Viscosity of Nitrobenzene–*n*-Pentane and Nitrobenzene–*n*-Heptane Systems

Eizo Sada,* Katsuroku Takahashi, and Mitsuhiro Hamada
Department of Chemical Engineering, University of Nagoya, Nagoya, Japan

The viscosities for two systems, nitrobenzene–*n*-pentane and nitrobenzene–*n*-heptane, have been measured for various concentrations and temperatures between 20 and 40 °C. The viscosity in the neighborhood of critical point of solution becomes anomalously large. The excess viscosity at the critical point leads to a cusp rather than an infinity.

The anomalous increase in viscosity for a binary mixture in the neighborhood of the critical point of solution has been known since the beginning of this century. Fixman (*5*) first theoretically treated this phenomena on the basis of the mean field theory, and predicted a strong divergence in viscosity near the critical point. Woermann and Sarholz (*12*) and other investigators (*3, 10*) tried to compare the measured data with Fixman's theory, and the comparison was found to be satisfactory only when the temperature was not too close to the critical temperature. On the other hand, Kadanoff and Swift (*7*) predicted on the basis of the dynamical scaling law that the singularity of the viscosity at a critical point was at most a very weak divergent or perhaps a cusp. This prediction was confirmed by many measurements (*1, 2, 6, 9*). Recently Kawasaki (*8*) reported on the basis of the mode–mode coupling theory, that the viscosity could not diverge at the critical point. The measurements by Stein et al. (*11*) supported this qualitative prediction.

In this work, the viscosities for two systems, nitrobenzene–*n*-pentane and nitrobenzene–*n*-heptane, have been measured for various concentrations. The viscosities in the neighborhood of the critical point have been minutely measured, and the excess viscosities and the temperature and concentration ranges with the anomalous increase in viscosity are discussed.

Experimental Section

Wako special-grade nitrobenzene, *n*-pentane, and *n*-heptane were used without further purification. The purity of these materials was checked by the analytical gas chromatography using a Porapak Q column. The minimum purity of these materials was recorded to be 99.9 mole %.

Viscosity data were obtained with a standard Ostwald-type capillary viscometer. The viscometer was sealed with the Teflon stopper. The seal was found to be so effective that the phase-separation temperature of the mixture in the neighborhood of the critical mixture did not change in the viscometer even when the viscometer was soaked in a water bath for a few days. The flow time of liquid mixture through the capillary was measured within 0.2%. The viscometer was calibrated with pure substances such as water, nitrobenzene, *n*-pentane, and *n*-heptane.

Table I. Viscosity and Density for the Nitrobenzene–*n*-Pentane System

Mole fraction	Viscosity, cP								Density, g cm^{-3}	
x_{NB}	20 °C	24 °C	24.02 °C	24.5 °C	25 °C	26 °C	32 °C	40 °C	(25 °C)	$10^3(-d\rho/dt)$
0.0998	0.272	0.262		0.261	0.260	0.257	0.245	0.229	0.6704	0.995
0.1994	0.336	0.322		0.321	0.319	0.316	0.298	0.277	0.7266	0.976
0.2990		0.420	0.420	0.415	0.411	0.404	0.373	0.342	0.7833	0.967
0.3491		0.520	0.517	0.488	0.476	0.461	0.417	0.380		
0.3832			0.614	0.532	0.515	0.498	0.447	0.403		
0.3990		0.596	0.591	0.550	0.536	0.518	0.466	0.424	0.8408	0.963
0.4589		0.603	0.602	0.592	0.584	0.571	0.520	0.471		
0.4940		0.623	0.623	0.616	0.610	0.600	0.551	0.503	0.8961	0.964
0.5984	0.790	0.748		0.743	0.738	0.729	0.677	0.616	0.9567	0.968
0.6995	0.972	0.921		0.915	0.909	0.897	0.831	0.753	1.0165	0.974
0.7997	1.221	1.150		1.142	1.134	1.118	1.031	0.929	1.0754	0.980
0.9000	1.549	1.452		1.441	1.430	1.406	1.284	1.143	1.1345	0.986

