Volumetric Properties of 2-Alkylamines (2-Aminobutane and 2-Aminooctane) at Pressures up to 140 MPa and Temperatures between (293.15 and 403.15) K[†]

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This work reports the density data (352 points) of two 2-alkylamines (2-aminobutane and 2-aminooctane; branched amines) at 12 temperatures between (293.15 and 403.15) K and pressures up to 140 MPa (every 10 MPa) which allows studying the influence of the chain length. An Anton Paar vibrating tube densimeter, calibrated with an uncertainty of $\pm 5 \cdot 10^{-4}\ \text{g} \cdot \text{cm}^{-3}$ was used to perform these measurements. The experimental density data were fitted with the Tait-like equation with low standard deviations (less than $2 \cdot 10^{-4}\ \text{g} \cdot \text{cm}^{-3}$). These data were used to derive the isobaric thermal expansivity and the isothermal compressibility.

1. Introduction

In a recent work by Miyake et al.,[1] it has been underlined that there is a lack of information on the volumetric and thermoelastic properties of amine compounds with a large number of carbon atoms. The database for thermophysical properties of these fluids, at present, is scarce and limited to narrow temperature and pressure intervals. Moreover, the study of this chemical family presents both fundamental and industrial interests in engineering applications. We have published some experimental data concerning primary amines (pentyl-, hexyl-, and heptylamine) versus pressure up to 140 MPa in the temperature interval (293.15 to 403.15) K.[1] To our knowledge, there are no experimental data about density versus pressure concerning the secondary amines (branched amines 2-alkylamines). In particular, the experimental study of the branching effect could be of interest for the people dealing with the modeling and theory of density.

Consequently, with the aim of completing a database relative to this chemical family, in this work, the densities ρ (352 experimental data) for two 2-alkylamines consisting of 2-aminobutane ($CH_3CH_2CH(NH_2)CH_3$, 172 points) and 2-aminooctane ($CH_3(CH_2)_5CH(NH_2)CH_3$, 180 points) have been measured up to 140 MPa (by steps of 10 MPa) between (293.15 and 403.15) K (by steps of 10 K). Figure 1 shows their molecular structure. The measured densities are used to derive the isobaric thermal expansivity, $\alpha_p = (-1/\rho)(\partial\rho/\partial T)_p$, and the isothermal compressibility, $\kappa_T = (1/\rho)(\partial\rho/\partial p)_T$.

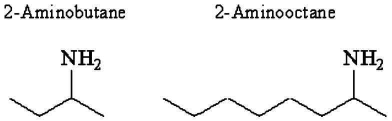

Figure 1. Molecular structure of the 2-aminobutane and of the 2-aminooctane.

2. Experimental Section

2.1. Materials. 2-Aminobutane ($C_4H_{11}N$, molar mass M = 73.14 $\text{g} \cdot \text{mol}^{-1}$, boiling point at atmospheric pressure T_b = 336.15 K, CAS number 693-16-3), 2-aminooctane ($C_8H_{19}N$, M = 129.24 $\text{g} \cdot \text{mol}^{-1}$, T_b = 438.15 K, CAS number 13952-84-6), and decane ($C_{10}H_{22}$, M = 73.14 $\text{g} \cdot \text{mol}^{-1}$, T_b = 446.9 K, CAS number 124-18-5) were obtained from Sigma-Aldrich with a purity of, respectively, (99.9, 99.41, and 99.44) % (GC analysis certified). These chemicals were subject to no further purification and directly injected into the high-pressure cell as soon as the bottle was opened.

2.2. Experimental Procedure. Measurement Technique. An Anton-Paar DMA HPM high-pressure vibrating tube densimeter was used to measure the density ρ as a function of pressure p (up to 140 MPa) and temperature T (between (293.15 and 403.15) K). The experimental setup was similar to the one described in a paper by Watson et al.[2] The calibration of the densimeter was performed according to the new procedure described by Comuñas et al.[3] which is a modification of the procedure previously proposed by Lagourette et al.[4] The calibration of our apparatus is based on the measurement of the oscillation periods of the U-tube filled with water (as a function of temperature and pressure), with decane (at high temperature and at atmospheric pressure), and under vacuum (as a function of temperature). These measurements are used to determine the values of the coefficients of the working equation of the apparatus giving the density as a function of the oscillation period.

(a) At $0.1 \le p/\text{MPa} \le 140$ and $293.15 \le T/\text{K} \le 363.15$. The densimeter calibration over these temperature and pressure intervals has been performed by using the procedure previously proposed by ref 4. The density values of water have been taken from the equation of state (EoS) reported by Wagner and Pruss.[5] The uncertainty in density of this EoS is 0.0001 % at 0.1 MPa in the liquid phase, 0.001 % at pressures between (0.1 and 10) MPa and temperatures to 423 K, and 0.003 % at pressures in the interval (10 to 100) MPa and temperature up to 423 K. The uncertainty is of the order of 0.02 % at 1000 MPa.

[†] Part of the special section "2008 European Conference on Thermophysical Properties".

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10.1021/je800786k CCC: $40.75

(b) At $p = 0.1$ MPa and $T \geq 373.15$ K. The limitation of the procedure described in ref 4 appears when the measurements are performed at 0.1 MPa and at temperatures greater than or equal to the boiling point of water (373.15 K). In this case, decane has been selected as a reference substance at the conditions $p = 0.1$ MPa and $T \geq 373.15$ K because its density is well-known at atmospheric pressure over wide temperature intervals.[6]

(c) At $p > 0.1$ MPa and $T \geq 373.15$ K. One can assume that, in the interval (0.1 to 1 MPa), as the pressure expansion coefficient of the cell is very low, the volume of the cell does not significantly change with pressure. Following the new procedure proposed in ref 3, the reference pressure for water density is 1 MPa instead of 0.1 MPa. It is necessary to measure the oscillation period of the cell under vacuum (over the entire temperature interval) and full of water and the density of water (for $p > 0.1$ MPa and for $T \geq 373.15$ K). Over those T, p intervals, only one reference fluid is necessary (water) together with the period of the evacuated cell.

After the densimeter was filled with the sample to be studied, the sample was brought to the desired temperature and pressure of interest and measured when thermal and mechanical equilibrium were reached.[2] The temperature of the high-pressure vibrating-tube cell of the densimeter was controlled by an external circulating temperature-controlled fluid and was measured inside the high-pressure cell. The temperature was measured with an uncertainty of ± 0.01 K between (293.15 and 353.15) K (Anton-Paar CKT100) and an uncertainty of ± 0.05 K above 353.15 K (AOIP PHP 602). Above atmospheric pressure, the pressure was measured with a HBM manometer with an uncertainty of ± 0.2 MPa.

