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Supplementary Material Available. The complete Table VIII will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 20× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche, referring to code number JCED-73-253.

Heat of Mixing and Vapor-Liquid Equilibrium of Acetophenone-2-Butanol System

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The heat of mixing of the acetophenone–2-butanol system exhibits an endothermic maximum of 541 cal/mol of solution close to 0.50 mole fraction at temperatures close to 25°C. Vapor-liquid equilibrium data of this system are reported at 1 atm pressure over the entire composition range.

The acetophenone–2-butanol system can be expected to deviate from ideality owing to hydrogen bonding between both like and unlike species. This work is part of a continuing study of phase equilibria and heat of mixing of alcohol-ketone systems. The heat of mixing absorbed in this system indicates the degree of the formation of alcohol-ketone hydrogen bonds with the loss of alcohol-alcohol hydrogen bonds, with the endothermic heat of mixing indicating a net decrease in number of hydrogen bonds. Activity coefficients calculated from the vapor-liquid equilibria data of this system also indicate solution nonideality.

Experimental

Details of the apparatus and the experimental methods used in this work have been described (*2, 6*). The 2-butanol used was reagent grade, obtained from Eastman Kodak Co., acetophenone used was chromatoquality, obtained from Matheson Coleman & Bell. Reagents were purified by fractional distillation. Boiling points and refractive indices at 25°C of 2-butanol and acetophenone used were 99.5°C and 1.3946 and 202.1°C and 1.5313, respectively. Equilibrium data were obtained by use of an improved Othmer still, and refractive index measurements were used for analysis. The overall reliability of equilibrium data is estimated to be ±0.005 mole fraction.

The calorimeter consisted of a 500-cm^3 Dewar flask fitted with a Beckman and a standardized calorimetric thermometer and a stirrer. Liquids were mixed in all cases by crushing a thin-walled bulb of a capsule containing one component against the bottom of the Dewar flask which contained the other component. Heat capacity of the system was determined by passing a known current through a calibrated resistance wire which was wound about the glass stirrer. The power supply used was a Kepco unit, Model 430D, and was voltage regulated. The calorimeter was warmed prior to mixing to give a temperature change with an average temperature of 25°C.

Results and Discussion

Experimental results are shown in Figures 1 and 2 and tabulated in Tables I and II. The activity coefficients calculated and shown in Table I indicate considerable nonideality. The latter nonideality is supported by the heat of mixing absorbed for the system at 25°C as seen in Figure 2, which exhibits a maximum of 541 cal/mol of solution at approximately 0.5 mole fraction.