Table II. Viscosity and Density for the Nitrobenzene–*n*-Heptane System

Mole fraction	Viscosity, cP							Density, g cm^{-3}	
x_{NB}	19.03 °C	19.5 °C	20 °C	22 °C	26 °C	32 °C	40 °C	(20 °C)	$10^3(-d\rho/dt)$
0.1490			0.482	0.471	0.451	0.423	0.391	0.7421	0.879
0.2214			0.532	0.517	0.498	0.463	0.425	0.7724	0.888
0.2746			0.580	0.562	0.539	0.503	0.459	0.7954	0.894
0.3291	0.642	0.636	0.631	0.611	0.579	0.536	0.491	0.8198	0.897
0.4214	0.805	0.777	0.759	0.720	0.670	0.615	0.558	0.8632	0.904
0.4477	0.906	0.831	0.805	0.759	0.702	0.643	0.580		
0.4729	1.017	0.875	0.845	0.790	0.730	0.678	0.602		
0.4886	0.999	0.891	0.862	0.808	0.746	0.681	0.613	0.8965	0.913
0.5628	0.965	0.951	0.937	0.896	0.836	0.764	0.689	0.9348	0.922
0.6392	1.033	1.025	1.016	0.984	0.926	0.850	0.770	0.9765	0.930
0.7954			1.313	1.274	1.201	1.104	0.984	1.0682	0.948
0.8751			1.517	1.475	1.385	1.260	1.124	1.1186	0.955

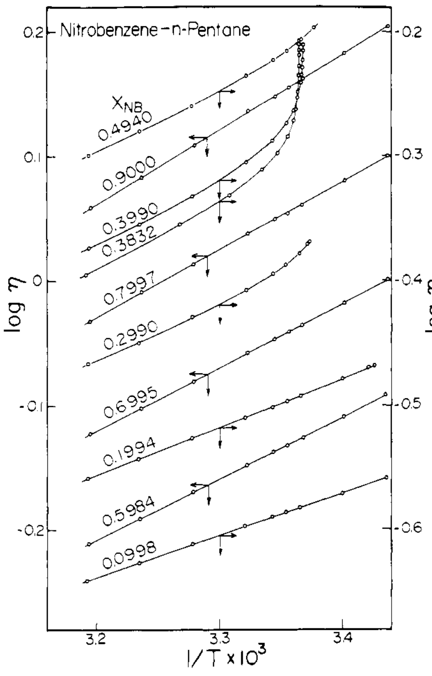

Figure 1. Log η vs. $1/T$ for the nitrobenzene-*n*-pentane system.

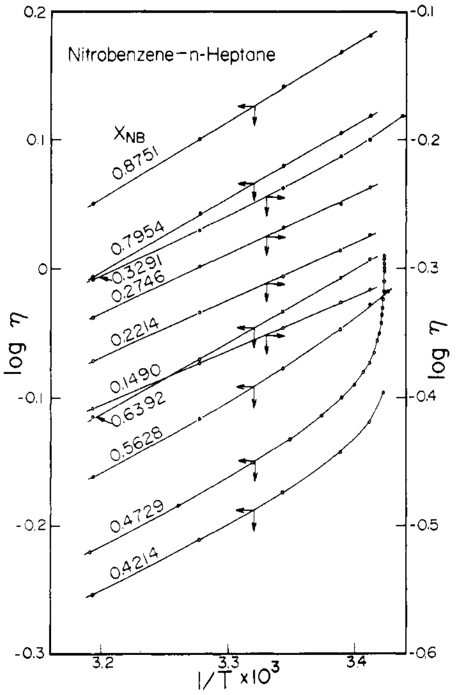

Figure 2. Log η vs. $1/T$ for the nitrobenzene-*n*-heptane system.

A pycnometer, consisting of the seal stopper, the graduated capillary part, and the bulb part, was used to determine the density of the binary mixture, and it was calibrated with pure water. The viscometer and the pycnometer were kept in a water bath controlled to ±0.001 °C. The temperature was measured by a Beckmann thermometer and a digital thermister.

