Pressure and temperature effects on the density and viscosity of DMF-water mixtures

M Ueno, R Mitsui, H Iwahashi, N Tsuchihashi and K Ibuki
Dept. of Molecular Chemistry & Biochemistry, Doshisha University, Kyotanabe, Kyoto, 610-0321, Japan
E-mail: mueno@mail.doshisha.ac.jp

Abstract. Densities and Viscosities of N, N-dimethylformamide (DMF)–water (D_2O, H_2O) mixtures were measured at 5, 25, and 45°C under high pressure up to 196.1 MPa. The isothermal compressibility of the mixtures shows a minimum against the composition in the water-rich region and the depth of the minimum is larger at lower pressures and temperatures. The viscosity of the mixture exhibits a remarkable maximum in the water-rich region, and its maximum becomes larger with an increase in pressure and with a decrease in temperature. These results are discussed in terms of the interactions between DMF and water molecules, especially, the hydrophobic hydration around the methyl groups of DMF molecules.

1. Introduction
Amides of (R_1, R_2)-NCHO type (R_1, R_2 = H and/or an alkyl group) possess a large dipole moment and a hydrophilic property, so that they mix well with water. On the other hand, we can introduce various kinds of alkyl group to amides systematically, and get information on the interactions between an alkyl group and water molecules. Amides are good model compounds of peptides in water, and the hydration of amides has been investigated vigorously at atmospheric pressure[1-6]. However, high pressure studies are few except for the density measurement by Uozaki et al.[7] Previously we have measured the density and viscosity of formamide (FA), N-methylformamide (NMF), and N, N-dimethylformamide (DMF)-H_2O mixtures at 25°C under high pressure up to 196.1 MPa[8]. Here, we report those of DMF-D_2O and DMF-H_2O mixtures at 5, 25, and 45°C under high pressure, and discuss mainly the pressure and temperature effects on the isothermal compressibility (κ_T) and viscosity (η) of these mixtures.

2. Experiments
N, N-dimethylformamide (99.50%, Nacali Tesque) was used without purification. Heavy water (99.90% D_2O, Euriso-Top) was distilled under a nitrogen atmosphere, and light water (H_2O) was deionized by ion-exchange resin after distillation. All the sample solutions were made by weight.

Relative densities (d_r = d_P / d_0.1) of the mixtures at pressure P, where d_P and d_0.1 are the density of the mixture at pressure P and at 0.1 MPa, respectively, were measured using a metal bellows volumometer up to 196.1 MPa at each temperature within an accuracy of ±0.2%. The densities of the mixtures at atmospheric pressure and at each temperature were determined by means of a vibrating densimeter (SS-D-200, Shibayama Scientific). The details of the density measurement have been written in the previous papers[8,9].
A rolling-ball type of viscometer (Hikari Koatsu) was used to determine the viscosities of the mixtures up to 196.1 MPa at each temperature. The viscosity was estimated from the rolling time \((t)\) by the following equation:

\[
\eta = Ct(d_B - d_F) \tag{1}
\]

where \(\eta\) is the viscosity, \(C\) is an apparatus constant, and \(d_B \) and \(d_F \) are the densities of the ball and the fluid, respectively. Ignoring the pressure dependence of \(C\) and \(d_B\), we determined the relative viscosities \((\eta_r = \eta / \eta_0)\) of the mixtures up to 196.1 MPa at each temperature within an accuracy of ±5%. The viscosities of the mixtures at atmospheric pressure were obtained with an Ubbelohde viscometer. The details of the viscosity measurement have been described elsewhere\[8,9\].

3. Results and Discussion

3.1. Density

Densities of DMF-D_2O mixtures decrease with an increase in DMF content at all the pressures studied, and those of DMF-H_2O mixtures tend to decrease mildly as shown in Fig. 1. It is interesting that the densities of DMF-H_2O mixtures show a maximum in the water-rich region at 5°C.

The isothermal compressibility \((\kappa_T)\) was calculated based on the density data. Figure 2 shows the composition dependence of \(\kappa_T\) for DMF-D_2O and DMF-H_2O mixtures at 5, 25, and 45°C under high pressure. Although \(\kappa_T\) of DMF is larger than that of water, \(\kappa_T\) of both mixtures shows a minimum against the composition in the water-rich region at all the pressures and temperatures studied; the depth of the minimum is larger at lower pressures and temperatures. Previously we examined the composition dependence of \(\kappa_T\) for FA-H_2O mixtures at 25°C\[8\]; \(\kappa_T\) decreases monotonously with an increase in the FA content. Therefore, the appearance of the minimum in \(\kappa_T\), especially at lower temperatures, can mainly be ascribed to the interactions between methyl groups of DMF and water molecules, i.e., hydrophobic hydration, and indicates that the structure of hydrophobic hydration resists to compression more strongly than the hydrogen-bonded structure in pure water because of the compactness of the former. The liquid structures of FA, NMF, and DMF at atmospheric pressure have been studied by the X-ray diffraction and the \textit{ab initio} LCG-MO-SCF calculations\[10\]. Most of DMF molecules oriented randomly without making hydrogen bonds. When water is added to DMF, the dipole-dipole interaction between DMF and water molecules would arise and the free volume in the mixture would decrease gradually. This would be the reason why \(\kappa_T\) decreases with an increase in the water content in the DMF-rich region.

