

Survey of dilution or adsorption enthalpies of a series of hygroscopic sorption materials

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ABSTRACT

In order to assess the thermal behavior of water based sorption systems, isothermal titration calorimetry (ITC) experiments were done to measure the integral dilution enthalpies (ΔH_D) of concentrated salt solutions via stepwise addition of water. Moreover the adsorption enthalpy (ΔH_A) of different solids were measured with ITC as well. The data showing values of ΔH_D in the range from 14 kJ/kg (KNO_3) to -415 kJ/kg (NaOH) and ΔH_A values from around 0.3 kJ/kg (MIL-53-AL) to -1380 kJ/kg (Zeolite XBF 13). Furthermore the titration results of the solid materials enable the possibility to calculate the adsorption capacity of these substances.

1. Introduction

Thermal energy storage is a sustainable possibility to improve the efficiency of air conditioning systems and moreover, is suitable for industrial drying applications [1,2]. The prevailing systems are based on sensible heat storage, phase change materials [3,4], and sorption processes (water) [1,2,5]. For sorption based technical implementations the increased demand for limited resources such as lithium compounds calls for alternative sorbent materials. Therefore, experimental data for potential alternative sorbent materials are required for model simulations allowing new or improved technical implementations [5,6,7].

The absorber is a central component of a sorption storage system. With regard to the materials in use, the systems can be divided in mainly two parts, which use on the one hand solids like silica gel or zeolites [8] or on the other hand hygroscopic fluids usually electrolyte solutions. The liberated heat of the sorption process (condensation + dilution enthalpy of water) can be used for air conditioning or for industrial drying applications. Owing to the high efficiency of the drying process of ambient air, this step can be used to reduce the electric power consumption of compressor based air conditioning devices by a pre-dehumidification step [9–12] resulting in an increased efficiency of about 50% referring to primary energy resources [13].

With respect to the working principle of absorption systems, the two most important parameters are a low water vapor pressure and a high dilution enthalpy, which is, with a fixed condensation enthalpy, the only possibility to improve the released energy/molecule. The latter can be measured with high precision isothermal titration calorimetry (ITC) experiments but also by using differential or Calvet-type calorimeters [14]. ITC experiments are a well-established method in biological [15,16] and

coordination chemistry [17,18], but all these measurements are done in liquid phase, which allows stirring of the solutions and a fast distribution of the titrated liquid. In contrast ITC experiments with a solid sample are rare.

In this paper we report results of ITC experiments on a selection of concentrated hygroscopic salt solutions and solid materials to provide experimental data for assessing their usability in ab-/adsorption storage systems. The focus of our investigations aims at maximized energy values over a wide concentration range, to improve the storage capacity of storage systems based on the respective materials.

2. Experimental

2.1. Materials

The inorganic salts, and SiO_2 were purchased from SIGMA Aldrich or Fisher scientific in analytical quality. Binder-free zeolite 13 XBF was provided by AEE INTEC (Austria). The MOFs MIL-53-AL/Cr/Fe were purchased from the Materials-Center University of Dresden. All substances were dried under vacuum (10^{-3} mbar) and a temperature of 200°C in an individually designed drying apparatus, before setting up the used concentration (salts) or using them in the measurements (solids).

2.2. ITC

The thermal analysis of the dilution enthalpy of the concentrated salt solutions and the adsorption enthalpy of the solid materials were carried out by ITC with a TAM III from TA Instruments, equipped with a nanocalorimeter. The specifications of the calorimeter are listed in Table 1:

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Table 1
Calorimeter specifications of the TAM III.

Thermostat temperature range	15 °C–150 °C
accuracy	< ± 0.1 °C
long term stability	< ± 100 µK/24 h
short term stability	< ± 10 µK/(p-p)
scanning rate	< ± 2 °C/h (20 °C – 150 °C)
Nanocalorimeter short term noise	< ± 10 nW
baseline drift	< 40 nW/24 h
accuracy	< 1%
precision	± 100 nW

The Isothermal Titration Calorimetry (ITC) was carried out in 1 mL and 4 mL glass ampoules. The ITC measurements were carried out with the respective salt solutions in water, with stirring frequencies between 100 rpm and 200 rpm using a gold propeller. The solid materials were measured without stirring. For the titrations the sample is transferred into the glass ampoule which is then attached to the titration module and inserted into the calorimeter following the standard procedure of the manufacturer. Upon successful calibration and recording of a constant baseline (slope < 500 nW/h), titration steps are performed by addition of water (5 µL–10 µL, error < 0.5%) via a cannula connected to a Hamilton syringe in discrete time intervals. Heat effects are tracked relative to an identical reference cell, which is filled with water or sand, in the accuracy specified in Table 1. The added amount of water and the operating time between injections were adjusted to the respective experiment. It should be noted, that the statistic error of each measurement is smaller, if more measurements are taken in this concentration range. The concentration given in mass percent ([wt%], mass ratio [%] or [mol/L]) always refers to the concentration at the start of the injection of water. The concentration range for each electrolyte is detailed in the Supporting information for each titration step. The larger the amount of water with respect to the sample mass, the wider the concentration range covered in the measurement.

