Excess Enthalpies of Mixing and Excess Heat Capacities of Binary Mixtures of Formic Acid and Pyridine at 30 °C

Arun K. Nandi and Sailendra N. Bhattacharyya*

Polymer Science Unit, Indian Association for the Cultivation of Science, Jadavpur, Calcutta 700 032, India

Molar excess enthalpies of mixing (H^E) and molar excess heat capacities at constant pressure (C_p^E) of the binary mixtures of pyridine (PY) and formic acid (FA) at different compositions were measured at 30 °C using a modified Arnett-type solution calorimeter. Data indicate solvation of the pyridinium complex at higher formic acid content mixtures.

Introduction

Formic acid and pyridine behave as solvents toward some polymers (1). Due to the acid–base behavior of these solvents it was of interest to study the solubility behavior of a polymer in the mixtures of the two solvents. We reported a thermodynamic study of such systems earlier (2, 3). In connection with the above study we measured calorimetrically the excess enthalpies of mixing of formic acid and pyridine at different compositions. The excess heat capacities of the mixtures at different compositions were also measured in a separate experiment, and both the data have been presented in this paper.

Experimental Section

Calorimeter. A simple and easy to build submarined calorimeter was designed and fabricated in this laboratory. It was a modified form of the solution calorimeter of Arnett et al. (4). It was a glass vessel having a long-necked inlet tube connected acentrically at the top and was fitted with a small heater and a thermistor in two mercury-filled wells of the vessel (Figure 1). The thermistor was connected to a recorder through a suitable bridge circuit and a millimicrovoltmeter (Keithley Instruments, 149 model). Samples in small batches can be added with the help of long-stemmed capillary tubes that terminate into a small reservoir (1–5 cm³ capacity). The bottom of the reservoir was closed by a thin flat glass membrane and can rest on a glass anvil attached to the calorimeter. The sample tubes can be inserted in the calorimeter through the inlet tube and were guarded with Teflon rings to check evaporation. The liquid inside the calorimeter was stirred by a glass-encapsuled magnetic stirrer. The glass vessel was placed in a brass jacket which was connected to a high-vacuum line. The whole assembly was immersed in a thermostatic water bath whose temperature was regulated within ±0.01 °C. The bath temperature was measured by a Hewlett-Packard (model 240A) quartz thermometer.

Testing of the Calorimeter. The calorimeter was tested by measuring the enthalpy of neutralization of 0.18 M hydrochloric acid and 0.018 M sodium hydroxide solution. A 10 cm³ volume of sodium hydroxide solution was taken in the calorimeter, and 1 cm³ of hydrochloric acid solution was introduced through the inlet tube. After equilibration for 2 h the glass seal was broken. The deflection obtained in the recorder was converted to energy by the standard procedure of calibrating it against a known joule heating produced inside the calorimeter through the heater incorporated therein. All the deflections were corrected for cooling. The enthalpy of
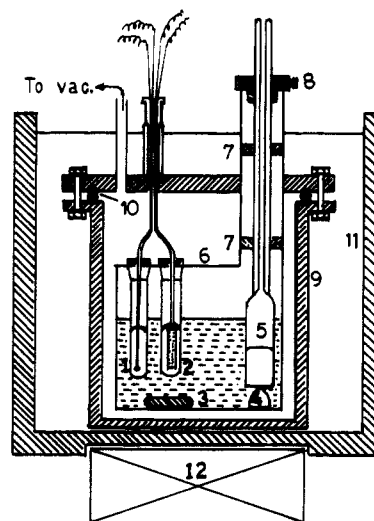

Figure 1. Schematic diagram of the calorimeter: 1, thermistor; 2, heater; 3, magnetic needle; 4, glass anvil; 5, glass container for adding liquid (sample tube); 6, calorimetric vessel; 7, Teflon rings; 8, Teflon ring with screw; 9, metal jacket; 10, rubber O ring; 11, water thermostat; and 12, magnetic stirrer.

mixing was calculated from the relation

$$Q = IVt(h_1/h_2) \tag{1}$$

where h_1 and h_2 are the deflections due to the mixing process and calibration. I, V, and t are current, voltage, and time, respectively. The measurement was repeated several times. The agreement of the literature value (5) with the individual value of all the measurements was within ±0.5%.

The energy evolved during such an experiment was approximately 8 J. The accuracy of the measurements was thus better than ±0.5% for enthalpy values equal or greater than this amount produced actually in the calorimeter. Below this level, the accuracy will decrease and will depend on the actual energy produced. The precision of the measurement was estimated to be 80 mJ/mm at this level.

