JOURNAL OF CHEMICAL & ENGINEERING DATA

ARTICLE

pubs.acs.org/jced

Vapor Pressures and Enthalpies of Vaporization of a Series of Low-Volatile Alkanolamines

Sergey P. Verevkin*

Department of Physical Chemistry and Department of Science and Technology of Life, Light and Matter, Faculty of Interdisciplinary Research, University of Rostock, Dr-Lorenz-Weg 1, D-18059, Rostock, Germany

Bo Tong and Urs Welz-Biermann

China Ionic Liquid Laboratory, Dalian Institute of Chemical Physics, Group 207, Chinese Academy of Sciences, 457 Zhongshan Road, Catalysis Building, 116023 Dalian, P. R. China

Yury Chernyak

Huntsman Corporation, Advanced Technology Centre, 8600 Gosling Rd., The Woodlands, 77381, Texas, United States

S *Supporting Information*

ABSTRACT: Vapor pressures of four alkanolamines (2-[(2-aminoethyl)amino]-ethanol [CAS No. 111-41-1], 2-[[2-(dimethylamino)ethyl]methylamino]-ethanol [CAS No. 2212-32-0], 2-(2-aminoethoxy)-ethanol [CAS No. 929-06-6], and 2-(2-dimethylaminoethoxy)ethanol [CAS No. 1704-62-7]) have been measured by the transpiration method. Molar enthalpies of vaporization were obtained from the temperature dependence of the vapor pressure. Primary experimental data on temperature on vapor pressures of alkanolamines have been collected from the literature and have been treated uniformly to derive vaporization enthalpies at the reference temperature $T = 298.15$ K. An internal consistency check of the reported enthalpy of vaporization values has been performed. Low-volatile alkanolamines studied in this work have been considered as suitable candidates for use in mixtures with ionic liquids in industrial processes of CO_2 and H_2S capture.

INTRODUCTION

Post-combustion CO_2 capture has received worldwide attention because of it possible impact on climate change. Also, the purification of natural gas, H_2S removal, as well as the sweetening of gas streams in petroleum refining, petrochemical plants, coal gasification, and hydrogen production is of major importance for both energy and environmental purposes. The core technology for these processes is the absorption of acid gases into aqueous solutions of alkanolamines. Although monoethanolamine (MEA) and diethanolamine (DEA) dominated the gas treatment industry for many decades,[1] there has been a continuous search for more efficient systems. Davis and co-workers[2] were the first to report specially designed ionic liquids (ILs) with an amine-functionalized cation in an IL system that reversibly bound nearly 0.5 mol of CO_2 per mole of IL. Noble and co-workers[3] suggested IL/MEA and IL/DEA mixtures to chemically bind CO_2. Numerous ILs have also been explored for CO_2 capture successfully.[4,5] One of the weaknesses of the commonly used liquid chemicals for treating is relatively high vapor pressure and, consequently, high loss of the gas treating agent during the process. Thus, it is reasonable to extend the search for more effective alkanolamines to materials with low vapor pressure. Indeed, IL-based solvents for postcombustion CO_2 capture and natural gas sweetening with innovative alkanolamines, such as methyldiethanolamine and triethanolamine, have gained ground in recent years because they can selectively absorb hydrogen sulfide in the presence of carbon dioxide and because of their low vapor pressure, high capacity, and low heat of reaction with CO_2 and H_2S.[1] Four low-volatility alkanolamines studied in this work (Figure 1) were considered as good candidates for further development of alkanolamines/IL gas treating mixtures. The reaction of CO_2 with alkanolamines in ILs was observed to proceed rapidly and efficiently. CO_2 could be readily decomplexed from the resulting carbamate salt by increasing the temperature and/or applying partial vacuum.[4] IL—alkanolamine solutions behave similarly to the aqueous amine solutions currently used for CO_2 capture and offer to significantly reduce solvent volatility and improve energy efficiency.[4] However, at least three important issues should be carefully studied before practical application of alkanolamines: vapor pressure of pure alkanolamines, volatility of IL—alkanolamine mixtures, and miscibility of alkanolamines in the IL. The viscosity of the alkanolamines is also a very important consideration for gas processing. Unfortunately, measured values of the viscosities of the alkanolamines under study in this work are not available in the literature. However, from our experience with such compounds

Special Issue: Kenneth N. Marsh Festschrift

Received: March 11, 2011
Accepted: June 7, 2011
Published: June 29, 2011

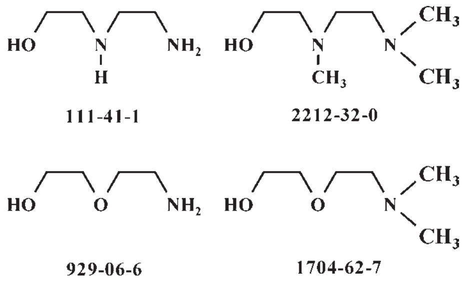

Figure 1. Compounds studied in this work: 2-[(2-aminoethyl)amino]-ethanol (**A**) [111-41-1], 2-[[2-(dimethylamino)ethyl]methylamino]-ethanol (**B**) [2212-32-0], 2-(2-aminoethoxy)-ethanol (**C**) [929-06-6], 2-(2-dimethylaminoethoxy)ethanol (**D**) [1704-62-7].

we could assess the order of viscosity of (50 to 150) cP (at room temperature), which is more or less the same as the viscosities of the common ILs such as [C_2mim][NTf_2] and [C_2mim][$EtSO_4$]. As an initial step of this development work, pure component properties of alkanolamines such as vapor pressure and enthalpy of vaporization have been investigated.

This study also extends our previous work on thermochemical properties of pure ethanolamines[6] and aliphatic polyamines.[7] The enthalpies of vaporization, $\Delta_l^g H_m$, have been obtained from the temperature dependence of the vapor pressures measured by the transpiration method. These data together with those available from the literature were used to establish the general regularities in the $\Delta_l^g H_m$ and the vapor pressures within this homologous series.

