Solubilities of Small Hydrocarbons, Viscosities of Diluted Tetraalkylphosphonium Bis(2,4,4-trimethylpentyl) Phosphinates

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Tetraalkylphosphonium bis(2,4,4-trimethylpentyl)phosphinates show large solubilities for methane, ethane, ethylene, and propane. In these ionic liquids, solubilities of ethane are larger than those of ethylene. Therefore, these ionic liquids may be useful solvents for separation of ethane and ethylene; because the vapor pressure of ethylene is higher than that of ethane, the relative volatility ethylene/ethane is enhanced. However, the viscosities of these ionic liquids are too high for an industrial process. Low-viscosity 1-butyl-3-H-imidazolium acetate([BHMIM][AC]) is a suitable diluent for reducing the large viscosities of trihexyl tetradecylphosphonium bis(2,4,4-trimethylpentyl) phosphinate ([P(14)666][TMPP]) and tetrabutylphosphonium bis(2,4,4-trimethylpentyl) phosphinate ([P4444][TMPP]). Addition of 20 wt % [BHMIM][AC] gives a dramatic drop in the viscosities of these ionic liquids. Mixtures of [P(14)666][TMPP] or [P4444][TMPP] with 20 or 50 wt % [BHMIM][AC] show high solubilities for the four solutes when compared with those in other ionic liquids. In these mixtures, the solubility for ethane is higher than that for ethylene. © 2014 American Institute of Chemical Engineers *AIChE J*, 60: 2607–2612, 2014

Keywords: solubility, density, viscosity, phosphonium-based ionic liquids, diluent, mixtures of ionic liquids

Introduction

Because of their negligible vapor pressure, nonflammability, and chemical stability,[1–3] ionic liquids are potential substitutes for conventional solvents for an absorption-based separation process. Gas solubilities in ionic liquids are important for designing separation process. The solubilities of small hydrocarbons in ionic liquids have been investigated by several authors, for example, by Finotello et al.[4] who studied the solubilities of methane in [emim][Tf2N], [emim][BF4], [hmim][Tf2N], and [mmim][MeSO4] as a function of temperature from 298 to 343 K; by Jacquemin et al.[6] who presented the solubilities of ethane and methane in [BMIM][PF6] as a function of temperature between 283 and 343 K; by Lee et al.[5] who presented the solubilities of propane and propylene in [bmim][Tf2N] from 280 to 340 K. Earlier,[7] we found that ionic liquid trihexyl tetradecylphosphonium bis(2,4,4-trimethylpentyl) phosphinate ([P(14)666][TMPP]) showed solubilities for small hydrocarbons (C = 1, 2, 3) higher than those in other ionic liquids. Solubilities for paraffins are higher than those of the corresponding olefins, contrary to solubilities in conventional ionic liquids. With these advantages, [P(14)666][TMPP] may be a good solvent for storage or separation of small

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hydrocarbons. Because, at a fixed temperature, the vapor pressure of an olefin is higher than that of its corresponding paraffin, this ionic liquid enhances the separation factor. However, the viscosity of [P(14)666][TMPP] (1004 cP at 298 K) is too high for an industrial process.[8] Hoping that the viscosity may fall with decreasing length of alkyl chains on the cations,[9,10] we custom-synthetized three other tetraalkylphosphonium bis(2,4,4-trimethylpentyl) phosphinate ionic liquids with alkyl chains on the cations shorter than those in [P(14)666][TMPP].[11] However, the viscosities of these ionic liquids are also very high,[7] although they also show high solubilities for small hydrocarbons.[12,13]

The viscosities of ionic liquids can be reduced by adding water or conventional solvents, for example, monoethanolamine or acetone.[14] But these diluents have low boiling points or they may have unfavorable flammability and corrosivity. For dilution, we prefer to use a high-boiling ionic liquid with low viscosity because an ionic liquid is more stable than conventional solvents and shows high solubility for small hydrocarbons. A good diluent is 1-butyl-3-H-imidazolium acetate ([BHMIM][AC]) because it has a low viscosity (6.6 cP at 298 K) and because it shows high solubility for ethane and ethylene.[15]

In this work, we report viscosities of mixtures of [P4444][TMPP] and [BHMIM][AC] from 298 to 343 K at atmospheric pressure. We also present solubilities for methane, ethane, ethylene, and propane in mixtures of [P(14)666][TMPP] or [P4444][TMPP] with 20 or 50 wt % [BHMIM][AC] and in pure [BHMIM][AC] from 298 to 324 K up to 5 MPa.

