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Improved Efficiency of Ethylene/Ethane Separation Using a Symmetrical Dual Nitrile-Functionalized Ionic Liquid

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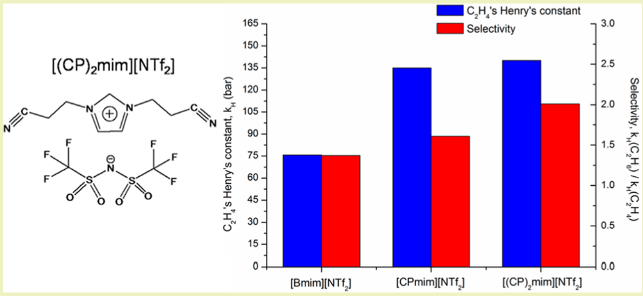
Ⓢ *Supporting Information*



ABSTRACT: As green and designable solvents, ionic liquids (ILs), have great potential in the separation of olefins and paraffins. The introduction of functional groups into ILs enhances its separation selectivity for olefin to paraffin; however, the absorption capacities of such functionalized ILs obviously decrease due to the strong polarity of the functional group. In this work, we designed a symmetrical dual nitrile-functionalized IL 1,3-dibutyronitrile-imidazolium bis((trifluoromethyl)sulfonyl)imide ($[(CP)_2im][NTf_2]$) and determined the solubility of ethylene and ethane at 303.15 K in three ILs: nonfunctionalized 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ($[Bmim][NTf_2]$), single-functionalized 1-butyronitrile-3-methylimidazolium bis((trifluoromethyl)sulfonyl)imide ($[CPmim][NTf_2]$), and dual-functionalized $[(CP)_2im][NTf_2]$. The experimental results showed that enhanced separation selectivity for ethylene/ethane could be achieved in the symmetrical dual-functionalized $[(CP)_2im][NTf_2]$ with only a slight reduction of absorption capacity. A COSMO-RS calculation was carried out to understand the underlying dissolution mechanism of ethylene and ethane in ILs and showed that the polarity of the IL and its misfit interaction with gases were the major factors in determining the solubilities of ethylene and ethane in it. In addition, a silver-containing IL was also tested because of its higher absorption capacity for olefins. It was found that the silver-containing IL was superior to any of the common ILs in the separation of ethylene/ethane, particularly $[Bmim][NTf_2]$. A simple equilibrium model was used to describe the absorption of ethylene in the silver-containing IL.

KEYWORDS: *Ionic liquids, Dual nitrile-functionalized, Absorption, π-Complexation, Symmetrical*

■ INTRODUCTION

The separation of olefin and paraffin mixtures is one of the most energy-intensive separation processes in the petrochemical industry because of the usually very small relative volatility and similar molecular sizes of olefin and paraffin. Recently, ionic liquids (ILs) have attracted great attention as alternative solvents/entrainers in absorption,[1−4] extraction,[5] and membrane[6−8] processes for olefins and paraffins. ILs have intrinsic advantages over volatile organic solvents because of their ultralow volatilities and good thermal stabilities,[12−14] which enable a relatively easy recovery without any loss under appropriate conditions and prevent cross-contamination of the gas stream. In addition, the physicochemical properties of ILs can be fine-tuned by combining the various cations and anions or even attaching specific functional groups to the common ions to improve separation efficiency.[12,15] Generally, the solubility of olefins in ILs can be enhanced by using phosphonium or ammonium ions as cations,[16,17] and it increases with lengthening of the alkyl chain of the cation.[9,18,19] However, the selectivity for olefin to paraffin in phosphonium-based ILs is very low (e.g., selectivity for 1-butene to butane is between 1.10 to 1.46[16]). Mokrushina et al.[20] screened more than 20 ILs for the propene/propane separation, and the results showed that the introduction of nitrile (−CN) functional groups into either the anion or cation (single −CN group in cation) could lead to a strongly enhanced selectivity. Domańska et al. found that 1-alkyl-3-methylimidazolium IL with SCN^- as the anion had a good selectivity for 1-hexene to hexane.[21,22] Camper et al.[10] measured the solubility of ethylene and ethane in 1-ethyl-3-methylimidazolium-based ILs with different anions. The ILs with $N(CN)_2^-$ or PF_6^- as anions showed better selectivity than the other ILs, and the selectivity values reached 1.95 and 1.81, respectively. However the solubilities of ethylene in these ILs were low[10,20−23] (Henry's constant k_H is 337 bar for $[Emim]N(CN)_2$). Zhang et al.[23] measured Henry's constant (k_H) for ethylene in several ILs by gas chromatography at infinite dilution and showed that a single −CN group substitution on the alkyl chain of the cation resulted in a remarkable decrease in the solubility of ethylene in the IL. Thus, the main challenge in using functionalized ILs for olefin and paraffin separation so far is that improved selectivity is always at the expense of decreasing capacity.[11,23,24]

