

Comparison between Phosphonium Docusate Ionic Liquids and Their Equimolar Mixtures with Alkanes: Temperature-Dependent Viscosity, Glass Transition, and Fragility

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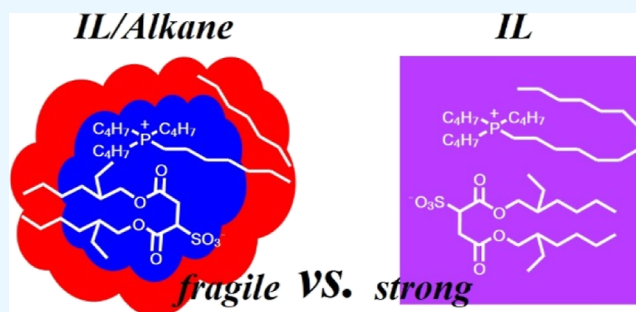


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ABSTRACT: In this study, we determined the temperature-dependent viscosities, glass transition temperatures, and fragilities of tetraalkylphosphonium docusate ionic liquids (ILs) and their equimolar mixtures with alkanes to elucidate the effects of the alkyl groups on the phosphonium cation. The target ILs were the docusate salts with tributylheptylphosphonium ($[P_{4447}][doc]$), tributyltetradecylphosphonium ($[P_{444,14}][doc]$), butyltrihexylphosphonium ($[P_{4666}][doc]$), trihexylheptylphosphonium ($[P_{6667}][doc]$), and trihexyltetradecylphosphonium cations ($[P_{666,14}][doc]$). The comparable IL/alkane mixtures were equimolar mixtures of IL and alkane with the same carbon numbers of the target ILs: $[P_{4447}][doc]$ /hexane to $[P_{6667}][doc]$; $[P_{4447}][doc]$ /heptane to $[P_{444,14}][doc]$; $[P_{444,14}][doc]$ /hexane to $[P_{666,14}][doc]$; $[P_{4666}][doc]$ /decane to $[P_{666,14}][doc]$; and $[P_{6667}][doc]$ /heptane to $[P_{666,14}][doc]$. The viscosities and glass transition temperatures of the neat ILs were higher than those of their respective IL/alkane mixtures. Based on the analysis of temperature-dependent viscosities, including a viscosity value of 10^{13} mPa·s at the glass transition temperature using the Vogel–Fulcher–Tammann equation, the neat ILs were stronger liquids than the corresponding IL/alkane mixtures. By comparing several combinations of the neat ILs and IL/alkane mixtures, we found that the larger the alkane, the more fragile the mixture.



1. INTRODUCTION

Ionic liquids (ILs) are salts with melting points lower than 373 K and unique properties depending on the ion species. Typical ILs are composed of an amphiphilic cation with a relatively long alkyl group and a compact anion.^{1–6} The alkyl group of cations plays a crucial role in the various physical properties, such as density, viscosity, and surface tension, of ILs.^{7–13} The alkyl group on the cations in ILs also affects the liquid structure at the microscopic/mesoscopic level, which was revealed by X-ray diffraction,^{14–16} as well as molecular dynamics (MD) simulations.^{17–19} The longer alkyl group of the cation provides a more segregated structure in ILs. Recently, MD simulations by Margulis and co-workers clarified the origins of the low-Q peaks of ILs: the highest one (resulting from adjacency correlations between neighboring atoms), the intermediate one (resulting from charge alternation), and the lowest one (attributed to polarity alteration).^{20–22} The alkyl group of ILs (often cations) also influences the liquid and reaction dynamics in ILs.^{23–29} Because the viscosity of IL depends on the length of the alkyl group, we expected that the liquid and reaction dynamics in ILs are influenced by the alkyl group of ILs through the viscosity. However, the process is not that straightforward. For

example, the microenvironment of the solute in an IL is often a key factor in its solvation and reaction dynamics.

As mentioned above, the alkyl group affects the liquid properties and structure, as well as the liquid and reaction dynamics in ILs, to a large extent. Now, the following questions arise: Does the alkyl group behave like a simple nonpolar environment? Does the alkyl group play any other role in the liquid properties in addition to causing a nonpolar environment on the ILs? To address these questions, we have attempted to compare an IL with an equimolar mixture of an IL with a short alkyl group and an alkane. However, this is difficult because ILs with short alkyl groups are insoluble in nonpolar solvents.

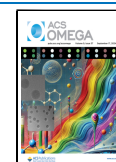
Recently, surfactant ILs (or IL-like surfactants) have been developed as surface-active materials.^{30–40} Typical surfactant ILs are composed of common cations (such as imidazolium and ammonium cations) paired with docusate anion. Sodium

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docusate (or sodium bis(2-ethylhexyl) sulfosuccinate), also known as Aerosol OT, is well-known as an anionic surfactant that forms organized systems such as reverse micelles.⁴¹ Some ILs containing the docusate anion [doc]⁻ (Figure 1) dissolve in nonpolar solvents, including alkanes, at certain relatively high concentrations^{32,36} likely due to its long alkyl groups and reverse micelle-like aggregations.

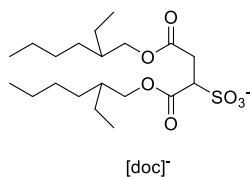


Figure 1. Chemical formula of the docusate anion.

