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Vapor Pressure Measurements of Bis(hydroxyethyl)piperazine and Tris(hydroxyethyl)ethylenediamine

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Vapor pressures of bis(hydroxyethyl)piperazine (BHEP) and tris(hydroxyethyl)ethylenediamine (THEED) were measured in the temperature ranges of (412.65 to 507.15) K and (372.55 to 472.35) K using the static and gas saturation techniques, respectively. The experimental data are well represented by the modified Antoine and the integrated Clausius−Clapeyron equations, and their coefficients are reported. The enthalpies of vaporization were found to be (62.76 ± 5.33) and (89.96 ± 3.91) kJ/mol for BHEP and THEED, respectively.

Introduction

Aqueous solutions of diethanolamine (DEA) are commonly used to remove acid gases (including hydrogen sulfide and carbon dioxide) from natural, refinery, and other industrial gas streams. Although the acid gas−amine reactions are reversible, some irreversible reactions may also occur under industrial conditions resulting in products from which the amines are not easily recovered. This phenomenon is called amine degradation (Meisen and Kennard, 1982). Industrial degraded DEA solutions usually contain hydroxyethyl oxazolidone (HEOD), bis(hydroxyethyl)piperazine (BHEP), and tris(hydroxyethyl)ethylenediamine (THEED), in addition to small concentrations of higher boiling degradation compounds (Kennard and Meisen, 1985). The presence of contaminants in amine solutions creates operational problems (Hall et al., 1981) including foaming, fouling, and corrosion as well as a reduction in active amine content and an increase in solution viscosity. In the United States alone, solvent losses in alkanolamine gas and liquid-treating plants amount to 95 million pounds per year valued at more than $60 million (Stewart, 1991). To maintain process efficiency, the contaminated amine solutions must be partially or completely replaced periodically with virgin amines. Typically, waste solutions contain over 80% of the original active amine (Dawodu et al., 1993). The current practices of deep well injection and incineration of the waste amine solutions are not only environmentally unattractive but also constitute a loss of valuable amine. A better option is to develop processes for reclaiming contaminated solutions, and distillation appears to be most promising since it is capable of separating a wide range of impurities including solids, heat stable salts, and organic degradation products. As part of our ongoing work into the development of distillation processes for purifying degraded amine solutions, we needed to determine the vapor pressures of BHEP and THEED since they had not been reported previously. HEOD can be reverted to DEA by caustic treatment and was therefore not considered.

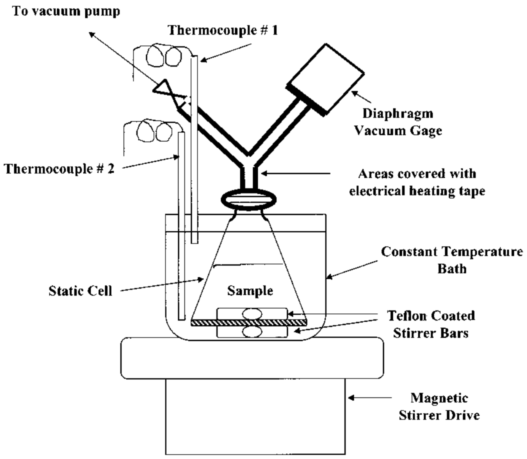
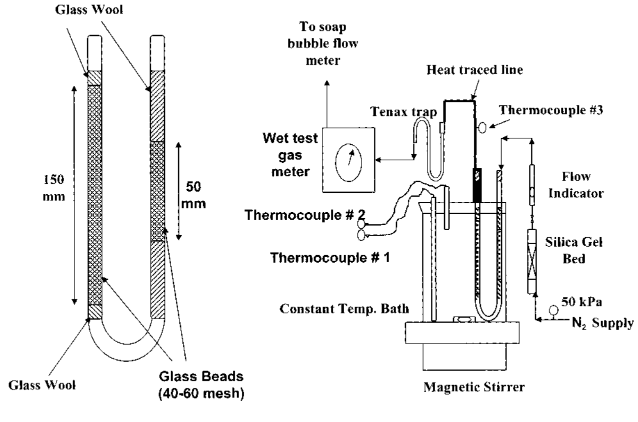


Figure 1. Schematic diagram of the static cell apparatus.