EXPERIMENTAL SECTION

Materials. Samples of alkanolamines were carefully purified at Huntsman Advanced Technology Center by repeated vacuum distillation. The degree of purity of the samples was determined before experiments using a Hewlett-Packard gas chromatograph 5890 Series II equipped with a flame ionization detector and a Hewlett-Packard 3390A integrator. The carrier gas (nitrogen) flow was 12.1 $cm^3 \cdot s^{-1}$. A capillary column HP-5 (stationary phase cross-linked 5 % phenyl methyl silicone) was used with a column length of 30 m, an inside diameter of 0.32 mm, and a film thickness of 0.25 mm. The standard temperature program of the GC was T = 333.15 K for 180 s followed by a heating rate of 0.167 $K \cdot s^{-1}$ to T = 523.15 K. No total impurities (greater than mass fraction 0.005) could be detected in the samples used for the vapor pressure measurements.

Vapor Pressures and Enthalpies of Vaporization Using the Transpiration Method. Vapor pressures were determined using the method of transpiration in a saturated nitrogen stream.[8,9] Enthalpies of vaporization were obtained applying the Clausius–Clapeyron equation. About 0.5 g of the sample was mixed with glass beads and placed in a thermostatted U-shaped tube having a length of 20 cm and a diameter of 0.5 cm. Glass beads with diameter of 1 mm provide surface which was sufficient for the vapor–liquid equilibration. At a constant temperature (± 0.1 K), a nitrogen stream was passed through the U-tube, and the transported amount of gaseous material was collected in a cooling trap. The mass of compound collected within a certain time interval was determined by dissolving it in a suitable solvent with certain amount of external standard (n-decane, n-undecane, n-dodecane). This solution was analyzed using a gas chromatograph equipped with an autosampler. The peak area of the compound

Table 1. Experimental Vapor Pressure, p, and Enthalpy of Vaporization, $\Delta_l^g H_m$(298.15 K), of Alkanolamines A to D

T[a]	m[b]	$V_{(N2)}$[c]	gas-flow	p[d]	$(p_{exp} - p_{calc})$	$\Delta_l^g H_m$
K	mg	dm^3	$dm^3 \cdot h^{-1}$	Pa	Pa	$kJ \cdot mol^{-1}$
(**A**) [111-41-1]; $\Delta_l^g H_m$ (298.15 K) = (75.06 ± 0.26) $kJ \cdot mol^{-1}$						
$\ln(p/Pa) = \frac{328.37}{R} - \frac{99005.44}{R \cdot (T/K)} - \frac{80.3}{R} \ln\left(\frac{T/K}{298.15}\right)$						
323.2	2.60	9.55	3.18	6.47	−0.01	73.06
323.2	1.41	5.13	5.14	6.52	0.05	73.06
324.2	2.50	8.70	3.18	6.81	−0.23	72.98
324.2	1.41	4.77	5.14	7.11	0.07	72.98
326.1	2.56	7.41	3.18	8.20	−0.05	72.82
326.2	1.34	3.92	5.12	8.09	−0.22	72.82
329.2	1.39	3.02	3.18	10.89	0.28	72.57
329.2	1.80	3.85	5.14	11.07	0.46	72.57
332.1	0.87	1.48	3.17	13.96	0.59	72.34
332.2	1.59	2.74	5.14	13.76	0.29	72.33
335.1	2.66	3.69	3.17	17.07	0.17	72.10
335.2	1.35	1.98	4.24	16.19	−0.84	72.09
335.2	4.86	6.91	5.12	16.68	−0.35	72.09
336.9	1.15	1.42	3.70	19.17	−0.23	71.96
338.1	0.92	1.00	3.16	21.71	0.46	71.86
338.1	1.46	1.60	3.20	21.63	0.38	71.86
341.2	1.57	1.41	4.24	26.42	−0.38	71.61
341.2	1.40	1.23	3.70	26.92	0.12	71.61
344.2	1.10	0.778	1.95	33.67	0.29	71.37
344.2	1.43	1.06	3.18	31.90	−1.48	71.37
345.2	1.39	0.922	3.69	35.73	−0.16	71.29
347.2	2.33	1.34	4.24	41.21	−0.18	71.13
350.2	1.89	0.870	2.90	51.59	0.48	70.89
353.2	3.10	1.20	4.24	61.34	−1.49	70.65
356.2	3.65	1.148	2.87	75.50	−1.43	70.41
359.2	3.13	0.778	1.95	95.33	1.54	70.17
359.2	3.45	0.902	3.18	90.76	−3.03	70.17
362.2	3.36	0.711	2.84	112.07	−1.83	69.92
365.2	3.42	0.584	1.95	139.12	1.31	69.68
368.2	3.77	0.531	1.88	168.32	2.23	69.44
371.2	4.08	0.485	1.94	199.88	0.42	69.20
373.2	4.71	0.486	1.95	229.96	5.06	69.04
374.2	4.82	0.475	1.90	241.04	2.36	68.96
(**B**) [2212-32-0]; $\Delta_l^g H_m$ (298.15 K) = (65.16 ± 0.14) $kJ \cdot mol^{-1}$						
$\ln(p/Pa) = \frac{321.62}{R} - \frac{89521.29}{R \cdot (T/K)} - \frac{81.7}{R} \ln\left(\frac{T/K}{298.15}\right)$						
293.4	0.84	1.63	1.63	8.74	0.25	65.55
295.2	0.80	1.33	4.42	10.13	0.14	65.41
297.5	0.91	1.22	3.32	12.63	0.35	65.22
299.6	0.86	0.989	1.80	14.78	0.02	65.05
301.4	0.84	0.829	3.32	17.13	−0.12	64.90
303.4	0.89	0.749	1.80	20.03	−0.43	64.74
305.4	1.34	0.929	1.80	24.42	0.22	64.57
307.2	1.66	0.995	3.32	28.22	0.13	64.43
309.2	0.87	0.450	1.80	32.92	−0.15	64.26
311.2	1.73	0.748	1.80	39.12	0.31	64.10

