

Effect of NaCl or KCl on the Excess Enthalpies of Alkanol + Water Mixtures at Various Temperatures and Salt Concentrations

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Excess enthalpies of methanol, ethanol, 1-propanol, or 2-propanol + aqueous solution of NaCl or KCl were measured using flow-mix calorimetry at various temperatures. Mixtures with all alkanols were investigated at 285.65, 298.15, 308.15, and 323.15 K; those with ethanol and both propanols were additionally investigated at 338.15 K. Furthermore, mixtures with 1-propanol were investigated at 353.15 K. The concentration of the salt water component was varied between 0 and 10 wt % salt in water. Due to the calorimetric flow-mix setup, the total salt concentration in the mixture decreases with increasing mole fraction of alkanol. The reliability of the experimental setup has already been verified in a previous work (Friese et al., 1998) by comparison with literature data. The measured excess enthalpies of alkanol (1) + (water (2) + salt (3)), h_{1+23}^E , are given along with a formula for calculating the excess enthalpies h_{123}^E occurring when mixing the three components in their reference states, that is pure liquids and infinitely diluted salt, respectively.

Introduction

In many chemical engineering processes one has to be aware of the influence of electrolytes on the phase equilibria. Apart from processes where electrolyte solutions occur as unwanted byproducts which demand further treatment, for example neutralization reactions or gas scrubbing, the purposeful use of electrolytes in separation techniques is of increasing interest. For example, the relative volatility of mixed solvent systems is affected by the addition of salt (salting-in or salting-out) (Mock et al., 1986). Regarding azeotropic mixtures, this change in phase equilibrium can be used to design more effective and more economical distillation operations because the azeotrope can be shifted or can even be broken by using salt as extractive agent (Gironi and Lamberti, 1995). Therefore, appropriate thermodynamic models are required in order to predict phase equilibria of liquid mixtures under the influence of inorganic salts. Most of the g^E models in the literature are semiempirical; that is, they contain parameters that have to be fitted to experimental data. For salt-free systems, parameters are usually fitted not only to vapour–liquid equilibrium (VLE) data but also to activity coefficients at infinite dilution as well as to excess enthalpy data in order to increase the thermodynamic consistency of the model. Against this background, the parameters of g^E models for the prediction of the salt effect on the behavior of liquid mixtures should be fitted to several kinds of experimental data, as well. However, only VLE data are available in the literature to a satisfying extent. Thus, there is a demand for further data for the systems mentioned, especially concerning excess enthalpy data (Loeche and Donohue, 1997; Renon, 1996; Achard et al., 1994). In order to create such a data base, the focus of this work was to investigate the influence of salt on the excess enthalpy of alkanol + water over a wide temperature range.

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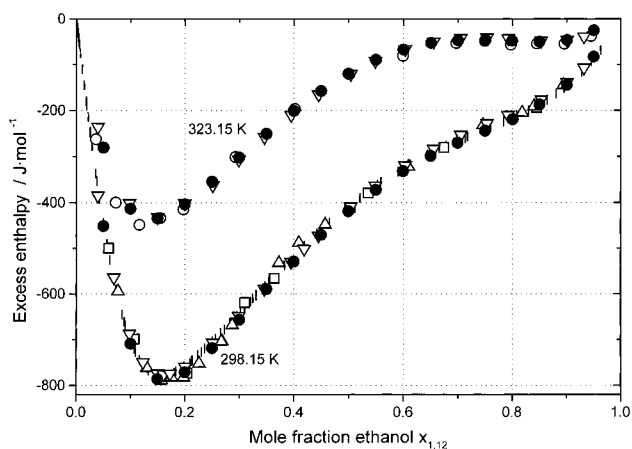


Figure 1. Comparison of salt-free excess enthalpy isotherms of ethanol (1) + water (2) with the literature: (□) Costigan et al., 1980; (□) Boyne and Williamson, 1967; (△) Chand and Fenby, 1978; (▽) Löwen, 1995; (○) Larkin, 1975; (●) this laboratory (Friese et al., 1998).

Table 1. Solvents and Salts

| component | supplier | purity (as reported by the supplier) |
|--------------------|-----------------------|--------------------------------------|
| methanol | Roth, Roti Solv. HPLC | ≥99.9% |
| ethanol | Fluka, puriss. p.a. | ≥99.8% |
| 1-propanol | Roth, Rotipuran | ≥99.5% |
| 2-propanol | Merck, gradient grade | ≥99.8% |
| sodium chloride | Fluka, puriss. p.a. | ≥99.5% |
| potassium chloride | Fluka, puriss. p.a. | ≥99.5% |

Experimental Section

Materials. Table 1 displays the substances of interest along with their respective suppliers and purities. Before the salt water solution was prepared, the salts were dried under vacuum for at least 24 h at 240 °C. Water was distilled and filtered four times (conductivity ≤ 1 μS·cm⁻¹). The organic solvents were used without further purification. They were dried with molecular sieves of 3 Å pore diameter supplied by Fluka (Dehydrat Fluka with indica-

Table 2. Excess Enthalpies of Methanol (1) + (Water (2) + NaCl (3))

| $x_{1,123}$ | $h_{1+23}^E/\text{J}\cdot\text{mol}^{-1}$ | $x_{1,123}$ | $h_{1+23}^E/\text{J}\cdot\text{mol}^{-1}$ | $x_{1,123}$ | $h_{1+23}^E/\text{J}\cdot\text{mol}^{-1}$ | $x_{1,123}$ | $h_{1+23}^E/\text{J}\cdot\text{mol}^{-1}$ | $x_{1,123}$ | $h_{1+23}^E/\text{J}\cdot\text{mol}^{-1}$ |
|---|---|-------------|---|-------------|---|-------------|---|-------------|---|
| $T = 285.65 \text{ K}, w_{3,23} = 1.00 \text{ wt } \%$ | | | | | | | | | |
| 0.050 | -367.9 | 0.250 | -945.6 | 0.450 | -894.1 | 0.650 | -710.1 | 0.850 | -392.6 |
| 0.100 | -635.7 | 0.300 | -958.5 | 0.500 | -857.9 | 0.700 | -645.0 | 0.900 | -279.9 |
| 0.150 | -804.7 | 0.350 | -951.3 | 0.550 | -813.9 | 0.750 | -571.7 | 0.950 | -149.2 |
| 0.200 | -900.5 | 0.400 | -926.1 | 0.600 | -765.4 | 0.800 | -488.6 | | |
| $T = 285.65 \text{ K}, w_{3,23} = 5.00 \text{ wt } \%$ | | | | | | | | | |
| 0.040 | -279.1 | 0.200 | -846.5 | 0.360 | -904.9 | 0.520 | -816.2 | 0.680 | -662.8 |
| 0.080 | -507.0 | 0.240 | -893.3 | 0.400 | -890.9 | 0.560 | -782.7 | 0.720 | -611.8 |
| 0.120 | -668.6 | 0.280 | -910.2 | 0.440 | -868.5 | 0.600 | -748.0 | 0.760 | -555.0 |
| 0.160 | -780.9 | 0.320 | -914.1 | 0.480 | -846.1 | 0.640 | -706.7 | 0.800 | -489.2 |
| $T = 285.65 \text{ K}, w_{3,23} = 10.00 \text{ wt } \%$ | | | | | | | | | |
| 0.035 | -227.2 | 0.175 | -748.2 | 0.315 | -853.5 | 0.455 | -815.8 | 0.595 | -722.8 |
| 0.070 | -411.0 | 0.210 | -796.6 | 0.350 | -851.6 | 0.490 | -796.8 | 0.630 | -690.4 |
| 0.105 | -555.2 | 0.245 | -829.1 | 0.385 | -845.6 | 0.525 | -774.7 | 0.665 | -659.1 |
| 0.140 | -667.5 | 0.280 | -847.9 | 0.420 | -832.9 | 0.560 | -751.1 | 0.700 | -618.5 |
| $T = 298.15 \text{ K}, w_{3,23} = 1.00 \text{ wt } \%$ | | | | | | | | | |
| 0.050 | -324.7 | 0.250 | -859.8 | 0.450 | -835.1 | 0.650 | -667.2 | 0.850 | -355.2 |
| 0.100 | -558.9 | 0.300 | -884.4 | 0.500 | -805.3 | 0.700 | -617.1 | 0.900 | -276.3 |
| 0.150 | -718.4 | 0.350 | -881.4 | 0.550 | -770.1 | 0.750 | -549.3 | 0.950 | -145.0 |
| 0.200 | -815.3 | 0.400 | -864.2 | 0.600 | -724.6 | 0.799 | -472.4 | | |
| $T = 308.15 \text{ K}, w_{3,23} = 1.00 \text{ wt } \%$ | | | | | | | | | |
| 0.035 | -210.6 | 0.246 | -794.5 | 0.456 | -778.4 | 0.631 | -652.9 | 0.806 | -437.9 |
| 0.070 | -388.7 | 0.281 | -810.7 | 0.491 | -757.4 | 0.666 | -619.0 | 0.841 | -379.9 |
| 0.105 | -531.1 | 0.316 | -815.5 | 0.526 | -736.6 | 0.701 | -581.4 | 0.876 | -309.7 |
| 0.141 | -637.2 | 0.351 | -816.0 | 0.561 | -712.1 | 0.736 | -538.9 | 0.911 | -234.6 |
| 0.176 | -711.7 | 0.386 | -806.7 | 0.596 | -685.0 | 0.771 | -491.6 | 0.945 | -150.9 |
| 0.211 | -763.5 | 0.421 | -793.3 | | | | | | |
| $T = 308.15 \text{ K}, w_{3,23} = 5.00 \text{ wt } \%$ | | | | | | | | | |
| 0.035 | -200.1 | 0.246 | -742.8 | 0.456 | -742.9 | 0.631 | -632.2 | 0.806 | -439.8 |
| 0.070 | -366.3 | 0.280 | -763.4 | 0.491 | -725.7 | 0.666 | -603.7 | 0.841 | -380.3 |
| 0.105 | -494.9 | 0.315 | -770.4 | 0.526 | -708.0 | 0.701 | -569.2 | 0.876 | -317.4 |
| 0.140 | -591.7 | 0.351 | -770.5 | 0.561 | -685.6 | 0.736 | -531.4 | 0.911 | -244.3 |
| 0.175 | -666.9 | 0.386 | -765.4 | 0.595 | -660.7 | 0.770 | -490.7 | 0.945 | -154.8 |
| 0.211 | -714.9 | 0.421 | -757.8 | | | | | | |
| $T = 308.15 \text{ K}, w_{3,23} = 10.00 \text{ wt } \%$ | | | | | | | | | |
| 0.035 | -177.3 | 0.245 | -676.4 | 0.421 | -696.0 | 0.596 | -623.7 | 0.771 | -475.0 |
| 0.070 | -329.4 | 0.281 | -694.6 | 0.456 | -684.7 | 0.631 | -600.8 | 0.806 | -428.9 |
| 0.105 | -446.2 | 0.316 | -702.5 | 0.491 | -675.8 | 0.666 | -574.3 | 0.840 | -376.0 |
| 0.140 | -537.1 | 0.351 | -707.2 | 0.526 | -660.5 | 0.700 | -545.8 | 0.876 | -313.4 |
| 0.175 | -602.5 | 0.386 | -703.6 | 0.561 | -640.9 | 0.735 | -515.0 | 0.910 | -241.4 |
| 0.211 | -647.5 | | | | | | | | |
| $T = 323.15 \text{ K}, w_{3,23} = 1.00 \text{ wt } \%$ | | | | | | | | | |
| 0.035 | -175.8 | 0.210 | -646.6 | 0.385 | -687.5 | 0.560 | -618.7 | 0.700 | -495.8 |
| 0.070 | -371.6 | 0.245 | -669.2 | 0.420 | -687.6 | 0.595 | -592.5 | 0.735 | -475.1 |
| 0.105 | -461.2 | 0.280 | -681.3 | 0.455 | -669.9 | 0.630 | -560.6 | 0.840 | -332.0 |
| 0.140 | -553.3 | 0.315 | -695.7 | 0.490 | -658.1 | 0.665 | -536.7 | 0.874 | -283.1 |
| 0.175 | -617.9 | 0.350 | -687.3 | 0.525 | -626.6 | | | | |

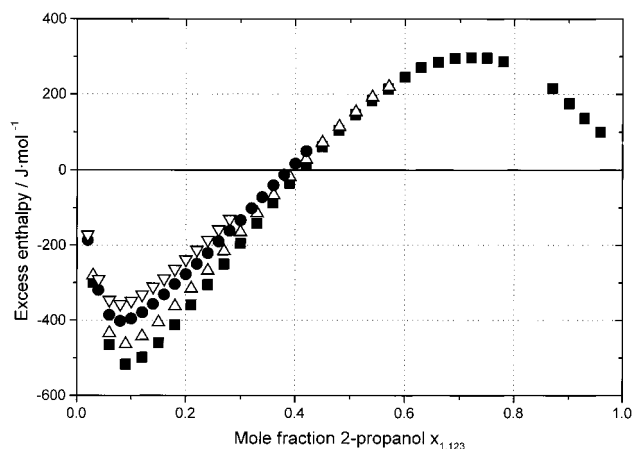


Figure 2. Effect of NaCl on the excess enthalpy of 2-propanol (1) + (water (2) + NaCl (3)) at 308.15 K: (Δ) 2.50 wt % $w_{3,23}$ (NaCl); (\bullet) 5.00 wt % $w_{3,23}$ (NaCl); (∇) 7.50 wt % $w_{3,23}$ (NaCl); (\blacksquare) salt-free system.

tor). Prior to the measurements, all organic liquids were degassed by use of a water-jet vacuum pump.

