Enthalpies of Mixing for the Liquid System Formic Acid + Acetic Acid

R. Haase, H.-J. Jansen, K. Puder, and B. Winter
Institut für Physikalische Chemie
der Technischen Hochschule Aachen

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After a short description of the evaluation of the calorimetric measurements, we give the results for the enthalpies of mixing in the liquid system formic acid + acetic acid. The molar excess enthalpy $\bar{H}^E$ has been determined as a function of the mole fraction x of acetic acid at 18 °C, 20 °C, 25 °C, 30 °C, and 40 °C. The function $\bar{H}^E(x)$ is always positive and nearly symmetric (with a maximum at about $x = 0.5$) and increases with increasing temperature. A three-parameter fit of the function $\bar{H}^E(x)$ has been achieved for each temperature.

Some time ago [1], we described measurements of the enthalpies of mixing for the liquid system water + acetic acid, carried out with a newly developed calorimeter 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 now want to present some results obtained with the same type of calorimeter in the case of the enthalpies of mixing for the liquid system formic acid + acetic acid. Though we have measured [2] the electric conductivity in the last liquid mixture, it may be considered to be a nonelectrolyte solution in the present context.

Before giving the experimental results for our special case, we shall shortly explain the principles of evaluating the calorimetric measurements.

If dashed symbols (′) refer to the calorimeter (including the liquid system) plus the electric heater and doubly dashed symbols (″) to the thermocouple (with its two junctions), we find for the increase ΔH of the enthalpy H:

$$\Delta H' = W'_{\mathrm{el}} + Q', \quad \Delta H'' = W''_{\mathrm{el}} + Q'', \tag{1}$$

where W_{el} is the (measurable) electric work done on the system (product of electric potential difference, electric current and time) and Q is the heat supplied to the system. (Here the fact that each system is closed and at constant pressure has been taken into account.)

Considering that the only exchange of heat with the surroundings taking place in the system ′ is that due to the contact with the thermocouple at one of its junctions (subscript 1), we obtain:

$$Q' = -Q''_1, \quad Q'' = Q''_1 + Q''_2, \tag{2}$$

Q''_2 being the heat supplied to the thermocouple everywhere except at the junction mentioned ($Q''_1 > 0$, $Q''_2 < 0$).

The experimental conditions are such that the temperatures in both systems are independent of time. Thus we have:

$$\Delta H' = \Delta_{\mathrm{m}} H, \quad \Delta H'' = 0. \tag{3}$$

Here $\Delta_{\mathrm{m}} H$ is the enthalpy of mixing.

Combining Eqs. (1), (2), and (3), we derive:

$$\Delta_{\mathrm{m}} H = W'_{\mathrm{el}} + Q', \tag{4}$$

$$Q' = W''_{\mathrm{el}} + Q''_2. \tag{5}$$

For a calibration experiment in the case $\Delta_{\mathrm{m}} H = 0$ ($W'_{\mathrm{el}} = W_0$), there results from (4):

$$W_0 = -Q'. \tag{6}$$

Now, for the thermocouple, in both the calibration and the mixing experiment, the temperatures, the potential difference and the current have the same values. Hence, it follows from (5) that, for a given time, Q' has a fixed value. Thus we conclude from (4) and (6) that

$$\Delta_{\mathrm{m}} H = W'_{\mathrm{el}} - W_0, \tag{7}$$

the final formula for the evaluation of the measurements. So we can easily compute the molar excess enthalpy (molar enthalpy of mixing) $\bar{H}^E = \Delta_{\mathrm{m}} H / n$ (n: total amount of substance of the mixture).

We thus determine $\bar{H}^E$ for the liquid system formic acid + acetic acid in the whole range of compositions at 18 °C, 20 °C, 25 °C, 30 °C, and 40 °C. The equation (typical for binary nonelectrolyte solutions)

$$\bar{H}^E = x(1-x)[b_0 + b_1(2x-1) + b_2(2x-1)^2] \tag{8}$$

fits the results. Here x is the mole fraction of acetic acid while b_0, b_1, and b_2 are empirical parameters depending on the temperature. These parameters, computed directly from the experimental data [3, 4], are listed in Table 1.

Reprint requests to Prof. Dr. R. Haase, Institut für Physikalische Chemie, Technische Hochschule Aachen, D-5100 Aachen.

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Table 1. Parameters of Eq. (8) for the temperatures investigated.

	$\frac{b_0}{\text{J mol}^{-1}}$	$\frac{b_1}{\text{J mol}^{-1}}$	$\frac{b_2}{\text{J mol}^{-1}}$
18 °C	533	− 25	− 108
20 °C	536	− 27	− 114
25 °C	561	− 29	− 122
30 °C	566	− 29	− 112
40 °C	592	− 29	− 137

The molar excess enthalpy $\bar{H}^E$ is always positive so that the process of mixing the pure liquid components is endothermic. The function $\bar{H}^E(x)$ is nearly symmetric (with a maximum at about $x = 0.5$) at all temperatures. For given composition, $\bar{H}^E$ increases with increasing temperature. All this can be seen in Figure 1.

For experimental details the reader should consult the original comprehensive reports [3, 4].

As far as the authors are aware, there are no literature data for the enthalpies of mixing of the system considered here.

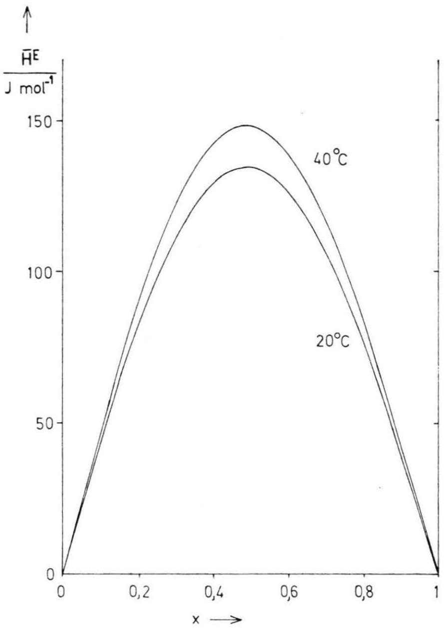

Fig. 1. Molar excess enthalpy $\bar{H}^E$ of the liquid system formic acid + acetic acid against mole fraction x of acetic acid at 20 °C and 40 °C.

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