Herein, we studied the temperature-dependent viscosity, glass transition temperature (T_g), and fragility parameter of several tetraalkylphosphonium docusate ILs and compared them with their respective mixtures of tetraalkylphosphonium docusate ILs having shorter alkyl groups and alkanes (e.g., tributyltetradecylphosphonium docusate [P_{444,14}][doc] vs an equimolar mixture of tributylheptylphosphonium docusate [P₄₄₇][doc] and heptane). In this study, tetraalkylphosphonium cations were chosen (Figure 2) because phosphonium-

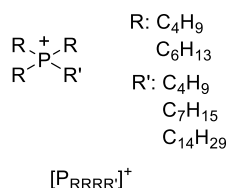


Figure 2. Chemical formulas of the phosphonium cations of ILs in this study.

based ILs are liquid for cations with a relatively long alkyl group and are less viscous than their ammonium counterparts (having the same alkyl groups).^{42–44} We systematically clarified the difference in temperature-dependent viscosities, glass transition temperatures, and fragility parameters between the ILs and the respective equimolar mixtures of ILs and alkanes. In the ILs studied here, the viscosity and glass transition temperature were large, and the fragility parameter was small compared to the respective equimolar mixtures of ILs and alkanes. Such information on the fragilities and glass transition temperatures of the present ILs and IL mixtures might be helpful for the potential applications of these liquid materials at low temperatures.

2. EXPERIMENTAL SECTION

2.1. Sample Preparations. The target ILs in this study included [doc]⁻ with tributylheptylphosphonium ([P₄₄₇]⁺), tributyltetradecylphosphonium ([P_{444,14}]⁺), butyltrihexylphosphonium ([P₄₆₆₆]⁺), trihexylheptylphosphonium ([P₆₆₆₇]⁺), and trihexyltetradecylphosphonium ([P_{666,14}]⁺) cations. The IL synthesis was based on standard procedures. The precursors of the ILs (phosphonium bromides and chlorides) were synthesized as previously established in our group.^{45,46} Anion exchange using sodium docusate (Sigma-Aldrich, >99%) was based on reported procedures.³⁷ The identities of the synthesized ILs were confirmed by ¹H NMR (see Figures

S1–S5 in Supporting Information) and elemental analysis (<0.4%). As an example, the procedures for [P₄₄₇][doc] are described as follows. 1-Bromoheptane (6.5 mL, 41.4 mmol) was added to tributylphosphine (5.0 mL, 20.3 mmol) in nitrogen atmosphere in a flask equipped with a reflux condenser and a magnetic stirrer. The solution was stirred and then heated to ca. 75 °C in an oil bath for 12 h while stirring. After the flask was allowed to cool to room temperature, high viscosity liquid was obtained. The liquid was then dissolved in acetonitrile and washed three times with hexane with twice the volume of the acetonitrile. The solution was evaporated and treated with activated carbon to remove contaminants. Subsequently, the high viscosity liquid was dried in vacuo at 100 °C for 3 days. After confirmation by ¹H NMR, tributylheptylphosphonium bromide, which was obtained by previous procedure, and sodium docusate (Aldrich, 10.2 g, 22.3 mmol) was dissolved in dichloromethane and the solution was stirred for 3 days at room temperature. The solution was allowed to stand at –20 °C for 3 days to allow solid impurities (NaBr) to settle out, and the solid was removed by passing through a filter. This procedure was repeated twice. Then, the solvent was removed with a rotary evaporator. The remaining liquid was dissolved in dichloromethane and washed with small amounts of water at least 10 times. A standard AgNO₃ test confirmed that the water fraction was bromide free. The yield was 80% (11.7 g, 16.2 mmol). Details of the synthesis procedures of the other ILs are summarized in the Supporting Information. Since extra peaks were not found in the ¹H NMR charts of the synthesized ILs within the baseline, the purity of ILs was estimated to be >99% (99.6–99.8%) from the spectral intensity of the band at $\delta = 3.27$ (dd, $J = 11.8$ and 19.6 Hz, 1H, OCCH(SO₃)CH₂CO) and the amplitude of the baseline fluctuation in the range of $\delta = 4.5$ –6.8. The water content of the ILs (liquid at room temperature) was estimated using Karl Fischer titrations using a coulometer (Hiranuma AQ-300). The results indicated that the water content was less than 150 ppm for all ILs ([P₄₄₇][doc]: 89 ppm; [P_{444,14}][doc]: 104 ppm; [P₄₆₆₆][doc]: 69 ppm; [P₆₆₆₇][doc]: 145 ppm; [P_{666,14}][doc]: 115 ppm). The water content of about 150 ppm in typical ILs could drop their viscosities by about 1% or below.⁴⁷ We thus think the effect of water on the IL viscosity in this study is negligibly small. The alkanes, hexane (Sigma-Aldrich, >99%), heptane (Kanto, >99%), and decane (Kanto, >99%), were used after drying them with molecular sieves 4A (Wako). For preparations of the equimolar mixture samples, the IL and alkane were weighed with appropriate amounts (within the error of ± 0.002 of the mole fraction in the worst case) and mixed together well.

