Enthalpies of Mixing for Binary Liquid Mixtures of Monocarbonic Acids and Alcohols

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We present the results of calorimetric measurements of the molar enthalpy of mixing (molar excess enthalpy) $\bar{H}^E$ as a function of temperature and composition (described by the mole fraction x of the alcohol) for 18 binary liquid systems consisting of an aliphatic monocarbonic acid (formic, acetic, propionic, butyric, valeric acids) and an aliphatic alcohol (methanol, ethanol, 1-propanol, 2-propanol, 1-butanol, 2-methyl-2-propanol). The experiments cover temperatures between 298.15 K and 318.15 K and the whole range of compositions (usually nearly 40 compositions at each temperature). There is a great variety of behaviour as far as the function $\bar{H}^E(x)$ for T = const is concerned. Many systems show endothermic mixing ($\bar{H}^E > 0$), other systems exothermic mixing ($\bar{H}^E < 0$), again other systems partly endothermic, partly exothermic behaviour. There is one case (acetic acid + 2-methyl-2-propanol) where $\bar{H}^E(x)$ changes its sign twice and the molar excess heat capacity exhibits unusually large negative values.

Previous calorimetric work in this laboratory concerns the enthalpies of mixing (excess enthalpies) for the binary liquid systems water + acetic acid [1, 2], formic acid + acetic acid [3, 4] as well as formic acid + propionic acid and acetic acid + propionic acid [4]. We now turn to a comprehensive study [5] of 18 binary liquid systems among the 30 possible combinations of the type acid + alcohol formed from the components formic acid, acetic acid, propionic acid, butyric acid, valeric acid (aliphatic monocarbonic acids) and methanol, ethanol, 1-propanol, 2-propanol, 1-butanol, 2-methyl-2-propanol (aliphatic alcohols) at temperatures between 298.15 K and 318.15 K and over the whole range of compositions (usually nearly 40 compositions at each temperature). The systems investigated are shown in Table 1.

Our calorimeter [5] is an improved construction of a flow-type calorimeter described earlier [4], based on the principle of continuous flow and of continuous compensation of temperature changes by simultaneous use of an electric heater and a Peltier-effect device.

The quantity derived from the measurements is the molar enthalpy of mixing (molar excess enthalpy) $\bar{H}^E$ as a function of the temperature T and

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Table 1. Systems investigated with respect to molar excess enthalpy $\bar{H}^E$ as a function of the mole fraction x of the alcohol at temperature T. The column "Type" indicates the type of the $\bar{H}^E(x)$-diagramm: the signs + and − refer to positive values of $\bar{H}^E$ (endothermic mixing) and to negative values of $\bar{H}^E$ (exothermic mixing), respectively.

System	T	Type
Formic acid + 1-propanol	298.15 K	−
+ 2-propanol	298.15 K	−
+ 1-butanol	298.15 K	+ −
+ 2-methyl-2-propanol	303.15 K	−
Acetic acid + methanol	298.15 K and 318.15 K	+ −
+ ethanol	298.15 K	+
+ 1-propanol	298.15 K	+
+ 2-propanol	298.15 K and 318.15 K	+
+ 1-butanol	298.15 K and 318.15 K	+
+ 2-methyl-2-propanol	303.15 K	+
+ 2-methyl-2-propanol	312.15 K and 312.85 K	+−+
+ 2-methyl-2-propanol	318.15 K	+−
Propionic acid + methanol	298.15 K and 318.15 K	+−
+ 2-propanol	298.15 K and 318.15 K	+
+ 1-butanol	298.15 K and 318.15 K	+
+ 2-methyl-2-propanol	303.15 K	+
Butyric acid + methanol	298.15 K	+−
Valeric acid + methanol	298.15 K and 318.15 K	+
+ 2-propanol	298.15 K and 318.15 K	+
+ 1-butanol	298.15 K and 318.15 K	+