Experimental

Methane, ethane, ethylene, and propane were purchased from Praxair with purities ≥99.9%. [P(14)666][TMPP], [P4444][TMPP], and [BHMIM][AC] were purchased from Ionic Liquid Technologies (Io-Li-Tec); their purities are higher than 95, 97, and 98%, respectively. The ionic liquids were further purified by drying at 373 K for 24 h under vacuum. After drying, water contents of ionic liquids were measured using the Karl-Fischer method (Aquaastar C2000 Titrator). Water contents are less than 0.6 wt %. Chloride contents in [P(14)666][TMPP], [P4444][TMPP], and [BHMIM][AC] are less than 2810, 1000, and 7200 ppm, respectively. Bromide contents in [P(14)666][TMPP] and [BHMIM][AC] are less than 8030 and 3540 ppm, respectively; no bromide was detectable in [P4444][TMPP] as reported by Ionic Liquid Technologies. The mixtures were prepared gravimetrically using a high-precision balance with uncertainty $\leq \pm 0.0001g$. Complete miscibility was observed after 48 h.

A Brookfield viscometer (model DVII + Pro) was used to measure the viscosities for pure [BHMIM][AC] and for mixtures of ionic liquids; uncertainties are within 3%. An Anton Paar vibrating-tube densimeter (model DMA 5000M) was used to measure the densities for pure [BHMIM][AC] and for mixtures of ionic liquids; uncertainties are within 0.0001 g cm^{-3}. Experimental details are given in a previous publication.[8]

The solubilities of methane, ethane, ethylene, and propane in pure [BHMIM][AC] and in mixtures of ionic liquids were measured using an isochoric saturation method; this method requires densities for the ionic liquids. A previous publication[16] gives details of experimental apparatus and procedure.

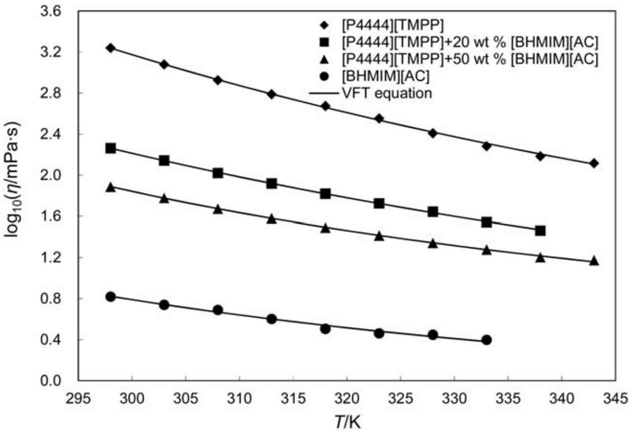

Figure 1. Viscosities for mixtures of [P4444][TMPP] and [BHMIM][AC].

Experimental viscosities for [P4444][TMPP] are from Ref. 11. Experimental results (points) are well represented by the VFT equation (lines). VFT equation is Vogel–Fulcher–Tammann (VFT) equation.[17]