Taking into account the accuracy of the temperature, the pressure, the period of oscillation measurement for water, vacuum, and the studied systems, and the water density accuracy, the overall experimental uncertainty in the reported density values is estimated to be $\pm 5 \cdot 10^{-4}$ $\text{g} \cdot \text{cm}^{-3}$ (i.e., around 0.05 % for density close to water density). This uncertainty is similar to that reported in several studies: Watson et al.,[2] Comuñas et al.,[3] Zéberg-Mikkelsen et al.,[7] Milhet et al.,[8] Miyake et al.,[9] and Boned et al.[10] However, for measurements at atmospheric pressure at T = (373.15, 383.15, 393.15, and 403.15) K, we used decane as reference fluid. The uncertainty of the decane density data reported in ref 6 (of the order of 10^{-4} $\text{g} \cdot \text{cm}^{-3}$) is greater than that of water, and consequently, for these four data points the uncertainty on the measured density is greater than 0.05 %.

A correction, due to the viscosity, can be included in the measurement procedure of the vibrating tube densimeter (Fandiño et al.[11] and Anton Paar Company[12]). However, in this work, such correction is much lower than the experimental uncertainty as the maximum estimated viscosity is around 4 mPa·s (extrapolating at 140 MPa and 293.15 K from experimental data currently done in the laboratory up to 100 MPa with a high-pressure falling body viscometer).

It is important to point out that the calibration of the densimeter is regularly checked. We chose toluene as a reference compound due to the fact that there are two good reference correlations in the literature by Cibulka and Takagi[13] and Lemmon and Span.[14] For instance, in ref 3 we indicate an AAD of 0.07 % and a maximum deviation DMax of 0.18 % by comparison with ref 13. The National Institute of Standards and Technology (NIST) utilizes, for toluene, the equation of state recently proposed by Lemmon and Span,[14] and in ref 3 we indicate an AAD of 0.07 %, a maximum deviation DMax of 0.16 % by comparison with the data generated by this equation of state. This comparison is regularly made every time that a new calibration with water, decane, and vacuum is done.

Finally, it should be mentioned that we have still not found in the literature any available density data measured with this apparatus up to 140 MPa, except some measurements that we made about diethyl adipate,[3] some linear alkylamines,[1] and 1-pentanol.[10]

3. Results and Discussion

The measured densities of 2-aminobutane and 2-aminooctane are reported in Table 1 along 12 isotherms between (293.15 and 403.15) K at pressures up to 140 MPa. As the boiling temperature at atmospheric pressure for 2-aminobutane is 336.15 K, the measurements have been limited to 323.15 K at atmospheric pressure for this compound. As already indicated, to our knowledge there are no experimental data about density versus pressure concerning the 2-alkylamines. Comparison with literature data has only been made at atmospheric pressure although there are very few data. For 2-aminobutane, Rao et al.[15] measured the density of 2-aminobutane, using a capillary pycnometer, and gave the value 0.71363 $\text{g} \cdot \text{cm}^{-3}$ at $T = 303.15$ K (we found 0.7151 $\text{g} \cdot \text{cm}^{-3}$). Notice also that for 2-aminobutane ACS SciFinder indicates in the "Details of substances. Experimental properties values" values of 0.7155 $\text{g} \cdot \text{cm}^{-3}$ and 0.724 $\text{g} \cdot \text{cm}^{-3}$ at T = 293.15 K (we found 0.7253 $\text{g} \cdot \text{cm}^{-3}$). For 2-aminooctane, the value indicated by ACS SciFinder is 0.7829 $\text{g} \cdot \text{cm}^{-3}$ at T = 293.15 K (we found 0.7720 $\text{g} \cdot \text{cm}^{-3}$). This important difference is perhaps linked to some purity problem. As previously indicated, the calibration of the densimeter is regularly checked with toluene reference data.

The experimental density values were correlated by the following Tait-like equation as in previous works:[1,3,7–10,16]

$$\rho(T,p) = \frac{\rho_0(T)}{1 - C \ln\left(\dfrac{B(T) + p}{B(T) + p_0}\right)} \tag{1}$$

where $\rho_0(T)$ is the temperature-dependent function of the density at the pressure p_0 expressed as

$$\rho_0(T) = A_0 + A_1T + A_2T^2 + A_3T^3 \tag{2}$$

Parameter C in eq 1 was assumed to be temperature independent, and $B(T)$ is the following polynomial function

$$B(T) = B_0 + B_1T + B_2T^2 \tag{3}$$

The values of the eight parameters in eqs 1 to 3, for each compound, have been adjusted against our experimental data over the entire T, p intervals.

To compare the experimental density values with those obtained with the Tait correlation, we have used the absolute average deviation (AAD), the maximum deviation (DMax), the average deviation (Bias), and the standard deviation (σ), which are defined as follows

$$\text{AAD} = \frac{100}{N}\sum_{i=1}^{N}\left|\frac{\rho_i^{\text{exp}} - \rho_i^{\text{calc}}}{\rho_i^{\text{exp}}}\right| \tag{4}$$

$$\text{DMax} = \text{Max}\left(100\left|\frac{\rho_i^{\text{exp}} - \rho_i^{\text{calc}}}{\rho_i^{\text{exp}}}\right|\right) \tag{5}$$

$$\text{Bias} = \frac{100}{N}\sum_{i=1}^{N}\frac{\rho_i^{\text{exp}} - \rho_i^{\text{calc}}}{\rho_i^{\text{exp}}} \tag{6}$$

$$\sigma = \sqrt{\frac{\sum_{i=1}^{N} (\rho_i^{\text{exp}} - \rho_i^{\text{calc}})^2}{N - m}} \tag{7}$$

where N is the number of experimental data for 2-aminobutane ($N = 172$) and 2-aminooctane ($N = 180$); m is the number of parameters ($m = 8$); and ρ_i^{exp} and ρ_i^{calc} are the experimental density of this work and that calculated with eq 1, respectively.

We mention here that the values of A_i, B_i, and C parameters were determined by correlating simultaneously all the experimental density values versus pressure and temperature, for each pure compound. The Tait-correlation parameters, along with the AAD, DMax, Bias, and σ, obtained with this correlation, are shown in Table 2 for the two compounds with $p_0 = 0.1$ MPa. Notice that the standard deviation is lower than the experimental uncertainty. Consequently, eqs 1 to 3 make it possible to interpolate our values at any T, p conditions. However, with $p_0 = 0.1$ MPa, the density $\rho_0(T)$ has no physical meaning above 336.15 K for 2-aminobutane. So we also made a fitting with $p_0 = 10$ MPa. The results given in Table 2 show that the fitting is not improved. The maximum deviation still occurs at $T = 373.15$ K and $p = 50$ MPa, around 0.095 %, but it is interesting to notice that the absolute average deviation is, in both cases, lower than 0.06 %, except for this single point. Figure 2 shows the deviation versus pressure between the experimental data and the Tait values for the 2-aminobutane ($p_0 = 0.1$ MPa and $p_0 = 10$ MPa) and the 2-aminooctane ($p_0 = 0.1$ MPa).