2.2. Viscosity Measurements. The IL viscosities, η , were measured using a reciprocating electromagnetic piston viscometer (Cambridge Viscosity, ViscoLab 4100) equipped with a circulating water bath (Yamato, BB300) with the uncertainty temperature of ± 0.2 K. Five pistons with different viscosity ranges were used: 0.2–2, 0.5–10, 5–100, 50–1000, and 500–10,000 mPa·s. Standard oils (Nippon Grease, JS10, JS50, JS100, JS500, JS1000, JS2000, and JS14000) and common solvents (diethyl ether, acetone, methanol, water, benzonitrile, dimethyl sulfoxide, *t*-butanol, benzyl alcohol, ethylene glycol, and diethylene glycol)⁴⁸ were used to convert the readings to be the real η values. Four or five standard liquids among the above liquids were used to calibrate each piston. The viscosity measurements of each sample were made twice, and the values were averaged. The reproducibility of the

Table 1. Viscosities of ILs, Equimolar IL/Alkane Mixtures, and Alkanes at 298 K

IL	η^a (mPa·s)	IL/alkane	η^a (mPa·s)	alkane	η^a (mPa·s)
[P ₄₄₄₇][doc]	2883	[P ₄₄₄₇][doc]/hexane	340.2	hexane	0.293
[P _{444,14}][doc]	2032	[P ₄₄₄₇][doc]/heptane	313.3	heptane	0.391
[P ₄₆₆₆][doc]	1975	[P _{444,14}][doc]/hexane	460.3	decane	0.865
[P ₆₆₆₇][doc]	1664	[P ₄₆₆₆][doc]/decane	193.7		
[P _{666,14}][doc]	1925	[P ₆₆₆₇][doc]/heptane	287.2		

^a±5%.

viscosity measurement using each piston was estimated to be ±1.9% (the largest uncertainty piston: 500–10,000 mPa·s) from the standard oils and common solvents used for the calibration. The uncertainty of the viscosity value coming from the viscometer was ±0.5%. The combined standard uncertainty estimated from the reproducibility of viscosity measurements, the uncertainties of viscometer, measurement temperature, IL purity, and water effect on the viscosity,⁴⁷ and the batching error was ±2.2%. The expanded uncertainty at the 95% confidence level for the viscosity values was thus ±4.4% (<±5%). The viscosities of a standard IL, 1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)amide, at 290, 310, and 330 K were also measured and confirmed that the values agreed with their reference values⁴⁹ within ±5% (Table S1).

2.32.3. Differential Scanning Calorimetry Measurements. The melting points, T_m , and glass transition temperatures, T_g , of the ILs and IL/alkane mixtures were estimated using a differential scanning calorimetry (DSC) apparatus (Shimadzu, DSC-60 Plus). Approximately 10–20 mg of the dried IL was put in an aluminum pan and it was shielded by an aluminum plate. The liquid samples were cooled to 143 K and then heated to 323 or 333 K, depending on the sample T_m to eliminate their thermal histories. The T_m and T_g values were determined during the second heating process. The scanning rate was set at 5 K min⁻¹. Solid indium was used as the standard. The reproducibility of transition temperature was approximately ±1 K.

3. RESULTS

3.1. Viscosity Measurements. Table 1 lists the viscosities of the ILs and IL/alkane mixtures determined at 298 K. The viscosities of the neat alkanes at 298 K are also listed in this table. The order of the viscosities in the neat ILs studied here was: [P₆₆₆₇][doc] < [P_{666,14}][doc] < [P₄₆₆₆][doc] < [P_{444,14}][doc] ≪ [P₄₄₄₇][doc]. The viscosities of the equimolar IL/alkane mixtures were significantly lower than those of the respective neat ILs. Comparing the viscosities of the three IL/alkane mixtures with different alkanes, the mixtures containing decane showed the largest reduction in viscosity. The viscosities of the alkanes studied here are in good agreement with previously reported values.⁴⁸

Figure 3 shows the plots of η vs $1/T$ for the neat ILs. The viscosity data for the ILs at various temperatures are summarized in Table S1. Figure 3 clearly indicates that the temperature-dependent viscosities do not show an Arrhenius-type behavior. Among the five ILs, [P₄₄₄₇][doc] clearly shows the highest viscosity among the present ILs. In addition, Figure 3 shows a slightly stronger temperature dependence of the viscosity of [P₄₄₄₇][doc] than the other ILs.

In Figure 4, we compare various plots of η vs $1/T$ for the ILs and their corresponding IL/alkane mixtures. The viscosity data for the IL/alkane mixtures at various temperatures are

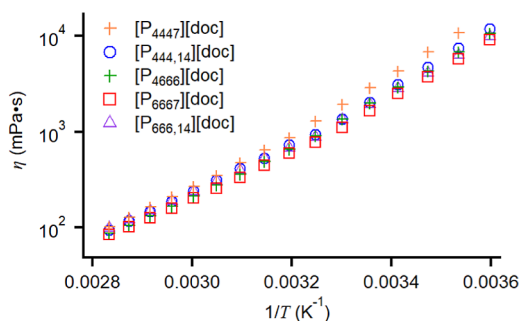


Figure 3. Plots of η vs $1/T$ for neat ILs, [P₄₄₄₇][doc] (brown plus signs), [P_{444,14}][doc] (blue circles), [P₄₆₆₆][doc] (green crosses), [P₆₆₆₇][doc] (red squares), and [P_{666,14}][doc] (purple triangles).

summarized in Table S1. Specifically, Figure 4a compares the plots of η vs $1/T$ between [P_{444,14}][doc] and [P₄₄₄₇][doc]/heptane, as well as [P_{666,14}][doc] and [P₄₆₆₆][doc]/decane and [P₆₆₆₇][doc]/heptane. The goal was to see the effect of a long alkyl group on the cation on the temperature-dependent viscosity. Figure 4b compares the plots for [P₆₆₆₇][doc] and [P₄₄₄₇][doc]/hexane together with [P_{666,14}][doc] and [P_{444,14}][doc]/hexane to elucidate the effect of three short alkyl groups on the cation on the temperature-dependent viscosity. Figure 4c compares the plots for [P_{666,14}][doc] with [P_{444,14}][doc]/hexane, [P₆₆₆₇][doc]/heptane, and [P₄₆₆₆][doc]/decane.