A. Saturating tube B. Experimental set-up

Figure 2. Schematic diagram of gas saturation apparatus.

Comprehensive reviews on techniques for determining vapor pressures have been reported in the literature (e.g., Boublik et al., 1975). In the static method, the equilibrium vapor pressure of a pure compound is determined in a thermostated cell by means of an appropriate total pressure measuring device. However, the static method is not well suited for compounds with low vapor pressures because impurities and the thermomolecular pressure effect (ther-

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Table 1. Vapor Pressures of Water, DEA, and Hexadecane Measured in This Work and Reported Previously

	P/kPa	
(T ± 0.2)/K	measured ± 0.07	lit.
	Water	
294.34	2.40	2.52
303.65	4.13	4.36
308.55	5.60	5.75
313.35	7.33	7.45
322.25	11.73	11.79
332.25	19.06	19.10
342.15	29.46	29.83
351.95	44.52	45.09
	DEA[a]	
392.55	0.27	0.21
411.95	0.80	0.67
422.45	1.33	1.17
432.35	2.00	1.92
442.15	3.07	3.04
452.35	4.53	4.77
461.95	7.33	7.13
471.45	10.66	10.39
	Hexadecane[a]	
119.6	0.27	0.30
139.2	0.93	0.84
149.2	1.60	1.34
163.9	2.93	2.54
178.8	4.70	4.59
193.6	8.00	7.85
204.0	11.33	11.15
208.7	13.20	12.99

[a] Literature data for pressures below 5 kPa were extrapolated using the Antoine parameters. Vapor pressures above 5.00 kPa were reported for DEA and hexadecane in the literature (Ohe, 1976).

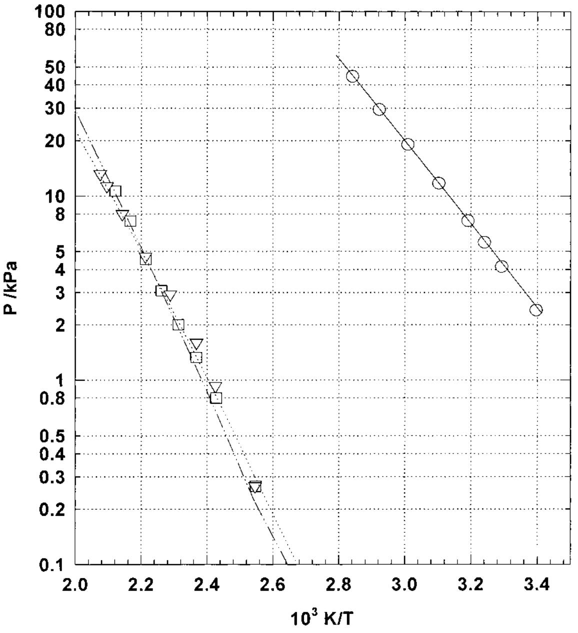

Figure 3. Vapor pressure of water, DEA, and hexadecane: (○) water—present work; (—) steam table—data from Weast (1986); (□) DEA—present work; (—••—) DEA—data from Ohe (1976); (▽) hexadecane—present work; (•••) hexadecane—data from Ohe (1976).

mal transpiration) often become significant (Patterson, 1956).

An alternate general method is the gas saturation (also referred to as the transport, entrainment or flow) technique, which is appropriate for substances with vapor pressures below approximately 100 Pa. A nonreactive, insoluble gas is passed over the test sample under conditions that yield complete gas saturation, and the rate of sample removal and/or the saturated vapor concentration in the gas is determined.

