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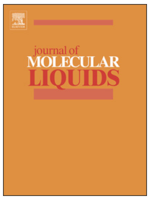

Vapor–liquid equilibria of N,N,N′,N′ tetramethylethylenediamine (TMEDA), tetramethylpropylenediamine (TMPDA) and their aqueous solutions

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ABSTRACT

The vapor pressures of (N,N,N′,N′ tetramethylethylenediamine (TMEDA) + water), (tetramethylpropylenediamine (TMPDA) + water) binary mixtures, and of pure N,N,N′,N′ tetramethylethylenediamine and tetramethylpropylenediamine components were measured by means of two static devices 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 order Redlich–Kister equation using the Barker's method. The two binary systems show a positive azeotropic behavior. The TMEDA aqueous solution exhibits positive deviations in G^E for all investigated temperatures over the whole composition. The (TMPDA + water) system shows the same behavior except for T = 273.15 and 283.15 K where a sinusoidal shape is observed. Additionally, the NRTL and UNIQUAC models have been used for the correlation or prediction of the total pressure.

1. Introduction

Aqueous solutions of alkanolamines are widely employed in the industry for removal of acidic gases such as CO_2 and H_2S from natural gas and flue gas streams. In recent years the existing gas treating technology was getting increased attention due to its potential for carbon capture applications in the power generating industry [1].

Various amines including aliphatic diamines and polyamines, as well as their mixtures with ionic liquids are considered as promising candidates for CO_2 removal [2,3]. Basic physical property information for this class of components is still under development among which vapor–liquid equilibria (VLE).

The present paper is part of a research program of VLE of aqueous mixtures of alkanolamines or amines [4–6]. The vapor–liquid equilibria of pure N,N,N′,N′ tetramethylethylenediamine (TMEDA), (tetramethylpropylenediamine (TMPDA) and their aqueous solutions were studied in the present work. The NRTL and UNIQUAC models were used to correlate the vapor pressures of pure and mixed liquids.

A survey of the literature shows that there is no data available on the open literature for the investigated binary systems.

2. Experimental section

2.1. Materials

The diamines were supplied by Aldrich Chem. (Milwaukee, WI, USA), Table 1. The mass fraction purity, tested by GLC, is better than 0.99. The water content in the amines (important in the case of pure amine study) was determined by the Karl Fischer method and it was less than 30 ppm. The aqueous mixtures were prepared by weighing. Deionized water was used (18 MΩ·cm) and the weighing balance uncertainty is ±0.0004 g.

2.2. VLE measurements

The vapor pressure measurements for the pure components and aqueous solutions were carried out using a static device [5,6]. The apparatus is equipped with a differential manometer from MKS, model 616A. 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 (±0.001 K, ITS 90) and a Leeds & Northrup bridge (±10^{-4} Ω). The differential pressure gage was calibrated against a U-manometer filled

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

Compound	CAS#	Temperature/K	*A*	*B*	*C*	100 (δP / P)
TMEDA	110-18-9	273.10–363.33	8.829	1221	−74,16	0.54
TMPDA	110-95-2	273.10–363.30	8.373	1132	−89,040	1.55
Water [5]	7732-18-5	273.12–363.31	10.384	1832	−32,49	0.50

$$100\,\delta P/P=\frac{1}{N}\sum_{i=1}^{N}100\left(\frac{Pcalc-Pexp}{P\,exp}\right),$$

where *N* is the total number of experimental values.

with mercury or Apiezon oil depending on pressure range. The levels in both arms of the U-shaped manometer were read by a cathetometer (reference 70298, from Bouty France) to the nearest 0.001 mm. The calibration was then checked by measuring the vapor and the sublimation pressures of water and naphthalene [7,8]. The uncertainty of the measurements is estimated to be: $u(P\,/\,\text{Pa}) = 0.03 * P$ for $P < 600$ Pa; $u(P\,/\,\text{Pa}) = 0.01 * P$ for P in the range (600 to 1300 Pa), $u(P\,/\,\text{Pa}) = 0.003 * P$ for P over 1300 Pa, and $u(T) = \pm 0.02$ K for the temperature range $243 \leq T/\text{K} \leq 473$. Mixtures were prepared by mass and thoroughly degassed by distillation as described previously [6]. Once the VLE measurements were carried out, the liquid phase is recovered and the molar fraction of the components was determined by gas chromatography. The estimated uncertainty of the molar fraction is $u\,(x_i) = 0.0002$.

