# Vapor Pressures and Vaporization Enthalpies of a Series of Ethanolamines

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The vapor pressures and molar enthalpies of vaporization, $\Delta_l^g H_m$, of 2-amino-ethanol, 2-(methylamino)-ethanol, 2-(ethylamino)-ethanol, 2-(dimethylamino)-ethanol, and 2-(diethylamino)-ethanol have been determined using the transpiration method. The strength of intermolecular hydrogen bonding in ethanolamines has been derived and discussed in terms of the difference between the enthalpy of vaporization of an alkanolamine and an appropriate homomorph (alkylamine).

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## Introduction

Alkanolamines are widely used in the petroleum and natural gas industry for the removal of acid gas impurities such as $CO_2$ and $H_2S$ from gas mixtures. The design of gas treating processes requires knowledge of the vapor−liquid equilibrium behavior of the aqueous acid gas + alkanolamine systems as well as knowledge of the vapor pressures of pure alkanolamines at ambient temperature. Alkanolamines are high boiling liquids. Precise measurement of the vapor pressures of low volatile compounds at ambient temperature is usually difficult; that is why the most published data are referred to elevated temperatures (from 353 to 373 K up to the boiling point). In this work, we have applied the transpiration method,[1,2] which is suitable for performing vapor pressure measurements of high boiling liquids in a temperature range essentially close to ambient temperature and to the reference temperature 298.15 K. Additionally, we collected from the literature[3−17] a large number of the primary experimental results on the temperature dependencies of vapor pressures and treated them in order to derive vaporization enthalpies at the reference temperature 298.15 K. Our collection together with our own results helps to assess the strength of hydrogen bonding in alkanolamines. It is well established that the presence of more than one electronegative group in amino-alcohols and their derivatives stabilizes certain molecular conformations by intramolecular hydrogen bonding. Intramolecular hydrogen bonding of aliphatic amino-alcohols has therefore been extensively studied by IR, dipole moment, NMR, and microwave techniques.[18−21] From the IR frequency shifts, it has been found that, among the various substituted alcohols, $X(CH_2)_nOH$, where X = $NH_2$, $NR_2$, OH, or a halogen, the nitrogen-substituted derivatives gave the largest frequency shifts, pointing to the important role of basicity in hydrogen bonding.[21] On the other hand, in such a liquid phase, also intermolecular association between amino-alcohols has to be considered. In this work, we studied the vapor pressures of 2-amino-ethanol, 2-(methylamino)-ethanol, 2-(ethylamino)-ethanol, 2-(dimethylamino)-ethanol, and 2-(diethylamino)-ethanol and derived their enthalpies of vaporization at the reference temperature 298.15 K. The latter values give some insight into the character and strength of hydrogen bonding in pure liquid ethanolamines.

## Experimental Section

The samples of alkanolamines studied in this work were of commercial origin; 2-amino-ethanol, 2-(methylamino)-ethanol, 2-(ethylamino)-ethanol, and 2-(dimethylamino)-ethanol were purchased from Aldrich, and 2-(diethylamino)-ethanol was purchased from Fluka. Their purities determined by gas chromatography (GC) were better than 0.999 mole fraction.

The vapor pressures and enthalpies of vaporization of ethanolamines were determined using the transpiration method[1,2] in a saturated nitrogen stream and applying the Clausius−Clapeyron equation. About 0.5 g of the sample was mixed with glass beads and placed in a thermostated U-shaped tube having a length of 20 cm and a diameter of 0.5 cm. Glass beads with a diameter of the glass spheres of 1 mm provide a surface large enough for rapid vapor−liquid equilibration. At 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 flow rate of the nitrogen stream was measured using a soap bubble flow meter and was optimized in order to reach the saturation equilibrium of the transporting gas at each temperature under study. The flow rate of the nitrogen stream in the saturation tube should not be too slow in order to avoid the transport of material from the U-tube due to diffusion. On the other hand, the flow rate should not be too fast in order to ensure the saturation of the nitrogen stream with the vaporizing species. We tested our apparatus at different flow rates of the carrier gas in order to check the lower boundary of the flow below which the contribution of the vapor condensed in the trap by diffusion becomes comparable to the transported one. In our apparatus, the contribution due to diffusion was negligible at a flow rate down to 0.45 $dm^3 \cdot h^{-1}$. The upper limit for our apparatus where the speed of nitrogen could already disturb the equilibration was found at a flow rate of 9.0 $dm^3 \cdot h^{-1}$. Thus, we carried out the experiments in the flow rate interval (2.5 to 4.8) $dm^3 \cdot h^{-1}$ which ensured that the transporting gas was in saturated equilibrium with the coexisting liquid phase in the satura-

