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Solubility of N_2O in Aqueous Solution of Diethylenetriamine

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The solubilities of N_2O in aqueous diethylenetriamine (DETA) solution at different mass fractions (15, 30, 45, 60, 75, 90, and 100) % of DETA were measured at different temperatures of (297.7 to 360.7) K. The solubility of N_2O in aqueous DETA solution is strongly dependent on both temperature and mass fraction of DETA. A semiempirical model considering the excess quantity of Henry's constant was correlated with the Redlich−Kister equation. The model gave satisfactory agreement with the experimental data.

Introduction

The development of affordable and environmentally acceptable solutions for the capture of CO_2 is one of the most important technological tasks we face. Absorption with amine-based absorbents is the most common technology for CO_2 removal today, using typically commercial alkanolamines such as MEA (2-aminoethanol), DEA (2-diethylaminoethanol), and MDEA (2-(2-hydroxyethyl-methyl-amino)ethanol). Even though CO_2 absorption is an established and proven technology, it is still very energy intensive. The overall challenge is to reduce energy requirement, the environmental impact, and the capture cost. A better solvent candidate should have a higher capacity, faster absorption rate, and lower enthalpy of absorption than those in use.

DETA (diethylenetriamine), having three amine functionalities, can be expected to have a high loading capacity, and to characterize DETA, several studies have been undertaken.[1,2]

Measurement of the free CO_2 solubility in aqueous alkanolamines at various concentrations and temperatures is essential in developing a kinetic model and also for correct implementation of the thermodynamic system. Inconsistencies in the solubility data may contribute to inconsistent results for the reaction kinetics study.[3] Another source mentions that 10 % uncertainty in solubility data can result in 20 % uncertainty in the apparent kinetics constant.[4] Due to the reactive nature of any absorbent with CO_2, it is not possible to measure the solubility of CO_2 in the absorbent solutions directly. This property must therefore be estimated indirectly from corresponding data of similar nonreacting gases using an analogy. The solubility of CO_2 can be inferred using the N_2O analogy, originally proposed by Clarke,[5] verified by Laddha et al.,[6] and frequently used for various amine systems, such as: single amines MDEA,[7−10] DEA,[8,11] MEA,[11] TEA,[11] AMP,[11−13] and PE[14] and blended amines (MEA + MDEA, MEA + AMP)[15,16] and (DEA + MDEA, DEA + AMP),[17] respectively. Where TEA = 2-(bis(2-hydroxyethyl)amino)-ethanol, AMP = 2-amino-2-methyl-propan-1-ol and PE = 2-(1-piperidyl)ethanol, respectively.

To predict the N_2O solubility data for different single or/and blended alkanolamine systems, various models have been suggested, such as empirical polynomial equation,[8,9] semiempirical models,[11,14−17] those based on work by Wang et al.,[18] and those based on extended scaled-particle theory.[19,20]

In this work, the solubility of N_2O into aqueous solutions of DETA was measured at different compositions and temperatures, and by using an excess quantity, the solubility data were correlated using the Redlich−Kister equation.

Experimental Section

Aqueous solutions of DETA were prepared by mass (balance model Mettler Toledo PB1502-L with uncertainty ± 0.01 g). DETA (99 % pure by mass) from Acros Organic, without further purification, was dissolved in deionized water. The gas N_2O (99.9991 % pure by volume) was supplied from commercial cylinders from AGA Gas GmbH.

The solubility apparatus consisted of a stirred jacketed glass vessel (V_R) with volume of $7.76 \cdot 10^{-4}$ m^3 and a stainless steel gas holding vessel (V_V) with volume of $1.17 \cdot 10^{-3}$ m^3. A known mass of solvent (V_S) (around half of reactor volume) was weighed and transferred to the glass vessel. The amount of solvent added was calculated by difference (D*m*). The solution was thereafter degassed by vacuum until around 2 kPa at ambient temperature until vapor−liquid equilibrium was established (see Figure 1). To minimize the solvent losses during degassing, the glass vessel was equipped with an outlet of condenser which used cooling medium at around 3.5 °C circulated using a Julabo F25 water bath. During the solubility measurement, the cooling system was switched off and the gas outlet closed. The temperature of the stirred jacketed glass vessel was adjusted by a heating medium circulating through a Lauda E300 water bath with uncertainty ± 0.1 K. N_2O gas was added to the glass vessel by opening the valve to the steel gas holding vessel shortly. Equilibrium was then established after around 4 h, and then pressure was recorded by two pressure transducers (Druck PTX 610 and PTX 7517-1 with uncertainty ± 0.08 % (800 kPa) and ± 0.1 % (200 kPa) of full scale, respectively). Two K-type thermocouples recorded temperatures in the jacketed glass vessel and in the stainless steel gas supply vessel, respectively, with uncertainty ± 0.1 K.