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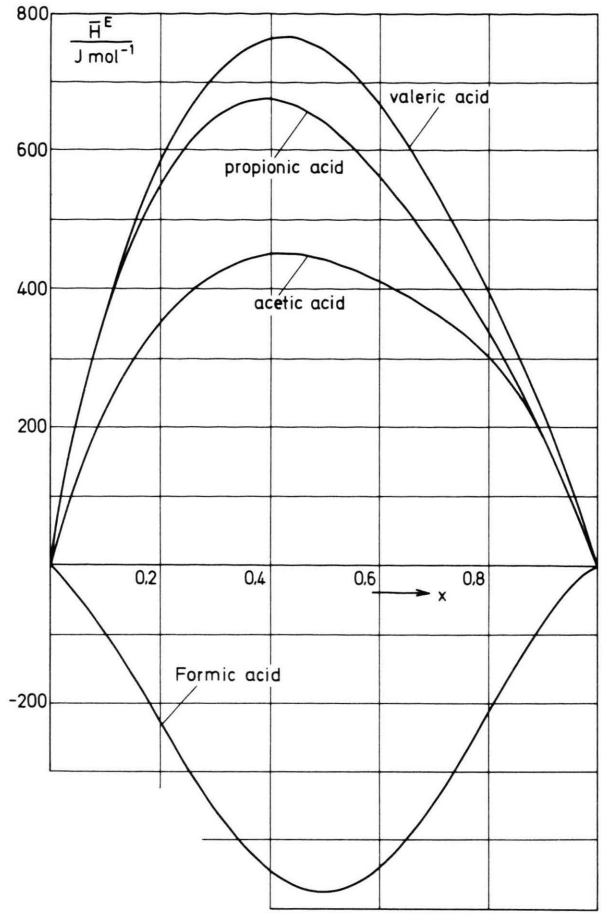

Fig. 1. Molar excess enthalpy $\bar{H}^E$ as function of the mole fraction x of the alcohol for binary liquid mixtures of carbonic acids and 2-propanol at 298.15 K.

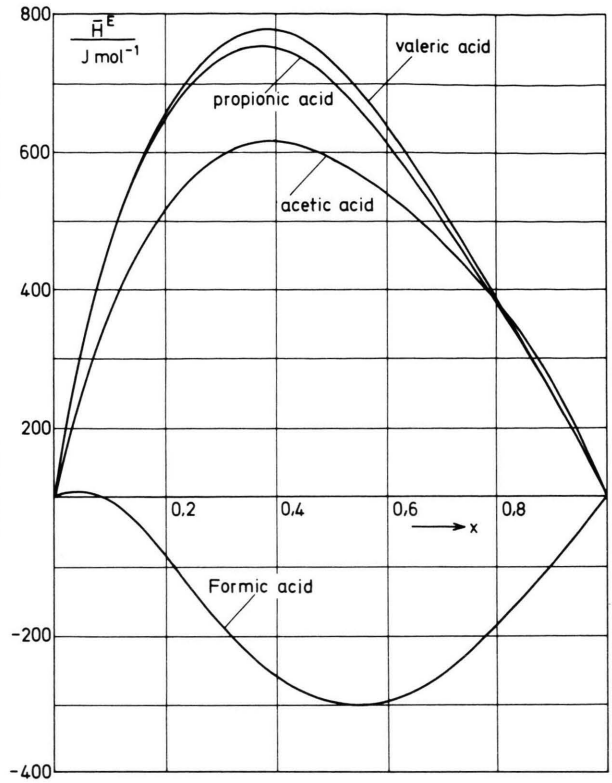

Fig. 2. Function $\bar{H}^E(x)$ for carbonic acids + 1-butanol at 298.15 K.

Table 2. Parameters a_k of (1) for the indicated systems (σ: standard deviation).

System	T / K	a_0 / J mol^{-1}	a_1 / J mol^{-1}	a_2 / J mol^{-1}	a_3 / J mol^{-1}	a_4 / J mol^{-1}	a_5 / J mol^{-1}	a_6 / J mol^{-1}	σ / J mol^{-1}
Formic acid + 1-Propanol	298.15	−1757.9	28.5	327.1	794.5	1833.8	−675.0	−1684.3	1.8
+ 2-Propanol	298.15	−1905.4	−84.3	1483.6	215.5	−118.3	−349.7		1.6
+ 1-Butanol	298.15	−1187.9	337.5	454.5	592.3	1865.5	−364.7	−1634.5	2.7
+ 2-Methyl-2-propanol	303.15	−3381.8	813.9	1853.4	599.8	−1185.1	−503.8	1378.2	4.3
Acetic acid + Methanol	298.15	−458.4	995.3	510.2	−52.1	351.8	347.7		1.7
+ Methanol	318.15	−385.3	956.1	634.0	110.4	100.1	91.9		2.2
+ Ethanol	298.15	599.4	865.5	451.5	166.4	202.0			2.8
+ 1-Propanol	298.15	1561.3	700.5	438.1	−413.3	214.0	569.1		1.6
+ 2-Propanol	298.15	1761.4	472.3	638.9	−1060.9	257.6	1010.8		2.8
+ 2-Propanol	318.15	1553.7	372.1	604.6	−774.1	268.0	699.5		1.9
+ 1-Butanol	298.15	1956.7	797.4	523.2	−535.0	223.1	648.1		3.1
+ 1-Butanol	318.15	1966.5	704.7	460.3	−523.4	−230.4	546.3	456.3	2.8
+ 2-Methyl-2-propanol	303.15	763.3	749.7	789.0	−930.2	−142.5	751.3		1.3
+ 2-Methyl-2-propanol	312.85	166.4	922.2	565.8	−685.8	509.9	448.3	−514.2	1.4
+ 2-Methyl-2-propanol	318.15	−201.1	1007.8	672.2	−523.7	−113.3	88.1		1.7