As shown in Figure 4a–c, the viscosity of the neat IL was much higher than that of the respective IL/alkane mixture(s). The reduction in the viscosity of the equimolar IL/alkane mixture was larger overall in the larger (or longer) alkane. Additionally, the temperature dependence of the viscosity of the neat IL was significantly different from those of the respective IL/alkane mixture(s). Furthermore, the temperature-dependent viscosity of each IL/alkane mixture is unique, but it appears that the alkanes substantially influence the temperature dependence of the viscosity (Figure 4c).

3.2. DSC Measurements. Figure 5a,b show the DSC charts of the neat ILs and the IL/alkane mixtures, respectively. All neat ILs showed a glass transition. The IL/alkane mixtures also became glass, but the DSC chart of [P₄₆₆₆][doc]/decane showed a glass transition at 187 K and a melting process at 236 K. Because the melting point of [P₄₆₆₆][doc]/decane is close to that of the neat decane (vide infra, 242 K), the large volume fraction of decane might tend to a larger heterogeneity and thus a solidification than the equimolar mixtures with hexane and heptane. The glass transition temperature and melting point were determined by the intersection of the two tangent lines. Table 2 lists the glass transition temperatures of the ILs and IL/alkane mixtures. The glass transition temperature for the neat ILs becomes slightly lower with the ILs that have a longer alkyl group. Compared with [P_{666,14}]⁺ based-ILs with the other common anions, such as bis-(trifluoromethylsulfonyl)amide, dicyanamide, tricyanometha-

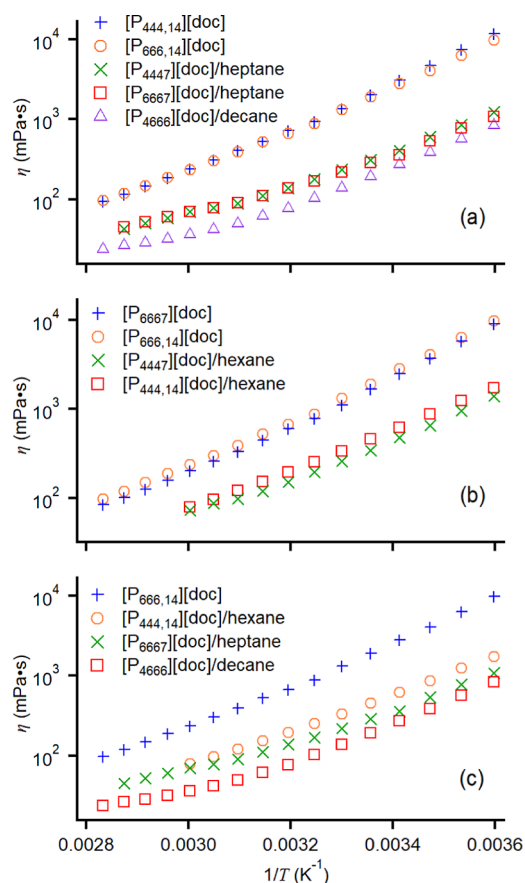


Figure 4. Arrhenius plots of η vs $1/T$ for (a) $[P_{444,14}][doc]$ (blue plus signs), $[P_{666,14}][doc]$ (brown circles), $[P_{4447}][doc]/heptane$ (green crosses), $[P_{6667}][doc]/heptane$ (red squares), and $[P_{4666}][doc]/decane$ (purple triangles), (b) $[P_{6667}][doc]$ (blue plus signs), $[P_{666,14}][doc]$ (brown circles), $[P_{4447}][doc]/hexane$ (green crosses), and $[P_{444,14}][doc]/hexane$ (red squares), and (c) $[P_{666,14}][doc]$ (blue plus signs), $[P_{444,14}][doc]/hexane$ (brown circles), $[P_{6667}][doc]/heptane$ (green crosses), and $[P_{4666}][doc]/decane$ (red squares).

nide, and chloride, the glass transition temperature of $[P_{666,14}][doc]$ is about 10–30 K low.⁵⁰ This can be accounted for by the long alkyl groups of $[doc]^-$. The IL/alkane mixtures showed lower glass transition temperatures than the respective neat ILs. The neat alkanes showed only the melting process in the DSC charts with the same temperature range as Figure 5a,b (Figure S6). The melting points of the hexane, heptane, and decane were 177, 182, and 242 K, respectively. These values were very close to the standard values in the CRC Handbook.⁴⁸