Results and Discussion

Table S1 (Supporting Information) shows densities for [P4444][TMPP] with 20 or 50 wt % [BHMIM][AC] and for pure [BHMIM][AC] from 293 to 343 K at atmospheric pressure. Densities were reported earlier (Liu et al., Submitted) for [P(14)666][TMPP] with 20 or 50 wt % [BHMIM][AC] from 293 to 343 K at atmospheric pressure. Equations 1–5, respectively, give densities for pure [BHMIM][AC], [P(14)666][TMPP] + 20 wt % [BHMIM][AC], [P(14)666][TMPP] + 50 wt % [BHMIM][AC], [P4444][TMPP] + 20 wt % [BHMIM][AC], and [P4444][TMPP] + 50 wt % [BHMIM][AC]

$$\rho=-8.2073\cdot 10^{-4}T+1.2368 \tag{1}$$

$$\rho=-6.3236\cdot 10^{-4}T+1.0941 \tag{2}$$

$$\rho=-6.9782\cdot 10^{-4}T+1.1415 \tag{3}$$

$$\rho=-6.4473\cdot 10^{-4}T+1.1262 \tag{4}$$

$$\rho=-7.0855\cdot 10^{-4}T+1.1664 \tag{5}$$

where ρ is in g cm^{-3} and T is in kelvin.

Table S2 (Supporting Information) and Figure 1 present experimental viscosities for [P4444][TMPP] with 20 or 50 wt % [BHMIM][AC] from 298 to 343 K at atmospheric pressure. Figure 2 shows previously reported viscosities (Liu et al., Submitted) for [P(14)666][TMPP] with 20 or 50 wt % [BHMIM][AC] from 298 to 343 K. As expected, viscosities for binary systems [P4444][TMPP] + [BHMIM][AC] and [P(14)666][TMPP] + [BHMIM][AC] decrease with rising temperature and with rising [BHMIM][AC] content. Addition of [BHMIM][AC] gives a dramatic drop in the viscosities of [P4444][TMPP] and [P(14)666][TMPP]: at 298 K, viscosities of [P4444][TMPP] and [P(14)666][TMPP] drop by 89% (1740–183 cP) and 84% (1004–160 cP) when the [BHMIM][AC] content of is 20 wt %, respectively; by 96% (1740–77 cP) and 97% (1004–33 cP) when the [BHMIM][AC] content is 50 wt %, respectively.

The temperature dependence of the viscosities of mixtures [P4444][TMPP] + [BHMIM][AC] and [P(14)666][TMPP] + [BHMIM][AC] are well represented by the Vogel–Fulcher–Tammann (VFT) equation[17]

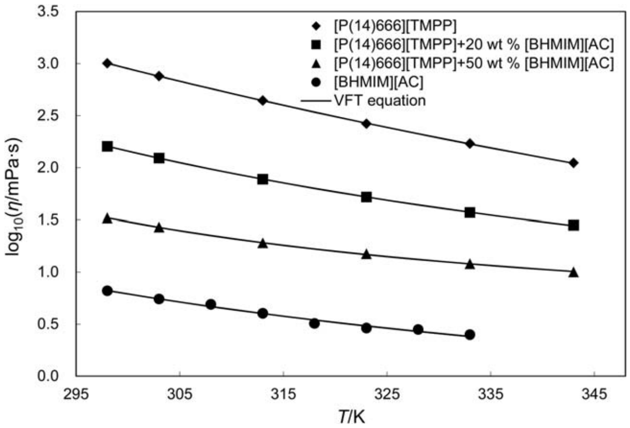

Figure 2. Viscosities for mixtures of [P(14)666][TMPP] and [BHMIM][AC].

Experiment viscosity data for [P(14)666][TMPP] with and without [BHMIM][AC] are from Ref. 8 (Liu et al., Submitted). Experimental results (points) are well represented by the VFT equation (lines). FT equation is Vogel–Fulcher–Tammann (VFT) equation.[17]

$$\eta = AT^{0.5}\exp\left(\frac{k}{T-T_0}\right) \tag{6}$$

where η is viscosity in cP, T is temperature in kelvin, k, A, and T_0 are adjustable parameters. Table S3 (Supporting Information) shows the adjustable VFT parameters for viscosities of [P4444][TMPP] or [P(14)666][TMPP] with varying [BHMIM][AC] content.

