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Heat Capacities, Speeds of Sound, and Isothermal Compressibilities of Some *n*-Amines and Tri-*n*-amines at 298.15 K

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The isothermal compressibilities at 298.15 K of primary amines (propylamine, butylamine, pentylamine, hexylamine, and octylamine) and tertiary amines (triethylamine, tripropylamine, trihexylamine, and trioctylamine) were determined from the measurements of heat capacities at constant pressure, densities, and speeds of sound.

Introduction

Isothermal compressibility, as well as heat capacity at constant pressure, is one of the most important thermodynamical properties which characterize chemical compounds. These quantities provide important information, necessary for a better understanding of the molecular structure and intermolecular interactions of pure liquids and solutions. One of the commonly used methods which need isothermal compressibilities (κ_T) is scaled particle theory (SPT).[1] Lately, we used the SPT method to calculate volumetric functions of interactions occurring between cholesterol and series of alkanes and alkan-1-ols.[2] Unfortunately, there was no possibility to apply this method for the homologous series of some other solvents including primary and tertiary amines, because of the lack of κ_T values at 298.15 K in the literature. This was the main reason we have determined the isothermal compressibilities of series of primary and tertiary amines with chain length up to eight carbon atoms. In this paper we attempt to express isothermal compressibilities as functions, which can be useful to predict the values of κ_T for homologues, for which there are no literature data.

Experimental Section

Materials. Amines (Fluka, purities > 99.5 mass %) were distilled over sodium in a nitrogen atmosphere. The middle fractions (about one-third) of distillates were used for measurements. Final purities were checked with gas−liquid chromatography and estimated as 99.5% to 99.7%. Liquids were stored in dry-box over phosphoric pentoxide and degassed by ultrasound just before the experiment.

Apparatus and Procedure. The isobaric heat capacity per unit volume $C_{p,v}$ was measured under atmospheric pressure by means of a high sensitivity differential scanning calorimeter Micro DSC III (Setaram, France) based on the Calvet's principle. The $C_{p,v}$ measurements were carried out within the temperature range 295 K to 301 K using the "continuous with reference" method recently analyzed in detail by Cerdeirina et al.[3] In this method the differential heat flow between a cell filled with the investigated liquid and a reference occurring during the continuous increase of calorimeter temperature is determined. In the temperature range under investigation, the scanning rate was 0.15 K min^{-1}. For measurements we used an "open" cell of about 1.3 cm^3 volume with a capillary inlet and an outlet placed outside the detection zone of the calorimeter. This allows us to avoid a vapor space over the liquid and provides constant pressure within the temperature range under investigation. The $C_{p,v}$ values for 298.15 K were calculated from the $C_{p,v} = f(T)$ function, by interpolation. As a reference of known heat capacity,[4] redistilled and degassed heptane was used. The uncertainty in $C_{p,v}$ is estimated to be smaller than 0.2%.

The densities of solvents were measured using a digital flow densimeter (Sodev, model 03, Sherbrook, Quebec). The densimeter was calibrated with reference to pure water and nitrogen gas (absolute 1 atm). The density of water was taken from ref 5, and that of nitrogen was calculated by means of the van der Waals equation of state. The reproducibility of the density measurements was ±0.01 kg m^{-3}, and the uncertainty was estimated as ±0.05 kg m^{-3}.

Speeds of sound were measured using an MPFU velocimeter (Ecolab, Poland). The device was calibrated with water by its producer, and the uncertainty in measurement can be estimated as ±0.5 ms^{-1}. Nevertheless, for testing we measured speeds of sound for some *n*-alkan-1-ols (C_1 to C_4) and heptane, and the difference between the literature[6] and experimental data was ±0.2−0.3 ms^{-1}. Values of speeds of sound at 298.15 K were calculated by interpolation from the linear $u = f(T)$ function in the temperature range 298.00 K to 298.30 K.

Experimental data of densities, heat capacities, and speeds of sound are compared with values available in the literature and listed in Table 1.

Results

The isothermal compressibility can be calculated from the equation

$$\kappa_T = \kappa_S + \frac{\alpha^2 VT}{C_p} \qquad (1)$$

where κ_S is the isentropic compressibility of the liquid at temperature T, V is the molar volume, C_p is the molar isobaric heat capacity, and α is the thermal expansion coefficient.