Figure 3 shows the variation of density as a function of temperature for the two 2-alkylamines at $p = 70$ MPa. Figures 4a and 4b show the variation of density as a function of temperature for the two 2-alkylamines at several pressures. The density decreases with increasing temperature over the entire pressure range for the two compounds. These two figures show

Table 1. Experimental Densities ρ (g·cm^{-3}) at Various Temperatures T (K) and Pressures p (MPa)

	T/K											
p/MPa	293.15	303.15	313.15	323.15	333.15	343.15	353.15	363.15	373.15	383.15	393.15	403.15
	ρ/g·cm^{-3}											
	2-Aminobutane											
0.1	0.7253	0.7151	0.7050	0.6947								
10	0.7336	0.7243	0.7148	0.7054	0.6954	0.6859	0.6758	0.6657	0.6555	0.6455	0.6349	0.6239
20	0.7412	0.7324	0.7234	0.7145	0.7052	0.6966	0.6871	0.6780	0.6689	0.6599	0.6505	0.6406
30	0.7481	0.7397	0.7311	0.7228	0.7140	0.7060	0.6972	0.6885	0.6801	0.6719	0.6631	0.6545
40	0.7545	0.7463	0.7382	0.7304	0.7220	0.7143	0.7058	0.6978	0.6900	0.6823	0.6743	0.6661
50	0.7604	0.7525	0.7447	0.7372	0.7292	0.7219	0.7140	0.7062	0.6982	0.6914	0.6843	0.6763
60	0.7661	0.7583	0.7508	0.7436	0.7358	0.7288	0.7212	0.7139	0.7070	0.6996	0.6930	0.6853
70	0.7713	0.7637	0.7565	0.7495	0.7421	0.7353	0.7280	0.7210	0.7140	0.7073	0.7009	0.6936
80	0.7763	0.7689	0.7619	0.7552	0.7480	0.7413	0.7342	0.7275	0.7209	0.7144	0.7082	0.7011
90	0.7811	0.7738	0.7670	0.7604	0.7534	0.7471	0.7401	0.7336	0.7272	0.7208	0.7149	0.7082
100	0.7855	0.7784	0.7718	0.7654	0.7586	0.7524	0.7457	0.7394	0.7332	0.7269	0.7212	0.7149
110	0.7897	0.7829	0.7764	0.7702	0.7635	0.7574	0.7510	0.7448	0.7387	0.7327	0.7272	0.7211
120	0.7939	0.7872	0.7808	0.7747	0.7681	0.7623	0.7560	0.7499	0.7440	0.7382	0.7328	0.7269
130	0.7978	0.7912	0.7851	0.7790	0.7725	0.7670	0.7607	0.7548	0.7491	0.7433	0.7381	0.7323
140	0.8015	0.7952	0.7891	0.7832	0.7769	0.7713	0.7653	0.7595	0.7539	0.7482	0.7429	0.7374
	2-Aminooctane											
0.1	0.7720	0.7640	0.7558	0.7481	0.7396	0.7315	0.7232	0.7147	0.7060	0.6976	0.6890	0.6801
10	0.7787	0.7713	0.7635	0.7560	0.7481	0.7405	0.7330	0.7249	0.7172	0.7094	0.7016	0.6935
20	0.7848	0.7778	0.7704	0.7632	0.7555	0.7486	0.7416	0.7340	0.7266	0.7195	0.7123	0.7050
30	0.7906	0.7838	0.7767	0.7699	0.7626	0.7560	0.7493	0.7420	0.7352	0.7285	0.7217	0.7148
40	0.7961	0.7892	0.7825	0.7760	0.7690	0.7627	0.7562	0.7493	0.7429	0.7364	0.7300	0.7235
50	0.8012	0.7945	0.7881	0.7816	0.7750	0.7689	0.7627	0.7561	0.7499	0.7438	0.7379	0.7315
60	0.8060	0.7995	0.7932	0.7871	0.7806	0.7747	0.7687	0.7624	0.7568	0.7506	0.7449	0.7387
70	0.8106	0.8042	0.7981	0.7922	0.7858	0.7802	0.7744	0.7683	0.7628	0.7568	0.7514	0.7454
80	0.8150	0.8087	0.8027	0.7970	0.7909	0.7853	0.7797	0.7738	0.7685	0.7627	0.7575	0.7516
90	0.8191	0.8130	0.8071	0.8015	0.7955	0.7902	0.7847	0.7790	0.7738	0.7681	0.7632	0.7575
100	0.8232	0.8171	0.8114	0.8059	0.8000	0.7949	0.7895	0.7839	0.7789	0.7733	0.7686	0.7631
110	0.8269	0.8210	0.8155	0.8101	0.8044	0.7992	0.7941	0.7885	0.7837	0.7783	0.7736	0.7683
120	0.8306	0.8248	0.8194	0.8141	0.8085	0.8034	0.7984	0.7930	0.7883	0.7830	0.7784	0.7732
130	0.8342	0.8285	0.8231	0.8180	0.8125	0.8075	0.8023	0.7973	0.7928	0.7875	0.7828	0.7779
140	0.8376	0.8320	0.8267	0.8216	0.8163	0.8114	0.8063	0.8014	0.7968	0.7918	0.7872	0.7824

Table 2. Obtained Parameters and Deviations for Density Correlation by Using Equation 1

	2-aminobutane	2-aminobutane	2-aminooctane
coefficients	$p_0 = 0.1$ MPa	$p_0 = 10$ MPa	$p_0 = 0.1$ MPa
A_0/g·cm^{-3}	1.07695	1.00762	1.04649
A_1/g·cm^{-3}·K^{-1}	$-1.79501 \cdot 10^{-3}$	$-1.07549 \cdot 10^{-3}$	$-1.23212 \cdot 10^{-3}$
A_2/g·cm^{-3}·K^{-2}	$3.35796 \cdot 10^{-6}$	$9.38907 \cdot 10^{-7}$	$1.56498 \cdot 10^{-6}$
A_3/g·cm^{-3}·K^{-3}	$-4.52474 \cdot 10^{-9}$	$-1.56682 \cdot 10^{-9}$	$-1.89178 \cdot 10^{-9}$
B_0/MPa	402.973	403.674	407.929
B_1/MPa·K^{-1}	−1.58302	−1.56074	−1.45949
B_2/MPa·K^{-2}	$1.57642 \cdot 10^{-3}$	$1.51271 \cdot 10^{-3}$	$1.35818 \cdot 10^{-3}$
C	$8.99794 \cdot 10^{-2}$	$9.23440 \cdot 10^{-2}$	$8.73111 \cdot 10^{-2}$
σ/g·cm^{-3}	0.000175	0.000180	0.000143
AAD/%	0.0195	0.0203	0.0154
DMax/%	0.0948	0.0958	0.0486
Bias/%	−0.0002	−0.0010	0.00076

