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# Experimental Investigation of the Influence of NaCl on the Vapor−Liquid Equilibrium of $CH_3OH + H_2O$

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New experimental results for the vapor−liquid equilibrium of the system sodium chloride + methanol + water are presented at (salt-free) solvent mixture methanol mole fractions from about 0.03 to 0.54, at sodium chloride molalities up to about 5.4 mol·kg$^{-1}$ of the solvent mixture (but always below the solubility limit of the salt), at temperatures from about (313 to 397) K, and at total pressures from about (10 to 500) kPa.

## Introduction

Models for describing the thermodynamic properties of salt-containing (aqueous as well as nonaqueous) mixed solvents (for example, the vapor−liquid equilibrium and salt solubilities) are required for the adequate design and optimization of many separation processes. Many such models are reported in the literature. (See, for example, the review by Anderko et al.[1]) To enhance their reliability, as well as to develop new models, it is desirable to extend the experimental database on which these models are founded. For most systems, that data is very scarce and restricted to very narrow ranges (e.g., in temperature and pressure (around 298 K and/or 0.1 MPa)).

In this publication, new experimental data for the influence of a single salt (sodium chloride) on the vapor−liquid equilibrium of an aqueous organic mixture (water + methanol) are presented for temperatures of about (314.6, 353.0, and 395.7) K. The salt-free mole fraction of methanol in the solvent mixture, the sodium chloride molality, and the total pressure range up to about 0.54, 5.4 mol·kg$^{-1}$ of the solvent mixture (always below the solubility limit of the salt), and 0.5 MPa, respectively.

## Experimental Section

***Apparatus.*** A special thin-film evaporator apparatus is used for the vapor−liquid equilibrium experiments. That apparatus has been used and described before (Hasse[2] and Albert et al.[3]); therefore, only an outline is repeated here. The thin-film evaporator consists of a rotating coil (made up of glass fiber-reinforced Teflon) inside a stainless steel tube. That coil spreads the thermostated liquid feed on the inner surface of the tube. The tube is heated from the outside by a liquid that is thermostated to a few kelvins above the temperature of the liquid feed. The heating results in a partial evaporation of the liquid feed at nearly constant pressure. That pressure is supplied by a back-pressure regulator. For measurements above ambient pressure, the evaporator chamber is pressurized from a storage tank (filled with nitrogen gas). For measurements at lower pressures, the storage tank is replaced by a buffer container that is connected to a vacuum pump and a nitrogen flask. After passing the heated section of the tube, the coexisting and equilibrated phases are separated. The liquid phase is subcooled, and the gaseous phase is completely condensed. Both are separately collected in vials.

The temperature is measured (with an accuracy of ±0.1 K) with a calibrated platinum resistance thermometer. The pressure is measured with two absolute pressure transducers that ranged up to (0.25 and 0.6) MPa (WIKA, Klingenberg, Germany) with an accuracy of ±0.1% of each transducer's range. Before and after a series of measurements, the transducers were calibrated against a high-precision pressure gauge (Desgranges & Huot, Aubervilliers, France) for pressures above ambient pressure and against a mercury manometer for pressures below ambient pressure. The salt molality in the liquid phase is determined gravimetrically by slowly heating the sample in an oven and thereby completely evaporating the solvent. Each sample is analyzed three times, and relative deviations between the single results are below 2% in most cases. The (salt-free) composition of the coexisting phases is determined by gas chromatography. Commercial GC equipment is used (Hewlett-Packard: GC model HP-5890, autosampler model HP-7673; column packing: Porapak T from Alltech, Unterhaching, Germany; thermal conductivity detector). Generally, for calibration (for analysis), each sample is analyzed at least five (three) times. Absolute deviations between the single results in the (salt-free) molar fraction of methanol were below ±0.007 mol/mol.

***Substances and Sample Pretreatment.*** Methanol (≥99.8 mol %, Honeywell Specialty Chemicals Seelze, Seelze, Germany) was degassed under vacuum. Deionized water was degassed by vacuum distillation. Sodium chloride (≥99.5 mass %) was purchased from Merck GmbH, Darmstadt, Germany, and was degassed and dried under vacuum. The liquid feed mixtures were gravimetrically prepared.

