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**SELECTIVE WATER SORBENTS FOR MULTIPLE APPLICATIONS, 3.
CaCl₂ SOLUTION CONFINED IN MICRO- AND MESOPOROUS
SILICA GELS: PORE SIZE EFFECT ON THE "SOLIDIFICATION-
MELTING" DIAGRAM**

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Abstract

In this communication we present a low-temperature "solidification-melting" phase diagram for CaCl₂/H₂O solutions confined in KSK and KSM silica gels. At salt concentrations of 0 - 48 wt. %, the diagram has been found to lie below the diagram reported for the bulk system by 15-30°C. It shows a depression of the solution melting point due to its confinement to the pores. Several other peculiarities of melting and solidification in this system are also reported and discussed. Beside fundamental interest, the data obtained could be of importance in many commercial areas such as refrigeration, accumulation of low temperature heat, frost prevention in building materials, *etc.*

Keywords: Melting, CaCl₂/H₂O solution, pore size effect, phase diagram

INTRODUCTION

Recently we have reported water sorption properties of CaCl₂ confined to *micro-* and *mesoporous* silica gels [1,2]. The results give indirect evidence for the melting temperature (T_m) depression of CaCl₂ tetra- and hexahydrates confined in the mesoporous host matrix. A similar behavior has been observed for highly concentrated CaCl₂ aqueous solutions in microporous silica gel. The effect becomes stronger as one goes from meso- to micropores. The melting temperature of the 86 wt. % CaCl₂/H₂O solution has been found to be lower by at

least 200 K in 3.5 nm diameter pores than in the ordinary bulk solution [2]. Here we present a direct DSC study of this effect carried out for $\text{CaCl}_2/\text{H}_2\text{O}$ solutions confined in the KSK and KSM silica gels. Low-temperature "solidification-melting" phase diagram of this system was measured at concentrations varied from 0 to 48 wt.%. The diagram has been found to lie below the diagram reported for the bulk system by 15-30 K [3-6]. It confirms the indirect indication for T_m depression mentioned above. This depression exemplifies the size effect resulting from the CaCl_2 confinement to the porous matrix. Several other peculiarities of melting and solidification in this system are also reported and discussed. Beside fundamental interest, the data obtained could be of importance in many commercial areas such as refrigeration, accumulation of low temperature heat, frost prevention in building materials, *etc.*

EXPERIMENTAL

Two commercial silica gels with well-defined pore structures were used as host materials: KSKG (specific surface area $S_{sp} = 350 \text{ m}^2/\text{g}$, pore volume $V = 1.0 \text{ cm}^3/\text{g}$, average pore diameter $d = 15 \text{ nm}$) and KSM ($S_{sp} = 600 \text{ m}^2/\text{g}$, $V = 0.3 \text{ cm}^3/\text{g}$, $d = 3.5 \text{ nm}$). Both silica gels were obtained from Reachim (former USSR). Their pores were filled with a CaCl_2 aqueous solution until the pore filling $\gamma = 0.97 - 1.09$ was reached. The solution salt concentration (C) was varied from 0 to 48 wt.%.

DSC-111 "SETARAM" unit was used for phase transition detection and heat capacity measurement in the temperature range of 170 - 320 K. A sample ($m_0 \approx 30 \text{ mg}$) was placed in a standard platinum crucible, cooled down to 170 K at a constant rate (5 K/min), maintained at this temperature for 10 min and finally heated at the same rate up to 320 K. The thermograms for the cooling and heating modes were recorded under the dry nitrogen flow. Short runs were performed at lower heating rates (0.67 and 1 K/min) in standard aluminium crucibles covered with a lid. The melting temperature was detected either as a temperature corresponding to the maximum of a DSC peak or by a standard "onset" method.

Thermomechanical analysis of $\text{CaCl}_2/\text{H}_2\text{O}/\text{SiO}_2$ (KSM) was performed as follows. The sample was pressed in a mold and protected with a tin foil to obtain a rod with size suited for mechanical measurements ($1.5 \times 11.3 \times 10 \text{ mm}^3$). Internal friction ($\tan \delta$) and dynamic module (E') were measured at the frequencies of 1 and 10 Hz by means of a Rheometric Scientific dynamic mechanical analyzer (DMTA). During the measurements, a controlled nitrogen atmosphere was maintained in the experimental chamber to avoid water condensation. The temperature was increased from 120 to 230 K at a linear heating rate of 3 K/min.