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Table 1. Properties of ILs and Henry's Constants (k_H) of Ethylene and Ethane at 303.15 K in This Work and Literatures

IL	MW (g mol^{-1})	ρ (g cm^{-3})	η (mPa s)	k_H (bar)		$k_H(C_2H_6)/k_H(C_2H_4)$
				C_2H_4	C_2H_6	
[Bmim][NTf$_2$][a]	419.37	1.43[30]	40.0[30]	75.7 ± 0.5	104.4 ± 1.0	1.37
[CPmim][NTf$_2$][a]	430.35	1.51[31]	147.0	135.1 ± 0.9	218.0 ± 1.1	1.61
[(CP)$_2$im][NTf$_2$][a]	483.41	1.47	668.7	140.1 ± 0.9	282.0 ± 1.8	2.01
[Emim][NTf$_2$][b]	391.31	1.51[30]	26.7[30]	99 ± 4.2	148 ± 6.2	1.49
[Bmpy][BF$_4$][b]	237.05	1.19	147.3	164 ± 7	282.2 ± 16.9	1.72
[Bmim][MeSO$_4$][b]	250.32	1.20	160.9[34]	119.4 ± 6.8	227.4 ± 16.0	1.90
[Bmim][N(CN)$_2$][b]	205.26	1.06	24.4	200.0 ± 21.0	425.0 ± 28.0	2.12
[Bmim][SCN][b]	197.30	1.07	41.9[35]	131.4 ± 4.7	227.7 ± 14.6	1.73
[Bmpy][SCN][b]	208.32	1.06		134.2 ± 5.4	225.4 ± 11.8	1.68

[a]This work. The errors of k_H are the slope errors of the linear isotherms. [b]Literature: refs 32 and 33.

One of the main reasons for the decreasing solubility of an olefin in functionalized ILs is that by introducing functional groups the polarity of functionalized ILs is usually enhanced.[11,23] Therefore, in this work, a dual-functionalized IL (1, 3-dibutyronitrile-imidazolium bis((trifluoromethyl)-sulfonyl)imide, [(CP)$_2$im][NTf$_2$]), with two symmetrical butyronitrile groups in the cation was prepared and used for separating ethylene and ethane for the first time. It was expected that the polarity of this functionalized IL would be weaker than in the common single-functionalized ILs because of its symmetrical dual-functionalized structure. In addition, the ability of IL to recognize ethylene could be improved by increasing the number of nitrile group in the structure of IL. One reason we chose NTf_2^- as the anion is that the solubility of ethylene in NTf_2^--based ILs is relatively larger than in other ILs. The solubilities of ethylene and ethane in conventional IL ([Bmim][NTf$_2$]), with single- and dual-functionalized ILs ([CPmim][NTf$_2$], [(CP)$_2$im][NTf$_2$]) were determined at 303.15 K, with the experimental pressure in the range of 0.5−2.5 bar. The dissolution mechanism of ethylene and ethane in those ILs was investigated using the conductor-like screening model for real solvents, the (COSMO-RS) method.

Meanwhile, Ortiz et al.[19,25,26] and Galán et al.[27] have described the selective separation of olefins from their mixtures with paraffins by chemical complexation to silver ions dissolved in ILs; the silver-containing ILs showed a higher absorption capacity for olefins than the corresponding pure ILs. So, in this work, we also tested the performance of silver-containing ILs as absorbents to improve the separation of ethylene and ethane, and an absorption equilibrium model was developed to describe ethylene absorption in silver-containing ILs at different pressures.

EXPERIMENTAL SECTION

Chemicals and Reagents. Ionic liquids, [Bmim][NTf$_2$] and [CPmim][NTf$_2$], were obtained from Green Chemistry and Catalysis, LICP, CAS (China). The water mass fractions of the ILs were determined by a Karl Fischer titrator, and the values were below 0.06% in mass fraction. The silver salt, AgNTf$_2$, was prepared by the reaction of Ag_2CO_3 (Aladdin, AR) with HNTf$_2$ (Aladdin, 95%). Ethylene (99.99%) and ethane (99.99%) were purchased from Hangzhou Jingong Material Co., Ltd. (China).

Preparation of [(CP)$_2$im][NTf$_2$] and Measurement of Density and Viscosity. The [(CP)$_2$im][NTf$_2$] was prepared by a method similar to that reported in the literature.[28,29] 1-(Trimethylsilyl)-imidazole (15.43 g, 0.11 mol) was added drop-by-drop to 4-chlorobutyronitrile ($Cl(CH_2)_3CN$) (35.21 g, 0.34 mol) at 80 °C under stirring for 24 h, and the resulting white solid was washed with diethyl ether. The product was dried under vacuum for 24 h at 80 °C, and [(CP)$_2$im]Cl was obtained. Then equimolar [(CP)$_2$im]Cl and lithium trifluoromethane-sulfonimide (LiNTf$_2$) aqueous solution were mixed and stirred at room temperature for 10 h to form [(CP)$_2$im][NTf$_2$]. The product [(CP)$_2$im][NTf$_2$] was extracted from aqueous solution with dichloromethane. Finally, [(CP)$_2$im]-[NTf$_2$] was dried under vacuum to remove water and dichloromethane.

