

# Densities and Isothermal Compressibilities at Pressures up to 20 MPa of the Systems *N,N*-Dimethylformamide or *N,N*-Dimethylacetamide + 1-Chloroalkane

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Densities of *N,N*-dimethylformamide or *N,N*-dimethylacetamide + 1-chlorobutane, or + 1-chlorohexane, or + 1-chlorooctane at 298.15 K and at pressures up to 20 MPa have been measured. Isothermal compressibilities of the pure liquids and their mixtures were obtained.

## Introduction

Thermodynamic properties for binary mixtures have been studied for testing some theories of the liquid state and for understanding the strength and nature of the intermolecular interactions in these mixtures. With this target, we studied the thermodynamic properties of different halogenated aliphatic compounds and their mixtures.<sup>1–7</sup> We present here the density,  $\rho$ , at 298.15 K and at pressures,  $p$ , up to 20 MPa of *N,N*-dimethylformamide or *N,N*-dimethylacetamide + 1-chlorobutane, or + 1-chlorohexane, or + 1-chlorooctane. Amides are of interest because they are used as simple models in biochemistry.<sup>8–10</sup> The study of liquid mixtures containing amides could contribute to an understanding of complex molecules of biological interest. On the other hand, monohaloalkanes represent a class of technically important compounds, used in industry as intermediates or as final products. This work is part of research to study the intermolecular interactions present in mixtures such as amide + 1-chloroalkane; these interactions could be dipolar as those in the pure 1-chloroalkanes and amides and also acceptor–donor interactions present in the mixtures of these compounds.

Densities,  $\rho$ , of the pure liquids (*N,N*-dimethylformamide, *N,N*-dimethylacetamide, and 1-chloroalkane) were measured at 288.15 K, 298.15 K, 308.15 K, and 318.15 K at pressures up to 20 MPa, and from them, thermal expansion coefficients,  $\alpha$ , were derived.

The isothermal compressibility,  $\kappa_T$ , of the pure liquids and their mixtures was calculated, and the excess isothermal compressibility,  $\kappa_T^E$ , of the mixtures was derived. As far as we know, there are no previous measurements on these mixtures in the literature.

## Experimental Section

**Materials.** *N,N*-Dimethylformamide (mole fraction > 99 %) and 1-chlorooctane (mole fraction > 98 %) were obtained from Fluka AG Buchs; 1-chlorohexane (mole fraction 99.0 %) was obtained from Aldrich Chem. Co.; and *N,N*-dimethylacetamide (mole fraction ≥ 99 %) and 1-chlorobutane (mole fraction ≥ 99.8 %) were obtained from Riedel-de Häen. All the liquids were used without further purification.

The measured densities,  $\rho$ , and isothermal compressibilities,  $\kappa_T$ , are compared with literature values in Table 1.

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**Table 1. Densities,  $\rho$ , and Calculated Isothermal Compressibility,  $\kappa_T$ , Values for the Pure Components at Atmospheric Pressure and 298.15 K and Those from the Literature**

component	$\rho/\text{g}\cdot\text{cm}^{-3}$		$10^4\kappa_T/\text{MPa}^{-1}$	
	exptl	lit.	exptl	lit.
<i>N,N</i> -dimethylformamide	0.9438	0.94387 <sup>11</sup>	6.51	6.50 <sup>11</sup>
<i>N,N</i> -dimethylacetamide	0.9370	0.93634 <sup>11</sup>	6.71	6.39 <sup>15</sup>
1-chlorobutane	0.8806	0.88075 <sup>12</sup>	12.05	12.13 <sup>16</sup>
1-chlorohexane	0.8731	0.87333 <sup>13</sup>	10.16	10.07 <sup>17</sup>
1-chlorooctane	0.8688	0.86883 <sup>14</sup>	8.98	

**Apparatus and Procedure.** The mixtures were prepared by mass, and the mole fraction uncertainty was estimated to be  $\pm 10^{-4}$ . For the pure components, experimental densities,  $\rho$ , were measured at 288.15 K, 298.15 K, 308.15 K, and 318.15 K at pressures,  $p$ , up to 20 MPa. For binary mixtures, experimental densities were measured at 298.15 K at pressures up to 20 MPa. The measured densities were obtained with a vibrating-tube densimeter with a DMA 512 high-pressure cell. High pressures were generated by a liquid pump (model LC-10 AT of Shimadzu).

