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Solubilities of R32, R245fa, R227ea and R236fa in a phosphonium-based ionic liquid

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ABSTRACT

New solubility data for difluoromethane (R32), 1,1,1,3,3-pentafluoropropane (R245fa), 1,1,2,2,3,3,3-heptafluoropropane (R227ea) and 1,1,1,3,3,3-hexafluoropropane (R236fa) in trihexyltetradecylphosphonium bis(2,4,4-trimethylpentyl)phosphinate ([P14666][TMPP]) at temperatures from 292 K to 344 K and at pressures from 0.01 MPa to 1.07 MPa is presented in this work. Low temperature and high pressure can improve the solubilities of hydrofluorocarbons in [P14666][TMPP]. Hydrofluorocarbons are more soluble in [P14666][TMPP] than their corresponding alkanes. Dispersive force, dipole–dipole interaction and hydrogen bond interaction were considered to exist between HFC and [P14666][TMPP]. A modified Krichevsky-Kasarnovsky equation was used to correlate the solubilities of R32, R227ea, R236fa and R245fa in [P14666][TMPP] with the mean absolute relative deviations and the maximum absolute relative deviations less than 2.0% and 4.3%, respectively.

1. Introduction

Recently, ionic liquid and hydrofluorocarbon (HFC) have attracted much attentions as a promising working pair for the absorption refrigeration cycles [1–9], which can overcome the disadvantages of the two commonly used working pairs $NH_3 + H_2O$ and H_2O + LiBr, such as toxicity, crystallization and corrosivity [10–11]. The solubility behavior of HFC in ionic liquid has an important influence on the performance of the absorption refrigeration cycle [12–13]. Moreover, the solubility data of HFCs in ionic liquid are also required for the separation of HFCs using ionic liquid as a solvent [14–15]. Many works have been carried out on the solubilities of HFCs in ionic liquids to provide information for designing high-performance ionic liquids for the refrigeration and separation processes. Shiflett et al. [16–26] have reported a large amount of solubility data for fluorinated methanes and fluorinated ethanes in imidazolium-based ionic liquids. They claimed that the hydrogen bond interaction plays an important role in the solubility behavior of HFC in ionic liquid. This conclusion is supported by the works of others [12,27–32]. In order to investigate the solubility behavior of HFCs in phosphonium-based ionic liquids, we have presented solubility data for five fluorinated ethanes R161, R143a, R134a, R125 and R152a in [P14666][TMPP] [33]. By comparing the solubilities of fluorinated ethanes and ethane in different ionic liquids, we found that the solubilities of fluorinated ethanes were larger than that of ethane [34]; the cations and the anions of ionic liquids had important influence on the solubilities of fluorinated ethanes. We believe that the hydrogen bond interaction also plays an important role in the solubility behavior of fluorinated ethanes in phosphonium-based ionic liquids. In addition, Sousa et al. [35,36] studied the solubilities of R-23, R-32 and R-41 in four phosphonium-based ionic liquids. However, it is still needed to gain further insight into the solubility behavior of HFCs in ionic liquids.

This work aims to study the solubilities of R32, R227ea, R236fa and R245fa in [P14666][TMPP]. The solubility measurements were carried out at temperatures from 292 K to 344 K and at pressures from 0.01 to 1.07 MPa. The solubility data was correlated by a modified Krichevsky-Kasarnovsky equation.

2. Experimental section

2.1. Materials

R32, R227ea, R236fa and R245fa were provided by Zhejiang Sinoloong Refrigerant Co., Ltd. with purities ≥99.9 wt.%. [P14666][TMPP] was provided by Strem Chemicals, Incorporated with a purity ≥95.0 wt.%. Information provided by supplier shows that [P14 666][TMPP] contains 2140 ppm chloride and 6510 ppm bromide. The volatile substances in the ionic liquid were further removed by drying at 393 K for 48 h in vacuum drying oven. The characteristics of the studied chemicals in this work are summarized in Table 1.

2.2. Solubility apparatus

A detailed description of the experimental apparatus and procedure was given in our previous works [31–32]. As it is shown in Fig. 1, the main parts of the apparatus are the equilibrium cell, the gas reservoir,

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Table 1
The chemicals used in this work.

Chemical name	Supplier	Purity in mass fraction	Purification method	Water content in mass fraction
[P14666][TMPP][a]	Strem Chemicals, Incorporated	≥95.0%	Vacuum drying	0.01%[b]
Difluoromethane (R32)	Zhejiang Sinoloong Refrigerant Co., Ltd.	≥99.9%	None	–
1,1,1,3,3-pentafluoropropane (R245fa)	Zhejiang Sinoloong Refrigerant Co., Ltd.	≥99.9%	None	–
1,1,2,2,3,3,3-heptafluoropropane (R227ea)	Zhejiang Sinoloong Refrigerant Co., Ltd.	≥99.9%	None	–
1,1,1,3,3,3-hexafluoropropane (R236fa)	Zhejiang Sinoloong Refrigerant Co., Ltd.	≥99.9%	None	–

[a] Trihexyltetradecylphosphonium bis(2,4,4-trimethylpentyl)phosphinate.
[b] Measured with a Metrohm 831 Karl Fischer titrator.

