Thermodynamic Excess Functions for the Liquid System Water + Acetic Acid from Calorimetric Data

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For the liquid system water + acetic acid, we give the results of new calorimetric measurements regarding the molar excess enthalpy $\overline{H}^E$ for 25 °C, 30 °C, 35 °C, 40 °C, 55 °C, and 70 °C, covering nearly the entire range of compositions. The experimental data show that $\overline{H}^E$ is positive for all compositions and temperatures except in the region of low acid concentrations at temperatures below 55 °C where the process of mixing the pure liquid components is exothermic ($\overline{H}^E < 0$). Using values of the molar excess Gibbs function $\overline{G}^E$ (always positive) derived from earlier data on vapour-liquid equilibria, we compute the molar excess entropy $\overline{S}^E$ which is always negative. The "symmetry rule" concerning the composition dependence of $\overline{G}^E$ (as compared to that of $\overline{H}^E$ and $\overline{S}^E$) has again been confirmed. The composition dependence of $\overline{S}^E$ is similar to that of the molar excess volume.

To extend the range of our computations of thermodynamic excess functions from calorimetric experiments[1] and vapour-liquid-equilibrium data[2,3] for the liquid system water + acetic acid, we developed a new calorimeter[4] 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. This calorimeter may be used for the measurement of heats of mixing for binary liquid mixtures, in particular for those in which both endothermic and exothermic mixing occurs.

We measured the molar excess enthalpy (molar heat of mixing) $\overline{H}^E$ for water + acetic acid in the whole range of compositions (except at 70 °C) for the temperatures 25 °C, 30 °C, 35 °C, 40 °C, 55 °C, and 70 °C. Thus former experimental data[1, 5, 6] could be checked or corrected and extended. The new calorimetric measurements are more reliable than the old ones, especially in the region of high dilution.

The new results are given in Tables 1 to 6 where $\overline{H}^E$ is represented as a function of the mole fraction x of acetic acid for all six temperatures. The estimated error is about 2%.

We again find a small exothermix region ($\overline{H}^E < 0$) for low acid concentrations at temperatures below 55 °C while otherwise the process of mixing the pure liquid components is endothermic ($\overline{H}^E > 0$).

Table 1. System water + acetic acid at 25 °C: Molar excess enthalpy $\overline{H}^E$ and product of thermodynamic temperature T and molar excess entropy $\overline{S}^E$ for different values of the mole fraction x of acetic acid (see also Figure 1 and Figure 2).

x	$\frac{\overline{H}^E}{\text{J mol}^{-1}}$	$\frac{T\,\overline{S}^E}{\text{J mol}^{-1}}$
0.107	−1	−285
0.224	113	−371
0.305	186	−386
0.459	290	−365
0.505	312	−355
0.663	355	−282
0.794	328	−227
0.819	312	−197
0.893	240	−160
0.960	120	−86

Table 2. System water + acetic acid at 30 °C: Molar excess enthalpy $\overline{H}^E$ and product of thermodynamic temperature T and molar excess entroy $\overline{S}^E$ for different values of the mole fraction x of acetic acid (see also Figure 2).

x	$\frac{\overline{H}^E}{\text{J mol}^{-1}}$	$\frac{T\,\overline{S}^E}{\text{J mol}^{-1}}$
0.104	10	−270
0.223	154	−340
0.353	235	−399
0.475	306	−388
0.584	349	−345
0.710	359	−299
0.820	316	−243
0.898	235	−192
0.954	146	−139

Table 3. System water + acetic acid at 35 °C: Molar excess enthalpy $\overline{H}^E$ and product of thermodynamic temperature T and molar excess entropy $\overline{S}^E$ for different values of the mole fraction x of acetic acid (see also Figure 2).