Table S4 (Supporting Information) shows solubilities for methane, ethane, ethylene, and propane in mixtures of [P4444][TMPP] or [P(14)666][TMPP] with [BHMIM][AC] from 298 to 324 K up to 5 MPa. The uncertainty in mole fraction x is less than ±5%. Figures 3, 4, S1, and S2 (Supporting Information) show P-x data for methane, ethane, ethylene, and propane in the binary systems [P4444][TMPP] + [BHMIM][AC] and [P(14)666][TMPP] + [BHMIM][AC] at 298, 313, and 323 K. As expected, the solubilities for all four solutes in mixtures of [P4444][TMPP] + [BHMIM][AC] and [P(14)666][TMPP] + [BHMIM][AC] increase with rising pressure and decrease with rising temperature. Solubilities for the four solutes in [P4444][TMPP] and [P(14)666] TMPP] decrease when the concentration of [BHMIM][AC] increases. However, these solubilities are higher than those in conventional ionic liquids.[7,12]

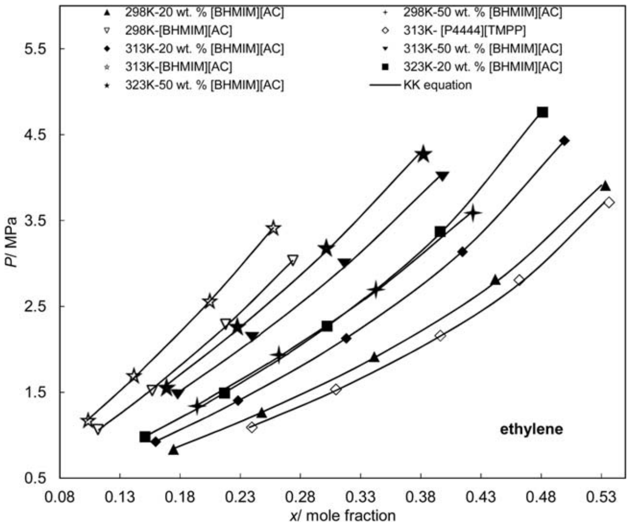

Figure 3. Solubilities for ethylene in mixtures of [P4444][TMPP] and [BHMIM][AC].

Solubilities for ethylene in [P4444][TMPP] are from Ref. 12. Experimental results (points) are well represented by the KK equation (lines). KK equation is Eq. 8.

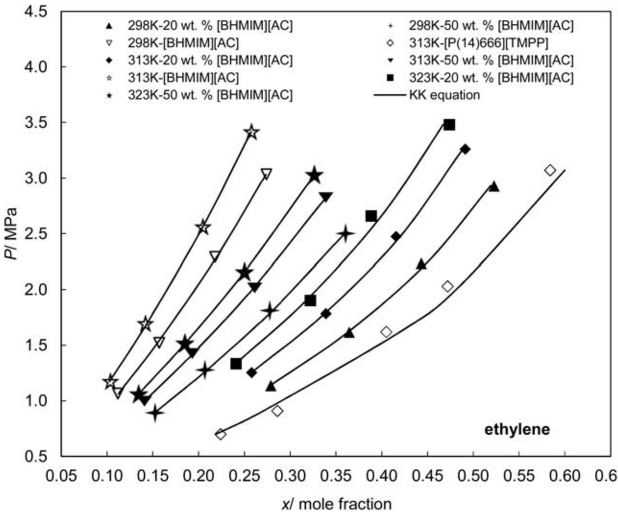

Figure 4. Solubilities for ethylene in mixtures of [P(14)666][TMPP] and [BHMIM][AC].

Solubilities for ethylene in [P(14)666][TMPP] are from Ref. 7. Experimental results (points) are well represented by the KK equation (lines). KK equation is Eq. 8.