We estimated the partial molar volume of DMF in aqueous solution \((\bar{V})\) using the data on the density of mol fraction \(x = 0-0.15\), and calculated the difference between \(\bar{V}\) and the molar volume of DMF: \((\Delta \bar{V} = \bar{V} - \bar{V}_{\text{m}})\). The values of \(\Delta \bar{V}\) are negative at all the pressures and temperatures. For example, in DMF-D_2O mixtures \(\Delta \bar{V} = -5.8, -4.3, \) and \(-3.5 \text{ cm}^3 \text{ mol}^{-1}\) at 25°C and 0.1, 98.1, and 196.1 MPa,
respectively. These results also suggest that the hydrophobic hydration is formed around the methyl group and its structure is compact. On the other hand, $\Delta V$ of $D\text{}_2\text{O}$ in DMF solution estimated with the data on $x = 0.6\sim1.0$ at 25°C are -2.5, -1.6, and -1.1 cm$^3$ mol$^{-1}$ at 0.1, 98.1, and 196.1 MPa, respectively. This suggests that the open structure of water disappears in the DMF-rich region.

3.2. Viscosity

Figure 3 shows the composition dependence of $\eta$ for the mixtures at 5, 25, and 45°C under high pressure.

![Graphs showing composition dependence of $\kappa_T$ and $\eta$ for DMF mixtures at various pressures and temperatures.](image)

Fig. 2. Composition dependence of $\kappa_T$ for the DMF mixtures at 5, 25, and 45°C under high pressure.

![Graphs showing composition dependence of $\eta$ for DMF mixtures at various pressures and temperatures.](image)

Fig. 3. Composition dependence of $\eta$ for the DMF mixtures at 5, 25, and 45°C under high pressure.
Fig. 4. Composition dependence of $\Delta E_{\text{vis}}$ for DMF-D$_2$O mixtures under high pressure.

Although the viscosities of D$_2$O and H$_2$O are not so much different from that of DMF, e.g., $\eta$(D$_2$O) = 1.097, $\eta$(H$_2$O) = 0.8903, and $\eta$(DMF) = 0.717 mPa s at 25°C, $\eta$ for DMF-water mixtures shows a maximum against the composition in the water-rich region, and the maximum becomes larger at higher pressures and lower temperatures as shown in Fig. 3. The isotope effect on $\eta$ and $\kappa_T$ appears more clearly at lower temperatures: $\eta$ of DMF-D$_2$O mixtures is apparently larger than that of DMF-H$_2$O mixtures at 5°C. In contrast to the case of DMF-water mixtures, $\eta$ for FA-H$_2$O mixtures at 25°C increases monotonously with an increase in the FA content[8]. Thus the presence of the maximum in the dynamic property of $\eta$ in the water-rich region can also be ascribed to the formation of hydrophobic hydration around the methyl groups of DMF as in the case of the static property of $\kappa_T$, though the compositions for the maximum in $\eta$ are different from those for the minimum in $\kappa_T$.

Activation energies for $\eta$ were obtained by the following equation:

$$\Delta E_{\text{vis}} = R \left( \frac{\partial \ln \eta}{\partial (1/T)} \right)_P$$

(2)

As is depicted in Fig. 4, $\Delta E_{\text{vis}}$ for DMF-D$_2$O mixtures is larger than that for DMF-H$_2$O mixtures, especially, in the water-rich region and $\Delta E_{\text{vis}}$ for both mixtures also shows a maximum in the water-rich region at all the pressures studied. The composition for the maximum shifts to the DMF-rich side with increasing pressure: it is about $x = 0.2$ and 0.3 at 0.1 and 196.1 MPa for DMF-D$_2$O mixtures, respectively. The values of $\Delta E_{\text{vis}}$ were determined within an accuracy of ±1 J mol$^{-1}$, so that the phenomena mentioned above are significant. $\Delta E_{\text{vis}}$ for water decreases with increasing pressure, which may be due to the distortion of hydrogen bonds between water molecules caused by compression. This tendency continues up to $x = 0.10$, and in the region over $x = 0.2$ $\Delta E_{\text{vis}}$ increases with increasing pressure. The compression not only brings about the distortion of hydrogen bonds but also puts the molecules closer each other and strengthens the dipole-dipole interactions in the mixtures. The latter factor is one of the reasons for the increase in $\Delta E_{\text{vis}}$ with pressure in the region over $x = 0.2$.

References
[1] Assarsson P and Eirich F R 1968 J. Phys. Chem. 72 2710
[2] Rohdewald P and Moldner M 1973 J. Phys. Chem. 77 373
[3] de Visser C, Perron G, Desnoyers J E, Heuvelsland W J M and Somsen G 1977 J. Chem. Eng. Data 22 74
[4] Kawaizumi F, Ohno M and Miyagawa Y 1977 Bull. Chem. Soc. Jpn. 50 2229
[5] Davis M I and Hernandez M E 1995 J. Chem. Eng. Data 40 674
[6] Garcia B, Alcalde R, Leal J M and Matos J S 1997 J. Phys. Chem. B 101 7991
[7] Uosaki Y, Iwama F and Moriyoshi T 1992 J. Chem. Thermodynamics 24 797
[8] Ueno M, Mizumaki Y, Tsuchihashi N and Ibuki K 2003 Rev. High Pres. Sci. Tech. 13 134
[9] Ueno M, Ueyama S, Hashimoto S, Tsuchihashi N and Ibuki K 2004 J. Solution Chem. 33 782
[10] See for example, Ohtaki H, Itoh S, Rode B M 1986 Bull. Chem. Soc. Jpn. 59 271