresponding to $V^{\mathrm{E}}=0$ is shifted to the left in comparison with curve 3. For curves 5, 6, and 7, the mole fractions giving maximum V^{E} values differ from

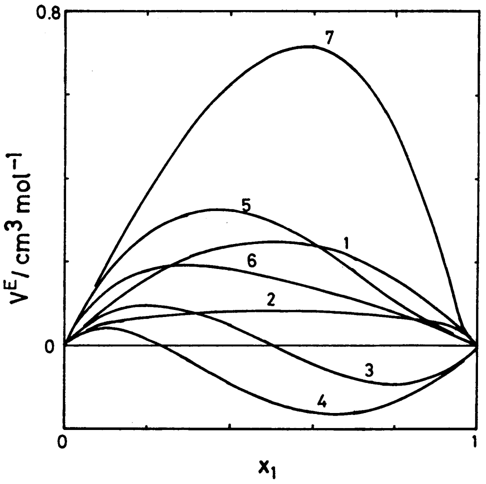

Fig. 1. Dependence of V^{E} curves on the value of parameters.

Curve	Λ_{21}	Λ_{12}	$\frac{V_1^\infty-V_1^*}{\mathrm{cm^3\ mol^{-1}}}$	$\frac{V_2^\infty-V_2^*}{\mathrm{cm^3\ mol^{-1}}}$
1	1.0	1.0	1.0	1.0
2	0.1	0.1	1.0	1.0
3	1.0	1.0	1.0	−1.0
4	0.3	1.0	1.0	−1.0
5	1.0	1.0	2.0	0.4
6	0.2	0.2	2.0	0.4
7	5.0	0.2	2.0	0.4

Table 1. Volume parameters and standard deviation at 298.15 K

Components		Parameters				$\sigma/10^{-4}$ cm^3 mol^{-1} [a)]		Literature
First	Second	$\frac{V_1^\infty-V_1^*}{\mathrm{cm^3\ mol^{-1}}}$	$\frac{V_2^\infty-V_2^*}{\mathrm{cm^3\ mol^{-1}}}$	Λ_{21}	Λ_{12}	Eq. 9	Polyn.	
Methanol	1-Butanol	0.1671	0.5788	0.628	0.408	2	3	14
1-Butanol	1-Octanol	0.1552	0.2144	1.088	0.136	5	5	14
1-Butanol	1-Hexanol	0.0502	0.0692	0.255	0.408	4	4	14
1-Butanol	1-Decanol	0.3020	0.4356	0.574	0.366	4	4	14
Methanol	1-Octanol	0.1901	2.3321	0.283	0.183	20	11	14
Ethanol	1-Octanol	0.1110	0.7798	0.211	0.192	4	3	14
1-Propanol	1-Octanol	0.1846	0.3532	0.449	0.304	4	3	14
1-Hexanol	1-Octanol	0.0343	0.0499	0.290	0.630	3	3	14
Benzene	*o*-Xylene	0.8848	1.1398	1.292	0.926	8	8	15
Benzene	*m*-Xylene	0.9627	1.4015	1.060	0.945	21	22	15
Benzene	*p*-Xylene	0.7256	0.9934	0.249	0.705	9	9	15
Methanol	Benzene	0.356	−0.468	0.225	0.161	30	16	16
Water[b)]	2-Butoxyethanol	−1.9074	−4.8736	0.276	0.421	280	289	17
Ethanol	Toluene	1.045	−1.164	0.164	0.352	45	30	18
Ethanol	*o*-Xylene	1.527	−0.818	0.157	0.479	63	40	18
Ethanol	*m*-Xylene	1.664	−0.359	0.199	0.799	77	37	18
Ethanol	*p*-Xylene	1.153	−0.930	0.198	0.359	35	17	18

a) $\sigma=\sqrt{\frac{\Sigma(V^{\mathrm{E}}_{\mathrm{calcd}}-V^{\mathrm{E}}_{\mathrm{obsd}})^2}{N-2}}$, the standard deviation, where N is the number of data points. $V^{\mathrm{E}}_{\mathrm{calcd}}$ and $V^{\mathrm{E}}_{\mathrm{obsd}}$ denote the calculated and observed values of V^{E}, respectively. b) At 300.15 K.

each other. It is found that the shape of the V^E curve is primarily determined by the signs and magnitudes of $V_1^\infty - V_1^*$ and $V_2^\infty - V_2^*$.

