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A simple correlation to predict high pressure solubility of carbon dioxide in 27 commonly used ionic liquids

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ABSTRACT

Engineers often demand the availability of easy correlations without difficult and time-consuming calculations. Up till now, there has been a lack of such correlations for mixtures of CO_2 + ionic liquids. This work proposes a correlation to predict CO_2 solubility in 27 common ionic liquids. The main advantages are its simplicity and minimal input data, namely temperature and pressure. The ionic liquids investigated ranged within a variety of families, having various anions and cations. Compared with the popular engineering models of Peng–Robinson (PR) and Soave–Redlich–Kwong (SRK), the present correlation is much easier to use, yet it is also more accurate (PR, SRK and the proposed model had AARD% values of 43.5%, 44.3% and 4.9%, respectively for a total of 3073 data), even when binary interaction coefficients of PR and SRK are optimized to experimental data (AARD% values of 17.2%, 16.9% and 4.9% for PR, SRK and the proposed model, respectively).

1. Introduction

Ionic liquids (ILs) are organic salts that are liquid at, or near, room temperature. They generally consist of large asymmetric organic cations and either an organic or inorganic anion. Melting points of ionic liquids are low because of the asymmetry of the cation, while the nature of the anion has a major role to control many of the physical properties of the ionic liquids, for example, their miscibility with conventional solvents and their hygroscopicity [1]. Ionic liquids can also be task-specific compounds, since the cation and anion of the ionic liquid can be molecularly-engineered for specific physico-chemical properties for use in a variety of fields [2,3]. The most striking property of ILs is their negligible vapor pressure [4]. This suggests that ILs can replace conventional solvents with insignificant vapor emissions. Some ILs have selective solubilities for particular components in mixtures. In separation processes, such ILs are most interesting candidates where they can serve as extraction media [5]. Other fields of possible applications for ILs include: homogeneous catalysis for a variety of organic systems [6–8], electrolytes [9,10] for batteries and fuel cells, lubricants, thermo fluids, plasticizers [4,5,11]. Knowledge of the solubility and the rate of solubility (i.e. diffusion coefficients of gases at various temperatures and pressures) is important for the evaluation of ionic liquids (ILs) for potential industrial processes [12].

Mixtures of CO_2 and ILs have received particular attention due to the very high solubilities of carbon dioxide in ILs, while the ionic liquids are insoluble in the pure CO_2 phase, even at high pressures. Example applications include a range of homogeneously catalyzed systems, the use of supercritical CO_2 as a green solvent to extract organic products or contaminants from ILs, and the separation of organic liquids and water from ILs by inducing a liquid–liquid split using CO_2. Due to such great potentials, in the past few years, a growing number of experimental studies have reported the solubility of CO_2 in various ILs, and such information is becoming increasingly available in the literature [13].

However, due to the difficulties of experimental measurements and the costly nature of ILs, it is recommended to develop predictive methods for estimating the phase behavior of these kinds of systems. In recent years, many researchers attempted to model solubility in ionic liquids. For this purpose, various methods have been proposed, progressing from simple to more complex models. Researchers have used simple cubic equation of states such as the Peng–Robinson (PR) [14] and Soave–Redlich–Kwong (SRK) [15]. In these methods, the ionic liquid was considered as a whole molecule with a certain volume and cohesive energy, rather than a combination of an anion and a cation [16]. Other efforts for ionic liquid modeling included the activity coefficient models and group contribution methods. Studies investigated several excess Gibbs energy models, such as the Wilson's equation [17], the Non-Random Two-Liquid (NRTL) model [18], UNIQUAC [19], and the group contribution method of UNIFAC [20]. In addition, since some of the characteristics of ionic liquids, such as negligible vapor pressures and long alkyl chains on the cations, give them some

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Table 1
Pressure, temperature and carbon dioxide solubility range of used ionic liquids in this study.