Table 1. Continued

T^a	m^b	$V_{(N2)}{}^c$	gas-flow	p^d	$(p_{exp} - p_{calc})$	$\Delta_l^g H_m$
K	mg	dm^3	dm$^3 \cdot$h^{-1}	Pa	Pa	kJ$\cdot$mol^{-1}
313.2	2.20	0.829	3.32	44.91	−0.56	63.94
315.2	2.83	0.926	1.79	51.64	−1.48	63.77
317.2	2.38	0.653	2.18	61.74	−0.18	63.61
319.2	3.87	0.940	3.32	69.49	−2.52	63.45
321.2	2.41	0.485	1.71	83.88	0.32	63.28
323.2	2.57	0.448	1.79	97.24	0.50	63.12
325.2	5.53	0.829	3.32	112.71	0.95	62.96
327.2	4.83	0.649	2.05	125.86	−2.98	62.79
329.2	4.59	0.538	1.79	144.24	−3.97	62.63
331.2	5.15	0.520	2.08	167.62	−2.53	62.47
333.2	5.15	0.446	1.67	195.46	0.52	62.30
335.2	6.62	0.510	1.80	219.41	−3.50	62.14
337.2	9.04	0.622	2.07	245.85	−8.54	61.98
339.2	11.94	0.678	1.63	297.73	7.96	61.81
341.2	9.07	0.450	1.80	340.94	11.50	61.65
343.2	11.41	0.517	2.07	372.80	−1.07	61.49
345.2	12.29	0.488	1.63	425.60	2.08	61.32
347.2	12.87	0.450	1.80	483.08	4.14	61.16
349.2	18.99	0.585	2.06	548.84	8.19	61.00
351.2	18.86	0.516	2.06	617.98	8.70	60.83
353.2	18.48	0.450	1.80	694.24	8.75	60.67

(**C**) [929-06-6]; $\Delta_l^g H_m$ (298.15 K) = (75.92 ± 0.43) kJ$\cdot$mol^{-1}

$$\ln(p/\mathrm{Pa}) = \frac{339.99}{R} - \frac{99293.44}{R\cdot(T/\mathrm{K})} - \frac{78.4}{R}\ln\left(\frac{T/\mathrm{K}}{298.15}\right)$$

T^a	m^b	$V_{(N2)}{}^c$	gas-flow	p^d	$(p_{exp} - p_{calc})$	$\Delta_l^g H_m$
303.2	5.39	34.4	2.02	3.68	−0.15	75.53
306.2	1.64	7.71	4.02	5.00	−0.12	75.29
308.2	1.62	6.04	4.03	6.30	0.08	75.13
311.2	3.28	9.72	4.02	7.93	−0.31	74.90
313.2	1.69	4.15	4.02	9.58	−0.33	74.74
316.2	1.69	3.02	4.02	13.14	0.14	74.51
318.2	1.76	2.55	4.03	16.24	0.70	74.35
321.3	2.74	3.13	5.08	20.53	0.16	74.11
324.3	2.34	1.98	3.72	27.80	1.47	73.87
326.3	2.46	1.85	3.83	31.21	0.08	73.72
329.2	2.76	1.55	3.73	41.65	2.10	73.49
331.3	2.39	1.20	3.79	46.70	−0.18	73.32
334.2	3.22	1.22	1.88	61.92	2.87	73.10
336.3	2.79	0.948	3.79	69.06	−0.52	72.93
339.2	5.71	1.51	1.89	88.54	1.61	72.70
341.3	4.50	1.01	3.79	104.58	2.73	72.54
344.3	2.46	0.470	1.88	123.11	−4.12	72.30
346.2	4.85	0.801	3.20	142.19	−3.94	72.16
349.2	4.68	0.630	1.89	174.82	−6.38	71.92
351.2	5.31	0.604	2.42	206.44	−2.19	71.76
353.2	5.09	0.503	2.01	237.50	−2.25	71.61
356.2	7.55	0.604	2.42	293.77	−0.55	71.37
359.2	7.69	0.508	2.03	355.61	−4.23	71.14

(**D**) [1704-62-7]; $\Delta_l^g H_m$ (298.15 K) = (63.80 ± 0.20) kJ$\cdot$mol^{-1}

$$\ln(p/\mathrm{Pa}) = \frac{319.10}{R} - \frac{88158.59}{R\cdot(T/\mathrm{K})} - \frac{81.7}{R}\ln\left(\frac{T/\mathrm{K}}{298.15}\right)$$

T^a	m^b	$V_{(N2)}{}^c$	gas-flow	p^d	$(p_{exp} - p_{calc})$	$\Delta_l^g H_m$
K	mg	dm^3	dm$^3 \cdot$h^{-1}	Pa	Pa	kJ$\cdot$mol^{-1}
293.3	1.00	1.62	4.42	11.46	0.60	64.20
295.4	1.08	1.47	4.42	13.64	0.55	64.03
297.5	1.09	1.22	3.32	16.69	0.96	63.86
299.6	1.01	0.989	1.80	19.06	0.21	63.69
301.4	1.01	0.829	3.32	22.65	0.70	63.54
303.4	1.05	0.749	1.80	25.96	0.02	63.37
305.4	1.49	0.929	1.80	29.72	−0.85	63.21
307.2	1.84	0.995	3.32	34.20	−1.18	63.06
309.2	0.97	0.450	1.80	40.00	−1.49	62.90
311.2	1.91	0.748	1.80	47.39	−1.16	62.74
313.2	2.44	0.829	3.32	54.66	−2.01	62.57
315.2	3.26	0.926	1.79	65.31	−0.69	62.41
317.2	2.64	0.653	2.18	75.04	−1.63	62.25
319.2	4.27	0.940	3.32	84.33	−4.55	62.08
321.2	2.66	0.485	1.71	101.93	−0.87	61.92
323.2	2.85	0.448	1.79	118.02	−0.63	61.76
325.2	5.97	0.829	3.32	133.56	−3.08	61.59
327.2	5.35	0.649	2.05	152.92	−4.11	61.43
329.2	5.09	0.538	1.79	175.43	−4.66	61.27
331.2	5.70	0.520	2.08	203.41	−2.72	61.10
333.2	5.70	0.446	1.67	237.21	1.74	60.94
335.2	7.31	0.510	1.80	266.14	−2.31	60.78
337.2	10.01	0.622	2.07	298.74	−6.75	60.61
339.2	12.79	0.678	1.63	350.13	3.16	60.45
341.2	9.97	0.450	1.80	411.60	18.24	60.29
343.2	12.58	0.517	2.07	451.20	6.03	60.12
345.2	13.53	0.488	1.63	514.55	11.65	59.96
347.2	19.06	0.644	1.84	549.06	−18.07	59.80
349.2	21.00	0.585	2.06	666.30	27.82	59.63
351.2	20.85	0.516	2.06	750.34	32.72	59.47
353.2	20.42	0.460	1.84	823.29	18.05	59.31