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Table 1. Properties of Primary Amines at 298.15 K

	$\rho/(\mathrm{kg \cdot m^{-3}})$		$C_p/(\mathrm{J \cdot mol^{-1} \cdot K^{-1}})$		$u/(\mathrm{m \cdot s^{-1}})$	
	this work	lit.	this work	lit.	this work	lit.
n-propylamine	710.69	712.3,[13] 710.86[14]	161.9	160,[18] 162.5[19]	1215.4	1224[21]
n-butylamine	733.02	732.25,[15] 733.08[14]	191.7	188[18]	1249.8	1259,[21] 1247.8[7]
n-pentylamine	747.87	748.56,[16] 749.6[17]	220.4	218[18]	1278.0	
n-hexylamine	760.13	760.27,[16] 761.4[17]	251.0	252[18]	1304.7	
n-octylamine	777.19	778.08,[16] 778.5[17]	311.6	303.9[20]	1344.2	

Table 2. Densities, Speeds of Sound, Isentropic Compressibilities, Thermal Expansion Coefficients, Molar Volumes, Isobaric Heat Capacities and Isothermal Compressibilities ofPrimary and Tertiary Amines at 298.15 K

	$\rho/(\mathrm{kg \cdot m^{-3}})$	$u/(\mathrm{m \cdot s^{-1}})$	$10^9\kappa_S/(\mathrm{Pa^{-1}})$	$10^3\alpha/(\mathrm{K^{-1}})$	$10^6V/(\mathrm{m^3 \cdot mol^{-1}})$	$C_p/(\mathrm{J \cdot mol^{-1} \cdot K^{-1}})$	$10^9\kappa_T/(\mathrm{Pa^{-1}})$
n-propylamine	710.69	1215.4	0.953	1.47[13]	83.17	161.9	1.284
n-butylamine	733.02	1249.8	0.873	1.30[7]	99.78	191.7	1.136
n-pentylamine	747.87	1278.0	0.816	1.20[16]	116.56	220.4	1.043
n-hexylamine	760.13	1304.7	0.773	1.13[16]	133.12	251.0	0.975
n-octylamine	777.19	1344.2	0.712	1.04[16]	166.30	311.6	0.884
triethylamine	722.26	1115.1	1.113	1.24[13]	140.10	221.20	1.404
tri-*n*-propylamine	752.03	1191.3	0.937	0.99[13]	190.51	301.00	1.122
tri-*n*-butylamine	773.84	1246.9	0.831	0.974	239.53	391.83	1.004
tri-*n*-hexylamine	794.71	1315.5	0.727	0.876	339.14	568.12	0.864
tri-*n*-octylamine	808.17	1363.2	0.666	0.870	437.63	751.43	0.797

Table 3. Coefficients of Eq 4, Correlation Coefficients, and Standard Deviations

	a	b	c	R	σ
primary *n*-amines	0.315 ± 0.023	1.986 ± 0.062	0.314 ± 0.019	1.0000	0.000 876
tertiary *n*-amines	0.528 ± 0.044	1.503 ± 0.050	0.621 ± 0.076	0.9985	0.007 10
n-alkan-1-ols	0.200 ± 0.078	1.985 ± 0.376	0.183 ± 0.048	0.9987	0.005 55
1-chloro-*n*-alkanes	0.763 ± 0.013	2.291 ± 0.112	1.152 ± 0.061	0.9999	0.001 28

Table 4. Properties of 1-Chloro-*n*-decane and 1-Chloro-*n*-hexadecane at 298.15 K

	$\rho/(\mathrm{kg \cdot m^{-3}})$	$u/(\mathrm{m \cdot s^{-1}})$	$10^9\kappa_S/(\mathrm{Pa^{-1}})$	$10^3\alpha/(\mathrm{K^{-1}})$	$10^6V/(\mathrm{m^3 \cdot mol^{-1}})$	$C_p/(\mathrm{J \cdot mol^{-1} \cdot K^{-1}})$	$10^9\kappa_T/(\mathrm{Pa^{-1}})$
1-chloro-*n*-decane	865.68	1295.45	0.688	0.919[22]	204.15	335.27	0.842
1-chloro-*n*-hexadecane	860.86	1370.49	0.618	0.829[22]	303.06	522.07	0.737

Values of isentropic compressibilities can be readily determined from the values of speed of sound u and density ρ:

$$\kappa_S = \frac{1}{u^2\rho} \tag{2}$$

Thermal expansion coefficients were calculated from density data at different temperatures

$$\alpha = -\frac{1}{\rho}\left(\frac{\partial\rho}{\partial T}\right)_p \tag{3}$$

from our experimental data or from the literature.

All the data used to calculate isothermal and isentropic compressibilities from eqs 1 and 2 are listed in Table 2.