4. DISCUSSION

4.1. Effects of Alkyl Group in Neat ILs. It is well-known that the viscosity of common simple monocationic ILs, such as 1-alkyl-3-methylimidazolium-, *N*-alkylpyridinium-, and *N*-alkyl-*N*-methylpyrrolidinium-based ILs, depends on the alkyl group; the longer the alkyl group, the larger is the viscosity.^{1,7–10,12,13} However, the present phosphonium docusate ILs do not follow this trend. As shown in Table 1, the viscosity of ILs with shorter alkyl groups is essentially higher than that of ILs with longer alkyl group(s): $[P_{4447}][doc] > [P_{444,14}][doc]$, $[P_{4666}][doc] \approx [P_{666,14}][doc] > [P_{6667}][doc]$, and $[P_{4447}][doc] > [P_{6667}][doc]$. $[P_{4666}][doc]$, $[P_{6667}][doc]$, and $[P_{666,14}][doc]$ do not fit the general pattern. Notably, the

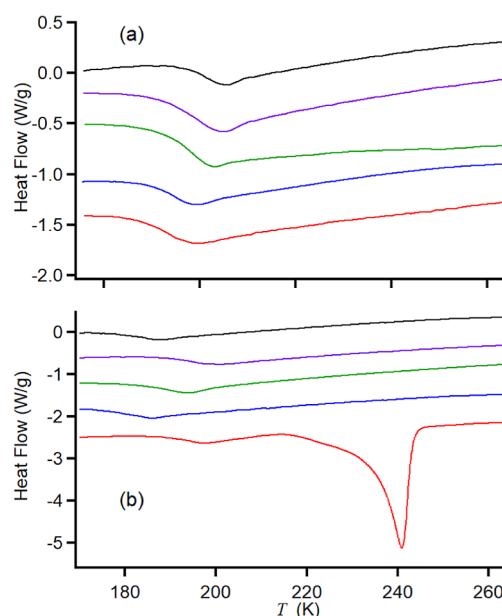


Figure 5. DSC charts of (a) neat ILs ($[P_{4447}][doc]$: black; $[P_{444,14}][doc]$: purple; $[P_{4666}][doc]$: green; $[P_{6667}][doc]$: blue; $[P_{666,14}][doc]$: red) and (b) IL/alkane mixtures ($[P_{4447}][doc]/heptane$: black; $[P_{4447}][doc]/hexane$: purple; $[P_{444,14}][doc]/hexane$: green; $[P_{6667}][doc]/heptane$: blue; $[P_{4666}][doc]/decane$: red). Offsets are given to clarify each trace.

Table 2. Glass Transition Temperature T_g of ILs and IL/Alkane Mixtures

IL	T_g^a (K)	IL/alkane	T_g^a (K)
$[P_{4447}][doc]$	197	$[P_{4447}][doc]/hexane$	183
$[P_{444,14}][doc]$	195	$[P_{4447}][doc]/heptane$	183
$[P_{4666}][doc]$	193	$[P_{444,14}][doc]/hexane$	183
$[P_{6667}][doc]$	189	$[P_{4666}][doc]/decane$	187
$[P_{666,14}][doc]$	188	$[P_{6667}][doc]/heptane$	173

^a ± 1 K.

viscosity of tetrabutylphosphonium docusate at 298 K is 4141 mPa·s, which is even higher than that of $[P_{4447}][doc]$.⁴⁰

The viscosities of the phosphonium ILs did not exhibit a simple dependence on the alkyl group, unlike typical ILs such as 1-alkyl-3-methylimidazolium-, *N*-alkylpyridinium-, and *N*-alkyl-*N*-methylpyrrolidinium-based ILs.^{1,7–10,12,13} However, some phosphonium-based ILs with cations that have a relatively long alkyl group (larger than the butyl group) also show such a viscosity trend.^{50,51} This complicated viscosity behavior in phosphonium-based ILs is attributed to the morphology, symmetry, and packing efficiency of the cation.⁵⁰ In addition, the larger ion volume and the greater flexibility of alkyl group conformation can influence the reduction in the viscosity of these ILs.

The trend of the glass transition temperatures of the present ILs is clear; that is, the longer alkyl group provides the lower glass transition temperature (Table 2). Considering the trend of the viscosities of the ILs, the less viscous IL seems to be the lower glass transition temperature overall. Thus, the mobility in the ILs likely influences the glass transition. The reason for $[P_{666,14}][doc]$, which shows a higher viscosity than $[P_{6667}][doc]$, shows the lowest glass transition temperature is likely due to a greater number of degrees of freedom of the conformations of the alkyl groups.

When the viscosity of glass-forming liquids does not exhibit the Arrhenius behavior, the Vogel–Fulcher–Tammann (VFT) equation^{52–55} is often used. The VFT equation is given by

$$\eta(T) = \eta_0 \exp\left(\frac{DT_0}{T - T_0}\right) \quad (1)$$

where T is the temperature, η_0 is the reference viscosity at which the argument of the exponential term is zero, D is a fragility-related parameter (inversely proportional to the fragility),^{56,57} and T_0 is the characteristic temperature at which the viscosity diverges. T_0 and η_0 are often located far away from the measured viscosity and temperature ranges, and thus the fit parameters simply obtained by eq 1 include a certain uncertainty. However, Angell and co-workers proposed that consistent VFT parameters from temperature-dependent shear viscosity data within a limited temperature range could be obtained by VFT fits incorporating a shear viscosity value of 10^{13} mPa·s at the glass transition temperature.⁵⁸ The logarithmic form of eq 1 ($\ln(\eta(T)) = \ln(\eta_0(T)) + [DT_0/(T - T_0)]$) was used to fit the data to properly manage the deviations across several orders of magnitude in η (a few mPa·s at high temperature range to 10^{13} mPa·s at the glass transition point). Figure 6 shows the semilogarithmic plots of η vs T together with the η value of 10^{13} mPa·s at T_g for the neat ILs. The fit parameters are listed in Table 3.

