Experimental Vapor Pressures of 2-Phenylethylamine, Benzylamine, Triethylamine, and *cis*-2,6-Dimethylpiperidine in the Range between 0.2 Pa and 75 kPa

Ilham Mokbel,* Antonio Razzouk, Terufat Sawaya, and Jacques Jose

UMR 5180, Equipe "Thermodynamique et Analyse", Laboratoire des Sciences Analytiques, Université Claude Bernard Lyon 1, 43 bd du 11 Novembre 1918, 69622 Villeurbanne, France

In this study, we reported experimental vapor pressures of several amines presenting different molecular structures, 2-phenylethylamine, benzylamine, triethylamine and *cis*-2,6-dimethylpiperidine, using a static apparatus. The pressure range is comprised between 0.2 Pa and 75 kPa, and the temperature range is between (273 and 365) K. From the temperature dependence of the vapor pressures, the molar enthalpies of vaporization at the mean temperature of the experimental range were derived from the Clausius−Clapeyron equation. From these results, the standard enthalpies of vaporization at $T = 298.15$ K were calculated and compared with the open literature values.

Introduction

At the present time, it is admitted that the climate change results from the increase in CO_2 and other greenhouse gases rates in the earth atmosphere. Therefore, it is urgent to deploy technologies to reduce emissions of greenhouse gases promoted by the combustion of fossil fuels for power generation. CO_2 capture and storage is an interesting technology that has the potential to make significant reductions in emissions. Widespread use of this technique could be achieved without the need for rapid change in the energy supply infrastructure. Actually, the standard process used to capture CO_2 is based on chemical absorption with aqueous monoethanolamine (MEA). MEA is widely used because of its high reactivity, low solvent cost, low molecular weight (which results in high absorption capacity at moderate concentrations), reasonable thermal stability, and low thermal degradation rate.[1–3] However, MEA has several disadvantages. It has a high reaction enthalpy, which leads to a high solvent regenerator energy consumption and therefore increases the cost of the process. MEA also reacts with NO_2 and SO_2 to form thermally stable salts that reduce the CO_2 absorption capacity of the solvent. Current research is aimed at identifying new solvent systems that require less energy for regeneration, are economical to produce, and are compatible with environmental constraints. Vapor−liquid equilibrium measurements for these solvents are needed to improve the overall performance of the system, especially in the recycling step of the solvent. In this study, we determined the vapor pressures of four amines (2-phenylethylamine, benzylamine, triethylamine, and *cis*-2,6-dimethylpiperidine) by means of a static apparatus. The data were fitted to Antoine and Clausius−Clapeyron equations and compared with literature values when available.

Experimental Section

Static Apparatus. Vapor pressure measurements were carried out using a static apparatus. The description of the apparatus and the experimental procedure can be found elsewhere,[4–7] thus

only the most salient information are given here. The apparatus was equipped with a differential manometer from MKS, type 670, 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, IPTS 90) and a Leeds & Northrup bridge (± 10^{-4} Ω). During measurements, the stability of the temperature was ± 0.02 K. The differential pressure gauge was calibrated against a U manometer filled with mercury or apiezon oil depending on the 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.[5]

The uncertainty in the measurements is estimated to be: $\sigma(T) = 0.02$ K for the temperature range $203 \leq T/K \leq 463$; $\sigma(P) = 0.01$ Pa + 0.03 P/Pa for pressures lower than 600 Pa; $\sigma(P) = 0.01$ P/Pa for the pressure range 600 < P/Pa < 1300; and $\sigma(P) = 0.003$ P/Pa for pressure over 1300 Pa.

Materials. All compounds were purchased from Aldrich. The purity was better than 99 % except for *cis*-2,6-dimethylpiperidine (98 %). The different compounds were dehydrated using molecular sieve and controlled by coulometric Karl Fisher analysis, which showed the presence of water below 0.04 % (mass percent) in the different amines.

Results and Discussion

The experimental T and P values of the different amines are reported in Table 1. The data were fitted using the Antoine equation

$$\log P/\text{Pa} = A - \frac{B}{C + T/\text{K}} \qquad (1)$$

by minimizing the objective function, S

* To whom correspondence should be addressed. E-mail: mokbel@univ-lyon1.fr.

