

Summary

One main cause of the deterioration of porous materials are soluble salts present in the pore space. These salts, especially their thermodynamic behaviour, are influenced by the environmental conditions. Changes in temperature and relative humidity (RH) cause crystallisation, dissolution, also called deliquescence, as well as hydration and dehydration. During crystallisation and hydration the porous structure is damaged by mechanical stresses due to growing crystals. This effect is also called salt weathering. Damage is more severe in case of cyclic processes of crystallisation/deliquescence and hydration/dehydration, respectively. For example, artefacts in museum cabinets are damaged by salt weathering. In order to prevent the damage of the porous materials one has to know the climatic conditions, where these cyclic processes are interrupted. That means one has to know the thermodynamic properties of the salts with respect to the influence of temperature and relative humidity on crystallisation, deliquescence, hydration and dehydration. The thermodynamic behaviour of electrolyte solution is successfully described by the ion interaction approach of PITZER since many years. The so called PITZER model is semi-empirical, hence, experimental data are required for obtaining the corresponding model parameters. With respect to the salt weathering of museum artefacts there is one particular salt system, Ca²⁺/Na⁺/OAc⁻/Cl⁻/H₂O, which is of practical interest. Due to the lack of data for an accurate description of the properties of the a.m. electrolyte system by using the PITZER model the determination of such databases is urgently required.

Thus, an appropriate methodology for the measurement of salt solubilities, one type of data which can be used for obtaining the PITZER model parameters, was elaborated. Solubilities were determined in the NaOAc/H₂O and Ca(OAc)₂/H₂O systems at 278.15 K, 298.15 K, 313.15 K, 323.15 K, and 333.15 K, respectively. The measurements for the ternary systems NaOAc/NaCl/H₂O, Ca(OAc)₂/NaOAc/H₂O and Ca(OAc)₂/CaCl₂/H₂O were carried out at 278.15 K, 298.15 K, and 323.15 K. For the determination of the solubility equilibria both, the salt solutions and the corresponding solid phases have to be investigated. Thus, two different procedures were used. The saturated salt solutions were kept at constant temperature. The estimated accuracy in the temperature was approximately 0.05 K. The equipment used for the sampling procedure – e.g. syringes, cannulas, filters – were thermo stated accordingly in order to avoid changes in the equilibrium compositions. By applying sampling after certain time periods it was possible to proof whether the salt solutions reached equilibrium with respect to the solubility. After the final sampling the relative humidities above the salt solutions were measured. These RH data were used as appropriate conditions for the subsequent investigations of the solid phases by humidity and temperature controlled X-ray diffraction (RHXR). The solid phases were separated from the saturated salt solutions by filtration under controlled RH in conjunction with thermo stated filtration units. The accuracy in temperature was approximately 0.1 K. Besides RHXR the method of SCHREINEMAKERS was applied for determining the composition of the solid phases, where necessary.

The concentrations in the saturated solutions were measured by anion exchange chromatography (AEC) and inductively coupled plasma optical emission spectrometry (ICP-OES). The trueness of the AEC was increased by using quadratic calibration functions instead of the usually applied linear calibration. The cause of the non-linearity was found as the carbonate contamination of the sodium hydroxide eluents. The carbonate content was estimated as 0.2 to 0.5 mmol/L. In addition, the results of the ion chromatographic determinations were checked by classical titration. With respect to the application of the ICP-OES no matrix effects of the sample solutions were observed. The accuracy of the whole procedure for the determination of the salt solubilities was around ±5 %. To judge the trueness of the individual results the ion balances were calculated by measuring both, the anion and the cation concentrations.

The stable solid phases in the NaOAc/H₂O system were determined as sodium acetate trihydrate and the anhydrous sodium acetate as previously described in the literature. The whole phase diagram was calculated, including the ice curve, the solubility curves of both a.m. solid phases as well as the boiling temperature curve. In comparison with the experimental data the calculated curves are within the experimental errors.