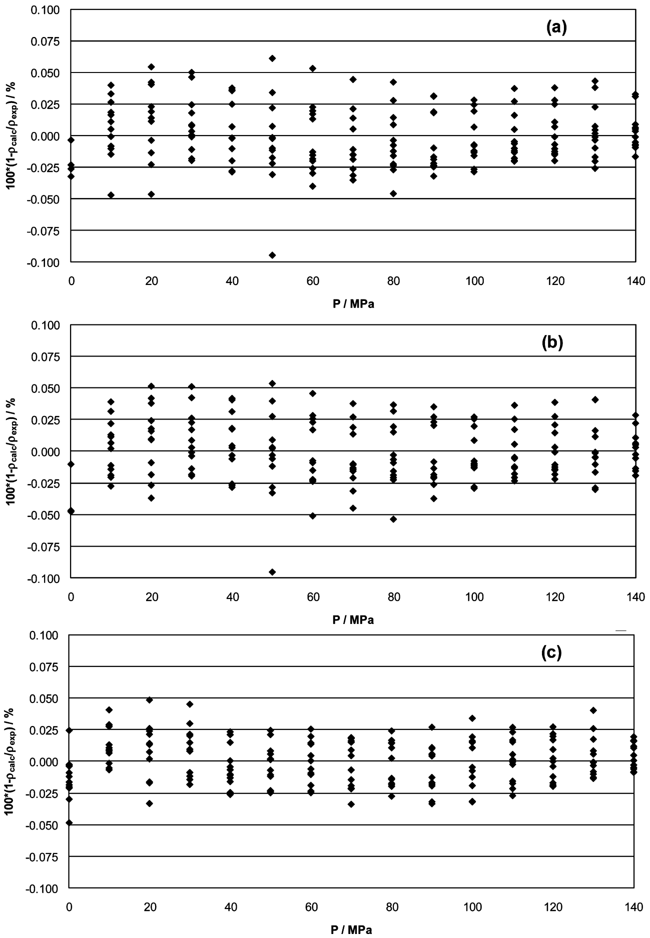

Figure 2. Deviation versus pressure between experimental density and Tait calculated density. (a) 2-Aminobutane, $p_0 = 0.1$ MPa; (b) 2-aminobutane, $p_0 = 10$ MPa; (c) 2-aminooctane, $p_0 = 0.1$ MPa.

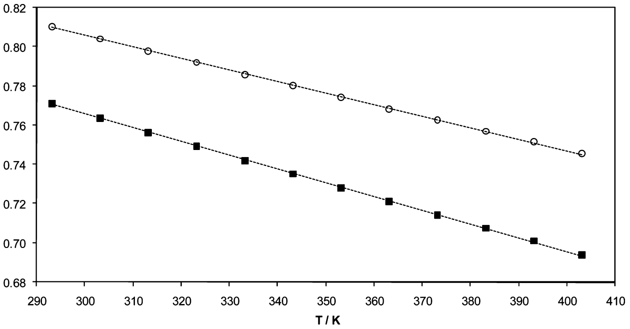

Figure 3. Variation of the density as a function of temperature at $p = 70$ MPa: ■, 2-aminobutane; and ○, 2-aminooctane.

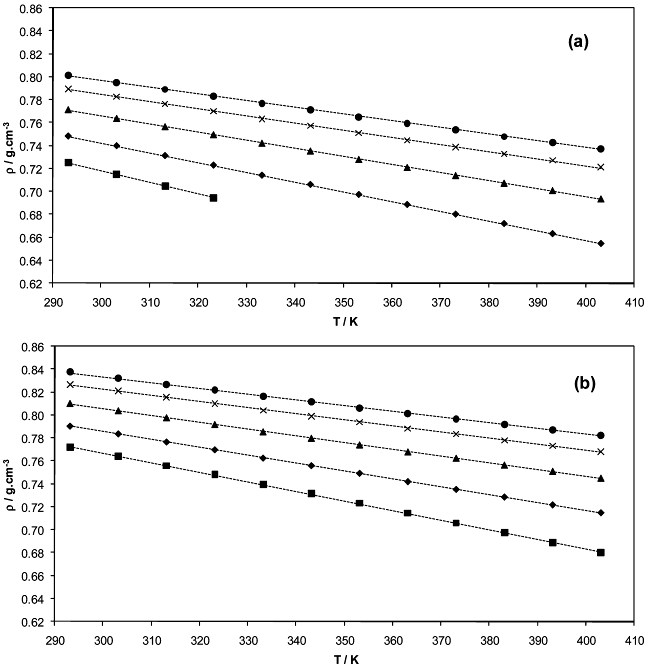

Figure 4. Variation of the density as a function of temperature at ■, $p = 0.1$ MPa; ◆, 30 MPa; ▲, 70 MPa; ×, 110 MPa; and ●, 140 MPa. (a) 2-Aminobutane. (b) 2-Aminooctane.

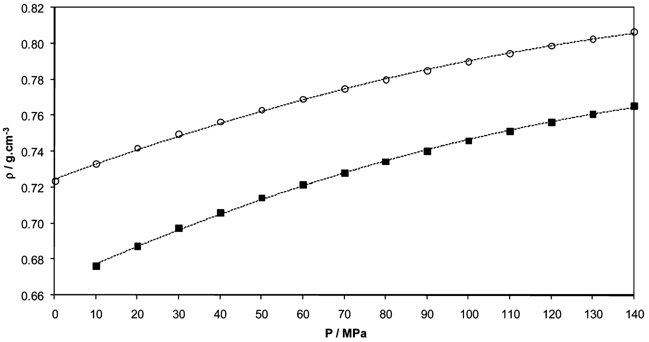

Figure 5. Variation of the density as a function of pressure at $T = 353.15$ K: ■, 2-aminobutane; and ○, 2-aminooctane.

Table 3. Influence of the Degree of the Polynomial Function $\rho_0(T)$, for 2-Aminobutane

	$n = 1$	$n = 2$	$n = 3$
σ/g·cm^{-3}	0.000490	0.000133	0.000137
AAD/%	0.053	0.011	0.010
DMax/%	0.118	0.028	0.028
Bias/%	0.0005	−0.00002	−0.0011

that in the temperature interval considered here the density versus temperature is practically linear.

We have studied, for 2-aminobutane, the influence of the choice of the degree of the polynomial function $\rho_0(T)$ to choose the most relevant one. The results are given in Table 3. The cubic polynomial, eq 2, gives the lowest values of AAD, DMax, and σ. Consequently, to get a better estimation of some derivative properties (see paragraph 4), we made the fitting of (T, p, ρ) data with eq 2, as the derivative properties are sensitive to the expression of the $\rho_0(T)$ density versus temperature.

Figure 5 shows the variation of density as a function of pressure for the two 2-alkylamines of this work at $T = 353.15$ K. As usual, density increases with the increase of pressure. At constant temperature, the curves are concave, which is associated with a negative second-order derivative. The shape of the isothermal curves of the density versus pressure is compatible with the logarithmic relationship included in the Tait-type density relation used to correlate our (T, p, ρ) data. Figures 6a and 6b show the variation of the density as a function of pressure for the two 2-alkylamines at several temperatures.