Table 1. Experimental Vapor Pressures of Benzylamine, Triethylamine, 2-Phenylethylamine, and *cis*-2,6-Dimethylpiperidine

benzylamine		triethylamine		2-phenylethylamine		*cis*-2,6-dimethylpiperidine	
T/K	P_{exptl}/Pa	T/K	P_{exptl}/Pa	T/K	P_{exptl}/Pa	T/K	P_{exptl}/Pa
292.74	62.2	273.04	2456	273.26	5.57	294.80	1558
302.68	130	292.87	7014	283.18	13.5	304.79	2680
312.69	259	312.82	17433	293.12	31.0	314.76	4415
322.67	494	332.78	38045	303.06	65.7	324.78	7037
332.7	878	352.77	74941	313.07	133	334.94	10916
342.68	1523			323.06	257	344.96	16773
352.67	2512			333.11	476	354.98	24532
362.67	4071			343.08	839	365.00	34944
				351.79	1333		

Table 2. Antoine Equation Parameters, Standard Deviation, σ, and Mean Relative Deviation, d[a]

compound	temp range T	A	B	C	
	K	(σ_A)	(σ_B)	(σ_C)	$100 \cdot d$
benzylamine	292.74 to 362.67	9.582	1793	−62.52	0.38
	(0.139)		(73)	(5.29)	
triethylamine	273.04 to 352.77	9.174	1334	−42.35	0.21
	(0.077)		(41)	(4.09)	
2-phenylethylamine	273.26 to 351.79	10.062	2132	−44.39	0.18
	(0.052)		(28)	(1.69)	
cis-2,6-dimethylpiperidine	294.80 to 365.00	9.713	1749	−26.65	0.43
	(0.206)		(124)	(10.6)	

[a] $d = (1/n) \sum (|P_{exptl} - P_{calcd}|)/(P_{exptl})$.

$$S = \sum_{i=1}^{n} \left(\frac{P_{exptl} - P_{calcd}}{P_{exptl}} \right)^2 \qquad (2)$$

The constants A, B, and C determined from least-squares fitting and the mean relative deviation d (n, number of experimental points) are reported in Table 2.

$$d = \frac{1}{n} \sum \frac{|P_{exptl} - P_{calcd}|}{P_{exptl}} \qquad (3)$$

The mean relative deviation, d, is comprised between 0.18 % and 0.69 %.

From the fits of the vapor pressures by the Clausius−Clapeyron equation, the enthalpies of vaporization, $\Delta_{vap}H_m$ (T_m), at the mean temperature of the experiments, T_m, were determined and are presented in Table 3. Vaporization enthalpies at the temperature 298.15 K were derived from the vaporization enthalpies calculated at the mean temperature, T_m, of the experiments using Chickos and Acree[15] equations

$$\Delta_{vap}H_m(298.15 \text{ K})/\text{J·mol}^{-1} = \Delta_{vap}H_m(T_m)$$
$$+ [10.58 + 0.26C_p(298.15 \text{ K})](T_m - 298.15) \quad (4)$$

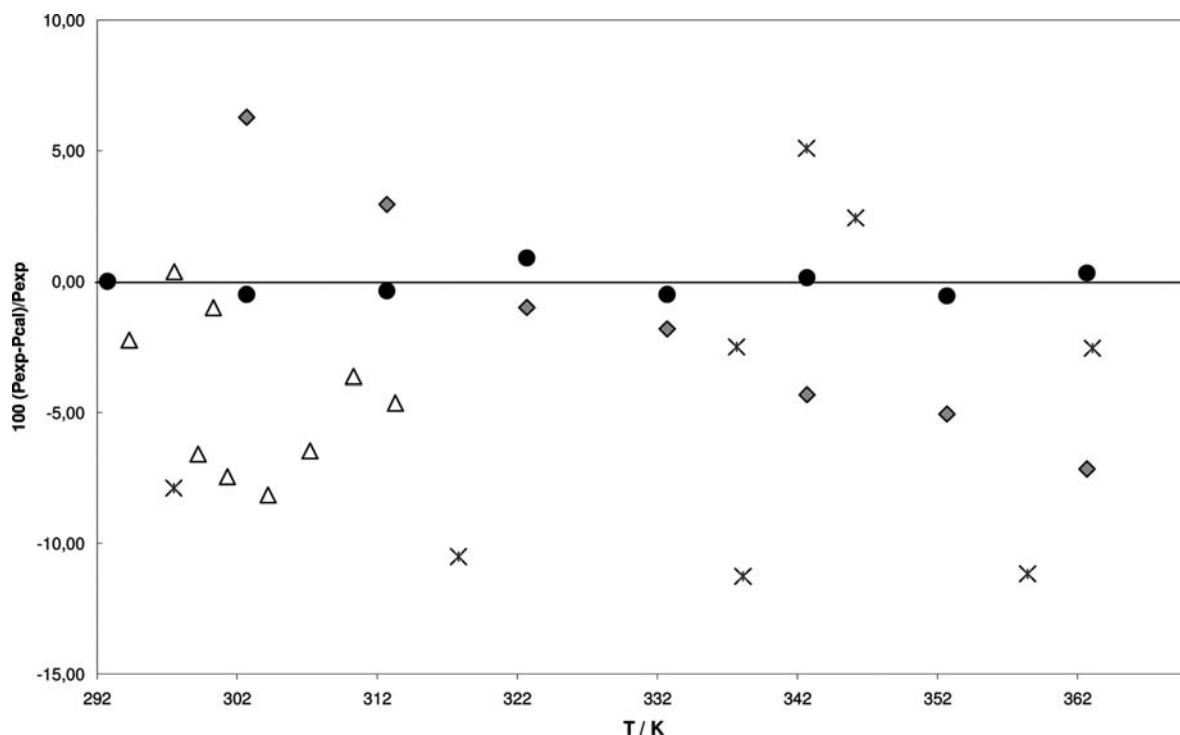The heat capacities of C_p were calculated using the group