[a] Temperature of saturation. [b] Mass of transferred sample condensed at T = 243.15 K. [c] Volume of nitrogen used to transfer mass m of sample. [d] Vapor pressure at temperature T calculated from m and the residual vapor pressure at the cooling temperature T = 243.15 K.

related to the peak of the external standard (hydrocarbon n-C_nH_{2n+2}) is a direct measure of the mass of the compound condensed into the cooling trap, provided that a calibration of the system has been made. The saturation vapor pressure p_i^{sat} at each temperature T_i (maintained and measured ± 0.1 K) was calculated from the amount of product collected within a definite period of time. Assuming that Dalton's law of partial pressures applied to the nitrogen stream saturated with the substance i of interest is valid, values of p_i^{sat} were calculated:

$$p_i^{sat} = m_i \cdot R \cdot T_a / V \cdot M_i; \qquad V = V_{N2} + V_i; \qquad (V_{N2} \gg V_i) \qquad (1)$$

where R = 8.314472 J$\cdot$K$^{-1}\cdot$mol^{-1}; m_i is the mass of transported compound, M_i is the molar mass of the compound, and V_i is its volume contribution to the gaseous phase. V_{N2} is the volume of transporting gas, and T_a is the temperature of the soap bubble meter. The volume of transporting gas V_{N2} was determined from the flow rate and time measurements. Data of p_i^{sat} have been obtained as a function of temperature and were fitted using the

Table 2. Summary on Enthalpy of Vaporization, $\Delta_l^g H_m$(298.15 K), of Alkanolamines A to D from Different Data Sources

	CAS no.	technique[a]	T-range K	C_p^l $(-\Delta_l^g C_p)^b$ $\mathrm{J\cdot mol^{-1}\cdot K^{-1}}$	$\Delta_l^g H_m(T_{av})$ $\mathrm{kJ\cdot mol^{-1}}$	$\Delta_l^g H_m(298.15\ \mathrm{K})^c$ $\mathrm{kJ\cdot mol^{-1}}$	ref	
A	111-41-1	E	447.5−533.6	268.0	68.4	83.6 ± 1.8	13	91dau
		S	323.2−433.2	(80.3)	58.2	64.2 ± 1.6	14	01xie-che
		LRTFM	719.2−738.8		66.1	100.8 ± 2.0	15	02wil-von
		T	323.2−374.2		71.2	**75.1 ± 0.3**		this work
B	2212-32-0	T	293.4−353.2	273.4(81.7)	63.2	65.2 ± 0.2		this work
C	929-06-6	E	391.0−516.1	261.0 [12]	59.4	71.2 ± 0.6	16	94cam-jon
		LRTFM	500.9−719.4	(78.4)	50.2	74.0 ± 0.4	17	06von-wil
		T	303.2−359.2		73.4	**75.9 ± 0.4**		this work
D	1704-62-7	E	333−423	273.7	-	62.5	18	70qui-hof
		S	283.2−373.1	(81.7)	56.6	58.7 ± 0.1	19	11bel-mok
		T	293.3−353.2		61.9	**63.8 ± 0.2**		this work

[a] Techniques: E = ebulliometry; S = static method; T = transpiration; LRTFM = flow method with ultralow residence times. [b] Values of $\Delta_l^g C_p$ have been derived from the isobaric molar heat capacity of the liquid esters C_p^l according to procedure developed by Chickos et al.[10] and modified in ref 11. [c] Vapor pressure data available in the literature were treated using eqs 2 and 3 to evaluate enthalpy of vaporization at T = 298.15 K in the same way as our own results in Table 1.

following equation:[11]

$$R\cdot\ln p_i^{sat} = a + \frac{b}{T} + \Delta_l^g C_p\cdot\ln\left(\frac{T}{T_0}\right) \qquad (2)$$

where a and b are adjustable parameters and $\Delta_l^g C_p$ is the difference of the molar heat capacities of the gaseous and the liquid phase, respectively. T_0 appearing in eq 2 is an arbitrarily chosen reference temperature (which has been chosen to be 298.15 K). Consequently, from eq 2 the expression for the vaporization enthalpy at temperature T is derived:

$$\Delta_l^g H_m(T)/\mathrm{J\cdot mol^{-1}} = -b + (\Delta_l^g C_p/\mathrm{J\cdot mol^{-1}\cdot K^{-1}})\cdot T \qquad (3)$$

Values of $\Delta_l^g C_p$ have been calculated according to a procedure developed by Chickos and Acree[10] using the experimental values of C_p(l) reported in the literature.[11,12] Our own experimental results and parameters, a and b, are listed in Table 1. The errors in the enthalpies of vaporization are calculated from eq 2 by using the method of least-squares and uncertainties in values of $\Delta_l^g C_p$ are not taken into account. We have checked experimental and calculation procedure with measurements of vapor pressures of n-alcohols.[12] The uncertainty of the GC analysis of transported mass of the material, δm_i = (1 to 3) %, was the main contributor to the total experimental error of vapor pressure data, δp_i = (1 to 3) %, measured by the transpiration method.