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The amount added of N_2O, $n_{N_2O}^{added}$, was calculated from the difference in pressure of the gas supply vessel before and after feeding N_2O as

$$(n_{N_2O}^{added}) = \frac{V_V}{RT_V}\left[\frac{P_{V_1}}{z_1} - \frac{P_{V_2}}{z_2}\right] \qquad (1)$$

Here P_V, T_V, z_1, z_2, and R are the pressure, the temperature of the stainless steel gas holding vessel, the compressibility factor of gas (at initial and final condition), and universal gas constant, respectively.

The amount of N_2O in the gas phase, $n_{N_2O}^{g}$, can then be calculated as

$$(n_{N_2O}^{g}) = \frac{P_{N_2O}(V_R - V_S)}{z_{N_2O}RT_R} \qquad (2)$$

where P_{N_2O}, T_R, and z are the partial pressure of N_2O, jacketed glass vessel temperature, and compressibility factor of N_2O after reaching equilibrium, respectively. The compressibility factor, z, was calculated using the Peng−Robinson equation of state. The amount of N_2O absorbed in the liquid phase, $n_{N_2O}^{l}$, can then be calculated as the difference between N_2O added and the increase of N_2O in the gas phase by

$$(n_{N_2O}^{l}) = (n_{N_2O}^{added}) - (n_{N_2O}^{g}) \qquad (3)$$

The concentration of N_2O, C_{N_2O}, can be calculated by

$$C_{N_2O} = \frac{(n_{N_2O}^{l})}{V_S} \qquad (4)$$

Density measurements[2] are needed to calculate the volume of solvent, V_S, added to the stirred jacketed glass vessel. The partial pressure of N_2O, P_{N_2O}, at equilibrium was calculated as the difference of measured total pressure in the jacketed glass vessel, P_R, and the solvent vapor pressure, P_S°, by

$$P_{N_2O} = P_R - P_S^{\circ} \qquad (5)$$

The solvent vapor pressure, P_S°, was directly measured at the desired temperature before adding N_2O.

Table 1. Measured Henry's Law Constant of N_2O in Water

T/K	k_H/Pa·m^3·mol^{-1}
298.3	4146
298.2	4048
303.8	4842
303.9	4909
313.7	6010
313.7	5897
323.4	7246
323.4	7446
333.3	8920
333.4	8890
342.7	10368
343.5	10268
353.3	12205
353.4	12375

The solubility was expressed by a Henry's law constant, according to the equation

$$P_{N_2O} = k_{H_{N_2O}} C_{N_2O} \qquad (6)$$

All operating conditions, including temperature and pressure, were recorded using a FieldPoint and LabVIEW data acquisition system. The scheme of the experimental setup is shown in the Figure 1.

Result and Discussion

To validate the solubility apparatus and the experimental procedures, the solubilities of N_2O in water and CO_2 in water at different temperatures (298.2 to 353.4) K were measured and compared to the literature. Measured Henry's constants for N_2O in water in this experiment are shown in Table 1 and for CO_2 in water shown in Table 2, whereas the comparison with several literature references is shown the in Figure 2 for N_2O in water and for CO_2 in water in Figure 3. It can be seen that the measured solubilities of N_2O and CO_2 in water agree very well with the literature values. All experiments were done at least twice, and the uncertainty is within 3 %.

Solubility of N_2O in aqueous DETA solution at different mass fractions (15, 30, 45, 60, 75, 90, and 100) % of DETA was measured at different temperatures, (297.7 to 360.7) K, and the

