shear viscosity anomaly near the critical binary system of nitrobenzene and n-heptane
Shear Viscosity Anomaly near the Critical Binary System of Nitrobenzene and n-Heptane
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ABSTRACT

Shear viscosity measurements were made as a function of temperature near the critical point and critical concentration for the binary system of nitrobenzene and n-heptane. The results above the critical temperature $T_c$ were analyzed by the mode coupling theory and the Debye momentum cutoff was determined. The anomaly of viscosity was detected as a function of temperature and concentration.

I. INTRODUCTION

Nitrobenzene and n-heptane system has an upper critical solution temperature. The critical region of this system has been studied to determine the phase coexistence curve by viscosity coefficient measurements$^{[1,2,3]}$. Other properties of the system nitrobenzene and n-heptane which have been previously studied include: the absorption and velocity of ultrasound$^{[4]}$, diffusion coefficient$^{[5,6,7]}$, light-scattering$^{[8,9]}$, interferometric$^{[10]}$ and dilatometric measurements$^{[11]}$.

The critical temperature of this solution is $T_c=19.10^\circ C$, while the critical concentration in nitrobenzene mole fraction is $x_c=0.470$.

In the present work, further coefficients of shear viscosity are measured over a wide range of temperature and concentration using the mode coupling approach of Kawasaki$^{[12,13]}$, and Perl and Ferrell$^{[14]}$.

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II. THEORETICAL CONSIDERATIONS

The critical anomaly of the shear viscosity was predicted by the mode coupling theory of Kawasaki, and Perl and Ferrell according to the law \(^{(12,13,14)}\)

\[
\frac{\eta - \eta_c}{\eta} = \frac{A \eta}{\eta} = A \ln q_D + A \ln \xi
\]

where \(q_D\) is a Debye momentum cutoff which measures the reciprocal of correlation length, \(A\) is a constant which was calculated by D'Arrigo et al.\(^{(14)}\)

to be \(8 \frac{8}{5 \pi^2} \approx 0.054\). The shear viscosity \(\eta\) is temperature dependent at the critical concentration \(x_c\) which is given by the power law\(^{(15)}\)

\[
\eta = \eta_0 t^{-\beta_y}
\]

Here \(\eta_0\) is the noncritical or background part of the measured viscosity \(\eta\), and \(x_0, \beta_y\) are critical exponents\(^{(14,15)}\), \(x_0 \beta_y = 0.04\), where \(t = \frac{T - T_c}{T_c}\) is the reduced temperature (measuring the distance from the critical temperature \(T_c\)).

In addition the correlation length \(\xi\) is related to the reduced temperature \(t\) near the critical temperature and at critical concentration by the power law\(^{(14)}\)

\[
\xi = \xi_0 t^{\gamma}
\]

Where \(\xi_0\) is the coherence length of the concentration fluctuations and \(\gamma = 0.64\) is a critical exponent\(^{(14,15)}\)

III. EXPERIMENTAL TECHNIQUE

The viscosity was measured by using a Brookfield Digital Viscometer which rotates a sensing element in a fluid and measures the torque necessary to overcome the viscous resistance to the induced movement\(^{(16,17)}\). This is accomplished by driving the spindle through a beryllium copper spring. To control the temperature of the sample, a water jacket is provided with inlet and outlet attached to a thermostatic device consisting of a constant temperature water bath and water-pump circulating system. Thermostatic control error was \(\pm 0.01^\circ\)C. The purified chemicals were obtained from Fisher Scientific and were used without any further purification. The purity of both chemicals was 99%. The samples were prepared by weight using an Ohans 1600 series balance instrument and a Sartorius scale with a precision of 0.0001gm.
To ensure that the viscometer was operating properly, the shear viscosity of a standard liquid sample provided by the Brookfield Engineering Laboratories, Inc. was measured. The agreement of the measurements with the standard sample was good. Each viscosity value represents the average of several measurements. The error in the viscosity measurements was less than 0.2%.

IV. RESULTS AND DISCUSSION

The critical temperature $T_c$ for the system nitrobenzene and n-heptane is (equal to) 19.10 °C. The corresponding critical concentration $x_c$ is 0.470 mole fraction of nitrobenzene.

The data of shear viscosity were fit to the power law $\eta = \eta_0 \lambda^{-x_c \gamma}$, where $x_c$ and $\gamma$ are critical exponent,\(^{[14,15]}\), $x_c \gamma = 0.04$. A least square fit near the critical temperature yields value of $\eta_0 = 0.70$ centipoise. The noncritical part of viscosity $\eta_0$ is necessary to obtain the Debye momentum cutoff. A least square fit is shown in Fig.(1).

The viscosity at different concentrations is plotted versus temperature in Fig(2). The temperature dependence at critical concentration $x_c = 0.470$ indicates the presence of anomaly in the neighborhood of the critical temperature.

Fig(3) shows the viscosity versus concentration for five different temperatures (isothermal lines). An increase in the viscosity can also be seen approaching the critical temperature and concentration.

The light-scattering measurements of Brumberger and Pancirov\(^{[18]}\) give the range of intermolecular forces for the nitrobenzene n-heptane system $l = 9.3 \pm 0.04$ Å (Debye parameter).

The values of the range $l$ of the intermolecular forces and the coherence length of concentration $\xi_0$ can be compared. The coherence length of concentration $\xi_l = 0.2 l$ as shown by Klein and Woermann\(^{[15]}\) can be calculated to be 1.87 Å. The coherence length of concentration $\xi_0$, which can be determined by light-scattering experiments is defined by the power law Eq.(3):

$$\xi = \xi_0 l^\gamma$$

The critical exponent has a value of $\gamma = 0.64^{[14,15]}$. Using the mode coupling approach,
\[ \frac{\Delta \eta}{\eta} = \eta - \eta_r = A \ln q_d + A \ln \xi \]

and plotting the relative anomalous viscosity \( \frac{\Delta \eta}{\eta} \) versus the logarithm of the correlation length \( \xi \), the constant \( A \) and \( q_d \) can be determined. Fig. (4) shows that the slope of the straight line is the constant \( A = 0.058 \pm 0.002 \).

The Debye momentum cutoff can be determined from the intercept of Fig. (4), where \( q_d = 0.5 \AA \). Swinney and Henry\(^{(18)}\) and D’Arrigo et al\(^{(14)}\) obtained the constant \( A \) experimentally to be 0.054 and 0.056 respectively. Our value of \( A \) is in good agreement with the literature values\(^{(14, 18)}\).

References
Fig. (2): The experimental shear viscosity as a function of temperature and concentration.

Fig. (1): The measured values of the shear viscosity and n-heptane critical mixture.
Fig. (4): The relative anomaly of shear viscosity \( \nu_s \).

The correlation length

(3) The measured values of the shear viscosity \( \nu_s \) concentration for different temperatures.

(\text{concentration})