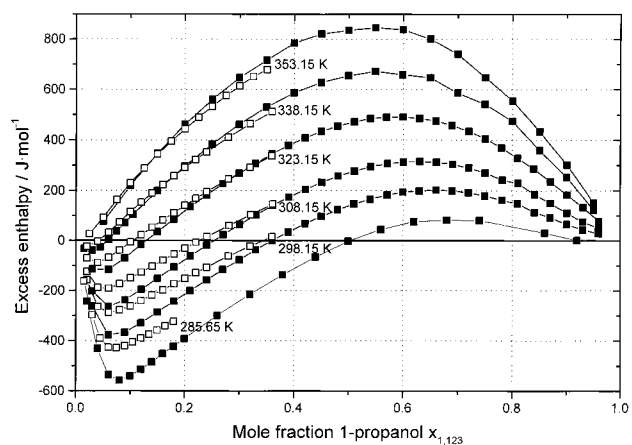


Figure 3. Temperature dependence of the excess enthalpy of 1-propanol (1) + (water (2) + NaCl (3)) at constant salt concentration $w_{3,23}$ (NaCl): (\square) 5.00 wt %; (\blacksquare) salt-free system.

Experimental Procedure. The experimental setup has been described in detail previously (Friese et al., 1998). Salt water solutions were prepared by mass using a Sartorius

Table 3. Excess Enthalpies of Methanol (1) + (Water (2) + KCl (3))

| $x_{1,123}$ | $h_{1+23}^E/\text{J}\cdot\text{mol}^{-1}$ | $x_{1,123}$ | $h_{1+23}^E/\text{J}\cdot\text{mol}^{-1}$ | $x_{1,123}$ | $h_{1+23}^E/\text{J}\cdot\text{mol}^{-1}$ | $x_{1,123}$ | $h_{1+23}^E/\text{J}\cdot\text{mol}^{-1}$ | $x_{1,123}$ | $h_{1+23}^E/\text{J}\cdot\text{mol}^{-1}$ |
|--|---|-------------|---|-------------|---|-------------|---|-------------|---|
| $T = 285.65 \text{ K}, w_{3,23} = 1.00 \text{ wt } \%$ | | | | | | | | | |
| 0.050 | -365.1 | 0.250 | -946.5 | 0.450 | -895.8 | 0.650 | -703.9 | 0.851 | -382.3 |
| 0.100 | -635.6 | 0.300 | -959.9 | 0.500 | -855.4 | 0.700 | -642.2 | 0.900 | -277.1 |
| 0.150 | -804.7 | 0.350 | -950.0 | 0.550 | -812.5 | 0.750 | -568.6 | 0.950 | -143.8 |
| 0.200 | -901.5 | 0.400 | -927.4 | 0.600 | -762.7 | 0.800 | -485.2 | | |
| $T = 285.65 \text{ K}, w_{3,23} = 5.00 \text{ wt } \%$ | | | | | | | | | |
| 0.030 | -219.5 | 0.150 | -774.6 | 0.270 | -928.0 | 0.390 | -916.0 | 0.480 | -857.0 |
| 0.060 | -409.7 | 0.180 | -834.6 | 0.300 | -933.7 | 0.420 | -897.2 | 0.510 | -838.8 |
| 0.090 | -561.8 | 0.210 | -884.1 | 0.330 | -932.7 | 0.450 | -879.9 | 0.540 | -809.6 |
| 0.120 | -681.2 | 0.240 | -911.7 | 0.360 | -927.7 | | | | |
| $T = 285.65 \text{ K}, w_{3,23} = 7.50 \text{ wt } \%$ | | | | | | | | | |
| 0.030 | -216.7 | 0.150 | -754.3 | 0.240 | -896.6 | 0.330 | -917.8 | 0.420 | -885.0 |
| 0.060 | -399.4 | 0.180 | -820.3 | 0.270 | -908.4 | 0.360 | -913.6 | 0.450 | -868.4 |
| 0.090 | -547.5 | 0.210 | -866.9 | 0.300 | -917.9 | 0.390 | -900.1 | 0.480 | -848.4 |
| 0.120 | -669.9 | | | | | | | | |
| $T = 298.15 \text{ K}, w_{3,23} = 1.00 \text{ wt } \%$ | | | | | | | | | |
| 0.040 | -265.5 | 0.200 | -822.6 | 0.360 | -882.1 | 0.520 | -795.9 | 0.680 | -638.4 |
| 0.080 | -481.7 | 0.240 | -861.5 | 0.400 | -865.7 | 0.560 | -759.1 | 0.720 | -587.7 |
| 0.120 | -638.4 | 0.280 | -881.6 | 0.440 | -848.0 | 0.600 | -725.0 | 0.760 | -536.8 |
| 0.160 | -746.5 | 0.320 | -888.6 | 0.480 | -820.3 | 0.640 | -683.9 | | |
| $T = 298.15 \text{ K}, w_{3,23} = 5.00 \text{ wt } \%$ | | | | | | | | | |
| 0.020 | -130.6 | 0.140 | -674.6 | 0.260 | -849.2 | 0.380 | -851.1 | 0.480 | -803.5 |
| 0.040 | -254.3 | 0.160 | -725.3 | 0.280 | -855.8 | 0.400 | -847.1 | 0.500 | -795.5 |
| 0.060 | -368.1 | 0.180 | -759.2 | 0.300 | -860.5 | 0.420 | -839.2 | 0.520 | -781.6 |
| 0.080 | -462.9 | 0.200 | -793.5 | 0.320 | -861.3 | 0.440 | -826.5 | 0.540 | -769.5 |
| 0.100 | -548.2 | 0.220 | -818.6 | 0.340 | -856.9 | 0.460 | -814.0 | 0.560 | -745.6 |
| 0.120 | -618.5 | 0.240 | -834.5 | 0.360 | -852.7 | | | | |
| $T = 298.15 \text{ K}, w_{3,23} = 7.50 \text{ wt } \%$ | | | | | | | | | |
| 0.020 | -130.6 | 0.120 | -600.6 | 0.220 | -795.5 | 0.320 | -839.7 | 0.400 | -824.5 |
| 0.040 | -244.8 | 0.140 | -654.7 | 0.240 | -810.5 | 0.340 | -834.4 | 0.420 | -818.5 |
| 0.060 | -358.3 | 0.160 | -702.9 | 0.260 | -825.7 | 0.360 | -835.9 | 0.440 | -807.7 |
| 0.080 | -449.9 | 0.180 | -742.6 | 0.280 | -832.6 | 0.380 | -831.3 | 0.460 | -801.0 |
| 0.100 | -532.1 | 0.200 | -773.6 | 0.300 | -836.4 | | | | |
| $T = 308.15 \text{ K}, w_{3,23} = 1.00 \text{ wt } \%$ | | | | | | | | | |
| 0.025 | -164.0 | 0.176 | -711.2 | 0.326 | -814.1 | 0.476 | -765.8 | 0.626 | -654.3 |
| 0.050 | -293.7 | 0.201 | -749.5 | 0.351 | -814.9 | 0.501 | -751.3 | 0.651 | -628.1 |
| 0.075 | -412.0 | 0.226 | -776.8 | 0.376 | -810.0 | 0.526 | -733.3 | 0.676 | -602.7 |
| 0.100 | -509.7 | 0.251 | -796.2 | 0.401 | -802.2 | 0.551 | -715.9 | 0.701 | -576.5 |
| 0.125 | -594.6 | 0.276 | -807.7 | 0.426 | -791.6 | 0.576 | -696.7 | 0.726 | -544.7 |
| 0.151 | -660.5 | 0.301 | -814.4 | 0.451 | -780.4 | 0.601 | -676.2 | 0.750 | -514.2 |
| $T = 308.15 \text{ K}, w_{3,23} = 5.00 \text{ wt } \%$ | | | | | | | | | |
| 0.020 | -120.0 | 0.140 | -618.8 | 0.260 | -783.6 | 0.380 | -796.0 | 0.481 | -752.3 |
| 0.040 | -233.6 | 0.160 | -665.5 | 0.281 | -795.6 | 0.401 | -789.4 | 0.501 | -740.6 |
| 0.060 | -334.0 | 0.180 | -701.3 | 0.300 | -800.6 | 0.420 | -782.3 | 0.521 | -732.4 |
| 0.080 | -421.9 | 0.200 | -732.2 | 0.321 | -801.0 | 0.441 | -772.7 | 0.541 | -718.4 |
| 0.100 | -498.4 | 0.220 | -755.4 | 0.341 | -802.6 | 0.460 | -765.0 | 0.561 | -703.3 |
| 0.120 | -565.6 | 0.241 | -772.1 | 0.361 | -800.1 | | | | |
| $T = 308.15 \text{ K}, w_{3,23} = 7.50 \text{ wt } \%$ | | | | | | | | | |
| 0.020 | -116.6 | 0.120 | -539.2 | 0.220 | -725.5 | 0.321 | -772.3 | 0.400 | -761.2 |
| 0.040 | -222.1 | 0.140 | -593.5 | 0.240 | -742.6 | 0.341 | -773.7 | 0.421 | -755.9 |
| 0.060 | -319.5 | 0.160 | -637.4 | 0.260 | -754.5 | 0.361 | -772.2 | 0.440 | -749.2 |
| 0.080 | -406.5 | 0.180 | -673.8 | 0.280 | -763.8 | 0.380 | -768.8 | 0.461 | -740.2 |
| 0.100 | -478.5 | 0.200 | -703.1 | 0.300 | -769.9 | | | | |
| $T = 323.15 \text{ K}, w_{3,23} = 1.00 \text{ wt } \%$ | | | | | | | | | |
| 0.025 | -126.9 | 0.175 | -606.1 | 0.325 | -685.0 | 0.475 | -658.7 | 0.625 | -573.4 |
| 0.050 | -258.4 | 0.200 | -622.7 | 0.350 | -694.0 | 0.500 | -647.3 | 0.650 | -551.0 |
| 0.075 | -382.1 | 0.225 | -660.0 | 0.375 | -700.1 | 0.525 | -628.3 | 0.675 | -530.3 |
| 0.100 | -452.7 | 0.250 | -677.6 | 0.400 | -691.0 | 0.550 | -619.8 | 0.700 | -507.8 |
| 0.125 | -509.9 | 0.275 | -677.1 | 0.425 | -687.9 | 0.575 | -606.9 | 0.725 | -482.4 |
| 0.150 | -570.3 | 0.300 | -684.5 | 0.450 | -673.8 | 0.600 | -589.5 | 0.750 | -458.0 |
| $T = 323.15 \text{ K}, w_{3,23} = 5.00 \text{ wt } \%$ | | | | | | | | | |
| 0.040 | -185.6 | 0.160 | -583.3 | 0.280 | -674.0 | 0.380 | -660.7 | 0.480 | -636.0 |
| 0.060 | -267.6 | 0.180 | -598.3 | 0.300 | -671.9 | 0.400 | -666.5 | 0.500 | -617.1 |
| 0.080 | -339.3 | 0.200 | -609.2 | 0.320 | -676.8 | 0.420 | -658.1 | 0.520 | -612.9 |
| 0.100 | -401.9 | 0.220 | -621.2 | 0.340 | -673.7 | 0.440 | -653.3 | 0.540 | -597.9 |
| 0.120 | -502.5 | 0.240 | -640.3 | 0.360 | -667.7 | 0.460 | -647.0 | 0.560 | -596.9 |
| 0.140 | -542.3 | 0.260 | -663.3 | | | | | | |
| $T = 323.15 \text{ K}, w_{3,23} = 7.50 \text{ wt } \%$ | | | | | | | | | |
| 0.020 | -92.1 | 0.120 | -501.5 | 0.240 | -609.8 | 0.320 | -652.1 | 0.400 | -643.5 |
| 0.040 | -182.6 | 0.140 | -527.8 | 0.260 | -621.0 | 0.340 | -656.6 | 0.420 | -633.9 |
| 0.060 | -296.6 | 0.160 | -563.4 | 0.280 | -638.3 | 0.360 | -650.2 | 0.440 | -631.0 |
| 0.080 | -401.6 | 0.200 | -585.7 | 0.300 | -650.0 | 0.380 | -650.1 | 0.460 | -621.8 |
| 0.100 | -456.0 | 0.220 | -594.6 | | | | | | |