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tion tube. The amount of condensed substance was determined by GC analysis using an external standard (hydrocarbon $n$-$C_nH_{2n+2}$). The saturation vapor pressure, $p_i^{\mathrm{sat}}$, at each temperature, $T_i$, was calculated from the amount of the 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, we calculated the values of $p_i^{\mathrm{sat}}$ with

$$p_i^{\mathrm{sat}} = m_i R T_{\mathrm{a}}/V M_i; \quad V = V_{\mathrm{N_2}} + V_i; \quad (V_{\mathrm{N_2}} \gg V_i) \qquad (1)$$

where $R = 8.314\,51\ \mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}$, $m_i$ is the mass of the transported compound, $M_i$ is the molar mass of the compound, and $V_i$ is its volume contribution to the gaseous phase. $V_{\mathrm{N_2}}$ is the volume of the carrier gas, and $T_{\mathrm{a}}$ is the temperature of the soap bubble meter. The volume of the carrier gas, $V_{\mathrm{N_2}}$, was determined from the flow rate and the time measurement. Data of $p_i^{\mathrm{sat}}$ have been obtained as a function of temperature and were fitted by using the equation[1]

$$R \ln p_i^{\mathrm{sat}} = a + \frac{b}{T} + \Delta_{\mathrm{l}}^{\mathrm{g}} C_{\mathrm{p}} \ln\left(\frac{T}{T_0}\right) \qquad (2)$$

where $a$ and $b$ are adjustable parameters and $\Delta_{\mathrm{l}}^{\mathrm{g}} C_{\mathrm{p}}$ is the difference of the molar heat capacities of the gaseous and liquid phases, 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 the temperature $T$ is given by

$$\Delta_{\mathrm{l}}^{\mathrm{g}} H_{\mathrm{m}}(T) = -b + \Delta_{\mathrm{l}}^{\mathrm{g}} C_{\mathrm{p}} T \qquad (3)$$

Values of $\Delta_{\mathrm{l}}^{\mathrm{g}} C_{\mathrm{p}}$ (see Table 2) have been derived using experimental values of the isobaric molar heat capacities, $C_{\mathrm{p}}^{\mathrm{l}}$, of ethanolamines[22] according to a procedure developed by Chickos et al.[23,24] If experimental data on the $\Delta_{\mathrm{l}}^{\mathrm{g}} C_{\mathrm{p}}$ values of ethanolamines were not available, they were calculated using the group-additivity method suggested by Chickos et al.[23,24] The latter method has been checked for reliability using experimental results from Maham et al.[22] The experimental results, the parameters $a$ and $b$ are listed in Table 1. Enthalpies of vaporization measured by the transpiration method are usually accurate within ±(0.3 to 0.5) kJ·mol$^{-1}$. This error was determined by the average deviation of experimental $\ln(p_i^{\mathrm{sat}})$ from the linear correlation presented in eq 2. The dominant source of the experimental error was the uncertainty in the amount of transported mass, $m_i$, determined by GC analysis which was assessed to be reliable within (1 to 3)%. The accuracy of the volume, $V_{\mathrm{N_2}}$, measurements from the flow rate was established to be ±0.001 dm$^3$. The accuracy of maintaining and measuring the temperature was within ±0.1 K. However, the two latter factors hardly contribute to the experimental error.

## Results and Discussion

The vapor pressures of ethanolamines (see Table 2) have been reported in refs 3−17, but these authors (except for Steele et al.[14,17]) did not calculate the enthalpy of vaporization from their results. Therefore, enthalpies of vaporization, $\Delta_{\mathrm{l}}^{\mathrm{g}} H_{\mathrm{m}}$(298.15 K), have been derived in this work for the first time using eqs 2 and 3 and the data obtained have been compared with our results (see Table 2). The comprehensive compilation by Stephenson and Malanowski[9] contains vapor pressure results for some ethanolamines over a wide temperature range. The origin of the data presented there is unclear, and the methods of measurement as well as the errors of the measurements and purities of the compounds investigated are unknown. Despite this, we also treated the results from ref 9 using eqs 2 and 3 and calculated $\Delta_{\mathrm{l}}^{\mathrm{g}} H_{\mathrm{m}}$(298.15 K) for the sake of comparison with our results. However, the agreement or disagreement with our data in each case should be questionable (see Table 2).

