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Low and medium density fluids have a large space to rearrange the solvent molecules around the solute molecule, though the solute molecules are closely packed in the liquid (high density fluid). The large fluctuation in medium density fluids brings about an unusual behavior of the chemical equilibrium such as the positive configurational volume change accompanying the dimerization reaction.[1] Especially, if we closely approach to the critical point of the reaction mixture, the fluctuation is enhanced and we may find a critical anomaly of the chemical equilibrium.

The singular behavior of the chemical equilibria near the critical point had been reported by Krichevskii and co-workers.[2] However, several authors attributed the anomaly to the critical opalescence,[3] and claimed that the critical anomaly of the chemical equilibrium should be too weak to detect in a conventional measurement as used by Krichevskii and co-workers. We tried to detect a critical anomaly of the chemical equilibrium of keto-enol equilibrium of acetylacetone in trifluoromethane (CHF$_3$, T_C = 298.8 K and ρ_C = 526 kg m^{-3}) by using FT-NMR spectroscopy at 300 ± 0.5 K, and found no anomaly around the critical point as predicted theoretically.[3]

The tautomeric equilibrium of acetylacetone has been studied exhaustively, and it has been known that the keto form is preferable in polar solvents[4] or in compression of the reaction mixture.[5] Recent work[6] in trifluoromethane, however, shows that the equilibrium constant is almost constant at 307 K.

Keto Form   **Enol Form**
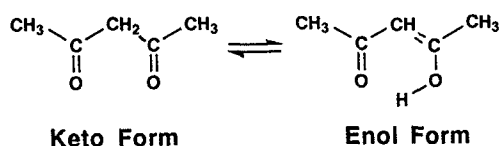
The equilibrium constant, K = [enol]/[keto], was determined from the areas under enol and keto methyl signals at 300 ± 0.5 K from 130 to 800 kg m^{-3}. NMR spectra were obtained by using an FT-MNR spectrometer (JEOL GX-400). The uncertainty of equilibrium constant was ca. 20% in the medium density region and up to 40% in the low density region (<200 kg m^{-3}), because the equilibrium lies so far to the enol form especially in the low density region. The samples were made by condensation of the gaseous mixture of acetylacetone and trifluoromethane in a pyrex glass capillary (about 1 mm o.d.) with liquid nitrogen, and sealed with torch. The obtained equilibrium constants were not dependent on the mol fraction of acetylacetone in the range of 0.01 to 0.03. Since the solubility of acetylacetone in trifluoromethane is not so large at 300 K in the density region lower than 200 kg m^{-3}, we measured the equilibrium constants in these samples at 328 K and 363 K, and extrapolated to 300 K by means of van't Hoff plot at constant volume. The phase separation was not

detected for the higher density samples even around the critical density. The density of each sample was determined by the gas-liquid ratio at 273 K and 195 K by using the saturation line of pure trifluoromethane. The validity of the method of determining density was confirmed by the changes of mass accompanied by breaking several sample capillaries. The error in the density was estimated as ±10%.

Figure 1 shows the density dependence of the equilibrium constant. Increasing the solvent density, the equilibrium constant decreases rapidly in the low density region (<200 kg m^{-3}), and the decreasing rate reduces in the medium density region within 300 kg m^{-3} and 800 kg m^{-3}. The density dependence of the equilibrium constant around the critical density is small, and no remarkable anomaly is detected. No anomaly was also found when increasing the temperature of several samples of the density close to the critical density within the experimental error. As Wheeler and Petscheck have been pointed out,[3(a)] chemical reactions of this type are expected to have, at most, weak anomaly. To detect a weak anomaly, high accuracy and a close approach to the critical point are required.

Although the critical anomaly was not detected, a large density dependence in the low density region is inter-
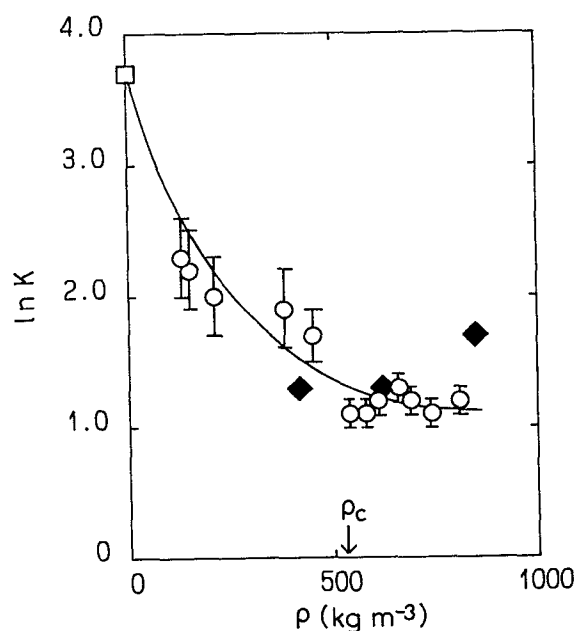
FIG. 1. Density dependence of the keto-enol tautomeric equilibrium constant of acetylacetone in CHF$_3$ at 300 K. ○, present results; □, Ref. 7, ◆, Ref. 6 with extrapolation from 307 K to 300 K by using van't Hoff equation.

esting from the viewpoint of the solvent effect on the chemical reaction. The density dependence of the equilibrium constant at sufficiently low density corresponds to the difference of the mixed virial coefficient. The slope at low density region of Fig. 1 corresponds to the difference of more than 300 cm^3 mol^{-1} in the mixed virial coefficients of CHF_3 with the keto and enol form of acetylacetone. It is not a surprising value when we take into account the fact that the mixed virial coefficient of $CHCl_3$ is -2005 cm^3 mol^{-1} for acetone and -1400 cm^3 mol^{-1} for ethyl ether at 333 K:[8] The hydrogen bonding between $CHCl_3$ and the oxygen atom in the carbonyl group is much stronger than the hydrogen bond between $CHCl_3$ and the oxygen in the epoxy group. The rapid reduction of the density dependence of the equilibrium constant at the medium density region suggests that the hydrogen bond between CHF_3 and acetylacetone is rapidly saturated with increasing the density of CHF_3. Present results will complement the extensive studies in the liquid phase[4,5] for understanding the solvent effect on the chemical equilibrium in fluids.

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