J. Chem. Eng. Data **2006,** *51,* 609−611

Critical Pressures and Temperatures of *n*-Diaminoalkanes (C_2 to C_{12})

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The critical temperatures and pressures of eight *n*-diaminoalkanes $NH_2(CH_2)_nNH_2$ with $n = 2$, 3, 4, 6, 8, 9, 10, and 12 have been measured. The method of pulse heating of a wire probe immersed into the liquid under study has been used. Residence times are from (0.03 to 1) ms. The critical properties of diaminoalkanes have been estimated by the group-contribution methods by Joback and Reid, Constantinou and Gani, and Marrero and Gani. These properties have also been calculated using a method based on the assumption that the functions describing the dependence of the critical properties of homologous series on the number of mers in a molecule should be self-similar and provide the scaling behavior for long-chain molecules. The last method provides the best accuracy in calculating the critical properties of diaminoalkanes. For this method, the average absolute errors are equal to 0.4 % for the critical temperature and about 2 % for the critical pressure.

Introduction

Diaminoalkanes $NH_2(CH_2)_nNH_2$ are widely employed in various organic syntheses. For example, 1,6-diaminohexane is well-known to be used in manufacturing nylon 6,6; 1,12-diaminododecane is a source of 12 carbon chains for medical drugs and so on. However, the critical constants of diaminoalkanes have probably been measured only for 1,2-diaminoethane.[1] In this paper, we report the experimental critical temperatures and pressures of eight diaminoalkanes with $n =$ 2, 3, 4, 6, 8, 9, 10, and 12. The pulse-heating method was used for the measurements.

Experimental Section

Method. The pulse-heating apparatus and procedures have been described in detail earlier.[2−4] The method consists of measuring the pressure dependence of the temperature of the attainable superheat (spontaneous boiling-up) of a liquid with the help of a thin wire probe heated by pulses of electric current. When the pressure in the liquid approaches the critical pressure, the temperature of the attainable superheat approaches the critical temperature. The values of the critical pressure (p_c^m) and the critical temperature (T_c^m) obtained in the course of the measurements should be corrected in accordance with the following equation:

$$p_c = p_c^m/\pi_0 \quad T_c = T_c^m/\tau_0 \tag{1}$$

Here $1/\pi_0$ and $1/\tau_0$ are correction factors.[2,5] In the calculation of the correction factors, use is made of the similarity parameter of a substance suggested by Filippov, which is analogous to the acentric factor:[6]

$$A = 100\frac{p_s(T/T_c = 0.625)}{p_c}$$

where p_s is the vapor pressure. The Filippov parameters and the critical constants of diaminoalkanes were calculated by an iteration method. For the first iteration, p_c^m and T_c^m were used as the critical constants; the vapor pressure of diaminoalkanes with $n = 2$ was estimated by the Antoine equation,[7] with $n =$ 3 to 10 by the Clapeyron equation and normal or reduced pressure boiling points taken in accordance with the NIST recommendation.[7] Then the values of π_0 and $\tau_0$were calculated and with the use of eq 1, p_c and T_c were calculated. For the second iteration, the Filippov parameter and the critical constants were calculated using the values obtained after the first iteration. Two iterations were enough because the values of π_0 and τ_0 are little affected by the variations of Filippov's parameter. We failed to find in the literature the vapor pressure of 1,12-diaminododecane ($n = 12$). The Filippov parameter of this compound was estimated by the following equation:

$$\ln A = a_0 + a_1 n^{2/3}$$

the form of which was suggested in our previous publications.[8,9] The constants a_0 and a_1 were determined by processing the Filippov parameters for $n = 2$ to 4, 6, 9, and 10: $a_0 = 0.92424$, $a_1 = -0.39542$.

For the calculation of the correction factors, the ideal gas heat capacity of the substance under study and the factor G_T are also needed. The ideal gas heat capacity was estimated by the method of Rihani and Doraiswamy as presented by Reid et al.[10] The factor $G_T \equiv \partial \ln J/\partial T$, where J is the rate of bubble nucleation in a superheated liquid, was measured in one experiment with the critical constants and estimated at 1.5 K^{-1}. The procedure of measuring this factor was described in our previous paper.[2]

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10.1021/je050424e CCC: \$33.50

Table 1. Sources and Purities of Compounds Used in Critical Point Measurements

			purity/%				
			before measuring critical constants			after measuring critical constants	
compound	CASRN[a]	supplier	supplier[b]	GC	PMS	GC	PMS
1,2-diaminoethane	107-15-3	Fluka	99.5	99.9	99.9	99.9	99.9
1,3-diaminopropane	109-76-2	Aldrich	100.00	98.5	100.0	100.0	100.0
1,4-diaminobutane	110-60-1	Aldrich	99.20	99.7	99.9	99.7	99.9
1,6-diaminohexane	124-09-4	Sigma	99.9	99.9	99.8	99.9	99.9
1,8-diaminooctane	373-44-4	Fluka	99.7	100	99.9	99.8	99.8
1,9-diaminononane	646-24-2	Aldrich	97.8/99.10	100	99.9	100	99.9
1,10-diaminodecane	646-25-3	Aldrich	98.20/99.40	99.8	100	99.8	100
1,12-diaminododecane	2783-17-7	Aldrich	99.9/99.2	100	99.8	99.8	100

[a] CAS Registry Number. [b] For a given lot (GC/titration vs $HClO_4$).