The structure and purity of synthesized [(CP)$_2$im][NTf$_2$] were evaluated by ^{1}H NMR spectrum (($CD_3)_2SO$, 500 Hz, δ/ppm): 9.24(s, 1H), 7.82(d, 2H), 4.25(t, 4H), 2.59(t, 4H), 2.15(m, 4H). The IR spectrum of [(CP)$_2$im][NTf$_2$] is shown in the Supporting Information. [(CP)$_2$im][NTf$_2$] has a good thermal stability, and its decomposition temperature is higher than 300 °C (results of DTG analysis of [(CP)$_2$im][NTf$_2$] are shown in the Supporting Information).

The density of [(CP)$_2$im][NTf$_2$] was determined at 30 °C using an Anton Paar DMA-5000 vibrating-tube densimeter. The viscosities of [CPmim][NTf$_2$] and [(CP)$_2$im][NTf$_2$] were measured using a Brookfield LVDV-II +pro Cone/Plate viscometer at 30 °C. The properties of the studied ILs are listed in Table 1.

Apparatus and Method for Gas Solubility Measurements. The experimental apparatus (Figure 1) used during the gas solubility measurements is based on an isochoric saturation technique. The apparatus was equipped with K-type thermocouples (accuracy ±0.15 K) and with a pressure transducer for measuring pressures close to atmospheric pressure (Druck RPT 350, 3.5−350 kPa, accuracy ±0.01% full scale).

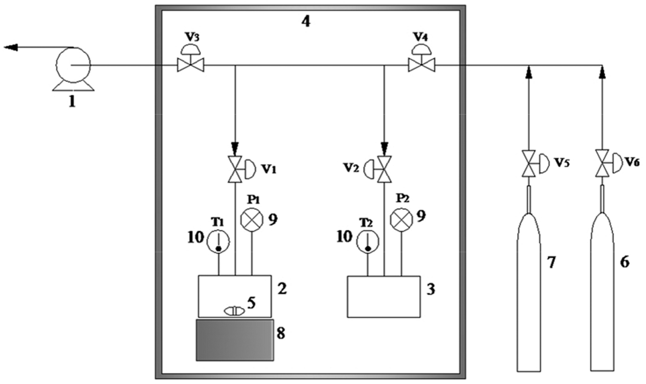

Figure 1. Schematic diagram of experimental apparatus. 1. Vacuum pump. 2. Equilibration cell. 3. Gas chamber. 4. Thermostated bath. 5. Magneton. 6. Ethylene. 7. Ethane. 8. Magnetic stirrer. 9. Pressure transducer. 10. Temperature sensor.

In a typical experiment, a pre-weighed amount of the IL was introduced into the equilibrium cell, and the system was evacuated with valves V1, V2, and V3 open. Then the valves to the vacuum pump (V3) and the equilibrium cell (V1) were closed, and a charge of gas component was introduced into the tube and gas chamber. Afterward, valve V2 was closed, and the equilibrium pressure p_0 and temperature T_0 in the chamber were measured. The gas in the pipeline was evacuated with valves V1 and V3 open. Then the valve to the vacuum pump (V3) was closed. The valve to the equilibrium cell (V2) was opened to introduce a certain amount of gas into the equilibration cell. Then the valve V2 was closed. The ILs were stirred vigorously with a magnetic stirrer to facilitate absorption. Equilibrium was assumed when the pressure of equilibration cell (p_1) changed less than 1 Pa within 10 min. The pressure p_1 and temperature T_1 in the equilibrium cell and the pressure p_2 and temperature T_2 in the gas chamber were measured at equilibrium. After the absorption reached equilibrium, the valve V2 was opened, and more gas was added to the equilibration cell. By repeating the absorption measurement, a new equilibrium was obtained.

The solubility of gas in the IL, n, was calculated by subtracting the moles of gas in the pure gas phase (above the IL) at equilibrium, n', from the total moles of gas introduced into the system, n_0. The moles of gas present in the pure gas phase were calculated with the equilibrium temperature and pressure and the volume of the pure gas phase by subtracting the volume occupied by the IL from the total system volume.