Table 2. (Continued)

System	T / K	a_0 / J mol^{-1}	a_1 / J mol^{-1}	a_2 / J mol^{-1}	a_3 / J mol^{-1}	a_4 / J mol^{-1}	a_5 / J mol^{-1}	a_6 / J mol^{-1}	σ / J mol^{-1}
Propionic acid + Methanol	298.15	858.1	2068.5	719.2	470.8	777.4	−258.3	−480.4	2.2
+ Methanol	318.15	906.2	2047.3	614.6	315.9	1009.7	−284.8	−935.7	1.8
+ 2-Propanol	298.15	2557.0	1141.9	172.0	−81.5	1731.4	−67.0	−1390.9	2.6
+ 2-Propanol	318.15	2484.6	1007.4	−153.5	−73.7	2823.3	144.1	−2319.4	3.8
+ 1-Butanol	298.15	2417.4	1410.3	−56.4	−219.6	1981.3	476.0	−1465.5	3.2
+ 1-Butanol	318.15	2513.4	1360.2	127.6	−425.1	1206.8	684.9	−610.4	3.0
+ 1-Methyl-2-propanol	303.15	1668.5	1091.4	100.8	−697.9	2094.3	444.4	−1701.6	3.4
Butyric acid + Methanol	298.15	1014.1	2091.3	793.0	65.2	−87.9	−247.3		2.7
Valeric acid + Methanol	298.15	1534.5	1932.4	900.2	369.9	−276.7	−632.8		3.5
+ Methanol	318.15	1966.7	2036.4	716.5	137.7	151.6	−66.8		2.9
+ 2-Propanol	298.15	2973.5	965.4	−142.1	323.0	822.6	−480.0		3.2
+ 2-Propanol	318.15	3073.4	854.0	235.1	781.2	383.7	−846.		6.8
+ 1-Butanol *	298.15	2539.3	1407.2	−408.5	−581.4	2947.4	1742.8	−3228.8	3.4
+ 1-Butanol	318.15	2809.5	1310.1	−315.9	237.1	2201.1	−83.1	−1515.6	3.8

* Use parameters only for $x \leq 0{,}8$!

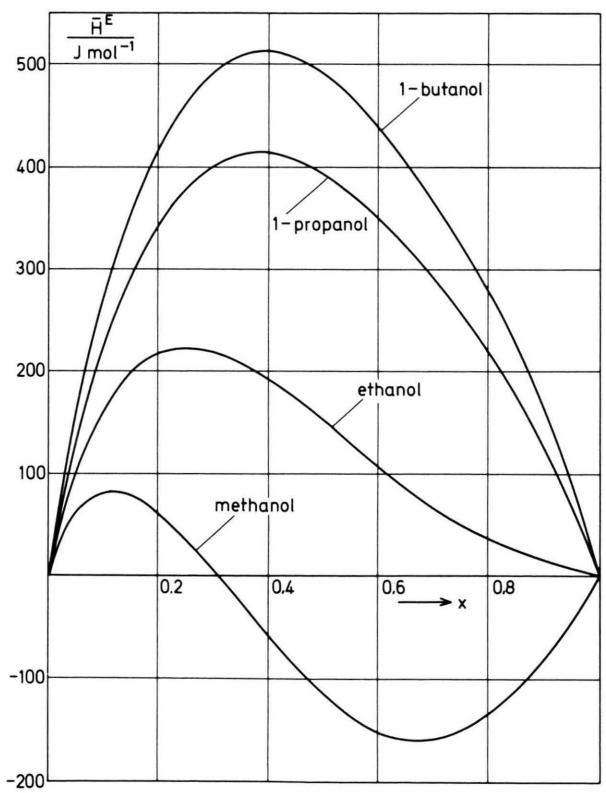

Fig. 3. Function $\bar{H}^E(x)$ for acetic acid + alcohols at 298.15 K.