Results and Discussion

The experimental data of the viscosity of the binary system nitrobenzene-*n*-pentane over the various compositions and temperatures are listed in Table I. In this table the densities at 25 °C and the temperature dependencies of the density are also cited. The similar data of the nitrobenzene-*n*-heptane system are given in Table II. The composition and temperature of the critical point of solution for the nitrobenzene-*n*-pentane system are 0.383 and 24.01 °C, and those for the nitrobenzene-*n*-heptane system are 0.473 and 19.03 °C.

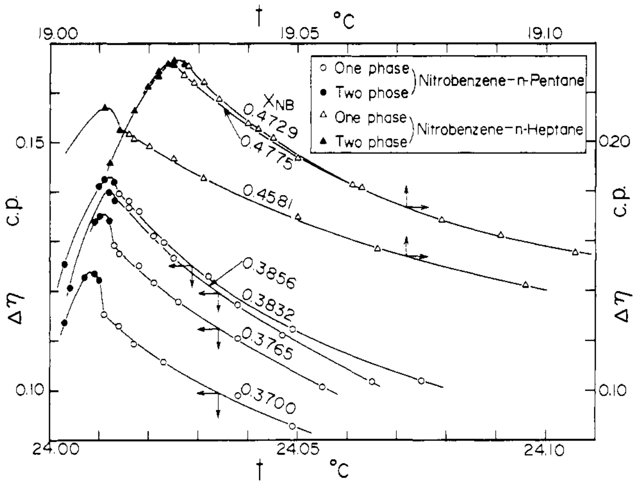

Figure 3. Excess viscosity in the neighborhood of the critical point.

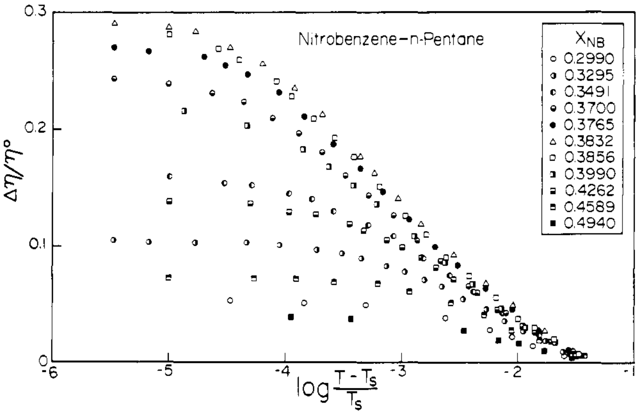

Figure 4. Relative excess viscosity of the nitrobenzene-*n*-pentane system.

Common logarithms of the viscosity for the nitrobenzene-*n*-pentane and the nitrobenzene-*n*-heptane systems, are plotted against $1/T$ in Figures 1 and 2, respectively. The values of log η in both systems rapidly increase with $1/T$ in the neighborhood of the critical point because of the singular behavior of the viscosity, but otherwise the points in these figures fall on the straight line and obey the Arrhenius relation

$$\log \eta = A\left(\frac{1}{T}\right) + B \tag{1}$$

When the viscosities for both systems were plotted against the composition of mixture, it was noticed that there is no anomalous increase of the viscosity at the temperature of 40 °C even for the composition of critical mixture. In the neighborhood of the critical point, the viscosity is divided into the ideal part η^0 and the excess part $\Delta\eta$. The ideal viscosity η^0 is assumed to obey the Arrhenius relation and is estimated by eq 1. In this estimation A in eq 1 is obtained by the interpolation from the values of the mixtures far from the critical point, and B is determined by using the viscosity at 40 °C. The excess viscosity $\Delta\eta = \eta - \eta^0$ in the neighborhood of the critical point is shown in Figure 3. It increases with the decrease of temperature in the homogeneous phase. When the temperature is decreased beyond the phase-separation point, $\Delta\eta$ becomes maximum and decreases rapidly with the further decrease of temperature. The temperature at

