Cation Effects on Physical Properties of Acetate-Based Ionic Liquids

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Abstract

This study reports the cation effects on the physical properties of acetate ($[AcO]^-$) based ILs before and after the CO_2 absorption. The cations of $[AcO]^-$ ILs were 1-ethyl-3-methylimidazolium ($[emim]^+$), *N,N*-diethyl-*N*-methyl-*N*-heptyl-ammonium ($[N_{1227}]^+$), *N,N*-diethyl-*N*-methyl-*N*-(6-hydroxyhexyl)-ammonium ($[N_{1226OH}]^+$), and dodecyltributyl-phosphonium ($[P_{444,12}]^+$). 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 hydroxy group, except for $[P_{444,12}][AcO]$. The density and molar volume of the IL + CO_2 mixtures were slightly higher or comparable to those of the corresponding neat ILs. The CO_2-saturated $[emim][OH-Piv]$, $[N_{1227}][AcO]$, and $[N_{1226,OH}][AcO]$ were more viscous than the neat ILs. 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 kinds of CO_2 adducts and the hydroxy group.

Keywords

Ionic liquid, Acetate, Physical property

1. Introduction

Ionic liquids (ILs) are salts with melting points being at or below ambient temperature. They generally consist of a bulky organic cation and an organic or inorganic anion. There are various ionic species, and thus, the natures of ILs can be optimized for individual applications by combining ions and chemical modifications. Because ILs have unique characteristics, e.g., negligibly vapor pressure, non-flammability, electrical conductivity, and miscibility with various chemicals, they have attracted much attention as potential solvents in various fields. A promising technology using IL is gas absorption, in particular, selective removal of acidic gases like CO_2. In the last decade, a variety of ILs for CO_2 chemisorption have been investigated to understand the natures of ILs and develop more efficient absorbents [1-12].
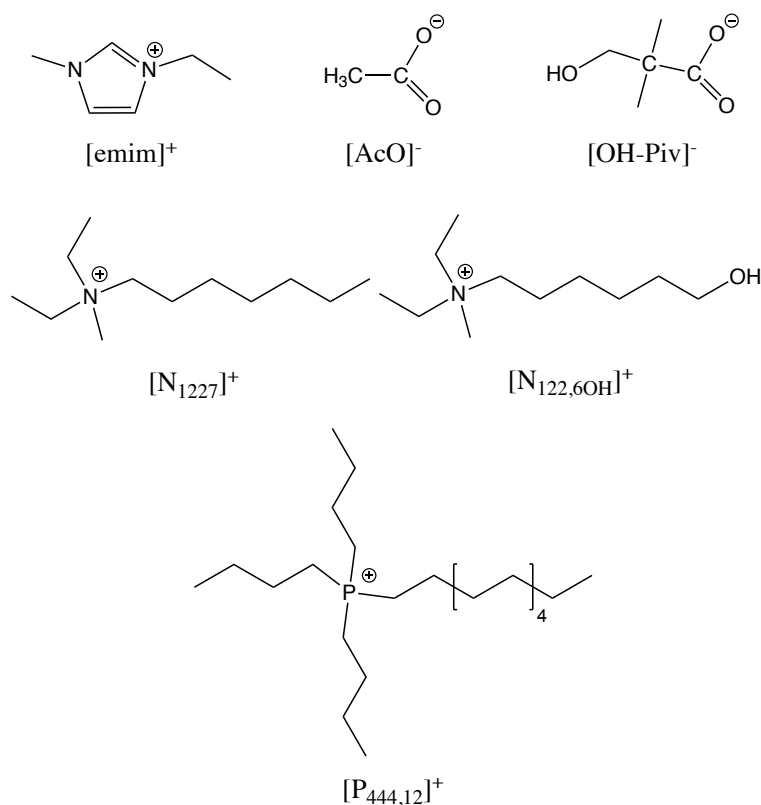

Fig. 1 Chemical structures and abbreviations of ionic species.