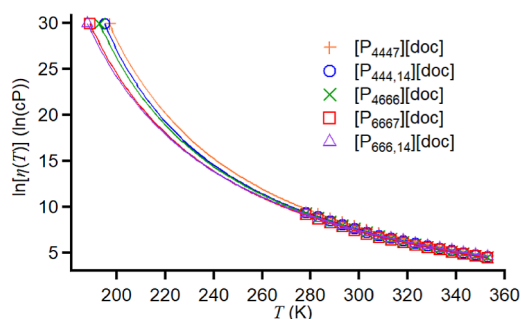


Figure 6. (a) Temperature-dependent viscosities with the viscosity value of 10^{13} mPa·s at the glass transition temperature for neat ILs, $[P_{4447}][doc]$ (brown plus signs), $[P_{444,14}][doc]$ (blue circles), $[P_{4666}][doc]$ (green crosses), $[P_{6667}][doc]$ (red squares), and $[P_{666,14}][doc]$ (purple triangles). Fits by the VFT function are also shown by the respective colored lines in the figure.

Table 3. VFT Fit Parameters for ILs and IL/Alkane Mixtures

	$\ln(\eta_0 \text{ (mPa}\cdot\text{s)})^a$	D^b	$T_0^c \text{ (K)}$
$[P_{4447}][doc]$	−5.176	15.4	137
$[P_{444,14}][doc]$	−4.374	13.6	140
$[P_{4666}][doc]$	−4.860	15.1	135
$[P_{6667}][doc]$	−4.943	16.2	129
$[P_{666,14}][doc]$	−4.668	16.2	128
$[P_{4447}][doc]/hexane$	−3.576	11.0	138
$[P_{4447}][doc]/heptane$	−2.761	9.32	142
$[P_{444,14}][doc]/hexane$	−3.734	11.8	135
$[P_{4666}][doc]/decane$	−3.423	8.84	148
$[P_{6667}][doc]/heptane$	−2.956	11.5	128

^a ±8%. ^b ±5%. ^c ±1%.

The liquid fragility is proportional to D^{-1} ,^{56,57} and thus, a larger D value denotes a stronger liquid and a smaller D value a

weaker liquid. The fragility is the degree to which the temperature-dependent viscosity deviates from Arrhenius behavior: Fragile liquids show a larger deviation from Arrhenius behavior, and strong liquids show a more Arrhenius behavior.^{56,57} Thus far, some trends of the D parameter with respect to the ion structure (or ion species) of IL have been revealed. For example, a longer alkyl group of cations provides a stronger liquid in 1-alkyl-3-methylimidazolium hexafluorophosphates.^{5,9} The D parameters of bis-(trifluoromethylsulfonyl)amide salts with butyldiethylmethylammonium and triethyloctylammonium cations were 10.26 and 7.715, respectively.⁶⁰ This study has also revealed that *N*-butylpyridinium bis(trifluoromethylsulfonyl)amide possess a lower D parameter (4.159) than 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)amide (5.664) and *N*-butyl-*N*-methylpyrrolidinium bis(trifluoromethylsulfonyl)amide (6.458).⁶⁰ When 1-methyl-3-propylimidazolium bis(trifluoromethylsulfonyl)amide and 1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)amide are compared with their respective dicationic ILs (e.g., 1,6-bis(3-methylimidazolium-1-yl)hexane bis(trifluoromethylsulfonyl)amide and 1,12-bis(3-methylimidazolium-1-yl)dodecane bis(trifluoromethylsulfonyl)amide), the D parameters of the dicationic ILs are approximately 5% smaller than those of the respective monocationic ILs.⁶¹ Comparing benzyl and cyclohexylmethyl groups in 1-alkyl-3-methylimidazolium, *N*-alkyl-*N*-methylpyrrolidinium, and *N*-pyridinium bis(trifluoromethylsulfonyl)amides showed a smaller D parameter in the benzyl group substituted ILs compared with the respective cyclohexylmethyl group substituted ILs.⁶² Comparing the substitution effect from an alkyl group with its respective group in cations showed that the D parameter was lower in bis(fluoromethylsulfonyl)amide and bis(trifluoromethylsulfonyl)amide salts.^{63,64} On the other hand, the D parameter of 1-(2-methoxyethyl)-1-methylpyrrolidinium cyclohexafluoropropane-1,3-bis(sulfonyl)amide was slightly higher than that of *N*-butyl-*N*-methylpyrrolidinium cyclohexafluoropropane-1,3-bis(sulfonyl)amide.⁶³ These results indicate that the combination of cation and anion intricately affects the fragility of ILs. Tetraalkylphosphonium ILs showed smaller D parameters than comparable tetraalkylammonium (having the same alkyl groups) ILs.^{45,60}