RESULTS AND DISCUSSION

Vapor Pressures and Enthalpies of Vaporization. $p-T$ data measured in this work and reported in the literature[13−19] were correlated with eqs 2 and 3 to derive vaporization enthalpy $\Delta_l^g H_m$(298.15 K) of alkanolamines **A** to **D**. The summary on $\Delta_l^g H_m$(298.15 K) values is given in Table 2 for comparison and analysis.

2-[(2-Aminoethyl)amino]-ethanol [111-41-1], ***A***. Vapor pressures of **A** available from the literature are very inconsistent (Figure 2). Vapor pressures measured by Xie and Cheng[14] using a static apparatus were in total disagreement with all other available data. This difference could be due to residual water in the sample or due to a leak in the measuring cell. Experimental vapor pressures reported by Daubert[13] also demonstrated some inconsistency especially in the temperature range (504 to 534) K. These high-temperature data have been disregarded in the same way as it was done in ref 15. Wilson et al.[15] measured vapor pressure in a high-temperature range in the vicinity of the critical point. There was no overlap between temperature intervals used this work and refs 13 and 15 with the temperature gap being too large to make any meaningful vapor pressure data comparison. Enthalpies of vaporization calculated from the experimental vapor pressures[13−15] reflect the inconsistency of these data and spread over 30 kJ·mol^{-1}. Such a difference could be partly explained as a consequence of the large extrapolation of data in refs 13 and 15 to the reference temperature 298.15 K.

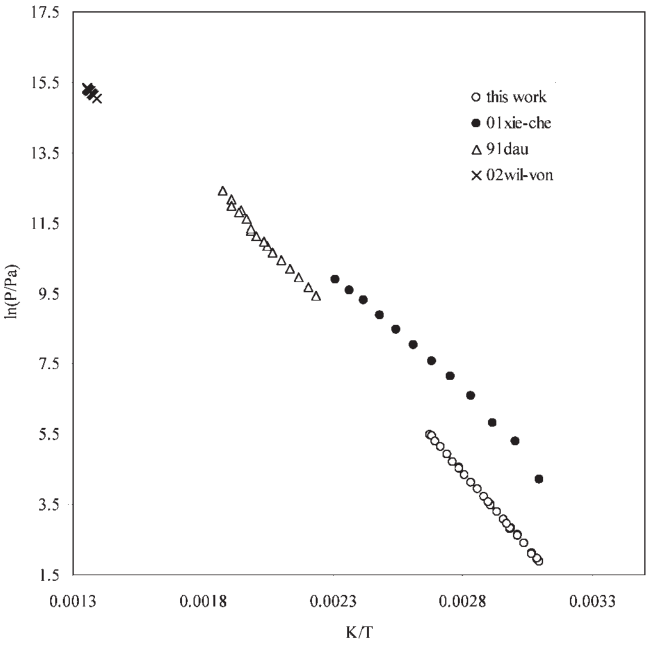

Figure 2. Plot of vapor pressure against reciprocal temperature for **A** [111-41-1].

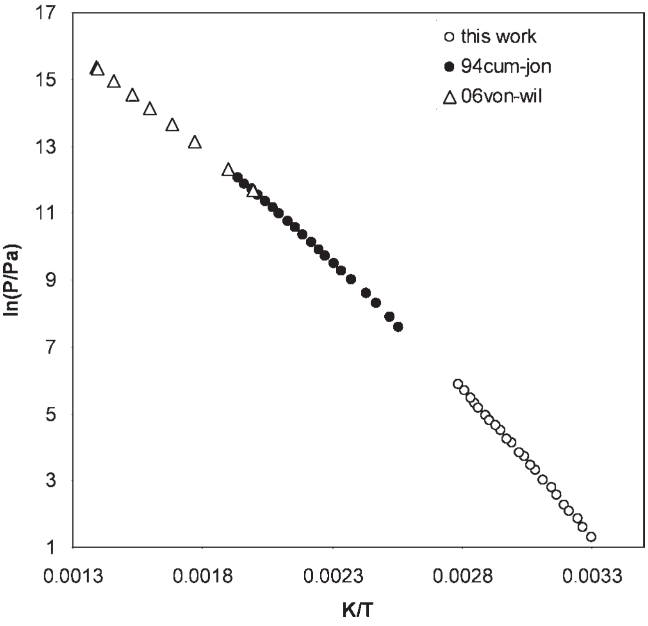

Figure 3. Plot of vapor pressure against reciprocal temperature for **C** [929-06-6].

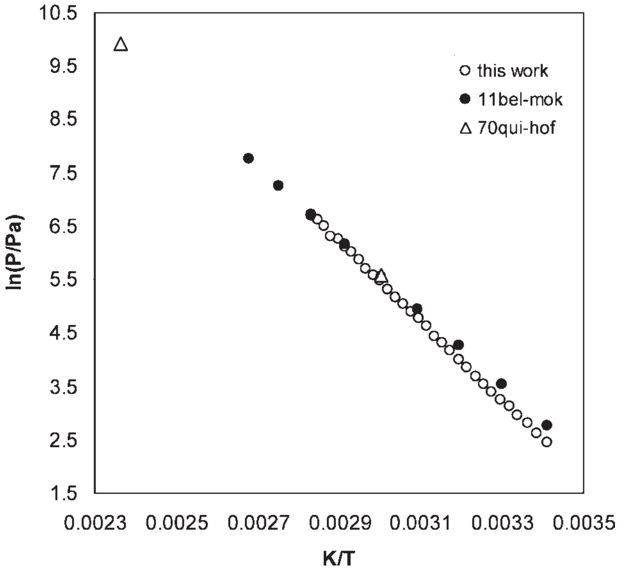

Figure 4. Plot of vapor pressure against reciprocal temperature for **D** [1704-62-7].

Table 3. Vapor Pressure Coefficients of eq 2 for Amino-Ethanols A to D

compound	temperature range, K	a	b	$\Delta_l^g C_p$
A, [111-41-1][a]	323.2−504.1	341.18	−103365.9	80.3
B, [2212-32-0]	293.4−353.2	321.62	−89521.29	81.7
C, [929-06-6][b]	303.2−516.1	328.95	−95678.44	78.4
D, [1704-62-7][c]	293.3−423	319.59	−88312.98	81.7

[a] Joint treatment of the results from this work together with the data from ref 13 in the T range (447.5 to 504) K. [b] Joint treatment of the results from this work together with the data from refs 16 and 17. [c] Joint treatment of the results from this work together with the data from ref 18 as well as from ref 19 in the T range (333.1 to 373.1) K.