Table 4. Excess Enthalpies of Ethanol (1) + (Water (2) + NaCl (3))

| $x_{1,123}$ | $h_{1+23}^E/\text{J}\cdot\text{mol}^{-1}$ | $x_{1,123}$ | $h_{1+23}^E/\text{J}\cdot\text{mol}^{-1}$ | $x_{1,123}$ | $h_{1+23}^E/\text{J}\cdot\text{mol}^{-1}$ | $x_{1,123}$ | $h_{1+23}^E/\text{J}\cdot\text{mol}^{-1}$ | $x_{1,123}$ | $h_{1+23}^E/\text{J}\cdot\text{mol}^{-1}$ |
|---|---|-------------|---|-------------|---|-------------|---|-------------|---|
| $T = 285.65 \text{ K}, w_{3,23} = 1.00 \text{ wt } \%$ | | | | | | | | | |
| 0.025 | -280.5 | 0.150 | -933.2 | 0.250 | -858.4 | 0.380 | -677.8 | 0.540 | -483.3 |
| 0.050 | -519.4 | 0.175 | -934.7 | 0.275 | -825.0 | 0.420 | -623.0 | 0.580 | -445.1 |
| 0.075 | -707.3 | 0.200 | -914.6 | 0.300 | -789.3 | 0.460 | -574.3 | 0.620 | -407.1 |
| 0.100 | -835.2 | 0.225 | -889.8 | 0.340 | -733.5 | 0.500 | -526.2 | 0.660 | -375.7 |
| 0.125 | -905.6 | | | | | | | | |
| $T = 285.65 \text{ K}, w_{3,23} = 3.96 \text{ wt } \%$ | | | | | | | | | |
| 0.020 | -211.1 | 0.100 | -770.0 | 0.180 | -853.3 | 0.260 | -778.6 | 0.340 | -682.1 |
| 0.040 | -402.4 | 0.120 | -823.0 | 0.200 | -841.1 | 0.280 | -756.7 | 0.360 | -657.4 |
| 0.060 | -561.0 | 0.140 | -850.6 | 0.220 | -824.2 | 0.300 | -731.8 | 0.380 | -633.1 |
| 0.080 | -682.6 | 0.160 | -858.1 | 0.240 | -801.5 | 0.320 | -707.4 | | |
| $T = 285.65 \text{ K}, w_{3,23} = 5.00 \text{ wt } \%$ | | | | | | | | | |
| 0.025 | -255.5 | 0.150 | -827.3 | 0.275 | -737.3 | 0.375 | -621.6 | 0.475 | -511.0 |
| 0.050 | -472.1 | 0.175 | -827.4 | 0.300 | -711.1 | 0.400 | -592.7 | 0.500 | -485.2 |
| 0.075 | -637.9 | 0.200 | -813.9 | 0.325 | -680.2 | 0.425 | -565.1 | 0.525 | -460.8 |
| 0.100 | -746.0 | 0.225 | -792.6 | 0.350 | -651.4 | 0.450 | -538.4 | 0.550 | -437.2 |
| 0.125 | -806.2 | 0.250 | -767.9 | | | | | | |
| $T = 285.65 \text{ K}, w_{3,23} = 5.98 \text{ wt } \%$ | | | | | | | | | |
| 0.020 | -199.0 | 0.080 | -646.4 | 0.140 | -798.5 | 0.200 | -788.8 | 0.260 | -732.8 |
| 0.040 | -381.3 | 0.100 | -726.2 | 0.160 | -803.7 | 0.220 | -772.3 | 0.280 | -712.9 |
| 0.060 | -532.7 | 0.120 | -773.4 | 0.180 | -800.2 | 0.240 | -754.9 | 0.300 | -690.5 |
| $T = 285.65 \text{ K}, w_{3,23} = 10.00 \text{ wt } \%$ | | | | | | | | | |
| 0.020 | -181.1 | 0.100 | -640.3 | 0.180 | -698.2 | 0.240 | -662.5 | 0.300 | -611.4 |
| 0.040 | -341.7 | 0.120 | -677.5 | 0.200 | -689.7 | 0.260 | -646.9 | 0.320 | -593.4 |
| 0.060 | -476.4 | 0.140 | -695.7 | 0.220 | -676.8 | 0.280 | -630.1 | 0.340 | -574.7 |
| 0.080 | -573.7 | 0.160 | -700.4 | | | | | | |
| $T = 298.15 \text{ K}, w_{3,23} = 1.00 \text{ wt } \%$ | | | | | | | | | |
| 0.050 | -440.2 | 0.250 | -697.3 | 0.450 | -459.7 | 0.650 | -294.7 | 0.850 | -188.3 |
| 0.100 | -688.6 | 0.300 | -636.7 | 0.500 | -409.0 | 0.700 | -267.5 | 0.900 | -149.8 |
| 0.150 | -762.8 | 0.350 | -575.5 | 0.550 | -364.7 | 0.750 | -243.1 | 0.950 | -85.6 |
| 0.200 | -745.8 | 0.400 | -515.5 | 0.600 | -326.1 | 0.801 | -217.8 | | |
| $T = 298.15 \text{ K}, w_{3,23} = 10.00 \text{ wt } \%$ | | | | | | | | | |
| 0.020 | -151.2 | 0.120 | -541.6 | 0.220 | -528.0 | 0.320 | -451.1 | 0.420 | -369.4 |
| 0.040 | -285.8 | 0.140 | -553.1 | 0.240 | -515.2 | 0.340 | -434.6 | 0.440 | -353.3 |
| 0.060 | -385.7 | 0.160 | -554.3 | 0.260 | -499.2 | 0.360 | -418.2 | 0.460 | -337.6 |
| 0.080 | -453.4 | 0.180 | -550.1 | 0.280 | -483.8 | 0.380 | -401.1 | 0.480 | -323.7 |
| 0.100 | -513.9 | 0.200 | -540.7 | 0.300 | -468.4 | 0.400 | -384.4 | 0.500 | -312.3 |
| $T = 308.15 \text{ K}, w_{3,23} = 1.00 \text{ wt } \%$ | | | | | | | | | |
| 0.040 | -306.8 | 0.241 | -557.2 | 0.442 | -342.8 | 0.641 | -201.2 | 0.801 | -149.6 |
| 0.080 | -508.3 | 0.281 | -514.4 | 0.482 | -306.5 | 0.681 | -185.2 | 0.841 | -141.2 |
| 0.121 | -597.9 | 0.321 | -470.0 | 0.522 | -274.5 | 0.721 | -172.2 | 0.881 | -113.1 |
| 0.161 | -614.2 | 0.361 | -425.0 | 0.561 | -247.0 | 0.762 | -160.1 | 0.921 | -84.0 |
| 0.201 | -593.3 | 0.402 | -383.2 | 0.601 | -220.7 | | | | |
| $T = 308.15 \text{ K}, w_{3,23} = 5.00 \text{ wt } \%$ | | | | | | | | | |
| 0.030 | -218.1 | 0.151 | -535.7 | 0.271 | -456.2 | 0.392 | -342.2 | 0.511 | -244.9 |
| 0.060 | -379.2 | 0.181 | -527.1 | 0.301 | -427.5 | 0.421 | -316.2 | 0.541 | -225.4 |
| 0.091 | -480.0 | 0.211 | -507.4 | 0.331 | -398.5 | 0.451 | -290.8 | 0.572 | -207.7 |
| 0.121 | -524.6 | 0.241 | -483.6 | 0.361 | -370.3 | 0.481 | -266.8 | 0.601 | -192.2 |
| $T = 308.15 \text{ K}, w_{3,23} = 10.00 \text{ wt } \%$ | | | | | | | | | |
| 0.020 | -129.9 | 0.121 | -431.3 | 0.221 | -403.9 | 0.301 | -345.2 | 0.381 | -281.7 |
| 0.040 | -240.0 | 0.141 | -436.5 | 0.241 | -390.4 | 0.321 | -328.7 | 0.401 | -265.4 |
| 0.060 | -323.4 | 0.161 | -434.0 | 0.261 | -375.8 | 0.341 | -312.5 | 0.421 | -251.4 |
| 0.080 | -380.2 | 0.181 | -427.0 | 0.281 | -360.2 | 0.361 | -297.2 | 0.442 | -236.5 |
| 0.100 | -414.9 | 0.201 | -416.5 | | | | | | |
| $T = 323.15 \text{ K}, w_{3,23} = 1.00 \text{ wt } \%$ | | | | | | | | | |
| 0.040 | -228.0 | 0.240 | -349.8 | 0.440 | -154.1 | 0.639 | -51.4 | 0.799 | -48.2 |
| 0.080 | -363.4 | 0.280 | -308.4 | 0.480 | -123.7 | 0.680 | -45.2 | 0.840 | -50.9 |
| 0.120 | -415.6 | 0.320 | -266.5 | 0.520 | -98.4 | 0.720 | -43.7 | 0.879 | -50.9 |
| 0.160 | -412.9 | 0.360 | -226.6 | 0.560 | -77.2 | 0.760 | -44.4 | 0.921 | -43.7 |
| 0.200 | -386.1 | 0.400 | -188.7 | 0.600 | -62.0 | | | | |
| $T = 323.15 \text{ K}, w_{3,23} = 5.00 \text{ wt } \%$ | | | | | | | | | |
| 0.030 | -160.4 | 0.150 | -356.4 | 0.270 | -267.1 | 0.390 | -158.9 | 0.510 | -76.8 |
| 0.060 | -274.1 | 0.180 | -341.4 | 0.300 | -238.4 | 0.420 | -135.4 | 0.540 | -62.4 |
| 0.090 | -337.5 | 0.210 | -319.4 | 0.330 | -210.2 | 0.450 | -113.9 | 0.570 | -50.1 |
| 0.120 | -357.7 | 0.240 | -294.0 | 0.360 | -184.1 | 0.480 | -93.6 | 0.600 | -40.2 |
| $T = 323.15 \text{ K}, w_{3,23} = 10.00 \text{ wt } \%$ | | | | | | | | | |
| 0.020 | -95.8 | 0.120 | -281.2 | 0.220 | -229.4 | 0.300 | -169.4 | 0.380 | -108.7 |
| 0.040 | -173.5 | 0.140 | -277.7 | 0.240 | -216.2 | 0.320 | -153.2 | 0.400 | -94.7 |
| 0.060 | -227.5 | 0.160 | -268.9 | 0.260 | -201.1 | 0.340 | -138.7 | 0.420 | -80.9 |
| 0.080 | -260.6 | 0.180 | -258.0 | 0.280 | -185.7 | 0.360 | -123.2 | 0.440 | -68.2 |
| 0.100 | -276.9 | 0.200 | -244.7 | | | | | | |

Table 4 (Continued)

| $x_{1,123}$ | $h_{1+23}^E/\text{J}\cdot\text{mol}^{-1}$ | $x_{1,123}$ | $h_{1+23}^E/\text{J}\cdot\text{mol}^{-1}$ | $x_{1,123}$ | $h_{1+23}^E/\text{J}\cdot\text{mol}^{-1}$ | $x_{1,123}$ | $h_{1+23}^E/\text{J}\cdot\text{mol}^{-1}$ | $x_{1,123}$ | $h_{1+23}^E/\text{J}\cdot\text{mol}^{-1}$ |
|---|---|-------------|---|-------------|---|-------------|---|-------------|---|
| $T = 338.15 \text{ K}, w_{3,23} = 1.00 \text{ wt } \%$ | | | | | | | | | |
| 0.040 | -156.9 | 0.240 | -150.9 | 0.440 | 38.2 | 0.600 | 103.9 | 0.799 | 62.2 |
| 0.080 | -234.5 | 0.280 | -108.2 | 0.480 | 62.4 | 0.639 | 101.8 | 0.840 | 38.0 |
| 0.120 | -249.0 | 0.320 | -67.3 | 0.519 | 81.8 | 0.680 | 101.0 | 0.879 | 31.9 |
| 0.160 | -231.0 | 0.360 | -29.0 | 0.560 | 95.8 | 0.720 | 86.6 | 0.921 | 26.6 |
| 0.200 | -194.5 | 0.400 | 7.9 | | | | | | |
| $T = 338.15 \text{ K}, w_{3,23} = 5.00 \text{ wt } \%$ | | | | | | | | | |
| 0.030 | -109.1 | 0.150 | -191.1 | 0.270 | -77.5 | 0.390 | 24.9 | 0.510 | 93.7 |
| 0.060 | -177.3 | 0.180 | -166.8 | 0.300 | -50.7 | 0.420 | 46.3 | 0.540 | 103.9 |
| 0.090 | -209.1 | 0.210 | -137.9 | 0.330 | -22.5 | 0.450 | 65.0 | 0.570 | 109.2 |
| 0.120 | -205.5 | 0.240 | -109.3 | 0.360 | 1.3 | 0.480 | 80.4 | 0.600 | 114.4 |
| $T = 338.15 \text{ K}, w_{3,23} = 10.00 \text{ wt } \%$ | | | | | | | | | |
| 0.020 | -62.6 | 0.120 | -146.3 | 0.220 | -67.1 | 0.300 | 5.9 | 0.380 | 67.4 |
| 0.040 | -109.9 | 0.140 | -133.2 | 0.240 | -45.8 | 0.320 | 21.6 | 0.400 | 79.4 |
| 0.060 | -139.7 | 0.160 | -122.3 | 0.260 | -30.0 | 0.340 | 38.0 | 0.419 | 92.8 |
| 0.080 | -151.5 | 0.180 | -102.1 | 0.280 | -11.1 | 0.360 | 54.4 | 0.439 | 104.8 |
| 0.100 | -153.3 | 0.200 | -83.6 | | | | | | |