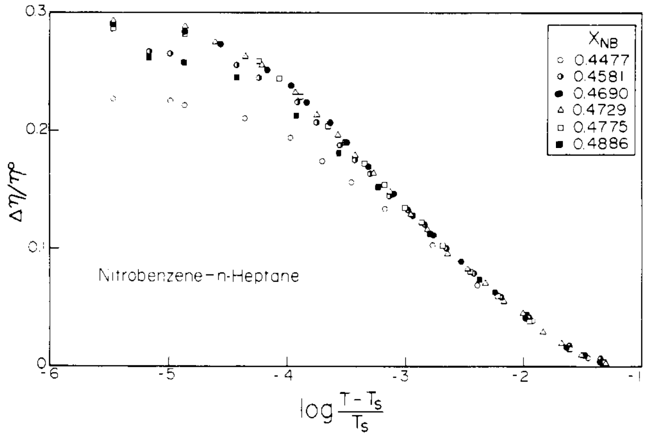

Figure 5. Relative excess viscosity of the nitrobenezene-*n*-heptane system.

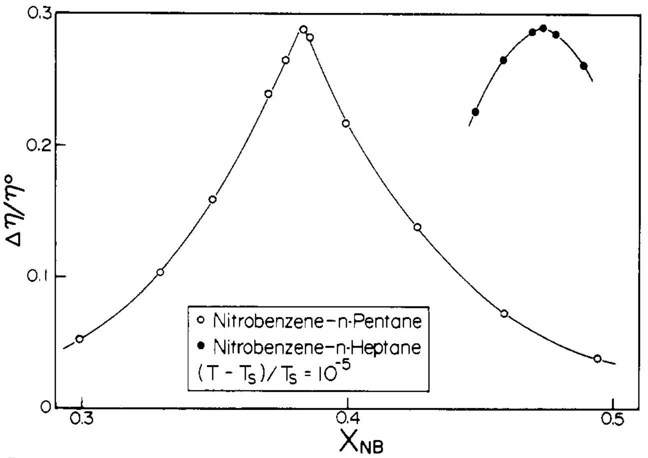

Figure 6. Relative excess viscosity at temperatures of $(T - T_s)/T_s = 10^{-5}$.

Table III. Viscosity for Critical Mixture of Nitrobenzene-*n*-Pentane ($x_{NB,c} = 0.383$, $t_c = 24.013$ °C)

t, °C	η, cP	$\Delta\eta$, cP	t, °C	η, cP	$\Delta\eta$, cP
24.014	0.620	0.140	24.187	0.558	0.075
24.016	0.619	0.138	24.292	0.546	0.067
24.018	0.617	0.136	24.452	0.535	0.057
24.023	0.610	0.130	24.849	0.520	0.044
24.032	0.604	0.123	25.606	0.504	0.032
24.049	0.593	0.112	26.732	0.489	0.023
24.075	0.583	0.102	29.13	0.466	0.012
24.143	0.565	0.085	32.84	0.442	0.007

Table IV. Viscosity for Critical Mixture of Nitrobenzene-*n*-Heptane ($x_{NB,c} = 0.473$, $t_c = 19.027$ °C)

t, °C	η, cP	$\Delta\eta$, cP	t, °C	η, cP	$\Delta\eta$, cP
19.028	1.022	0.231	19.247	0.906	0.117
19.031	1.015	0.225	19.352	0.889	0.102
19.034	1.008	0.217	19.476	0.878	0.092
19.040	0.999	0.208	19.694	0.859	0.075
19.045	0.992	0.202	20.010	0.845	0.064
19.061	0.973	0.183	20.42	0.831	0.055
19.079	0.959	0.168	21.02	0.812	0.042
19.106	0.945	0.155	21.94	0.794	0.034
19.137	0.931	0.141	23.27	0.768	0.021
19.183	0.919	0.129	25.51	0.736	0.011

which $\Delta\eta$ becomes maximum is about 0.002 °C lower than the phase-separation temperature. It is difficult to determine the composition of critical mixture from the phase-separation temperature, because the temperature varies little with the composition of mixture in the neighborhood of the critical point. On the other hand, the maximum excess viscosity considerably varies with the composition of mixture in the neighborhood of the critical point. The composition of mixture which gives the largest maximum excess viscosity is regarded as the composition of critical mixture. From the curve of the critical mixture in Figure 3, the viscosity does not seem to diverge to infinity at the critical point.