Out of the solvents studied κ_S values at 298.15 K can be found in the literature only for butylamine[7] (0.8766×10^{-9} Pa^{-1}) and triethylamine[8] (1.099×10^{-9} Pa^{-1}). The values determined in this work are 0.873×10^{-9} Pa^{-1} and 1.113×10^{-9} Pa^{-1}, respectively, and show a good agreement with literature data.

The only data available in the literature referring to the isothermal compressibilities of amines at 298.15 K concern tri-*n*-butylamine:[9] $\kappa_T = 0.99 \times 10^{-9}$ Pa^{-1}. This value was determined from direct measurements of density as a function of pressure. The value determined by us via eq1 is 1.004×10^{-9} Pa^{-1} and remains also in very good agreement with the value cited by Serratrice and Delpuech.[9]

Discussion

For series of primary and tertiary amines, with the increase of hydrocarbon chain length (N), values of isothermal compressibilities decrease exponentially. The same character of change of κ_T is shown by the homologous series of other polar compounds such as *n*-alkan-1-ols or 1-chloro-*n*-alkanes. The corresponding values for these solvents are plotted in Figure 1.

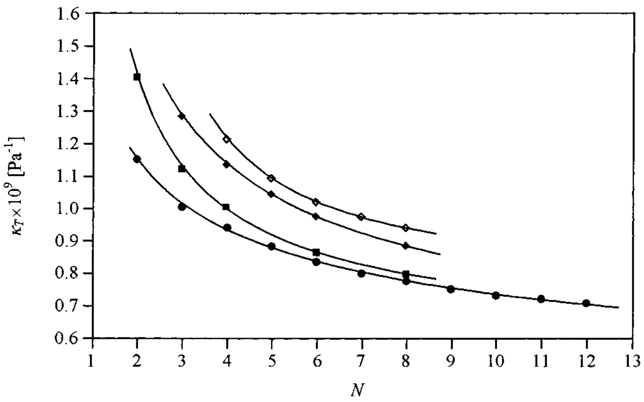

Figure 1. Isothermal compressibilities against number of carbon atoms in the molecule. Values of κ_T for *n*-alkan-1-ols were taken from ref 10, and those for 1-chloro-*n*-alkanes were taken from ref 11. ◆, primary *n*-amines; ■, tertriary *n*-amines; ●, *n*-alkan-1-ols; ◇, 1-chloro-*n*-alkanes.

The exponential decrease of values of $\kappa_T = f(N)$ can be described with an empirical equation as follows:

$$\kappa_T = a \exp\left(\frac{b}{N^c}\right) \tag{4}$$

where a, b, and c are constants for each homologous series. Although eq 4 describes well the dependence of κ_T on chain length for the set of data already possessed, the determination of κ_T from eq 4 by extrapolation to high values of N

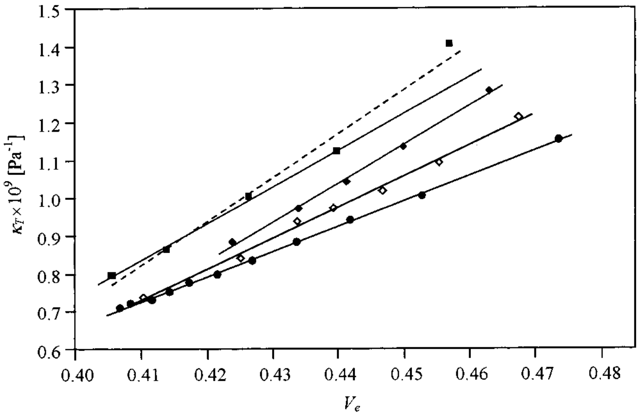

Figure 2. Isothermal compressibilities against contribution of "empty volume" in the solvent volume. The solid line for tertiary amines excluded triethylamine. The dashed line is for the whole series of tertiary amines. ◆, primary *n*-amines; ■, tertriary *n*-amines; ●, *n*-alkan-1-ols; ◇, 1-chloro-*n*-alkanes.

does not seem to be very precise. The parameters of eq 4 listed in Table 3, nevertheless, could be useful in the estimation by interpolation of κ_T values.

Isothermal compressibility defines the ability of a substance to change its volume under external pressure. From this point of view this parameter should be related to the existence of an empty space between molecules of liquids. This "empty" volume can be easily estimated as the difference between the molar volume of liquids at a defined temperature and the intrinsic volume, for example, the van der Waals volume. The relation between κ_T and the contribution of empty volume in the solvent volume is showed in Figure 2.