Figure 1. Relative deviation of the experimental vapor pressures of benzylamine from values obtained with Antoine equation as a function of temperature T/K: ●, this work; △, ref 8; ◇, ref 9; ×, ref 10.

Table 3. Clausius−Clapeyron Equation Parameters A and B, Standard Deviation, σ, Mean Relative Deviation, d, $B = \Delta_{vap}H_m (T_m)/R$ with $R = 8.314$ J·K^{-1}·mol^{-1}, Mean Temperature of the Experiments, T_m, and Vaporization Enthalpy at 298.15 K, $\Delta_{vap}H_m$ (298.15 K)[a,b]

	temp range T	T_m	A	B		$\Delta_{vap}H_m (T_m)$	$\Delta_{vap}H_m$ (298.15 K)
amine	K	K	(σ_A)	(σ_B)	$100 \cdot d$	kJ·mol^{-1} (σ)	kJ·mol^{-1}
benzylamine	292.74 to 362.67	328	25.82 (0.12)	6340 (38)	1.8	52.7 (0.3)	54.6 (0.3)
triethylamine	273.04 to 352.77	313	22.99 (0.09)	4133 (29)	1.4	34.4 (0.2)	35.4 (0.2)
2-phenylethylamine	273.26 to 351.79	313	26.28 (0.09)	6704 (30)	1.9	55.7 (0.2)	56.8 (0.2)
cis-2,6-dimethylpiperidine	294.80 to 365.00	330	23.55 (0.04)	4773 (15)	0.64	39.7 (0.1)	41.3 (0.1)