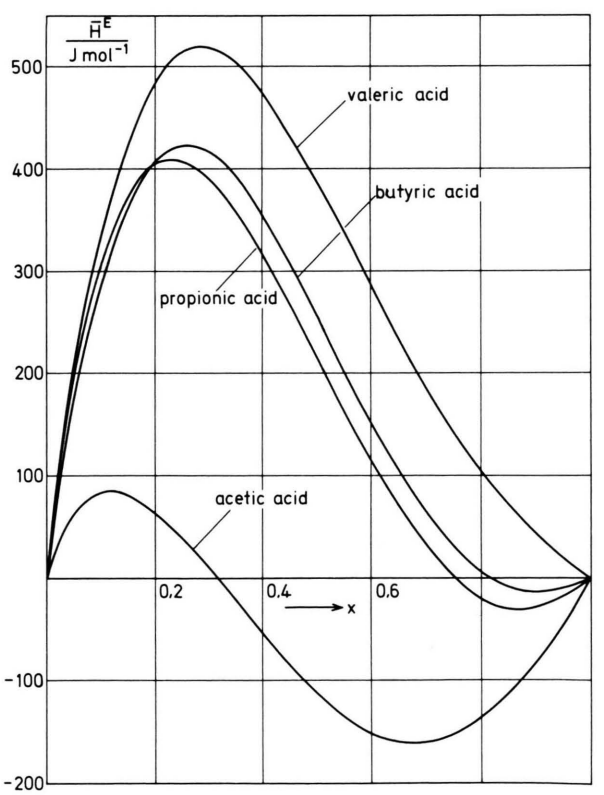

Fig. 4. Function $\bar{H}^E(x)$ for carbonic acids + methanol at 298.15 K.