Experimental solubilities are fitted to the Krichevsky–Kasarnovsky (KK) equation[18]: For gas 1 in Solvent 2

$$\ln\frac{f_1}{x_1} = \ln H + \frac{V_1^{\infty}(P-P_2^S)}{RT} \tag{7}$$

wheref_1, the fugacity of gas 1, is calculated using the REFPROP computer program[19]; x_1 is the mole fraction of Solute 1 in Solvent 2 at pressure P; H is Henry's constant for Solute 1 in Solvent 2 when total pressure P equals solvent vapor pressure P_2^S; $V_1^{\infty}$is the partial molar volume of solute in the solvent at infinite dilution. For an ionic liquid at normal temperature, $P_2^S$is essentially zero. Equation 7 becomes

$$\ln\frac{f_1}{x_1} = \ln H + \frac{V_1^{\infty}P}{RT} \tag{8}$$

At a fixed temperature, for a particular solute in a particular solvent, H and V_1^{∞} are obtained from the intercept and slope of a plot of $\ln(f_1/x_1)$ vs. P. Figures 3 and 4 show that the KK equation gives a good representation of experimental data. Parameters of the KK equation for the four solutes in pure [P(14)6666][TMPP] and [P4444][TMPP] are obtained from experimental data in the literature.[7,12] Table 1 shows Henry's constants and partial molar volumes at infinite dilution for methane, ethane, ethylene, and propane in mixtures of [P4444][[TMPP] or [P(14)666][TMPP] with 20 or 50 wt % [BHMIM][AC].

Table 1 shows that partial molar volumes at infinite dilution for methane, ethane, ethylene, and propane in [P(14)666] [TMPP] or [P4444][TMPP] with 20 or 50 wt % [BHMIM][AC] fall with increasing [BHMIM][AC] content, and increase in the order methane < ethylene < ethane < propane.

Table 1. Parameters of Eq. 8 for Four Solutes in Two Ionic Liquids and in Their Mixtures with [BHMIM][AC]

T/K	H/MPa	$V_1^{\infty\,\mathrm{a}}$	T/K	H/MPa	V_1^{∞}	T/K	H/MPa	V_1^{∞}	T/K	H/MPa	V_1^{∞}
	Methane			Ethane			Ethylene			Propane	
[P(14)666][TMPP]											
313	7.8	223	314	1.9	496	314	2.6	375	313	0.6	2039
333	8.6	212	333	2.4	428	333	3.2	344	333	1.0	1520
353	9.1	230	353	3.0	381	353	4.0	299	353	1.4	1195
[P(14)666][TMPP]+ 20 wt % [BHMIM][AC]											
299	13.7	80	298	2.5	384	299	3.3	297	299	0.8	2049
313	15.0	74	313	3.2	321	313	4.0	275	313	1.1	1836
323	15.9	64	323	3.9	221	323	4.6	244	323	1.4	1696
[P(14)666][TMPP]+ 50 wt % [BHMIM][AC]											
299	24.3	47	299	4.4	143	299	5.4	111	299	1.5	882
313	26.0	45	313	5.4	120	313	6.5	99	313	2.0	526
323	27.6	32	323	6.1	116	323	7.2	96	323	2.5	409
[P4444][TMPP]											
314	12.6	127	314	3.0	331	313	3.9	280	314	1.0	1544
323	13.3	125	333	3.7	341	333	4.7	272	323	1.2	1729
333	13.9	125	343	4.0	322	353	5.3	290	333	1.4	1551
[P4444][TMPP]+ 20 wt % [BHMIM][AC]											
299	16.1	110	299	3.4	184	299	4.3	189	299	1.1	1327
314	17.8	107	313	4.2	174	314	5.2	179	314	1.5	842
324	19.2	106	324	4.8	149	323	5.9	173	323	1.9	468
[P4444][TMPP]+ 50 wt % [BHMIM][AC]											
299	26	34	299	5.3	86	299	6.2	68	299	2.1	334
314	29	28	314	6.6	69	314	7.5	61	314	2.7	288
324	30	24	323	7.6	61	324	8.4	59	324	3.3	251
[BHMIM][AC]											
299	51.7	10	299	9.5	28	299	8.7	48	299	3.5	207
314	53.6	9	313	11.3	26	313	10.6	39	313	4.6	125

[a] V_1^{∞} is in cm^3 mol^{-1}.