x	$\frac{\overline{H}^E}{\text{J mol}^{-1}}$	$\frac{T\,\overline{S}^E}{\text{J mol}^{-1}}$
0.121	31	−286
0.237	144	−375
0.344	232	−406
0.456	300	−400
0.556	346	−374
0.660	372	−330
0.797	350	−240
0.921	211	−156
0.959	140	−119

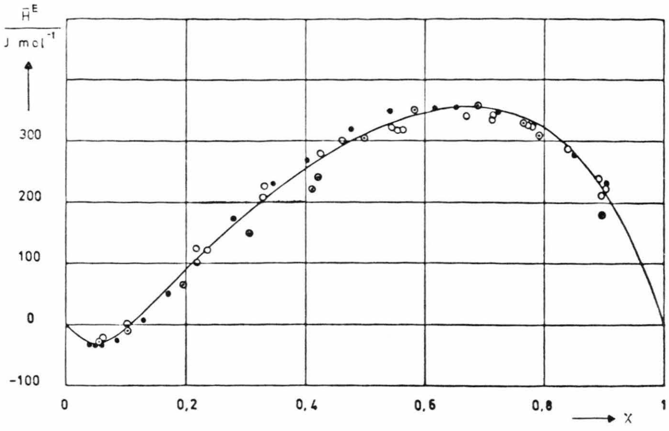

Fig. 1. System water + acetic acid at 25 °C: Molar excess enthalpy $\overline{H}^E$ against mole fraction x of acetic acid from new measurements (curve). ○ data of Campbell and Gieskes[5] (1965); ⊙ data of Haase, Steinmetz, and Dücker[1] (1972); ● data of Vilcu and Lucinescu[6] (1974).

Table 4. System water + acetic acid at 40 °C: Molar excess enthalpy $\overline{H}^E$ and product of thermodynamic temperature T and molar excess entropy $\overline{S}^E$ for different values of the mole fraction x of acetic acid (see also Figure 2).

x	$\overline{H}^E$ / J mol^{-1}	$T\,\overline{S}^E$ / J mol^{-1}
0.118	43	−273
0.240	158	−357
0.335	240	−389
0.437	309	−384
0.542	359	−370
0.612	377	−340
0.755	370	−263
0.876	280	−213
0.932	194	−167

Table 5. System water + acetic acid at 55 °C: Molar excess enthalpy $\overline{H}^E$ and product of thermodynamic temperature T and molar excess entropy $\overline{S}^E$ for different values of the mole fraction x of acetic acid (see also Figure 2).

x	$\overline{H}^E$ / J mol^{-1}	$T\,\overline{S}^E$ / J mol^{-1}
0.148	116	−327
0.288	248	−394
0.402	330	−394
0.524	390	−378
0.572	405	−355
0.690	409	−292
0.764	378	−231
0.851	294	−176
0.936	180	− 90

Table 6. System water + acetic acid at 70 °C: Molar excess enthalpy $\overline{H}^E$ and product of thermodynamic temperature T and molar excess entropy $\overline{S}^E$ for different values of the mole fraction x of acetic acid (see also Figure 2).

x	$\overline{H}^E$ / J mol^{-1}	$T\,\overline{S}^E$ / J mol^{-1}
0.151	161	−320
0.283	276	−392

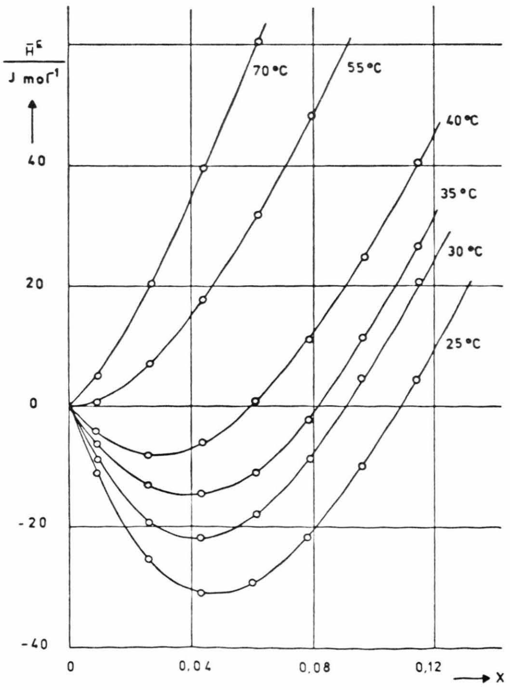

Fig. 2. System water + acetic acid: Molar excess enthalpy $\overline{H}^E$ against mole fraction x of acetic acid for six temperatures in the region of small acid concentrations.