RESULTS AND DISCUSSION

A typical thermogram of the system involved has two peaks (Fig. 1). The low-temperature peak appears at 214 K (onset temperature is equal to 205 K). Its position does not change with the solution concentration and is likely to correspond to the eutectic mixture melting. At CaCl_2 concentrations lower than 30 wt.%, this peak may not be present due to a supercooling effect that will be specially discussed elsewhere. The position of the second peak depends strongly on the solution concentration and represents the melting point of the system in the pores.

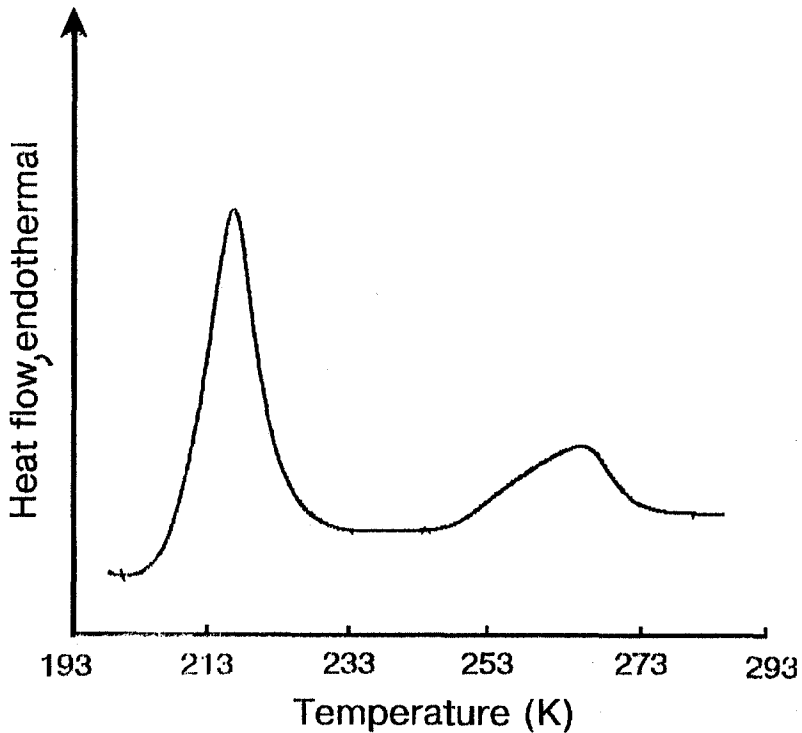


Fig. 1. DSC thermogram of the CaCl_2 aqueous solution ($C = 37$ wt.%) confined to the pores of the KSKG silica gel. The heating rate is 5 K/min

The solution confinement in the silica gel pores has been found to affect its properties leading to a melting behavior different from that of an ordinary bulk fluid. The main effect consists in a melting temperature (T_m) depression of the solution in the pores. In the case of microporous silica gel KSM, neither

solidification nor melting peaks were detected down to 170 K. Possible reasons of this effect are discussed below. For the mesoporous host material, the typical depression (ΔT_m) was about 10-30 K.

The phase diagram for aqueous CaCl_2 solutions confined to the KSKG pores (Fig. 2) appears to belong to the same simple eutectic type as for the bulk solution [3-6]. The diagram clearly shows the melting temperature depression over the whole concentration range from pure water to the highest stoichiometric crystalline hydrate ($\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$). It is noteworthy that the phase diagrams both for the bulk and dispersed solutions do not follow the Schreder equation [7], indicating a strong deviation from the behavior typical for ideal binary solutions.

