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Chemical Reactions in Medium Density Fluids.
Inversion of Density Dependence of the Dimerization Equilibrium of 2-Methyl-2-nitrosopropane in Carbon Dioxide

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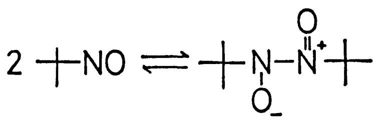
Pressure effect on the dimerization-dissociation reaction of 2-methyl-2-nitrosopropane was studied in supercritical carbon dioxide. The configurational volume change for the dimerization, which was negative at high density, was found to be positive in a medium density region.

It is well known that ordinary liquids are regarded as high density fluids the structure of which is dominated by the repulsive intermolecular interactions; the attractive interactions between the molecules have little effect on its structure.$^{1)}$ In the liquid state, therefore, the configurational volume changes for chemical reactions$^{2)}$ are determined mainly by the packing effect, and the apparent desolvation effect is observed only for ionic reactions. However when we decrease the density of a liquid, the packing effect is weakened and the attractive interactions between the molecules come to dominate the structure of the fluid. As a result, the effect of solvation is strengthened, and the desolvation effect is expected to be observed even in the nonionic reaction in such a fluid.

We attempt to demonstrate the above prospect by studying the dimerization-dissociation reaction of 2-methyl-2-nitrosopropane (MNP) in carbon dioxide. The reaction scheme of MNP is given as follows:$^{3,4)}$



$$2\,{+}\mathrm{NO} \rightleftharpoons {+}\underset{\mathrm{O}^-}{\underset{|}{\mathrm{N}}}-\overset{\mathrm{O}}{\overset{\|}{\mathrm{N}^{+}}}{+} \qquad (1)$$

The behavior of the equilibrium constant was not so abnormal in the density region between 750 and 1100 kg m^{-3} at 25.0 °C.[5] In the present work, however, we have found the inversion of the density dependence of the equilibrium constant by studying the system in a wider density range at 35.0 °C.

The experimental procedure and apparatus are the same as those in the previous report.[5] Since the solubility of MNP in carbon dioxide below 200 kg m^{-3} is not so large, the equilibrium constant could not be measured below 200 kg m^{-3}. Figure 1 shows the isothermal lines of carbon dioxide. The density of carbon dioxide was calculated by means of the empirical equation of state.[6] At 35.0 °C, the density increases rapidly from 200 to 700 kg m^{-3} with an increase in pressure, and then rather slowly; since the accuracy of the pressure measurement was ±1 bar in the present work, the maximum uncertainty of the density was about ±30 kg m^{-3}.

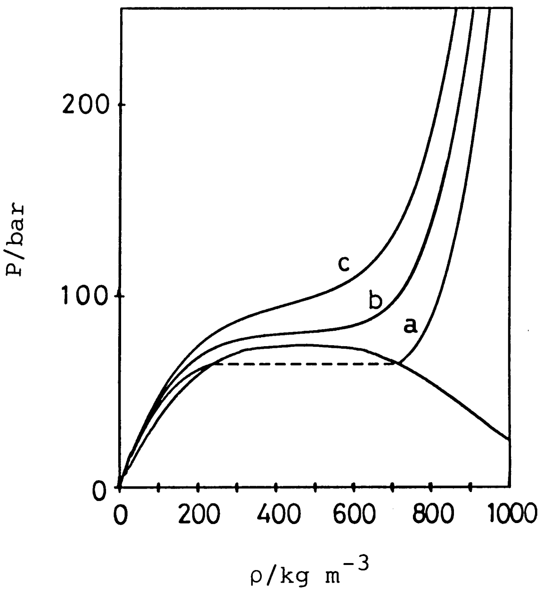


Fig. 1. Isothermal lines of carbon dioxide at several temperature: a, 25.0 °C; b, 35.0 °C; c, 45.0 °C.

