Isentropic Compressibility of an Ideal Ternary Solution

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An equation is given for the isentropic compressibility of an ideal ternary solution and is used to calculate excess isentropic compressibilities of *o*-xylene + acetone + benzene, *o*-xylene + acetone + cyclohexane, and *o*-xylene + acetone + carbon tetrachloride mixtures. The results of these calculations indicate that the three ternary mixtures do not exhibit the large deviations from ideality as had been suggested by the earlier calculations of Prasad and Prakash.

In several recent publications appearing in this journal (1-3), the excess isentropic compressibility K_s^{ex} of a liquid mixture was defined as the difference between the observed isentropic compressibility and that of an ideal solution K_s^{ideal} as in eq 1.

$$K_s^{\text{ex}} = K_s - K_s^{\text{ideal}} \quad (1)$$

The isentropic compressibility of the ideal solution was represented as the mole fraction average of the isentropic compressibilities of the pure liquids K_s° , (eq 2). While many

$$K_s^{\text{ideal}} = \sum_{i=1}^N X_i K_s^{\circ} \quad (2)$$

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 of any solution is related to the isothermal compressibility K_t by

$$K_s = K_t(C_v/C_p) \quad (3)$$

$$K_s = -(\partial \ln V / \partial P)_S \quad (4)$$

$$K_t = -(\partial \ln V / \partial P)_T \quad (5)$$

Table I. Excess Isentropic Compressibilities of Several Ternary Mixtures

X_2	X_3	$10^{12}K_s^{\circ}$, cm ² dyn ⁻¹	K_s^{ex}	
			eq 1 and 2	eq 1 and 9
<i>o</i> -Xylene + Acetone + Benzene				
0.00	0.60	64.22	-0.59	-0.76
0.10	0.50	65.24	-1.73	-1.02
0.20	0.40	66.33	-2.80	-1.55
0.30	0.30	67.66	-3.63	-1.90
0.40	0.20	69.44	-4.01	-1.84
0.50	0.10	71.15	-4.46	-1.91
0.60	0.00	73.55	-4.22	-1.35
0.50	0.50	74.92	-2.61	-1.60
<i>o</i> -Xylene + Acetone + Cyclohexane				
0.00	0.60	72.04	-1.86	-1.72
0.10	0.50	72.69	-1.85	-1.22
0.20	0.40	73.02	-2.17	-1.09
0.30	0.30	73.30	-2.54	-0.98
0.40	0.20	73.45	-3.03	-1.44
0.50	0.10	73.53	-3.60	-1.14
0.60	0.00	73.55	-4.22	-1.35
0.50	0.50	86.68	+1.58	+2.26
<i>o</i> -Xylene + Acetone + Carbon Tetrachloride				
0.00	0.60	67.11	-1.65	-1.59
0.10	0.50	67.59	-2.67	-2.01
0.20	0.40	68.19	-3.57	-2.41
0.30	0.30	69.24	-4.03	-2.36
0.40	0.20	70.68	-4.09	-1.92
0.50	0.10	72.07	-4.20	-1.80
0.60	0.00	73.55	-4.22	-1.35
0.50	0.50	78.30	-2.52	-1.50

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

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

the coefficient of thermal expansion ($\alpha = (\partial \ln V / \partial T)_P$). The isothermal compressibility of an ideal solution can easily be

shown to equal the volume fraction (ϕ_i) average of the isothermal compressibilities of the pure liquids

$$K_t^{\text{ideal}} = \sum_{i=1}^N \phi_i K_{t,i}^{\circ} \quad (7)$$

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

$$C_p^{\text{ideal}} = \sum_{i=1}^N x_i C_{p,i}^{\circ} \quad (8)$$

Combination of eq 3–8 gives the following expression for the isentropic compressibility of an ideal ternary solution

$$K_s^{\text{ideal}} = \sum_{i=1}^3 \phi_i \{ K_{s,i}^{\circ} + TV^{\circ}_i (\alpha^{\circ}_i)^2 / C_{p,i}^{\circ} \} - T \left[\sum_{i=1}^3 x_i V^{\circ}_i \right] \left[\sum_{i=1}^3 \phi_i \alpha^{\circ}_i \right]^2 / \left[\sum_{i=1}^3 x_i C_{p,i}^{\circ} \right] \quad (9)$$

which in no way resembles a mole fraction average of the individual $K_{s,i}^{\circ}$, except in the very special case when the molar volumes, isobaric heat capacities, and isobaric thermal expansivities of all three components are identical. It should be noted that eq 9 is identical with equations derived by Bertrand and Smith (4) and Benson and Kiyohara (5, 6) for binary mixtures.

In Table I, I compare the excess isentropic compressibilities as calculated by Prasad and Prakash (7), using eq 1 and 2, to those values calculated from eq 1 and 9 for the ternary systems *o*-xylene + acetone + benzene, *o*-xylene + acetone + cyclohexane, and *o*-xylene + acetone + carbon tetrachloride. The isobaric heat capacities of the pure components were taken directly from the literature (7) and the numerical values of the thermal expansivities were calculated from the density data of the pure liquids at several different temperatures (8). Most noticeable in this comparison is the fact that the three ternary mixtures do not exhibit the large deviations from ideality as had been suggested by the earlier calculations of Prasad and Prakash.

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