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Pressure Effects on the Viscosity of Substituted Benzenes

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In the previous work,¹ the viscosity of liquid benzene was investigated as a function of pressure and temperature and the dependency was explained in terms of the variation in its free volume.^{2,3} An empirical formula was devised to relate the viscosity of benzene to the pressure and temperature variation. The investigation has been extended toward a variety of thermodynamic functions of substituted benzenes including toluene and chlorobenzene as well as benzene. In this work, we measured the viscosity of benzene, toluene and chlorobenzene under the pressure of 1 through 1,000 bar at 20 °C and 60 °C. The same method as that of the previous work was applied to the viscosity measurement.¹

According to the Newton's law of viscosity, the shear stress is equal in magnitude to the momentum flux and is proportional to the velocity gradient of the momentum transfer.⁴ In the steady state, as the velocity gradient is constant, the shear stress must be the same throughout the system. Considering only the viscous force of the fluid, we can formulate the free energy change of the fluid due to the movement of an object through it as

$$dG = V dP - S dT + \eta A d v \quad (1)$$

where η is the viscosity of the fluid, A the resisting area, v the velocity of the moving object, and G , V , S , P and T are the general thermodynamic state functions. The shear free energy, G_{vis} , is defined as in the following.

$$G_{vis} = \eta = \frac{1}{A} \left(\frac{\partial G}{\partial v} \right)_{T,P} \quad (2)$$

The measured shear free energies are plotted as the func-

tion of pressure at 20 °C and at 60 °C in Figure 1 (A) and (B), respectively. The shear free energy increases as the pressure is raised. In the low pressure region, G_{vis} of chlorobenzene is higher and G_{vis} of toluene is lower than that of benzene, respectively. At 20 °C, G_{vis} of benzene rises more rapidly with pressure than that of other substituted benzenes and becomes the highest of the three above the pressure of about 900 bar. At 60 °C, G_{vis} of benzene still rises more rapidly relative to that of toluene or chlorobenzene, but not enough to make the curve crossing upto the pressure of 1,000 bar.

In a condensed phase such as the liquid state of substituted benzenes, intermolecular forces are large and play a dominant role in determining its physical properties. The viscosity, a macroscopic property, reflects the molecular cohesive forces.⁵ We can understand the relatively larger shear free energy of chlorobenzene in terms of the electronic charge distribution. Chlorobenzene has dipole-dipole interactions in addition to the dispersion interaction of benzene. When the pressure is low, the electrostatic interaction makes a first order contribution to the molecular cohesive force of chlorobenzene and results in the largest shear free energy among the three substituted benzenes.

In general, since the molecular interactions strongly depend on the intermolecular distance, the cohesive force has an inverse relation to the free volume of the system. The lower shear free energy of toluene can be explained in terms of molecular interaction. Because of the motion of the methyl group, a toluene molecule has larger free volume than benzene. In other words, benzene is more closely packed and experiences stronger cohesive force against the viscous flow than toluene.

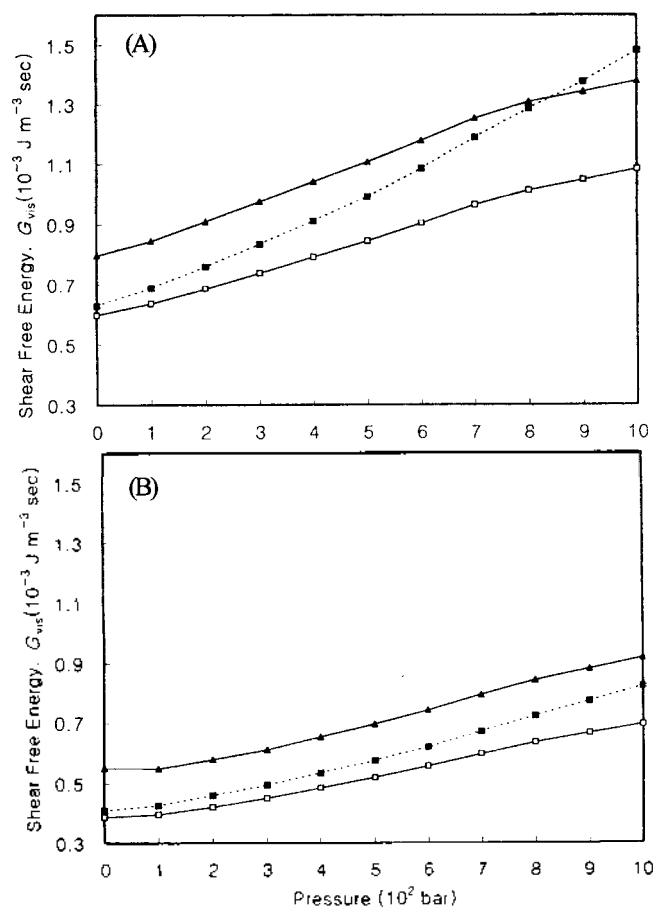


Figure 1. The Shear Free Energies of Fluids as a Function of Pressure at 20 °C (A) and 60 °C (B): —□— Toluene, ...■... Benzene, —▲— Chlorobenzene.

As the pressure is raised, the density of a fluid is increased and the intermolecular distance is decreased. Therefore, the free volume of the fluid is diminished and molec-

ules get more tightly packed at high pressure.⁶ This molecular event manifests as the increment in the shear free energy. The free volume reduction rate of benzene is greater than that of substituted benzenes as the pressure is raised. The slopes of the curves in Figure 1 indicate the trend. At low temperature, the free volume reduction, *i.e.*, molecular packing against the viscous flow, is more effectively enhanced for benzene as compared to substituted benzenes. At high temperature, however, increased thermal motion acts against molecular packing. Therefore, favorable packing of benzene does not result in excessive shear free energy over that of chlorobenzene upto 1,000 bar at 60 °C.

We can quantitatively understand the molecular interaction potential and molecular kinetic energies by examining the viscosity, a simple bulk property, at the molecular level. A detailed evaluation of molecular interactions can be performed through molecular simulations. A set of molecular dynamics simulations and complementary experiments with a diversity of substituted benzenes under extended pressure and temperature conditions are in progress.

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Resonance Energy Transfer in the Equilibrated Unfolding States of Human Tumor Necrosis Factor- α

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The protein folding study has attracted wide attentions in recent years as one of the most puzzling problems in the respect of the intermediates involved in the kinetic and equilibrium folding pathways.¹ The human Tumor Necrosis Factor- α (hTNF- α), a cytokine which has potent roles in a

wide range of cell regulatory, immune and inflammatory functions,² is ideal for folding studies because of its interesting trimeric native structure and β -sheet property.³ For these reasons, hTNF- α has been extensively investigated with regard to its structure, thermodynamics and kinetics of folding and unfolding.⁴

Resonance energy transfer is widely used in studies of

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