3. Results and discussion

The experimental vapor pressure data were fitted to the Antoine equation:

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

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 overall mean relative deviation in pressure is:

$$\frac{\delta P}{P}\% = \frac{100}{N}\sum\left(\frac{P_{calc} - P_{exp}}{P_{exp}}\right) \tag{3}$$

where *N* is the total number of experimental values.

The explored temperature range, the coefficients *A*, *B*, and *C* of the Antoine equation and the overall mean relative deviation in pressure for the pure amines are listed in Table 1. Water data were taken from the literature [9]. Experimental results of TMEDA and TMPDA and relative deviations obtained using Antoine equation are given in Table 2.

For pure TMEDA our vapor pressure data agree to within 4% with those reported by Dahmani et al. [10] in the temperature range (303.15 to 343.15 K), where for pure TMPDA, our vapor pressures agree with those reported by Verevkin and Chernyak [11] to within 5% in the temperature range (273 to 323 K).

For the two binary mixtures, the vapor pressures were measured at temperatures between 293.15 K and 363.15 K and the results fitted to the Antoine equation. Molar excess Gibbs functions G^E were estimated from the Redlich–Kister equation using the Barker's [12] method:

$$G^E = x_1(1-x_1)\sum_{j=1}^{m} R\ T\ G_j(2x_1-1)^{j-1} \tag{4}$$

Table 2
Experimental and calculated (with the Antoine equation (Eq. (1))) vapor pressures of pure TMEDA, TMPDA and water.

T/K	*P*exp / Pa	*P*cal / Pa	δP / P (%)
TMEDA			
273.10	489	491	−0.39
283.06	966	964	0.24
293.08	1790	1784	0.32
313.11	5275	5235	0.76
333.23	12,888	13,056	−1.30
343.26	19,474	19,564	−0.46
353.30	28,606	28,485	0.43
363.33	40,570	40,389	0.45
100 δP / P			0.54
TMPDA			
273.10	166	167	−0.45
283.09	344	345	−0.31
293.06	666	666	−0.01
303.08	1225	1211	1.15
313.11	2131	2090	1.93
323.16	3493	3444	1.43
333.17	5288	5434	−2.77
343.20	8047	8283	−2.93
353.23	12,096	12,230	−1.11
363.30	18,195	17,570	3.43
100 δP / P			1.55

Note: $u(P\,/\,\text{Pa}) = 0.03 * P$ for $P < 600$ Pa; $u(P\,/\,\text{Pa}) = 0.01 * P$ for P in the range (600 to 1300 Pa), $u(P\,/\,\text{Pa}) = 0.003 * P$ for $P > 1300$ Pa, and $u(T) = \pm 0.02$ K for the temperature range $203 \leq T/\text{K} \leq 463$.

where x_1 is the molar fraction for the diamine. The coefficients G_j were determined by regression through minimization of the sum of residuals between experimental and calculated pressures.

Activity coefficients, γ_i, are rigorously calculated using the following equation:

$$y_iP\ \phi_i \exp\int_{P}^{Pi_i^s}\frac{V_i^L}{RT}dP = \phi_i^s\gamma_i x_i P_i^s \tag{5}$$

where y_i and x_i are respectively the molar fraction in the vapor and in the liquid phase of component *i*, *P* is the total pressure, P_i^S is the saturated vapor pressure of pure component *i* (determined in this work), ϕ_i is the fugacity coefficient of component *i* in the vapor phase and ϕ_i^s is the fugacity coefficient of the pure component *i* at saturation. The exponential term $\exp\int_{P}^{Pi_i^s}\frac{V_i^L}{RT}dP$ is the Poynting factor. At low pressures (below 2 bars, which is our case), vapor phases usually approximate ideal gases, for which $\phi_\text{i} = \phi_i^s = 1$ and the Poynting factor may be neglected. Therefore for low pressure, VLE data reduces to Eq. (6):

$$y_i = \frac{x_i\gamma_i P_i^s}{P}. \tag{6}$$

The vapor pressures as a function of the mole fraction for each binary mixture are listed in Tables 3 and 4. The G_j coefficients and standard deviations $\sigma(G_j)$ for TMEDA and TMPDA aqueous solutions are reported in Table 5.

For each system, the molar excess Gibbs functions G^E at different temperatures, calculated from our vapor pressure data, are plotted against the mole fraction x_1, Figs. 1 and 2.

The aqueous solution containing TMEDA exhibits positive deviations in G^E over the whole composition range and the G^E curves are slightly asymmetrical. The (TMPDA + water) binary mixture exhibits the same behavior except for T = 273.15 and 283.15 K where a sinusoidal shape is observed.