Henry's constants are represented by[20]

$$\ln H = \frac{A}{T} + B \qquad (9)$$

where Henry's constant H is in MPa, temperature T is in kelvin, A (in kelvin) and B are adjustable parameters. Table S5 (Supporting Information) gives parameters A and B. The absolute average deviations between experimental Henry's constant and those calculated from Eq. 9 are less than 1.3%.

A high Henry's constant corresponds to a low solubility. Figure 5 shows Henry's constants for four solutes in pure solvents [P4444][TMPP], [P(14)666]TMPP], and [BHMIM][AC] and in mixtures of [P4444][TMPP] or [P(14)666]TMPP] with 20 or 50 wt % [BHMIM][AC]. Table 1 and Figure 5 show that Henry's constants for the four solutes in [P(14)666][TMPP] and [P4444][TMPP] increase with rising temperature and with rising concentration of [BHMIM][AC]. At 313 K, Henry's constants for methane, ethane, ethylene, and propane in [P(14)666][TMPP] increase by about 92, 32, 26, and 25%, respectively, when the [BHMIM][AC] content is 20 wt %, and by about 233, 184, 148, and 213%, respectively, when [BHMIM][AC] content is 50 wt %. At 313 K, with addition of 20 wt % [BHMIM][AC], Henry's constants for methane, ethane, ethylene, and propane in [P4444][TMPP] increase by about 42, 17, 16, and 10%, respectively, and by about 132, 128, 103, and 170%, respectively, when the [BHMIM][AC] content in [P4444][TMPP] is 50 wt %. At the same [BHMIM][AC] concentration, solubilities in [P(14)666][TMPP] are higher than those in [P4444][TMPP].

Figures 6 and 7 and Tables S6 and S7 (Supporting Information) show Henry's constants for ethylene in several ionic liquids[21–26] at 303 and 313 K. Mixtures of [P(14)666][TMPP] or [P4444][TMPP] with 20 wt % [BHMIM][AC] show that the solubilities for ethylene are similar to those in [N(1)888][Tf2N], [P(14)666]DCA], [P(14)666][Cl], [P(14)444][DBS], [P(14)666][Tf2N], [P(14)666][TMPP], and [P4444][TMPP]. The viscosities of these solvents are higher than 440 cP.[8,21,27] However, they show solubilities for ethylene higher than those in other types of ionic liquids. Mixtures of [P(14)666][TMPP] or [P4444][TMPP] with 50 wt % [BHMIM][AC] show solubilities for ethylene slightly lower than those in [N(1)888][Tf2N], [P(14)666]DCA], [P(14)666][Cl], [P(14)444][DBS], [P(14)666][Tf2N], [P(14)666][TMPP], and [P4444][TMPP], although they show solubilities for ethylene higher than those in other types of ionic liquids.

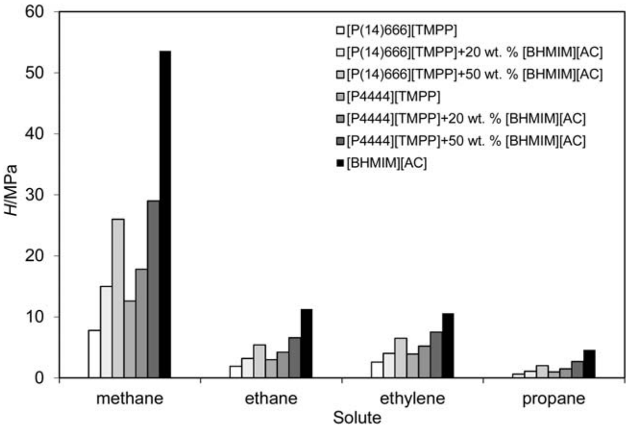

Figure 5. Henry's constants for four solutes in mixtures of ionic liquids at 313 K.

A low Henry's constant corresponds to a high solubility.

