Enthalpies of Mixing for Binary Liquid Mixtures of Acids

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For the binary liquid systems formic acid + acetic acid, formic acid + propionic acid, and acetic acid + propionic acid, we give the results of new calorimetric measurements of the molar excess enthalpy $\bar{H}^E$ at 25 °C, 30 °C, 40 °C, and 60 °C, covering the entire range of compositions. $\bar{H}^E$ is always positive, increases linearly with the temperature, and is slightly asymmetric with respect to the mole fraction x. The composition at the maximum of the function $\bar{H}^E(x)$ is independent of the temperature.

Previous calorimetric work refers to the enthalpies of mixing for the liquid systems water + acetic acid [1, 2] and formic acid + acetic acid [3]. We now deal with the corresponding measurements for the three binary liquid systems which can be formed from the components formic acid, acetic acid, and propionic acid.

Taking account of experiences made earlier in our laboratory [4], we developed an improved calorimeter [5] based on the principle of continuous flow and of continuous compensation of temperature changes by simultaneous use of an electric heater and of a Peltier-effect device. We also reconsidered [5] the equations describing the balance of mass and energy and thus established precise formulae for the evaluation of the experimental data. Hence, we were able to determine, in a rigorous way, heats of mixing in a wide range of temperatures for both endothermic and exothermic conditions.

Table 1. Values of the parameters b_0, b_1, b_2 in (1) for different systems and temperatures.

System and temperature	b_0 / J mol^{-1}	b_1 / J mol^{-1}	b_2 / J mol^{-1}
Formic acid + acetic acid			
25 °C	537	53	−110
30 °C	566	80	−110
40 °C	573	83	−125
60 °C	639	77	−150
Formic acid + propionic acid			
25 °C	2250	−728	−400
30 °C	2310	−657	−240
40 °C	2420	−465	510
60 °C	2690	−531	610
Acetic acid + propionic acid			
25 °C	266	−48	− 65
30 °C	274	−46	−105
40 °C	302	−74	− 85
60 °C	392	50	− 10

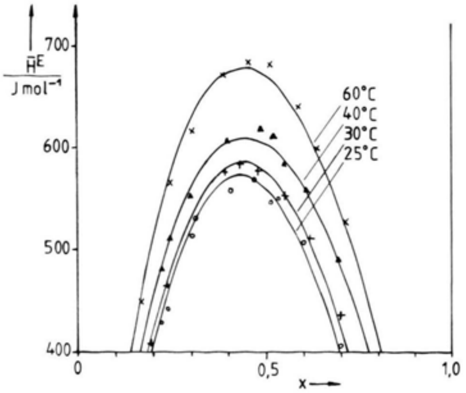

Fig. 1. Liquid system formic acid + propionic acid (as an example): Molar excess enthalpy $\bar{H}^E$ against mole fraction x of propionic acid at 25 °C, 30 °C, 40 °C, and 60 °C [curves calculated according to (1) with parameters in Table 1, marked points: measured values].

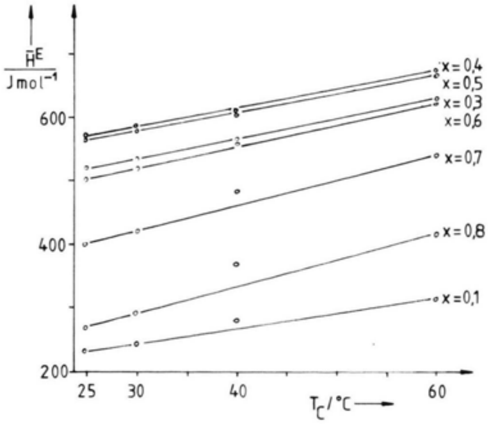

Fig. 2. Liquid system formic acid + propionic acid: Molar excess enthalpy $\bar{H}^E$ against Celsius temperature T_C for different values of mole fraction x of propionic acid (compare Figure 1).

Though the electric conductivity of the system formic acid + acetic acid, for example, is measurable [6], the three liquid systems treated here may be considered to be nonelectrolyte solutions in the present context.

The experiments [5] have been carried out in the whole range of compositions (between 11 and 25 compositions at each temperature) at 25 °C, 30 °C, 40 °C, and 60 °C. The equation (typical for binary nonelectrolyte solutions)

$$\bar{H}^E = x(1-x)[b_0 + b_1(2x-1) + b_2(2x-1)^2] \quad (1)$$

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fits the results. Here $\bar{H}^{\mathrm{E}}$ denotes the molar excess enthalpy (molar enthalpy of mixing or molar heat of mixing), x the mole fraction of the second component, while b_0, b_1, b_2 represent empirical parameters depending on the temperature and on the nature of the system (see Table 1).

The values of $\bar{H}^{\mathrm{E}}$ are always positive, indicating that in each case the process of mixing the pure liquid components is endothermic. The function $\bar{H}^{\mathrm{E}}(x)$ is slightly asymmetric, the composition at the maximum being independent of the temperature (see Fig. 1 and Table 2). For given composition, $\bar{H}^{\mathrm{E}}$ increases linearly with the temperature T (see Fig. 2). This means that $\partial \bar{H}^{\mathrm{E}}/\partial T$ (molar excess heat capacity at constant pressure) is positive and a function of composition only. The values of $\bar{H}^{\mathrm{E}}$ (for given temperature and composition) as well as the maximum of the function $\bar{H}^{\mathrm{E}}(x)$ (for given temperature) increase in the order of increasing difference between the components (see Fig. 3 and Table 2).

Table 2. Maximum $\bar{H}^{\mathrm{E}}_{\max}$ (experimental values) of molar excess enthalpy $\bar{H}^{\mathrm{E}}$ (with respect to composition) for different systems and temperatures (x: mole fraction of second component at maximum).

System and temperature	x	$\bar{H}^{\mathrm{E}}_{\max}/\mathrm{J\ mol^{-1}}$
Formic acid + acetic acid	0.55	
25 °C		137
30 °C		139
40 °C		143
60 °C		160
Formic acid + propionic acid	0.45	
25 °C		568
30 °C		585
40 °C		620
60 °C		690
Acetic acid + propionic acid	0.47	
25 °C		68
30 °C		72
40 °C		79
60 °C		106

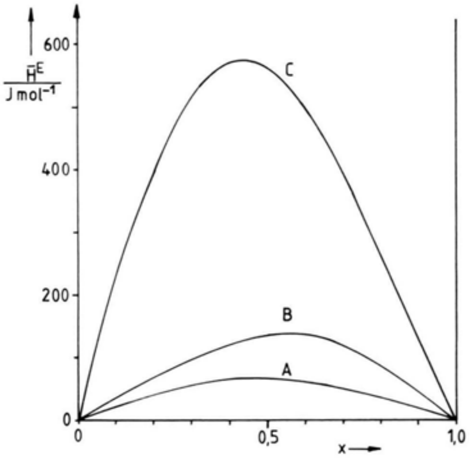

Fig. 3. Liquid systems acetic acid + propionic acid (A), formic acid + acetic acid (B), and formic acid + propionic acid (C): Molar excess enthalpy $\bar{H}^{\mathrm{E}}$ against mole fraction x of second component at 25 °C (measured values).

For details the reader should consult the original comprehensive report [5].

Obviously the water-free liquid systems investigated here show less complicated behaviour than the system water + acetic acid [1, 2] where a change of sign occurs in $\bar{H}^{\mathrm{E}}$.

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