The solubility measurements in the system Ca(OAc)₂/H₂O are consistent with literature data up to 323.15 K. However, the solubilities at 328.15 K and 333.15 K are significantly lower than literature data, caused by the change of the solid phase from calcium acetate monohydrate to calcium acetate hemi-hydrate. In the literature the existence of a calcium acetate dihydrate is also postulated, which could not be confirmed by the investigations in this work, however. The complete phase diagram as in the case of the NaOAc/H₂O system was calculated and agreement with the experimental data to within the experimental error was obtained. The transition point for change of the solid phase from the monohydrate to the hemi- hydrate was calculated as 2.083 mol/kg at 320.15 K.

Experimental Determination and Thermodynamic Modelling of Solubility Equilibria in the System Na-Ca-OAc-Cl-H₂O

The investigation of the solubilities in the ternary system NaOAc/NaCl/H₂O at 278.15 K to 323.15 K revealed sodium acetate trihydrate and anhydrous sodium chloride as the stable solid phases. The invariant equilibrium shifts with increasing temperature to decreasing NaCl- and increasing NaOAc molalities, respectively. For the parameterisation of the ternary interaction parameters $\theta_{\text{OAc,Cl}}$ and $\Psi_{\text{OAc,Cl,Na}}$ the solubility data from this work were used in conjunction with literature data for activity and osmotic coefficient data. The ternary interaction parameters were obtained by using a least square fitting procedure. For all three isotherms, there is excellent agreement between calculated solubilities and experimental data from this work. Also, the literature data are described accurately by the fit to within their respective uncertainties.

Investigation of the ternary Ca(OAc)₂/NaOAc/H₂O system led to the stable solid phases calcium acetate monohydrate, calcium acetate hemi-hydrate, and sodium acetate trihydrate, respectively. The experimental data are in good agreement with the calculated solubilities to within the error of the solubility measurement procedure. Due to the lack of literature data, only solubility data of this work were used for the determination of the ternary interaction parameters. The parameterisation for $\Psi_{\text{Ca,Na,OAc}}$ was done by using an empirical procedure, instead of the least square fitting procedure used for the determination of the ternary parameters of the NaOAc/NaCl/H₂O system, because the parameter $\theta_{\text{Ca,Na}}$ was already fixed by former investigations.

The third investigated ternary system was Ca(OAc)₂/CaCl₂/H₂O. It is the most complex system due to the existence of double salts. At 278.15 K and 298.15 K calcium acetate monohydrate, calclacite (calcium acetate chloride pentahydrate) and calcium chloride hexahydrate are the stable solid phases. At 323.15 K additional double salts were found, di-calcium acetate calcium chloride pentahydrate and anhydrous calcium acetate chloride, respectively. Instead of calcium acetate monohydrate and calcium acetate hexahydrate –calcium acetate hemi-hydrate and calcium chloride dihydrate were present. In analogy to the— system Ca(OAc)₂/NaOAc/H₂O, the θ_{ij} parameter, $\theta_{\text{OAc,Cl}}$, was fixed from parameterisation of the NaOAc/NaCl/H₂O system. Hence, the parameter $\Psi_{\text{Ca,OAc,Cl}}$ was determined empirically. In general, the calculated solubilities for all three isotherms are in agreement with the experimental data both, from this work and from the literature. Though the scatter in the literature data is considerably greater. A complete calculation of the isothermal solubility curve at 323.15 K was not possible due to the lack of data for higher calcium chloride molalities.

Together with existing parameterisations for the systems NaCl/H₂O, CaCl₂/H₂O and CaCl₂/NaCl/H₂O, respectively, the ternary parameterisations of this work allow the calculation of solubility equilibria in the system Ca²⁺/Na⁺/OAc⁻/Cl⁻/H₂O including the prediction of crystallisation pathways, deliquescence humidities, and hydration/dehydration equilibria, respectively. This is the first time, that it is possible to predict appropriate ambient conditions of temperature and relative humidity in order to prevent salt damage in porous material such as museum artefacts contaminated with mixtures of acetate, chloride, sodium and calcium ions. In future under controlled temperature and relative humidity conditions expensive restorations and the deterioration or total loss of unique cultural heritage can be avoided.