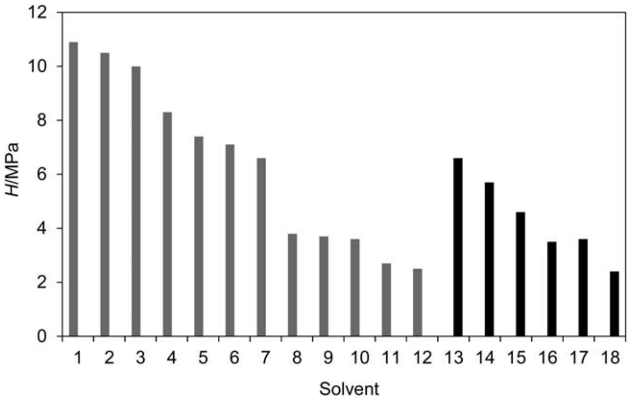

Figure 6. Henry's constants for ethylene in a variety of ionic liquids at 303K.

1:[N(4)111][Tf2N][21]; 2: [N(4)113][Tf2N][21]; 3: [N(6)111][Tf2N][21]; 4: [P2444][DEP][22]; 5: [N(10)111][Tf2N][21]; 6: [N(10)113][Tf2N][21]; 7: [N(6)222][Tf2N][21]; 8: [N(1)888][Tf2N][21]; 9: [P(14)666]DCA][22]; 10: [P(14)666][Cl][22]; 11: [P(14)444][DBS][22]; 12: [P(14)666][Tf2N][22]; 13: [P4444][TMPP]+50 wt % [BHMIM][AC]; 14: [P(14)666][TMPP]+50 wt % [BHMIM][AC]; 15: [P4444][TMPP]+20 wt % [BHMIM][AC]; 16: [P(14)666][TMPP]+20 wt % [BHMIM][AC]; 17: [P4444][TMPP][12]; 18: [P(14)666][TMPP].[7] Solvent 18 has highest solubility for ethylene. Solvents 15 and 16 have solubilities for ethylene similar to those in Solvents 8–12, 17, and 18. Solubilities for ethylene in Solvents 13, 14 are lower than those in Solvents 8–12, 17, and 18.

In earlier work,[7,12] we found that, contrary to conventional ionic liquids,[24,26] [P(14)666][TMPP] and [P4444][TMPP] show solubilities for ethane higher than those for ethylene, as indicated in Figure 8 and Table S7 (Supporting Information). The larger solubility of ethane may be useful to enhance the relative volatility ethylene/ethane, because the vapor pressure of ethylene is higher than that of ethane. Figure 8 shows that in mixtures of [P(14)666][TMPP] or [P4444][TMPP] with 20 or 50 wt % [BHMIM][AC], solubilities for ethane are higher than those for ethylene. To illustrate, at 313 K, the relative volatility ethylene/ethane ($H_{\text{ethylene}}/H_{\text{ethane}}$) in [P(14)666][TMPP] + 20 wt % [BHMIM][AC] is 1.3, whereas in [EMIM][Tf2N] it is 0.7.

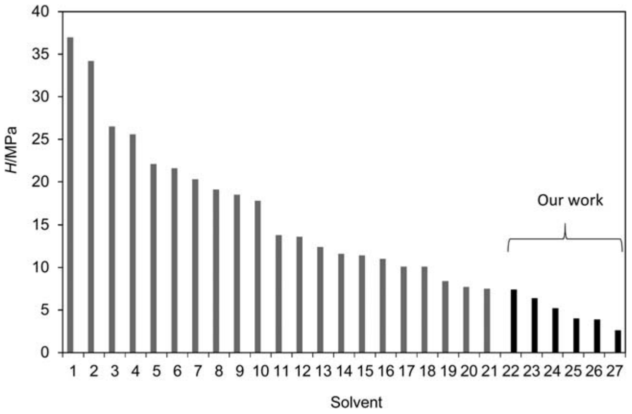

Figure 7. Henry's constants for ethylene in a variety of ionic liquids at 313 K.