The vapor pressures of 2-amino-ethanol have been measured in this work in the temperature range (279.0 K to 324.4 K). Although 2-amino-ethanol has a melting temperature of 283.8 K, the rate of crystallization of the sample in our experiments was very slow and the sample was measured as an undercooled liquid down to 279.0 K. the values of the enthalpy of vaporization, $\Delta_{\mathrm{l}}^{\mathrm{g}} H_{\mathrm{m}}$(298.15 K), of 2-amino-ethanol derived from the vapor pressures available from the literature obtained by ebulliometric and static measurements are very close to our result, (59.6 ± 0.3) kJ·mol$^{-1}$. The agreement of our results for the vapor pressures at different temperatures with the literature data is illustrated in Figure 1.

The enthalpies of vaporization, $\Delta_{\mathrm{l}}^{\mathrm{g}} H_{\mathrm{m}}$(298.15 K), of 2-(methylamino)-ethanol and 2-(dimethylamino)-ethanol derived in this work are in remarkable agreement with those calculated from vapor pressures available in the literature (see Table 2). The agreement of our results for the vapor pressures at different temperatures with the literature data is presented in Figure 2.

The disagreement with the vaporization enthalpies of 2-(diethylamino)-ethanol available from the literature (see Table 2) is larger than that for other ethanolamines; however, our result, $\Delta_{\mathrm{l}}^{\mathrm{g}} H_{\mathrm{m}}$(298.15 K) = (52.5 ± 0.2) kJ·mol$^{-1}$, coincides with those derived from the recent high temperature (332.5 to 475.6 K) ebulliometric measurements done by Steele et al.[17]

Close agreement of the enthalpies of vaporization, $\Delta_{\mathrm{l}}^{\mathrm{g}} H_{\mathrm{m}}$(298.15 K), of ethanolamines derived by different experimental techniques (see Table 2) has shown the reliability of our results derived by the transpiration method. Thus, we have been encouraged to use our own values of $\Delta_{\mathrm{l}}^{\mathrm{g}} H_{\mathrm{m}}$(298.15 K) for further thermochemical calculations as follows.

The existence of intramolecular hydrogen bonding in ethanolamines is well documented by spectroscopic measurements in the gaseous phase and dilute solutions in nonassociating inert solvents documented by IR-spectroscopic results in $CCl_4$ and $C_2Cl_4$.[19,20] However, exact quantification of intramolecular hydrogen bonds in the pure liquid state is difficult because both kinds of hydrogen bonding, inter- and intramolecular bonding, are expected to be present in liquid ethanolamines. The extent of intermolecular hydrogen bonding in ethanolamines can be assessed with the help of the vaporization enthalpies and the concept of homomorph compounds. Similar calculations have been performed recently[1] for the comparison of the enthalpies of vaporization of $n$-alkanols and those of alkanes. Indeed, for alkanes, only nonassociating intermolecular van der Waals interactions determine the values of their enthalpies of vaporization. The enthalpies of vaporization of alkanes which are obtained by replacing the OH group by a $CH_3$ group (R−$CH_3$) will essentially represent the nonassociative contribution of the alcohol (R−OH) to its enthalpy of vaporization. The difference of the enthalpies of vaporization between alkanols, ROH, and its homomorph, $RCH_3$, presents a crude measure for the

**Table 1. Results for the Vapor Pressure, $p$, and Enthalpy of Vaporization, $\Delta_l^g H_m$, Obtained by the Transpiration Method**