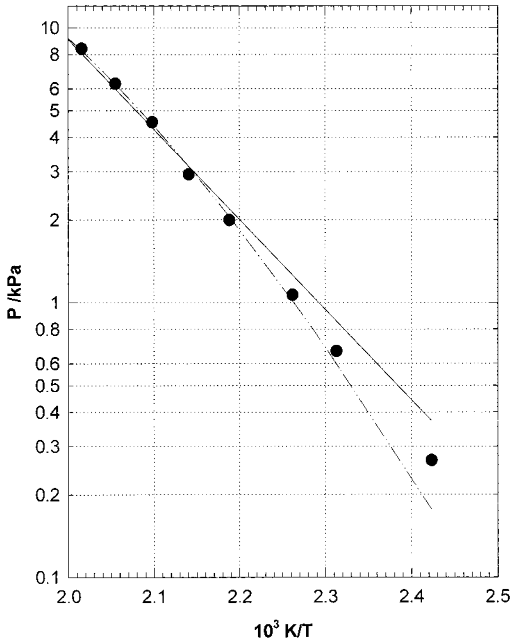

Figure 4. Vapor pressure of BHEP: (●) present experimental data; (—) integrated Clausius—Clapeyron equation; (—••—) modified Antoine equation.

Table 2. Vapor Pressure of BHEP Measured by the Static Cell Technique

	P/kPa		
		estimated	
(T ± 0.2)/K	measured ± 0.07	modified Antoine eq	integrated Clausius—Clapeyron eq
412.65	0.27	0.18	0.37
432.35	0.67	0.60	0.86
442.15	1.07	1.01	1.26
470.05	2.00	2.06	2.20
467.15	2.93	3.13	3.14
476.65	4.53	4.47	4.34
486.65	6.26	6.24	6.00
496.15	8.40	8.27	8.27
507.15	10.93	11.01	11.24

The vapor pressures of BHEP and THEED were found by the static and gas saturation methods, respectively. For the temperature range of interest in connection with reclaiming industrial amine solutions, the BHEP vapor pressures are fairly high (>400 Pa) and enable the use of cells equipped with total pressure sensors. The high melting point of BHEP (410 K) creates serious problems for other techniques. THEED has very low vapor pressures (<27 Pa) in the temperature range of interest and cannot be easily measured directly unless sample purities are very high. The gas saturation technique is relatively insensitive to low concentrations of impurities.

Experimental Section

Materials. BHEP with a purity exceeding 99% was supplied by Aldrich Chemical Co. (Milwaukee, WI) and was used without further purification. THEED was specially prepared with a purity exceeding 95% (Abedinzadegan Abdi, 1997). Its primary impurities were BHEP and DEA in almost equal percentages.

BHEP Apparatus and Procedures. The equipment shown schematically in Figure 1 was used for the BHEP

Table 3. Parameters in the Vapor Pressure Equations (Eq 1, Modified Antoine Equation; Eq 2, Integrated Clausius−Clapeyron Equation)

		parameters			standard deviation			
compound	eq	A	B/K	C/K^{-1}	σ_A	σ_B/K	σ_C/K^{-1}	$r^{2\,a}$
BHEP	1	84.281	22,106.0	−0.062	13.24	3,247.0	0.014	0.9998
	2	10.514	−3,277.8		0.238	118.1		0.9984
THEED	1	0.4369	1,035.0	0.0161	0.028	240.6	0.008	0.9999
	2	11.432	−4698.1		0.136	64.3		0.9977

[a] $r^2 = 1 - \sum_{i=1}^{n}(P_{\mathrm{meas}} - P_{\mathrm{calc}})^2/\sum_{i=1}^{n}(P_{\mathrm{meas}} - P_{\mathrm{avg}})^2$.

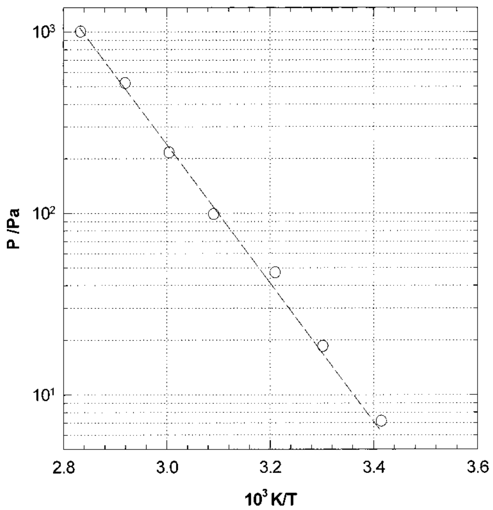

Figure 5. Vapor pressure of naphthalene: (○) present experimental data; (− −) data from Wania et al. (1994).