1: [DMIM][MeHPO3][23]; 2: [EMIM][DCA][24]; 3: [DMIM][Me2PO4][23]; 4: [BMIM][BF4][23]; 5: [BMIM][MeSO4][23]; 6: [EMIM][CF3SO3][24]; 7: [EMIM][EtHPO3][25]; 8: [BMIM][PF6][24]; 9: [BMIM][MeHPO3][23]; 10: [BMIM][OAc][23]; 11: [BMIM][TFA][23]; 12: [BMIM][Me2PO4][23]; 13: [EMIM][Tf2N][24]; 14: [BEIM][EtHPO3][22]; 15: [BMPyrr][OAc][23]; 16: [BMIM][BuHPO3][23]; 17: [BMPyrr][BuHPO3][23]; 18: [BHMIM][AC]; 19: [BMIM][Tf2N][23]; 20: [BMPyrr][Tf2N][23]; 21: [HMPY][Tf2N][26]; 22: [P4444][TMPP]+50 wt % [BHMIM][AC]; 23: [P(14)666][TMPP]+50 wt % [BHMIM][AC]; 24: [P4444][TMPP]+20 wt % [BHMIM][AC]; 25: [P(14)666][TMPP]+20 wt % [BHMIM][AC]; 26: [P4444][TMPP][12]; 27: [P(14)666][TMPP].[7] Solvents 21–27 have solubilities for ethylene higher than those in the other solvents. Solvent 27 is best.

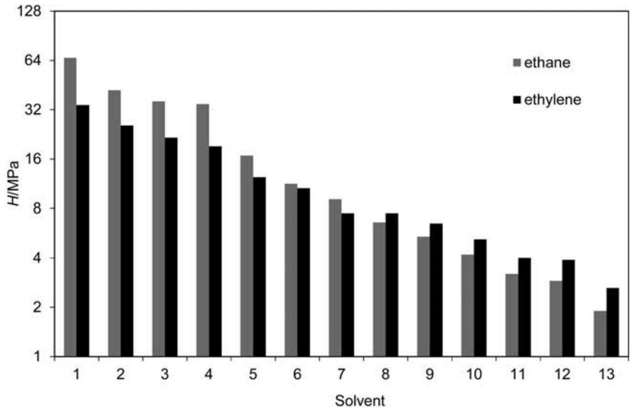

Figure 8. Henry's constants for ethane and ethylene in several ionic liquids at 313 K.

1: [EMIM][DCA][24]; 2: [EMIM][CF3SO3][24]; 3:[BMIM][PF6][24]; 4: [EMIM][Tf2N][24]; 5: [BMIM][PF4][24]; 6: [BHMIM][AC]; 7: [HMPY][Tf2N][26]; 8: [P4444][TMPP]+50 wt % [BHMIM][AC]; 9: [P(14)666][TMPP]+50 wt % [BHMIM][AC]; 10: [P4444][TMPP]+20 wt % [BHMIM][AC]; 11: [P(14)666][TMPP]+20 wt % [BHMIM][AC]; 12: [P4444][TMPP][12]; 13: [P(14)666][TMPP].[7] Highest solubilities are in Solvent 13. Solvents 8–13 show solubilities for ethane larger than those for ethylene.

Conclusions

[BHMIM][AC] is a useful diluent to reduce the large viscosities of two tetraalkyl phosphonium-based ionic liquids: [P(14)666][TMPP] and [P4444][TMPP]. Viscosities of [P(14)666][TMPP] and [P4444][TMPP] drop dramatically with addition of 20 wt % [BHMIM][AC]. With addition of 20 or 50 wt % [BHMIM][AC], [P(14)666][TMPP] and [P4444][TMPP] show high solubilities for small hydrocarbons when compared to solubilities in other ionic liquids. Mixtures of [P(14)666][TMPP] and [P4444][TMPP] with 20 or 50 wt % [BHMIM][AC] show that the solubilities for ethane are larger than those for ethylene, enhancing the relative volatility ethylene/ethane. To reduce the large viscosity of an ionic-liquid solvent, [BHMIM][AC] is a suitable diluent. The diluted ionic liquids [P(14)666][TMPP] and [P4444][TMPP] may be useful for a separation process or for storage of small hydrocarbons.

Acknowledgments

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