Table 5. Excess Enthalpies of Ethanol (1) + (Water (2) + KCl (3))

| $x_{1,123}$ | $h_{1+23}^E/\text{J}\cdot\text{mol}^{-1}$ | $x_{1,123}$ | $h_{1+23}^E/\text{J}\cdot\text{mol}^{-1}$ | $x_{1,123}$ | $h_{1+23}^E/\text{J}\cdot\text{mol}^{-1}$ | $x_{1,123}$ | $h_{1+23}^E/\text{J}\cdot\text{mol}^{-1}$ | $x_{1,123}$ | $h_{1+23}^E/\text{J}\cdot\text{mol}^{-1}$ |
|--|---|-------------|---|-------------|---|-------------|---|-------------|---|
| $T = 285.65 \text{ K}, w_{3,23} = 1.00 \text{ wt } \%$ | | | | | | | | | |
| 0.025 | -285.2 | 0.150 | -942.6 | 0.275 | -833.0 | 0.375 | -687.8 | 0.475 | -559.5 |
| 0.050 | -525.9 | 0.175 | -943.1 | 0.300 | -796.1 | 0.400 | -653.5 | 0.500 | -530.5 |
| 0.075 | -713.4 | 0.200 | -925.8 | 0.325 | -760.9 | 0.425 | -620.8 | 0.525 | -501.3 |
| 0.100 | -841.6 | 0.225 | -898.9 | 0.350 | -724.0 | 0.450 | -590.1 | 0.550 | -476.0 |
| 0.125 | -912.9 | 0.250 | -865.9 | | | | | | |
| $T = 285.65 \text{ K}, w_{3,23} = 5.00 \text{ wt } \%$ | | | | | | | | | |
| 0.020 | -214.1 | 0.100 | -781.2 | 0.180 | -867.1 | 0.260 | -798.0 | 0.340 | -697.9 |
| 0.040 | -405.4 | 0.120 | -837.0 | 0.200 | -859.5 | 0.280 | -773.5 | 0.360 | -675.9 |
| 0.060 | -568.6 | 0.140 | -865.5 | 0.220 | -842.0 | 0.300 | -751.1 | 0.380 | -649.3 |
| 0.080 | -692.0 | 0.160 | -873.9 | 0.240 | -819.3 | 0.320 | -725.3 | | |
| $T = 285.65 \text{ K}, w_{3,23} = 7.50 \text{ wt } \%$ | | | | | | | | | |
| 0.020 | -204.6 | 0.080 | -665.2 | 0.140 | -826.5 | 0.200 | -821.1 | 0.260 | -767.9 |
| 0.040 | -392.3 | 0.100 | -747.8 | 0.160 | -835.1 | 0.220 | -805.8 | 0.280 | -747.3 |
| 0.060 | -546.0 | 0.120 | -799.5 | 0.180 | -834.1 | 0.240 | -788.0 | 0.300 | -726.5 |
| $T = 298.15 \text{ K}, w_{3,23} = 1.00 \text{ wt } \%$ | | | | | | | | | |
| 0.030 | -276.6 | 0.150 | -757.7 | 0.270 | -670.4 | 0.390 | -528.6 | 0.510 | -398.3 |
| 0.060 | -499.4 | 0.180 | -754.4 | 0.300 | -635.4 | 0.420 | -491.9 | 0.540 | -371.6 |
| 0.090 | -648.2 | 0.210 | -733.7 | 0.330 | -594.9 | 0.450 | -457.5 | 0.570 | -346.5 |
| 0.120 | -727.7 | 0.240 | -704.5 | 0.360 | -562.3 | 0.480 | -426.8 | 0.600 | -325.4 |
| $T = 298.15 \text{ K}, w_{3,23} = 5.00 \text{ wt } \%$ | | | | | | | | | |
| 0.030 | -257.2 | 0.120 | -668.2 | 0.210 | -668.7 | 0.300 | -585.7 | 0.390 | -487.5 |
| 0.060 | -459.2 | 0.150 | -689.2 | 0.240 | -645.1 | 0.330 | -553.6 | 0.420 | -454.0 |
| 0.090 | -575.5 | 0.180 | -687.9 | 0.270 | -615.0 | 0.360 | -517.9 | 0.450 | -423.6 |
| $T = 298.15 \text{ K}, w_{3,23} = 7.50 \text{ wt } \%$ | | | | | | | | | |
| 0.020 | -173.0 | 0.100 | -603.3 | 0.180 | -657.8 | 0.240 | -622.2 | 0.300 | -567.5 |
| 0.040 | -322.3 | 0.120 | -638.1 | 0.200 | -652.1 | 0.260 | -604.2 | 0.320 | -545.6 |
| 0.060 | -443.3 | 0.140 | -658.8 | 0.220 | -638.4 | 0.280 | -585.3 | 0.340 | -515.7 |
| 0.080 | -543.8 | 0.160 | -664.6 | | | | | | |
| $T = 308.15 \text{ K}, w_{3,23} = 1.00 \text{ wt } \%$ | | | | | | | | | |
| 0.030 | -240.9 | 0.151 | -623.5 | 0.271 | -533.9 | 0.391 | -399.7 | 0.511 | -289.8 |
| 0.060 | -426.8 | 0.181 | -616.2 | 0.301 | -499.2 | 0.421 | -368.7 | 0.542 | -266.3 |
| 0.091 | -546.2 | 0.211 | -595.4 | 0.331 | -465.5 | 0.452 | -340.6 | 0.572 | -245.9 |
| 0.121 | -606.5 | 0.241 | -565.8 | 0.362 | -430.9 | 0.481 | -315.0 | 0.602 | -227.6 |
| $T = 308.15 \text{ K}, w_{3,23} = 5.00 \text{ wt } \%$ | | | | | | | | | |
| 0.020 | -155.1 | 0.121 | -555.1 | 0.221 | -534.8 | 0.321 | -439.7 | 0.402 | -361.5 |
| 0.040 | -288.0 | 0.141 | -567.0 | 0.241 | -517.0 | 0.342 | -419.5 | 0.422 | -342.3 |
| 0.060 | -396.4 | 0.161 | -567.4 | 0.261 | -498.1 | 0.361 | -399.7 | 0.442 | -324.5 |
| 0.080 | -473.4 | 0.181 | -560.9 | 0.281 | -478.9 | 0.381 | -380.0 | 0.461 | -308.1 |
| 0.101 | -525.4 | 0.201 | -549.3 | 0.301 | -459.0 | | | | |
| $T = 308.15 \text{ K}, w_{3,23} = 7.50 \text{ wt } \%$ | | | | | | | | | |
| 0.020 | -147.3 | 0.101 | -495.8 | 0.181 | -526.3 | 0.241 | -485.7 | 0.301 | -432.3 |
| 0.040 | -275.8 | 0.121 | -521.7 | 0.201 | -515.3 | 0.261 | -468.4 | 0.321 | -414.4 |
| 0.060 | -376.0 | 0.141 | -532.6 | 0.221 | -501.4 | 0.281 | -450.4 | 0.341 | -396.8 |
| 0.080 | -449.2 | 0.161 | -532.8 | | | | | | |
| $T = 323.15 \text{ K}, w_{3,23} = 1.00 \text{ wt } \%$ | | | | | | | | | |
| 0.030 | -187.4 | 0.150 | -424.2 | 0.270 | -326.2 | 0.390 | -203.2 | 0.510 | -108.3 |
| 0.060 | -313.0 | 0.180 | -409.9 | 0.300 | -293.3 | 0.420 | -176.2 | 0.540 | -90.6 |
| 0.090 | -389.1 | 0.210 | -386.5 | 0.330 | -263.8 | 0.450 | -151.4 | 0.570 | -76.4 |
| 0.120 | -421.6 | 0.240 | -357.0 | 0.360 | -231.7 | 0.480 | -128.2 | 0.599 | -64.5 |

Table 7 (Continued)

| $x_{1,123}$ | $h_{1+23}^E/\text{J}\cdot\text{mol}^{-1}$ | $x_{1,123}$ | $h_{1+23}^E/\text{J}\cdot\text{mol}^{-1}$ | $x_{1,123}$ | $h_{1+23}^E/\text{J}\cdot\text{mol}^{-1}$ | $x_{1,123}$ | $h_{1+23}^E/\text{J}\cdot\text{mol}^{-1}$ | $x_{1,123}$ | $h_{1+23}^E/\text{J}\cdot\text{mol}^{-1}$ |
|--|---|-------------|---|-------------|---|-------------|---|-------------|---|
| $T = 298.15 \text{ K}, w_{3,23} = 3.00 \text{ wt } \%$ | | | | | | | | | |
| 0.020 | -176.5 | 0.100 | -314.1 | 0.160 | -242.8 | 0.240 | -139.3 | 0.360 | -0.1 |
| 0.040 | -295.9 | 0.120 | -291.2 | 0.180 | -215.5 | 0.280 | -90.7 | 0.400 | 41.4 |
| 0.060 | -338.7 | 0.140 | -266.4 | 0.200 | -190.8 | 0.320 | -44.1 | 0.441 | 79.2 |
| 0.080 | -332.7 | | | | | | | | |
| $T = 298.15 \text{ K}, w_{3,23} = 5.00 \text{ wt } \%$ | | | | | | | | | |
| 0.020 | -169.5 | 0.080 | -305.7 | 0.140 | -243.7 | 0.200 | -174.5 | 0.280 | -86.5 |
| 0.040 | -279.9 | 0.100 | -287.7 | 0.160 | -220.5 | 0.220 | -154.3 | 0.320 | -41.4 |
| 0.060 | -314.3 | 0.120 | -266.9 | 0.180 | -193.3 | 0.240 | -132.6 | 0.360 | 2.5 |
| $T = 308.15 \text{ K}, w_{3,23} = 1.00 \text{ wt } \%$ | | | | | | | | | |
| 0.020 | -144.5 | 0.120 | -187.3 | 0.231 | -24.9 | 0.351 | 127.1 | 0.471 | 244.0 |
| 0.040 | -232.8 | 0.141 | -159.1 | 0.261 | 14.6 | 0.381 | 159.1 | 0.501 | 266.2 |
| 0.060 | -254.8 | 0.171 | -108.3 | 0.291 | 54.8 | 0.411 | 190.5 | 0.531 | 281.9 |
| 0.080 | -239.8 | 0.201 | -66.4 | 0.321 | 92.4 | 0.442 | 219.0 | 0.561 | 295.4 |
| 0.100 | -214.9 | | | | | | | | |
| $T = 308.15 \text{ K}, w_{3,23} = 3.00 \text{ wt } \%$ | | | | | | | | | |
| 0.020 | -139.3 | 0.101 | -194.5 | 0.161 | -114.9 | 0.241 | -8.1 | 0.362 | 134.7 |
| 0.040 | -219.7 | 0.121 | -168.3 | 0.181 | -88.0 | 0.281 | 41.4 | 0.402 | 176.2 |
| 0.060 | -233.0 | 0.141 | -141.9 | 0.201 | -61.4 | 0.321 | 89.5 | 0.441 | 211.9 |
| 0.080 | -219.0 | | | | | | | | |
| $T = 308.15 \text{ K}, w_{3,23} = 5.00 \text{ wt } \%$ | | | | | | | | | |
| 0.020 | -132.3 | 0.080 | -196.2 | 0.141 | -123.3 | 0.201 | -48.7 | 0.281 | 44.7 |
| 0.040 | -205.2 | 0.100 | -173.1 | 0.161 | -98.2 | 0.221 | -23.2 | 0.321 | 88.9 |
| 0.060 | -214.2 | 0.120 | -149.3 | 0.181 | -73.3 | 0.241 | -1.2 | 0.361 | 133.5 |
| $T = 323.15 \text{ K}, w_{3,23} = 1.00 \text{ wt } \%$ | | | | | | | | | |
| 0.020 | -85.8 | 0.120 | -12.7 | 0.230 | 165.5 | 0.350 | 330.0 | 0.470 | 443.2 |
| 0.040 | -121.6 | 0.140 | 21.2 | 0.260 | 211.0 | 0.380 | 363.3 | 0.500 | 461.5 |
| 0.060 | -110.2 | 0.170 | 71.2 | 0.290 | 253.2 | 0.410 | 394.2 | 0.530 | 476.1 |
| 0.080 | -79.9 | 0.200 | 119.3 | 0.320 | 292.4 | 0.440 | 421.2 | 0.560 | 483.9 |
| 0.100 | -46.5 | | | | | | | | |
| $T = 323.15 \text{ K}, w_{3,23} = 3.00 \text{ wt } \%$ | | | | | | | | | |
| 0.020 | -81.0 | 0.100 | -33.1 | 0.160 | 62.3 | 0.240 | 180.6 | 0.360 | 333.6 |
| 0.040 | -110.3 | 0.120 | -1.1 | 0.180 | 93.4 | 0.280 | 236.2 | 0.400 | 373.0 |
| 0.060 | -96.1 | 0.140 | 30.5 | 0.200 | 122.4 | 0.320 | 286.3 | 0.440 | 409.3 |
| 0.080 | -65.7 | | | | | | | | |
| $T = 323.15 \text{ K}, w_{3,23} = 5.00 \text{ wt } \%$ | | | | | | | | | |
| 0.020 | -76.9 | 0.080 | -53.6 | 0.140 | 39.5 | 0.200 | 127.4 | 0.280 | 235.5 |
| 0.040 | -101.2 | 0.100 | -22.7 | 0.160 | 68.2 | 0.220 | 155.9 | 0.320 | 283.9 |
| 0.060 | -83.2 | 0.120 | 8.0 | 0.180 | 97.6 | 0.240 | 183.5 | 0.360 | 324.3 |
| $T = 338.15 \text{ K}, w_{3,23} = 1.00 \text{ wt } \%$ | | | | | | | | | |
| 0.020 | -37.4 | 0.120 | 130.9 | 0.230 | 337.8 | 0.350 | 513.2 | 0.470 | 623.1 |
| 0.040 | -33.0 | 0.140 | 171.4 | 0.260 | 387.0 | 0.380 | 548.1 | 0.500 | 638.0 |
| 0.060 | 1.0 | 0.170 | 229.7 | 0.290 | 433.1 | 0.410 | 578.5 | 0.530 | 647.7 |
| 0.080 | 44.9 | 0.200 | 285.4 | 0.320 | 475.2 | 0.439 | 602.2 | 0.559 | 650.0 |
| 0.100 | 88.9 | | | | | | | | |
| $T = 338.15 \text{ K}, w_{3,23} = 3.00 \text{ wt } \%$ | | | | | | | | | |
| 0.020 | -33.7 | 0.100 | 95.3 | 0.160 | 208.9 | 0.240 | 348.0 | 0.359 | 513.2 |
| 0.040 | -26.0 | 0.120 | 132.9 | 0.180 | 246.5 | 0.280 | 410.1 | 0.400 | 557.1 |
| 0.060 | 7.8 | 0.140 | 171.5 | 0.200 | 281.0 | 0.320 | 465.5 | 0.440 | 587.1 |
| 0.080 | 53.3 | | | | | | | | |
| $T = 338.15 \text{ K}, w_{3,23} = 5.00 \text{ wt } \%$ | | | | | | | | | |
| 0.020 | -30.7 | 0.080 | 58.7 | 0.140 | 173.6 | 0.200 | 279.1 | 0.280 | 402.4 |
| 0.040 | -19.6 | 0.100 | 97.9 | 0.160 | 210.4 | 0.220 | 312.0 | 0.320 | 454.8 |
| 0.060 | 18.8 | 0.120 | 137.6 | 0.180 | 244.9 | 0.240 | 343.0 | 0.359 | 502.9 |
| $T = 353.15 \text{ K}, w_{3,23} = 1.00 \text{ wt } \%$ | | | | | | | | | |
| 0.020 | 7.2 | 0.120 | 279.8 | 0.230 | 527.5 | 0.350 | 725.5 | 0.470 | 830.6 |
| 0.040 | 57.7 | 0.140 | 330.8 | 0.260 | 585.8 | 0.380 | 760.5 | 0.500 | 845.5 |
| 0.060 | 107.3 | 0.170 | 401.9 | 0.290 | 636.3 | 0.410 | 791.4 | 0.530 | 846.8 |
| 0.080 | 170.2 | 0.200 | 466.4 | 0.320 | 682.3 | 0.440 | 815.8 | 0.560 | 848.5 |
| 0.100 | 227.3 | | | | | | | | |
| $T = 353.15 \text{ K}, w_{3,23} = 3.00 \text{ wt } \%$ | | | | | | | | | |
| 0.030 | 29.7 | 0.120 | 276.6 | 0.210 | 478.2 | 0.300 | 635.7 | 0.390 | 753.7 |
| 0.060 | 112.0 | 0.150 | 351.7 | 0.240 | 536.6 | 0.330 | 683.1 | 0.420 | 785.7 |
| 0.090 | 196.8 | 0.180 | 416.7 | 0.270 | 590.8 | 0.360 | 720.2 | 0.450 | 806.9 |
| $T = 353.15 \text{ K}, w_{3,23} = 5.00 \text{ wt } \%$ | | | | | | | | | |
| 0.025 | 20.6 | 0.100 | 226.0 | 0.175 | 404.1 | 0.250 | 542.1 | 0.325 | 659.8 |
| 0.050 | 88.0 | 0.125 | 287.3 | 0.200 | 449.2 | 0.275 | 584.2 | 0.350 | 693.6 |
| 0.075 | 157.1 | 0.150 | 344.4 | 0.225 | 496.6 | 0.300 | 622.1 | | |