Excess Enthalpy of Mixing. A 10 cm³ volume of component 1 (either formic acid or pyridine) was taken in the calorimeter to start with and equilibrated in the bath for 2 h. A weighed amount of the other component (~1 g) in a sample tube was inserted into the calorimeter through the inlet tube. After equilibration for another ¹/₂ h, the glass seal was broken. The energy evolved was measured as described earlier. The sample tube was then withdrawn, and another such tube with about 1 g of pure component 2 was

Table I. Excess Enthalpies (H^E) of x Pyridine + (1 − x) Formic Acid at 30 °C

x	H^E/(kJ mol^{-1})	x	H^E/(kJ mol^{-1})	x	H^E/(kJ mol^{-1})
0.023	−1.194	0.240	−8.359	0.402	−7.974
0.045	−2.314	0.259	−8.475	0.414	−7.873
0.069	−3.390	0.276	−8.528	0.424	−7.889
0.091	−4.348	0.292	−8.528	0.453	−7.587
0.110	−5.095	0.308	−8.484	0.488	−7.209
0.128	−5.811	0.322	−8.443	0.528	−6.718
0.140	−6.222	0.334	−8.399	0.574	−6.116
0.162	−6.877	0.349	−8.320	0.631	−5.371
0.184	−7.461	0.364	−8.219	0.688	−4.569
0.203	−7.871	0.377	−8.152	0.764	−3.480
0.222	−8.167	0.390	−8.071	0.866	−1.973

Table II. Heat Capacities (C_p) of x Pyridine + (1 − x) Formic Acid at 30 °C

| x	C_p/ (J K^{-1} mol^{-1})	x	C_p/ (J K^{-1} mol^{-1})	x	C_p/ (J K^{-1} mol^{-1})
0.00	102.9	0.318	110.3	0.656	212.3
0.104	104.3	0.484	114.7	0.858	135.1
0.190	107.7	0.540	119.2	1.000	148.1

inserted into the calorimeter. The enthalpy change of component 2 with the earlier solution was then measured. The excess enthalpy of mixing for the new resulting composition was then calculated from the values obtained from the two experiments. The process was repeated with successive additions of component 2 up to nearly 0.4 mole fraction of pyridine. The components were then reversed, and measurement was done from the other end of the composition scale until the compositions merged. During each withdrawal of the sample tube a small amount of the solution was found to adhere to the sample tube. It was accounted for by weighing. With this kind of experiment error tends to accumulate with each addition of component 2. So the error would be maximum near 0.4 mole fraction pyridine when components are switched. The cumulative error around this mole fraction could be as large as ±5%. But the excellent overlap of the two sets of measurements indicates that the actual error is much less.

Excess Heat Capacities. For excess heat capacity measurements, samples of known composition and of known weight were taken into the calorimeter. One probe of the quartz thermometer guarded by Teflon rings was inserted into the calorimeter in place of the sample tube to measure directly the temperature change of the calorimeter. The calibrating heater of the calorimeter was then used to heat the solution from 28.5 to 31.5 °C. The specific heat at the average temperature of 30 °C was obtained from the following equation:

$$(ms + ws_1)(T_2 - T_1) = IVt \tag{2}$$

where m and s are the mass and heat capacity of the solution, w is the water equivalent of the calorimeter, s_1 is the heat capacity of water at 30 °C, and $T_2 - T_1$ is the rise of the temperature of the solution. The water equivalent of the calorimeter had been determined separately using a known amount of distilled water (s_1 = 4.1785 J/g at 30 °C) as the calorimetric liquid.

The heat capacity measurements are not of high accuracy, and from the scatter of the excess heat capacity data the accuracy of the excess heat capacity measurement is estimated to be around ±10%. But these are direct measurements and hopefully give better results than one would obtain from temperature variation of excess enthalpies.
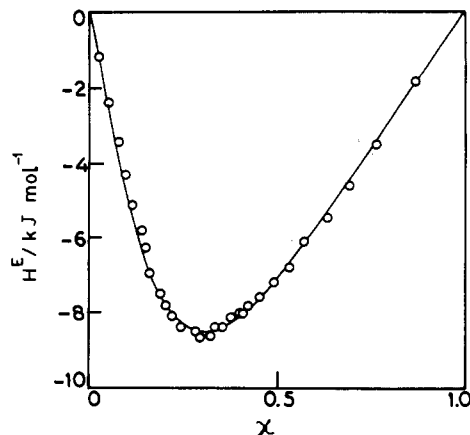
Figure 2. H^E of (1 − x) formic acid + x pyridine mixtures at different mole fractions of pyridine (the solid curve is according to eq 4 and open circles represent the experimental points).
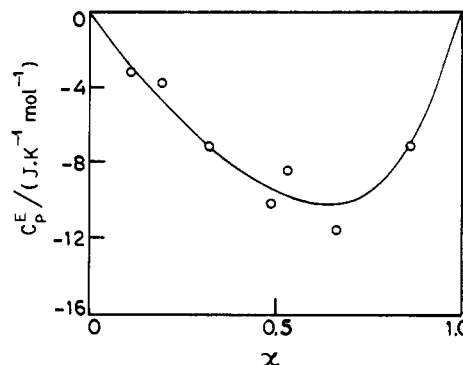
Figure 3. C_p^E of (1 − x) formic acid + x pyridine mixtures at different mole fractions of pyridine (the solid curve is according to eq 4 and open circles represent the experimental points).