The total moles of pure gas introduced into the system were

$$n_0 = p_0 V_2 / Z_0 R T_0 \tag{1}$$

The moles of pure gas present in the pure gas phase at equilibrium were

$$n' = n_1 + n_2 = p_1 (V_1 - V_{\mathrm{IL}}) / Z_1 R T + p_2 V_2 / Z_2 R T_2 \tag{2}$$

The solubility of pure gas in ionic liquid was

$$n = n_0 - n' = p_0 V_2 / Z_0 R T_0 - p_1 (V_1 - V_{\mathrm{IL}}) / Z_1 R T_1 - p_2 V_2 / Z_2 R T_2 \tag{3}$$

where p_0 and T_0 are the pressure and temperature of the total gas introduced into the system, and p_1, T_1 and p_2, T_2 are the pressure and temperature in the equilibration cell and gas chamber at equilibrium. V_1, V_2, and V_{IL} are the total volume of the equilibration cell (106.3 mL), gas chamber (including the pipeline, 111.6 mL), and the IL in equilibration cell (7 mL). Z_0, Z_1, and Z_2 are the compressibility factors for the pure gas at different equilibrium states. The solubility can then be expressed as a mole fraction

$$x = n / (n + n_{\mathrm{IL}}) \tag{4}$$

or as Henry's constant

$$k_{\mathrm{H}} \approx p / x \tag{5}$$

where n_{IL} is the mole of IL in the equilibration cell, x is the mole fraction of gas dissolved in the liquid phase, and p is the pressure of the gas at equilibrium. On the basis of the solubility data, Henry's coefficient was obtained from the slope of a linear isotherm of pressure versus the mole fraction of gas dissolved in the liquid phase. In this work, all the squares of regression coefficients (R^2) are more than 0.999 (Table S2) and indicate that the experimental results are stable and reproducible.

Preliminary experiments were carried out to test the accuracy of the apparatus, and the solubility of ethylene in [Bmim][NTf$_2$], [Bmim][BF$_4$] and [Bmim][PF$_6$] was determined. Compared with the literature data,[3,10] the relative deviations were less than ±5% (Table S1, Supporting Information). Therefore, the apparatus can be used for measuring the solubility of gas in IL with high reliability.

Selectivity of IL for ethylene to ethane can be defined as the ratio of ethylene to ethane.[19] The molar selectivity toward ethylene was calculated from the individual gas absorption data according to eq 6.

$$\text{Selectivity} = k_{\mathrm{H,C_2H_6}} / k_{\mathrm{H,C_2H_4}} \tag{6}$$

■ COMPUTATIONAL DETAILS

The COSMO-RS calculations were performed considering the ILs as independent counterions. In this work, the molecular geometries of the gaseous solutes and the ILs were optimized on the density functional theory level, utilizing the BP (B88-VWN-P86) functional with RI (resolution of identity) approximation and a triple-z valence polarized basis set (TZVP). The molecular geometry optimization for each compound was performed using the quantum chemical TURBOMOLE 6.3 program package,[36] and the COSMO file for each compound was obtained. Subsequently, using the COSMO file, the COSMO-RS calculation for infinite dilution activity coefficients, Henry's constants, energy, and screening charges on the molecular surface for each species was performed with the COSMOthermX program[37] in BP_TZVP_C30_1201 parametrization.

For the calculation of the activity coefficient at infinite dilution, the mole or mass fraction of the compound of interest (ethylene and ethane) has to be set to zero in the composition of the solution. The chemical potentials $\mu_{\mathrm{j}}^{(\mathrm{p})}$ of all pure compounds j and the chemical potentials $\mu_{\mathrm{j}}^{(\mathrm{i})}$ in the liquid phase (compound i or compound mixture, respectively) are calculated. The infinite dilution activity coefficients γ^{∞} are then calculated as $\ln(\gamma^{\infty}) = (\mu_{\mathrm{j}}^{(\mathrm{i})} - \mu_{\mathrm{j}}^{(\mathrm{p})})/RT$. In the COSMO-RS calculation of this study, the ILs are treated as independent counterions, and the activity coefficients are calculated at infinite dilution. Thus, the COSMOtherm calculation is based on a ternary mixture: cation, anion, and solute, with the boundary condition that the molar amount of anion equals the molar amount of cation in the mixture. Henry's constant k_{H} is calculated from the γ^{∞} and the vapor pressures of the compounds. Actually, the mixture of IL and gas is a binary system, so the values of γ^{∞} and k_{H} that are directly acquired from the COSMOtherm software are corrected by dividing them by two.

■ RESULTS AND DISCUSSION

Separation of Ethylene and Ethane Using the Symmetrical Dual Nitrile-Functionalized IL. The solubilities of ethylene and ethane in [Bmim][NTf$_2$], the single-functionalized IL ([CPmim][NTf$_2$]) and the dual-functionalized IL ([(CP)$_2$im][NTf$_2$]), were measured at a temperature of 303.15 K and pressure of 0.5 to 2.5 bar; the experimental results are shown in Figure 2. As shown in Figure 2, the solubilities of ethylene in [bmim][NTf$_2$], [CPmim][NTf$_2$] and [(CP)$_2$im][NTf$_2$] are 0.048, 0.026, and 0.022 mol/L at about 1.0 bar, and the solubilities of ethane are 0.036, 0.016 and 0.012, respectively. It is obvious that the solubility of ethylene is larger than that of ethane in the same IL. On the basis of the experimental solubility data, Henry's constants k_{H} for ethylene and ethane in different ILs were calculated, and the results are shown in Table 1. It was found that the selectivity of ethylene to ethane in IL increased from 1.37 to 1.61 with the introduction of a nitrile group into the alkyl chain of the cation. However, the solubility of ethylene decreased sharply, with k_{H} for ethylene increasing from 75.7 to 135.1, when only a single nitrile group was introduced into the cation. After introducing one more nitrile group into the cation to form a symmetrical structure ([(CP)$_2$im][NTf$_2$]), the selectivity of ethylene to ethane increased remarkably from 1.61 to 2.01. However, the solubility of ethylene in IL decreased only a little with Henry's constant increasing marginally from 135.1 to