The relative excess viscosities for various compositions of mixture are plotted against log $[(T - T_s)/T_s]$ in Figures 4 and 5 for the nitrobenzene-*n*-pentane and the nitrobenzene-*n*-heptane systems, respectively, where T_s is the phase-separation temperature. The excess viscosity increases with the decrease of $(T - T_s)/T_s$, and it becomes larger as the composition of the mixture approaches that of the critical mixture. When the composition of the mixture is far from the critical mixture, $\Delta\eta/\eta^0$ varies little for the small value of $(T - T_s)/T_s$. For any composition of the mixtures, $\Delta\eta/\eta^0$ becomes zero at almost the same value of $(T - T_s)/T_s$; that is, the excess viscosity $\Delta\eta$ is zero when $(T - T_s)$ is larger than about 10 K. Figure 4 in comparison with Figure 5 shows that the curves for the critical mixture of the two systems are quite alike.

The relative excess viscosities at $(T - T_s)/T_s = 10^{-5}$ are shown in Figure 6. The excess viscosity is maximum at the critical mixture, and it symmetrically decreases with the change of composition of the mixture. For the nitrobenzene-*n*-pentane system the excess viscosity sharply changes in the neighborhood of the critical mixture, while it changes rather slowly in the same region for the nitrobenzene-*n*-heptane system. The relative excess viscosities at the critical point are about 0.29 for both systems.

The viscosity and the excess viscosity of the critical mixture are given in Tables III and IV for the nitrobenzene-*n*-pentane and the nitrobenzene-*n*-heptane systems, respectively. These data were fitted to the following equation

$$\Delta\eta = \left(\frac{A}{\alpha}\right)(\epsilon^{-\alpha} - 1) + B \qquad (2)$$

where ϵ is $(T - T_c)/T_c$ and T_c is the critical temperature. Fisher (*4*) pointed out that a value of α in $-1 < \alpha < 0$ gives a cusp, $\alpha = 0$ a logarithmic divergence, and that in $\alpha > 0$ a power-law divergence. The fitted parameters are: for nitrobenzene-*n*-pentane, $A = 0.0594 \pm 0.0114$, $B = -0.182 \pm 0.008$, $\alpha = -0.154 \pm 0.051$, for $3.4 \times 10^{-6} < \epsilon < 10^{-2}$; and for nitrobenzene-*n*-heptane, $A = 0.0859 \pm 0.0123$, $B = -0.273 \pm 0.019$, $\alpha = -0.135 \pm 0.039$, for $3.4 \times 10^{-6} < \epsilon < 10^{-2}$. The values of the exponent are of the same order for these two systems, and they are both negative. The values are close to those obtained by Allegra et al. (*1*) for the isobutyric acid–water system. The present results seem to support the prediction of Kadanoff–Swift that the singularities of the viscosity at the critical point lead to a cusp rather than an infinity.

Glossary

t	temperature, °C
t_c	critical temperature, °C
T	temperature, K
T_c	critical temperature, K
T_s	phase-separation temperature, K
x_{NB}	mole fraction of nitrobenzene
$x_{NB,c}$	mole fraction of nitrobenzene of critical mixture
ϵ	$(T - T_c)/T_c$
η	viscosity, cP
η^0	ideal viscosity, cP
$\Delta\eta$	excess viscosity, cP
ρ	density, g cm^{-3}

