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Solubilities of ammonia in choline chloride plus urea at (298.2–353.2) K and (0–300) kPa

Fu-Yu Zhong, Kuan Huang *, Hai-Long Peng *

Key Laboratory of Poyang Lake Environment and Resource Utilization of Ministry of Education, School of Resources Environmental and Chemical Engineering, Nanchang University, Nanchang, Jiangxi 330031, China

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ABSTRACT

The solubilities of ammonia (NH_3) in deep eutectic solvents (DESs) comprising of choline chloride (ChCl) and urea at the temperature ranging from (298.2 to 353.2) K and pressure ranging from (0 to 300.0) kPa were determined by a volumetric method. The molar ratios of ChCl to urea in selected DESs were 1:1.5, 1:2.0 and 1:2.5. It is found that the solubility of NH_3 increases with the increase of pressure, but decreases with the increase of temperature. In addition, the solubilities of NH_3 in ChCl + urea (1:2.0) are slightly higher than those in ChCl + urea (1:1.5) and ChCl + urea (1:2.5) at 313.2 K, while the difference in NH_3 solubilities of ChCl + urea mixtures is negligible at 323.2–353.2 K. By fitting the experimental data with Henry's law equation, the Henry's law constants of NH_3 in ChCl + urea mixtures were obtained. According to the relationship between Henry's law constant and temperature, the thermodynamic properties of NH_3 absorption in ChCl + urea mixtures such as Gibbs free energy changes, enthalpy changes and entropy changes were also calculated.

1. Introduction

Ammonia (NH_3), an alkaline gas with pungent odor, is mainly emitted from the tail gas of ammonia and urea synthesis processes [1]. It is not only corrosive to equipments and pipelines, but also the precursor of fog and haze [2]. On the other hand, NH_3 is an important raw material for the production of nitrogenous fertilizers and freezing media [3]. Therefore, the efficient capture and recycling of NH_3 from industrial exhaust gas is highly demanded to achieve environmental and economic benefits [4].

The currently available technologies for NH_3 capture in the industry include absorption [5], catalytic conversion [6], and biodegradation [7]. Among these technologies, absorption is the most commonly used. Some typical absorbents are water [8], acids, and ionic liquids (ILs) [9,10]. However, these absorbents have many inherent defects. For example, water is highly volatile, and the NH_3 absorption capacity is quite low; acids exhibit strong chemical reactivity to NH_3, resulting in the irreversible absorption of NH_3; ILs suffer from complicated synthesis and high cost, which limit their practical applications in the industry [11]. Therefore, it is of great significance to develop new absorbents for NH_3 capture.

Recently, deep eutectic solvents (DESs) have attracted tremendous attentions because of their unique properties such as extremely low volatility, wide liquid range and structural designability [12–14]. They are also regarded as IL analogues, and a class of green solvents with potential application in gas separation [15]. Unlike ILs which are pure compounds, DESs are mixtures comprising of hydrogen-bond acceptors and donors. Therefore, DESs are advantageous over ILs in synthesis and price. It has been demonstrated that DESs are promising absorbents for acid gases such as CO_2 and SO_2 [16–19]. However, there are very few reports on the use of DESs for NH_3 capture. To the best of our knowledge, the only example is from Yang et al., who reported the efficient absorption of NH_3 in phenol-based DESs [20].

To date, the detailed solubilities of NH_3 in DESs and the thermodynamic properties of NH_3 absorption in DESs are still very scarce in the literature. These data are very important for evaluating the potential application of DESs in NH_3 capture, as well as the process design. In this work, the solubilities of NH_3 in DESs comprising of choline chloride (ChCl) and urea at different temperatures and pressures were determined. ChCl and urea are two most common compounds for the construction of DESs [21]. Their chemical structures are shown in Scheme 1. The molar ratios of ChCl to urea in selected DESs were 1:1.5, 1:2.0 and 1:2.5. The Henry's law constants of NH_3 in ChCl + urea mixtures were obtained by fitting the experimental data with Henry's law equation. The thermody-

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* Corresponding authors.
E-mail addresses: huangk@ncu.edu.cn (K. Huang), peng_hailong@aliyun.com (H.-L. Peng).

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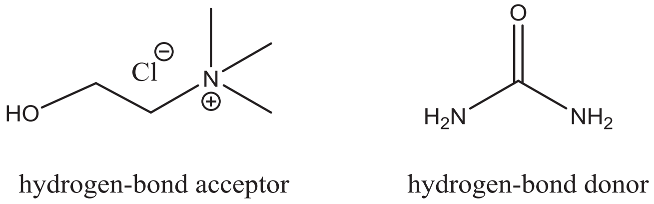


Scheme 1. Chemical structures of DESs investigated in this work.

namic properties of NH_3 absorption in ChCl + urea mixtures such as Gibbs free energy changes, enthalpy changes and entropy changes were also calculated according to the relationship between Henry's law constant and temperature.

2. Experimental

2.1. Materials

NH_3 was supplied by Huasheng Special Gas Co. Ltd., China. ChCl and urea were purchased from Adamas Co. Ltd., China. The basic information of chemicals used in this work are presented in Table 1. All the chemicals were used as received. DESs were prepared by stirring the mixtures of ChCl and urea at 333.2 K until clear liquids were obtained. The water contents in prepared DESs were determined by Karl-Fisher titration on a 787KF Titrino instrument. The basic information of DESs prepared in this work are presented in Table 2.