| $T$[a] | $m$[b] | $V_{N_2}$[c] | $p$[d] | $(p_{exptl} - p_{calcd})$ | $\Delta_l^g H_m$ | $T$[a] | $m$[b] | $V_{N_2}$[c] | $p$[d] | $(p_{exptl} - p_{calcd})$ | $\Delta_l^g H_m$ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| K | mg | dm$^3$ | Pa | Pa | kJ·mol$^{-1}$ | K | mg | dm$^3$ | Pa | Pa | kJ·mol$^{-1}$ |
| 2-Amino-ethanol; $\Delta_l^g H_m(298.15\ K) = (59.63 \pm 0.28)$ kJ·mol$^{-1}$<br>$\ln(p/Pa) = (285.55/R) - [75\,702.78/R(T/K)] - (53.9/R)\ln[(T/K)/298.15]$ | | | | | | | | | | | |
| 279.0 | 6.31 | 30.57 | 8.48 | 0.0 | 60.67 | 309.4 | 4.50 | 1.71 | 105.6 | −1.4 | 59.03 |
| 281.1 | 6.51 | 25.26 | 10.55 | 0.3 | 60.55 | 312.4 | 4.46 | 1.34 | 133.7 | 0.4 | 58.87 |
| 294.0 | 4.33 | 5.44 | 32.21 | 0.3 | 59.86 | 315.4 | 4.54 | 1.08 | 168.9 | 3.5 | 58.71 |
| 297.2 | 3.85 | 3.80 | 40.90 | −0.6 | 59.69 | 318.4 | 5.06 | 1.00 | 202.7 | −1.4 | 58.54 |
| 300.2 | 4.21 | 3.20 | 53.03 | 0.2 | 59.52 | 321.4 | 3.93 | 0.620 | 255.9 | 5.0 | 58.38 |
| 303.2 | 4.21 | 2.68 | 63.30 | −3.5 | 59.36 | 324.5 | 4.21 | 0.541 | 313.4 | 4.4 | 58.21 |
| 306.3 | 4.33 | 2.09 | 83.66 | −1.1 | 59.20 | | | | | | |
| 2-(Methylamino)-ethanol; $\Delta_l^g H_m(298.15\ K) = (57.84 \pm 0.21)$ kJ·mol$^{-1}$<br>$\ln(p/Pa) = (293.13/R) - [75\,847.15/R(T/K)] - (60.4/R)\ln[(T/K)/298.15]$ | | | | | | | | | | | |
| 274.9 | 3.09 | 7.521 | 13.94 | −0.3 | 59.25 | 296.3 | 4.23 | 1.511 | 92.12 | 1.2 | 57.95 |
| 277.9 | 8.41 | 14.969 | 18.89 | 0.0 | 59.07 | 299.2 | 3.90 | 1.115 | 114.92 | 0.8 | 57.78 |
| 282.1 | 7.48 | 9.032 | 27.60 | 0.0 | 58.81 | 302.3 | 4.89 | 1.115 | 144.04 | −0.8 | 57.59 |
| 285.1 | 3.24 | 2.987 | 35.99 | 0.1 | 58.63 | 308.4 | 3.24 | 0.468 | 227.06 | −0.5 | 57.22 |
| 288.2 | 3.45 | 2.447 | 46.63 | −0.2 | 58.44 | 311.4 | 3.03 | 0.355 | 279.89 | −2.1 | 57.04 |
| 291.1 | 5.25 | 2.843 | 60.98 | 1.4 | 58.27 | 314.3 | 5.25 | 0.497 | 346.76 | 1.3 | 56.87 |
| 291.2 | 2.97 | 1.631 | 60.03 | −0.1 | 58.26 | 317.2 | 5.19 | 0.408 | 417.20 | −4.2 | 56.69 |
| 293.2 | 5.25 | 2.447 | 70.77 | −0.1 | 58.14 | 320.2 | 3.90 | 0.248 | 514.60 | −0.7 | 56.51 |
| 2-(Ethylamino)-ethanol; $\Delta_l^g H_m(298.15\ K) = (61.01 \pm 0.44)$ kJ·mol$^{-1}$<br>$\ln(p/Pa) = (309.40/R) - [81\,848.12/R(T/K)] - (60.4/R)\ln[(T/K)/298.15]$ | | | | | | | | | | | |
| 282.5 | 1.59 | 2.745 | 16.25 | −0.4 | 62.10 | 306.2 | 1.53 | 0.359 | 118.62 | −7.3 | 60.45 |
| 284.5 | 1.04 | 1.445 | 20.09 | 0.0 | 61.97 | 308.5 | 1.68 | 0.305 | 152.81 | 2.6 | 60.29 |
| 287.3 | 1.05 | 1.120 | 26.12 | 0.2 | 61.77 | 309.2 | 1.75 | 0.300 | 161.15 | 2.7 | 60.24 |
| 290.3 | 1.04 | 0.849 | 34.03 | 0.2 | 61.56 | 311.5 | 1.83 | 0.269 | 188.40 | 0.1 | 60.08 |
| 293.2 | 1.00 | 0.650 | 43.00 | −0.6 | 61.36 | 312.2 | 3.34 | 0.450 | 205.17 | 6.8 | 60.03 |
| 296.3 | 1.56 | 0.762 | 56.71 | 0.0 | 61.14 | 315.3 | 3.04 | 0.338 | 249.17 | 0.2 | 59.81 |
| 299.3 | 1.59 | 0.581 | 75.86 | 3.2 | 60.93 | 318.3 | 2.85 | 0.263 | 300.21 | −8.3 | 59.60 |
| 302.3 | 1.59 | 0.472 | 93.31 | 0.7 | 60.72 | 321.3 | 3.80 | 0.282 | 373.95 | −6.7 | 59.39 |
| 305.5 | 1.71 | 0.395 | 120.37 | 1.2 | 60.50 | | | | | | |
| 2-(Dimethylamino)-ethanol; $\Delta_l^g H_m(298.15\ K) = (46.51 \pm 0.38)$ kJ·mol$^{-1}$<br>$\ln(p/Pa) = (274.71/R) - [65\,563.83/R(T/K)] - (63.9/R)\ln[(T/K)/298.15]$ | | | | | | | | | | | |