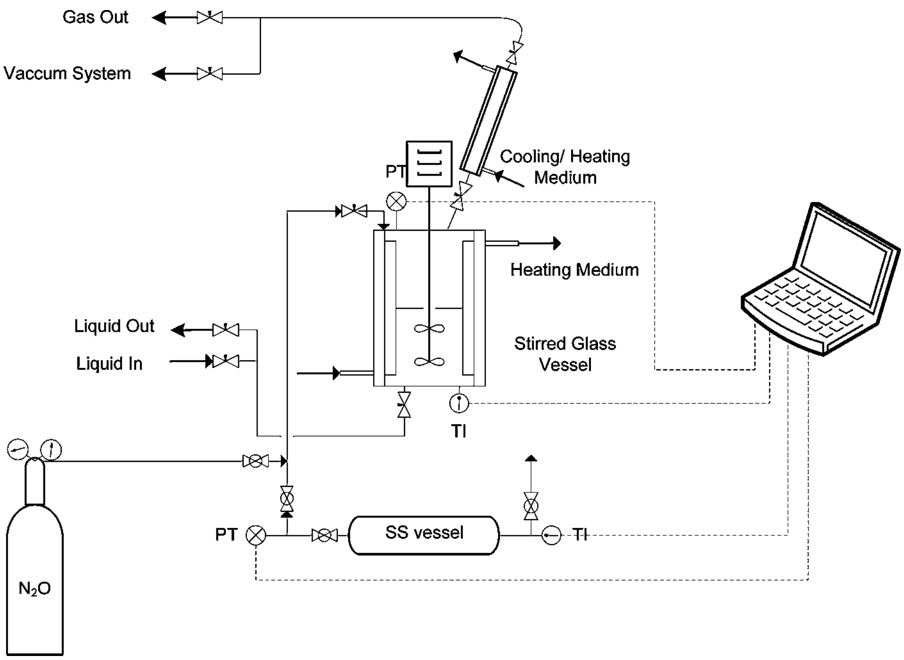

Figure 1. Solubility apparatus.

Table 2. Measured Henry's Law Constant of CO_2 in Water

T/K	k_H/Pa·m^3·mol^{-1}
298.3	3022
298.3	2991
303.4	3462
303.3	3401
313.3	4327
313.4	4328
323.0	5233
322.9	5184
332.7	6168
332.7	6128
332.8	6203
343.0	7111
342.9	7215
353.1	8359
352.1	8331

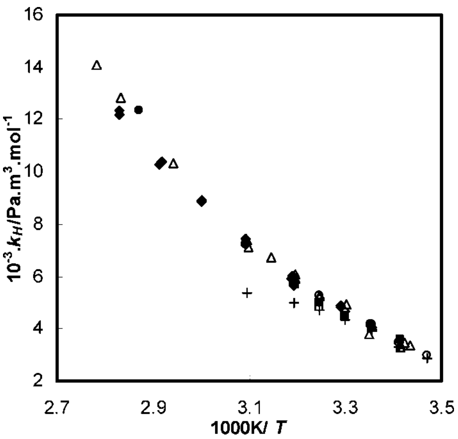

Figure 2. Henry's Law constant of N_2O in water: ♦, this work; ○, ref 7; Δ, ref 8; +, ref 9; ◇, ref 11; ●, ref 12; □, ref 16; ■, ref 17.

experimental results are shown in Table 3 and Figures 4 and 5. The solubility is strongly dependent on temperature. Generally, as expected, the solubility decreases with increasing temperature. The change with concentration is more complex. Generally, the solubility goes through a minimum value at around (50 to 60) % of DETA and then shifts to higher values in the amine region for the water-rich region. At low temperature, the solubility decreases with increasing DETA content, whereas at the highest temperature the reverse trend is seen. This behavior could be related to the packing structure of the solution itself since the density of the aqueous solution of DETA also reaches a maximum value at around (50 to 60) % of DETA,[2] thereby leaving less "free" volume of the solution available to dissolve gas.

The Redlich−Kister equation was used to correlate the solubility at various concentrations and temperatures via the

Table 3. Measured Henry's Law Constant of N_2O in Water (1) + DETA (2) Solution (w_2)

$w_2 = 15$ %		$w_2 = 30$ %		$w_2 = 45$ %		$w_2 = 60$ %	
T	k_H	T	k_H	T	k_H	T	k_H
K	Pa·m^3·mol^{-1}	K	Pa·m^3·mol^{-1}	K	Pa·m^3·mol^{-1}	K	Pa·m^3·mol^{-1}
297.7	4685	297.8	5532	297.8	8740	297.7	9662
297.7	4824	298.0	5552	297.9	8567	303.2	10215
298.5	4794	298.3	6114	298.2	8475	312.8	11792
303.2	5303	298.6	5894	298.2	8611	312.9	10835
307.9	5812	303.0	5966	303.1	9111	322.3	12443
308.0	5890	303.1	6077	303.2	9206	331.9	12821
312.9	6310	303.1	6107	312.7	10041	331.9	12231
322.5	7430	303.1	6412	312.9	10169	341.8	13298
332.0	8668	312.6	7022	322.3	11127	351.0	12090
341.7	9860	312.7	7198	322.3	11411	351.5	14134
351.5	11508	312.8	6981	322.4	11542	360.7	15236
360.7	13175	322.4	8681	332.0	12370	360.7	15236
360.8	13061	322.4	8653	341.8	13494		
361.0	13175	322.5	8737	351.2	14437		
		332.1	9638	361.0	16191		
		332.2	9813				
		341.7	10970				
		341.7	11051				
		351.4	12408				
		351.5	12579				
		360.1	13958				
		360.1	13834				