Table 2. Critical Temperatures of *n*-Diaminoalkanes $NH_2(CH_2)_nNH_2$: Experimental and Calculated Values

			T_c/K			
n	T_b[a]/K	T_c/K	ref 14	ref 15	ref 16	ref 17
2	391	614 ± 6 613.1 ± 0.2[b]	592.5	593.0	593.0	608
3	413.2	632 ± 6	612.6	602.5	599.5	630
4	431.7	651 ± 7	627.1	623.9	621.5	650
6	477.7	685 ± 7	669.0	660.4	660.0	685
8	498.7	712 ± 7	676.8	690.7	693.0	715
9	531.8	726 ± 7	711.7	704.1	707.9	728
10		736 ± 7		716.7	721.9	740
12		767 ± 8		739.4	747.6	763
AAPE[c]/%			3.26	3.51	3.29	0.40
MAPE[d]/%			4.94	4.67	5.14	0.93

[a] T_b is the normal boiling point; according to NIST recommendation.[7] [b] Data by Wilson et al.[1] [c] AAPE = $(1/N)(\Sigma|T_c^{exp} - T_c^{calc}|/T_c^{exp}) \times 100$ %, where N is the number of experimental data points, T_c^{exp} is the experimental value of the critical temperature, and T_c^{calc} is the calculated value of the critical temperature. [d] MAPE = $(|T_c^{exp} - T_c^{calc}|_{max}/T_c^{exp}) \times 100$ %.

Table 3. Critical Pressures of *n*-Diaminoalkanes $NH_2(CH_2)_nNH_2$: Experimental and Calculated Values

		p_c/MPa			
n	p_c/MPa	ref 14	ref 15	ref 16	ref 17
2	6.65 ± 0.20 6.707 ± 0.007[a]	5.954	6.290	6.290	6.30
3	5.59 ± 0.17	5.161	5.552	4.921	5.36
4	4.54 ± 0.14	4.516	4.799	4.243	4.63
6	3.59 ± 0.11	3.543	3.698	3.290	3.59
8	2.80 ± 0.08	2.854	2.946	2.667	2.89
9	2.63 ± 0.08	2.582	2.656	2.434	2.62
10	2.43 ± 0.07	2.347	2.409	2.238	2.39
12	2.01 ± 0.06	1.965	2.012	1.930	2.02
AAPE[b]/%		3.67	2.75	7.05	2.13
MAPE[c]/%		10.47	5.70	11.97	5.26

[a] Data by Wilson et al.[1] [b] AAPE = $(1/N)(\Sigma|p_c^{exp} - p_c^{calc}|/p_c^{exp}) \times 100$ %, where N is the number of experimental data points, p_c^{exp} is the experimental value of the critical pressure, and p_c^{calc} is the calculated value of the critical pressure. [c] MAPE = $(|p_c^{exp} - p_c^{calc}|_{max}/p_c^{exp}) \times 100$ %.

Table 4. Parameters of Equations 2 and 3

parameter	value
ν	3
a_1	$2.37112 \cdot 10^3$
a_2	$-7.6388 \cdot 10^{-1}$
a_3	$-3.734 \cdot 10^{-2}$
λ	5/3
b	6.036

The critical parameters determined in the way described above may depend on the time from the beginning of a heating pulse to the moment of boiling-up t^* due to the decomposition of a substance under study in the course of heating. The critical constants of diaminoalkanes were measured with the help of probes (1, 2, and 3) cm in length at heating times $t^* = (0.03, 0.06, 0.11, 0.22, 0.45, \text{and } 1.00)$ ms. Several portions (from 2 to 4) of each compound were used. No thermal decomposition of diaminoalkanes was observed in the course of measuring so the experimental data were averaged over all the probe lengths, heating times, and portions.

Sources and Purities of the Compounds Studied. The sources and purities of the diaminoalkanes studied are given in Table 1. Before and after measuring the critical constants, the purities of the samples were determined using gas chromatography (Shimadzu GS-Ha) and proton magnetic spectroscopy (Bruker DRX 400).

Uncertainties. The uncertainties of the critical constants measured by the pulse-heating method were discussed in detail in our previous papers.[11−13] We estimate the uncertainties for diamonoalkanes at 0.03 p_c and 0.01 T_c, where T_c is the absolute temperature. It corresponds to from (± 0.20 to ± 0.06) MPa for the critical pressure and from (± 6 to ± 8) K for the critical temperature (see Tables 2 and 3).