The comparison of the (T, p, ρ) data for these 2-alkylamines reveals that the density increases with the number of carbon atoms. Figure 7 shows the variation of the density versus the molar mass for various P, T conditions. At atmospheric pressure and $T = 293.15$ K, the data for butylamine (molar mass $M = 73.16$ g·mol^{-1}), octylamine ($M = 129.25$ g·mol^{-1}), nonylamine (molar mass $M = 143.28$ g·mol^{-1}), and decylamine ($M = 157.31$ g·mol^{-1}) are from Liew et al.[17] The values for pentylamine ($M = 87.16$ g·mol^{-1}), hexylamine (molar mass $M = 101.19$ g·mol^{-1}), and heptylamine ($M = 115.22$ g·mol^{-1}) at

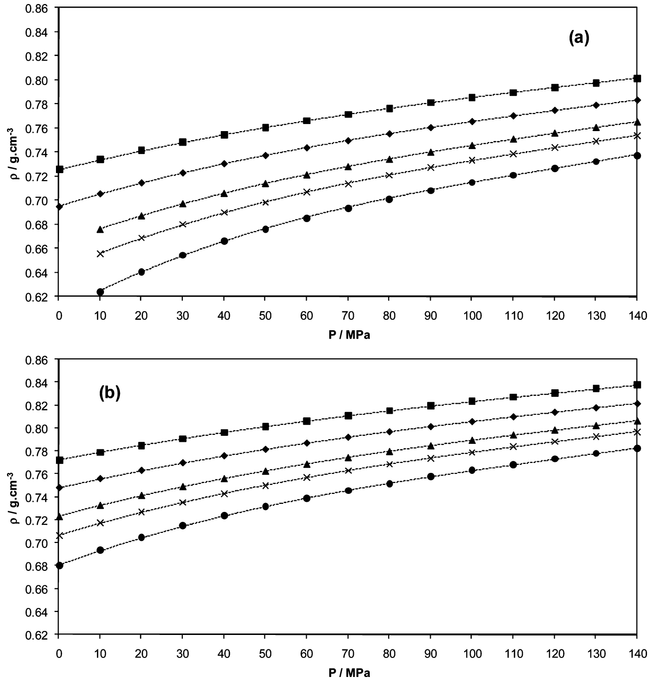

Figure 6. Variation of the density as a function of pressure at T = ■, 293.15 K; ◆, 323.15 K; ▲, 353.15 K; ×, 373.15 K; and ●, 403.15 K. (a) 2-Aminobuatne. (b) 2-Aminooctane.

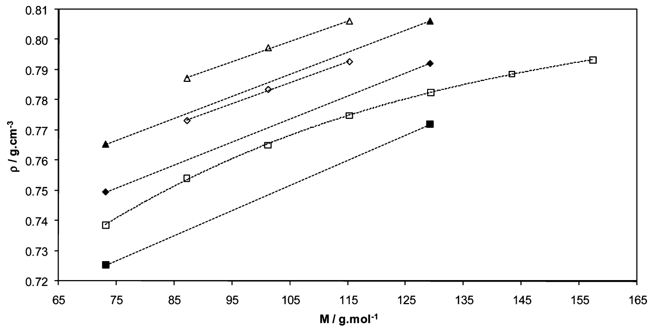

Figure 7. Density of 2-alkylamines (this work; closed symbols) and 1-alkylamines (Miyake,[1] Liew,[17] open symbols) versus molar mass M at various T, p conditions: ■, □, T = 293.15 K and p = 0.1 MPa; ◆, ◇, 323.15 K and 70 MPa; ▲, △, 353.15 K and 140 MPa.

all pressures are from ref 1. The density of the branched amines seems lower than the one of the linear amines. These figures show that the density increases with the number of carbon atoms. This is not systematically the case for all chemical families, such as for the alkylbenzene family which does not emphasize, for density, such a trend with the number of carbon atoms.[8] On the other hand, density is a ratio of two functions of molecular size as $\rho = M/V_m$ where M is the molar mass (which is strictly a linear function of the molar mass of the $-CH_2-$ group in this homologous series) and V_m is the molar volume (which is approximately the linear function of the molecular size as within the homologous series the increment is the "molar volume" of the $-CH_2-$ group). Molar volume might be a better property (compared to density) for the consideration of the effect of molecular size since differences between particular amines are directly related to molar volume contribution of the $-CH_2-$ group. Figure 8 shows the variation of the molar volume (V_m) versus the molar mass (M) for 2-alkylamines and 1-alkylamines.[1,17] Notice that the variations of 1-alkylamines are practically linear. The dotted line in this figure is the correlated straight line with $R^2 \geq 0.9998$. It can also be seen that the molar volume values of 2-alkylamines are slightly higher than for 1-alkylamines.

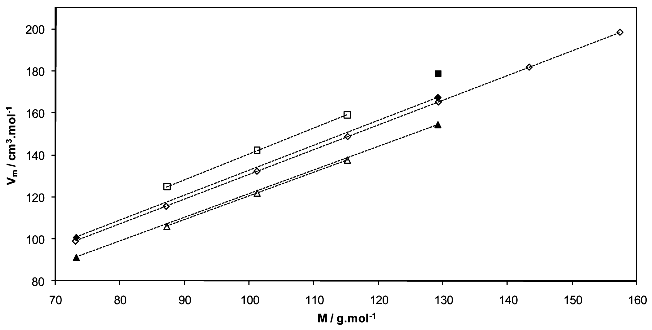

Figure 8. Variation of the molar volume V_m of 2-alkylamines (this work, closed symbols) and 1-alkylamines (Miyake,[1] Liew,[17] open symbols) versus the molar mass (M) for various T, p conditions. ■, □, T = 353.15 K and p = 0.1 MPa; ◆, ◇, 293.15 K and 0.1 MPa; ▲, △, 293.15 K and 140 MPa.

Finally, for the alkylbenzene family, in such a representation, as the density is practically constant with the number of carbon atoms,[8] the molar volume is a linear function of the molar mass.

4. Derived Thermodynamic Properties

The experimental densities can be used to derive other important quantities such as the isothermal compressibility, defined as $\kappa_T = (1/\rho)(\partial\rho/\partial p)_T$, and the isobaric thermal expansivity, defined as $\alpha_p = (-1/\rho)(\partial\rho/\partial T)_p$. In this work, the isothermal compressibility κ_T has been determined analytically by differentiating the Tait-like equation, which is used to correlate (T, p, ρ) data, with respect to pressure. The following expression is obtained from eq 1

$$\kappa_T = \left(\frac{1}{\rho}\right)\left(\frac{\partial\rho}{\partial p}\right)_T = \frac{C}{\left(1 - C\ln\left(\frac{B(T)+p}{B(T)+p_0}\right)\right)(B(T)+p)} \qquad (8)$$

The isobaric thermal expansivity (α_p) could also be obtained in the same manner with respect to temperature. However, some authors like Troncoso et al.,[18] Cerdeiriña et al.,[19] and Jacquemin et al.[20] mention that α_p could highly depend on the form of temperature-dependent functions $\rho_0(T)$ and B(T) in eq 1 and recommend to derive α_p numerically from the isobaric density values. As we supposed in previous works[1−3,10] that the density at each isobar can be correlated with temperature with a simple cubic polynomial function

$$\rho_p(T) = a_0 + a_1T + a_2T^2 + a_3T^3 \qquad (9)$$

α_p is then expressed as follows

$$\alpha_p = -\left(\frac{1}{\rho}\right)\left(\frac{\partial\rho}{\partial T}\right)_p = -\frac{a_1 + 2a_2T + 3a_3T^2}{a_0 + a_1T + a_2T^2 + a_3T^3} \qquad (10)$$

The uncertainties for κ_T and α_p are estimated as 1 % and 3 %, respectively.[1−3,10] The values of κ_T and α_p calculated with the procedures explained above are indicated in Tables 4 and 5.