$w_2 = 75$ %		$w_2 = 90$ %		$w_2 = 100$ %	
T	k_H	T	k_H	T	k_H
K	Pa·m^3·mol^{-1}	K	Pa·m^3·mol^{-1}	K	Pa·m^3·mol^{-1}
297.8	6891	298.4	3139	297.8	1970
303.2	7097	303.2	3344	298.1	2013
312.7	7441	312.7	3635	298.1	2013
322.5	7702	312.7	3644	298.2	1989
331.9	8062	322.2	4002	303.0	2098
341.3	8365	331.6	4229	312.7	2324
351.0	8639	350.9	4830	322.3	2468
360.8	9067	351.5	4824	322.3	2552
		360.3	5004	322.4	2350
				331.9	2783
				341.6	3025
				351.1	3100
				351.2	3286
				360.3	3462
				360.7	3571

Table 4. Redlich−Kister Coefficients (A_n) for the Excess Henry Law Constants of N_2O in Water (1) + DETA (2) Solution

T/K	A_1	A_2	A_3	A_4	A_5	A_6	σ
298.1	1.4335	−3.4287	6.7697	−9.8325	−5.8956	13.3899	0.0464
303.2	1.2489	−3.1677	6.7568	−9.7989	−5.9376	13.2174	0.0574
312.9	0.9042	−2.6804	6.7327	−9.7362	−6.0162	12.8953	0.0562
322.5	0.5601	−2.1940	6.7086	−9.6736	−6.0946	12.5738	0.0463
332.2	0.2146	−1.7056	6.6844	−9.6107	−6.1733	12.2510	0.0422
342.0	−0.1353	−1.2109	6.6599	−9.5470	−6.2531	11.9240	0.0435
351.6	−0.4807	−0.7227	6.6357	−9.4841	−6.3318	11.6014	0.0357
360.6	−0.7999	−0.2715	6.6133	−9.4260	−6.4045	11.3031	0.0397

excess properties of the solubility data. The excess Henry's constant, $\hat{A}$, is calculated by an additive logarithmic rule[21,22] and defined by

$$\hat{A} = \ln(k_{\mathrm{H_m}}) - x_1 \ln(k_{\mathrm{H_1}}) - x_2 \ln(k_{\mathrm{H_2}}) \tag{7}$$

where $K_{\mathrm{H_m}}$, $K_{\mathrm{H_1}}$, and $K_{\mathrm{H_2}}$ represent Henry's Law constant of N_2O into the mixture, in pure DETA (2), and in water (1), respectively. The excess Henry's constant, $\hat{A}$, was correlated to the Redlich−Kister[23] equation by

$$\hat{A} = x_1 x_2 \sum_{n=1} A_n (1 - 2x_2)^{n-1} \tag{8}$$

where x_1, x_2 are the mole fractions of water (1) and DETA (2), respectively, and A_n are the Redlich−Kister coefficients. The Redlich−Kister coefficients A_n were determined for each temperature by regression and are presented in Table 4 along with the standard deviation, σ, corresponding to each fit.

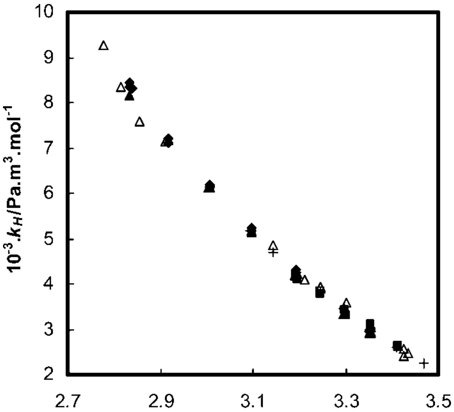

Figure 3. Henry's Law constant of CO_2 in water: ♦, this work; Δ, ref 8; +, ref 9; □, ref 16; ■, ref 17; ▲, ref 24.