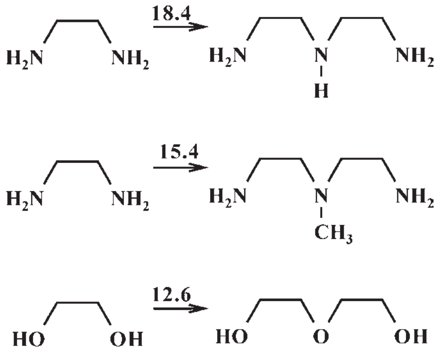

Figure 5. Differences between enthalpies of vaporization of the pairs of structurally related compounds to obtain contributions for units ($-CH_2-NH-CH_2-$), [$-CH_2-N(CH_3)-CH_2-$], and ($-CH_2-O-CH_2-$) used for consistency test of the data (see text).

2-[[2-(Dimethylamino)ethyl]methylamino]-ethanol [2212-32-0], ***B***. The vapor pressures and enthalpy of vaporization of this compound have been studied for the first time.

2-(2-Aminoethoxy)-ethanol [929-06-6], ***C***. In contrast to compound **A**, literature vapor pressures of compound **C** were remarkably consistent (Figure 3), and as the result, vaporization enthalpies derived from these vapor pressures were in good agreement with $\Delta_l^g H_m$(298.15 K) = (75.9 ± 0.4) kJ·mol^{-1} measured in this work. The acceptable discrepancies in vaporization enthalpies are rather due to long extrapolation of data in refs 16 and 17 to the reference temperature T = 298.15 K.

2-(2-Dimethylaminoethoxy)ethanol [1704-62-7], ***D***. Vapor pressures (Figure 4) of compound **D** measured in this work agreed reasonably well with the ebulliometric data of Quitzsch et al.[18] However, low-temperature vapor pressure values obtained by Belabbaci et al.[19] in static-cell experiments were noticeably larger than those developed in this work. From our experience such a disagreement is possible if the sample under study in the static apparatus is not completely dry. In contrast, the possible effect of residual water on the reliability of the vapor pressure data in the transpiration method is avoided because the sample under study is subjected to a preconditioning procedure and the moisture is usually withdrawn from the sample before the beginning of the data collection. Our value $\Delta_l^g H_m$(298.15 K) = (63.8 ± 0.2) kJ·mol^{-1} is in fair agreement with Quitsch et al.[18] but is 5 kJ·mol^{-1} different than vaporization enthalpy derived from Belabbaci et al.[19]

Experimental vapor pressure measurements performed in this work have been done in the temperature range possibly close to the reference temperature T = 295.15 K which is why values of $\Delta_l^g H_m$(298.15 K) measured in this study could be recommended for thermochemical calculations since they are less affected by extrapolation than other data sets.[13−17]

Vapor Pressure Correlations for Alkanolamines. Taking the generally good agreement between vapor pressure data reported in this work and the literature into account, the experimental data (if it has been possible) were regressed together to develop correlations for accurately describing the vapor pressure of alkanolamines over a temperature range from ambient to the elevated temperatures. Table 3 summarizes coefficients of the vapor pressure correlation (eq 3) for alkanolamines, which could be used for thermochemical and technical calculations.

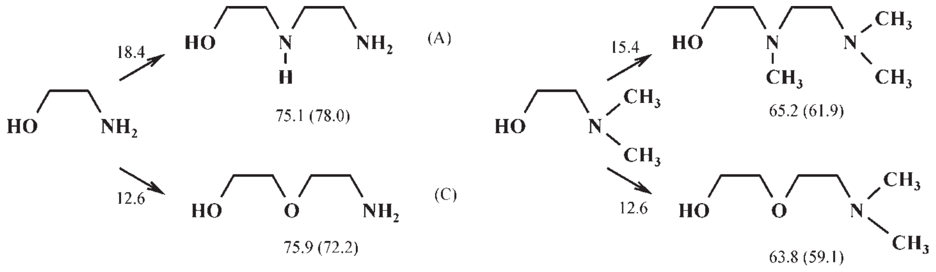

Figure 6. Calculation of enthalpies of vaporization of alkanolamines starting from aminoethanol and *N*,*N*-dimethyl-2-aminoethanol (see text).

