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Note

EXCESS THERMODYNAMIC FUNCTIONS FOR A SIMPLE EUTECTIC: *m*-AMINOPHENOL–PYROGALLOL SYSTEMS

U.S. RAI, O.P. SINGH and N.P. SINGH
Department of Chemistry, B.H.U. Varanasi (UP) (India)

NARSINGH BAHADUR SINGH
Materials Research Center, R.P.I. Troy, NY 12180 (U.S.A.)

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Recently, Singh and Singh [1] reported the results of relative undercooling, linear velocity of crystallization microstructure and zone-melting studies of the *m*-aminophenol–pyrogallol eutectic system. In the absence of heats of fusion data they could not test the validity of the mixture law. The purpose of the present communication is to report details of excess thermodynamic functions, such as excess free energy, entropy and enthalpy, for this system. These parameters were computed on the basis of experimentally determined phase diagram and heats of fusion data.

Details of the experimental techniques are described in ref. 2.

From the general condition of phase equilibrium for the two phases

$$U_i^l = U_i^s \tag{1}$$

i.e.

$$U_i^{0l} + RT\ln(X_i^l\gamma_i^l) = U_i^{0s} + RT\ln(X_i^s\gamma_i^s) \tag{2}$$

where X_i and γ_i are the mole fraction and activity coefficient, respectively, of component i at a given temperature T in the solid or liquid phase (described by superscripts s and l, respectively. By simple thermodynamic relations, eqn. (2) gives eqn. (3) which can be used for computing the ideal phase boundary.

$$\ln\frac{X_i^l\gamma_i^l}{X_i^s\gamma_i^s} = -\frac{\Delta_f h_i^0}{R}\left(\frac{1}{T}-\frac{1}{T_i^0}\right) + \frac{\Delta_f C_{pi}^0}{R}\left(\ln\frac{T_i^0}{T}+1-\frac{T_i^0}{T}\right) \tag{3}$$

where T_i and $\Delta_f h_i^0$ are the melting temperature and heat of fusion, respectively, for component i. Assuming that heat of fusion is independent of temperature and the two components are miscible in the liquid phase only, eqn. (3) can be written as

$$-\ln X_i^l\gamma_i^l = \Delta_f h_i^0/R\left(1/T - 1/T_i^0\right) \tag{4}$$

TABLE 1

Heats of fusion

Material	$\Delta_f h$ (kJ mole^{-1})
m-Aminophenol	22.98
Pyrogallol eutectic;	18.55
Experimental	19.94
Mixture law	20.94

Equation (4) was used to calculate the activity coefficient of *m*-aminophenol and pyrogallol at the eutectic point. The results are given in Table 1. Assuming that $\gamma_i^l = 1$, the ideal phase boundary was computed for the whole composition range, and the results are shown in Fig. 1 along with the experimental data.

If the eutectic is assumed to be a simple mechanical mixture, the heat of fusion is given as

$$(\Delta_f h)_e = \sum X_i, \Delta_f h_i^0 \tag{5}$$

where $(\Delta_f h)_e$ is the heat of fusion for the eutectic mixture. For the present eutectic, the experimental value was much less than that predicted by the mixture law. This indicates some kind of association or clustering in the eutectic melt. In order to clarify this, we computed the excess thermody-

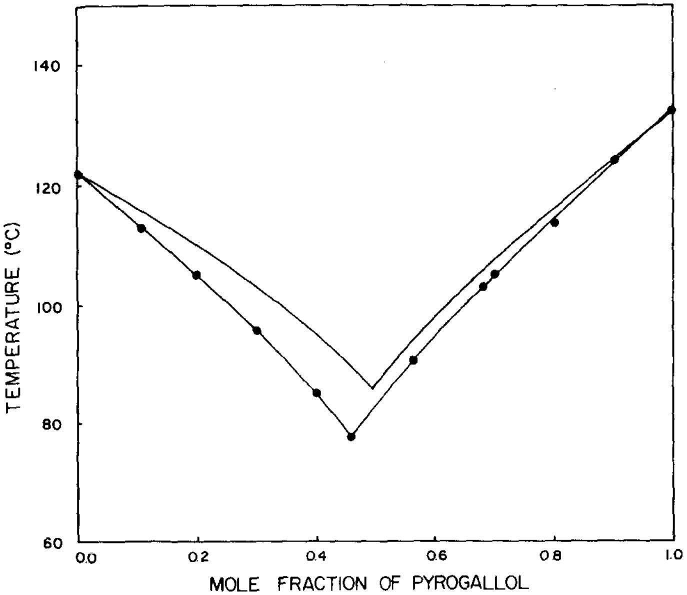

Fig. 1. Mole fraction of pyrogallol. ———, ideal phase boundary; ●———●, experimental phase boundary.

TABLE 2

Values of $\ln \gamma_i^l$ and $\partial \ln \gamma_i^l/\partial T$ at the eutectic temperature

Material	$\ln \gamma_i^l$	$\partial \ln \gamma_i^l/\partial T$
m-Aminophenol	−0.2333	−0.0016
Pyrogallol	−0.0834	−0.0093

TABLE 3

Excess thermodynamic functions for the eutectic

Functions	Values (J mole^{-1})
g^E	−478.0
s^E	−11.1
h^E	−1044.0

namic functions given by [3] the equations

$$g^E = RT\left(X_1 \ln \gamma_1^l + X_2 \ln \gamma_2^l\right) \tag{6}$$

$$s^E = -R\left(X_1 \ln \gamma_1^l + X_2 \ln \gamma_2^l + X_1 T\partial \ln \gamma_1^l/\partial T + X_2 T\partial \ln \gamma_2^l/\partial T\right) \tag{7}$$

$$h^E = -RT^2\left(X_1\partial \ln \gamma_1^l/\partial T + X_2\partial \ln \gamma_2^l/\partial T\right) \tag{8}$$

$\ln \gamma_i^l$ was calculated from eqn. (4) and $\partial \ln \gamma_i^l/\partial T$ was computed as follows. Differentiation of eqn. (4) gives

$$\frac{\partial \ln \gamma_i^l}{\partial T} = \Delta_f h_i^0/RT^2 - \partial X_i/X_i\partial T \tag{9}$$

$\partial X_i/\partial$T was evaluated by taking two points near the eutectic point and arranging in the form

$$X_i = A + BT_i \tag{10}$$

where $B = \partial X_i/\partial T$. Since other parameters of eqn. (9) are known, the $\partial \ln \gamma_i^l/\partial T$ values were computed for both components at the eutectic temperature. These values are also recorded in Table 2. The excess thermodynamic functions computed by eqns. (6), (7) and (8) are shown in Table 3. These values are negative, indicating some sort of molecular clustering in the eutectic melt.

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