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Concentration and Temperature Dependence of Shear Viscosity of the Critical Mixture of Nitroethane and 3-Methylpentane

لزوجة الخليط نيترويثين و٣ - ميثيلبنتين واعتماده على درجة الحرارة والتركيز

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Abstract

Shear viscosity coefficients of nitroethane and 3-methylpentane mixture have been measured using digital viscometer. The measured values were over the entire concentration range above the critical temperature (T_c = 299.590 K) in the range 0.040 $\leq$ T- T_c $\leq$ 18.570 K. The results above the critical temperature T_c were analyzed by the mode coupling theory. The anomaly of shear viscosity was detected as a function of temperature and concentration. A least square fit near the critical temperature yields a value of noncritical part of shear viscosity η_0 = 0.358 cP. The Debye momentum cutoff q_D and the constant A in the mode coupling approach were determined. Our values of η_0 and A are in good agreement with the literature values.

ملخص

لقد تم دراسة اللزوجة واعتمادها على درجات الحرارة للخليط الثنائي نيترويثين – ٣ – ميثيلبنتين في حالة التركيز الحرج وفوق درجة الحرارة الحرجة للخليط. وقد استخدمت نظرية الازدواج في تحليل النتائج، وأظهرت الدراسة ظاهرة غير عادية للزوجة نتيجة اعتمادها على درجات الحرارة وتركيز الخليط.

وأظهرت النتائج توافق كبير بين النتائج العملية والنظرية

I. Introduction

The existence of shear viscosity anomaly has been experimentally observed in some binary liquid systems near the critical temperature and concentration [1,2,3]. The critical region of the Nitroethane and 3-methylpentane system (NE + 3MP) has been studied to determine the phase coexistence curve using a visual and a float technique [4]. This system has an upper critical solution temperature T_c = 299.590 K. The tracer diffusion coefficients of the binary mixture have been determined at several temperatures [5]. The acoustic velocity and attenuation behavior of NE + 3MP have been investigated by Harada *et al* [6] and Garland *et al* [7]. The asymptotic critical behavior of the thermal expansion coefficient and of the specific heat were determined and reported [8]. By varying the static pressure, the adiabatic thermal pressure coefficient and the adiabatic coupling constant near the critical point have been obtained [9].

Experimental data of shear viscosity coefficients are important for the scientists working on the improvement of molecular theories.

In the present work, we have measured the shear viscosities over the entire composition range and over a large temperature range including temperatures very close to critical temperature T_c to determine the Debye momentum cutoff and a constant A in the mode-coupling theory. [1,10] Determining this constant using nitroethane and 3-methylpentane system for the first time supports the mode-coupling theory of the anomalous viscosity. In general, our constants determined by experimental measurements of the chosen system will support the constants obtained by theoretical calculations using mode-coupling theory.

II. Theory

The mode coupling approach of Kawasaki [1] and Perl and Ferrell [10] predicts a critical anomaly of the shear viscosity coefficient according to the law

$$(\eta-\eta_0)/\eta = \Delta\eta/\eta = A \ln \xi + A \ln q_D,$$

where η_0 is the noncritical part of the measured shear viscosity η. The constant A was calculated by D'Arrigo *et al* [11] and given by $A = 8/15\pi^2 \approx 0.054$, and q_D is a Debye momentum cutoff.

The shear viscosity η is temperature dependent at the critical concentration which is given by the power law [12]:

$$\eta = \eta_0 \, t^{-x\eta\nu}.$$

Here x_η and ν are critical exponents [11,13], $x_\eta\nu = 0.04$, $t = (T- T_c) / T_c$ is the reduced temperature, which measures the relative distance from the critical temperature T_c. The correlation length ξ is related to the reduced temperature t near the critical temperature and at critical concentration by the power law [12]:

$$\xi = \xi_0 \, t^{-\nu}$$

where ξ_0 is the coherence length of the concentration fluctuations, and $\nu = 0.64$ is a critical exponent [11,13].