experiments. The cell was a 25 mL flask with glass ball and socket joints, which could seal the system at very low pressures. Three calibrated type K-type thermocouples were used and their readings displayed on a digital temperature indicator (model L-08435-41, Cole Parmer Instruments Co., Chicago, IL) with a precision of ±0.2 K. Two thermocouples were placed in the constant temperature bath to monitor the temperatures of its lower and upper regions to ensure that the stirring was sufficient to provide isothermal conditions. The third thermocouple was inserted in the line connecting the cell to the pressure sensor and vacuum pump. All lines were kept at least 1 K above the cell temperature to avoid condensation. The cell contents were stirred to ensure complete thermal equilibrium between the inside and outside of the cell. Heating was provided by a 500 W electrical tape wrapped around the 100 mL thermal bath, and the temperature was controlled within ±0.1 K of the set point with an electronic controller (model CN 76000, Omega Technologies, Stamford, CT). The pressure was measured with a 0−200 kPa diaphragm vacuum gauge (model L-68801-53, Cole Parmer Instruments Co., Chicago, IL) with a resolution of 25 Pa and an accuracy of better than ±0.5% of readings. The pressure sensor was calibrated for pressures ranging from high vacuum to atmospheric pressure.

About 15−20 g of the BHEP sample was melted and degassed by boiling it at low pressures for at least 15 min. The temperature was then briefly raised to 453 K and the pressure somewhat reduced so that the liquid boiled severely for a short while to avoid thermal breakdown. The temperature was then lowered to approximately 412 K (i.e., above the BHEP melting point), and a vacuum was applied. The cell was then sealed by closing the valve connecting the cell to the vacuum pump. The total pressure was recorded at the desired temperature once the system had reached equilibrium. It typically took less than 15 min for equilibrium to be established. The experiments were repeated at least three times, and the precision of the pressure measurement was 65 Pa.

Table 4. Vapor Pressures of THEED Measured by the Gas Saturation Technique

	P /Pa	
(T ± 0.2)/K	measured ± σ	estimated^a
372.55	0.06 ± 0.02	0.066
392.45	0.33 ± 0.03	0.290
412.65	1.10 ± 0.06	1.114
432.65	4.09 ± 0.55	3.742
472.35	28.12 ± 2.10	30.604

[a] Estimate is based on eq 2.

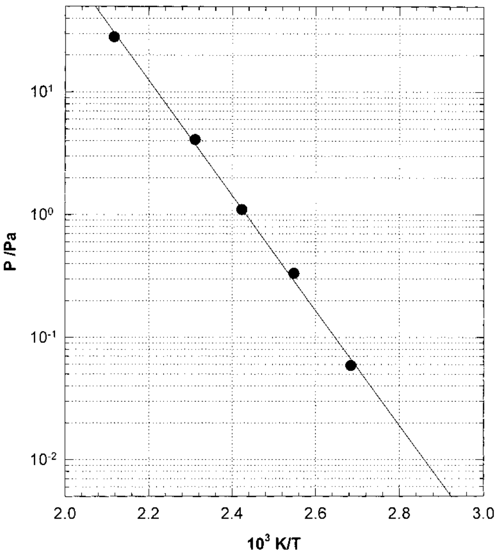

Figure 6. Vapor pressure of THEED: (●) present experimental data; (—) integrated Clausius−Clapeyron equation.

THEED Apparatus and Procedures. The experimental apparatus is shown in Figure 2A,B. A U-shaped Pyrex glass tube (8 mm i.d., 350 mm long) was used as the gas saturator. The tube was filled with 40−60 mesh glass beads. One gram of the THEED sample was dissolved in 10 g of methanol, and about 1 mL of the solution was charged into the gas saturator. The liquid mixture penetrated into and remained in the void space as a thin film coating the beads. The methanol was subsequently removed by gently heating the U-tube under reduced pressures for almost 2 h before starting the vapor pressure measurements. Ultrapure nitrogen was supplied from cylinders and was pretreated by passing it through a bed of silica gel beads (Chromatographic Specialties, 35/60 mesh). The nitrogen stream was then thermally equilibrated and saturated by passing it through the U-tube. A 6 mm i.d., 250 mm long stainless steel tube filled with Tenax TA 60/100 mesh (Supelco Inc., Oakville, Ontario) was used as the trap to adsorb the vaporized material