## Experimental Results

The vapor−liquid equilibrium of the system NaCl + $CH_3OH + H_2O$ was investigated at temperatures of about (314.6, 353.0, and 395.7) K. The liquid feed solutions contained up to about 54 mol % methanol in the salt-free solvent mixture. The maximum salt concentration was 5.4 mol·kg$^{-1}$ of the solvent mixture (but it was always below the solubility limit of the salt). The total pressure was

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**Table 1. Experimental and Calculation Results[10] for the Vapor−Liquid Equilibrium of the System ($CH_3OH + H_2O + NaCl$)[a]**

| $\frac{T}{K}$ | $\tilde{x}_M$ | $\frac{\bar{m}_{NaCl}}{mol \cdot kg^{-1}}$ | $y_{M,exptl}$ | $y_{M,calcd}$ | $\frac{p_{exptl}}{kPa}$ | $\frac{p_{calcd}}{kPa}$ |
|---|---|---|---|---|---|---|
| 316.4 | 0.0368 | 0 | 0.212 | 0.240 | 10.00 | 11.11 |
| 315.3 | 0.0314 | 1.42 | 0.236 | 0.257 | 10.00 | 10.18 |
| 315.5 | 0.0325 | 2.78 | 0.278 | 0.313 | 10.00 | 10.42 |
| 315.6 | 0.0324 | 4.14 | 0.319 | 0.365 | 10.00 | 10.54 |
| 315.3 | 0.0312 | 5.38 | 0.352 | 0.402 | 10.00 | 10.25 |
| 315.8 | 0.0762 | 0 | 0.383 | 0.391 | 13.00 | 12.93 |
| 315.3 | 0.0776 | 1.10 | 0.425 | 0.439 | 13.00 | 12.91 |
| 314.8 | 0.0784 | 2.16 | 0.469 | 0.483 | 13.00 | 12.91 |
| 314.7 | 0.0857 | 3.26 | 0.506 | 0.545 | 13.00 | 13.56 |
| 314.5 | 0.0763 | 4.35 | 0.539 | 0.560 | 13.00 | 13.14 |
| 314.1 | 0.216 | 0 | 0.631 | 0.640 | 18.00 | 17.44 |
| 313.6 | 0.221 | 0.536 | 0.657 | 0.664 | 18.00 | 17.43 |
| 313.6 | 0.223 | 1.07 | 0.674 | 0.683 | 18.00 | 17.73 |
| 313.3 | 0.213 | 1.65 | 0.695 | 0.691 | 18.00 | 17.34 |
| 313.0 | 0.207 | 2.21 | 0.703 | 0.701 | 18.00 | 17.10 |
| 314.6 | 0.466 | 0 | 0.799 | 0.807 | 25.00 | 25.00 |
| 314.4 | 0.466 | 0.195 | 0.807 | 0.812 | 25.00 | 24.92 |
| 314.3 | 0.470 | 0.389 | 0.815 | 0.819 | 25.00 | 24.96 |
| 314.3 | 0.463 | 0.577 | 0.809 | 0.820 | 25.00 | 24.81 |
| 314.3 | 0.463 | 0.775 | 0.816 | 0.825 | 25.00 | 24.88 |
| 353.1 | 0.0317 | 0 | 0.222 | 0.196 | 58.54 | 56.93 |
| 353.9 | 0.0395 | 0.552 | 0.246 | 0.248 | 60.94 | 61.23 |
| 352.7 | 0.0404 | 1.13 | 0.256 | 0.272 | 58.24 | 58.70 |
| 352.3 | 0.0328 | 2.21 | 0.275 | 0.269 | 55.54 | 55.22 |
| 353.9 | 0.0282 | 5.01 | 0.328 | 0.333 | 55.94 | 56.02 |
| 353.2 | 0.0780 | 0 | 0.376 | 0.367 | 70.66 | 69.58 |
| 352.6 | 0.0849 | 0.455 | 0.395 | 0.405 | 70.36 | 70.21 |
| 353.1 | 0.0892 | 1.67 | 0.429 | 0.461 | 71.06 | 74.01 |
| 353.9 | 0.0906 | 2.21 | 0.434 | 0.484 | 73.87 | 77.17 |
| 354.3 | 0.0850 | 3.31 | 0.473 | 0.509 | 74.47 | 77.87 |
| 352.8 | 0.247 | 0 | 0.617 | 0.633 | 97.72 | 100.6 |
| 352.6 | 0.237 | 0.597 | 0.642 | 0.646 | 97.72 | 99.93 |
| 352.7 | 0.246 | 1.20 | 0.669 | 0.674 | 98.52 | 102.6 |
| 352.5 | 0.224 | 1.73 | 0.647 | 0.670 | 98.32 | 99.43 |
| 352.5 | 0.217 | 2.30 | 0.651 | 0.681 | 102.0 | 99.18 |
| 352.9 | 0.493 | 0 | 0.767 | 0.783 | 126.4 | 130.6 |
| 352.9 | 0.509 | 0.203 | 0.760 | 0.797 | 126.3 | 132.2 |
| 352.8 | 0.488 | 0.394 | 0.760 | 0.793 | 126.3 | 130.4 |
| 352.8 | 0.527 | 0.597 | 0.772 | 0.815 | 126.3 | 134.2 |
| 352.9 | 0.512 | 0.778 | 0.786 | 0.814 | 127.2 | 133.5 |
| 393.9 | 0.0357 | 0 | 0.217 | 0.188 | 250.2 | 242.8 |
| 396.2 | 0.0384 | 1.39 | 0.242 | 0.236 | 262.7 | 261.2 |
| 396.2 | 0.0347 | 2.76 | 0.204 | 0.257 | 252.8 | 253.1 |
| 396.6 | 0.0339 | 4.10 | 0.293 | 0.292 | 250.0 | 251.4 |
| 396.3 | 0.0323 | 4.84 | 0.299 | 0.303 | 245.6 | 244.3 |
| 396.4 | 0.0960 | 0 | 0.351 | 0.372 | 313.2 | 320.7 |
| 395.9 | 0.0929 | 0.792 | 0.379 | 0.395 | 310.9 | 315.7 |
| 396.5 | 0.0936 | 1.81 | 0.385 | 0.430 | 314.9 | 323.7 |
| 396.9 | 0.0870 | 3.28 | 0.445 | 0.461 | 316.8 | 321.4 |
| 396.9 | 0.0861 | 4.41 | 0.483 | 0.492 | 312.0 | 320.5 |
| 396.8 | 0.191 | 0 | 0.512 | 0.528 | 390.6 | 395.1 |
| 395.2 | 0.261 | 0.865 | 0.647 | 0.634 | 404.0 | 423.4 |
| 395.1 | 0.273 | 1.10 | 0.651 | 0.651 | 402.2 | 429.6 |
| 395.0 | 0.235 | 1.74 | 0.644 | 0.638 | 402.3 | 411.5 |
| 395.2 | 0.219 | 2.26 | 0.617 | 0.637 | 404.5 | 405.2 |
| 394.3 | 0.492 | 0 | 0.728 | 0.748 | 485.6 | 499.3 |
| 395.0 | 0.492 | 0.199 | 0.738 | 0.755 | 498.4 | 510.7 |
| 395.0 | 0.535 | 0.392 | 0.730 | 0.781 | 498.3 | 524.8 |
| 395.0 | 0.517 | 0.590 | 0.740 | 0.778 | 498.4 | 519.8 |
| 395.0 | 0.520 | 0.799 | 0.742 | 0.785 | 498.5 | 521.1 |

