Melting point depression of ionic liquids confined in nanospaces†

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A new physical method was proposed to control the liquid properties of room temperature ionic liquids (RT-ILs) in combination with nanoporous materials; the melting point of ILs confined in nanopores remarkably decreases in proportion to the inverse of the pore size.

Over the past decade, room temperature ionic liquids have attracted considerable attention as feasible "green" media for reaction and separation chemistry and electrolyte devices owing to a negligibly small vapor pressure, high thermal and chemical stability, and sufficient electrochemical competence.[1] Many researchers have synthesized a lot of ILs with different cation and anion structures in order to decrease the melting points and viscosities[2] and also to functionalize them as novel task-specific ILs.[3] Such chemical manipulations have produced a variety of RT-ILs; however, there have been very a few reports on physical attempts to improve the properties of ILs. Among such attempts, the discovery that drastic changes in the phase behavior of ILs, *i.e.*, the melting point depression of salts[4] and the phase separation between ILs and liquids,[5] can be induced by high-pressure CO_2 is rather interesting because a multiphasic system composed of IL and supercritical CO_2 has several advantages over IL/conventional-solvent systems as previously pointed out.[6]

On the other hand, it has been demonstrated that fluids confined in nanospaces show anomalous phase behaviors, which are typically illustrated by melting point depression, boiling point increase, and a shift of the critical point.[7] For example, many researchers have found that water and aqueous solutions with hydrogen bonding abilities have very unique properties in carbon nanotubes.[8] Moreover, the phase behaviors and liquid properties of confined fluids can be tuned by the size of the space, the structure, and surface conditions. In this paper, we propose a new physical method to control the liquid properties of ILs in combination with nanoporous materials, and reveal the freezing/melting behaviors of ILs under such limited spaces. Confinement of ILs in nanospaces promises to open up new chemistry in a variety of chemical fields.

Differential scanning thermal calorimetry (DSC) was carried out for ILs confined in a series of porous silica glasses, whose the physical properties are well-known.[9] In the present work, several hydrophobic and hydrophilic ionic liquids were deliberately selected because most ILs show no distinct freezing/melting behavior in DSC.[10] Frequently, a small amount of impurities such as water remarkably affects the properties of ILs;[11] therefore, the ILs were synthesized and purified carefully in our lab. The detailed procedure is given in the Supplementary Information together with the water contents.† The confined samples were prepared by mixing the nanoporous materials with the purified ILs under an Ar atmosphere, and then the excess ILs were removed by filtration. The typical DSC scans are shown in Fig. 1 for two ILs of the 1-butyl-3-methylimidazolium (BMIM) cation with $[CF_3SO_3]^-$ and $[(CF_3SO_2)_2N]^-$ anions in bulk liquid and confined in controlled-pore glasses (CPGs).[9] For bulk ILs, the results are in good agreement with the previous studies.[10] For confined ILs, a small endothermic peak still remains, independent of the pore size, at the same temperature as the bulk one, which can be attributed to residual ILs on the outer surface. In addition to the bulk melting peak, moreover, a new endothermic peak is clearly observed and assigned to be IL confined in nanopores. These DSC results indicate several important features: (i) the confined IL has a lower melting point, up to −30 °C, than the bulk one, (ii) this melting point depression is enhanced more remarkably by decreasing the pore size, and at the same time (iii) the pore melting peak is much more broadened as the pore size decreases. Note that the exothermic peak at the pore freezing point shows a similar tendency; however, other peaks due to glass transition and heat crystallization, if observed as is the case for $[BMIM][(CF_3SO_3)_2N]$ in Fig. 1(b), are originally so broad that we cannot detect any appreciable confinement effect.

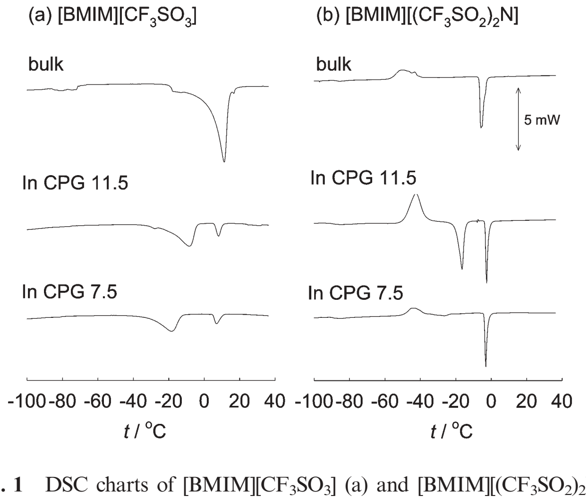

Fig. 1 DSC charts of $[BMIM][CF_3SO_3]$ (a) and $[BMIM][(CF_3SO_2)_2N]$ (b) in bulk liquid and confined in controlled-pore glasses (CPGs) with different pore diameters (11.5 and 7.5 nm). The measurements were carried out by first cooling the samples from 20 °C to −120 or −150 °C and then by heating up to 40 °C at a fixed scan rate of 5 K min^{-1} with a SII DSC6200. Only the heating part is given in this figure to clarify the melting behavior.