III. Experimental Technique

Measurements have been made with a Brookfield Digital DV-I + Viscometer. The Brookfield DV- I + Viscometer measures fluid viscosity at given shear rates. The principle of operation is to drive a spindle (which is immersed in the test fluid) through a calibrated spring. The viscous drag of the fluid against the spindle is measured by the spring deflection. Spring deflection is measured with a rotary transducer. The measurement range of a DV- I + (in centipoise or miliPascal seconds) is determined by the rotational speed of the spindle, the size and shape of the spindle, the container the spindle is rotating in, and the full scale torque of the calibrated spring [14].

The purified chemicals of nitroethane and 3-methylpentane were obtained from Fisher Scientific and used without any further purification. The 3-methylpentane was used with a purity better than 99.9% and nitroethane with a purity of 99%. The shear viscosity of a standard liquid sample provided by the Brookfield Engineering Laboratories Inc. was measured and showed a very good agreement with a standard value. Each measured datum of the viscosity of nitroethane and 3-methylpentane samples represents the average of five measurements. The error in the viscosity measurement was less than 0.2%.

IV. Experimental Results and Discussion:

The critical temperature T_c for the system nitroethane and 3-methylpentane is $T_c = 299.6$ K. The corresponding critical concentration x_{cnit} is 0.51 mole fraction of nitroethane [7,9].

The values of shear viscosity coefficients at different temperatures across the entire composition range of nitroethane are shown in Fig.(1). The temperature dependence at critical concentration $x_{cnit} = 0.5078$ indicates the presence of anomaly in the neighborhood of the critical temperature. In addition, the temperature dependence of the viscosity at the critical composition is quite different from the behavior of the pure components indicating the absence of anomaly in the viscosity in the neighborhood of the critical temperature. The data of shear viscosity were fit to the power law $\eta = \eta_0 \ t^{-x\eta\nu}$, where x_η and ν are critical exponents [11,13]. A least square fit near the critical temperature yields value of $\eta_0 = 0.358$ centipoise. The noncritical part of viscosity η_0 is necessary to obtain the Debye momentum cutoff. A least square fit is shown in Fig. (2). Burstyn and Sengers [15] have obtained the value of η_0 to be 0.372 centipoise. Our value of η_0 is in good agreement with Burstyn and Sengers value.

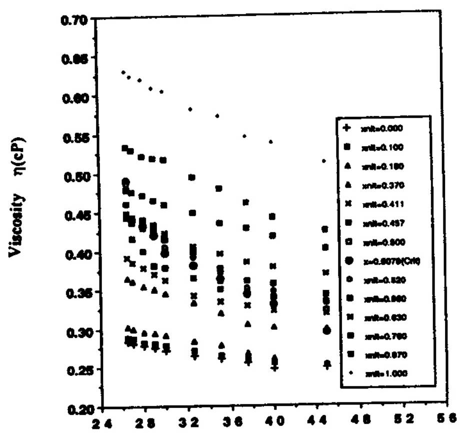

Figure 1: The experimental shear viscosity as a function of temperature and concentration.

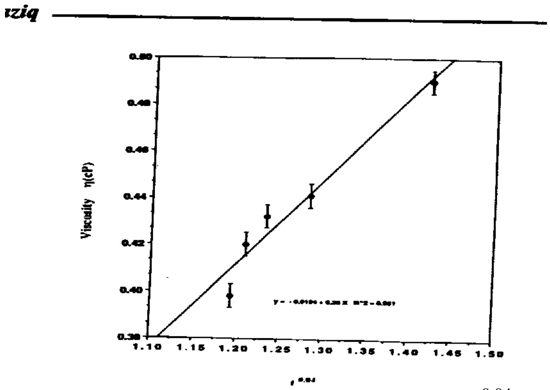

Figure 2: The measured values of the shear viscosity η(cP) Vs. $t^{-0.04}$ for nitroethane and 3-methylpentane critical mixture.

Fig. (3) shows the shear viscosity versus concentration for five different temperatures (isothermal lines). The large anomaly in the viscosity coefficient near the T_c becomes apparent. It is unexpected [1] that a slight anomaly is noticeable even at 32.5 ^{0}C, some 8 ^{0}C above the critical temperature. The correlation length ξ is related to the reduced temperature by light –scattering experiments by $\xi = \xi_0\, t^{-v}$, where ξ_0 = 2.13 is the critical amplitude coherence length of local concentration fluctuations [7,16]. The intermolecular force range L (Debye parameter) can be calculated from light-scattering experiment by the relation [13]:

$L = 2.45\, T_c^{[(\gamma-1)/2]}\, \xi_0$, where $\gamma = 1.25$. For $T_c \approx 300$ K we obtain, L = 10.65 .

