Liquid−vapor equilibria of pure and aqueous solutions of diethylenetriamine or dipropylenetriamine

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ABSTRACT

Vapor pressures of pure and aqueous diethylenetriamine (DETA) and dipropylenetriamine (DPTA) were measured by means of a static apparatus at temperatures between (283 and 363) K. The data were correlated with the Antoine equation and fitted to Redlich−Kister equation using Barker's method. Additionally, the NRTL, UNIQUAC models were used to correlate total pressures.

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1. Introduction

CO$_2$ capture using amine solutions, particularly aqueous monethalamine (MEA), is regarded as the most mature technology for post-combustion CO$_2$. The process is well-developed because it has been already used, since several decades, to remove CO$_2$ from natural gas. However it remains an expensive technology because of several reasons: high energy requirements in the regeneration step of MEA, degradation and corrosion properties of the amine, loss through emissions due to its volatility at the absorption and regeneration stage [1]. According to Rao and Rubin [2], the solvent makeup accounts to 10% of the total operating cost of the CO$_2$ capture technology when MEA is used. One solution to these requirements is to find a better solvent with high cyclic capacity, fast absorption rate, low enthalpy of absorption. Polyamines have more than one amine functionality and hence they can potentially have a high absorption rate and low volatility. They could be good candidate for CO$_2$ scrubbing from flue gas. Accurate liquid−vapor equilibrium of any new chemical solvent for carbon dioxide absorption is necessary in the design, optimization of the process.

With this aim we determined the vapor pressures of two triamines: diethylenetriamine (DETA), dipropylenetriamine (DPTA), and their aqueous mixtures. Experimental results were fitted by the Antoine equations and compared with the available literature data. A survey of the literature shows that there are no vapor pressures available for pure DPTA and for the aqueous solutions. The later were correlated using the NRTL and UNIQUAC models.

2. Experimental section

2.1. Materials

Diethylenetriamine and dipropylenetriamine were purchased from Sigma−Aldrich. Table 1 reports the purities stated by the supplier and those obtained by Gas Chromatography. The water content in the amines (important in the case of pure amine study), was determined by Karl Fischer method and it was less than

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Table 1
Purities (mass fraction) and CAS# of chemicals.

Compound	CAS#	Structure	Supplier purity	GC purity
Diethylenetriamine (DETA)	111-40-0		0.99	>0.99
Dipropylenetriamine (DPTA)	56-18-8		0.98	>0.99

30 ppm. The aqueous mixtures were prepared using deionized water (18 MΩ cm).

2.2. VLE measurements

The vapor pressure measurements for the pure components and binary systems were carried out using a static apparatus [3,4]. The apparatus is equipped with a differential manometer from MKS, type 670, model 616 A. Temperature measurements were carried out using a copper-constantan thermocouple calibrated against a 25 Ω platinum resistance standard thermometer ($\pm$0.001 K, IPTS 90) and a Leeds & Northrup bridge ($\pm 10^{-4}\Omega$). The uncertainty of the measurements are as follows: $U(P/Pa) = 0.1Pa + 0.03*P$ for $P < 600$ Pa; $U(P/Pa) = 0.01*P$ for P in the range (600–1300 Pa), $U(P/Pa) = 0.003*P$ for P over 1300 Pa and $U(T) = 0.02$ K. Mixtures were prepared by mass and thoroughly degassed by distillation. Once the VLE measurements were carried out, the liquid phase is recovered and the molar fraction of the components determined by gas chromatography. The estimated uncertainty of the molar fraction determination is $U(x_1) = 0.0005$.

3. Results and discussion

3.1. Pure compounds

Experimental results of DETA and DPTA are given in Table 2. Vapor pressures of water were taken from literature [5]. Experimental P/T were fitted to the Antoine equation and the coefficients reported in Table 3:

$$\log_{10}P/Pa = A - \frac{B}{(C + T/K)} \tag{1}$$

The objective function Q was the sum of the squared relative deviations in pressure:

$$Q = \sum \left(\frac{P_{calc} - P_{exp}}{P_{exp}}\right)^2 \tag{2}$$

The enthalpy of vaporization $\Delta_{vap}H_m(T_m)$ of the two triamines at the mean temperature of the experiments, T_m, was deduced from the fits of the experimental vapor pressures. In a second step, we used Chickos and Acree correlation [6] to determine $\Delta_{vap}H_m$ at the temperature 298.15 K, Table 4.

Several authors studied diethylenetriamine [7–10]. The vapor pressures data obtained in the present study are in agreement with values reported by Steele et al. [10] who used ebulliometric method. The mean relative deviation vary from 1.9% at T = 370.5 K–5.98% at T = 445.531 K. In addition, the enthalpy of vaporization deduced from the present study at 298.15 K is in a very good agreement with Steele et al. [10] value determined using a calorimeter (relative deviation of 1.5%). To the best of our knowledge, there are no values reported in the literature for the vapor pressures and enthalpy of vaporization of DPTA.

Table 2
Experimental vapor pressures of pure DETA and DPTA.

T/K	P_{exp}/Pa
DETA	
283.07	4.340
293.11	10.98
303.16	26.48
313.21	58.38
323.24	122.2
333.30	241.9
343.33	453.5
352.13	767.1
353.40	820.6
362.40	1357
372.39	2283
382.44	3676
392.48	5720
402.41	8703
412.38	12,788
422.28	18,433
432.28	26,483
442.17	36,029
DPTA	
293.09	2.725
303.14	6.161
313.11	13.55
323.16	28.13
333.18	57.33
343.23	111.1
353.29	210.6
363.37	382.0
372.35	621.6
382.45	1051
382.45	1050
382.45	1037
382.48	1052
392.53	1767
402.46	2839
412.49	4254
412.49	4276
422.32	6445
432.25	9444
432.25	9513
432.25	9498
432.25	9558
442.05	13,599

$U(P/Pa) = 0.1Pa + 0.03*P$ for $P < 600$ Pa; $U(P/Pa) = 0.01*P$ for P in the range (600–1300 Pa). $U(P/Pa) = 0.003*P$ for P over 1300 Pa and $U(T) = 0.02$ K.

Table 3
Coefficients A, B, and C and overall mean relative deviation in pressure of the Antoine equation (Eq. (1)).

Compound	Temperature/K	A	B	C	$100(\delta P/P)$
DETA	283.07 to 442.17	9.820	1952	−70.66	0.90
DPTA	293.09 to 442.05	11.015	2911	−18.39	1.28

$100\delta P/P = \frac{1}{N}\sum_{i=1}^{N} 100\left(\frac{P_{calc} - P_{exp}}{P_{exp}}\right)$, where N is the total number of experimental values.