[a] Calculation for preset temperature and liquid-phase composition.

below 0.5 MPa. The experimental results are given in Table 1.

The experimental results for the composition of the gaseous phase are shown as full symbols and plotted versus the molality of the salt (at about constant temperature and at about constant salt-free liquid mole fraction of methanol) in Figures 1 to 3. As expected, the concentration of methanol in the gaseous phase increases with increasing salt molality (i.e., methanol is "salted-out", whereas water is "salted-in"). This behavior is often attributed to the hydration of sodium chloride in the liquid phase, which "reduces" the concentration of "free" water.

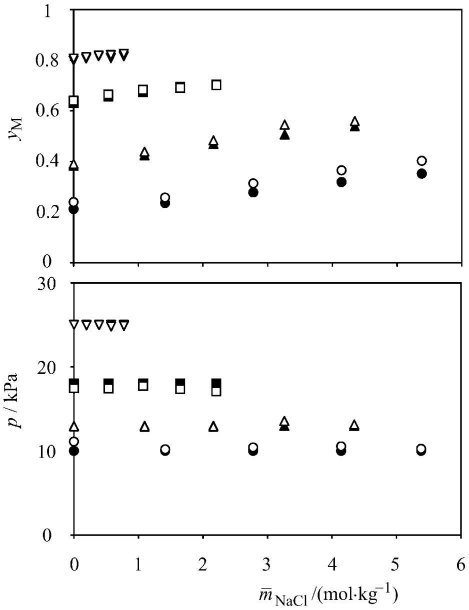

**Figure 1.** Mole fraction of methanol in the vapor phase (upper diagram) and total pressure (lower diagram) versus the molality of NaCl in aqueous solutions of methanol at $T \approx 314.6$ K (solid symbols: experimental data, this work; open symbols: calculation results, Pérez-Salado Kamps[10]): ● and ○, $\tilde{x}_M \approx 0.0328$; ▲ and △, $\tilde{x}_M \approx 0.0789$; ■ and □, $\tilde{x}_M \approx 0.216$; ▼ and ▽, $\tilde{x}_M \approx 0.466$.