Literature Cited

(1) Allegra, J. C., Stein, A., Allen, G. F., *J. Chem. Phys.*, **55**, 1716 (1971).
(2) Arcovito, G., Falaci, C., Roberti, M., Mistura, L., *Phys. Rev. Lett.*, **22**, 1040 (1969).
(3) Brunet, J., Gubbins, K. E., *Trans. Faraday Soc.*, **65**, 1255 (1969).
(4) Fisher, M. E., *Rep. Prog. Phys.*, **30**, 615 (1967).
(5) Fixman, M., *J. Chem. Phys.*, **36**, 310 (1962).
(6) Hung, J. S., Webb, W. W., *Phys. Rev. Lett.*, **23**, 160 (1969).
(7) Kadanoff, L. P., Swift, J., *Phys. Rev.*, **166**, 89 (1968).
(8) Kawasaki, K., *Ann. Phys. (N.Y.)*, **61**, 1 (1970).
(9) Leister, H. M., Allegra, J. C., Allen, G. F., *J. Chem. Phys.*, **51**, 3701 (1969).
(10) Masuda, U., Murata, N., Kajiwara, T., *Nihonkagakukaishi*, 1253 (1973).
(11) Stein, A., Davidson, S. J., Allegra, J. C., Allen, G. F., *J. Chem. Phys.*, **56**, 6164 (1972).
(12) Woermann, D., Sarholz, W., *Ber. Bunsenges.*, **69**, 319 (1965).

Received for review September 20, 1976. Accepted March 14, 1977.

The Equilibrium Phase Properties of the Nitrogen–Isopentane System

Thamra R. Krishnan, Harish Kalra, and Donald B. Robinson*
Department of Chemical Engineering, University of Alberta, Edmonton, Alberta, Canada T6G 2G6

Vapor and liquid equilibrium phase compositions and refractive indices have been determined for the nitrogen–isopentane system at 40.0, 99.8, 159.8, and 219.6 °F from the vapor pressure of isopentane to about 3000 psia. The equilibrium ratios for each component were calculated at each temperature from the phase composition data. The equilibrium phase densities were calculated from the measured phase compositions and refractive indices using the Lorentz–Lorenz molar refractivity relationship.

Nitrogen is frequently present in natural gas and related fluids and consequently its presence must be recognized when determining the thermodynamic properties of these multicomponent systems. As in the case of other nonhydrocarbon components, the binary interaction parameters between nitrogen and paraffin hydrocarbons are normally not small enough to be neglected. One way of obtaining these parameters is by using experimental data obtained by measuring equilibrium phase compositions. The object of the work undertaken in this study was to obtain phase behavior data on mixtures of nitrogen and isopentane at pressures up to about 3000 psia and over a temperature range from about 40 to 220 °F. As far as could be determined, no previous studies have been reported on this system.

Experimental Method

The experimental method used in this work was essentially the same as that used in several earlier studies on other systems. This was described in detail in papers by Besserer and Robinson (*2, 3*) and more recently by Kalra et al. (*8*). The equilibrium cell was of the variable volume type with provision for sampling both liquid and vapor phases at equilibrium and for determining the refractive index of each phase.

The system temperature was measured with a calibrated iron–constantan thermocouple relative to an ice junction such that the temperature is believed known to ±0.1 °F. The pressure was measured with a calibrated 0–3000 psi Heise gauge equipped with a type 316 stainless steel bourdon tube. The pressure measurements are thought to be reliable within ±0.1% full scale.

The phase compositions were determined with a Model 700 Hewlett-Packard chromatograph using a thermal conductivity cell detector. The chromatographic column was 3 ft long by ⅛ in. in diameter and was packed with Porapak QS. It was maintained at a temperature of 172 °C. The response factor for converting from area to mole fraction was 1.9889 for nitrogen relative to 1.0000 for isopentane. This factor was obtained by using pure component samples in a 0.5-mL sample loop at pressures up to about 200 mm of mercury. Over this range, the response was linear with sample size. The compositions are believed known to ±0.005 mole fraction.

Materials

The nitrogen used in this work was obtained from a local supplier and was stated to have a minimum purity of 99.99 mole %. A sample of the material was analyzed on a silica gel column and no impurity peaks were detected. The isopentane was Phillips petroleum research grade having a reported purity of 99.99+ and it was used without further treatment