Table 8. Excess Enthalpies of 2-Propanol (1) + (Water (2) + NaCl (3))

| $x_{1,123}$ | $h_{1+23}^E/\text{J}\cdot\text{mol}^{-1}$ | $x_{1,123}$ | $h_{1+23}^E/\text{J}\cdot\text{mol}^{-1}$ | $x_{1,123}$ | $h_{1+23}^E/\text{J}\cdot\text{mol}^{-1}$ | $x_{1,123}$ | $h_{1+23}^E/\text{J}\cdot\text{mol}^{-1}$ | $x_{1,123}$ | $h_{1+23}^E/\text{J}\cdot\text{mol}^{-1}$ |
|--|---|-------------|---|-------------|---|-------------|---|-------------|---|
| $T = 285.65 \text{ K}, w_{3,23} = 2.50 \text{ wt } \%$ | | | | | | | | | |
| 0.020 | -285.9 | 0.100 | -793.3 | 0.180 | -686.5 | 0.275 | -504.2 | 0.375 | -316.3 |
| 0.040 | -524.4 | 0.120 | -777.2 | 0.200 | -647.6 | 0.300 | -456.8 | 0.400 | -271.9 |
| 0.060 | -694.9 | 0.140 | -754.8 | 0.225 | -602.3 | 0.325 | -409.0 | 0.425 | -228.7 |
| 0.080 | -773.6 | 0.160 | -721.7 | 0.250 | -553.1 | 0.350 | -361.2 | | |
| $T = 285.65 \text{ K}, w_{3,23} = 5.98 \text{ wt } \%$ | | | | | | | | | |
| 0.015 | -197.1 | 0.074 | -664.1 | 0.119 | -658.3 | 0.164 | -610.2 | 0.208 | -537.6 |
| 0.030 | -372.9 | 0.089 | -679.2 | 0.134 | -644.8 | 0.179 | -582.0 | 0.223 | -516.0 |
| 0.045 | -523.3 | 0.104 | -674.2 | 0.149 | -623.4 | 0.193 | -558.7 | 0.238 | -491.5 |
| 0.059 | -617.7 | | | | | | | | |
| $T = 285.65 \text{ K}, w_{3,23} = 7.50 \text{ wt } \%$ | | | | | | | | | |
| 0.015 | -192.3 | 0.075 | -621.9 | 0.120 | -612.6 | 0.165 | -559.5 | 0.210 | -493.9 |
| 0.030 | -361.3 | 0.090 | -628.6 | 0.135 | -599.9 | 0.180 | -540.1 | 0.225 | -473.3 |
| 0.045 | -510.6 | 0.105 | -628.6 | 0.150 | -579.6 | 0.195 | -518.7 | 0.240 | -454.0 |
| 0.060 | -579.2 | | | | | | | | |
| $T = 298.15 \text{ K}, w_{3,23} = 2.50 \text{ wt } \%$ | | | | | | | | | |
| 0.030 | -338.7 | 0.151 | -544.5 | 0.271 | -340.7 | 0.392 | -145.4 | 0.512 | 55.2 |
| 0.060 | -540.5 | 0.181 | -486.5 | 0.301 | -288.8 | 0.422 | -94.0 | 0.542 | 82.4 |
| 0.090 | -593.1 | 0.211 | -450.4 | 0.331 | -238.4 | 0.452 | -48.2 | 0.572 | 122.8 |
| 0.121 | -582.6 | 0.241 | -402.0 | 0.361 | -182.8 | 0.482 | -0.3 | | |
| $T = 298.15 \text{ K}, w_{3,23} = 5.00 \text{ wt } \%$ | | | | | | | | | |
| 0.020 | -222.9 | 0.120 | -511.3 | 0.201 | -411.2 | 0.281 | -286.4 | 0.361 | -156.3 |
| 0.040 | -391.8 | 0.140 | -490.5 | 0.221 | -380.6 | 0.301 | -256.4 | 0.381 | -127.8 |
| 0.060 | -491.5 | 0.161 | -465.6 | 0.241 | -351.4 | 0.321 | -223.7 | 0.401 | -97.3 |
| 0.080 | -524.7 | 0.181 | -437.7 | 0.261 | -330.6 | 0.341 | -188.3 | 0.421 | -65.5 |
| 0.100 | -524.0 | | | | | | | | |
| $T = 298.15 \text{ K}, w_{3,23} = 7.50 \text{ wt } \%$ | | | | | | | | | |
| 0.020 | -204.3 | 0.080 | -467.4 | 0.140 | -431.6 | 0.201 | -359.9 | 0.241 | -307.2 |
| 0.040 | -361.3 | 0.100 | -463.3 | 0.161 | -408.1 | 0.221 | -332.7 | 0.261 | -274.4 |
| 0.060 | -442.9 | 0.120 | -450.9 | 0.181 | -385.0 | | | | |
| $T = 308.15 \text{ K}, w_{3,23} = 2.50 \text{ wt } \%$ | | | | | | | | | |
| 0.030 | -280.6 | 0.150 | -405.7 | 0.270 | -215.7 | 0.390 | -17.9 | 0.510 | 152.9 |
| 0.060 | -434.3 | 0.180 | -362.3 | 0.300 | -164.9 | 0.420 | 28.3 | 0.541 | 191.5 |
| 0.090 | -463.3 | 0.210 | -315.3 | 0.330 | -114.6 | 0.450 | 72.1 | 0.571 | 219.8 |
| 0.120 | -442.7 | 0.240 | -267.3 | 0.360 | -66.1 | 0.480 | 114.2 | | |
| $T = 308.15 \text{ K}, w_{3,23} = 5.00 \text{ wt } \%$ | | | | | | | | | |
| 0.020 | -186.3 | 0.120 | -378.9 | 0.200 | -277.2 | 0.280 | -161.1 | 0.360 | -40.0 |
| 0.040 | -319.4 | 0.140 | -356.6 | 0.220 | -249.6 | 0.300 | -132.8 | 0.380 | -12.3 |
| 0.060 | -385.7 | 0.160 | -330.9 | 0.240 | -220.8 | 0.320 | -101.3 | 0.400 | 16.7 |
| 0.080 | -402.1 | 0.180 | -303.7 | 0.260 | -189.5 | 0.340 | -72.0 | 0.420 | 49.4 |
| 0.100 | -395.4 | | | | | | | | |
| $T = 308.15 \text{ K}, w_{3,23} = 7.50 \text{ wt } \%$ | | | | | | | | | |
| 0.020 | -172.5 | 0.080 | -357.1 | 0.140 | -310.9 | 0.200 | -238.2 | 0.260 | -158.3 |
| 0.040 | -291.2 | 0.100 | -348.7 | 0.160 | -289.6 | 0.220 | -212.8 | 0.280 | -130.7 |
| 0.060 | -346.7 | 0.120 | -332.0 | 0.180 | -264.1 | 0.240 | -185.9 | | |
| $T = 323.15 \text{ K}, w_{3,23} = 2.50 \text{ wt } \%$ | | | | | | | | | |
| 0.030 | -198.9 | 0.150 | -204.3 | 0.270 | -16.9 | 0.390 | 164.8 | 0.510 | 315.1 |
| 0.060 | -276.5 | 0.180 | -159.3 | 0.300 | 29.0 | 0.420 | 208.4 | 0.540 | 342.3 |
| 0.090 | -276.1 | 0.210 | -113.8 | 0.330 | 75.4 | 0.450 | 246.5 | 0.571 | 368.1 |
| 0.120 | -244.6 | 0.240 | -66.0 | 0.360 | 121.7 | 0.480 | 282.7 | | |
| $T = 323.15 \text{ K}, w_{3,23} = 5.00 \text{ wt } \%$ | | | | | | | | | |
| 0.020 | -136.7 | 0.120 | -208.0 | 0.200 | -99.6 | 0.280 | 19.9 | 0.360 | 133.4 |
| 0.040 | -216.6 | 0.140 | -183.1 | 0.220 | -70.5 | 0.300 | 49.2 | 0.380 | 161.9 |
| 0.060 | -246.9 | 0.160 | -155.7 | 0.240 | -40.0 | 0.320 | 77.0 | 0.400 | 189.4 |
| 0.080 | -245.5 | 0.180 | -127.8 | 0.260 | -9.4 | 0.340 | 105.7 | 0.420 | 216.1 |
| 0.100 | -229.9 | | | | | | | | |
| $T = 323.15 \text{ K}, w_{3,23} = 7.50 \text{ wt } \%$ | | | | | | | | | |
| 0.020 | -122.9 | 0.080 | -209.1 | 0.140 | -145.2 | 0.200 | -67.1 | 0.260 | 17.3 |
| 0.040 | -193.3 | 0.100 | -190.5 | 0.160 | -119.2 | 0.220 | -39.3 | 0.280 | 42.0 |
| 0.060 | -215.0 | 0.120 | -168.5 | 0.180 | -92.4 | 0.240 | -10.3 | | |
| $T = 338.15 \text{ K}, w_{3,23} = 2.50 \text{ wt } \%$ | | | | | | | | | |
| 0.015 | -75.3 | 0.090 | -138.8 | 0.240 | 90.3 | 0.360 | 271.7 | 0.480 | 413.6 |
| 0.030 | -128.1 | 0.105 | -118.8 | 0.270 | 138.6 | 0.390 | 312.6 | 0.510 | 439.6 |
| 0.045 | -156.8 | 0.150 | -53.6 | 0.300 | 185.2 | 0.420 | 350.0 | 0.540 | 462.8 |
| 0.060 | -162.0 | 0.180 | -4.1 | 0.330 | 229.0 | 0.450 | 383.5 | 0.570 | 479.8 |
| 0.075 | -154.0 | 0.210 | 42.4 | | | | | | |
| $T = 338.15 \text{ K}, w_{3,23} = 5.00 \text{ wt } \%$ | | | | | | | | | |
| 0.020 | -96.3 | 0.120 | -66.6 | 0.200 | 47.5 | 0.280 | 169.5 | 0.360 | 280.4 |
| 0.040 | -129.3 | 0.140 | -39.1 | 0.220 | 79.4 | 0.300 | 196.7 | 0.380 | 303.0 |
| 0.060 | -135.4 | 0.160 | -11.2 | 0.240 | 109.5 | 0.320 | 222.8 | 0.400 | 328.4 |
| 0.080 | -119.7 | 0.180 | 19.2 | 0.260 | 137.9 | 0.340 | 250.2 | 0.420 | 351.8 |
| 0.100 | -95.0 | | | | | | | | |
| $T = 338.15 \text{ K}, w_{3,23} = 7.50 \text{ wt } \%$ | | | | | | | | | |
| 0.020 | -73.9 | 0.080 | -91.4 | 0.140 | -17.4 | 0.200 | 69.8 | 0.260 | 154.4 |
| 0.040 | -105.8 | 0.100 | -70.3 | 0.160 | 12.0 | 0.220 | 98.1 | 0.280 | 184.4 |
| 0.060 | -106.1 | 0.120 | -44.2 | 0.180 | 39.3 | 0.240 | 130.8 | | |