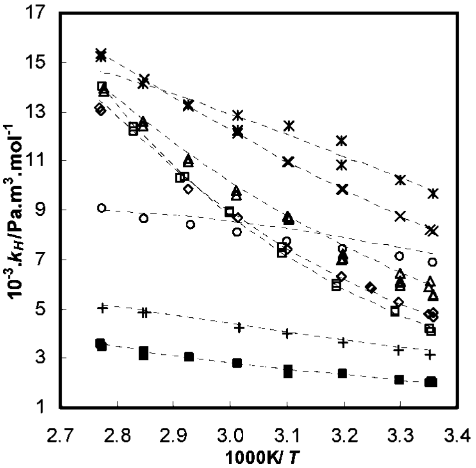

Figure 4. Henry's Law constant of N_2O in water (1) + DETA (2) solution at different mass fractions w_2: □, 0; ◇, 15; Δ, 30; ×, 45; *, 60; ○, 75; +, 90; ■, 100; - - -, model.

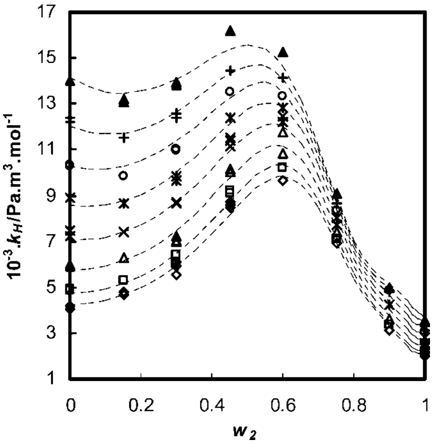

Figure 5. Henry's Law constant of N_2O in water (1) + DETA (2) solution at different temperatures: ◇, 298.1 K; □, 303.2 K; Δ, 312.9 K; ×, 322.5 K; *, 332.2 K; ○, 341.1 K; +, 351.6 K; ▲, 360.6 K; - - -, model.

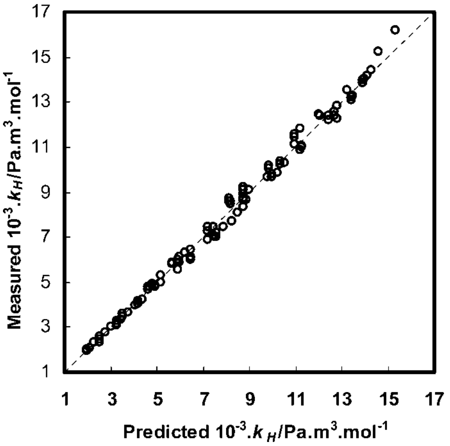

Figure 6. Parity plot for the measured and the predicted Henry's Law constant of N_2O in water (1) + DETA (2) using the parameters in Table 4 and Table 5.

$$\sigma = \left[\sum \frac{(\hat{A} - \hat{A}_{\mathrm{calc}})^2}{N_{\mathrm{exp}} - n} \right]^{1/2} \tag{9}$$

where N_{exp}, n, and $\hat{A}_{\mathrm{calc}}$ are the number of experiment, the number of parameters, and the predicted excess Henry's Law constant, respectively.

The temperature dependence of the Redlich−Kister coefficients, A_n, can be represented by polynomials (eq 10), and for DETA, a second-order polynomial was found sufficient as given in Table 5.

$$A_n = \sum_{n=1} a_n T^{n-1} \tag{10}$$

It can be seen from Figures 4 and 5 that the Redlich−Kister model agrees very well for all concentrations and temperatures,

Table 5. Coefficient of Temperature Dependence of Redlich−Kister Coefficients (a_n) for the Excess Henry's Law Constant of N_2O in Water (1) + DETA (2) Solution

	a_1	a_2
A_1	12.0832	−0.0357
A_2	−18.4837	0.0505
A_3	7.5154	−0.0025
A_4	−11.7707	0.0065
A_5	−3.4689	−0.0081
A_6	23.3404	−0.0334

indicating that this equation can be applied to correlate the solubility of N_2O in aqueous DETA solutions. Figure 6 is a plot of the experimental solubility data against the calculated result with eq 7 and shows an average deviation of 2.7 % and a maximum deviation of 8.7 %.

Conclusion

Solubility of N_2O in aqueous DETA solutions at different mass fractions, (15, 30, 45, 60, 75, 90, and 100) %, of DETA was measured at different temperatures, (297.7 to 360.7) K. The solubility of N_2O in aqueous DETA solution is strongly dependent on both temperature and concentration. A semiempirical model for the solubility considering the excess quantity of Henry's constant was developed using the Redlich−Kister equation. The model gave satisfactory agreement with the experimental data with an average deviation of 2.7 % and a maximum deviation of 8.7 %.

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