| 277.9 | 3.634 | 0.562 | 189.28 | 7.75 | 47.81 | 294.1 | 7.732 | 0.397 | 550.21 | −10.66 | 46.77 |
| 278.3 | 2.655 | 0.401 | 193.41 | 6.40 | 47.78 | 295.0 | 6.096 | 0.298 | 577.98 | −16.58 | 46.72 |
| 278.6 | 6.253 | 0.976 | 186.98 | −4.24 | 47.76 | 295.2 | 3.660 | 0.169 | 612.82 | 10.54 | 46.70 |
| 280.2 | 3.370 | 0.441 | 221.68 | 6.58 | 47.66 | 298.0 | 6.065 | 0.248 | 688.27 | −31.71 | 46.52 |
| 280.7 | 2.600 | 0.329 | 229.07 | 5.99 | 47.63 | 298.2 | 3.571 | 0.136 | 736.49 | 7.38 | 46.51 |
| 281.8 | 6.662 | 0.811 | 237.35 | −4.22 | 47.56 | 301.1 | 5.656 | 0.192 | 828.09 | −45.15 | 46.33 |
| 283.2 | 3.634 | 0.377 | 277.20 | 10.14 | 47.47 | 301.2 | 6.067 | 0.193 | 884.45 | 5.83 | 46.32 |
| 284.3 | 6.065 | 0.629 | 277.06 | −11.65 | 47.40 | 304.2 | 7.259 | 0.193 | 1056.43 | 2.33 | 46.13 |
| 286.2 | 3.766 | 0.313 | 343.79 | 14.01 | 47.28 | 304.2 | 5.813 | 0.160 | 1019.27 | −34.84 | 46.13 |
| 286.5 | 7.449 | 0.662 | 321.79 | −14.93 | 47.26 | 307.2 | 6.538 | 0.144 | 1266.71 | 7.50 | 45.94 |
| 289.2 | 5.217 | 0.353 | 419.95 | 14.83 | 47.09 | 307.2 | 7.103 | 0.160 | 1243.40 | −15.81 | 45.94 |
| 289.4 | 6.694 | 0.480 | 396.74 | −13.90 | 47.07 | 310.2 | 7.038 | 0.128 | 1531.84 | 33.86 | 45.75 |
| 290.6 | 7.040 | 0.464 | 430.81 | −14.37 | 47.00 | 313.3 | 5.928 | 0.088 | 1874.70 | 89.93 | 45.55 |
| 292.2 | 3.713 | 0.209 | 503.85 | 8.68 | 46.90 | 316.3 | 7.620 | 0.096 | 2207.22 | 101.13 | 45.36 |
| 292.4 | 6.191 | 0.364 | 481.71 | −20.04 | 46.88 | | | | | | |
| 2-(Diethylamino)-ethanol; $\Delta_l^g H_m(298.15\ K) = (52.45 \pm 0.16)$ kJ·mol$^{-1}$<br>$\ln(p/Pa) = (303.80/R) - [77\,076.22/R(T/K)] - (82.6/R)\ln[(T/K)/298.15]$ | | | | | | | | | | | |
| 278.2 | 2.38 | 1.010 | 51.47 | 2.0 | 54.10 | 296.0 | 4.31 | 0.450 | 204.13 | 5.9 | 52.63 |
| 278.6 | 1.732 | 0.718 | 50.86 | −0.3 | 54.07 | 296.3 | 4.33 | 0.462 | 199.38 | −3.2 | 52.61 |
| 279.8 | 2.409 | 0.916 | 55.44 | −1.1 | 53.97 | 296.3 | 2.346 | 0.248 | 199.78 | −2.8 | 52.61 |
| 281.2 | 2.36 | 0.808 | 63.47 | 0.0 | 53.85 | 297.3 | 4.03 | 0.387 | 221.33 | 3.7 | 52.52 |
| 282.7 | 1.842 | 0.557 | 69.73 | −2.0 | 53.73 | 298.2 | 3.873 | 0.354 | 232.89 | 0.8 | 52.45 |
| 284.2 | 2.38 | 0.631 | 81.26 | 0.4 | 53.61 | 299.2 | 2.315 | 0.198 | 246.38 | −2.7 | 52.37 |
| 285.1 | 2.41 | 0.575 | 90.24 | 3.4 | 53.53 | 301.2 | 3.936 | 0.288 | 288.73 | 2.4 | 52.20 |
| 285.3 | 1.937 | 0.471 | 86.81 | −1.5 | 53.51 | 302.2 | 2.30 | 0.161 | 302.99 | −3.8 | 52.12 |
| 287.3 | 2.25 | 0.480 | 100.81 | −2.4 | 53.35 | 302.2 | 5.24 | 0.362 | 307.03 | 0.2 | 52.12 |
| 288.0 | 2.28 | 0.450 | 108.90 | −0.1 | 53.29 | 304.2 | 3.952 | 0.238 | 350.91 | −0.7 | 51.95 |
| 288.3 | 2.31 | 0.437 | 113.48 | 1.9 | 53.27 | 307.2 | 4.046 | 0.200 | 426.67 | −2.8 | 51.71 |
| 290.2 | 2.33 | 0.391 | 127.40 | −1.6 | 53.11 | 310.2 | 3.684 | 0.150 | 517.99 | −4.2 | 51.46 |
| 291.0 | 4.01 | 0.625 | 137.38 | 0.3 | 53.04 | 313.2 | 3.747 | 0.125 | 632.21 | 0.3 | 51.21 |
| 292.3 | 4.25 | 0.600 | 151.34 | 0.2 | 52.94 | 316.3 | 4.550 | 0.125 | 767.66 | 1.8 | 50.95 |
| 293.3 | 4.63 | 0.606 | 162.91 | 0.2 | 52.85 | 318.3 | 5.195 | 0.125 | 876.55 | 11.7 | 50.79 |
| 295.3 | 4.015 | 0.455 | 188.11 | −0.3 | 52.69 | | | | | | |