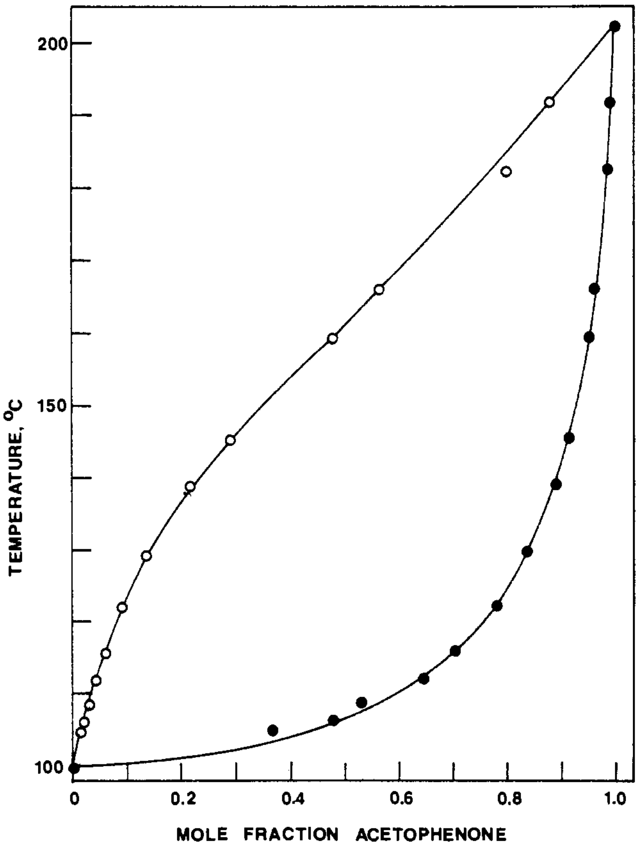

Figure 1. Boiling point–composition curve for acetophenone–2-butanol system

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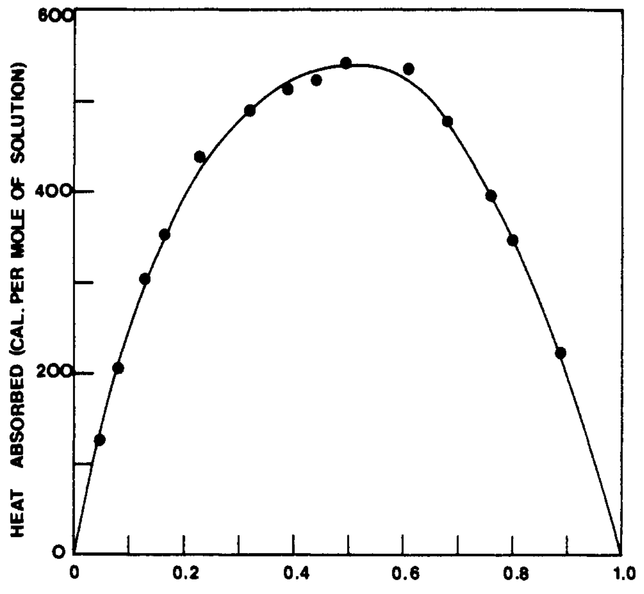

Figure 2. Heat of mixing-composition curve for acetophenone-2-butanol system

Activity coefficients were calculated, correcting for nonideal gas behavior (*4*), for experimental equilibrium points using the equation:

$$\gamma_i = \frac{Z_i y_i P}{x_i p_i^\circ} \qquad (1)$$

Vapor pressures used for calculation of γ_i were taken from smooth plots of data reported for 2-butanol (*1*) and for acetophenone (*5*).

As with many other systems where strong association owing to hydrogen bonding occurs, we could not satisfactorily represent the vapor-liquid equilibrium data of this system by use of the Gibbs-Duhem equation. Examination of an equation which can be derived from the Gibbs-Duhem equation shows that the heat of mixing per mole of solution, H^M, as a function of temperature, is necessary for a conclusive thermodynamic test of the data:

$$\Delta Q = \int_0^1 [\log \gamma_1/\gamma_2 - (H^M/4.576\, T^2) \times (dT/dx_1)_P]\, dx_1 = 0 \qquad (2)$$

where Q, the Redlich-Kister (*3*) function, is defined in terms of the excess free energy change per mole of solution, ΔG^E:

$$Q = \frac{\Delta G^E}{4.576\, T} = x_1 \log \gamma_1 + x_2 \log \gamma_2 \qquad (3)$$

In Equation 2, $(dT/dx_1)_P$ can be obtained from the liquid curve of Figure 1, but H^M must be known at the experimental temperatures involved. Such heat of mixing data as a function of temperatures are not presently available for this system.

Table I. Vapor-Liquid Equilibrium Data at 1 Atm Pressure of Acetophenone(1)-2-Butanol(2) System

Bp, °C	x_1	y_1	γ_1	γ_2
104.8	0.367	0.018	0.960	1.279
106.1	0.479	0.023	0.890	1.502
108.1	0.534	0.033	1.062	1.520
111.9	0.648	0.045	1.034	1.726
115.7	0.705	0.062	1.153	1.791
122.1	0.780	0.093	1.282	1.879
129.5	0.837	0.138	1.407	1.941
138.9	0.890	0.217	1.492	2.050
145.2	0.914	0.293	1.579	2.050
159.2	0.953	0.481	1.577	2.054
165.8	0.963	0.567	1.495	1.826
182.3	0.988	0.801	1.289	1.975
191.5	0.990	0.879	1.110	1.234

Table II. Heat of Mixing Data at 25°C of Acetophenone(1)-2-Butanol(2) System

x_1	H^M, cal/mol of solution
0.039	127
0.081	206
0.129	304
0.165	353
0.228	439
0.321	488
0.389	520
0.440	522
0.496	541
0.611	535
0.679	477
0.760	396
0.798	345
0.888	224

Nomenclature

γ_i = liquid phase activity coefficient of component i
P = total pressure, torr
p_i° = vapor pressure of pure component i, torr
x_i = mole fraction of component i in liquid phase
y_i = mole fraction of component i in vapor phase
Z_i = correction factor for perfect gas law deviations

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