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Excess Compressibility of Binary Liquid Mixtures

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Excess compressibility is an important quantity related to intermolecular forces between unlike molecules.[1]

The formulas of compressibility based on statistical theories have been derived by Prigogine,[2] Flory[3] and others. Flory's formula is very simple, and the values for nonpolar liquid mixtures calculated by the formula showed a fairly good fit with the observed data. Three parameters are included in Flory's solution theory and were determined experimentally.

A statistical thermodynamic theory for binary liquid mixtures based on the cell method and the Sutherland type potential function for pair interactions, has been successfully applied to nonpolar solutions.[*1,4] From the theory, the excess compressibility equation has been derived for the relation between the compressibility and intermolecular energy. It is believed that the compressibility data gives a severe test to the statistical theory of solution.

The equation of state for a binary mixture consisting of nonpolar rigid spherical molecules (A and B) differing in size is given by the following equation.

$$-p = \frac{2\pi}{3}\frac{N^2}{V^2}\left[(\gamma\varepsilon^*)_A \cdot r_A{}^{*3} \cdot x_A + (\gamma\varepsilon^*)_B \cdot r_B{}^{*3} \cdot x_B\right] - RT\left[\frac{x_A}{\beta a_A{}^2 \cdot (a_A - r_A{}^*)} + \frac{x_B}{\beta a_B{}^2 \cdot (a_B - r_B{}^*)}\right] \qquad (1)$$ [*2]

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1) G. H. Findenegg and F. Kohler, *Trans. Faraday Soc.*, **63**, 870 (1967); R. J. Fort and W. R. Moore, *ibid.*, **61**, 2102 (1965).

2) I. Prigogine, "The Molecular Theory of Solutions," North-Holland Publishing Co., Amsterdam (1957).

3) A. Abe and P. J. Flory, *J. Amer. Chem. Soc.*, **87**, 1838 (1965).

[*1] In the following, this paper is referred to as paper I and the number of the equation given in paper I is superscripted with a prime.

4) K. Arakawa and O. Kiyohara, This Bulletin, **43**, 975 (1970).

All notations used in the present note are the same as those in paper I.

Differentiating Eq. (1) with respect to pressure at constant temperature, we have

$$\left(\frac{\partial V}{\partial p}\right)_T = 1\Big/\Big[\frac{4\pi}{3}\cdot\frac{N^2}{V^3}\{(\gamma\varepsilon^*)_A\cdot r_A{}^{*3}\cdot x_A + (\gamma\varepsilon^*)_B\cdot r_B{}^{*3}\cdot x_B\} - \boldsymbol{R}T(k_A\cdot x_A + k_B\cdot x_B)\Big], \tag{2}$$

where

$$k_A = \left(\frac{1}{a_A{}^2\cdot(a_A - r_A{}^*)\cdot\beta}\right)^2\cdot\left(\frac{3a_A - 2r_A{}^*}{3a_A}\right) \text{ and}$$

$$k_B = \left(\frac{1}{a_B{}^2\cdot(a_B - r_B{}^*)\cdot\beta}\right)^2\cdot\left(\frac{3a_B - 2r_B{}^*}{3a_B}\right),$$

and, using the same approximate equation (Eqs. (17′)—(20′)), the isothermal compressibility κ_T for a binary mixture is expressed as follows.

$$\kappa_T^{(\mathrm{I})} = \frac{1}{3\boldsymbol{R}T}\cdot\frac{(V - V^*)^2}{V\cdot\left[\dfrac{1+3\rho_A}{1+\rho_A}\cdot x_A + \dfrac{1+3\rho_B}{1+\rho_B}\cdot x_B\right] - 2\cdot(V - V^*)}. \tag{3}$$

For a pure liquid A, we have

$$\kappa_{T\cdot\mathrm{A}}^{(\mathrm{I})} = \frac{1}{3\boldsymbol{R}T}\,\frac{(V_A{}^0 - V_{AA}{}^*)^2}{V_A{}^0\left[\dfrac{1+3\rho_{AA}}{1+\rho_{AA}}\right] - 2\cdot(V_A{}^0 - V_{AA}{}^*)} \tag{4}$$

where

$$\rho_A = \frac{V - V^*}{3V_A{}^*},\ \rho_B = \frac{V - V^*}{3V_B{}^*},$$

$$V^* = V_A{}^*\cdot x_A + V_B{}^*\cdot x_B,\quad x_A + x_B = 1.$$

x_A and x_B are the mole fraction for each species, $V_A{}^*$ and $V_B{}^*$ are the "*hard core volume*"[3,4] for each species in solution, and $V_{AA}{}^*$ and $V_{BB}{}^*$ are those in pure liquid, respectively. V and V^0 are the volume of solution and pure liquid each.