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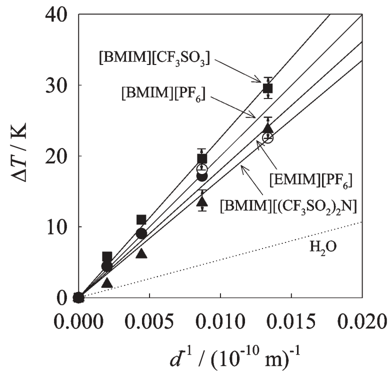

Fig. 2 Melting point depression of ILs as a function of the inverse of the pore diameter; [BMIM][CF_3SO_3] (■), [BMIM][PF_6] (●), [EMIM][PF_6] (○), [BMIM][$(CF_3SO_2)_2N$] (▲). The dotted line represents the melting point depression of H_2O. The arrows indicate the estimated errors of T_m(pore) within ± 1.5 K.

It was revealed that confinement can readily liquidize ILs at a much lower temperature. Moreover, we found that the melting point depression (ΔT) for ILs confined in nanopores shows a linear relationship with the inverse of the mean pore diameter ($1/d$), shown in Fig. 2, where ΔT is defined as the difference ($\Delta T = T_m - T_m$(pore)) of the melting points between bulk (T_m) and confined (T_m(pore)) ILs. This relationship can hold for all the confined ILs used here, and the lower shift is much larger than those of usual solvents, as is the case of water, for example, shown in Fig. 2. More interestingly, the slope of ΔT *vs.* $1/d$ is moderately dependent on a combination of the cation and anion species of ILs; it follows that $H_2O \ll$ [BMIM][$(CF_3SO_3)_2N$] < [EMIM][PF_6] < [BMIM][PF_6] < [BMIM][CF_3SO_3].

ΔT is commonly related to the molar volume (V_m), the inverse of the enthalpy of fusion ($1/\Delta H_f$), and the difference between the surface tensions of the solid-substrate (γ_{ss}) and liquid-substrate (γ_{ls}) interfaces in addition to T_m and $1/d$ on the basis of the Gibbs–Thomson equation:[7a]

$$\Delta T = \alpha(T_m V_m/\Delta H_f)(\gamma_{ss} - \gamma_{ls})/d. \quad (1)$$

Here, α is determined by the pore geometry and the contact angle, and the pore is assumed to be completely filled with IL. The proportional constant of $T_m V_m/\Delta H_f$ can be estimated form the properties of bulk ILs, which increases in the following order: [BMIM][$(CF_3SO_3)_2N$] < [EMIM][PF_6] < [BMIM][CF_3SO_3] < [BMIM][PF_6]. This would be in agreement with the tendency observed for hydrophobic ILs, but cannot explain the largest slope of hydrophilic [BMIM][CF_3SO_3]. One might consider that it is caused by higher water contents in hygroscopic [BMIM][CF_3SO_3]; however, the melting peaks of [BMIM][CF_3SO_3] on the outer surface in different porous glasses remain almost the same as that of the bulk one. Thus, the surface tension term, reflecting the interaction between the matrix and IL, should also be an important factor in the slope because α remains almost the same independent of ILs. Note that the magnitude of the slope increases with the empirically-known hydrophilicity of ILs.[1]

The matrices of CPGs used in this study have a moderately hydrophilic surface, which can be easily modified into a hydrophobic one with methyl groups by the silylation procedure without a significant change[12] in the pore distribution.[11] We studied the melting behaviors of ILs confined in a modified CPG with a pore diameter of 11.5 nm. However, the surface hydrophobization is not very effective and slightly weakens the melting point depression. On the other hand, ILs confined in a thirsty Vycor glass with a strongly hydrophilic surface and 7.0 nm pore diameter showed a remarkable change in the melting behaviors; the melting endotherms were observed at much lower temperatures and sometimes disappeared due to peak broadening. The results are supported by NMR experiments in which ^1H signals of ILs in Vycor, though much broadened, are observed at very low temperature (see Supplementary Information†), where the ILs are supposed to be frozen according to the melting points of ILs in CPGs. It was found as well that the dynamic motion of confined ILs is very slow and remarkably restricted, which no longer satisfies the extreme narrowing condition. These facts suggest that an appropriate surface modification can also tune the liquid properties of ILs confined in nanopores effectively and sophisticatedly. Several researchers[13] have recently reported a similar peculiarity in the liquid/gas interface of ILs.

In this study, we propose a new practical method to control the liquid properties of ILs in combination with nanoporous materials. The present method can be applied to every IL because it is based on a universal physical phenomenon. Our approach is useful, in particular, for ILs with higher melting points, which can preserve their own original liquid natures by confinement even at lower moderate temperatures. The physical concept of "nano-ILs" should be expanded to a wide range of chemical fields. In fact, some attempts have recently been performed in catalytic and electrochemical applications,[14] although the fundamental aspects of nano-ILs unfortunately have remained unrevealed. Nevertheless, excellent catalytic activities and high heat resistances have been found as a result of the confinement effect. Our results, in addition to high thermal stability, demonstrate that ILs confined in nanospaces have potential advantages at lower temperatures. From a practical viewpoint, moreover, the confined ILs used in this study were readily washed out from the nanoporous matrices with miscible organic solvents such as acetone or dichloromethane. Thus, the ILs and nanoporous materials can be separated for recycling. On the other hand, confinement restricts the dispersion of ILs from nanopores into poor solvents. This reduces contamination of ILs in bulk reaction/electrolysis media.

Recently, various nanoporous matrices have been synthesized from inorganic and organic materials and their hybrids. These matrices have well-defined pore distributions, controllable surfaces, and characteristic structures. Hence, further studies would create geometrically designed nano-ILs such as 1-dimensional ILs in channels and 2-dimensional ILs in slits. The combination of ILs and nanoporous materials is so wide that the IL-confinement system can be optimized for each purpose in a variety of chemical processes.

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