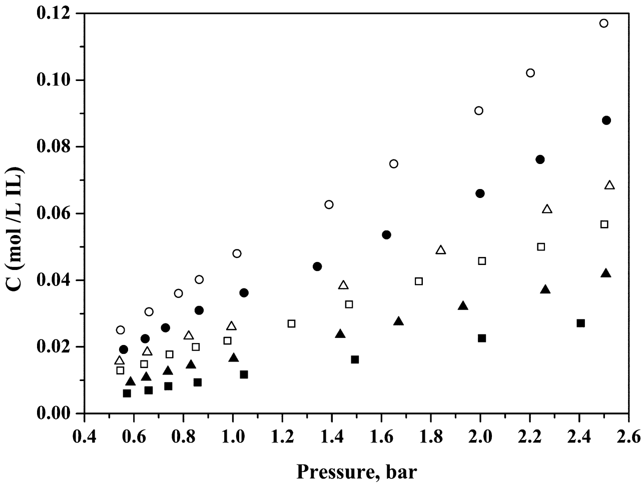

Figure 2. Solubility of ethylene and ethane in ionic liquids [Bmim][NTf$_2$], [CPmim][NTf$_2$], and [(CP)$_2$im][NTf$_2$] at 303.15 K. (○) C_2H_4-[Bmim][NTf$_2$]; (●) C_2H_6-[Bmim][NTf$_2$]; (Δ) C_2H_4-[CPmim][NTf$_2$]; (▲) C_2H_6-[CPmim][NTf$_2$]; (□) C_2H_4-[(CP)$_2$mim][NTf$_2$]; and (■) C_2H_6-[(CP)$_2$mim][NTf$_2$].

140.1 bar. In other words, our experimental result shows that enhanced selectivity for ethylene with respect to ethane could be achieved with the symmetrical dual-functionalized IL at only a small cost in absorption capacity. Making a comparison with the solubility data reported in the literature[10,32] (Table 1), we find that the separation efficiency of the dual-functionalized IL [(CP)$_2$im][NTf$_2$] is superior to that of most conventional ILs. Among previously reported ILs, 1-butyl-3-methylimidazolium dicynamide ([Bmim][N(CN)$_2$]), which has two nitrile groups in the anion, has shown the largest selectivity of ethylene to ethane. However, Henry's constant k_H for ethylene in [Bmim][N(CN)$_2$] is 200 bar, obviously larger than that in [(CP)$_2$im][NTf$_2$] and indicating a lower solubility of ethylene in [Bmim][N(CN)$_2$] than in [(CP)$_2$im][NTf$_2$]. The values of k_H for ethylene are 99 and 119.4 bar in [Emim][NTf$_2$] and [Bmim][MeSO$_4$], lower than that in [(CP)$_2$im][NTf$_2$], but the selectivities of ethylene to ethane using [Emim][NTf$_2$] and [Bmim][MeSO$_4$] are lower than that in [(CP)$_2$im][NTf$_2$]. [Bmim][SCN] and [Bmpy][SCN] could have ethylene solubilities similar to [(CP)$_2$im][NTf$_2$]; however, selectivities are obviously lower than those using [(CP)$_2$im][NTf$_2$] as absorbent.

A COSMO-RS calculation was carried to understand the underlying dissolution mechanism of ethylene and ethane in ILs. Figure 3 shows the σ-profiles of ethylene, ethane, Bmim$^+$, CPmim$^+$, and (CP)$_2$im$^+$, respectively. Of these, ethane is the least polar compound, reflected by the narrow distribution of the charge densities around zero within the nonpolar region from −0.005 to 0.005 e/Å^2. The two peaks can be assigned to the carbon atoms for positive values and to the hydrogen atoms for negative values. Ethylene has a broader distribution from −0.009 e/Å^2 to +0.011 e/Å^2, indicating that ethylene is a low polar molecule. From the σ-profiles of the three imidazolium-based cations, their polarity order can be confirmed by the different distribution of peaks in the σ-profile. Compared with the Bmim$^+$, the positive region extends from 0.005 to 0.015 e/Å^2 for CPmim$^+$ due to the introduction of the nitrile group. Thus, the polarity of [CPmim][NTf$_2$] is greater than that of [Bmim][NTf$_2$], and it affects the solubility of the weakly polar ethylene and the nonpolar ethane molecules. In addition, although (CP)$_2$im$^+$ possesses one more nitrile group than CPmim$^+$, the σ-profiles for CPmim$^+$ and (CP)$_2$im$^+$ have similar regions about −0.017 to 0.016 e/Å^2, indicating that the polarity will not change much after introducing a symmetric nitrile group in the CPmim$^+$, which is in favor of increasing the selectivity for ethylene/ethane at the least cost in absorption capacity.