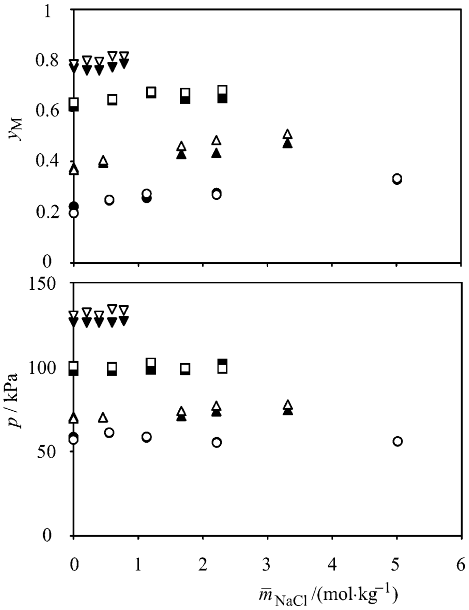

**Figure 2.** Mole fraction of methanol in the vapor phase (upper diagram) and total pressure (lower diagram) versus the molality of NaCl in aqueous solutions of methanol at $T \approx 353.0$ K (solid symbols: experimental data, this work; open symbols: calculation results, Pérez-Salado Kamps[10]): ● and ○, $\tilde{x}_M \approx 0.0345$; ▲ and △, $\tilde{x}_M \approx 0.0855$; ■ and □, $\tilde{x}_M \approx 0.234$; ▼ and ▽, $\tilde{x}_M \approx 0.506$.

## Modeling Results and Comparison with Literature Data

Some experimental information on the vapor−liquid equilibrium of the ternary system (methanol + water + NaCl) is available in the literature.[4−9] That information

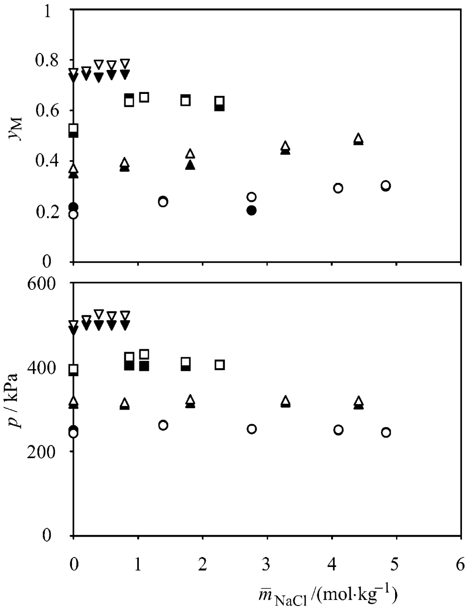

**Figure 3.** Mole fraction of methanol in the vapor phase (upper diagram) and total pressure (lower diagram) versus the molality of NaCl in aqueous solutions of methanol at $T \approx 395.7$ K (solid symbols: experimental data, this work; open symbols: calculation results, Pérez-Salado Kamps[10]): ● and ○, $\tilde{x}_M \approx 0.0350$; ▲ and △, $\tilde{x}_M \approx 0.0911$; ■ and □, $\tilde{x}_M \approx 0.236$; ▼ and ▽, $\tilde{x}_M \approx 0.511$.

contains altogether 91 experimental data points covering a temperature range from (298 to 382) K at pressures up to about 101 kPa and sodium chloride concentrations up to the solubility limit.

A model for describing the vapor−liquid equilibrium of salt-containing mixed solvent systems has recently been presented by Pérez-Salado Kamps.[10] That model has been applied for the simultaneous description of experimental data for the vapor−liquid-phase equilibrium of the system (methanol + water + NaCl) (from refs 4 to 9 and the present work), the mean ionic activity coefficient of sodium chloride,[11−17] and the solubility of sodium chloride in aqueous solutions of methanol.[4,18−20] A comparison between the experimental database and the calculations has been given by Pérez-Salado Kamps.[10] Therefore, the comparison between experimental results and calculation results is restricted here to the new experimental VLE data of the present work (Table 1). Figures 1 through 3 also show that comparison.