Consistency Test of $\Delta_{\mathrm{l}}^{\mathrm{g}}H_{\mathrm{m}}$ for Amino-Ethanols. Very pure agreement (see Table 2) among available vaporization enthalpies measured in this work with the literature data requires a test of our results for internal consistency. In our previous publication[7] we observed an interesting structure−property relation for vaporization enthalpies of ethylenediamine derivatives. In this work we extend this pattern to alkanolamines (see Figure 1 and Table 2). Indeed, the difference $\Delta(\Delta_{\mathrm{l}}^{\mathrm{g}}H_{\mathrm{m}})$ between enthalpies of vaporization of diethylenetriamine (CAS [111-40-0])[7] and ethylenediamine (CAS [107-15-3])[7,20] $\Delta(\Delta_{\mathrm{l}}^{\mathrm{g}}H_{\mathrm{m}}) = 63.4 - 45.0 = (18.4 \pm 0.7)\ \mathrm{kJ \cdot mol^{-1}}$ provided a value of a specific contribution for the ($-CH_2-NH-CH_2-$) unit (see Figures 5 and 6) in any polyamine. Having this group contribution, $\Delta_{\mathrm{l}}^{\mathrm{g}}H_{\mathrm{m}}$ values for other parent compounds, such as triethylenetetramine, tetraethylenepentamine, and longer polyamines could be predicted.[7] In this work we have used the same pattern to assess enthalpy of vaporization of the ethanolamine derivatives (see Figures 5 and 6) as follows. For compound (**A**): starting from the enthalpy of vaporization of ethanolamine[6] (CAS [141-43-5]) $\Delta_{\mathrm{l}}^{\mathrm{g}}H_{\mathrm{m}} = (59.6 \pm 0.3)\ \mathrm{kJ \cdot mol^{-1}}$ and the contribution for the ($-CH_2-NH-CH_2-$) unit $\Delta(\Delta_{\mathrm{l}}^{\mathrm{g}}H_{\mathrm{m}}) = (18.4 \pm 0.7)\ \mathrm{kJ \cdot mol^{-1}}$, an enthalpy of vaporization of 78.0 $\mathrm{kJ \cdot mol^{-1}}$ for **A** has been calculated. This estimate is somewhat larger than the experimental value (75.1 ± 0.3) $\mathrm{kJ \cdot mol^{-1}}$ for this compound (see Table 2). The discrepancy is possible to account for the stabilizing and destabilizing effects in alkanolamines due to the interplay of intra- and intermolecular hydrogen bonding specific for OH- and NH_2-groups.[6] Indeed, it is well-established that there are intramolecular hydrogen bonding in ethanol-amines, which is able to decrease the enthalpy of vaporization.[6] At the same time, in diamines (e.g., in ethylenediamine) the specific van der Waals interactions are able to increase the enthalpy of vaporization.[7] It is possible that in compound (**A**) these both specific interactions are available and their counterplay may cause deviation of the estimated value from the experimental one. Taking into account that stabilization due to the intramolecular hydrogen bonding in *N*-methyl-2-ethanolamine is on the level of $-2.5\ \mathrm{kJ \cdot mol^{-1}}$,[6] and at the same time the destabilization in ethylenediamine is on the level of 3 $\mathrm{kJ \cdot mol^{-1}}$,[7] our estimate, 78.0 $\mathrm{kJ \cdot mol^{-1}}$ for **A**, fits quite well with our expectation for competition between specific interactions in this compound.

To check the consistency of the vaporization enthalpy of compound **B**, the difference between enthalpies of vaporization of *N*-methyl-2,2-diamino-diethylamine[7] [CAS 4097-88-5], $\Delta_{\mathrm{l}}^{\mathrm{g}}H_{\mathrm{m}} = (60.4 \pm 0.5)\ \mathrm{kJ \cdot mol^{-1}}$, and ethylenediamine, $\Delta(\Delta_{\mathrm{l}}^{\mathrm{g}}H_{\mathrm{m}}) = 60.4 - 45.0 = (15.4 \pm 0.5)\ \mathrm{kJ \cdot mol^{-1}}$, provided a value of a specific contribution of the [$-CH_2-N(CH_3)-CH_2-$] unit (see Figure 5). For compounds **C** and **D** the difference between enthalpies of vaporization of diethylene glycol[21] [CAS 111-46-6] $\Delta_{\mathrm{l}}^{\mathrm{g}}H_{\mathrm{m}} = (78.6 \pm 0.6)\ \mathrm{kJ. \cdot mol^{-1}}$ and ethyleneglycol[22] [CAS 107-21-1] $\Delta_{\mathrm{l}}^{\mathrm{g}}H_{\mathrm{m}} = (66.0 \pm 0.2)\ \mathrm{kJ \cdot mol^{-1}}$ have been calculated: $\Delta(\Delta_{\mathrm{l}}^{\mathrm{g}}H_{\mathrm{m}}) = 78.6 - 66.0 = (12.6 \pm 0.6)\ \mathrm{kJ \cdot mol^{-1}}$ which is a specific contribution for the ($-CH_2-O-CH_2-$) unit (see Figure 5). With these two new structural units and the enthalpies of vaporization of ethanolamine[6] and *N*,*N*-dimethyl-2-aminoethanol[6] (CAS [108-01-0]) $\Delta_{\mathrm{l}}^{\mathrm{g}}H_{\mathrm{m}} = (46.5 \pm 0.4)\ \mathrm{kJ \cdot mol^{-1}}$, we were able to predict enthalpies of vaporization of alkanolamines **B**, **C**, and **D** (see numbers in Figure 6). Differences between experimental and estimated $\Delta_{\mathrm{l}}^{\mathrm{g}}H_{\mathrm{m}}$-values presented in Figure 6 do not exceed (3 to 4) $\mathrm{kJ \cdot mol^{-1}}$. An analysis of possible energetic interferences between stabilizing hydrogen bonding and destabilizing N−N repulsions in the alkanolamines studied matches our expectation and provides us with confidence on the consistency of the vaporization enthalpies derived in this study. This approach can be utilized in the analysis and vaporization enthalpy estimations of any other alkanolamines with similar functional groups.

■ OUTLOOK

A great number of process improvements can be developed around solvents that have no vapor pressure and are thermally stable and liquid over large temperature ranges. The combination of alkanolamines with ILs looks like a much more viable approach to achieve high levels of reversible CO_2 capture.[3] Amine−IL solutions are highly tunable systems for CO_2 capture, provided that such solutions have acceptably low pressure at processing temperatures. In addition to the results presented in this work we are currently examining vapor pressure and thermochemistry of pure ILs. The experimental study of vapor pressures for amine/IL mixtures seems to be a reasonable extension of the current work, and it could be important for improvement of current technologies for CO_2 capture and selective separation of H_2S from CO_2, which are often found together in natural gas wells.

■ ASSOCIATED CONTENT

Ⓢ **Supporting Information.** Physicochemical properties of the alkanolamines under study. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*Telephone: +49 381 498 6508. Fax: +49 381 498 6524. E-mail: sergey.verevkin@uni-rostock.de.

Funding Sources

This work has been supported by the German Science Foundation (DFG) in the frame of the priority program SPP 1191 "Ionic

Liquids". B.T. acknowledges gratefully a research scholarship from the DAAD (Deutscher Akademischer Austauschdienst).

■ REFERENCES

(1) Kohl, A.; Nielsen, R. *Gas Purification*, 5th ed.; Gulf Publishing Co.: Houston, TX, 1997.