The molar excess heat capacity values (C_p^E) were calculated from the equation

$$C_p^E = C_{p,m} - [(1 - x)C_{p,1} + xC_{p,2}] \tag{3}$$

where $C_{p,i}$ with the appropriate subscript is the molar heat capacity of the component i or the mixture and x is the mole fraction of component 2 (pyridine).

Materials. Formic acid (BDH) and pyridine (BDH) were of analytical reagent grade. They were dried over anhydrous sodium sulfate and solid potassium hydroxide, respectively, and fractionally distilled. Only the middle fractions were collected.

Results and Discussion

The excess enthalpy of mixing and heat capacity of the pyridine + formic acid system are given in Tables I and II, respectively. The excess enthalpy of mixing values and the curve of Figure 2 reveal that its maximum value is not located at 50 mol % pyridine, where a 1:1 complex is formed, but approximately at 25 mol % pyridine. The enthalpy of formation of the pyridine–formic acid (PY–FA) complex at different compositions of the mixture can be obtained from the straight lines drawn from H^E at x_{PY} = 0 to H^E at x_{PY} = 0.5 and H^E at x_{PY} = 1 to H^E at x_{PY} = 0.5 in the acid- and pyridine-rich regions, respectively. The results reveal that in the acid-rich zone there are larger excess negative enthalpies than are required for the complex formation. It was pointed out earlier that in the excess formic acid region solvation of the complex occurs through H-bonding of the pyridine formate with FA and it is absent in the pyridine-rich region (2). The

Table III. Adjustable Parameters of Equation 4 and Standard Deviations $\sigma(Q^E)$ for the Pyridine + Formic Acid System

Q^E	K	A_0	A_1	A_2	A_3	A_4	$\sigma(Q^E)$
H^E	0.7	−18.087	−4.19	−1.166	8.114	10.893	0.062
$C_p{}^E$	0.0	−37.948	20.019	−13.994			0.91

excess enthalpy of mixing of the pyridine + formic acid system is larger than that of the pyridine + acetic acid system (6) which corroborates the stronger acid character of formic acid than acetic acid.

The heat capacity values of the pure components and of the mixtures are given in Table II. The measured heat capacity of pure formic acid is 102.9 J K^{-1} mol^{-1} and compares favorably with the reported values for these systems in the literature, 99.1 and 100.35 J K^{-1} mol^{-1} (7,8). For pure pyridine the reported values of C_p are 135.1 J K^{-1} mol^{-1} at 17 °C (9) and 132.5 J K^{-1} mol^{-1} (extrapolated value) (10). The value obtained in this experiment is 148.6 J K^{-1} mol^{-1} at 30 °C. The discrepancy from the literature value in this case is somewhat higher compared to that of formic acid. The excess enthalpy (H^E) and excess heat capacity results (calculated from eq 3) were fitted in the equation

$$Q^E = \frac{x(1-x)\sum_{i=0}^{n-1}A_i(1-2x)^i}{1-K(1-2x)} \quad (4)$$

where $Q^E = H^E/(\text{kJ mol}^{-1})$ or $C_p/(\text{J mol}^{-1}\ \text{K}^{-1})$ and A_i and K are adjustable coefficients. The adjustable coefficients and the corresponding standard deviations $\sigma(Q^E)$ are given in Table III. In Figures 2 and 3 the solid curves represent the plot according to eq 4 for H^E and $C_p{}^E$ values, respectively. The experimental values are also included in the figures. The $C_p{}^E$ values for this system are negative for intermediate compositions. The only explanation that can be offered here for negative $C_p{}^E$ is that the C_p of 1 mol of the 1:1 complex PY–FA formed must be less than the total C_p of 1 mol of pyridine and 1 mol of formic acid required to form the complex.

Acknowledgment

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