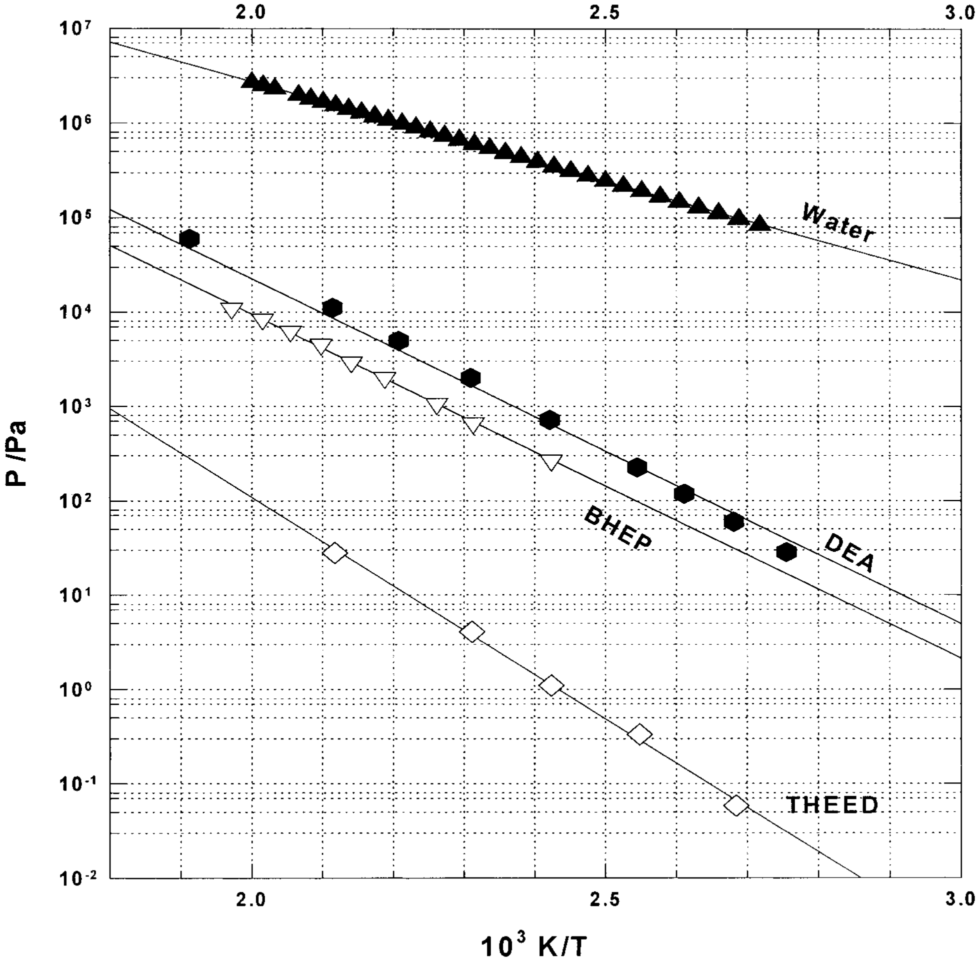

Figure 7. Vapor pressure of water, DEA, BHEP, and THEED as a function of temperature. (The solid lines represent the correlated result by the integrated Clausius−Clapeyron equation.)

carried by the nitrogen (see Figure 2B). After the experiment was completed, the trap was transferred to the oven of a gas chromatograph (model 5830A, Hewlett-Packard). A flame ionization detector calibrated with standard solutions of DEA, BHEP, and THEED was used (Abedinzadegan Abdi, 1997) to determine the quantity of eluting THEED.