The evaluation of the titration was performed using the TAM Assistant V. 1.3 program. This allows an numerical integration of the heat flow against the experiment time to calculate the dilution/adsorption energies for a given titration step [19]. The energy values obtained for each concentration are listed in the Supporting information besides being plotted in the figures of the following section. The corresponding enthalpies for each step are calculated as:

$$\text{enthalpy} = \frac{\text{energy}}{\text{mass}(\text{H}_2\text{O})}$$

3. Results

The dilution enthalpies has been measured for 19 concentrated salt solutions and 7 solids. For each substance category two groups with higher and lower dilution enthalpies can be classified, which are plotted in different diagrams to get a detailed overview of the respective measurements. Additionally, all values are listed in the SI. In Fig. 1 the salt solutions with lower energies are plotted against the concentration. Three different categories have been identified with respect to the dilution enthalpy delivered. Thus, LiAc, MgCl₂, LiOH and ZnAc₂ show an exothermic dilution enthalpy (Ac = acetate), KH₂PO₄ and KNO₃ deliver an endothermic signal and furthermore the solutions of MgSO₄ etc. are nearly thermoneutral in a stepwise dilution with H₂O. Furthermore, the dilution enthalpy depends on the choice of the cation (LiAc max. –21.8 kJ/kg (H₂O), NaAc –1.8 kJ/kg (H₂O) as well as from the used anion (KForm max. –0.3 kJ/kg (H₂O), KNO₃ 14.3 kJ/kg (H₂O); Form = formate).

In contrast to the plotted results of the dilution enthalpy in Fig. 1, the salt solutions in Fig. 2 have a solubility, which is approx. three times

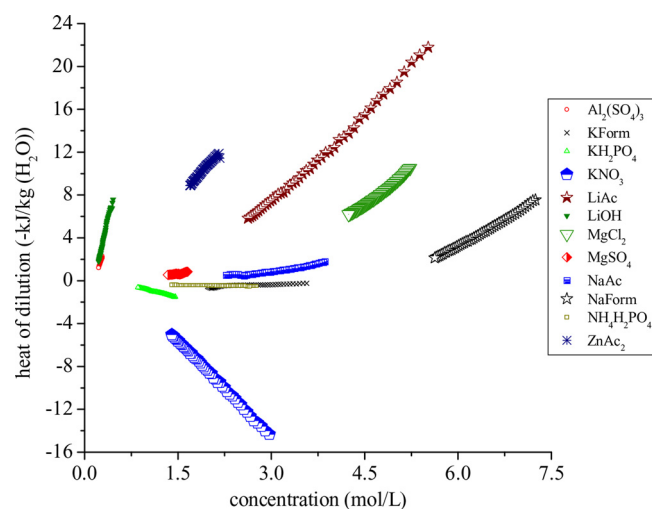


Fig. 1. Results of ITC-experiments for aqueous solutions of twelve salts with heat of dilution plotted against concentration. Cf. Supplementary information (SI) for specific values.

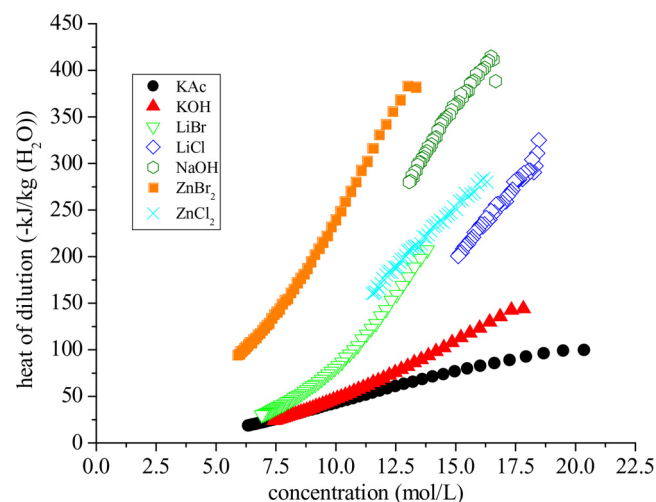


Fig. 2. Results of ITC-experiments for aqueous solutions of seven well soluble salts with heat of dilution plotted against concentration. Cf. SI for specific values.

higher. As a consequence, the ratio of water molecules which interact with the ions is different, resulting in a higher dilution enthalpy. Compared to the results presented above, these salt solutions delivered an approx. three times higher dilution enthalpy.

Fig. 2 shows, that the solutions of NaOH and ZnBr₂ delivered the highest dilution enthalpy (–414 kJ/kg (H₂O)) respectively –383 kJ/kg (H₂O)). The results of the ITC experiment of the LiCl solution with a dilution enthalpy of –325 kJ/kg are in agreement with the results in the literature (–330 kJ/kg) [20] and additionally in the range of the Li-mixtures LiBr/Li/LiCl/LiNO₃ (ratio:5:1:1:0.5) with a concentration of 64.5 wt% (–344 kJ/kg(H₂O)) [21]. As already mentioned before, the level of the dilution enthalpy for this seven salts depends on the nature of the ions. For example, the dilution enthalpy of the KOH solution is approx. 3-times smaller compared with NaOH due to the lower charge density of K⁺ compared with Na⁺. Consequently, the dilution enthalpy of LiOH-solution should be highest of the hydroxide salts. However, the solubility limits an increased value, as can be derived from Fig. 1 as well.

Since ITC-experiments of solid substances are rare, Fig. 3 shows a plot of the obtained heat flow obtained for a typical solid sample (Zeolite 13 XBF) over a prolonged time. Besides the calculation of the

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