We have focused on carboxylate-based ILs because their production costs are generally less expensive than other ILs for chemisorption. The CO_2 absorption and physical properties for various carboxylates have been reported in the earlier works [1,4,13-24]. Both the cation and anion species influence the properties of the carboxylate IL. The physical properties after the CO_2 absorption strongly associate with the ionic species; however, it has not been investigated experimentally yet for the acetate ILs other than the dialkylimidazolium acetate. The effects of the cation species on the physical properties of the CO_2-saturated acetate IL are

still unrevealed in detail. In the present study, we measured the density and viscosity before and after CO_2 absorption for acetate ILs. The cations of the present acetates were 1-ethyl-3-methylimidazolium ([emim]$^+$), *N,N*-diethyl-*N*-methyl-*N*-heptyl-ammonium ([N$_{1227}$]$^+$), *N,N*-diethyl-*N*-methyl-*N*-(6-hydroxyhexyl)ammonium ([N$_{122,6OH}$]$^+$), and dodecyltributyl-phosphonium ([P$_{444,12}$]$^+$). The properties of 1-ethyl-3-methylimidazolium 2,2-dimethyl-3-hydroxylpropionate ([emim][OH-Piv]) were also investigated to elucidate the effect of the hydroxy functionalization on the carboxylate. Fig. 1 shows the chemical structures and the abbreviations for the ions used in this work.

2. Experimental

The density, viscosity, and electrical conductivity of the neat ILs were measured using the same apparatus and procedure reported in our previous studies [25,26]. The density was determined with a vibrating tube densimeter (Anton Paar, DMA 500M). The viscosities were measured using a rotating-cylinder viscometer (Anton Paar, Stabinger SVM 3000). Each apparatus was calibrated with reference samples. The temperature was maintained within ±0.01 K at most. The instrumental accuracy for the density is less than ±0.05 kg m^{-3}, whereas the expanded uncertainty is ±0.1% because of impurities. The expanded uncertainty for the viscosity is less than ±2%. The experimental apparatus and procedure for the CO_2 solubility measurement at atmospheric pressure were described elsewhere [19]. The CO_2 solubility per mole of IL α_{CO2} was presented as $\alpha_{CO2} = (w_{CO2}/M_{CO2})/(w_{IL}/M_{IL})$. M_1 and M_2 stand for the molar masses of CO_2 and carboxylate ILs. The CO_2 pressure p_1 was 0.10 MPa, and the temperature T was kept constant within ±0.1 K. The uncertainty of α_1 is estimated to be less than 0.01. After the CO_2 solubility measurement, the IL solution was again saturated with CO_2 at 313 K. The saturated solution was transferred to the viscometer (Anton Paar, Stabinger SVM 3000) using an airtight syringe to avoid air exposure. The density and viscosity were measured at 313.15 K.

3. Results and Discussion

Fig. 2 presents the densities ρ of the present ILs at atmospheric pressure. Each IL showed an ordinary temperature profile; the density decreased with the elevated temperature. 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 thermal expansion coefficient β ($=(1/V)/(\partial V/\partial T)_p$) for [P$_{444,12}$][AcO] ($6.6822 \cdot 10^{-4}$ K^{-1}) was the largest followed by those for [emim][OH-Piv] ($6.2138 \cdot 10^{-4}$ K^{-1}), [N$_{1227}$][AcO] ($6.0856 \cdot 10^{-4}$ K^{-1}), [emim][AcO] ($5.5781 \cdot 10^{-4}$ K^{-1}), and [N$_{122,6OH}$][AcO] ($5.0932 \cdot 10^{-4}$ K^{-1}). The molar volumes V_m increased in the following order: [emim][AcO] (156.11 cm^3 mol^{-1}), [emim][OH-Piv] (208.31 cm^3 mol^{-1}), [N$_{122,6OH}$][AcO] (242.59 cm^3 mol^{-1}), [N$_{1227}$][AcO] (262.13 cm^3 mol^{-1}), and [P$_{444,12}$][AcO] (482.35 cm^3 mol^{-1}). The cations with the longer alkyl chains tend to decrease the density in the present study. This