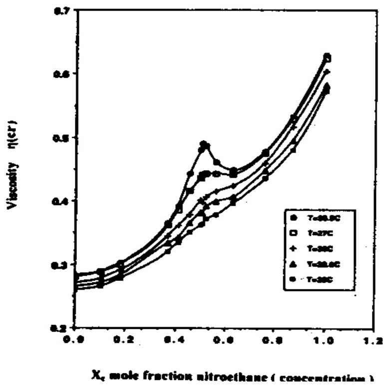

Figure 3: The measured values of shear viscosity Vs. concentration for different temperatures.

The relative anomalous viscosity $\Delta\eta/\eta$ is plotted versus the logarithm of the correlation length ξ in Fig. (4). For large values of ξ ($\xi \geq$ 45), we have straight line with the slope A = 0.054 ± 0.002 as determined by a visual fit. From the intercept we get q_D^{-1} = 3.64 , where q_D = 0.275 $^{-1}$ is the Debye momentum cutoff. Swinney and Henry [17], D'Arrigo *et al* (11) and Abdelraziq *et al* (14) obtained the constant A experimentally to be 0.054, 0.056 and 0.058, respectively. Our value of A is in good agreement with the literature values. We note that the product $A\nu$, which is the index for the anomalous viscosity along the critical concentration, has the value 0.035, which is identical with the results obtained by Ohta [18].

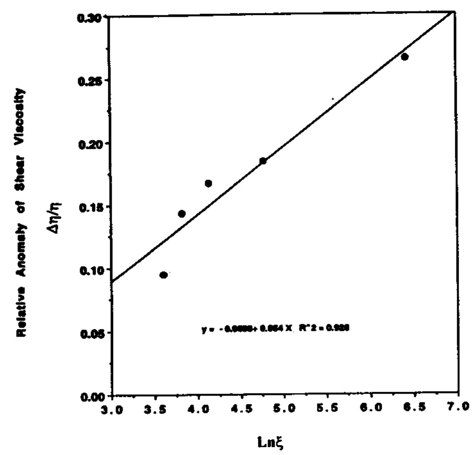

Figure 4: The relative anomaly of shear viscosity Vs. the correlation length.

Table (1) shows the measured and calculated values of the constant A in the mode-coupling theory using Nitroethane and 3-methylpentane and other different systems.

Table 1: The measured and calculated values of the constant A in this work and others for different binary mixture systems.

Binary mixture system	Calculated Constant A	Measured Constant A	Reference
Aniline-cyclohexane.		0.056	D'Arrigo (11)
Aniline- cyclohexane.	0.054		D'Arrigo (11)
Triethylamine-water.		0.054	Swinney and Henry (17)
Nitrobenzene n-heptane.		0.058	Abdelraziq (14)
Nitroethane and 3-methylpentane.		0.054	This work

It is apparent that the agreement of the constant A with the experimental results for different mixtures is quite good and independent on mixtures. The slightly different values are probably due to different evaluation of the background or non-critical part η_0 of the measured viscosity η. The intermolecular force range L (Debye parameter), has been obtained to be 10.65 . In addition, the Debye momentum cutoff. q_D is determined to be 0.275 $^{-1}$ Determining these constants using Nitroethane and 3-methylpentane system for the first time support the mode-coupling theory of the anomalous viscosity.

V. Conclusion

In this paper the noncritical part of shear viscosity has been determined. The intermolecular force range L (Debye parameter), has been obtained to be 10.65 . In addition, the Debye momentum cutoff, q_D, is determined to be 0.275 $^{-1}$.

The values of L, q_D and A constants, experimentally measured here for nitroethane and for 3-methylpentane systems, are in good agreement with our earlier samples containing organic systems. The overall data, experimentally measured in this laboratory, support the data obtained by theoretical calculations using the Mode coupling approach and add to its credibiltity.

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