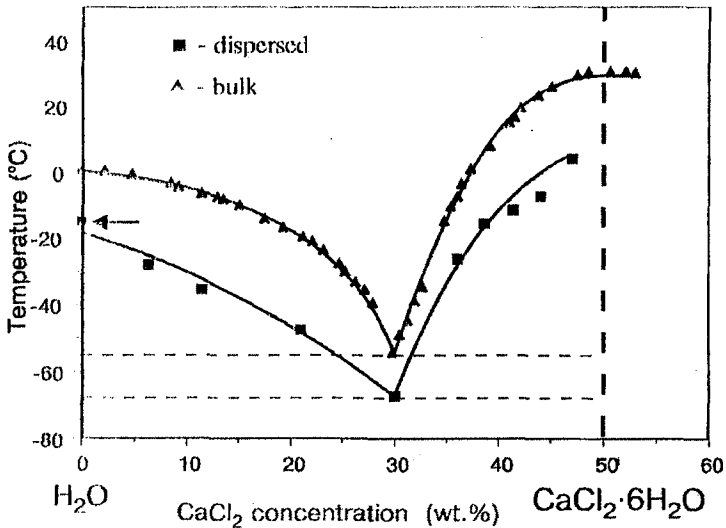


Fig. 2. "Solidification-melting" phase diagram for binary mixtures $\text{H}_2\text{O} - \text{CaCl}_2$:
s - bulk, n - dispersed in the KSKG silica gel

Such melting temperature depression has been established in the literature for single component systems like water, organic liquids, metal particles, *etc.* [8-13]. Very large effects are known for 5 nm gold particles. ΔT_m higher than 500 K has been reported for this system [13].

The Gibbs-Thomson thermodynamic analysis [9,14,15] predicts that the melting point depression $\Delta T_m(d) = T_m(\infty) - T_m(d)$ for a small crystal with typical size d is determined by the following equation:

$$\Delta T_m(d) = 4\sigma T_m(\infty)/(d \Delta H \rho) \sim 1/d \quad (1)$$

where $T_m(\infty)$ is the normal (bulk) melting point, σ is the surface energy of the solid-liquid interface, ΔH is the bulk fusion enthalpy, ρ is the solid density. To estimate a scale of the depression given by eq.1, let us calculate ΔT for pure water confined in the pores. It corresponds to a salt solution of zero concentration (see arrow in Fig. 2). Equation 1 gives $\Delta T_m = 9.0$ K for 15 nm pores. A more detailed thermodynamic analysis [10] suggested the melting temperature depression equal to 9.3 K for water in such pores (see eq. 19 in Ref. [10]). For water in the KSKG silica gel, we obtained $\Delta T_m = 14.8$ K with the onset method and $\Delta T_m = 2.6$ K from the peak position. The former value is likely to characterize water melting in the narrowest pores, whereas the latter corresponds to the largest ones. The melting temperature shift in average pores lies in between the two and can be briefly estimated as $\Delta T_m = (14.8 + 2.6)/2 = 8.7$ K. It is close to both values calculated from the literature data.

Assuming the $1/d$ dependence valid for micropores, it is easy to estimate T_m for water confined to the KSM pores: $T_m = 235$ K and 218 K from Ref. [9] and [10], respectively. So, the melting point of water or low concentration CaCl_2 solutions in the KSM pores should be within the tested temperature range $T > 170$ K. The established lack of solidification-melting transitions in this host material may be explained by the following reasons: a) relation 1 is not valid for so small pores and the actual T_m is lower than 170 K; b) the fusion enthalpy in small pores is strongly reduced below its bulk value [10,16,17], making the melting peak undetectable; c) the system is vitrified; d) water (or solution) in small pores is strongly supercooled [11,12] and its solidification temperature is lower than 170 K. Let us discuss these reasons in more detail.

1) One should expect that relation 1 is not valid for very small pores because it predicts $\Delta T_m \rightarrow \infty$ at $d \rightarrow 0$. As a result, it leads to an overestimation of the ΔT_m value and the real melting point depression is expected to be lower than that predicted by eq.1. It shows that the lack of melting transition in the KSM matrix can hardly be explained by a decrease of the thermodynamic melting point.

2) We have found the reduction of the fusion enthalpy (ΔH_f) for water confined to the KSKG pores. This value has been measured to be 264.5 kJ/g. It is by 61.5 kJ/g lower than the fusion heat in the ordinary bulk state. It is interesting to note that the value obtained by us is close to the one calculated in Ref. [10] for 15 nm water aggregates: $\Delta H_f = 262$ kJ/g. Since ΔH_f diminishes with

cooling, an additional decrease in the fusion heat of $\Delta(\Delta H_f)$ is expected to be caused by the melting point decrease in the pores $T_m(d) < T_m(\infty)$

$$\Delta(\Delta H_f) = \int_{T_m(\infty)}^{T_m(d)} [C_p^{liq}(T) - C_p^{sol}(T)] dT < 0$$

where c_p^{liq} and c_p^{sol} are specific heats for liquid and solid phases, respectively. Unfortunately, this temperature contribution cannot be carefully estimated at low temperatures because, to our knowledge, c_p^{liq} of liquid water is unknown for $T < 230$ K. The ΔH_f decrease estimated in the available range $273 \text{ K} \Rightarrow 230 \text{ K}$ appears to equal 96.5 kJ/g . This value makes 29.5% of ΔH_f at 273 K . It shows that the tentative ΔH_f decrease at $T = 170 - 230 \text{ K}$ may be significant.