[a] Temperature of saturation. $N_2$ gas flow (0.22 to 0.69) cm$^3$·s$^{-1}$. [b] Mass of transferred sample condensed at $T = 243$ K. [c] Volume of nitrogen used to transfer mass $m$ of the sample. [d] Vapor pressure at temperature $T$ calculated from $m$ and the residual vapor pressure at $T = 243$ K.

contribution to the enthalpy of vaporization due to the self-association of alcohols. A remarkable constancy of the difference in enthalpies of vaporization at 298.15 K of (21 to 25) kJ·mol$^{-1}$ was observed, indicating that the contribution to $\Delta_l^g H_m$ of alcohols due to *inter*molecular hydrogen bonding is nearly independent of the chain length. These results could be interpreted quantitatively using the extended real associated solution (ERAS) model.[1]

Following this pattern, experimental data of the vaporization enthalpies, $\Delta_l^g H_m$(298.15 K), of ethanolamines at 298.15 K (Table 2, this work) were compared with those of their homomorphs (alkylamines): (30.3 ± 0.1) kJ·mol$^{-1}$ for

**Table 2. Compilation of Data on the Enthalpies of Vaporization, $\Delta_l^g H_m$(298.15 K), of Aminoethanols**

| | technique[a] | temperature range | $\Delta_l^g C_p$[b] | $\Delta_l^g H_m$(298K)[c] | ref |
|---|---|---|---|---|---|
| | | K | $J \cdot mol^{-1} \cdot K^{-1}$ | $kJ \cdot mol^{-1}$ | |
| 2-amino-ethanol | | 341−453 | 53.9 | 57.9 | Wilson, 1935 |
| | E | 303−373 | | 57.4 | Leibush, 1947 |
| | E | 379.3−443.5 | | 59.5 | Matthews, 1950 |
| | E | 338.6−444.1 | | 60.3 | McDonald, 1959 |
| | S | 325.1−443.2 | | 57.7 | Danov, 1969 |
| | S | 293.1−297.6 | | 54.8 | Gustin, 1974 |
| | S | 298.2−308.2 | | 56.1 | Touhara, 1982 |
| | | 310−444 | | 60.8 | Stephenson, 1987 |
| | E | 351.5−613.2 | | 59.0 | Daubert, 1987 |
| | E | 357.6−439.7 | | 59.4 | Tochigi, 1999 |
| | T | 279.0−324.4 | | **59.6 ± 0.3** | this work |
| 2-(methylamino)-ethanol | S | 298.2−308.2 | 60.4 | 57.5 | Touhara, 1982 |
| | E | 351−410 | | 57.6 | Smirnova, 1987 |
| | S | 268.8−401.4 | | 57.9 | Noll, 1998 |
| | E | 340.3−461.0 | | 57.0 ± 0.5 | Steele, 1997 |
| | T | 274.9−320.2 | | **57.8 ± 0.2** | this work |
| 2-(dimethylamino)-ethanol | E | 333−423 | 63.9 | 47.6 | Quitzsch, 1970 |
| | S | 298.2−308.2 | | 47.9 | Touhara, 1982 |
| | | 350−387 | | 47.6 | Stephenson, 1987 |
| | | 323−408 | | 46.1 | Stephenson, 1987 |
| | T | 277.9−316.3 | | **46.5 ± 0.4** | this work |
| 2-(diethylamino)-ethanol | S | 283−318 | 82.6 | 58.5 ± 1.3 | Lebedeva, 1977 |
| | E | 332.5−475.6 | | 52.5 ± 0.2 | Steele, 2002 |
| | | 328−433 | | 55.1 | Stephenson, 1987 |
| | T | 278.2−318.3 | | **52.5 ± 0.2** | this work |