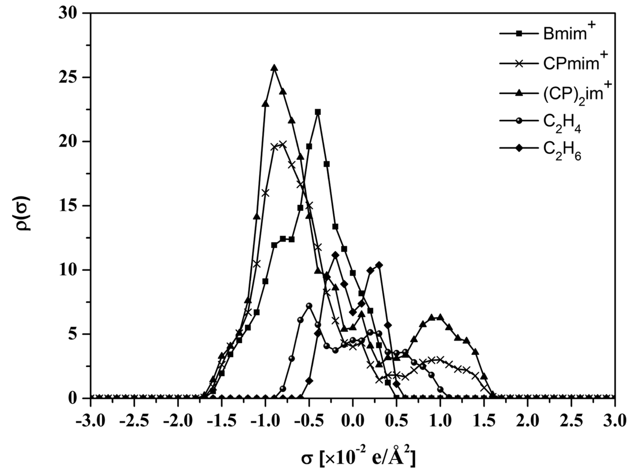

Figure 3. Probability distribution $\rho(\sigma)$ of the screening charge density σ.

The infinite dilution activity coefficients γ^∞ data provide valuable information for testing predictive models or computer simulation methods because values of γ^∞ give a direct measure of interactions between unlike molecules in the absence of solute−solute interactions. Therefore, the solubilization ability of the IL stationary phases for different kinds of solutes can be characterized through their values of γ^∞. The ratio of γ^∞ also can stand for the selectivity of two compounds. As the data listed in Table 2 show, the calculated infinite dilution activity coefficients γ^∞ and Henry's constants k_H of ethylene and ethane increase with the addition of a nitrile group in the alkyl chain of the cation, which is consistent with the experimental results such that introducing the nitrile group will decrease the capacity both for ethylene and ethane. Compared with the values in [CPmim][NTf$_2$], the γ^∞ and k_H of ethylene and ethane increase just slightly, and the selectivity is further enhanced in the symmetrical dual-functionalized nitrile-based IL [(CP)$_2$im][NTf$_2$]. Among the three descriptor parameters for the solvation interactions of ethylene and ethane with ILs (Table 3), the parameters for hydrogen bonding interaction (H_HB) are zero for ethane-IL, indicating that there is no hydrogen bonding interaction between ethane and the studied ILs. In ethylene-IL, the values of H_HB are negative, and the absolute values are very small, indicating that a weak hydrogen bonding interaction occurs.[38] Moreover, the hydrogen bonding interaction becomes slightly stronger after introducing the nitrile group. The parameter for the van der Waals interaction is strongly negative for all ILs and varies within a narrow range, and the absolute value decreases both in ethylene-IL and ethane-IL after introducing a nitrile group into [Bmim][NTf$_2$]. Nevertheless, when another nitrile group was introduced into [CPmim][NTf$_2$], the absolute value of the van der Waals interaction energy increases, indicating that the interaction between IL and gas molecule is enhanced. In COSMO-RS, an electrostatic interaction arises from the contact of two segments with different screening charge density. The specific interaction

Table 2. Calculated Infinite Dilution Activity Coefficients (γ^∞) and Henry's Constants (k_H) of Ethylene and Ethane in ILs at 303.15 K by COSMO-RS

	γ^∞			k_H (bar)		
IL	C_2H_4	C_2H_6	$\gamma^\infty(C_2H_6)/\gamma^\infty(C_2H_4)$	C_2H_4	C_2H_6	$k_H(C_2H_6)/k_H(C_2H_4)$
[Bmim][NTf_2]	0.84	1.84	2.19	65.82	163.28	2.48
[CPmim][NTf_2]	1.50	4.61	3.07	116.84	409.13	3.50
[$(CP)_2$im][NTf_2]	1.65	5.48	3.32	128.64	485.78	3.78

Table 3. Solvation Interactions of Ethylene and Ethane in Ionic Liquids at 303.15 K

species	H_MF[a]	ΔH_MF	H_HB[b]	ΔH_HB	H_vdW[c]	ΔH_vdW
[Bmim][NTf_2]-C_2H_4	4.72		−0.0048		−13.73	
[Bmim][NTf_2]-C_2H_6	4.70		0.0000		−14.62	
[CPmim][NTf_2]-C_2H_4	5.58	0.86[d]	−0.0062	−0.0014[d]	−13.65	0.08[d]
[CPmim][NTf_2]-C_2H_6	6.13	1.43[d]	0.0000	0.0000[d]	−14.40	0.22[d]
[$(CP)_2$im][NTf_2]-C_2H_4	5.89	0.31[e]	−0.0067	−0.0005[e]	−13.82	−0.17[e]
[$(CP)_2$im][NTf_2]-C_2H_6	6.51	0.38[e]	0.0000	0.0000[e]	−14.57	−0.17[e]