The vibrating-tube temperature,  $T$ , measured with an Anton-Paar CKT 100 digital thermometer, was stable to better than  $\pm 0.01$  K using a Grant LT D6G thermostat. Pressures,  $p$ , were measured with a pressure gauge (Gefran) calibrated with another pressure gauge (Druck, model DPI 145).

The forced path mechanical calibration (FPMC)<sup>18</sup> model was used to calibrate the densimeter. 1,2-Dichloroethane was used as a reference liquid<sup>19</sup> for calibration purposes. This liquid was chosen because it is widely studied in the literature and because its density,  $\rho$ , is higher than the values of density,  $\rho$ , studied in our research. The uncertainty of the reported densities was estimated to be  $10^{-4} \text{ g}\cdot\text{cm}^{-3}$ .

## Results and Discussion

The measured densities,  $\rho$ , for the pure liquids at 288.15 K, 298.15 K, 308.15 K, and 318.15 K and at pressures,  $p$ , up to 20 MPa are reported in Table 2. The isothermal compressibilities,  $\kappa_T$

$$\kappa_T = \rho^{-1}(\delta\rho/\delta P)_T \quad (1)$$

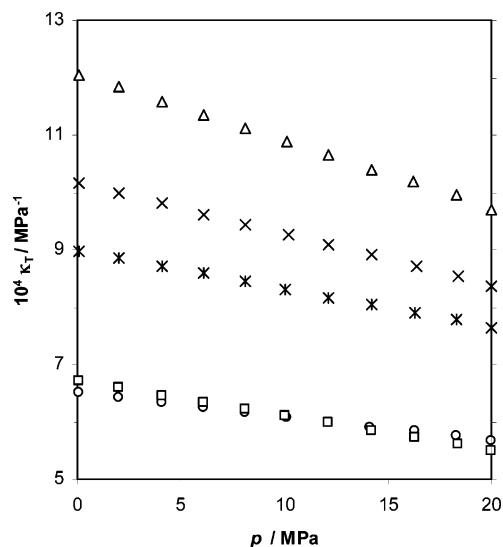
obtained at 288.15 K, 298.15 K, 308.15 K, and 318.15 K for the pure liquids are given in Table 2. Density data were fitted to linear equations, and analytical differentiation was done to obtain the isothermal compressibilities. The uncertainty of the











**Figure 1.** Isothermal compressibility,  $\kappa_T$ , of the pure components plotted against pressure at  $T = 298.15$  K.  $\circ$ ,  $N,N$ -dimethylformamide;  $\square$ ,  $N,N$ -dimethylacetamide;  $\triangle$ , 1-chlorobutane;  $\times$ , 1-chlorohexane;  $*$ , 1-chlorooctane.

literature for the pure liquids are  $\alpha$  ( $N,N$ -dimethylformamide)  $= 9.75 \cdot 10^{-4}$   $\text{K}^{-1}$ ,<sup>20</sup>  $\alpha$  ( $N,N$ -dimethylacetamide)  $= 9.60 \cdot 10^{-4}$   $\text{K}^{-1}$ ,<sup>21</sup>  $\alpha$  (1-chlorohexane)  $= 1.092 \cdot 10^{-3}$   $\text{K}^{-1}$ ,<sup>22</sup> and  $\alpha$  (1-chlorooctane)  $= 9.50 \cdot 10^{-4}$   $\text{K}^{-1}$ .<sup>23</sup> We did not find the value of the thermal expansion coefficient,  $\alpha$ , for 1-chlorobutane in the literature. As can be seen, there is a good agreement between the values of thermal expansion coefficients,  $\alpha$ , obtained by us and literature values.