These theoretical results were tested against data from the literature for 20 binary mixtures. As stated previously, two non-randomness factors can be readily calculated from accurately measured values of V^E. For this purpose, the V^E data at $x_1=0.3$ and $x_1=0.7$ obtained using a reported smoothing equation were used. The calculated non-randomness factors are listed in Table 1 with the standard deviations of the smoothing and the theoretical curves.

The agreement between the present equation and experiment is quite satisfactory. Typical examples are shown in Fig. 2. As is shown in Table 1, the standard deviations of V^E calculated from the smoothing equation and the new equation are of the same order for systems have V^E curves of simple shape. For systems having S-shaped V^E curves, such as the benzene+methanol system, however, the standard deviation calculated from the new equation is larger than that for the smoothing equation. This is probably due to the uncertainty in the $V_i^\infty - V_i^*$ value. Generally, for systems having S-shaped V^E curves, the $V_i^\infty - V_i^*$ calculated using the new equation appear to be larger than those using the smoothing equation. Small $|V_i^\infty - V_i^*|$ values produce small maximum or minimum values of the V^E curves. For systems having S-shaped V^E curves, very good estimates of V^E can be made utilizing the alternative equation with four adjustable parameters: two non-randomness factors and two partial molar volumes.

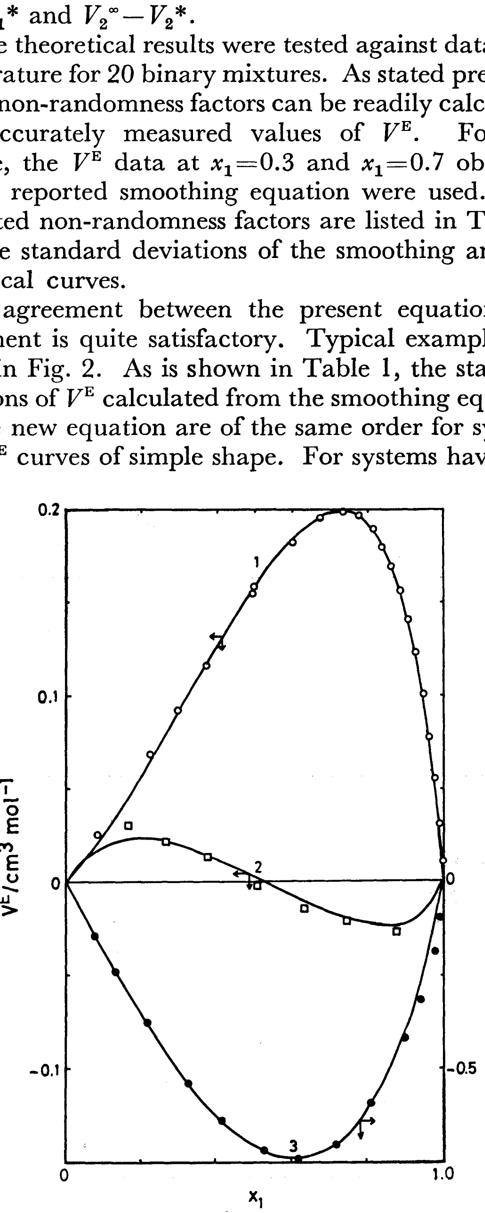

Fig. 2. The examples of the test of new equation for binary systems. Curve 1 corresponds to methanol+1-octanol system; curve 2, methanol+benzene; curve 3, water+2-butoxyethanol.