On examination of the D parameters of the present five neat ILs, it is less certain whether the differences in the alkyl groups of the phosphonium cations show a liquid fragility trend. But the data seem to suggest that the $[P_{666y}][doc]$ is a little stronger than the comparable $[P_{444y}][doc]$ (y is the same alkyl group). The trends observed for $[P_{444y}][doc]$ and $[P_{666y}][doc]$ are qualitatively consistent with the results of 1-alkyl-3-methylimidazolium hexafluorophosphates⁵⁹ and tetraalkylammonium bis(trifluoromethylsulfonyl)amides.⁶⁰ However, the length of the alkyl group denoted by y does not show a consistent effect on the liquid fragility in the $[P_{444y}][doc]$ and $[P_{666y}][doc]$. Because the viscosities of the present ILs (the values at 298 K are shown in Table 1) do not show a clear pattern, the liquid fragility might be strongly influenced by the viscosity (or fluidity) rather than the glass transition temperature, which shows clear x - and y -dependence of T_g in $[P_{xxyy}][doc]$ (Table 2).

4.2. Neat IL versus IL/Alkane Mixture. Comparisons of the viscosities of the IL and its respective equimolar IL/alkane mixture showed a substantial reduction in the mixture, as shown in Figure 4. The viscosity ratios at 298 K of the pairs of

[P_{444,14}][doc] and [P₄₄₄₇][doc]/heptane, [P₆₆₆₇][doc] and [P₄₄₄₇][doc]/hexane, [P_{666,14}][doc] and [P_{444,14}][doc]/hexane, [P_{666,14}][doc] and [P₆₆₆₇][doc]/heptane, and [P_{666,14}][doc] and [P₄₆₆₆][doc]/decane are 6.49, 4.90, 4.18, 6.70, and 9.94, respectively (Table 1). This indicates that the larger alkane in the equimolar mixture decreases the viscosity more, but the trends of the viscosity and dispersive force of the neat alkanes are opposite (Table 1). Thus, the dilution effect by the nonpolar solvent is dominant in the reduction of the viscosity of the IL.

Regarding the glass transition temperatures, the alkane dependence on the lowering of the glass transition temperature was also observed (Figure 5 and Table 2), but the trend was different from the viscosity. The difference in the glass transition temperatures of the pairs of [P_{444,14}][doc] and [P₄₄₄₇][doc]/heptane, [P₆₆₆₇][doc] and [P₄₄₄₇][doc]/hexane, [P_{666,14}][doc] and [P_{444,14}][doc]/hexane, [P_{666,14}][doc] and [P₆₆₆₇][doc]/heptane, and [P_{666,14}][doc] and [P₄₆₆₆][doc]/decane are 12, 6, 5, 15, and 1 K, respectively (Table 2). Namely, heptane decreases the glass transition temperature the most, hexane is in the middle, and decane decreases a little. The difference in the reduction of the glass transition temperatures between hexane and heptane might be attributed to the odd–even effect in the melting point of alkane. Since the melting point of heptane is lower than that of hexane, this could influence the glass transition temperature of the IL. The tiny reduction in the glass transition temperature of the [P₄₆₆₆][doc]/decane might come from the segregation. As shown in Figure 5, the DSC chart of [P₄₆₆₆][doc]/decane clearly showed both glass transition and melting processes. Because the melting point of [P₄₆₆₆][doc]/decane is close to that of neat decane, the glass transition temperature is essentially attributed to [P₄₆₆₆][doc].

Figure 7 shows the semilogarithmic plots of η vs T together with the η value of 10^{13} mPa·s at T_g for the neat ILs and their respective IL/alkane mixtures. The fits by the VTF equation are also shown in the figure. The fit parameters are listed in Table 3. Figure 7 shows that the curvatures of the IL/alkane mixtures are larger than those of comparable neat ILs. As shown in Table 3, the D parameters of the IL/alkane mixtures were smaller than those of the neat IL. Therefore, the IL/alkane mixtures were more fragile than the neat ILs, indicating that the alkyl groups on the phosphonium cations play a role in liquid fragility other than just the nonpolar environment of the ionic (polar) region.

Regarding the effect of the alkyl group y in [P_{xyxy}][doc] on the D parameter, Figure 7a and Table 3 indicate that the effects on reducing the D parameter value are similar on neat ILs and IL/alkane mixtures when the alkane is the same: 4.1 in [P_{444,14}][doc] \rightarrow [P₄₄₄₇][doc]/heptane and 4.5 in [P_{666,14}][doc] \rightarrow [P₆₆₆₇][doc]/heptane. In addition, we observed that longer alkanes in the IL/alkane mixtures reduce the D parameter more: 4.5 in [P_{666,14}][doc] \rightarrow [P₆₆₆₇][doc]/heptane and 7.36 in [P_{666,14}][doc] \rightarrow [P₄₆₆₆][doc]/decane.

The results of the effect of the alkyl group x in [P_{xyxy}][doc] on the D parameter (Figure 7b and Table 3) showed that the magnitudes of the reductions in the D parameters from the neat IL to the IL/alkane mixtures are also similar when the alkane is the same: 5.2 in [P₆₆₆₇][doc] \rightarrow [P₄₄₄₇][doc]/hexane and 4.4 in [P_{666,14}][doc] \rightarrow [P_{444,14}][doc]/hexane.

