Critical Dynamic Viscosities in a Binary Mixture

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Ultrasonic shear measurements were conducted on polystyrene-cyclohexane solutions at 3, 51, and 252 kHz using the crystal fork and torsion methods. The real and imaginary parts of the complex shear modulus above the critical point are compared with modified theoretical expressions derived within the framework of the decoupled-mode theory. For this comparison, a background part was assumed to be described by a scaling form proposed by de Gennes. Numerical analysis of the data shows a satisfactory agreement between the theory and the experiments for ultrasonic shear data over a wide range of reduced frequency $\omega^*$. In addition, it is shown that the description of the simple viscosity dynamical scaling function is broken at a high-frequency limit.

KEY WORDS: critical phenomena; cyclohexane; polystyrene; shear modulus; ultrasonics; viscosity.

1. INTRODUCTION

In a previous paper [1], ultrasonic shear data along the critical isochore in xenon and in the binary mixture nitrobenzene--$n$-hexane were interpreted in terms of modified theoretical expressions derived within the framework of decoupled-mode theory. Although the numerical analysis of the data has shown a rather satisfactory agreement between the theory and the experiments for ultrasonic shear data, we did not claim that these tests are...
conclusive because of the scattering of our experimental data. Furthermore, we desired to improve the ultrasonic shear measurements and investigate the viscosity over a wide range of frequency in various binary systems in order to obtain more conclusive results. To improve the measurements we used a network analyzer system described later. By choosing a polymer solution as the binary mixture, we were able to test the theory over a wide range of reduced frequency $\omega^*$, because the polymer solution is characterized by a high viscosity and a large correlation length in comparison with simple pure fluids and binary mixtures of low molecular weight.

In this paper, we report measurements on the ultrasonic shear viscosity for polystyrene in cyclohexane at the critical solution concentration in the one-phase region as a function of temperature and frequency. This system has been thoroughly examined over the past decade by coexistence-curve measurements [2], light-scattering measurements [2, 3], static shear viscosity measurements [4], and line-width measurements [5]. These data enabled us to test the theory of the dynamic viscosity over a wide range of $\omega^*$. Experiments were conducted with a carefully fractionated polymer sample to minimize the effect of the molecular weight distribution.

2. EXPERIMENTAL

The fork and torsion crystal techniques described in previous papers [6–8] were used for dynamic viscosity measurements. The vibration of the crystal is damped by immersing it in a liquid to be measured, and the properties of liquid in shear may be calculated from the resulting changes in the resonant frequency $\Delta f$ and in the resistance $\Delta r$ corresponding to the resonant frequency on the motional admittance circle of the crystal, compared with the corresponding values in air. These quantities are related to the real and imaginary parts ($R$ and $X$, respectively) of the shear mechanical impedance $Z$ by the equations

$$Z = R + iX$$  \hspace{1cm} (1)

$$R = \Delta r/2\sqrt{2K}$$  \hspace{1cm} (2)

$$X = \Delta f/\sqrt{2K}$$  \hspace{1cm} (3)

where $K$ is a constant for a particular crystal and is determined from Newtonian liquids through the equation,

$$K = \Delta f/\sqrt{\rho_N \eta_N \omega}$$  \hspace{1cm} (4)

where $\rho_N$ and $\eta_N$ are the density and the viscosity in Newtonian liquids,