(2) Bates, E. D.; Mayton, R. D.; Ntai, I.; Davis, J. H. CO_2 Capture by a Task-Specific Ionic Liquid. *J. Am. Chem. Soc.* **2002**, *124*, 926–927.

(3) Bara, J. E.; Camper, D. E.; Gin, D. L.; Noble, R. D. Room-Temperature Ionic Liquids and Composite Materials: Platform Technologies for CO_2 Capture. *Acc. Chem. Res.* **2010**, *43*, 152–159.

(4) Camper, D.; Bara, J. E.; Gin, D. L.; Noble, R. D. Room-Temperature Ionic Liquid-Amine Solutions: Tunable Solvents for Efficient and Reversible Capture of CO_2. *Ind. Eng. Chem. Res.* **2008**, *47*, 8496–8498.

(5) Gurkan, B.; Goodrich, B. F.; Mindrup, E. M.; Ficke, L. E.; Massel, M.; Seo, S.; Senftle, T. P.; Wu, H.; Glaser, M. F.; Shah, J. K.; Maginn, E. J.; Brennecke, J. F.; Schneider, W. F. Molecular Design of High Capacity, Low Viscosity, Chemically Tunable Ionic Liquids for CO_2 Capture. *J. Phys. Chem. Lett.* **2010**, *1*, 3494–3499.

(6) Kapteina, S.; Slovik, K.; Verevkin, S. P.; Heintz, A. Vapor Pressures and Vaporization Enthalpies of a Series of Ethanolamines. *J. Chem. Eng. Data* **2005**, *50*, 398–402.

(7) Efimova, A. A.; Emel'yanenko, V. N.; Verevkin, S. P.; Chernyak, Y. Vapour Pressure and Enthalpy of Vaporization of Aliphatic Poly-Amines. *J. Chem. Thermodyn.* **2010**, *42*, 330–346.

(8) Verevkin, S. P. Pure Component Phase Changes Liquid and Gas. Chapter 1 in *Experimental Thermodynamics: Measurement of the thermodynamic properties of multiple phases*; Weir, R. D., De Loos, Th. W., Eds.; Elsevier: New York, 2005; Vol. 7, pp 6—30.

(9) Kulikov, D. V.; Verevkin, S. P.; Heintz, A. Enthalpies of vaporization of a series of linear aliphatic alcohols. Experimental measurements and application of the ERAS-model for their prediction. *Fluid Phase Equilib.* **2001**, *192*, 187–202.

(10) Chickos, J. S.; Acree, W. E., Jr. Enthalpies of Vaporization of Organic and Organometallic Compounds, 1880—2002. *J. Phys. Chem. Ref. Data* **2003**, *32*, 519–878.

(11) Maham, Y.; Hepler, L. G.; Mather, A. E.; Hakin, A. W.; Marriott, R. A. Molar heat capacities of alkanolamines from 299.1 to 397.8 K. Group additivity and molecular connectivity analyses. *J. Chem. Soc., Faraday Trans.* **1997**, *93*, 1747–1750.

(12) Chiu, L.-F.; Li, M.-H. Heat Capacity of Alkanolamine Aqueous Solutions. *J. Chem. Eng. Data* **1999**, *44*, 1396–1401.

(13) Daubert, T. E. Vapor pressure of 13 pure industrial chemicals. Experimental Results for Phase Equilibria and Pure Comnponent Properties; *DIPPR Data Series 1*; AIChE: New York, 1991; pp 80—95.

(14) Xie, R.; Cheng, Y. Thermodynamic properties of 2-(2-aminoethylamino)ethanol and ethylenediamine system. *Huagong Xuebao (Chin. Ed.)* **2001**, *52*, 650–653.

(15) Wilson, G. M.; von Niederhausern, D. M.; Giles, N. F. Critical Point and Vapor Pressure Measurements for Nine Compounds by a Low Residence Time Flow Method. *J. Chem. Eng. Data* **2002**, *47*, 761–764.

(16) Cunningham, J. R.; Jones, D. K., Eds. Experimental Results for DIPPR 1990—1991 Projects on Phase Equilibria and Pure Component Properties. *DIPPR Data Ser.* **1994**, *2*, 154—172.

(17) von Niederhausern, D. M.; Wilson, G. M.; Giles, N. F. Critical Point and Vapor Pressure Measurements for 17 Compounds by a Low Residence Time Flow Method. *J. Chem. Eng. Data* **2006**, *51*, 1990–1995.

(18) Quitzsch, K.; Hofmann, H. P.; Hering, D.; Salzer, R.; Geiseler, G. Isobaric liquid-vapor equilibriums of binary and ternary mixtures of methyl glycol, dimethylaminoethanol, and 2-[2-(dimethylamino)-ethoxy]ethanol. *Z. Phys. Chem. (Leipzig)* **1970**, *243* (5—6), 321–339.

(19) Belabbaci, A.; Mokbel, I.; Kaci, A. A.; Jose, J.; Negadi, L. Phase equilibrium properties of binary aqueous solutions of benzylamine, 1,2-bis(2-aminoethoxy)ethane, or 2-[2-(dimethylamino)ethoxy]ethanol. *J. Chem. Thermodyn.* **2011**, *43*, 17–21.

(20) Wadso, I. Enthalpies of vaporization of organic compounds. *Acta Chem. Scand.* **1969**, *23*, 2061–2064.

(21) Steele, W. V.; Chirico, R. D.; Cowell, A. B.; Knipmeyer, S. E.; Nguyen, A. Thermodynamic Properties and Ideal-Gas Enthalpies of Formation for Methyl Benzoate, Ethyl Benzoate, (R)-(+)-Limonene, tert-Amyl Methyl Ether, trans-Crotonaldehyde, and Diethylene Glycol. *J. Chem. Eng. Data* **2002**, *47*, 667–688.

(22) Verevkin, S. P. Determination of vapor pressures and enthalpies of vaporization of 1,2-alkanediols. *Fluid Phase Equilib.* **2004**, *224*, 23–29.