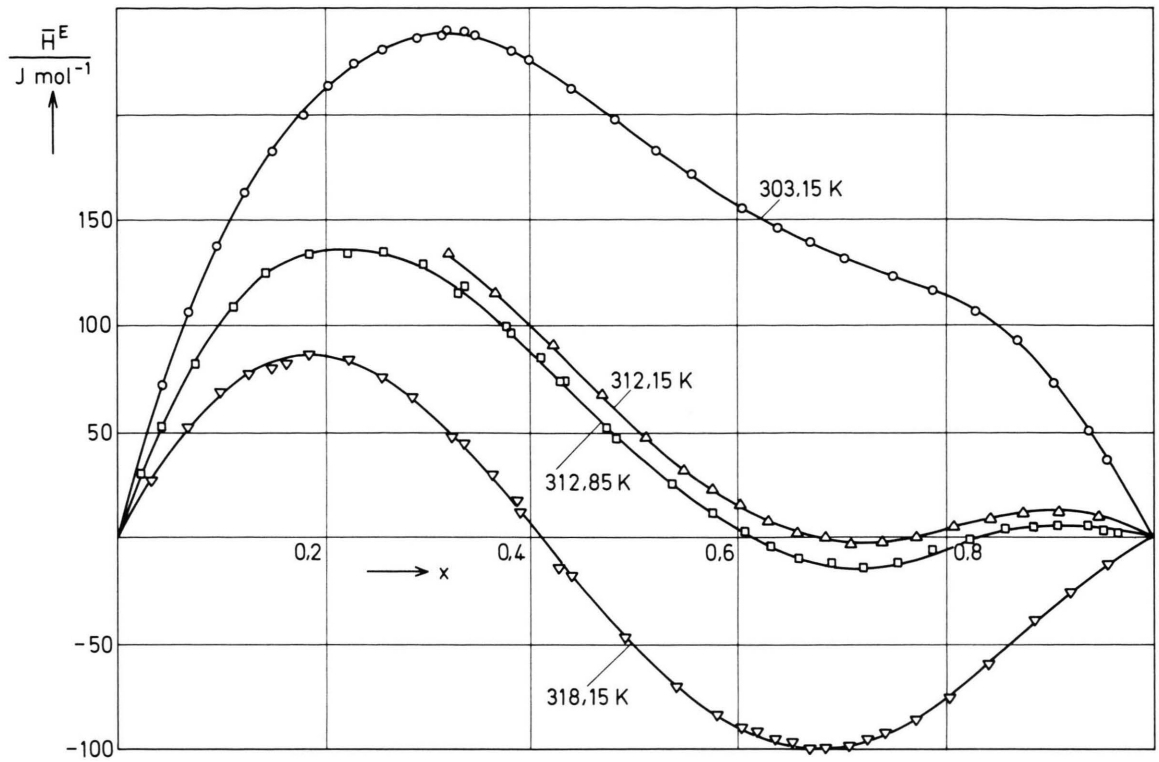

Fig. 5. Function $\bar{H}^E(x)$ for acetic acid + 2-methyl-2-propanol at four temperatures.

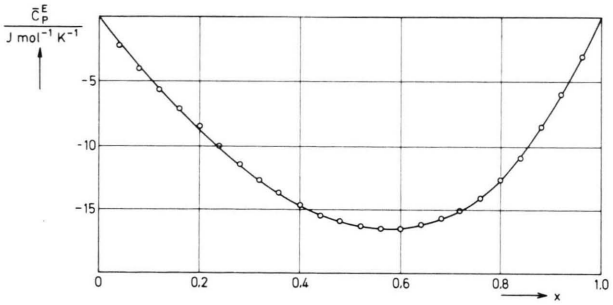

Fig. 6. Molar excess heat capacity $\bar{C}_P^E(x)$ for acetic acid + 2-methyl-2-propanol at 310.65 K (derived graphically from $\bar{H}^E$, see Figure 5).

of the mole fraction x of the alcohol, the pressure P being irrelevant.

We fit the experimental data to the power series

$$\bar{H}^E = x(1-x)\sum_{k=0}^{m} a_k (1-2x)^k = x(1-x) \cdot [a_0 + a_1(1-2x) + \ldots + a_m(1-2x)^m], \quad (1)$$

where the parameters a_k only depend on the temperature. We need up to 7 constants $(a_0, a_1, \ldots, a_6)$ at each temperature to fit our results (see Table 2, where the standard deviation σ is also given).

In some cases we may derive the molar excess heat capacity (at constant pressure)

$$\bar{C}_P^E = (\partial \bar{H}^E/\partial T)_{P,x} = x(1-x)\sum_{k=0}^{m} b_k (1-2x)^k \quad (2)$$

with [see (1)]

$$b_k = \mathrm{d}a_k/\mathrm{d}T \quad (3)$$

from experimental values of the function $\bar{H}^E(T, x)$.

Figures 1 to 5 and 6 give examples of measured values of $\bar{H}^E$ and $\bar{C}_P^E$, respectively. In the last case ($\bar{C}_P^E$ for acetic acid + 2-methyl-2-propanol at 310.65 K) the data have been fitted to (2) using the parameters [without reference to (3)]

$$b_0 = -64.4\ \mathrm{J\,K^{-1}\,mol^{-1}},$$
$$b_1 = \ \ 24.7\ \mathrm{J\,K^{-1}\,mol^{-1}},$$
$$b_2 = -\ \ 6.2\ \mathrm{J\,K^{-1}\,mol^{-1}},$$
$$b_3 = -13.3\ \mathrm{J\,K^{-1}\,mol^{-1}},$$

the standard deviation being $0.2\ \mathrm{J\,K^{-1}\,mol^{-1}}$.

We now briefly discuss the functions $\bar{H}^E(x)$ and $\bar{C}_P^E(x)$ for given temperatures. In most cases (see Table 1 and Figs. 1 to 5) the process of mixing the liquid components is endothermic ($\bar{H}^E > 0$) throughout. However, systems containing formic acid show – nearly throughout – exothermic behaviour ($\bar{H}^E < 0$). In systems consisting of methanol and carbonic acids (the system formic acid + methanol being too exothermic to be susceptible to measurements) the function $\bar{H}^E(x)$ is positive for small values of x (endothermic region), passes through zero, and is negative for large values of x (exothermic region), the last region becoming smaller with higher carbonic acids and disappearing in mixtures with valeric acid. Finally, the system acetic acid + 2-methyl-2-propanol exhibits an extraordinary behaviour (see Figures 5 and 6): In a certain range of temperatures, the function $\bar{H}^E(x)$ changes the sign twice, while the function $\bar{C}_P^E(x)$ has unusually large negative values.

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