Comparison of the D parameters of [P_{666,14}][doc] and [P_{444,14}][doc]/hexane, [P₄₆₆₆][doc]/decane, and [P₆₆₆₇][doc]/heptane shows the effect of the reduction in the D value from

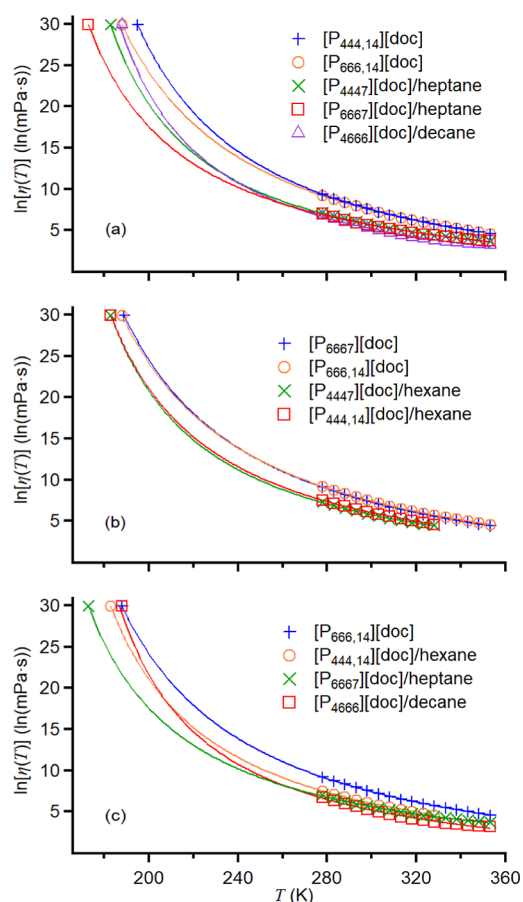


Figure 7. Temperature-dependent viscosities with the viscosity value of 10^{13} mPa·s at the glass transition temperature for IL/alkane mixtures, (a) [P_{444,14}][doc] (blue plus signs), [P_{666,14}][doc] (brown circles), [P₄₄₄₇][doc]/heptane (green crosses), [P₆₆₆₇][doc]/heptane (red squares), and [P₄₆₆₆][doc]/decane (purple triangles), (b) [P₆₆₆₇][doc] (blue plus signs), [P_{666,14}][doc] (brown circles), [P₄₄₄₇][doc]/hexane (green crosses), and [P_{444,14}][doc]/hexane (red squares), and (c) [P_{666,14}][doc] (blue plus signs), [P_{444,14}][doc]/hexane (brown circles), [P₆₆₆₇][doc]/heptane (green crosses), and [P₄₆₆₆][doc]/decane (red squares). Fits by the VTF function are also shown by the respective colored lines in the figure.

the IL and its respective IL/alkane mixture is almost the same in [P_{444,14}][doc]/hexane and [P₆₆₆₇][doc]/heptane. But [P₄₆₆₆][doc]/decane shows the larger reduction effect on the D parameter. On the basis of these comparisons (Figure 7a–c), we can conclude that the reduction of the D value from the IL to the IL/alkane mixture depends on the volume fraction of the alkane. It might be worth reminding that [P₄₆₆₆][doc]/decane showed both the glass transition and melting processes, but the other IL/alkane mixture systems indicated only the glass transitions. Because the melting point observed in [P₄₆₆₆][doc]/decane is close to that of the neat decane, the docusate ILs easily aggregate in alkane, and a larger alkane makes a clearer segregation structure in the mixtures. This heterogeneous nature may cause a reduction in liquid fragility.

5. CONCLUSIONS

In this study, we compared the temperature-dependent viscosities, glass transitions, and fragilities of [P₄₄₄₇][doc], [P_{444,14}][doc], [P₄₆₆₆][doc], [P₆₆₆₇][doc], and [P_{666,14}][doc]. Alkyl groups affect the temperature-dependent viscosities, glass

transitions, and fragilities of the docusate ILs. The viscosity and glass transition temperature of the phosphonium ILs with shorter alkyl groups are essentially higher than that of ILs with longer alkyl group(s). We also studied their respective equimolar IL/alkane mixtures: [P₄₄₄₇][doc]/hexane; [P₄₄₄₇][doc]/heptane; [P_{444,14}][doc]/hexane; [P₄₆₆₆][doc]/decane; [P₆₆₆₇][doc]/heptane. Essentially, the viscosities and glass transition temperatures of the IL/alkane mixtures were lower than those of their respective neat ILs. The fragility-related parameter *D*, estimated from the VFT equation fit, clearly showed that the IL/alkane mixtures were more fragile than their respective neat ILs. This indicated that the alkyl groups of the phosphonium cations play a role in the liquid fragility other than just the nonpolar environment of the ionic (polar) region. In addition, we observed that the reduction in the *D* parameter from the IL to the IL/alkane mixture depended on the size of the alkane: the larger the alkane, the lower the *D* parameter (more fragile). The observations, lowering the viscosity, decreasing the glass transition temperature, and more fragile nature of the equimolar IL/alkane mixtures than the comparable IL in this study suggest that IL/alkane mixtures would be useful for cryogenic application. Studies using X-ray scattering and spectroscopic techniques are promising to provide further insights into molecular-level aspects.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsomega.4c04681>.

Synthesis procedures and assignments of the ILs, viscosity data of the ILs, IL/alkane mixtures, and alkanes, and DSC charts of the neat alkanes (PDF)

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Notes

The authors declare no competing financial interest.

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