In a first step we used p_0 = 0.1 MPa for the calculation of κ_T. Figure 9 shows the isothermal compressibility (κ_T) as a function of temperature of the two 2-alkylamines at p = 70 MPa and Figure 10 shows the variation of κ_T as a function of temperature for 2-aminobutane at p = (0.1, 20, 40, 70, and 140) MPa. Figure 11 shows the variation of κ_T as a function of pressure of the two 2-alkylamines at T = 353.15 K, and Figure 12 shows the variation of κ_T as a function of pressure of 2-aminooctane at various temperatures. Of course, the study of two compounds is certainly not enough to take definitive conclusion, but with respect to the number of carbon atoms of

Table 4. Isothermal Compressibility, κ_T (10^{-4} MPa^{-1}) at Various Temperatures *T* and Pressure *p*

	T/K											
p/MPa	293.15	303.15	313.15	323.15	333.15	343.15	353.15	363.15	373.15	383.15	393.15	403.15
						$\kappa_T/10^{-4}$ MPa^{-1}						
						2-Aminobutane						
0.1	12.08	13.22	14.53	16.03								
10	10.78	11.69	12.69	13.83	15.10	16.54	18.16	20.00	22.08	24.43	27.09	30.07
20	9.74	10.47	11.28	12.17	13.14	14.23	15.42	16.73	18.17	19.75	21.48	23.35
30	8.89	9.50	10.16	10.88	11.66	12.50	13.42	14.42	15.49	16.64	17.87	19.17
40	8.18	8.70	9.25	9.84	10.48	11.17	11.91	12.69	13.52	14.41	15.34	16.31
50	7.58	8.03	8.50	9.00	9.54	10.11	10.71	11.35	12.02	12.73	13.47	14.23
60	7.07	7.46	7.86	8.30	8.75	9.24	9.74	10.28	10.84	11.42	12.02	12.64
70	6.63	6.97	7.32	7.70	8.10	8.51	8.95	9.40	9.87	10.36	10.87	11.39
80	6.24	6.54	6.85	7.19	7.53	7.90	8.27	8.67	9.07	9.50	9.93	10.37
90	5.89	6.16	6.45	6.74	7.05	7.37	7.70	8.05	8.40	8.77	9.15	9.53
100	5.59	5.83	6.09	6.35	6.63	6.91	7.21	7.51	7.83	8.15	8.48	8.82
110	5.31	5.54	5.77	6.01	6.25	6.51	6.78	7.05	7.33	7.62	7.92	8.22
120	5.07	5.27	5.48	5.70	5.92	6.16	6.40	6.64	6.90	7.16	7.42	7.70
130	4.84	5.03	5.22	5.42	5.63	5.84	6.06	6.28	6.51	6.75	6.99	7.24
140	4.64	4.81	4.99	5.17	5.36	5.56	5.76	5.96	6.17	6.39	6.61	6.84
						2-Aminooctane						
0.1	9.01	9.66	10.37	11.16	12.04	13.01	14.08	15.28	16.62	18.11	19.77	21.62
10	8.25	8.78	9.37	10.01	10.71	11.47	12.30	13.21	14.20	15.27	16.44	17.70
20	7.60	8.06	8.55	9.08	9.65	10.26	10.93	11.64	12.40	13.22	14.09	15.01
30	7.05	7.44	7.86	8.31	8.79	9.30	9.84	10.42	11.03	11.67	12.35	13.05
40	6.58	6.92	7.28	7.67	8.07	8.50	8.96	9.43	9.94	10.46	11.01	11.57
50	6.17	6.47	6.79	7.12	7.47	7.84	8.23	8.63	9.05	9.49	9.94	10.40
60	5.81	6.08	6.36	6.65	6.96	7.28	7.61	7.96	8.32	8.69	9.07	9.46
70	5.50	5.73	5.98	6.24	6.51	6.79	7.09	7.39	7.70	8.02	8.35	8.68
80	5.21	5.43	5.65	5.88	6.12	6.37	6.63	6.90	7.17	7.45	7.74	8.02
90	4.96	5.15	5.36	5.57	5.78	6.01	6.24	6.47	6.71	6.96	7.21	7.47
100	4.73	4.91	5.09	5.28	5.48	5.68	5.89	6.10	6.32	6.54	6.76	6.98
110	4.52	4.68	4.85	5.03	5.20	5.39	5.58	5.77	5.96	6.16	6.36	6.56
120	4.33	4.48	4.64	4.80	4.96	5.13	5.30	5.47	5.65	5.83	6.01	6.19
130	4.16	4.30	4.44	4.59	4.74	4.89	5.05	5.21	5.37	5.53	5.70	5.86
140	4.00	4.13	4.26	4.40	4.54	4.68	4.82	4.97	5.12	5.27	5.42	5.57

Table 5. Isobaric Thermal Expansivity, α_p (10^{-4} K^{-1}) at Various Temperatures *T* and Pressure *p*

