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Melting temperatures and solubilities of congruently melting salt hydrates confined in nanoporous materials

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The Gibbs energy of nanocrystals increases with decreasing crystal size due to an increasing surface to volume ratio (A/V) resulting in a solubility increase and a melting temperature decrease of small crystals. In the case of pure phases, the melting temperature decrease may be approximately represented by the Gibbs–Thomson (GT) equation. However, the melt of a salt hydrate is not a pure phase but rather a concentrated electrolyte solution. Hence, the GT equation does not apply and a different approach based on the solubility increase of small crystals is used here.
The additional energy of a small crystal is accounted for by the surface energy yielding an expression for the solubility increase of nanocrystals. For the thermodynamic solubility product of small crystals we obtain [1]:
lnK = lnK + (cl Vm/RT) (dA/dV) (1)
where K and K are the thermodynamic solubility products of the small and an infinitely large crystal, respectively, cl is the surface free energy of the crystal–liquid interface, Vm is the molar volume of the solid, R is the gas constant and T is the absolute temperature. The surface to volume ratio is inversely proportional to the crystal size. For a spherical crystal of radius r, dA/dV = 2/r. The solubility curve of a hydrated salt, i.e. the relation between composition of the saturated solution and temperature, is a continuous function with a maximum if temperature is the ordinate and composition the abscissa. The maximum of the curve is the melting temperature of the hydrated solid and the composition of the saturated solution (the solubility at the melting temperature) equals the composition of the solid. Therefore, as shown in Fig.1, the melting temperature decrease Tm of a small crystal corresponds to a solubility increase msat. Thus, the solubility increase of small crystals can be determined indirectly by measurement of the melting temperature. In the present study, we have determined the melting temperatures of nanocrystals of M(NO3)2·6H2O (M=Mg,Zn), confined in mesoporous materials with narrow pore size distributions and different pore diameters (Vycor glass, mesoporous silica). Using a molality based Pitzer model for the calculation of water activity and activity coefficients, the thermodynamic solubility products of the nanocrystals were calculated. Using Eq. (1) and treating cl as an adjustable parameter, the data were used to determine values of the surface free energy of the crystal–liquid interface.

References

[1] M. Steiger, J. Cryst. Growth 2005, 282, 470–481.

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