[a] Techniques: E, the ebulliometric method; T, the transpiration method; S, the static method. [b] The molar heat capacity difference between the liquid and gaseous phases (see text). [c] Derived using eqs 2 and 3 with the molar heat capacity difference, $\Delta_l^g C_p$.

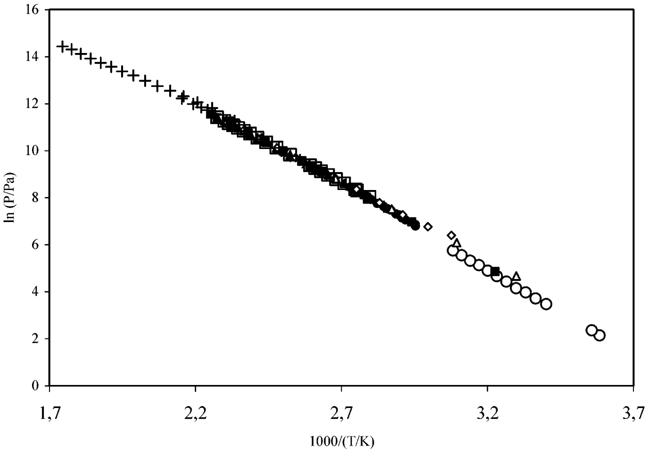

**Figure 1.** Experimental data of the vapor pressures of 2-amino-ethanol: ○, this work; ●, Matthews et al.;[5] ▲, Tochigi et al.;[11] ◇, Danov et al.;[7] ∗, McDonald et al.;[6] △, Leibush and Shorina;[4] +, Daubert et al.;[10] ■, Stephenson and Malanowski.[9]

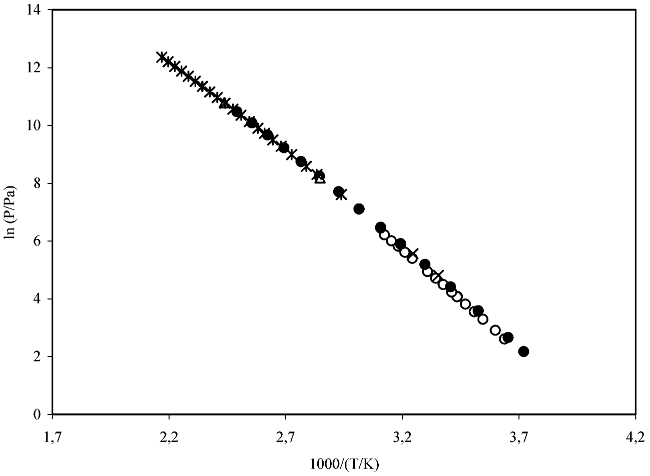

**Figure 2.** Experimental data of the vapor pressures of 2-(methylamino)-ethanol: ○, this work; ●, Noll et al.;[13] △, Smirnova et al.;[12] ◇, Danov et al.;[7] ×, Touhara et al.;[8] ∗, Steele et al.[14]

propylamine available from ref 25 as well as 31.2 $kJ \cdot mol^{-1}$ for (*N*-methyl)-propylamine, 35.7 $kJ \cdot mol^{-1}$ for (*N*-ethyl)-propylamine, 30.7 $kJ \cdot mol^{-1}$ for (*N,N*-dimethyl)-propylamine, and 39.9 $kJ \cdot mol^{-1}$ for (*N,N*-diethyl)-propylamine estimated according to the group-additivity procedure by Lebedev and Miroshnichenko.[26] The differences of the enthalpies of vaporization between ethanolamines and alkylamines are presented in Table 3. These differences could be interpreted as contribution to the enthalpy of vaporization due to intermolecular bonding in ethanolamines. In other words, these differences are a rough measure for the strength of *inter*molecular hydrogen bonding.

