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## Cation effects on physical properties of acetate-based ionic liquids

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Abstract (less than 300 words)

Ionic liquids (ILs) are salts with melting points being at or below ambient temperature. There are various ionic species, and thus, the natures of ILs can be optimized for individual applications by the combination of ions and chemical modification. Because ILs have unique characteristics like negligibly vapor pressure, non-flammability, and miscibility with various chemicals, they have attracted much attention as potential solvents in various fields. Here, we report the cation effects on the physical properties of acetate ([AcO] $^-$ ) based ILs before and after the CO<sub>2</sub> absorption. The cations of [AcO] $^-$  ILs were 1-ethyl-3-methylimidazolium ([emim] $^+$ ),  $N_iN_i$ -diethyl- $N_i$ -methyl- $N_i$ -heptyl-ammonium ([N<sub>1227</sub>] $^+$ ),  $N_iN_i$ -diethyl- $N_i$ -methyl- $N_i$ -(6-hydroxyhexyl)-ammonium ([N<sub>12260H</sub>] $^+$ ), and dodecyltributylphosphonium ([P<sub>444,12</sub>] $^+$ ). The physical properties of 1-ethyl-3-methylimidazolium 2,2-dimethyl-3-hydroxylpropionate ([emim][OH-Piv]) were also examined to elucidate the effect of the hydroxy-functionalized carboxylate.

The densities of  $[P_{444,12}][AcO]$ ,  $[N_{1227}][AcO]$ ,  $[N_{122,6OH}][AcO]$ , [emim][AcO], and [emim][OH-Piv] increased in this order at certain temperatures. The cations with the longer alkyl chains tended to decrease the densities of ILs. The hydroxy-functionalized ILs were denser than the corresponding non-functionalized ILs.  $[N_{122,6OH}][AcO]$  has the highest viscosity followed by [emim][OH-Piv],  $[N_{1227}][AcO]$ ,  $[P_{444,12}][AcO]$ , and [emim][AcO] over the present temperature range. This order is attributed to the cation size and the hydrogen bond via the hydroxyl group, except for  $[P_{444,12}][AcO]$ . The densities of the IL +  $CO_2$  mixtures were slightly higher or comparable to those of the corresponding neat ILs. The ratios of the densities between before and after  $CO_2$  absorption tended to be largely dependent on the  $CO_2$  solubility:  $[emim][AcO] > [N_{122,6OH}][AcO] > [P_{444,12}][AcO] > [N_{1227}][AcO]$ . The  $CO_2$ -saturated  $[N_{1227}][AcO]$  and  $[N_{1226,OH}][AcO]$  were more viscous than the neat ILs. The viscosity increment is typically observed for the  $CO_2$  chemical absorbent. In contrast, the viscosities of [emim][AcO] and  $[P_{444,12}][AcO]$  showed no appreciable change after  $CO_2$  absorption. This difference in viscosity change would arise from the kind of  $CO_2$  adducts.

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