The excess compressibility κ^E is given by the equation

$$\kappa^{\mathrm{E}} = \kappa - \frac{1}{V}(V_A{}^0\kappa_A{}^0 x_A + V_B{}^0\kappa_B{}^0 x_B) \tag{5}$$

where $\kappa_A{}^0$ and $\kappa_B{}^0$ are the compressibility for each pure liquid. The $\kappa_T^{E,(\mathrm{I})}$ calculated*3 from the observed excess molar volume V^E (the 3rd column of Table 1) using Eqs. (3), (4) and (5) are compared with experimental results in the 5th column of Table 1. As the values of molecular parameters (molar volume and thermal expansion coefficient of pure liquid), those listed in paper I have been used.

The agreement between calculated and observed results is satisfactory on the whole.

Equation (3) can be simplified further, and we have an extremely simplified formula

$$\kappa_T^{(\mathrm{II})} = \frac{1}{3\boldsymbol{R}T}\cdot\frac{(V - V^*)^2}{V}. \tag{6}^{*4}$$

Inserting Eq. (6) into Eq. (5), we obtain a simplified formula of excess compressibility as

$$\kappa_T^{\mathrm{E},(\mathrm{II})} = \frac{1}{3\boldsymbol{R}T}\cdot\frac{1}{V}\left[(V - V^*)^2 - \{(V_A{}^\circ - V_{AA}{}^*)^2\cdot x_A + (V_B{}^\circ - V_{BB}{}^*)^2\cdot x_B\}\right] \tag{7}^{5)}$$

The formula of $\kappa_T^{E,(\mathrm{II})}$ has been tested by the same procedure as described above, and the results are shown in the 6th column of Table 1. The agreement between the observed and calculated is

TABLE 1. EXCESS COMPRESSIBILITY FOR EQUIMOLAR MIXTURES

System	T (°C)	V^E (cc/mol) Obsd	$\kappa_T^E \times 10^3$ (cc/cal·mol) Obsd	Calcd (I)	Calcd (II)
CCl_4-$C(Me)_4$	0	−0.5[a)]	−0.95[b)]	−0.57	−0.33
CCl_4-$SiCl_4$	20	0.05[c)]	−0.02[d)]	−0.03	−0.01
CCl_4-$TiCl_4$	20	0.08[c)]	−0.03[d)]	0.07	0.05
CCl_4-$SnCl_4$	20	0.46[c)]	0.06[d)]	0.24	0.15
$SiCl_4$-$TiCl_4$	20	−0.36[c)]	−0.48[d)]	−0.24	−0.14
$SiCl_4$-$SnCl_4$	20	0.13[c)]	−0.12[d)]	0.04	0.03
$TiCl_4$-$SnCl_4$	20	0.08[c)]	−0.01[d)]	0.01	0.01
C_6H_6-CCl_4	25	0.01[e)]	0.04[f)]	0.01	0.01
	40	0.04[e)]	0.04[f)]	0.02	0.01
	70	0.11[c)]	0.05[f)]	0.05	0.03
C_6H_6-*c*-C_6H_{12}	25	0.65[g)]	0.14[f)]	0.30	0.19
	40	0.66[g)]	0.17[f)]	0.30	0.19
	70	0.67[g)]	0.24[f)]	0.31	0.18
CCl_4-*c*-C_6H_{12}	25	0.16[h)]	0.04[h)]	0.08	0.05
	40	0.16[h)]	0.04[h)]	0.08	0.05
	70	0.16[h)]	0.05[h)]	0.08	0.05

a) A. Englert-Chwoles, *J. Chem. Phys.*, **23**, 1168 (1955).

b) J. Jeener, *J. Chem. Phys.*, **25**, 584 (1956).

c) H. Sackmann and H. Arnold, *Z. Electrochem.*, **63**, 565 (1959).

d) H. Sackmann and A. Boczek, *Z. Physik. Chem.*, **29**, 329 (1961).

e) S.E. Wood and J.P. Brusie, *J. Amer. Chem. Soc.*, **65**, 189 (1943).

f) A. Abe and P.J. Flory, *ibid.*, **87**, 1838 (1965).

g) S.E. Wood and A.E. Austin, *ibid.*, **67**, 480 (1945).

h) M. D. Peña and M. L. McGlashan, *Trans. Faraday Soc.*, **57**, 1511 (1961).

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*2 Eq. (1) is easily derived by differentiation of Eq. (16′).

*3 The values κ_T^{E} can also be calculated using $V_{\mathrm{calc.}}^{\mathrm{E}}$ calculated from the observed excess enthalpy H^{E} (see Eq. (30′)).

*4 Eq. (6) is derived from Eq. (3) by assuming $\rho_{\mathrm{A}} < 1$ and $\rho_{\mathrm{B}}' < 1$, and thus, by ignoring $V - V^*$ compared with V.

5) O. Kiyohara and K. Arakawa, *ibid* **43**, 3037 (1970). The 14th Annual Symposium on Ultrasonic and Chemical Physics, Nov. 1969, Tokyo.

as good as one can expect from a simple equation.

It is to be noted that Eqs. (3)—(7) are functions of volume and temperature.