Compound	Abbreviation	$T_{min} - T_{max}$ (K)	$P_{min} - P_{max}$ (MPa)	CO_2 Solubility (mole fraction)	ndp[a]	Ref.	Maximum experimental error margin (mole fraction)
Trihexyltetradecylphosphoniumbis(trifluoromethylsulfonyl)imide	[P14,6,6,6][Tf_2N]	292.88–375.35	0.106–72.185	0.169–0.879	210	[25,26]	±0.005
1-Butyl-1-methylpyrrolidinium trifluoromethanesulfonate	[BMP][TfO]	303.15–373.35	1.880–70.200	0.2583–0.7058	64	[25]	±0.005
1-Ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide	[emim][Tf_2N]	283.15–344.55	0.200–43.200	0.06418–0.761	107	[2,27–30]	±0.013
1-Butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide	[bmim][Tf_2N]	279.98–636.41	0.250–49.990	0.0483–0.8041	441	[1,27,31–37]	±0.0149
1-Hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide	[hmim][Tf_2N]	281.9–348.6	0.214–39.000	0.053–0.8333	136	[2,27,29,38,39]	±0.0186
1-Octyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide	[omim][Tf_2N]	297.55–344.55	0.680–34.800	0.3019–0.8456	96	[27,34]	±0.0147
1-Butyl-3-methylimidazolium dicyanamide	[bmim][DCA]	293.36–363.25	1.018–73.640	0.2–0.601	79	[34–36]	NA[b]
1-Ethyl-3-methylimidazolium trifluoromethanesulfonate	[emim][TfO]	303.85–344.55	0.800–37.800	0.2613–0.6268	55	[40]	±0.0101
1-Butyl-3-methylimidazolium trifluoromethanesulfonate	[bmim][TfO]	298.2–344.55	0.850–37.500	0.1088–0.672	87	[34,40]	±0.0087
1-Hexyl-3-methylimidazolium trifluoromethanesulfonate	[hmim][TfO]	303.85–344.55	1.250–36.300	0.3566–0.7171	68	[40]	±0.0093
1-Octyl-3-methylimidazolium trifluoromethanesulfonate	[omim][TfO]	303.85–344.55	0.680–34.000	0.2166–0.7414	65	[40]	±0.0116
1-Butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide	[BMP][Tf_2N]	283.1–373.15	0.25–62.770	0.0576–0.803	107	[33,41]	±0.005
1-Hexyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide	[HMP][Tf_2N]	303.15–373.15	1.060–47.550	0.2778–0.8105	64	[42]	±0.005
1-Octyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide	[OMP][Tf_2N]	303.15–373.15	0.510–35.920	0.2409–0.8176	72	[42]	±0.005
Trihexyltetradecylphosphonium chloride	[P14,6,6,6][Cl]	302.55–363.68	0.168–24.570	0.119–0.8	69	[26]	NA
1-(2-Hydroxy ethyl)-3-methylimidazolium tetrafluoroborate	[hemim][BF_4]	303.15–353.15	0.114–1.194	0.004–0.102	44	[43]	±0.003
1-Butyl-3-methylimidazolium acetate	[bmim][Ac]	283.1–348.2	0.010–1.999	0.063–0.455	32	[44]	±0.006
1-Butyl-2,3-dimethylimidazolium hexafluorophosphate	[BMMIM][PF_6]	283.15–323.15	0.009–1.300	0.00926–0.219	105	[28]	NA
1-Ethyl-3-methylimidazolium ethylsulfate	[emim][$EtSO_4$]	303.15–353.15	0.122–9.461	0.01–0.457	55	[12,45]	±0.002
1-Hexyl-3-methylpyridinium bis[trifluoromethylsulfonyl]imide	[H3MP][Tf_2N]	283.18–323.15	0.007–1.300	0.00958–0.376	47	[46]	NA
Triisobutylmethylphosphonium p-toluenesulfonate	[P4,4,4,1][TOS]	323.1	0.050–1.300	0.00611–0.121	28	[33]	NA
1-Ethyl-3-methylimidazolium hexafluorophosphate	[emim][PF_6]	308.14–366.03	1.490–97.100	0.104–0.619	74	[47]	NA
1-Butyl-3-methylimidazolium hexafluorophosphate	[bmim][PF_6]	282.05–363.54	0.25–73.500	0.02927–0.729	418	[28,33,42,44,48–50]	±0.013
1-Hexyl-3-methylimidazolium hexafluorophosphate	[hmim][PF_6]	298.15–363.58	0.296–94.600	0.058–0.727	112	[29,51]	±0.007
1-Butyl-3-methylimidazolium tetrafluoroborate	[bmim][BF_4]	278.47–368.22	0.250–67.620	0.03–0.6017	250	[28,33,52,53]	±0.005
1-Hexyl-3-methylimidazolium tetrafluoroborate	[hmim][BF_4]	293.18–368.16	0.540–86.600	0.103–0.703	104	[29,54]	±0.002
1-Octyl-3-methylimidazolium tetrafluoroborate	[omim][BF_4]	307.79–363.28	0.571–85.800	0.10050.7523	100	[55]	±0.001
					3073[c]		

[a] ndp is the number of data.
[b] Not available.
[c] Total number of data.