trend was reported in the earlier work [27]. The thermal expansivities of the non-functionalized ILs showed the opposite behavior. The exchange of $[N_{1227}]^+$ with $[N_{122,6OH}]^+$ increased the density and decreased the thermal expansivity. In contrast, the hydroxyl carboxylate $[OH\text{-}Piv]^-$ increased both the density and thermal expansivity of the $[emim]^+$ IL compared to $[AcO]^-$.

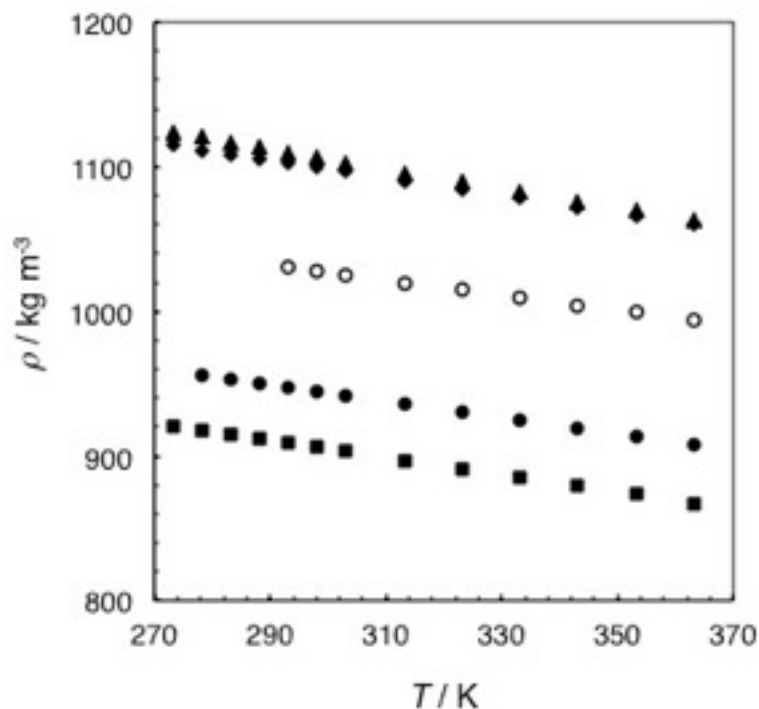**Fig. 2** Densities ρ of the present ILs at atmospheric pressure. Closed diamond, [emim][AcO] [28]; closed circle, $[N_{1227}][AcO]$; open circle, $[N_{122,6OH}][AcO]$; closed square, $[P_{444,12}][AcO]$; closed triangle, [emim][OH-Piv]. The closed diamonds overlap with the closed triangles.

Fig. 3 present the viscosities η against the temperature. The viscosity decreased with the temperature increasing. $[N_{122,6OH}][AcO]$ has the highest viscosity followed by [emim][OH-Piv], $[N_{1227}][AcO]$, $[P_{444,12}][AcO]$, and [emim][AcO] over the present temperature range. It is considered that this order is attributed to the cation size and the hydrogen bond via the hydroxy group, except for $[P_{444,12}][AcO]$. The lower viscosity of the phosphonium salt compared to the ammonium salt is also reported in the literature [29]. It was pointed out that the reason is the larger size of the charge center atom for the phosphonium cation compared to the ammonium cation. The temperature sensitivities $(-(1/\eta)/(\partial\eta/\partial T)_p)$ increased in the following order: [emim][AcO] $(4.92\cdot10^{-2}\ K^{-1})$ < $[P_{444,12}][AcO]$ $(5.80\cdot10^{-2}\ K^{-1})$ < $[N_{122,6OH}][AcO]$ $(7.71\cdot10^{-2}\ K^{-1})$ $\leq [N_{1227}][AcO]$ $(7.90\cdot10^{-2}\ K^{-1})$ < [emim][OH-Piv] $(8.32\cdot10^{-2}\ K^{-1})$. This order does not coincide with that for the density of the ILs investigated.