This is obvious from Figs. 1 and 2, both showing a plot of the function $\overline{H}^{\mathrm{E}}(x)$. Figure 1 refers to 25 °C and includes previous results [1, 5, 6]. Figure 2 relates to all six temperatures but is restricted to the region of small acid content where the change of sign of $\overline{H}^{\mathrm{E}}$ occurs.

We already derived [2, 3] the molar excess Gibbs function $\overline{G}^{\mathrm{E}}$ from vapour-liquid equilibria and found [2, 3] that $\overline{G}^{\mathrm{E}}$ is always positive. Plotting the molar Gibbs function of mixing $\Delta_{\mathrm{m}}\overline{G} = \Delta_{\mathrm{m}}\overline{G}^{\mathrm{id}} + \overline{G}^{\mathrm{E}}$ against x, the superscript id denoting an ideal mixture, we checked that our values of $\overline{G}^{\mathrm{E}}$ do not imply phase separation.

To complete the thermodynamic description of our system we compute the molar excess entropy $\overline{S}^{\mathrm{E}}$ (see Tables 1 to 6) and the molar entropy of mixing $\Delta_{\mathrm{m}}\overline{S}$ (not shown here) from the relations $T\overline{S}^{\mathrm{E}} = \overline{H}^{\mathrm{E}} - \overline{G}^{\mathrm{E}}$ (T: thermodynamic temperature) and $\Delta_{\mathrm{m}}\overline{S} = \Delta_{\mathrm{m}}\overline{S}^{\mathrm{id}} + \overline{S}^{\mathrm{E}}$. We notice that $\overline{S}^{\mathrm{E}}$ is always negative but that $\Delta_{\mathrm{m}}\overline{S}$ remains positive throughout since $|\overline{S}^{\mathrm{E}}|$ never exceeds $\Delta_{\mathrm{m}}\overline{S}^{\mathrm{id}}$ which is positive. In view of the general inequality $T\Delta_{\mathrm{m}}\overline{S} > \overline{H}^{\mathrm{E}}$, the case $\Delta_{\mathrm{m}}\overline{S} < 0$ is possible only for $\overline{H}^{\mathrm{E}} < 0$.

All the thermodynamic functions depend on the temperature T, on the pressure P, and on the mole fraction x of acetic acid, but here they always refer to normal pressure.

The liquid system water + acetic acid may be considered to be a nonelectrolyte solution except in the region of extremely low acid content where precise measurements are difficult.

In Fig. 3 the functions $\overline{G}^{\mathrm{E}}$, $\overline{H}^{\mathrm{E}}$, and $T\overline{S}^{\mathrm{E}}$ are plotted against x for 35 °C and 55 °C. These curves exhibit features similar to those stated in our previous papers [2, 3].

Taking into account the data for many other binary liquid mixtures (nonelectrolyte solutions and salt melt mixtures), we conclude that $\overline{G}^{\mathrm{E}}$, $\overline{H}^{\mathrm{E}}$, and $\overline{S}^{\mathrm{E}}$ may be positive or negative. We also notice [7, 8] that, for given values of T and P, the functions $\overline{H}^{\mathrm{E}}(x)$ and $\overline{S}^{\mathrm{E}}(x)$ often are extremely asymmetric and even change the signs while $\overline{G}^{\mathrm{E}}$ can still be roughly represented by $Bx(1-x)$ where the (positive or negative) quantity B depends on T and P. Hence, the following rule holds for most cases [9]: The function $\overline{G}^{\mathrm{E}}(x)$ does not change its sign and is nearly symmetric (parabolic), no matter how complicated the functions $\overline{H}^{\mathrm{E}}(x)$ and $\overline{S}^{\mathrm{E}}(x)$ are. This symmetry rule [7, 8] also applies to the liquid system water + acetic acid (see Figure 3).