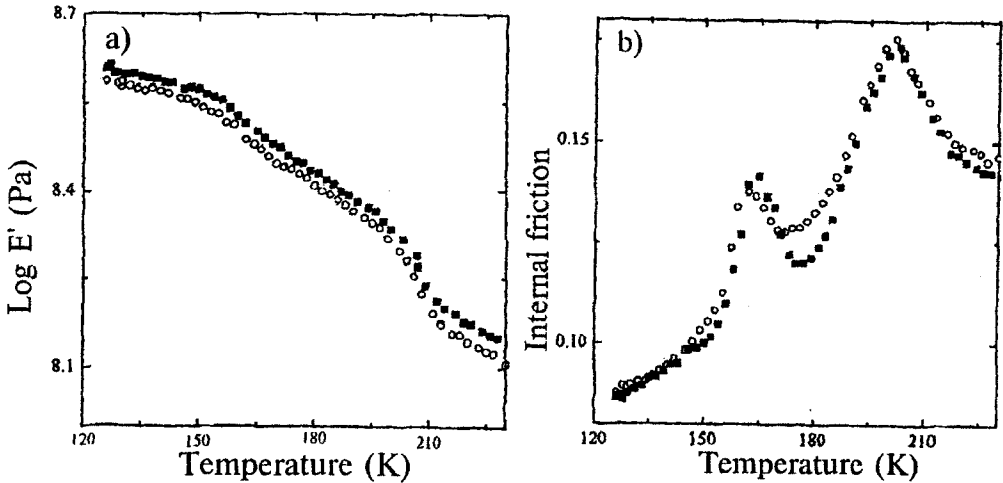


Fig. 3. Dynamic module E' (a) and internal friction $\tan \delta$ (b) as a function of temperature for the $\text{CaCl}_2/\text{H}_2\text{O}/\text{KSM}$ system at 1 Hz (m) and 10 Hz (n)

3) Evidence for possible vitrification of the solution in the micropores can be seen from thermomechanical spectra presented in Fig. 3. The spectra show the temperature behavior of the dynamic module and internal friction in the sample at frequencies of 1 and 10 Hz. The loss peak at 163 K and the corresponding inflection in the module shifted to higher temperatures when the frequency was increased. Such behavior is typical for thermally activated relaxation and may be tentatively associated with glass transition (T_G) of the solution in small pores [18]. The peak at 203 K and the relative module drop were not sensitive to the

frequency change. It is typical for first order transitions. The nature of the transition should be a subject of further studies. Note that in the experiments discussed the system was precooled down to 120 K.

4) In our opinion, strong supercooling is one of the most important factors that can lead to the absence of exo- and endoeffects for the liquid dispersed in the micropores. We have observed that even in the bulk aqueous solutions of CaCl_2 the solidification exo-peak shifted downwards compared to the melting point by tens of degrees. Restricted pore geometry of the KSKG silica gel enhances the supercooling effect. Namely, the solidification temperature decreases by 10-30 K compared to the bulk system. This means that the solution confinement to the silica gel pores strongly influences the nucleation process at low temperatures. Possible reasons of this effect may be in a considerable disordering of the solution structure in the vicinity of the pore surface, low liquid viscosity in the pores [12,19] or modification of thermodynamic fluctuations in the liquid confined in the restricted volume.

Several other peculiarities of supercooling, solidification and melting in the confined $\text{CaCl}_2/\text{H}_2\text{O}$ and $\text{LiBr}/\text{H}_2\text{O}$ systems will be reported elsewhere. Among them, a threshold effect of the pore filling on the solution solidification as well as solidification/melting of $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ microcrystals isolated in the silica gel pores will be reported.

All the phenomena discussed above show that size-dependent effects may come in many varieties and manifest in supercooling, solidification and melting behavior different from common bulk $\text{CaCl}_2/\text{H}_2\text{O}$ solutions. The most important effect is the depression of the system melting point, which appears not only at low but also at room and elevated temperatures and can influence the sorption properties of this system [1,2].

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