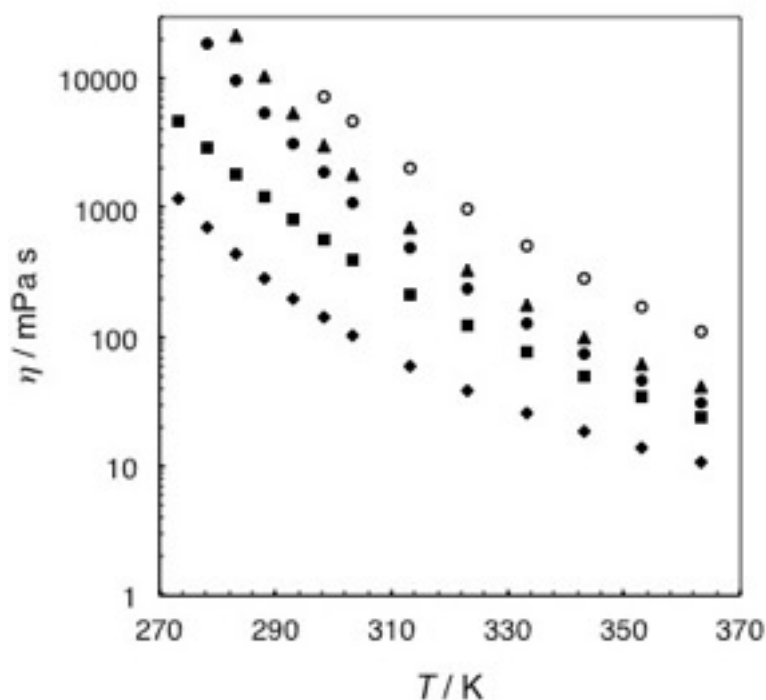**Fig. 3** Viscosities η of the present ILs at atmospheric pressure. Closed diamond, [emim][AcO] [28]; closed circle, [N$_{1227}$][AcO]; open circle, [N$_{122,6OH}$][AcO]; closed square, [P$_{444,12}$][AcO]; closed triangle, [emim][OH-Piv].

Table 1 summarizes the density ρ_{CO2}, molar volume $V_{m,CO2}$, and viscosity η_{CO2} of the CO_2-saturated carboxylates at 313.15 K. $V_{m,CO2}$ is defined as $(M_{IL}\cdot(1-x_{CO2})+(M_{IL}+M_{CO2})\cdot x_{CO2})/\rho_{CO2}$. x_{CO2} denotes the solubility (mole fraction scale) of CO_2. Table 1 lists the rate of change of the property $\Delta A = (A_{CO2} - A)/\alpha_{CO2}$ ($A=\rho$, V_m, or η) due to the CO_2 absorption. The densities and molar volumes of the IL + CO_2 mixtures were slightly higher or comparable to those of the corresponding pure ILs. $\Delta\rho_{CO2}$ decreased in the following order: [emim][AcO] > [emim][OH-Piv] > [N$_{122,6OH}$][AcO] > [P$_{444,12}$][AcO] > [N$_{1227}$][AcO]. In terms of $\Delta V_{m,CO2}$, [N$_{1227}$][AcO] showed the highest value followed by [P$_{444,12}$][AcO], [N$_{122,6OH}$][AcO], [emim][AcO], and [emim][OH-Piv]. The CO_2-saturated [N$_{1227}$][AcO], [N$_{1226,OH}$][AcO], and [emim][OH-Piv] 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. $\Delta\eta_{CO2}$ increased in the following order: [P$_{444,12}$][AcO] < [emim][AcO] < [N$_{1227}$][AcO] < [N$_{122,6OH}$][AcO] < [emim][OH-Piv].