the magnetic stirrer, the thermostat and the data acquisition system. Initially, the volumes of equilibrium cell and the gas reservoir were calibrated by gravimetric method. The experiment began with loading a certain amount of ionic liquid into the equilibrium cell. Then, the equilibrium cell was connected to the gas reservoir and put into the water thermostat for which the stability was maintained within ±0.04 K/30 min. After that, a certain amount of gas from the gas reservoir was injected into the equilibrium cell and the magnetic stirrer was used to accelerate the dissolve process. The equilibrium was reached when the pressure was stable. The temperatures and pressures inside the equilibrium cell and the gas reservoir were recorded during the whole experiment process using two platinum resistant thermometers (Fluke 5608) and two pressure sensors (Keller 33X), respectively. The expanded uncertainties of the platinum resistant thermometers and the pressure sensors are 0.02 K and 0.3 kPa (coverage factor $k = 2$, 0.95 level of confidence [37]), respectively. Taking the temperature fluctuation of the thermostat into account, the expanded uncertainty of the temperature in the equilibrium cell is estimated to be less than 0.1 K ($k = 2$). The uncertainties of temperature and pressure did not cause any significant change in the gas solubility measurement.

2.3. Calculation of gas solubility

The gas solubility is usually expressed as mole fraction of solute in the liquid phase x which is defined by

$$x = \frac{n_g^l}{n_l + n_g^l} \quad (1)$$

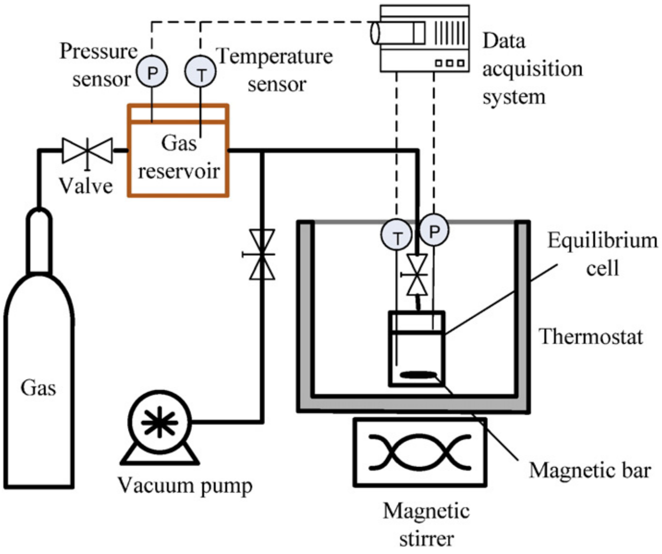

Fig. 1. Schematic of the experimental apparatus.

where n_l is the mole number of ionic liquid; n_g^l is the mole number of gas absorbed by the ionic liquid, which is calculated by

$$n_g^l = V_{GC}(\rho_i - \rho_f) - \rho_g(V_{EC} - V_l) \quad (2)$$

where V_{GC} is the volume of the gas reservoir; V_{EC} is the volume of the equilibrium cell; V_l is the volume of ionic liquid in the equilibrium cell. ρ_i and ρ_f are the molar densities of gas in the gas container before and after loading the gas into the equilibrium cell; ρ_g is the molar density of gas in the equilibrium cell when the equilibrium is reached. ρ_i, ρ_f and ρ_g were calculated by the REFPROP database [38]. The volume of ionic liquid in the equilibrium cell was calculated from the mass and density of ionic liquid. Densities of [P14666][TMPP] have been determined in literature [34] using a Anton-Paar vibrating-tube densimeter (DMA 5000 M). In literature [39,40], the volume change of ionic liquid caused by the dissolution of gas was usually neglected because the effect of it on solubility calculation for the isochoric saturation method is very small. For the system studied in this work, the calculated value of solubility with 20% volume expansion of ionic liquid only has less than 0.6% difference from the calculated value of solubility with the volume expansion neglected. Therefore, the effect of the volume change of ionic liquid caused by the dissolution of gas for the system in this work is very small, we neglected it when calculating the solubility. Our method was verified by measuring the solubilities of carbon dioxide in [HMIM][Tf$_2$N] [32]. Our experimental results agree well with those in literatures measured by different methods. The deviations of the data in our work and literature from the quadratic polynomial obtained by fitting the data at constant temperature are less than 3%. In addition, the solubilities of HFCs were also measured at different mass of [P14666][TMPP] in the equilibrium cell from 4 g to 8 g. There is virtually no difference between the experimental results, indicating that the effect of volume change of ionic liquid caused by the dissolution of gas on the solubility measurement is very small. Densities of [P14666][TMPP] can be correlated by a linear function of temperature:

$$\rho/\mathrm{g\ cm^{-3}} = -5.9125 \times 10^{-4}(T/K) + 1.0655. \quad (3)$$

The relative expanded uncertainty in mole fraction due to both random and systematic errors is estimated to be less than 4% ($k = 2$).

3. Results and discussion

Solubilities of R32, R227ea, R236fa and R245fa in [P14666][TMPP] were measured in the temperature range from 292 K to 344 K and in the pressure range from 0.01 MPa to 1.07 MPa. The solubility data are shown in Table 2 and Figs. 2–5. As expected, the solubilities of these four HFCs in [P14666][TMPP] rise with the increasing pressure and fall with the increasing temperature. Henry's constant of gas in solvent at