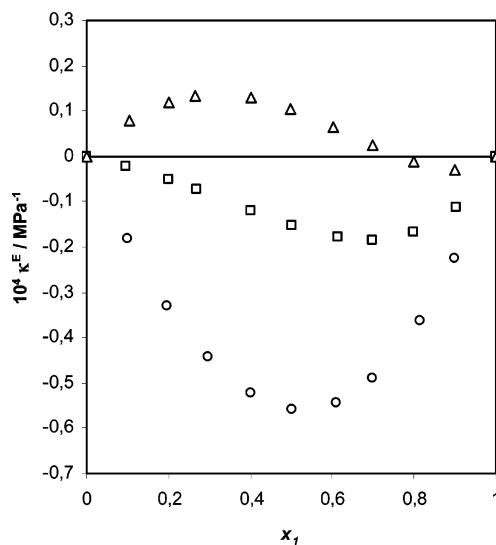
For  $N,N$ -dimethylformamide or  $N,N$ -dimethylacetamide + 1-chlorobutane, or + 1-chlorohexane, or + 1-chlorooctane mixtures, experimental densities,  $\rho$ , and isothermal compressibilities,  $\kappa_T$ , calculated with eq 1 are presented in Table 3. From the values of Table 3, it can be observed that the values of isothermal compressibility,  $\kappa_T$ , decrease as the length of the aliphatic chain of the 1-chloroalkane of the mixture increases. The same behavior is found in the literature for series of nonsaturated hydrocarbons,<sup>24</sup> alcohols,<sup>17,25</sup> etc. However, a different behavior is found for series such as *n*-alkane,<sup>26</sup> for example. Thereby, we can conclude that even though  $(\delta V^E / \delta P)_T$  and the isothermal compressibility,  $\kappa_T$ , are related properties, their behavior in function of the molecular structure related parameters, such as, for example, the length of the aliphatic chain, can be different. The reason could be that the isothermal compressibility,  $\kappa_T$ , depends on the molar volume of the studied system which involves the structural effects in the systems, besides the molecular interactions.

The “excess” compressibility,  $\kappa_T^E$ , defined as

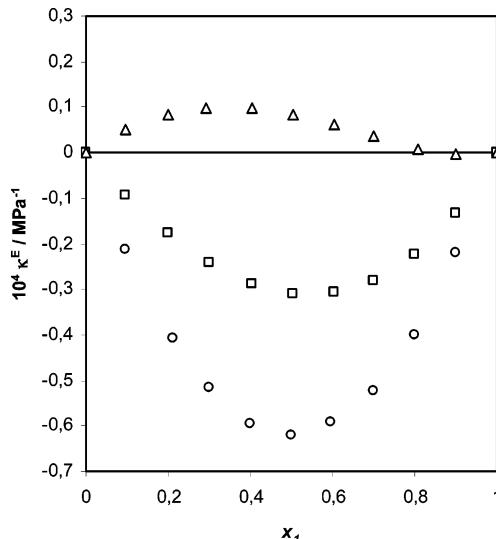
$$\kappa_T^E = -V^{-1}(\delta V^E / \delta P)_T = \kappa - \phi_1 \kappa_1 - \phi_2 \kappa_2 \quad (3)$$

where  $\phi_1$  and  $\phi_2$  are the volume fractions, is widely used. The values for  $\kappa_T^E$ , obtained with eq 3, are represented against the mole fraction of the amide,  $x$ , in Figures 2 and 3.

The excess isothermal compressibility,  $\kappa_T^E$ , values increase in the following sequence:  $N,N$ -dimethylformamide or  $N,N$ -dimethylacetamide + 1-chlorobutane <  $N,N$ -dimethylformamide or  $N,N$ -dimethylacetamide + 1-chlorohexane <  $N,N$ -dimethylformamide or  $N,N$ -dimethylacetamide + 1-chlorooctane. From the experimental data presented here, it can be seen that for a given chloroalkane the difference between the behavior of the



**Figure 2.** Excess isothermal compressibility,  $\kappa_T^E$ , represented against mole fraction of  $N,N$ -dimethylformamide for the mixtures with:  $\circ$ , 1-chlorobutane;  $\square$ , 1-chlorohexane; or  $\triangle$ , 1-chlorooctane at  $T = 298.15$  K.



**Figure 3.** Excess isothermal compressibility,  $\kappa_T^E$ , represented against mole fraction of  $N,N$ -dimethylacetamide for the mixtures with:  $\circ$ , 1-chlorobutane; or  $\square$ , 1-chlorohexane;  $\triangle$ , or 1-chlorooctane at  $T = 298.15$  K.

mixtures with the two studied amides is very small as the physical property values for these amides are alike.

We conclude that the excess isothermal compressibility,  $\kappa_T^E$ , values for the mixtures  $N,N$ -dimethylformamide or  $N,N$ -dimethylacetamide with 1-chlorobutane show the largest deviation from ideality, and the mixtures with 1-chlorooctane show the smallest deviation from ideality.

In any case, the explanation of the volumetric behavior of the studied mixtures is difficult from only this kind of measurements, given the variety and complexity of the interactional and geometric effects present in the pure 1-chloroalkanes and amides such as, for example, the dipole–dipole interactions and the specific acceptor–donor interactions present in the mixtures.

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