We define the contribution of "empty volume" to the solvent volume as

$$V_e = \frac{V_m - V_w}{V_m} \qquad (5)$$

where V_m is the molar volume of liquid calculated from the densities listed in Table 2, or from literature data,[10,11] and V_w is the van der Waals volume, calculated as a sum of atomic increments cited by Bondi.[12] Values of V_m, V_w, and V_e for investigated solvents are listed in Table 5. The relation $\kappa_T = f(V_e)$ shown in Figure 2 for studied series of solvents can be described with the linear equation

$$\kappa_T = a_1 + b_1 V_e \qquad (6)$$

with correlation coefficients from 0.9877 to 0.9991. Only in the case of tertiary amines does the high value of κ_T of triethylamine disturb the linear character of the function $\kappa_T = f(V_e)$. For tertiary amines of $N \geq 3$ the linear character of eq 6 is preserved ($R = 0.9967$).

The possibility of using eq 6 for estimating the values of isothermal compressibility by extrapolation was examined for 1-chlorodecane and 1-chlorohexadecane. Using the literature[11] data of κ_T for homologous series of 1-chloroalkanes with the number of carbon atoms $4 \leq N \leq 8$, we calculated values for 1-chlorodecane ($\kappa_T = 0.857 \times 10^{-9}$ Pa^{-1}) and 1-chlorohexadecane ($\kappa_T = 0.737 \times 10^{-9}$ Pa^{-1}) The values determined experimentally are respectively 0.842 $\times 10^{-9}$ Pa^{-1} and 0.737 $\times 10^{-9}$ Pa^{-1} (Table 4), and they are different from the extrapolated values only in the case of 1-chlorodecane of about 2%.

Table 5. Molar Volumes, van der Waals Volumes, and Contributions of "Empty Volume" in the Solvent Volume of Studied Liquids at 298.15 K

n-alkan-1-ols				1-chloro-*n*-alkanes			
N	$10^6 V_m$	$10^6 V_w$	V_e	N	$10^6 V_m$	$10^6 V_w$	V_e
	m^3·mol^{-1}	m^3·mol^{-1}			m^3·mol^{-1}	m^3·mol^{-1}	
2	58.66	30.89	0.4734	4	105.10	55.98	0.4674
3	75.13	41.12	0.4527	5	121.55	66.21	0.4553
4	91.98	51.35	0.4417	6	138.15	76.44	0.4467
5	108.70	61.58	0.4335	7	154.57	86.67	0.4393
6	125.27	71.81	0.4268	8	171.14	96.90	0.4338
7	141.81	82.04	0.4215	10	204.15	117.36	0.4251
8	158.32	92.27	0.4172	16	303.06	178.74	0.4102
9	174.97	102.50	0.4142				
10	191.58	112.73	0.4116				
11	207.81	122.96	0.4083				
12	224.52	133.19	0.4068				

tertiary *n*-amines				primary *n*-amines			
N	$10^6 V_m$	$10^6 V_w$	V_e	N	$10^6 V_m$	$10^6 V_w$	V_e
	m^3·mol^{-1}	m^3·mol^{-1}			m^3·mol^{-1}	m^3·mol^{-1}	
2	140.00	76.03	0.4569	3	83.17	44.67	0.4629
3	190.51	106.72	0.4398	4	99.78	54.90	0.4498
4	239.53	137.41	0.4263	5	116.56	65.13	0.4412
6	339.14	198.79	0.4138	6	133.12	75.36	0.4339
8	437.63	260.17	0.4055	8	166.30	95.82	0.4238

Table 6. Coefficients of Eq 6, Correlation Coefficients, and Standard Deviations

	a_1	b_1	R	σ
primary *n*-amines	−3.472 ± 0.146	10.255 ± 0.329	0.9969	0.009 84
tertiary *n*-amines[a]	−3.130 ± 0.166	9.675 ± 0.392	0.9967	0.010 19
n-alkan-1-ols	−2.003 ± 0.029	6.658 ± 0.067	0.9991	0.004 44
1-chloro-*n*-alkanes[b]	−2.597 ± 0.234	8.127 ± 0.522	0.9877	0.013 88
1-chloro-*n*-alkanes[c]	−2.641 ± 0.116	8.222 ± 0.265	0.9948	0.012 37

[a] For $N \geq 3$. [b] For $4 \leq N \leq 8$ from literature data.[11] [c] Including our experimental κ_T values for 1-chlorodecane and 1-chlorohexadecane.

The coefficients of eq 6 which give the possibility to predict the κ_T values for the homologous series under study are listed in Table 6.

Considering the simplicity of calculating the "empty volume" and the fact that the linear character of relation 6 is fulfilled for odd as well as for even homologues, it seems that the relation $\kappa_T = f(V_e)$ gives a good possibility of estimating isothermal compressibility.

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