According to Table 3, it is evident that 2-amino-ethanol exhibits the highest value assigned to the *inter*molecular hydrogen bond, −28.3 $kJ \cdot mol^{-1}$. This is close to the hydrogen bonding energy for 1 mol of the N−H· · ·O bonds and indicates that the majority of hydrogen bonds in 2-amino-ethanol are of *inter*molecular character. Obviously, spatial crowding of the nitrogen atom disturbs the formation of intermolecular hydrogen bonds in 2-(methylamino)-ethanol and 2-(ethylamino)-ethanol, since (−26.6 and −25.3) $kJ \cdot mol^{-1}$ are lower values in comparison to those of 2-amino-ethanol. Further N-substitution with methyl and ethyl in (dimethylamino)-ethanol (−15.8 $kJ \cdot mol^{-1}$) and 2-(diethylamino)-ethanol (−12.6 $kJ \cdot mol^{-1}$) causes a substantial decrease of the hydrogen bonding strength, and it is apparent that the most crowded 2-(diethylamino)-ethanol possesses the weakest intermolecular hydrogen bond. Although we cannot quantify the amount of *intra*molecular hydrogen bonds, it can be concluded that the portion of hydrogen bonding in amino-alcohols is shifted from intramolecular character to intermolecular character when the molecular density increases from the gaseous state or diluted solution to the bulk liquid state.

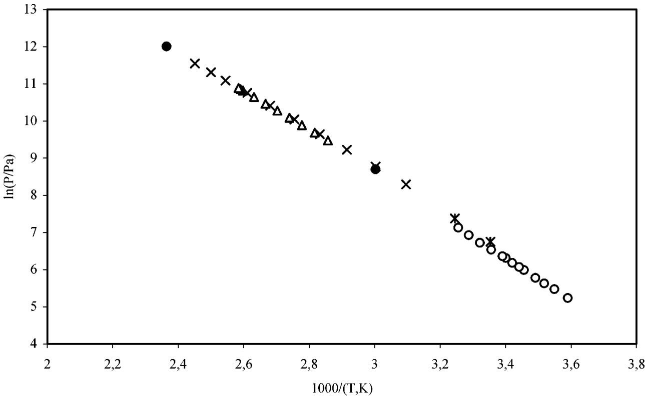

**Figure 3.** Experimental data of the vapor pressures of 2-(dimethylamino)-ethanol: ○, this work; ●, Quitzsch et al.;[15] △, Stephenson and Malanowski;[9] ×, Stephenson and Malanowski;[9] ∗, Touhara et al.[8]

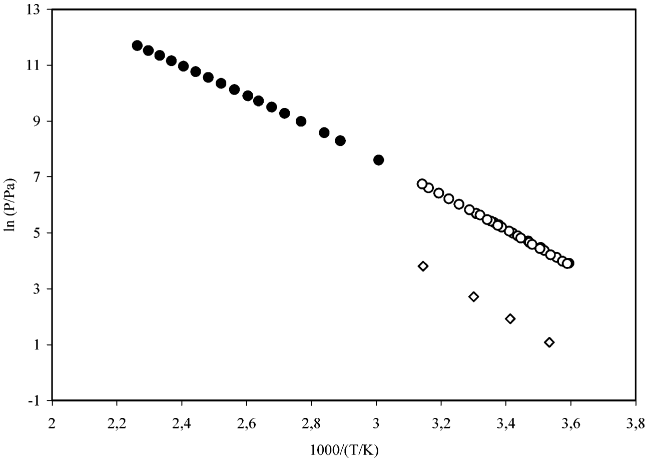

**Figure 4.** Experimental data of the vapor pressures of 2-(diethylamino)-ethanol: ○, this work; ●, Steele et al.;[17] ◇, Lebedeva et al.[16]

**Table 3. Interpretation of the Strength of the Intermolecular Hydrogen Bond from the Vaporization Enthalpies, $\Delta_l^g H_m$(298.15 K), of Ethanolamines (from This Work) and Their Homomorphs (in kJ·mol$^{-1}$)**

| $\Delta_l^g H_m$(298.15 K) amino-ethanol | $\Delta_l^g H_m$(298.15 K) amine | $\Delta^a$ |
|---|---|---|
| 2-amino-ethanol<br>59.6 | propan-1-amine<br>31.3$^b$ | −28.3 |
| 2-(methylamino)-ethanol<br>57.8 | *N*-methylpropan-1-amine<br>31.2$^c$ | −26.6 |
| 2-(ethylamino)-ethanol<br>61.0 | *N*-ethylpropan-1-amine<br>35.7$^c$ | −25.3 |
| 2-(dimethylamino)-ethanol<br>46.5 | *N*,*N*-dimethylpropan-1-amine<br>30.7$^c$ | −15.8 |
| 2-(diethylamino)-ethanol<br>52.5 | *N*,*N*-diethylpropan-1-amine<br>39.9$^c$ | −12.6 |

[a] Difference between column 2 and column 1 (see text). [b] From ref 25. [c] Estimated according to the group-additivity procedure by Lebedev and Miroshnichenko.[26]

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