The difference in viscosity change would arise from the kind of CO_2 adducts. As reported in our earlier study, [emim][AcO], [P$_{444,12}$][AcO], [N$_{122,6OH}$][AcO], and [emim][OH-Piv] generates acetic acid through the chemical reaction with CO_2 [15-17,30]. The formation of acetic acid decreases the viscosity of 1-butyl-3-methylimidazolium acetate ([bmim][AcO]) as

reported in the literatures [18,19]. The viscosity decrement in [emim][AcO] and [P$_{444,12}$][AcO] would arise from the formation of acetic acid as well as [bmim][AcO]. On the other hand, [N$_{122,6OH}$][AcO] and [emim][OH-Piv] became more viscous after the CO_2 absorption. We suggest that this viscosity increment is caused by the hydrogen bonding via the hydroxy group. The existence of the hydrogen bond network is supported by the smaller rate of change in the molar volumes of [N$_{122,6OH}$][AcO] and [emim][OH-Piv].

Table 1

CO_2 solubility, density, molar volume, and viscosity of the CO_2 saturated ILs at 313.15 K.

	[emim] [AcO]	[N$_{1227}$] [AcO]	[N$_{122,6OH}$] [AcO]	[P$_{444,12}$] [AcO]	[emim] [OH-Piv]
α_{CO2}	0.33$_4$	0.109	0.22$_8$	0.20$_7$	0.20$_6$
ρ/kg m^{-3}	1090.3$_4$	936.19$_9$	1019.7$_3$	897.08$_1$	1095.9$_2$
ρ_{CO2}/kg m^{-3}	1126	936.2	1039	905.5	1117
$\Delta\rho_{CO2}$ /kg m^{-3} (mol-CO$_2$)$^{-1}$	107	9.17×10^{-3}	84.5	40.7	102
V_m/cm^3 mol^{-1}	156.10$_6$	262.12$_5$	242.58$_9$	482.34$_6$	208.30$_6$
$V_{m,CO2}$/cm^3 mol^{-1}	160.9$_5$	266.7$_4$	245.9$_5$	486.5$_5$	211.1$_1$
$\Delta V_{m,CO2}$ /cm^3 mol^{-1} (mol-CO$_2$)$^{-1}$	14.5	42.4	14.8	32.0	13.6
η/mPa s	60.2$_6$	483.$_7$	$2.02_5\times10^3$	213.$_5$	719.$_1$
η_{CO2}/mPa s	60.1$_4$	657.$_1$	$3.00_7\times10^3$	211.$_4$	$2.22_1\times10^3$
$\Delta\eta_{CO2}$ /mPa s (mol-CO$_2$)$^{-1}$	-5.96×10^{-3}	1.59×10^3	4.31×10^3	-10.1	7.29×10^3

6. Conclusion

We measured the physical properties of [AcO]$^-$ based ILs before and after the CO_2 absorption to investigate the effect of cation species. The densities of [AcO]$^-$ ILs with [P$_{444,12}$]$^+$, [N$_{1227}$]$^+$, [N$_{122,6OH}$]$^+$, and [emim]$^+$ increased in this order at certain temperatures. [emim][OH-Piv] had the higher density than [emim][AcO]. [N$_{122,6OH}$]$^+$ IL has the highest viscosity followed by [N$_{1227}$]$^+$, [P$_{444,12}$]$^+$, and [emim]$^+$ over the present temperature range. The density and molar volume of the CO_2 saturated IL were slightly higher or comparable to those of the neat IL. The CO_2-saturated [emim][OH-Piv], [N$_{1227}$][AcO], and [N$_{1226,OH}$][AcO] were more viscous than the neat ILs. 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 arose from the kinds of CO_2 adducts and the functional group.

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