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Note

COMMENT ON "ULTRASONIC VELOCITY AND VISCOSITY OF BINARY LIQUID MIXTURES"

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ABSTRACT

The isentropic compressibility of an ideal binary solution is discussed from the standpoint of basic thermodynamic relationships. The derived expression clearly shows that ideal solution isentropic compressibility is not a simple mole fraction average of pure component isentropic compressibilities, but rather a fairly complex expression containing isobaric heat capacity and coefficient of thermal expansion terms.

In a recent paper appearing in this journal, Islam and Quadri [1] calculated the excess isentropic compressibilities of binary benzyl alcohol + isoamyl alcohol and benzyl alcohol + isopropyl alcohol mixtures as

$$\beta_s^{ex} = \beta_s^{mixture} - \beta_s^{ideal} \tag{1}$$

i.e. the difference between the observed isentropic compressibility and that of an ideal solution β_s^{ideal}. The isentropic compressibility of an ideal solution was represented as

$$\beta_s^{ideal} = X_1\beta_{s,1}^{\ominus} + X_2\beta_{s,2}^{\ominus} \tag{2}$$

i.e. the mole fraction average of the isentropic compressibilities of the pure liquids $\beta_{s,i}^{\ominus}$. The authors interpreted the very large negative β_s^{ex} values, particularly for the benzyl alcohol + isopropyl alcohol system, in terms of molecular interactions. Negative β_s^{ex} indicated that the association between unlike molecules predominates over the dissociation of aromatic alcohol molecules.

Interpretation of molecular interactions in solution requires the correct calculation of excess properties. While many thermodynamic and physical properties of an ideal solution are correctly described by mole fraction averages, the isentropic compressibility is not one of these properties. The isentropic compressibility is related to the isothermal compressibility K_t by

$$\beta_s = K_t(C_v/C_p) \tag{3}$$

$$\beta_s = -(\partial \ln V/\partial P)_S \tag{4}$$

$$K_t = -(\partial \ln V/\partial P)_T \tag{5}$$

i.e. the ratio of heat capacities at constant volume and pressure, which are themselves related through

$$C_p - C_v = \alpha^2 VT/K_t \qquad (6)$$

where the coefficient of thermal expansion $\alpha = (\partial \ln V/\partial T)_P$. The isothermal compressibility of an ideal binary solution can easily be shown to be equal to the volume fraction (ϕ_i) average of the isothermal compressibilities of the two pure liquids

$$K_t^{\text{ideal}} = \phi_1 K_{t,1}^{\ominus} + \phi_2 K_{t,2}^{\ominus} \qquad (7)$$

and the isobaric heat capacity to be equal to the mole fraction average of the heat capacities of the pure liquids

$$C_p^{\text{ideal}} = X_1 C_{p,1}^{\ominus} + X_2 C_{p,2}^{\ominus} \qquad (8)$$

Combining eqns. (3–8) gives the following expression for the isentropic compressibility of an ideal binary solution

$$\beta_s^{\text{ideal}} = \phi_1\left\{\beta_{s,1}^{\ominus} + TV_1^{\ominus}\left(\alpha_1^{\ominus}\right)^2/C_{p,1}^{\ominus}\right\} + \phi_2\left\{\beta_{s,2}^{\ominus} + TV_2^{\ominus}\left(\alpha_2^{\ominus}\right)^2/C_{p,2}^{\ominus}\right\}$$

$$- T\left(X_1V_1^{\ominus} + X_2V_2^{\ominus}\right)\left(\phi_1\alpha_1^{\ominus} + \phi_2\alpha_2^{\ominus}\right)^2/\left(X_1C_{p,1}^{\ominus} + X_2C_{p,2}^{\ominus}\right) \qquad (9)$$

which in no way resembles a mole fraction average of the individual $\beta_{s,i}^{\ominus}$, except in the very special case when the molar volumes, isobaric heat capacities and isobaric thermal expansivities of both components are identical. It should be noted that eqn. (9) is identical to equations derived by Bertrand and Smith [2] and Benson and Kiyohara [3,4]. The large deviations in β_s^{ex} noted by Islam and Quadri in the binary benzyl alcohol + isopropyl alcohol system may well vanish when the excess values are calculated properly. Benzyl alcohol and isopropyl alcohol are dissimilar in molecular size, with molar volumes of $V \approx 104.0$ and $77.3\ \text{cm}^3\ \text{mol}^{-1}$, respectively. Numerical differences will exist between mole fraction (eqn. (2)) and volume fraction (eqns. (7) and (9)) averages of pure component properties.

REFERENCES

1 M.R. Islam and S.K. Quadri, Thermochim. Acta, 115 (1987) 335.

2 G.L. Bertrand and L.E. Smith, J. Phys. Chem., 74 (1970) 4171.

3 G.C. Benson and O. Kiyohara, J. Chem. Thermodyn., 11 (1979) 1061.

4 O. Kiyohara and G.C. Benson, J. Chem. Thermodyn., 11 (1979) 861.