MNP shows an absorption around 291 nm mainly due to the dimer, and another around 674 nm due to the monomer. In the equilibrium state the following equation holds:

$$(\varepsilon^{D}_{291}/\varepsilon^{M\,2}_{674})K/\ell = (A_{291}/A_{674} - \varepsilon^{M}_{291}/\varepsilon^{M}_{674})/A_{674}, \qquad (2)$$

where K, A, ε, and ℓ denote the equilibrium constant, the absorbance, the molal absorption coefficient, and the path length, respectively; the superscripts M and D denote the monomer and the dimer, respectively. The subscript denotes the wavelength. In the density region below 200 kg m^{-3}, the shape of the monomer spectrum changes dramatically, but above 200 kg m^{-3} its shape changes a little; especially above 500 kg m^{-3} no essential change is observed. Therefore we ignore the pressure effect on the absorption coefficients and evaluate the pressure dependence of the equilibrium constant according to Eq. 2 . The density dependence of the equilibrium constant is shown in Fig. 2, together with the previous data at 25.0 °C. The value of $\varepsilon^{M}_{291}/\varepsilon^{M}_{674}$ (0.115) is optimized by using all the experimental data at 35.0 °C. In the reaction system studied here the configurational volume change for the dimerization (ΔV_{conf}) is expressed by

$$\Delta V_{\mathrm{conf}} = -\kappa kT\,\rho\frac{\partial}{\partial\rho}\ln[(A_{291}/A_{674} - \varepsilon^{\mathrm{M}}_{291}/\varepsilon^{\mathrm{M}}_{674})/A_{674}], \qquad (3)$$

where κ, ρ, k, and T denote the isothermal compressibility, the density of carbon dioxide, the Boltzmann constant, and the temperature, respectively. As shown in Fig. 2, ΔV_{conf} changes from negative to positive with decreasing density. The sign of ΔV_{conf} is reversed at about 750 kg m^{-3}. In the high density region, ΔV_{conf} is negative as expected for the bond formation reaction in the liquid state; above 800 kg m^{-3} it is almost constant (about -33 cm^3 mol^{-1}) and the effect of the desolvation is not apparently observed in this density range. In the density region below 750 kg m^{-3}, on the other hand, ΔV_{conf} has a very large positive value (about +1000 cm^3 mol^{-1}). In other words, the volume of the reactants increases during the course of the dimerization, probably because the destruction of the solvation shells of the monomers caused by the dimerization plays a key role in determining the configurational volume change in this density region.

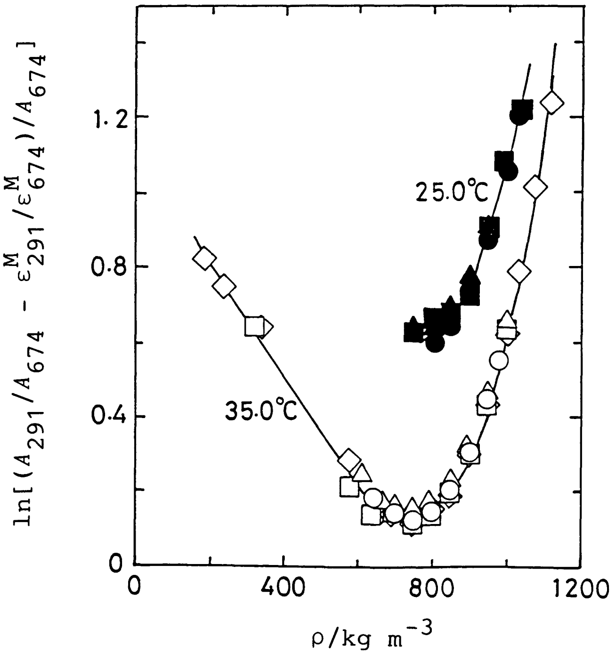


Fig. 2. Density dependence of the equilibrium constant of the dimerization-dissociation reaction of MNP in CO_2 at 35.0 and 25.0 °C. The total concentration of MNP ([M]+2[D]):◇, 1.84×10^{-2} M; □, 2.06×10^{-2} M;△, 2.13×10^{-2} M; ○, 2.94×10^{-2} M. The data at 25.0 °C are taken from Ref. 6. (1 M = 1 mol dm^{-3})

The density dependence of the equilibrium constant at 25.0 °C is quite similar to that at 35.0 °C. It suggests that the internal energy change for this reaction is determined mainly by the bond energy.

The density where the inversion of the sign of ΔV_{conf} occurs is much higher than the critical density of carbon dioxide (= 468 kg m^{-3}). This means that when the density is increased, the liquid-like behavior does not begin at the critical density from the view point of the configurational volume profile of this reaction. We consider that the critical density is a measure to characterize the medium density fluid which shows the anomalous behavior as found here.

The inversion of the density dependence of the equilibrium constant in the medium density fluid is observed for the first time in this study. In view of the reports where the reaction rate is simply accelerated in the medium density region,[7,8] further study is required to clarify the general aspects of the chemical reaction in the medium density fluid.

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