	T/K											
p/MPa	293.15	303.15	313.15	323.15	333.15	343.15	353.15	363.15	373.15	383.15	393.15	403.15
						$\alpha_p/10^{-4}$ K^{-1}						
						2-Aminobutane						
0.1	13.95	14.21	14.49	14.79								
10	12.74	13.02	13.31	13.63	13.98	14.36	14.76	15.20	15.67	16.18	16.72	17.31
20	12.12	12.25	12.40	12.57	12.77	12.99	13.24	13.51	13.82	14.15	14.52	14.92
30	11.33	11.46	11.59	11.74	11.88	12.04	12.20	12.36	12.53	12.71	12.90	13.10
40	10.77	10.87	10.97	11.06	11.16	11.26	11.36	11.45	11.55	11.65	11.74	11.83
50	10.18	0.00	10.42	10.52	10.60	10.67	10.72	10.76	10.78	10.77	10.75	10.71
60	10.06	10.04	10.02	10.01	10.02	10.03	10.06	10.10	10.15	10.21	10.29	10.38
70	9.60	9.59	9.59	9.59	9.60	9.60	9.61	9.62	9.64	9.65	9.67	9.69
80	9.31	9.28	9.25	9.23	9.22	9.21	9.20	9.20	9.20	9.21	9.22	9.24
90	9.03	9.00	8.96	8.93	8.90	8.88	8.85	8.83	8.81	8.80	8.78	8.77
100	8.69	8.67	8.65	8.63	8.60	8.57	8.54	8.50	8.46	8.42	8.37	8.33
110	8.38	8.39	8.38	8.37	8.35	8.31	8.27	8.22	8.15	8.07	7.99	7.89
120	8.24	8.22	8.19	8.15	8.10	8.05	8.00	7.94	7.87	7.79	7.71	7.62
130	8.02	7.99	7.96	0.00	7.87	7.82	7.77	7.71	7.64	7.57	7.49	7.41
140	7.76	7.75	7.73	7.70	7.67	7.63	7.58	7.53	7.46	7.39	7.32	7.23
						2-Aminooctane						
0.1	10.24	10.45	10.66	10.88	11.11	11.35	11.59	11.85	12.11	12.38	12.67	12.96
10	9.74	9.86	9.99	10.13	10.27	10.42	10.58	10.74	10.91	11.09	11.28	11.47
20	9.21	9.32	9.43	9.53	9.63	9.72	9.82	9.91	10.00	10.08	10.16	10.24
30	8.81	8.88	8.95	9.01	9.08	9.14	9.20	9.26	9.32	9.38	9.43	9.48
40	8.53	8.55	8.57	8.60	8.62	8.65	8.69	8.72	8.76	8.81	8.85	8.90
50	8.28	8.26	8.25	8.24	8.24	8.24	8.24	8.25	8.26	8.28	8.31	8.34
60	8.09	8.01	7.94	7.89	7.86	7.84	7.83	7.85	7.88	7.93	7.99	8.08
70	7.85	7.75	7.68	7.61	7.57	7.53	7.52	7.52	7.55	7.58	7.64	7.72
80	7.67	7.55	7.45	7.36	7.30	7.25	7.23	7.23	7.25	7.29	7.36	7.45
90	7.46	7.34	7.23	7.14	7.07	7.02	6.99	6.97	6.98	7.00	7.04	7.11
100	7.29	7.16	7.05	6.96	6.88	6.81	6.77	6.74	6.73	6.74	6.77	6.82
110	7.02	6.92	6.83	6.76	6.69	6.64	6.59	6.56	6.54	6.53	6.53	6.55
120	6.90	6.78	6.68	6.59	6.51	6.45	6.40	6.37	6.35	6.35	6.36	6.39
130	6.79	6.66	6.55	6.45	6.36	6.29	6.24	6.21	6.19	6.18	6.20	6.23
140	6.63	6.51	6.40	6.31	6.22	6.15	6.10	6.05	6.02	6.01	6.01	6.03

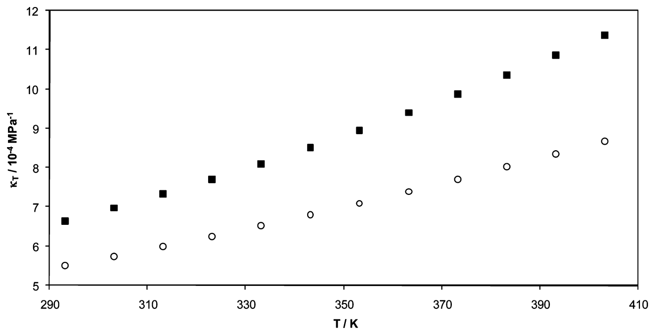

Figure 9. Isothermal compressibility κ_T as a function of temperature at p = 70 MPa (■, 2-aminobutane; and ○, 2-aminooctane).

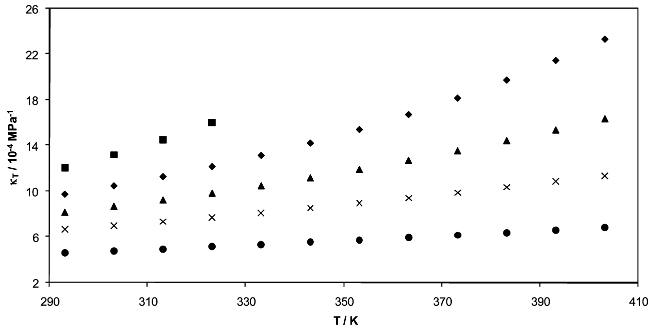

Figure 10. Isothermal compressibility κ_T as a function of temperature for 2-aminobutane at p = ■, 0.1 MPa; ◆, 20 MPa; ▲, 40 MPa; ×, 70 MPa; and ●, 140 MPa.

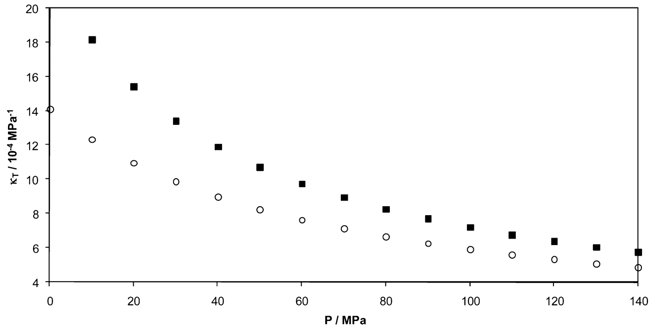

Figure 11. Isothermal compressibility κ_T as a function of pressure at T = 353.15 K (■, 2-aminobutane; and ○, 2-aminooctane).

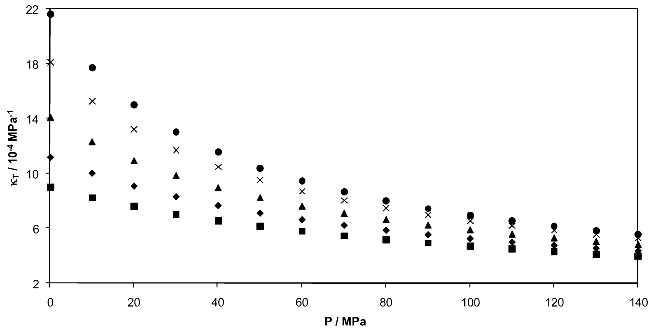

Figure 12. Isothermal compressibility κ_T as a function of pressure for 2-aminooctane at various temperatures (T = ■, 293.15 K; ◆, 323.15 K; ▲, 353.15 K; ×, 383.15 K; and ●, 403.15 K).

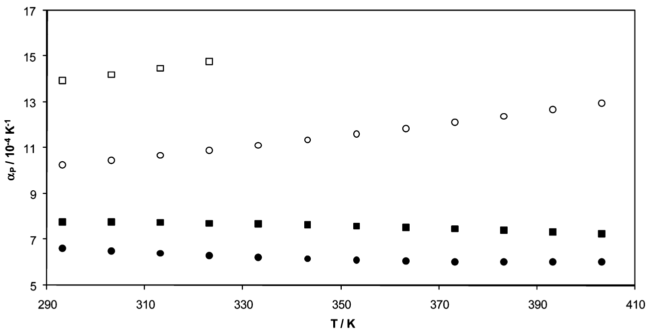

Figure 13. Isobaric thermal expansivity α_p as a function of temperature at p = 0.1 MPa (open symbols) and 140 MPa (filled symbols): □,■, 2-aminobutane; ○,●, 2-aminooctane.