Using density data of the literature, we obtain [4] the molar excess volume $\overline{V}^{\mathrm{E}}$ for our system. The quantity $\overline{V}^{\mathrm{E}}$ is found to be negative throughout and to be roughly proportional to $\overline{S}^{\mathrm{E}}$, as shown in Fig. 4 for 25 °C. This confirms a rule due to Rehage [11] which states that, for many binary nonelectrolyte solutions, the functions $\overline{S}^{\mathrm{E}}(x)$ and $\overline{V}^{\mathrm{E}}(x)$ have the same sign and approximately the same form [12].

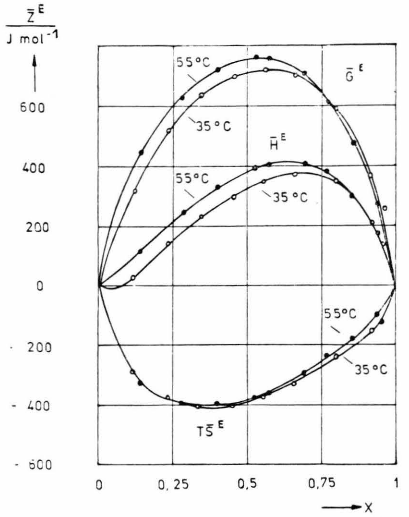

Fig. 3. System water + acetic acid at 35 °C and 55 °C: Molar excess functions $\overline{Z}^{\mathrm{E}}$ (molar excess Gibbs function $\overline{G}^{\mathrm{E}}$, molar excess enthalpy $\overline{H}^{\mathrm{E}}$, and product of thermodynamic temperature T and molar excess entropy $\overline{S}^{\mathrm{E}}$) against mole fraction x of acetic acid.

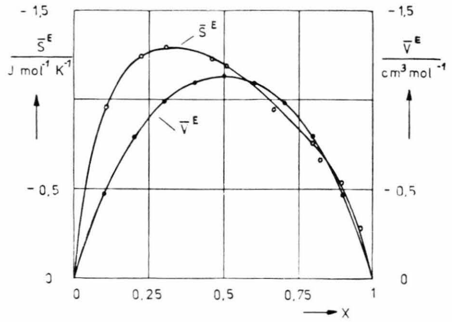

Fig. 4. System water + acetic acid at 25 °C: Molar excess entropy $\overline{S}^{\mathrm{E}}$ and molar excess volume $\overline{V}^{\mathrm{E}}$ against mole fraction x of acetic acid.

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[9] Lorrimer et al.[10] state that, in systems of the type toluene + sulfur dioxide, there occurs a change of sign in the function $\overline{G}^{\mathrm{E}}(x)$. According to Apelblat and Kohler[13], this change of sign is also found for the systems methanol + propionic acid and methanol + butyric acid. In all these cases $\overline{G}^{\mathrm{E}}$ was derived from total vapour pressures alone.

[10] J. W. Lorrimer, B. C. Smith, and G. H. Smith, J. C. S. Faraday I **71**, 2232 [1975].

[11] See R. Haase, Thermodynamik der Mischphasen, Springer-Verlag, Berlin-Göttingen-Heidelberg 1956, p. 447.

[12] There are exceptions to this rule. Thus, in the system chloroform + acetic acid at 25 °C, $\overline{S}^{\mathrm{E}}$ is negative while $\overline{V}^{\mathrm{E}}$ is positive[5].

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