For the salt-free system, the Gibbs excess energy equation applied by that model reduces to the UNIQUAC equation.[21] The binary UNIQUAC interaction parameters were adjusted to vapor−liquid equilibrium data (for temperatures from 298 K to 423 K) found in the literature (cf. ref 10). The average (and maximum) relative deviations between that literature data and calculation results for the pressure and the mole fraction of methanol in the vapor phase (for preset temperature and liquid-phase composition) amount to ±1.6% (16%) and ±2.5% (25.4%), respectively. Those deviations mainly result from the scattering of the experimental data. The average (and maximum) relative deviations between the new experimental data (for the salt-free system) and calculation results for the pressure and the mole fraction of methanol in the vapor phase (for preset temperature and liquid-phase composition) amount to ±2.9% (11.1%) and ±5.1% (13.3%), respectively. When the pressure is preset (instead of the temperature), the average (and maximum) deviation in the temperature amount to ±0.7 K (2 K), and the average (and maximum) relative deviation in the mole fraction of methanol in the vapor amount to ±5.2% (13.6%).

**Table 2. Comparison of the New Experimental Results for the Vapor−Liquid Equilibrium of the System ($CH_3OH$ + $H_2O$ + NaCl) with Calculation Results[10] [a,b]**

| ~$T$/K | $\tilde{x}_M$ | $100\cdot\lvert\overline{\Delta y_M}/y_{M,exptl}\rvert^c$ | $100\lvert\overline{\Delta p}/p_{exptl}\rvert^c$ | $\lvert\overline{\Delta T}/K\rvert^d$ |
|---|---|---|---|---|
| 314.6 | 0.0328 | 12.7 | 3.5 | 0.7 |
| | 0.0789 | 4.5 | 1.7 | 0.3 |
| | 0.216 | 0.8 | 3.3 | 0.7 |
| | 0.466 | 0.9 | 0.4 | 0.1 |
| 353.0 | 0.0345 | 2.8 | 0.5 | 0.1 |
| | 0.0855 | 7.3 | 3.4 | 0.8 |
| | 0.234 | 2.4 | 2.6 | 0.7 |
| | 0.506 | 4.6 | 4.8 | 1.3 |
| 395.7 | 0.0350 | 7.6 | 0.4 | 0.1 |
| | 0.0911 | 5.4 | 2.1 | 0.7 |
| | 0.236 | 1.6 | 3.5 | 1.2 |
| | 0.511 | 5.0 | 4.2 | 1.4 |

[a]
$$\left|\frac{\overline{\Delta Z}}{Z_{exptl}}\right| = \frac{1}{N}\sum_{i=1}^{N}\left|\frac{Z_{i,exptl} - Z_{i,calcd}}{Z_{i,exptl}}\right|$$

[b]
$$\left|\overline{\Delta Z}\right| = \frac{1}{N}\sum_{i=1}^{N}\left|Z_{i,exptl} - Z_{i,calcd}\right|$$

[c] $y_M$ and $p$ calculated at experimental temperature and liquid-phase composition. [d] $T$ calculated at experimental pressure and liquid-phase composition.

For the salt-containing system, the average (and maximum) relative deviations between experimental and calculation results for the pressure and the mole fraction of methanol in the vapor phase (for preset temperature and liquid-phase composition) amount to ±2.5% (6.8%) and ±4.6% (26%), respectively. If the pressure is preset instead of the temperature, then the average (and maximum) deviation in the temperature amount to ±0.7 K (2.3 K), and the average (and maximum) relative deviation in the mole fraction of methanol in the vapor amount to ±4.7% (25.9%). These deviations are similar to those for the salt-free system.

## Conclusions

New experimental data on the vapor−liquid equilibrium of the system methanol + water + sodium chloride, measured with a thin-film evaporator technique at temperatures (and pressures) ranging from about (313 to 397) K {and (10 to 500) kPa} and for sodium chloride concentrations below the solubility limit are presented. As expected, by increasing the concentration of the salt in the liquid (at constant temperature and at constant salt-free concentration of methanol in that liquid), an increase in the concentration of methanol in the gaseous phase is experimentally observed (i.e., methanol is "salted-out", and water is "salted-in").

## Nomenclature

| | |
|---|---|
| exptl | experimental |
| calcd | calculated |
| $\bar{m}_{NaCl}$ | (stoichiometric) molality of NaCl in the liquid phase in moles per kilogram of the (water + methanol) solvent mixture |
| $N$ | number of experimental points |
| $p$ | pressure |
| $T$ | absolute temperature |
| $\tilde{x}_M$ | mole fraction of methanol in the salt-free liquid phase (i.e., in the (water + methanol) solvent mixture) |
| $y_M$ | mole fraction of methanol in the gaseous phase |

$Z$ property $Z = y_M$, $T$, or $p$

$\overline{\Delta Z}$ average difference between experimental and calculated numerical values for property Z (see footnote of Table 2).

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