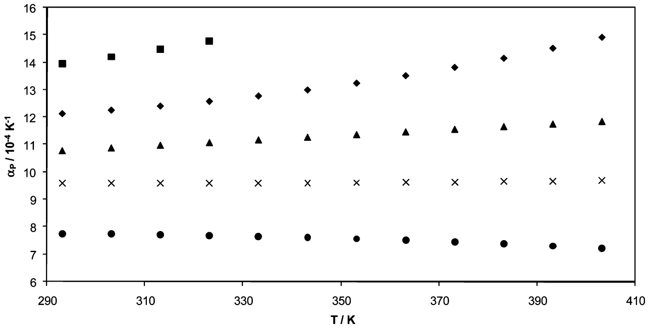

Figure 14. Isobaric thermal expansivity α_p as a function of temperature for 2-aminobutane at p = ■, 0.1 MPa; ◆, 20 MPa; ▲, 40 MPa; ×, 70 MPa; and ●, 140 MPa.

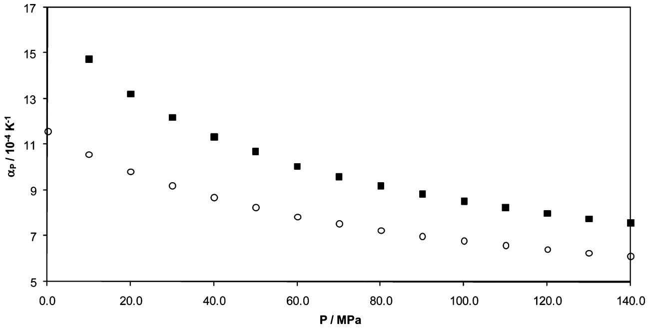

Figure 15. Isobaric thermal expansivity α_p as a function of pressure at T = 353.15 K (■, 2-aminobutane; and ○, 2-aminooctane).

the alkyl chain, it seems that the longer the alkyl chain is, the smaller the value of κ_T is (Figures 9 and 11) at the same p, T conditions. At each isobar, the value of κ_T increases with increasing temperature (Figures 9 and 10). At each isotherm, the value of κ_T decreases with increasing pressure (Figures 11 and 12). The temperature and pressure dependency of κ_T of the two 2-alkylamines roughly showed a similar tendency. In a second step, for 2-aminobutane we used the parameters calculated using p_0 = 10 MPa (Table 2). The average absolute deviation between the two sets of values is 0.27 % with a maximum deviation of 1.27 % (at T = 403.15 K and P = 10 MPa), with a Bias = 0.007 %. Recall that the uncertainty for κ_T is estimated as 1 %. This comparison shows that the value of the isothermal compressibility κ_T seems independent of the value chosen for p_0 (fitting of Tait equation).

Figure 13 shows the isobaric thermal expansivity (α_p) as a function of temperature for the two 2-alkylamines at p = 0.1 and 140 MPa. Figure 14 shows α_p as a function of temperature for 2-aminobutane at p = (0.1, 20, 40, 70, and 140) MPa. Figure 15 shows α_p as a function of pressure for the two 2-alkylamines at T = 353.15 K, and Figure 16 shows α_p as a function of pressure for the two 2-alkylamines at various temperatures. The value of α_p decreases with increasing pressure. With respect to the number of carbon atoms of the alkyl chain, it seems that the longer the alkyl chain, the smaller the value of α_p (Figures 13 and 15). The temperature dependency of α_p shows a different tendency according to pressure (Figures 13 and 14). For instance, in the case of 2-aminobutane, α_p increases with increasing

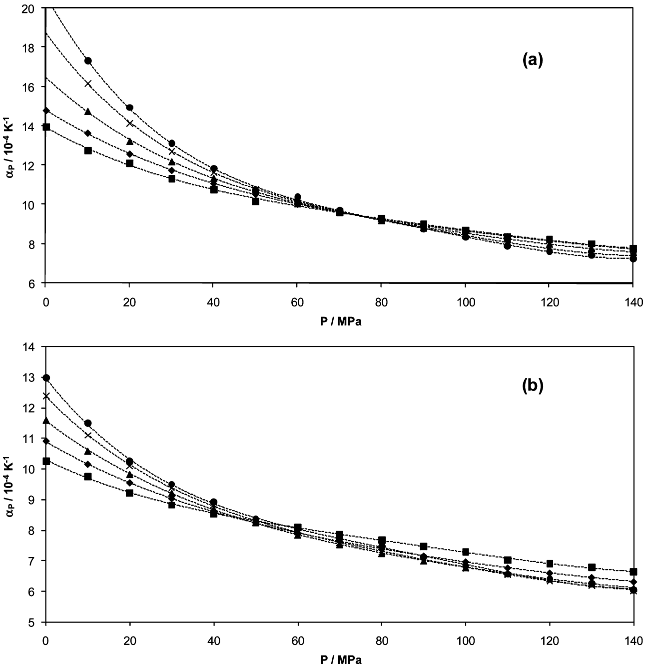

Figure 16. Isobaric thermal expansivity α_p as a function of pressure at various temperatures. (a) 2-Aminobutane. (b) 2-Aminooctane. ■, $T = 293.15$ K; ◆, 323.15 K; ▲, 353.15 K; ×, 383.15 K; and ●, 403.15 K.

temperature at $p = 0.1$ MPa but decreases with temperature at $p = 140$ MPa (Figure 13). The boundary pressure, at which the temperature dependence of α_p reverses, corresponds to the crossing point of isotherms seen in Figure 16. The crossing points appear between (70 and 80) MPa for 2-aminobutane and (45 and 55) MPa for 2-aminooctane, respectively. It seems that the pressure of the crossing point decreases when the number of carbon atoms increases. This is a tendency opposite to the case of 1-alkylamine.[1]

At the pressure corresponding to this intersection point, α_p is independent of the temperature. Notice that the crossover point seems to be really unique, despite the fact that the α_p values have been obtained versus pressure with different sets a_0, a_1, and a_2 at each T and despite the fact that the lines α_p versus P at given T are also fitted independently. Recent studies by Cerdeiriña et al.[19] and Gonzalez-Salgado et al.[21] have shown that association hardly affects κ_T behavior. Nevertheless, the specific behavior of the thermal expansion coefficient, that is, the locus of the crossover point, could be analyzed as a macroscopic manifestation of the association phenomenon occurring at molecular level (Randzio et al.,[22] Lafitte et al.[23]). With this idea in mind, recent developments[23] on the molecular equation of state (EOS)—those belonging to the SAFT family being a representative example—have shown the importance of adjusting their molecular parameters equations on phase properties affected by association. In the case of study including associative systems, this is the way to obtain a realistic balance between dispersive and associative energies.[23] Discussion is still open on the choice of the adequate properties, but the simultaneous knowledge of density and its derivative versus pressure and temperature constitute very relevant data for the study of global phase behavior of amines from SAFT like EOS.

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Received for review October 22, 2008. Accepted January 5, 2009.

JE800786K