[a] H_MF, misfit interaction energy in the mixture, kJ/mol. [b] H_HB, H-bond interaction energy in the mixture, kJ/mol. [c] H_vdW, van der Waals interaction energy in the mixture, kJ/mol. [d] ΔH is H([CPmim][NTf_2]-gas)-H([Bmim][NTf_2]-gas), the difference of corresponding energy after introducing a nitrile group to [Bmim][NTf_2] with the same gas solute, kJ/mol. [e] ΔH is H([$(CP)_2$im][NTf_2]-gas)-H([CPmim][NTf_2]-gas), the difference of corresponding energy after introducing a nitrile group to [CPmim][NTf_2] with the same gas solute, kJ/mol.

energy per unit area results from this "misfit" of screening charge density. This misfit interaction is defined as the electrostatic interaction between the two contacting molecules and can be regarded as a reflection of polarity. Its positive value in Table 3 indicates that the ionic characteristic of ILs is unfavorable for the dissolution of neutral and weak polar ethylene and ethane molecules. The increasing value of H_MF with the nitrile group denotes an increasing polarity of the cation and corresponding ILs and also indicates that a more polar IL militates against the dissolution of ethylene and ethane. Furthermore, the misfit interaction of ethane-IL increases more sharply than ethylene-IL, which probably leads to an enhanced selectivity of IL for ethylene to ethane. However, when the second nitrile group is introduced, the value of H_MF rises slightly, only 0.31 and 0.38 for ethylene and ethane, much smaller than the increase from [Bmim][NTf_2] to [CPmim][NTf_2]. This demonstrates that the polarity of the IL does not increase dramatically when a symmetrical nitrile group is introduced into [CPmim][NTf_2], and it also explains why the solubility of ethylene and ethane drops slightly in [$(CP)_2$im][NTf_2] compared with [CPmim][NTf_2].

Separation of Ethylene and Ethane Using IL Containing Silver Salt. The silver ion (0.25 mol/L) was added to IL to increase the selectivity of the ethylene to ethane. The solubilities of ethylene and ethane are shown in Figure 4. The experimental results showed that IL ([Bmim][NTf_2]) containing silver ions ($AgNTf_2$) had a much higher solubility for ethylene than ethane due to the chemical interaction between the silver and the double bond of ethylene. The solubility of ethane remained almost constant before and after the addition of silver ion, implying that there was only a physical interaction between ethane and the silver-containing IL. Therefore, the selectivity of ethylene to ethane reached 10.7 at a pressure of 0.56 bar and a temperature of 303.15 K in Ag-[Bmim][NTf_2]. In addition, a salting out effect was not observed because the presence of the salt did not decrease the solubility of ethane in the IL phase. All of these are consistent with the result of other silver-containing IL systems.[19,26,27] In addition, it was noted that the solubilities of ethylene in Ag-[CPmim][NTf_2] and Ag-[$(CP)_2$im][NTf_2] did not increase significantly when compared with its solubilities in [CPmim][NTf_2] and [$(CP)_2$im][NTf_2], respectively. One of the probable reasons is that the nitrile group has a strong interaction with the silver ion, which hinders the π-complexation of the silver ion with ethylene.

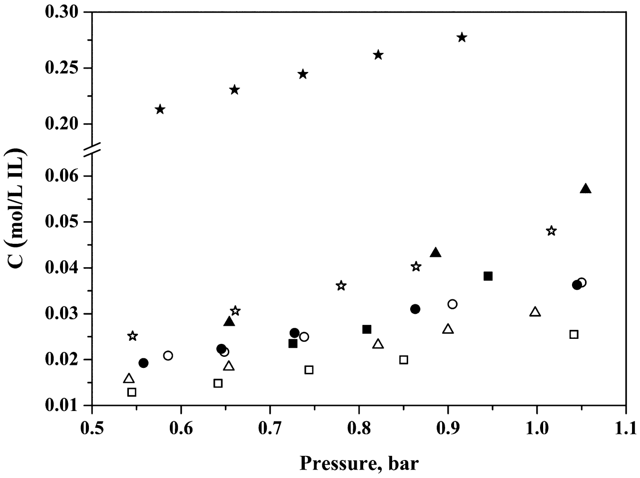

Figure 4. Solubility of ethylene and ethane in ionic liquids with and without silver ions at 303.15 K. (★) C_2H_4–Ag-[Bmim][NTf_2]; (☆) C_2H_4-[Bmim][NTf_2]; (●) C_2H_6-Ag-[Bmim][NTf_2]; (○) C_2H_6-[Bmim][NTf_2]; (▲) C_2H_4-Ag-[CPmim][NTf_2]; (Δ) C_2H_4-[CPmim]NTf_2]; (■) C_2H_4-Ag-[$(CP)_2$im][NTf_2]; and (□) C_2H_4-[$(CP)_2$im][NTf_2].