[a] $\ln P/\text{Pa} = A - (B/(T/\text{K}))$. [b] $d = (1/n) \sum (|P_{exptl} - P_{calcd}|)/(P_{exptl})$.
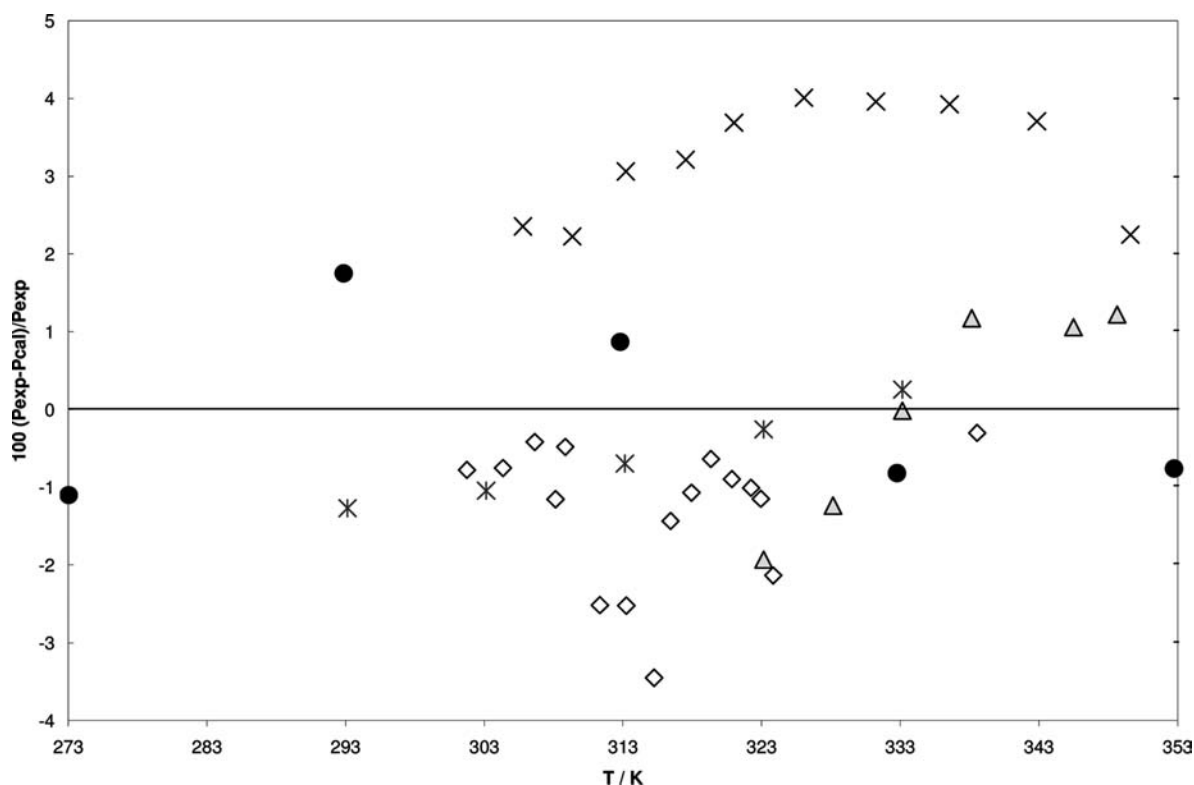

Figure 2. Relative deviation of the experimental vapor pressures of triethylamine from values obtained with Antoine equation as a function of temperature T/K: ●, this work; △, ref 10; *, ref 11; ◇, ref 12; ×, ref 13.

additivity method developed by Chickos and Acree.[15] The calculated values of the standard enthalpies of vaporization at $T = 298.15$ K are reported in Table 3.

Comparison with Literature Data. Several authors have studied benzylamine.[8–10] As shown in Figure 1, the experimental vapor pressures are in good agreement with Verevkin's[8] values and with Stull's[9] data. (For both authors, the mean relative deviation is 4 %.) As for the values of the DIPPR data series,[10] the relative deviation with the present work extends between 2 % and 16 %. The enthalpy of vaporization of benzylamine was determined by Carson et al.,[16] $\Delta_{vap}H_m$ (298.15 K) = (53.6 ± 2.1) kJ·mol^{-1}; by Majer and Svoboda,[17] $\Delta_{vap}H_m$ (298.15 K) = 60.16 kJ·mol^{-1}; and by Verevkin,[8] $\Delta_{vap}H_m$ (298.15 K) = (52.02 ± 0.57) kJ·mol^{-1}. The obtained value in the present study, $\Delta_{vap}H_m$ (298.15 K) = (54.6 ± 0.3) kJ·mol^{-1}, is in a good agreement with those from Carson et al. and Verevkin.

The experimental vapor pressures of triethylamine were compared with the values of Kokkonen and Arvola,[11] who used a static method, with Dutt et al.[12] measurements, which were obtained by ebulliometry, and with the data from the DIPPR data bank.[10] The present results are in very good agreement with the three sources of data, with a mean relative deviation below 1.5 % (Figure 2). However, a mean relative deviation of 3.2 % is observed between the present work and Majer et al.[13] data. With regard to *cis*-2,6-dimethylpiperidine, the sole datum

found in the literature is the enthalpy of vaporization measured by Ribeiro da Silva et al.[14] The $\Delta_{vap}H_m$ (298.15 K) obtained in this study, (41.3 ± 0.1) kJ·mol^{-1}, is in a good agreement with the Ribeiro Da Silva measurement, (42.4 ± 0.68) kJ·mol^{-1}. No literature data in the open literature were found to be compared with the vapor pressures or the vaporization enthalpy of 2-phenylethylamine presented in this work.

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