Table 9. Excess Enthalpies of 2-Propanol (1) + (Water (2) + KCl (3))

| $x_{1,123}$ | $h_{1+23}^E/\text{J}\cdot\text{mol}^{-1}$ | $x_{1,123}$ | $h_{1+23}^E/\text{J}\cdot\text{mol}^{-1}$ | $x_{1,123}$ | $h_{1+23}^E/\text{J}\cdot\text{mol}^{-1}$ | $x_{1,123}$ | $h_{1+23}^E/\text{J}\cdot\text{mol}^{-1}$ | $x_{1,123}$ | $h_{1+23}^E/\text{J}\cdot\text{mol}^{-1}$ |
|--|---|-------------|---|-------------|---|-------------|---|-------------|---|
| $T = 285.65 \text{ K}, w_{3,23} = 2.50 \text{ wt } \%$ | | | | | | | | | |
| 0.020 | -290.9 | 0.100 | -817.1 | 0.180 | -709.7 | 0.275 | -523.2 | 0.375 | -332.0 |
| 0.040 | -536.2 | 0.120 | -805.0 | 0.200 | -671.6 | 0.300 | -474.9 | 0.400 | -284.9 |
| 0.060 | -711.0 | 0.140 | -778.3 | 0.225 | -622.6 | 0.325 | -427.1 | 0.425 | -244.6 |
| 0.080 | -798.3 | 0.160 | -747.1 | 0.250 | -571.0 | 0.350 | -377.1 | | |
| $T = 285.65 \text{ K}, w_{3,23} = 5.00 \text{ wt } \%$ | | | | | | | | | |
| 0.020 | -280.2 | 0.060 | -673.0 | 0.100 | -766.7 | 0.140 | -723.0 | 0.180 | -659.4 |
| 0.040 | -509.9 | 0.080 | -747.2 | 0.120 | -749.4 | 0.160 | -694.1 | 0.200 | -623.4 |
| $T = 285.65 \text{ K}, w_{3,23} = 7.50 \text{ wt } \%$ | | | | | | | | | |
| 0.015 | -202.3 | 0.060 | -629.2 | 0.105 | -699.8 | 0.150 | -655.8 | 0.195 | -590.6 |
| 0.030 | -382.4 | 0.075 | -679.8 | 0.120 | -687.9 | 0.165 | -635.1 | 0.210 | -566.4 |
| 0.045 | -530.9 | 0.090 | -699.0 | 0.135 | -672.8 | 0.180 | -614.1 | 0.225 | -547.5 |
| $T = 298.15 \text{ K}, w_{3,23} = 2.50 \text{ wt } \%$ | | | | | | | | | |
| 0.030 | -342.7 | 0.151 | -564.2 | 0.271 | -363.7 | 0.391 | -149.3 | 0.481 | 5.7 |
| 0.060 | -557.2 | 0.181 | -515.9 | 0.301 | -313.1 | 0.421 | -100.1 | 0.511 | 50.5 |
| 0.090 | -614.6 | 0.211 | -467.1 | 0.331 | -257.9 | 0.451 | -53.9 | 0.542 | 109.5 |
| 0.121 | -603.1 | 0.241 | -417.1 | 0.361 | -199.5 | | | | |
| $T = 298.15 \text{ K}, w_{3,23} = 5.00 \text{ wt } \%$ | | | | | | | | | |
| 0.020 | -222.6 | 0.100 | -566.5 | 0.181 | -480.2 | 0.261 | -352.7 | 0.341 | -225.2 |
| 0.040 | -411.3 | 0.121 | -553.0 | 0.201 | -450.8 | 0.281 | -322.1 | 0.361 | -191.8 |
| 0.060 | -515.7 | 0.141 | -532.8 | 0.221 | -419.3 | 0.301 | -290.2 | 0.381 | -162.8 |
| 0.080 | -561.4 | 0.161 | -506.8 | 0.241 | -385.1 | 0.321 | -252.6 | | |
| $T = 298.15 \text{ K}, w_{3,23} = 7.50 \text{ wt } \%$ | | | | | | | | | |
| 0.020 | -216.8 | 0.080 | -516.6 | 0.141 | -487.1 | 0.201 | -410.7 | 0.261 | -321.6 |
| 0.040 | -385.9 | 0.100 | -518.3 | 0.160 | -463.8 | 0.221 | -382.2 | 0.281 | -283.4 |
| 0.060 | -482.2 | 0.121 | -504.4 | 0.181 | -433.9 | 0.241 | -352.7 | | |
| $T = 308.15 \text{ K}, w_{3,23} = 2.50 \text{ wt } \%$ | | | | | | | | | |
| 0.030 | -285.3 | 0.150 | -421.3 | 0.270 | -225.9 | 0.390 | -23.5 | 0.510 | 146.0 |
| 0.060 | -442.9 | 0.180 | -376.6 | 0.300 | -177.5 | 0.420 | 22.8 | 0.540 | 182.7 |
| 0.090 | -477.2 | 0.210 | -327.2 | 0.330 | -127.3 | 0.450 | 64.4 | 0.570 | 212.5 |
| 0.120 | -458.3 | 0.240 | -278.0 | 0.360 | -76.4 | 0.480 | 105.5 | | |
| $T = 308.15 \text{ K}, w_{3,23} = 5.00 \text{ wt } \%$ | | | | | | | | | |
| 0.020 | -191.3 | 0.100 | -431.2 | 0.180 | -339.8 | 0.260 | -220.4 | 0.340 | -97.2 |
| 0.040 | -333.8 | 0.120 | -414.9 | 0.200 | -310.8 | 0.280 | -188.0 | 0.360 | -61.0 |
| 0.060 | -409.9 | 0.140 | -392.9 | 0.220 | -282.2 | 0.300 | -157.3 | 0.380 | -31.1 |
| 0.080 | -434.3 | 0.160 | -369.1 | 0.240 | -252.1 | 0.320 | -125.8 | | |
| $T = 308.15 \text{ K}, w_{3,23} = 7.50 \text{ wt } \%$ | | | | | | | | | |
| 0.020 | -182.4 | 0.080 | -400.7 | 0.140 | -359.8 | 0.200 | -282.3 | 0.260 | -200.5 |
| 0.040 | -315.9 | 0.100 | -395.5 | 0.160 | -334.4 | 0.220 | -255.0 | 0.280 | -169.3 |
| 0.060 | -384.0 | 0.120 | -380.2 | 0.180 | -309.2 | 0.240 | -224.7 | | |
| $T = 323.15 \text{ K}, w_{3,23} = 2.50 \text{ wt } \%$ | | | | | | | | | |
| 0.030 | -204.2 | 0.150 | -221.9 | 0.270 | -31.3 | 0.390 | 152.8 | 0.510 | 305.6 |
| 0.060 | -290.2 | 0.180 | -175.9 | 0.300 | 15.9 | 0.420 | 196.3 | 0.540 | 335.0 |
| 0.090 | -291.8 | 0.210 | -129.1 | 0.330 | 63.3 | 0.450 | 236.5 | 0.570 | 359.2 |
| 0.120 | -262.1 | 0.240 | -80.3 | 0.360 | 109.6 | 0.480 | 272.5 | | |
| $T = 323.15 \text{ K}, w_{3,23} = 5.00 \text{ wt } \%$ | | | | | | | | | |
| 0.020 | -140.5 | 0.100 | -254.4 | 0.180 | -151.9 | 0.260 | -31.9 | 0.340 | 87.0 |
| 0.040 | -229.4 | 0.120 | -232.6 | 0.200 | -122.7 | 0.280 | -3.1 | 0.360 | 116.8 |
| 0.060 | -267.2 | 0.140 | -207.9 | 0.220 | -91.6 | 0.300 | 27.8 | 0.380 | 143.8 |
| 0.080 | -268.6 | 0.160 | -181.4 | 0.240 | -63.3 | 0.320 | 58.9 | | |
| $T = 323.15 \text{ K}, w_{3,23} = 7.50 \text{ wt } \%$ | | | | | | | | | |
| 0.020 | -132.2 | 0.080 | -242.1 | 0.140 | -183.5 | 0.200 | -102.2 | 0.260 | -16.3 |
| 0.040 | -213.6 | 0.100 | -227.1 | 0.160 | -157.9 | 0.220 | -74.7 | 0.280 | 15.2 |
| 0.060 | -244.0 | 0.120 | -207.6 | 0.180 | -130.3 | 0.240 | -47.2 | | |
| $T = 338.15 \text{ K}, w_{3,23} = 2.50 \text{ wt } \%$ | | | | | | | | | |
| 0.015 | -80.8 | 0.090 | -146.8 | 0.240 | 83.3 | 0.360 | 267.9 | 0.480 | 412.3 |
| 0.030 | -132.2 | 0.105 | -126.7 | 0.270 | 130.7 | 0.390 | 306.2 | 0.510 | 440.4 |
| 0.045 | -162.8 | 0.150 | -62.7 | 0.300 | 178.5 | 0.419 | 344.2 | 0.540 | 464.8 |
| 0.060 | -169.8 | 0.180 | -12.7 | 0.330 | 222.9 | 0.449 | 381.3 | 0.570 | 483.6 |
| 0.075 | -162.7 | 0.210 | 33.8 | | | | | | |
| $T = 338.15 \text{ K}, w_{3,23} = 5.00 \text{ wt } \%$ | | | | | | | | | |
| 0.020 | -92.0 | 0.100 | -115.0 | 0.180 | 3.5 | 0.260 | 124.5 | 0.340 | 240.1 |
| 0.040 | -142.7 | 0.120 | -87.5 | 0.200 | 33.6 | 0.280 | 153.8 | 0.360 | 269.8 |
| 0.060 | -153.6 | 0.140 | -58.5 | 0.220 | 63.0 | 0.300 | 184.0 | 0.380 | 294.5 |
| 0.080 | -138.5 | 0.160 | -27.5 | 0.240 | 93.6 | 0.320 | 211.0 | | |
| $T = 338.15 \text{ K}, w_{3,23} = 7.50 \text{ wt } \%$ | | | | | | | | | |
| 0.020 | -87.7 | 0.080 | -122.5 | 0.140 | -44.4 | 0.200 | 42.6 | 0.260 | 128.5 |
| 0.040 | -132.1 | 0.100 | -98.7 | 0.160 | -17.9 | 0.220 | 72.3 | 0.280 | 157.3 |
| 0.060 | -137.7 | 0.120 | -72.1 | 0.180 | 14.0 | 0.240 | 102.3 | | |

Table 10. Excess Enthalpies of Methanol (1) + Water (2)

| $x_{1,12}$ | $h_{1+2}^E/\text{J}\cdot\text{mol}^{-1}$ | $x_{1,12}$ | $h_{1+2}^E/\text{J}\cdot\text{mol}^{-1}$ | $x_{1,12}$ | $h_{1+2}^E/\text{J}\cdot\text{mol}^{-1}$ | $x_{1,12}$ | $h_{1+2}^E/\text{J}\cdot\text{mol}^{-1}$ | $x_{1,12}$ | $h_{1+2}^E/\text{J}\cdot\text{mol}^{-1}$ |
|------------------------|--|------------|--|------------|--|------------|--|------------|--|
| $T = 285.65 \text{ K}$ | | | | | | | | | |
| 0.050 | -363.1 | 0.250 | -947.9 | 0.450 | -898.7 | 0.650 | -706.3 | 0.850 | -386.0 |
| 0.100 | -644.1 | 0.300 | -962.6 | 0.500 | -857.3 | 0.700 | -643.8 | 0.900 | -275.4 |
| 0.150 | -795.6 | 0.350 | -954.0 | 0.550 | -813.1 | 0.750 | -567.8 | 0.950 | -145.0 |
| 0.200 | -901.5 | 0.400 | -928.1 | 0.600 | -761.7 | 0.800 | -485.0 | | |
| $T = 298.15 \text{ K}$ | | | | | | | | | |
| 0.050 | -330.3 | 0.250 | -879.8 | 0.450 | -850.8 | 0.650 | -680.2 | 0.850 | -385.3 |
| 0.100 | -570.9 | 0.300 | -895.2 | 0.500 | -815.0 | 0.700 | -619.6 | 0.900 | -270.1 |
| 0.150 | -739.4 | 0.350 | -888.4 | 0.550 | -779.3 | 0.750 | -555.3 | 0.950 | -136.4 |
| 0.200 | -832.9 | 0.400 | -873.4 | 0.600 | -737.8 | 0.800 | -476.3 | | |
| $T = 308.15 \text{ K}$ | | | | | | | | | |
| 0.050 | -281.8 | 0.251 | -802.2 | 0.451 | -785.1 | 0.651 | -632.1 | 0.851 | -356.8 |
| 0.100 | -509.0 | 0.301 | -820.4 | 0.501 | -756.3 | 0.701 | -580.6 | 0.900 | -256.6 |
| 0.150 | -663.2 | 0.351 | -817.6 | 0.551 | -722.1 | 0.751 | -515.2 | 0.950 | -134.3 |
| 0.201 | -753.9 | 0.401 | -806.0 | 0.600 | -680.2 | 0.800 | -444.5 | | |
| $T = 323.15 \text{ K}$ | | | | | | | | | |
| 0.050 | -289.1 | 0.250 | -677.2 | 0.450 | -683.3 | 0.650 | -558.0 | 0.850 | -314.0 |
| 0.100 | -492.7 | 0.300 | -696.4 | 0.500 | -658.5 | 0.700 | -509.0 | 0.900 | -225.5 |
| 0.150 | -575.1 | 0.350 | -706.7 | 0.550 | -623.1 | 0.750 | -457.1 | 0.950 | -112.5 |
| 0.200 | -635.8 | 0.400 | -703.0 | 0.600 | -595.6 | 0.800 | -393.7 | | |