2.2. Apparatus

The apparatus for the measurement of NH_3 solubilities in DESs is similar to the one reported in our previous work, as shown in Scheme 2 [22]. The apparatus has two chambers made of 316 L stainless steel. The smaller one is equipped with a magnetic stirrer and used as the equilibrium cell, while the bigger one is used as the gas reservoir to isolate the gas before it contacts with the absorbent loaded in the equilibrium cell. The volumes of two chambers including connecting parts are measured to be 105.34 cm^3 (V1) and 40.01 cm^3 (V2) respectively, by using helium as the probing gas with the standard uncertainty of 0.01 cm^3. The temperatures (T) of two chambers are controlled by a water bath with the standard uncertainty of 0.1 K. The pressures in two chambers are monitored by two pressure transducers (Wideplus-8) with the standard uncertainty of 1.2 kPa. The pressure transducers are connected to a digital displayer (Wideplus-80) to record the pressure change online.

2.3. Procedures

In a typical run, a specific amount of DES (~1.0 g) was loaded into the equilibrium cell. The mass of DES (w) was measured by an analytical balance with the standard uncertainty of 0.0001 g. The whole system was evacuated, and the residual pressure in equilibrium cell was recorded to be P_0 (0–0.3 kPa), approaching the detecting limit of pressure transducers. The residual pressure P_0 was recorded for 24 h before the measurement of NH_3 solubilities started. It was found that the increase in P_0 was less than 0.1 kPa, validating the good vacuum tightness of the whole system. The gas from cylinder was then fed into the gas reservoir to a pressure of P_1. The needle valve between two chambers was turned on to let the gas be introduced into the equilibrium cell. Absorption equilibrium was considered to be reached when the pressures of two chambers remained constant for at least 2 h. The equilibrium pressures were denoted as P_2 for equilibrium cell and P'_1 for gas reservoir. Thus, the gas partial pressure in equilibrium cell was $P_{NH3} = P_2\text{-}P_0$. The gas uptake $n(P_{NH3})$ was calculated using the following equation:

Table 1
Basic information of chemicals used in this work.

Chemicals	CAS number	M.W./($g{\cdot}mol^{-1}$)[a]	Purity
NH_3	7664-41-7	17.04	99.99 mol.%
ChCl	67-48-1	139.63	99 wt%
urea	57-13-6	60.06	99 wt%

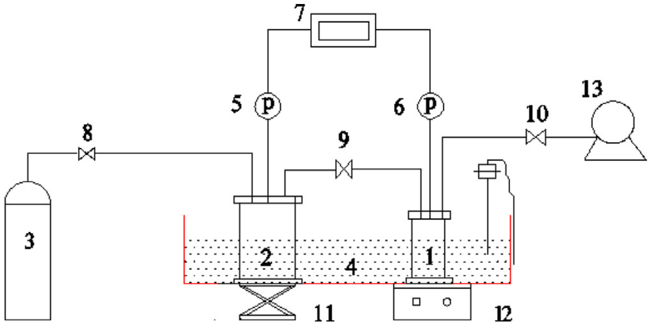
[a] M.W. is the molecular weight.

Table 2
Basic information of DESs prepared in this work[a].

DESs	n_{urea}/n_{ChCl}	$w_{H2O}/\%$
ChCl + urea (1:1.5)[b]	1.4982 ± 0.0001	0.13 ± 0.01
ChCl + urea (1:2.0)[b]	2.0013 ± 0.0001	0.11 ± 0.01
ChCl + urea (1:2.5)[b]	2.4991 ± 0.0001	0.15 ± 0.02

[a] n_{urea}/n_{ChCl} is the molar ratio of urea to ChCl; w_{H2O} is the weight percentage of water; standard uncertainties $u(n_{urea}/n_{ChCl})$ and $u(w_{H2O})$ are reported following the ±sign.

[b] Numbers in brackets are the molar ratios of ChCl to urea.



Scheme 2. Apparatus for measurement of NH_3 solubilities (1: equilibrium cell, 2: gas reservoir, 3: gas cylinder, 4: water bath, 5 and 6: pressure transducers, 7: digital displayer, 8–10: needle valves, 11: elevator platform, 12: magnetic stirrer, 13: pump).

$$n(P_{NH_3}) = \rho_g(P_1,T)V_1 - \rho_g(P'_1,T)V_1 - \rho_g(P_{NH_3},T)(V_2 - w/\rho_L) \quad (1)$$

where ρ_g (P_i, T) is the density of gas in $mol{\cdot}cm^{-3}$ at P_i (i = 1, NH_3) and T, and is acquired from NIST Chemistry WebBook [23]; ρ_L is the density of DES in $g{\cdot}cm^{-3}$ at T. It should be pointed out that the volume expansion of liquid phase should be very small, because the experimental pressure is not high. Furthermore, only small amount of liquid was loaded in the equilibrium cell, and the contribution of liquid phase expansion to the errors of taking $V_2\text{-}w/\rho_L$ as the gas phase volume in equilibrium cell can be neglected. Continuous measurements of gas solubilities at elevated pressures were performed by introducing more gas into the equilibrium cell to reach new equilibrium. The gas solubilities were defined as the molality of gas in DES phase. After the completion of measurements, the gas remaining in two chambers was swept into a tail-gas absorber containing aqueous solution of H_2SO_4 to prevent the gas from leaking into the atmosphere. Duplicate experiments were performed for each DES to give the average values of gas solubility data. The standard uncertainties of gas solubility data were estimated from the standard uncertainties of pressure by error propagation, as the contributions of the uncertainties of temperature, volume, mass and density to the total uncertainties of gas solubility data are very small and can thus be neglected [22].