For systems containing nitroethane, the temperature dependence of V^E has been investigated by Handa *et al.*[19] It is of interest to apply the new equation to those systems. The estimated non-randomness factors are listed in Table 2. In Table 2, the system containing 2-methylpentane at 298.15 K is qualitatively fitted by Eq. 9, because of the S-shaped V^E curve. As is shown, the non-randomness factors tend to increase with temperature, which means that the mixture becomes ideal. This tendency is consistent with the expected behavior for normal mixtures. However, the temperature dependence of the non-randomness factors is larger than that predicted from either definition by Wilson and Scatchard[9] or by Renon and Prausnitz.[10] It is assumed that the molecular distribution adjacent to the central molecule is determined by two factors, *i.e.*, a combinatorial factor depending on the molecular size and shape, and a residual factor depending on the molecular interaction energy, and that the non-randomness factors account for these two factors. Furthermore, we have no method to separate the excess volume into two factors. Thus, it appears difficult to exactly express the temperature dependence.

The non-randomness factors calculated from the V^E data are not necessarily consistent with those defined in the Wilson equation, which are calculated from G^E data. Nevertheless, the G^E values for several binary mixtures calculated by applying the present non-randomness factors to the Wilson equation are in qualitative agreement with the observed value. As is shown in Fig. 3, the calculated G^E values for the benzene +*m*-xylene[20] and for the methanol+benzene[16] systems are in relatively good agreement with the observed values, while the calculated G^E values for the water+2-

Table 2. The dependence of volume parameters on the temperature for systems containing nitroethane as the first component

Second component	Temperature / K	$V_1^\infty - V_1^*$ / cm^3 mol^{-1}	$V_3^\infty - V_2^*$ / cm^3 mol^{-1}	Λ_{21}	Λ_{12}	σ[a) / cm^3 mol^{-1}
2-Methylpentane	298.15	2.285	−0.503	0.214	0.193	0.011_2
	303.15	3.065	−0.403	0.159	0.244	0.005_9
	313.15	2.861	−0.497	0.193	0.394	0.004_5
2,3-Dimethylbutane	298.15	2.341	−0.671	0.156	0.254	0.004_7
	313.15	2.644	−0.768	0.179	0.348	0.006_4
2,2-Dimethylbutane	298.15	1.739	−1.735	0.147	0.426	0.009_9
	313.15	1.722	−1.968	0.224	0.607	0.004_3

a) The standard deviation is $\sigma=\sqrt{\dfrac{\Sigma(V^E_{\text{calcd}}-V^E_{\text{obsd}})^2}{N-2}}$, where N is the number of data points.

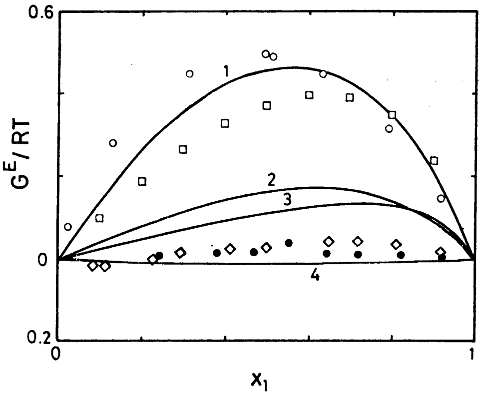

Fig. 3. Application of nonrandomness factor to Wilson equation. Curve 1 and ○ correspond to methanol+benzene system; curve 2 and □, water+2-butoxyethanol; curve 3 and ◇, methanol+1-butanol; curve 4 and ●, benzene+*m*-xylene.

butoxyethanol[17] and for the methanol+1-butanol[21] systems are in only qualitative agreement with the observed values. Recalling that the accuracy of the V^E data sensitively affect the reliability of the non-randomness factors, the poor agreement between the latter two systems is partly due to the uncertainty in the non-randomness factors.

Conclusion

The new equation with only two parameters successfully fits the excess volumes of binary mixtures to the same order as the smoothing equation. These two parameters have exact physical meanings, contrary to the traditional smoothing equation parameters. At the present stage, the G^E calculated from V^E data are in qualitative agreement with observed values.

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