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Phase equilibrium measurements and thermodynamic modeling of aqueous solutions of polyamines CO_2 absorbents: 3-aminopropylmethylamine, 3-aminopropyldimethylamine and N,N-diethyl 1,3-propanediamine at temperatures from 273 K to 363 K

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ABSTRACT

The vapor pressures of the pure components 3-aminopropylmethylamine (MAPA), 3-aminopropyldimethylamine (DMAPA) and N,N-diethyl 1,3-propanediamine (DEAPA) along with the binary mixtures (MAPA + water), (DMAPA + water) and (DEAPA + water) were measured by means of a static apparatus at temperatures between (273 and 363) K. The data were correlated with the Antoine equation. From these data, excess Gibbs functions (G^E) were calculated for several constant temperatures, and fitted to a three parameters Redlich–Kister equation using the Barker's method. Additionally, the NRTL and UNIQUAC models have been used for the correlation of the total pressure.

1. Introduction

CO_2 represents more than 70% of total greenhouse gas emissions due to anthropogenic activities, mainly the combustion of fossil fuels [1]. Several methods exist for the absorption of CO_2 from flue gas among which the chemical absorption technology. At the solvent regeneration step of the process, relatively pure CO_2 is obtained (purity 99%). The acid gas is then compressed and dedicated for geologic storage.

Despite its maturity, chemical absorption of CO_2 is financially nonviable and must be improved at the two stages of the capture process: absorption of CO_2 and solvent regeneration. An economical efficiency in the absorption process depends on a solvent presenting an increased capacity of CO_2 absorption than the currently most used solvent, aqueous monoethanolamine (MEA). This optimal solvent could be a polyamine. Due to its additional amine function, a polyamine is expected to have higher reaction rate with CO_2 compared to solvent with single amine function [2–4]. On another side, the polyamine solvent must not present some drawbacks, such as, toxicity and volatility.

In this work, vapor pressures of pure polyamines and their aqueous solutions are performed in order to estimate their volatility during CO_2 absorption and desorption, in the absorber and stripper respectively. Reliable measurements of vapor pressures are a key industrial interest when screening for new promising solvents for CO_2 capture and in the design of the water wash unit. On the other hand volatility, deduced from vapor pressures measurements using Barker's method, are essential for thermodynamic modeling of (amine + water) systems and in the understanding the molecular interactions of species in nonideal (amine + water) mixtures. Three polyamines were selected presenting each of them two amine functions. In all cases the compounds have a primary amine function where the additional amine function is a secondary amine function in the case of 3-aminopropylmethylamine, a tertiary amine function in the case of 3-Aminopropyldimethylamine and N,N-diethyl 1, 3-propanediamine.

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TABLE 1
CAS#, structures and purities of chemicals from Sigma-Aldrich.

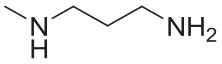
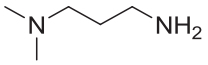
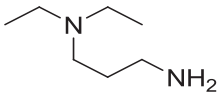
Compound	CAS #	Structure	Claimed purity (mass fraction)	GC purity (peak area)
3- Aminopropylmethylamine (MAPA)	6291-84-5		0.98	>0.99
3-Aminopropyldimethylamine (DMAPA)	109-55-7		0.99	>0.99
N,N-diethyl 1,3-propanediamine (DEAPA)	104-78-9		⩾0.99	>0.99

TABLE 2
Coefficients *A*, *B*, and *C* and overall mean relative deviation in pressure of the Antoine equation (Eq. (1)).

Compound	*T*/K	*A*	*B*	*C*	100 ($\delta P/P$)
MAPA	273.00 to 432.40	9.132	1361	−83.69	0.40
DMAPA	273.04 to 363.44	9.320	1485	−62.71	0.15
DEAPA	263.16 to 363.25	9.625	1755	−56.43	0.29

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

TABLE 3
Experimental and calculated (with the Antoine equation (Eq. (1)) vapor pressures of pure MAPA, DMAPA and DEAPA.

T/K	P_{exp}/Pa	P_{cal}/Pa	$\delta P/P$ (%)
	MAPA		
273.00	89	88	1.73
283.37	205	208	−1.16
293.47	431	442	−2.41
303.11	861	852	1.01
313.18	1607	1594	0.78
323.26	2830	2831	−0.02
323.26	2828	2831	−0.09
333.23	4764	4774	−0.21
333.25	4764	4779	−0.31
343.26	7745	7754	−0.11
343.28	7742	7763	−0.27
343.30	7740	7771	−0.40
352.54	11,854	11,766	0.75
352.54	11,847	11,766	0.69
353.24	12,137	12,128	0.08
362.82	18,101	18,069	0.18
362.84	18,106	18,086	0.11
372.74	26,606	26,562	0.17
372.76	26,609	26,586	0.09
382.84	38,343	38,312	0.08
382.87	38,346	38,344	0.01
392.92	53,963	53,906	0.11
392.95	53,959	53,949	0.02
402.59	73,401	73,278	0.17
402.59	73,398	73,278	0.16
402.61	73,412	73,333	0.11
422.46	129,798	130,425	−0.48
422.46	129,794	130,425	−0.49
422.51	129,836	130,602	−0.59
432.40	169,969	169,764	0.12
432.40	170,017	169,764	0.15
100$\delta P/P$			**0.40**
	DMAPA		
273.04	183	182	0.27
283.06	381	382	−0.13
293.13	749	752	−0.44
303.16	1396	1397	−0.05
313.21	2478	2472	0.22
323.27	4186	4186	0.00
333.32	6828	6814	0.20
343.37	10,727	10,714	0.12
343.37	10,725	10,715	0.09
353.41	16,311	16,315	−0.03
363.44	24,103	24,159	−0.23
100$\delta P/P$			**0.15**
	DEAPA		
263.16	14	14	0.04
273.05	34	33	0.57
283.27	77	78	−0.21
283.27	77	78	−0.11
293.22	163	164	−0.33
303.14	326	325	0.09
303.16	325	326	−0.23
313.16	616	617	−0.06
313.18	616	618	−0.19
323.16	1112	1113	−0.07
323.16	1114	1113	0.09
333.18	1940	1925	0.75
343.21	3234	3208	0.82
353.19	5161	5153	0.16
353.19	5162	5153	0.17
363.25	7965	8052	−1.09
100$\delta P/P$			**0.29**

Note: $u(P/Pa) = 0.03^{*}P$ 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 $P > 1300$ Pa, and $u(T) = \pm 0.02$ K for the temperature range $203 \leqslant T/K \leqslant 463$.

2. Experimental section

2.1. Materials

The diamines 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 30 ppm. The aqueous mixtures were prepared by weighing (uncertainty is ±0.0004 g). Deionized water was used (18 MΩ · cm) when preparing aqueous solution.

2.2. VLE measurements

The vapor pressure measurements for the pure components and binary systems were carried out using a static apparatus [5,6]. The apparatus is equipped with a differential manometer from MKS, model 616 A. The pressure measurement consisted of applying the vapor pressure of the sample on the measurement side of the gauge. The reference side was submitted to a permanent-dynamic pumping. The residual pressure was 10^{-4} Pa and therefore can be neglected. Temperature measurements were carried out using a copper-constantan thermocouple calibrated against a 25 Ω platinum resistance standard thermometer ($T = \pm 0.001$ K, IPTS 90) and a Leeds & Northrup bridge ($\pm 10^{-4}$ Ω). The differential