The equilibrium model was used to describe the absorption of ethylene in the silver-containing IL.[39,40] The ethylene reacts with the silver ion to form π-complexes in the Ag-[Bmim][NTf_2] mixture, which can be described by primary and secondary complexation reactions with different stoichiometries of ethylene and silver.

$$Ag^+ + C_2H_4 \leftrightarrow Ag^+(C_2H_4) \quad \text{primary complexation} \tag{7}$$

$$Ag^+(C_2H_4) + C_2H_4 \leftrightarrow Ag^+(C_2H_4)_2 \quad \text{secondary complexation} \tag{8}$$

The equilibrium constants are defined as

$$K_{\mathrm{eq}\,7} = [\mathrm{Ag}^{+}(\mathrm{C_2H_4})]/[\mathrm{Ag}^{+}][\mathrm{C_2H_4}] \tag{9}$$

$$K_{\mathrm{eq}\,8} = [\mathrm{Ag}^{+}(\mathrm{C_2H_4})_2]/[\mathrm{Ag}^{+}(\mathrm{C_2H_4})][\mathrm{C_2H_4}] \tag{10}$$

The equilibrium constants for the primary and secondary complexation reactions were calculated, and the values were 54.4 L/mol and 7.5 L/mol, respectively. The accuracy of the calculation results is presented in the parity graph shown in Figure 5, and the average absolute deviation is 0.16%. The equilibrium constants showed that the formation of the primary complex species is more favored than the secondary complex under similar operating conditions, which is in accordance with the result of the experiment for propylene/propane separation with silver- containing IL.[19,25]

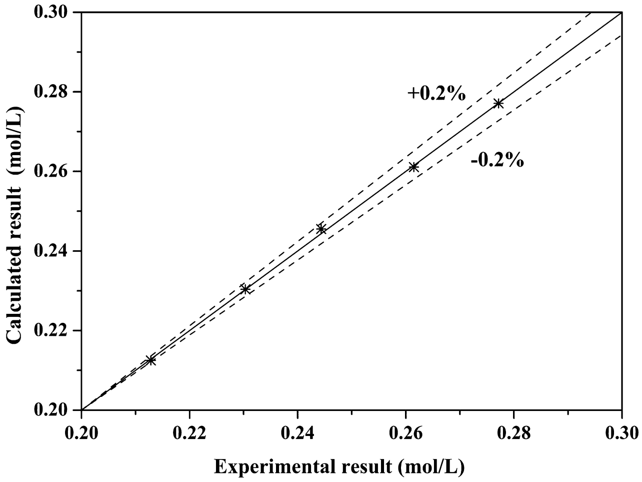

Figure 5. Parity graph of the calculated and experimental values of ethylene in [Bmim][NTf$_2$]-Ag (Ag$^+$ 0.25 mol/L).

CONCLUSIONS

The study demonstrates that the nitrile group functionalized ILs are promising solvents for ethylene/ethane separation. Remarkably, the symmetrical dual nitrile-functionalized IL [(CP)$_2$im][NTf$_2$] has a higher selectivity for the ethylene/ethane separation than the single nitrile-functionalized IL [CPmim][NTf$_2$] and the nonfunctionalized IL [Bmim][NTf$_2$]. Moreover, the absorption capacity of ethylene in [(CP)$_2$im][NTf$_2$] was only slightly lower than that in [CPmim][NTf$_2$]. The COSMO-RS calculation result indicates that misfit interaction and polarity are the major factors in the dissolution of ethylene and ethane in ILs. The polarity and misfit interaction energy of [CPmim][NTf$_2$] are greater than those of [Bmim][NTf$_2$] obviously; however, those of [(CP)$_2$im][NTf$_2$] are only slightly stronger than [CPmim][NTf$_2$]. This result indicates that the polarity of IL will not increase dramatically when a symmetrical nitrile group is introduced into [CPmim][NTf$_2$], which is in good accordance with the conclusion from the results of experimental solubility. The IL containing a silver ion performed much better than pure IL in the separation of ethylene/ethane, and the selectivity of ethylene to ethane reached 10.7 at a pressure of 0.56 bar and at 303.15 K in Ag-[Bmim][NTf$_2$]. But the solubility of ethylene in [CPmim][NTf$_2$] and [(CP)$_2$im][NTf$_2$] does not increase obviously after the introduction of the silver ion, probably due to the relatively strong interaction between the nitrile group in the cation and the silver ion.

ASSOCIATED CONTENT

Supporting Information

IR spectrum, DTG analysis of [(CP)$_2$im][NTf$_2$], experimental data for verification of the experiment, and solubility of ethylene and ethane. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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