Table 11. Excess Enthalpies of Ethanol (1) + Water (2)

| $x_{1,12}$ | $h_{1+2}^E/\text{J}\cdot\text{mol}^{-1}$ | $x_{1,12}$ | $h_{1+2}^E/\text{J}\cdot\text{mol}^{-1}$ | $x_{1,12}$ | $h_{1+2}^E/\text{J}\cdot\text{mol}^{-1}$ | $x_{1,12}$ | $h_{1+2}^E/\text{J}\cdot\text{mol}^{-1}$ | $x_{1,12}$ | $h_{1+2}^E/\text{J}\cdot\text{mol}^{-1}$ |
|------------------------|--|------------|--|------------|--|------------|--|------------|--|
| $T = 285.65 \text{ K}$ | | | | | | | | | |
| 0.025 | -288.5 | 0.150 | -958.5 | 0.275 | -845.2 | 0.540 | -490.5 | 0.780 | -291.6 |
| 0.050 | -534.3 | 0.175 | -958.2 | 0.300 | -806.8 | 0.600 | -430.2 | 0.840 | -242.7 |
| 0.075 | -723.9 | 0.200 | -938.5 | 0.360 | -717.2 | 0.660 | -381.3 | 0.901 | -178.2 |
| 0.100 | -854.9 | 0.225 | -910.7 | 0.420 | -635.7 | 0.720 | -335.4 | 0.959 | -86.0 |
| 0.125 | -929.4 | 0.250 | -879.3 | 0.480 | -559.8 | | | | |
| $T = 308.15 \text{ K}$ | | | | | | | | | |
| 0.050 | -378.8 | 0.251 | -569.2 | 0.451 | -344.3 | 0.651 | -201.2 | 0.801 | -150.8 |
| 0.100 | -585.6 | 0.301 | -512.8 | 0.502 | -298.6 | 0.701 | -182.0 | 0.851 | -137.0 |
| 0.151 | -639.8 | 0.352 | -453.4 | 0.551 | -257.8 | 0.752 | -159.9 | 0.901 | -103.9 |
| 0.201 | -618.2 | 0.401 | -396.8 | 0.602 | -227.2 | | | | |
| $T = 323.15 \text{ K}$ | | | | | | | | | |
| 0.050 | -280.1 | 0.250 | -354.4 | 0.450 | -157.6 | 0.650 | -52.6 | 0.850 | -50.6 |
| 0.100 | -413.0 | 0.300 | -301.8 | 0.500 | -119.7 | 0.700 | -47.3 | 0.901 | -46.7 |
| 0.150 | -434.3 | 0.350 | -250.5 | 0.550 | -89.6 | 0.751 | -46.2 | 0.950 | -25.4 |
| 0.200 | -403.6 | 0.400 | -200.6 | 0.600 | -67.5 | 0.800 | -48.0 | | |
| $T = 338.15 \text{ K}$ | | | | | | | | | |
| 0.025 | -108.8 | 0.150 | -253.3 | 0.350 | -49.0 | 0.550 | 87.7 | 0.750 | 83.1 |
| 0.050 | -188.6 | 0.175 | -232.5 | 0.400 | -2.8 | 0.600 | 99.5 | 0.849 | 42.3 |
| 0.075 | -238.5 | 0.200 | -208.9 | 0.450 | 36.2 | 0.650 | 102.1 | 0.901 | 30.7 |
| 0.100 | -261.9 | 0.250 | -156.9 | 0.500 | 66.7 | 0.700 | 96.8 | 0.950 | 23.7 |
| 0.125 | -263.9 | 0.300 | -100.6 | | | | | | |

LP1200S balance (accuracy, ± 2 mg; precision, ± 1 mg) for degassed water, and a Sartorius MC210P balance (accuracy, ± 10 μg ; precision, ± 20 μg) for the salt. Both components, the salt water as well as the alkanol, are delivered by syringe pumps through thermostated PTFE tubing to the measuring cell where they are mixed. The total flow rate of the mixture is kept constant at 0.08 $\text{mL}\cdot\text{min}^{-1}$. Starting with salt water, an excess enthalpy isotherm is measured by stepwise increase of the alkanol fraction. The maximum alkanol fraction is given by the maximum solubility of the salt in the solvent mixture (Wagner et al., 1998) or, for mixtures with propanols, by avoiding the occurrence of two liquid phases (Gomis et al., 1994, 1997); that is, the resulting mixture is always a homogeneous liquid phase. The mole fraction can be adjusted with a standard deviation < 0.008 . The standard deviation of the excess enthalpy is estimated to be $< 2\%$.

Results and Discussion

The results of the excess enthalpy measurements influenced by salt are given in Tables 2–9. Additionally, the excess enthalpies of the solvents without salt were mea-

sured after changes of alkanol or temperature in order to verify the reliability of the measurements periodically. The results of those measurements are shown in Tables 10–13. The excess enthalpies of the salt-free system ethanol + water at 298.15 K as well as the excess enthalpies of methanol + (water + NaCl) at 298.15 and 323.15 K for salt water concentrations of 5 and 10 wt %, respectively, are given in a previous work (Friese et al., 1998). In Figure 1, the good correspondence with literature regarding the excess enthalpies of salt-free systems is shown exemplarily for ethanol + water isotherms.

By means of Figures 2–5, the influence of salt on the excess enthalpy related to a variation in salt concentration, temperature, alkanol, or salt is illustrated.

In both the figures and tables, the following nomenclature is used to specify mole fractions or mass fractions, respectively: In the system alkanol (1) + water (2) + salt (3), for example, $w_{3,23}$ is the mass fraction of salt in the salt water solution or $x_{1,123}$ is the mole fraction of alkanol in the entire mixture.

An influence of salt on the excess enthalpy of alkanol + water mixtures can be observed already at low salt

Table 12. Excess Enthalpies of 1-Propanol (1) + Water (2)

| $x_{1,12}$ | $h_{1+2}^E/\text{J}\cdot\text{mol}^{-1}$ | $x_{1,12}$ | $h_{1+2}^E/\text{J}\cdot\text{mol}^{-1}$ | $x_{1,12}$ | $h_{1+2}^E/\text{J}\cdot\text{mol}^{-1}$ | $x_{1,12}$ | $h_{1+2}^E/\text{J}\cdot\text{mol}^{-1}$ | $x_{1,12}$ | $h_{1+2}^E/\text{J}\cdot\text{mol}^{-1}$ |
|------------------------|--|------------|--|------------|--|------------|--|------------|--|
| $T = 285.65 \text{ K}$ | | | | | | | | | |
| 0.060 | -536.3 | 0.140 | -484.3 | 0.260 | -299.3 | 0.500 | -1.6 | 0.740 | 81.2 |
| 0.080 | -557.7 | 0.160 | -451.8 | 0.320 | -214.7 | 0.559 | 44.6 | 0.860 | 31.4 |
| 0.100 | -539.9 | 0.180 | -421.8 | 0.380 | -136.8 | 0.620 | 76.7 | 0.920 | 0.7 |
| 0.120 | -513.5 | 0.200 | -391.3 | 0.439 | -65.6 | 0.680 | 82.9 | | |
| $T = 298.15 \text{ K}$ | | | | | | | | | |
| 0.030 | -261.2 | 0.240 | -157.4 | 0.450 | 97.2 | 0.630 | 200.0 | 0.810 | 148.6 |
| 0.060 | -376.8 | 0.270 | -116.3 | 0.480 | 123.1 | 0.660 | 202.8 | 0.841 | 113.2 |
| 0.090 | -366.7 | 0.300 | -76.5 | 0.510 | 147.0 | 0.690 | 199.9 | 0.870 | 92.5 |
| 0.120 | -328.8 | 0.330 | -36.9 | 0.540 | 165.7 | 0.719 | 191.7 | 0.900 | 65.8 |
| 0.150 | -286.1 | 0.360 | 1.0 | 0.571 | 182.6 | 0.749 | 179.3 | 0.930 | 43.2 |
| 0.180 | -242.1 | 0.390 | 34.5 | 0.600 | 194.3 | 0.781 | 162.1 | 0.960 | 29.0 |
| 0.210 | -200.2 | 0.420 | 68.1 | | | | | | |
| $T = 308.15 \text{ K}$ | | | | | | | | | |
| 0.030 | -201.8 | 0.241 | -18.7 | 0.451 | 232.7 | 0.631 | 315.3 | 0.810 | 229.6 |
| 0.060 | -263.4 | 0.271 | 23.4 | 0.481 | 258.2 | 0.661 | 312.8 | 0.841 | 184.6 |
| 0.090 | -237.5 | 0.301 | 64.8 | 0.511 | 277.5 | 0.691 | 304.0 | 0.870 | 149.5 |
| 0.120 | -195.2 | 0.331 | 103.0 | 0.541 | 294.8 | 0.720 | 289.8 | 0.901 | 110.5 |
| 0.150 | -150.2 | 0.361 | 140.8 | 0.571 | 306.8 | 0.750 | 270.7 | 0.931 | 74.8 |
| 0.181 | -105.6 | 0.391 | 173.8 | 0.601 | 313.6 | 0.782 | 242.1 | 0.960 | 50.5 |
| 0.211 | -61.6 | 0.421 | 204.3 | | | | | | |
| $T = 323.15 \text{ K}$ | | | | | | | | | |
| 0.030 | -114.2 | 0.240 | 181.9 | 0.450 | 434.1 | 0.630 | 486.1 | 0.809 | 328.0 |
| 0.060 | -115.8 | 0.270 | 226.4 | 0.480 | 455.3 | 0.660 | 476.2 | 0.840 | 286.8 |
| 0.090 | -69.5 | 0.300 | 267.9 | 0.510 | 472.3 | 0.689 | 457.9 | 0.870 | 234.9 |
| 0.120 | -16.2 | 0.330 | 307.7 | 0.540 | 484.8 | 0.720 | 434.3 | 0.901 | 182.8 |
| 0.150 | 34.7 | 0.360 | 344.5 | 0.569 | 490.3 | 0.750 | 406.1 | 0.931 | 133.1 |
| 0.180 | 85.2 | 0.390 | 379.2 | 0.600 | 491.5 | 0.780 | 369.7 | 0.960 | 78.2 |
| 0.210 | 134.7 | 0.420 | 408.6 | | | | | | |
| $T = 338.15 \text{ K}$ | | | | | | | | | |
| 0.015 | -32.1 | 0.090 | 70.6 | 0.299 | 461.8 | 0.549 | 671.1 | 0.800 | 475.5 |
| 0.030 | -39.6 | 0.105 | 104.4 | 0.349 | 530.1 | 0.599 | 658.3 | 0.851 | 359.1 |
| 0.045 | -25.9 | 0.150 | 199.2 | 0.400 | 586.1 | 0.649 | 647.0 | 0.901 | 252.4 |
| 0.060 | 3.7 | 0.200 | 296.0 | 0.450 | 627.9 | 0.699 | 585.9 | 0.951 | 121.5 |
| 0.075 | 37.3 | 0.250 | 383.6 | 0.499 | 654.1 | 0.750 | 542.1 | | |
| $T = 353.15 \text{ K}$ | | | | | | | | | |
| 0.050 | 74.6 | 0.250 | 560.2 | 0.450 | 820.7 | 0.650 | 800.6 | 0.851 | 433.2 |
| 0.100 | 219.9 | 0.300 | 645.7 | 0.500 | 835.5 | 0.700 | 740.8 | 0.901 | 301.9 |
| 0.150 | 347.5 | 0.350 | 716.4 | 0.550 | 845.7 | 0.750 | 646.9 | 0.951 | 150.8 |
| 0.200 | 461.6 | 0.400 | 784.1 | 0.600 | 837.6 | 0.800 | 556.1 | | |

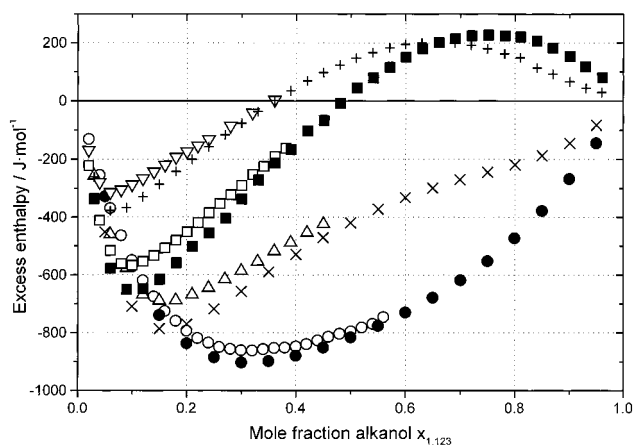


Figure 4. Effect of KCl on the excess enthalpy of different alkanols (1) + (water (2) + KCl (3)) at 298.15 K and $w_{3,23}(\text{KCl}) = 5.00 \text{ wt } \%$. Methanol: (●) salt-free; (○) with salt. Ethanol: (×) salt-free; (△) with salt. 1-Propanol: (+) salt-free; (▽) with salt. 2-Propanol: (■) salt-free; (□) with salt.

concentrations ($w_{3,23} = 1.00 \text{ wt } \%$). In Figure 2 it is shown that the difference with regard to the salt-free system becomes more significant if the salt concentration is increased. For the example given in Figure 2, this means that the excess enthalpy of a mixture of an aqueous solution containing 7.50 wt % sodium chloride with 2-pro-

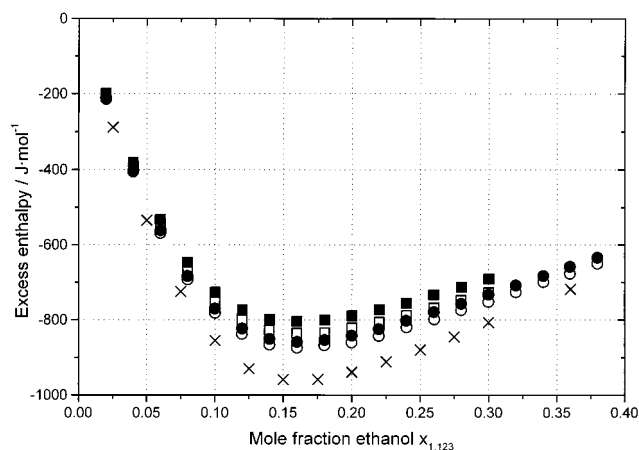


Figure 5. Effect of salt (3) (NaCl or KCl) on the excess enthalpy of ethanol (1) + water (2) at 285.65 K for 1.2558 mol % salt in water [(○) 5.00 wt % $w_{3,23}(\text{KCl})$; (●) 3.96 wt % $w_{3,23}(\text{NaCl})$] and 1.9216 mol % salt in water [(□) 7.50 wt % $w_{3,23}(\text{KCl})$; (■) 5.98 wt % $w_{3,23}(\text{NaCl})$]; (×) salt-free system.

panol at 308.15 K is finally reduced by about one third compared to that for the salt-free system.