Results and Discussion

Tables 2 and 3 present the critical temperatures and pressures of *n*-diaminoalkanes included in this study. Our data for 1,2-diaminoethane are in good agreement with the results by Wilson et al.[1] obtained by a flow method. Tables 2 and 3 contain the values estimated using the group-contribution methods by Joback and Reid,[14] Constantinou and Gani,[15] and Marrero and Gani[16] as well as the values calculated by the equations suggested in our previous paper:[17]

$$T_c(n) = [[a_1a_3(1-\nu)(n-k) + [T_c(k)^{a_3} + a_2]^{1-\nu}]^{1/1-\nu} - a_2]^{1/a_3} \tag{2}$$

$$p_c(n) = [p_c(k)^{1-\lambda} + b^{-\lambda}(\lambda - 1)(n-k)]^{1/1-\lambda} \tag{3}$$

Here n and k are the numbers of mers in a molecule. These equations were obtained from the idea that the functions describing the dependence of the critical properties of homologous series on the number of mers in a molecule should satisfy the two following requirements: (i) should be self-similar ones and (ii) should provide the scaling behavior for long-chain molecules. In addition, for homologous series with the same structure of mer, independently of the structure of end groups, these functions should give the same values of the limiting ($n \to \infty$) critical properties. The parameters of eqs 2 and 3 are given in Table 4. According to the theory developed in ref 17, the values of ν and λ are universal and depend on neither the structure of a mer nor the structure of end groups. The

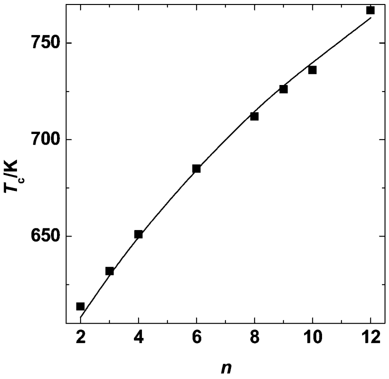

Figure 1. Critical temperatures of *n*-diaminoalkanes $NH_2(CH_2)_nNH_2$ vs the number of carbons in a molecule. The solid line corresponds to calculation by eq 2.

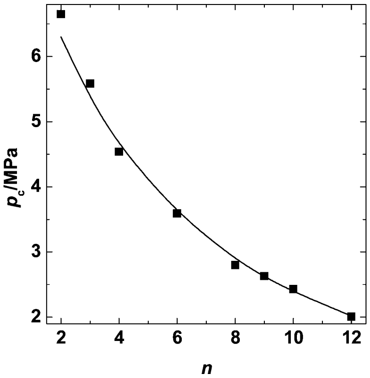

Figure 2. Critical pressures of *n*-diaminoalkanes $NH_2(CH_2)_nNH_2$ vs the number of carbons in a molecule. The solid line corresponds to calculation by eq 3.

parameters a_i and b depend on the structure of a mer but do not depend on the structure of end groups. These parameters were determined by processing experimental data for six homologous series with the common formula $H(CH_2)_nR$, where R was the following end groups: H (normal alkanes), C_2H_3 (1-alkenes), OH (1-alkanols), $COCH_3$ (2-alkanones), COC_2H_5 (3-alkanones), and COC_3H_7 (4-alkanones). These homologous series were chosen because their critical properties were studied most fully. The proposed equations allow predicting the critical temperatures or pressures of any member of a homologous series with the common formula $R_1(CH_2)_nR_2$ if the critical temperature $T_c(k)$/pressure $p_c(k)$ of one substance, which belongs to this series are known.

For diaminoalkanes, the base point k was taken equal to 6. For this point the experimental and the calculated values of the critical properties are absolutely equal. Tables 3 and 4 show that eqs 2 and 3 predict the critical constants of diaminoalkanes well enough. It is well to bear in mind that these equations were designed for calculating the critical properties of long-chain molecules. So it is not surprising that the maximum discrepancy between the experimental and calculated values of the critical temperature and pressure is observed for 1,2-diaminoethane ($n = 2$). The critical temperatures and pressures of *n*-diaminoalkanes are shown in Figures 1 and 2. The solid lines in these figures are the result of calculation using eqs 2 and 3.

The well-known group-contribution methods by Joback and Reid,[14] Constantinou and Gani,[15] and Marrero and Gani[16] give the critical temperatures that are on average lower by approximately 3 % than the experimental values (see Table 2). For the critical pressure, the method of Constantinou and Gani works better than the methods by Joback and Reid and Marrero and Gani.

Equations 2 and 3 provide the best accuracy in comparison with the group-contribution methods, especially for the critical temperature. It is not surprising because the critical temperature and pressure of one of diamonoalkanes (base point) are used in these equations.

Conclusion

The critical temperatures and pressures of eight *n*-diaminoalkanes have been measured by the pulse-heating technique. They have also been calculated using the group-contribution methods and a method based on the hypothesis of functional self-similarity and the scaling behavior of the critical constants of long-chain molecules. The last method provides the best accuracy in calculating the critical properties of diaminoalkanes. For this method, the average absolute errors are equal to 0.4 % for the critical temperature and about 2 % for the critical pressure.

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Received for review October 14, 2005. Accepted November 29, 2005. This study was supported by the Russian Foundation for Basic Research under Grant 04-02-16111a and the grant of the President of the Russian Federation NSh-905.2003.2.

JE050424E