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On the Thermodynamics of Binary Liquid Mixtures of *Scatchard—Hildebrand* Type at Infinite Dilution

Short Communication

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The excess Gibbs free energy G^E of binary liquid nonassociated mixtures may, to a first approximation, be formally expressed as the sum of a quantity which will be designated by G^* containing the contribution of the intermolecular force fields, and of a combinatorial part G^{Ec}:

$$G^E = G^* + G^{Ec}, \tag{1}$$

where $G^{Ec} = - T\,(\Delta\, S^c - \Delta\, S^{id})$ and $\Delta\, S^{id}$ is the ideal entropy of mixing. The combinatorial entropy $\Delta\, S^c$ was discussed recently by *Donohue* and *Prausnitz*[1] in terms of a generalized *Flory* model applicable to systems with molecules of arbitrary size and shape including as a limiting case the *Flory—Huggins* equation[2, 3] for mixtures of chainlike molecules.

In the present context, nonassociated mixtures in which at all concentrations G^* is positive and its temperature derivative negative, are termed "*Scatchard—Hildebrand* type" mixtures.

In regular solutions G^* is related to the solubility parameters by the *Scatchard—Hildebrand* equation[4]

$$G^* = \frac{x_1\, x_2\, V_1\, V_2\, (\delta_1 - \delta_2)^2}{x_1\, V_1 + x_2\, V_2}, \tag{2}$$

where x_1 and x_2 are the mole fractions, V_1 and V_2 the molar volumes of the pure liquid components. The solubility parameter of component i is denoted by $\delta_i = \sqrt{\Delta\, U_i^{vap}/V_i}$, where $\Delta\, U_i^{vap}$ is the energy change that accompanies isothermal vaporization of the saturated liquid to the ideal gas state.

If G^* is taken from eq. (2), $\Delta\, S^c$ represented by the simple *Flory—Huggins* term and the thermal expansivity of each component assumed to be equal to that of the mixture, α_m, one may derive[5] the following relationship between the enthalpy of mixing H^E and G^*:

$$H^E/G^* = 1 + 1{,}5\,\alpha_m\,T. \tag{3}$$

From eq. (3) it may be concluded

$$\lim_{x_i \to 0} (H^E/G^*) = 1 + 1{,}5\,\alpha_m\,T, \quad (i = 1, 2). \tag{4}$$

Limiting values of H^E/G^* extrapolated from observed excess properties of mixing have been reported elsewhere[5]. Taking the average of the obtained results, one may write

$$\lim_{x_i \to 0} (H^E/G^*) = 2, \quad (i = 1, 2). \tag{5}$$

Eq. (5) is in fair agreement with eq. (4) found from the temperature dependence of the solubility parameters.

Funk and *Prausnitz*[6] combined the relation between H^E, G^E and the excess volume V^E based on the regular solution theory[4]

$$H^E = G^E + V^E\,\alpha_m\,T/\beta_m, \tag{6}$$

β_m being the isothermal compressibility of the mixture, with the following approximation which interrelates the limiting values of the excess volume $V_i^{E\infty}$ and the excess chemical potential $\mu_i^{E\infty}$ of component i at $x_i \to 0$

$$V_i^{E\infty} = \mu_i^{E\infty}\,\beta_j/(\alpha_j\,T), \quad (i \neq j). \tag{7}$$

α_j and β_j are the thermal expansivity and the isothermal compressibility of component j, respectively.

To investigate the consequence of such a treatment to the value of H^E/G^E at infinite dilution, we rewrite eq. (6) into the form

$$H^E/G^E = 1 + (V^E/G^E)\,(\alpha_m\,T/\beta_m). \tag{8}$$

The limiting value is then

$$\lim_{x_i \to 0} (H^E/G^E) = 1 + \lim_{x_i \to 0} (V^E/G^E) \lim_{x_i \to 0} (\alpha_m\,T/\beta_m), \tag{9}$$

where

$$\lim_{x_i \to 0} (\alpha_m\,T/\beta_m) = \alpha_j\,T/\beta_j, \quad (i \neq j). \tag{10}$$

From *l'Hospital's* rule it follows

$$\lim_{x_i \to 0} (H^E/G^E) = H_i^{E\infty}/\mu_i^{E\infty} \tag{11a}$$

$$\lim_{x_i \to 0} (V^E/G^E) = V_i^{E\infty}/\mu_i^{E\infty}. \tag{11b}$$

Combination of eq. (11 b) with eq. (7) gives

$$\lim_{x_i \to 0} (V^E/G^E) = \beta_j/(\alpha_j T), \qquad (i \neq j). \tag{12}$$

Using eq. (12) and eq. (10), we now reduce eq. (9) to

$$\lim_{x_i \to 0} (H^E/G^E) = 2, \qquad (i = 1, 2). \tag{13}$$

It is interesting to note that in eq. (13) neither the expansivity, compressibility, nor the excess volume or the temperature appear as parameters. The approximation used in eq. (7) imposes, however, a restriction on the sign of the limiting values of the excess functions. Considering $\beta_j/(\alpha_j T) > 0$, the signs of $V_i^{E\infty}$ and $\mu_i^{E\infty}$ can not be different. Comparison of eq. (13) and eq. (11 a) shows, on the other hand, that the sign of $H_i^{E\infty}$ must agree with that of $\mu_i^{E\infty}$ and, as a consequence, also agree with that of $V_i^{E\infty}$.

Eq. (1) relates G^E to G^*. If ΔS^c is nearly ideal, then $G^E = G^*$ and eq. (13) becomes identical to the empirically obtained[5] eq. (5). It is possible to extend eq. (7) to include *Scatchard—Hildebrand* type solutions in which $H_i^{E\infty}$ and $V_i^{E\infty}$ are both positive and $\mu_i^{E\infty}$ may be negative, provided that $G^* > 0$ over the whole concentration range. Then in all relations the excess functions are to be replaced by G^* and its derivatives, H^E remaining unchanged ($H^E = H^*$), since the combinatorial part of eq. (1) does not contribute to the enthalpy of mixing. With regard to the restriction $G^* > 0$ required by the *Scatchard—Hildebrand* concept, the correlation scheme used by *Funk* and *Prausnitz* should not be applied to systems with $H_i^{E\infty}$ or $V_i^{E\infty} < 0$.

Knowledge of $\lim (H^E/G^*)$ at $x_i \to 0$ allows estimation of the enthalpy of mixing of binary nonassociated solutions at all compositions in cases where G^E is given at one temperature only[5].

References

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