The shift to less exothermic excess enthalpies due to salt as observed in Figure 2 cannot be generalized. The excess enthalpy isotherms of the salt-free system 1-propanol + water turn from predominantly exothermic values at

Table 13. Excess Enthalpies of 2-Propanol (1) + Water (2)

| $x_{1,12}$ | $h_{1+2}^E/\text{J}\cdot\text{mol}^{-1}$ | $x_{1,12}$ | $h_{1+2}^E/\text{J}\cdot\text{mol}^{-1}$ | $x_{1,12}$ | $h_{1+2}^E/\text{J}\cdot\text{mol}^{-1}$ | $x_{1,12}$ | $h_{1+2}^E/\text{J}\cdot\text{mol}^{-1}$ | $x_{1,12}$ | $h_{1+2}^E/\text{J}\cdot\text{mol}^{-1}$ |
|------------------------|--|------------|--|------------|--|------------|--|------------|--|
| $T = 285.65 \text{ K}$ | | | | | | | | | |
| 0.020 | -303.0 | 0.120 | -859.7 | 0.260 | -581.7 | 0.500 | -115.9 | 0.740 | 128.5 |
| 0.040 | -557.6 | 0.140 | -829.5 | 0.320 | -456.4 | 0.560 | -25.5 | 0.800 | 121.3 |
| 0.060 | -744.5 | 0.160 | -793.8 | 0.380 | -333.2 | 0.620 | 46.3 | 0.860 | 99.3 |
| 0.080 | -845.0 | 0.180 | -753.5 | 0.440 | -219.0 | 0.679 | 107.5 | 0.920 | 50.6 |
| 0.100 | -871.2 | 0.200 | -711.5 | | | | | | |
| $T = 298.15 \text{ K}$ | | | | | | | | | |
| 0.030 | -336.5 | 0.241 | -455.2 | 0.451 | -67.4 | 0.631 | 180.2 | 0.811 | 220.7 |
| 0.060 | -577.6 | 0.271 | -403.6 | 0.481 | -8.0 | 0.661 | 200.5 | 0.840 | 206.5 |
| 0.091 | -650.9 | 0.301 | -337.3 | 0.511 | 43.7 | 0.691 | 214.3 | 0.870 | 182.5 |
| 0.121 | -647.7 | 0.331 | -271.6 | 0.541 | 78.4 | 0.721 | 224.4 | 0.901 | 152.6 |
| 0.151 | -615.9 | 0.362 | -213.8 | 0.571 | 115.4 | 0.751 | 226.5 | 0.929 | 117.5 |
| 0.181 | -558.3 | 0.391 | -167.9 | 0.601 | 150.8 | 0.782 | 224.2 | 0.961 | 80.1 |
| 0.211 | -500.8 | 0.421 | -103.2 | | | | | | |
| $T = 308.15 \text{ K}$ | | | | | | | | | |
| 0.030 | -298.8 | 0.210 | -359.0 | 0.390 | -34.9 | 0.570 | 213.7 | 0.749 | 296.1 |
| 0.060 | -465.5 | 0.240 | -304.9 | 0.420 | 13.9 | 0.600 | 245.0 | 0.780 | 285.9 |
| 0.090 | -516.9 | 0.270 | -250.2 | 0.450 | 61.5 | 0.629 | 270.2 | 0.870 | 215.2 |
| 0.120 | -498.5 | 0.300 | -194.8 | 0.480 | 104.7 | 0.660 | 283.8 | 0.901 | 175.2 |
| 0.150 | -460.1 | 0.330 | -141.7 | 0.510 | 146.2 | 0.690 | 294.7 | 0.929 | 136.3 |
| 0.180 | -411.5 | 0.360 | -87.4 | 0.540 | 183.6 | 0.721 | 296.7 | 0.959 | 99.7 |
| $T = 323.15 \text{ K}$ | | | | | | | | | |
| 0.060 | -298.3 | 0.270 | -41.2 | 0.450 | 240.7 | 0.629 | 402.2 | 0.810 | 361.5 |
| 0.090 | -301.2 | 0.300 | 10.5 | 0.480 | 279.7 | 0.660 | 411.0 | 0.840 | 316.0 |
| 0.120 | -286.6 | 0.330 | 59.6 | 0.509 | 313.4 | 0.690 | 412.8 | 0.870 | 275.6 |
| 0.150 | -244.2 | 0.360 | 108.5 | 0.540 | 342.6 | 0.721 | 407.3 | 0.901 | 225.6 |
| 0.180 | -196.6 | 0.390 | 156.1 | 0.570 | 368.4 | 0.749 | 396.4 | 0.929 | 178.2 |
| 0.210 | -146.0 | 0.420 | 201.1 | 0.600 | 388.5 | 0.780 | 376.7 | 0.959 | 116.6 |
| 0.240 | -93.8 | | | | | | | | |
| $T = 338.15 \text{ K}$ | | | | | | | | | |
| 0.015 | -81.1 | 0.090 | -162.8 | 0.300 | 180.6 | 0.549 | 481.0 | 0.800 | 417.5 |
| 0.030 | -138.9 | 0.105 | -143.5 | 0.350 | 261.8 | 0.600 | 501.4 | 0.850 | 357.5 |
| 0.045 | -174.0 | 0.150 | -72.5 | 0.399 | 330.5 | 0.650 | 510.7 | 0.901 | 271.7 |
| 0.060 | -183.1 | 0.200 | 11.7 | 0.449 | 392.7 | 0.699 | 498.0 | 0.950 | 153.4 |
| 0.075 | -177.4 | 0.250 | 97.5 | 0.499 | 443.4 | 0.749 | 464.8 | | |

285.65 K to endothermic values over the whole mole fraction range at 353.15 K (see Figure 3; for better distinctness, the measured values are connected by lines). Along with this change in sign of the excess enthalpy with increasing temperature, the shift to less exothermic excess enthalpies under the influence of salt decreases and, for temperatures greater than 323.15 K, salt-free and salt-influenced isotherms intersect; that is, a shift to less endothermic excess enthalpies can be observed in relation to the salt-free isotherm if the alkanol mole fraction exceeds that at the point of intersection. With increasing temperature, this point is moved to lower alkanol mole fractions, although the total salt concentration $w_{3,123}$ rises with decreasing alkanol mole fractions. Regarding the 353.15 K isotherms, the behavior of the excess enthalpy in the alkanol mole fraction range from about 0.06 to 0.2 is hardly affected by the addition of salt even though the salt concentration in the mixture is relatively high.

In Figure 4, the influence of salt at the constant salt-water concentration $w_{3,23}(\text{KCl}) = 5.00 \text{ wt } \%$ and constant temperature is displayed for different alkanols. The difference with regard to the salt-free excess enthalpy isotherm due to the addition of salt is significantly smaller for mixtures with methanol, both relatively and absolutely, than for the other alkanols. The greatest effect can be observed at the minimum of the salt-free isotherm of each system. While in mixtures of ethanol, 1-propanol, or 2-propanol with water the addition of KCl causes a reduction of the exothermic effect of 13–16% at the isotherm's minimum, in mixtures with methanol only a reduction of about 5% can be achieved; that is, the interaction between methanol and water is much less affected by the addition of salt. Compared to the other alkanols, methanol is smaller

and more polar. Therefore, it is easier for a methanol molecule to interact with water molecules in the solvation shell of an ion or to replace it.

The influence of different kinds of salt on the excess enthalpy of alkanol + water mixtures can be shown by means of Figure 5. In this work sodium chloride and potassium chloride were investigated. Both are 1,1-electrolytes with chloride as the anion. Therefore, the differences in the salt influence on the excess enthalpy of the solvent mixture are likely to result from the type of cation. Generally speaking, for alkali halides, cations not anions are responsible for the observed shift in phase equilibria and in excess enthalpies because they are smaller and consequently carry a higher surface charge. Provided that the salt is completely dissociated, the influence of sodium and potassium ions can be compared if the same number of chloride moles is dissolved in the solvent mixture. The assumption of complete dissociation is at least valid at low mole fractions of alkanol. In Figure 5, two concentrations (1.2558 and 1.9216 mol % salt in water) were investigated for both sodium and potassium chloride. The excess enthalpy isotherm of ethanol + water at 285.65 K is slightly more affected by sodium chloride than by potassium chloride. This observation can also be attributed to the size of the cation because sodium ion is the smaller one with a higher surface charge.

The excess enthalpies h_{1+23}^E are measured by mixing alkanol with a salt water solution of constant mass fraction $w_{3,23}$, that is alkanol (1) + (water (2) + salt (3)). The total excess enthalpy h_{123}^E refers to a mixture of pure alkanol (1) + pure water (2) + salt at infinite dilution (3). It can be calculated according to

$$\frac{H_{123}^E}{n_1 + n_2 + n_3} = \frac{H_{1+23}^E}{n_1 + n_2 + n_3} + \frac{n_2 + n_3}{n_1 + n_2 + n_3} \cdot \frac{H_{23}^E}{n_2 + n_3} \quad (1)$$

$$h_{123}^E = h_{1+23}^E + (1 - x_{1,123}) \cdot h_{23}^E \quad (2)$$

In eq 2, the excess enthalpy h_{23}^E of a mixture of pure water with salt at infinite dilution cannot be measured directly, but it is part of the solution process of solid salt in water. In this experiment, the integral enthalpy of solution $H_{23}^{\text{sol,int}}$ is experimentally accessible as a function of temperature and final salt concentration for each salt. The quantity consists of an enthalpy $H_{23}^{\text{sol},\infty}$ describing the transformation of the salt from the solid state to infinite dilution and of the unknown excess enthalpy H_{23}^E for mixing water with infinitely diluted salt.

$$H_{23}^{\text{sol,int}} = H_{23}^E + H_{23}^{\text{sol},\infty} \quad (3)$$

After introducing specific variables, eq 3 yields the results

$$\frac{H_{23}^E}{n_2 + n_3} = \frac{n_3}{n_2 + n_3} \left(\frac{H_{23}^{\text{sol,int}}}{n_3} - \frac{H_{23}^{\text{sol},\infty}}{n_3} \right) \quad (4)$$

$$h_{23}^E = x_{3,23} (h_{23}^{\text{sol,int}} - h_{23}^{\text{sol},\infty}) \quad (5)$$

$$\text{with } h_{23}^{\text{sol},\infty} = \lim_{x_{3,23} \rightarrow 0} h_{23}^{\text{sol,int}} \quad (6)$$

If enthalpies of solution for salt in water are available as a function of temperature and salt concentration, excess enthalpies h_{123}^E can be calculated by means of eq 2 using the results for h_{1+23}^E given in this article.

Conclusion

The influence of salt on the excess enthalpies of alkanol + water mixtures was investigated by flow-calorimetric measurements. Results of h_{1+23}^E , that is the excess enthalpies of a mixture of alkanol (1) + salt water (23), are given for 117 isotherms along with 19 excess enthalpy isotherms for the salt-free binaries. Methanol, ethanol, 1-propanol, and 2-propanol were mixed with aqueous solutions of both sodium chloride and potassium chloride at different salt water mass fractions $w_{3,23}$. On the basis of the experimental results for h_{1+23}^E and considering different reference states, an equation is proposed for the calculation of excess enthalpies of pure alkanol + pure water + salt at infinite

dilution, h_{123}^E . The data presented in this work contain excess enthalpies for up to six temperatures over a broad temperature range from 285.65 to 353.15 K. Using the Gibbs–Helmholtz equation, parameters for g^E models can be fitted not only to VLE data but also to excess enthalpy data under the influence of salt in order to yield better thermodynamic consistency.

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