All lines and parts between the gas saturator and the Tenax trap were heat-traced to maintain temperatures at least 1 K above those of the constant temperature bath. The total volume of the inert gas was measured by a wet test gas meter (Precision Scientific Co., Chicago, IL). The gas meter was calibrated with a soap bubble flowmeter. The constant temperature bath was a 2 L Pyrex beaker filled with Paratherm heat transfer oil and was warmed with a 500 W electric tape. Two K-type thermocouples were placed into the bottom and top sections of the bath, and the oil was agitated with a magnetic stirrer bar to ensure thermal uniformity. The temperature was regulated with the controller already described in the section on BHEP.

Results and Discussion

BHEP. To verify that the static technique yielded accurate results, the vapor pressures of deionized water, DEA, and hexadecane were measured and compared with literature values (Ohe, 1976). As shown in Table 1 and illustrated in Figure 3, the agreement between the measured and previously reported values is satisfactory.

Table 2 summarizes the results of the BHEP vapor pressure measurements, and Figure 4 presents the data in graphical form. The modified Antoine equation (eq 1) and the integrated form of the Clausius−Clapeyron equation (eq 2) gave good fits with the experimental data:

$$\ln\{P\} = A - B/\mathrm{T} + C\mathrm{T} \qquad (1)$$

$$\log\{P\} = A + B/\mathrm{T} \qquad (2)$$

$$\text{where} \quad B = -\Delta_{\text{vap}}H/(2.303R)$$

Equation 2, subsequently referred to as the “integrated Clausius−Clapeyron equation”, is based on the assumptions that the latent heat of vaporization is constant and that the molar volume of the liquid phase is negligible compared with that of the vapor phase.

The numerical values of the coefficients and their units are given in Table 3.

THEED. To verify the reliability of the gas saturation method, the vapor pressure of naphthalene was determined. This compound has also been recommended by IUPAC as a reference material for determining enthalpies of sublimation (or vaporization). One gram of naphthalene was dissolved in 20 g of hexane, and 2 mL of the solution were charged into the U-tube. The solvent was then evaporated under low pressures. Measurements of the naphthalene vapor pressure at room temperature (293−298 K) were performed at three different flow rates ranging from (5 to 20) mL/min to determine whether gas saturation was achieved in the U-tube. No significant change in vapor pressure was observed with gas flow rates up to 20 mL/min. The gas rate was subsequently set to 10 mL/min. Since the volume of the gas saturator was approximately 17 mL and had a void volume of 50%, the residence time of the gas was about 50 s. This exceeds the residence times of 30 s, which had been reported as adequate to achieve equilibrium (Wania et al., 1994). All experiments were repeated at least three times, and the mean values of the vapor pressures were reported. The results of the naphthalene vapor pressure measurements are shown in Figure 5. Very good agreement was obtained with the literature values (Wania et al., 1994)

To calculate the vapor pressures, the following equation for vapor−liquid equilibria was used:

$$y_iP = x_i\gamma_iP_i^{\mathrm{s}} \tag{3}$$

The total system pressure (P) and composition in the vapor phase (y_i) were measured directly. Since the mole fraction (x_i) of the sample compound in the liquid phase was close to unity, the activity coefficient (γ_i) was assumed to be one. The vapor pressure (P_i^{s}) could therefore be calculated from eq 3. The results of the THEED vapor pressure measurements are summarized in Table 4 and shown graphically in Figure 6.

Figure 7 provides a comparison of the vapor pressures of compounds typically found in partially degraded DEA solutions. The integrated Clausius−Clapeyron equation (eq 2) was used to regress the experimental data. It is apparent that THEED is readily separable by distillation from BHEP, DEA, and water. However, the separation of BHEP from DEA is much more difficult due to the similarity of their vapor pressures.

The enthalpy of vaporization for BHEP and THEED can be calculated from parameter B in the integrated Clausius−Clapeyron equation (eq 2) and, with a 95% confidence level, were found to be (62.76 ± 5.33) and (89.96 ± 3.91) kJ/mol, respectively.

Conclusions

The vapor pressures of BHEP and THEED, determined by using the static cell and saturated gas methods, where found to be well represented by a modified Antoine and the integrated Clausius−Clapeyron equations. Their enthalpies of vaporization are reported. It is clear that THEED can be readily separated from contaminated DEA solutions by distillation whereas the removal of BHEP is more difficult.

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