

## Viscosity and Diffusivity of a Binary Liquid Mixture of Critical Composition: Study of the System 2-Butoxyethanol/Water

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Results of measurements of the temperature dependence of the shear viscosity and the mutual diffusion coefficient of a 2-butoxyethanol/water mixture of critical composition are reported. The shear viscosities are measured with a capillary viscometer, and the diffusion coefficients by dynamic light scattering. The viscosity data are used to determine the regular (background) and the singular (critical) part of the viscosity [ $\eta_b$ ;  $\eta = \eta_b(Q_0\xi)^{-\nu}$ ] and to analyze the crossover regime.  $Q_0$  has a value of  $Q_0 = (1.54 \pm 0.60) \times 10^6 \text{ cm}^{-1}$ , which is small for a binary mixture of components of small molar mass. The viscosity is dominated by singular contributions in a narrow temperature range ( $T_c - T \leq 1.2 \text{ K}$ ). The singular contributions can be neglected for temperatures ( $T_c - T \geq 11 \text{ K}$ ). The function  $\eta = \eta_b \exp\{z_\eta H\}$ , given in the literature, represents the viscosity data in the temperature range  $3 \text{ mK} \leq (T_c - T) \leq 25 \text{ K}$  using the asymptotic form of the function  $H$  for  $(q_d/q_c) \rightarrow 0$  ( $q_d, q_c$ , parameter of the theory). This limit corresponds to the case in which the background diffusion coefficient  $D_b$  can be neglected. The reduced diffusion coefficient  $D^*$  calculated from the light-scattering data as a function of the scaling variable  $x (= q\xi)$  is represented by the approximation of the dynamic scaling function proposed in the literature.

**KEY WORDS:** critical phenomena; shear viscosity; diffusivity; dynamic scaling.

### 1. INTRODUCTION

Approaching the critical point of a binary liquid mixture of critical composition from the homogeneous one-fluid phase region of the phase diagram, it is observed that the shear viscosity exhibits a weak divergence

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and the mutual diffusion coefficient a strong convergence (“critical slowing down”) [1–4]. In the treatment of dynamic critical phenomena [5–7], it is customary to separate the mutual diffusion coefficient and the viscosity into a regular background part and a singular critical part. The principle of dynamic scaling implies that the critical diffusion coefficient  $D_c$  should depend on the scaled variable  $x [= q\xi$ ;  $\xi$ , correlation length of local concentration fluctuations;  $q$ , absolute value of the scattering vector,  $q = (4\pi/\lambda) \sin(\Theta/2)$ ;  $\lambda$ , wavelength of incident light in the scattering medium;  $\Theta$ , scattering angle]. Burstyn et al. [9] have given an approximant for the dynamic scaling function of the form:

$$D_c = \Gamma_c/q^2 = R[k_B T/(6\pi\eta\xi)] \Omega_K(x)[1 + (x/2)^2]^{-z_\eta/2} \quad (1)$$

with

$$\Omega_K(x) = [3/(4x^2)][1 + x^2 + (x^3 - 1/x) \arctan(x)] \quad (2)$$

$$\eta = \eta_b(Q_0\xi)^{-z_\eta} \quad (3)$$

$\Gamma$  is the reciprocal of the time constant of the autocorrelation function of scattered intensity [assuming that the diffusion coefficient  $D (= D_c + D_b)$  is measured by dynamic light-scattering experiments];  $\Gamma_c$ , the singular contribution to  $\Gamma$ ;  $\Gamma_b$ , the background contribution to  $\Gamma$ ;  $R$ , the amplitude of the correction to the Stokes–Einstein diffusion law (universal constant  $R = 1.03$  [2]);  $k_B$ , the Boltzmann constant;  $\xi$ , the correlation length of local concentration fluctuations ( $\xi = \xi_0 t^{-\nu}$ ;  $t = |T - T_c|/T_c$ ;  $\nu$ , universal critical exponent, theoretical value  $\nu = 0.630$ );  $\Omega_K(x)$ , the Kawasaki function;  $z_\eta$ , the universal critical exponent, theoretical value  $z_\eta \approx 0.065$ ;  $\eta$ , the shear viscosity ( $\eta_b$ , background contribution); and  $Q_0$ , the system-specific critical amplitude of viscosity.

There are several theoretically calculated values of  $z_\eta$  in the literature ( $0.050 \leq z_\eta \leq 0.065$ ). A review of experimentally determined values of  $z_\eta$  has shown that a large number of experimental data are consistent with the theoretical value of  $z_\eta = 0.065$  [3, 4]. Equation (3) represents the asymptotic behavior of the viscosity near the critical temperature. Far away from  $T_c$  the viscosity should approach the background viscosity  $\eta_b$ . According to Bhattacharjee et al. [8, 9], the crossover behavior of the viscosity can be represented by Eq. (4):

$$\eta = \eta_b \exp\{z_\eta H\} \quad (4)$$

The function  $H$ , which is given by Eq. (2.18) in Ref. 8, is a function of the correlation length  $\xi$  and two system-specific parameters,  $q_c$  and  $q_d$ . They are related to the critical amplitude  $Q_0$  by Eq. (5):

$$Q_0^{-1} = [(1/2) \exp\{4/3\}][q_c^{-1} + q_d^{-1}] \quad (5)$$

The parameter  $q_c$  appears in the expression of the background diffusion coefficient  $D_b$  [9] [see Eq. (6)].

$$D_b = \Gamma_b/q^2 = [k_B T/(16\eta_b \xi)] [(1 + q^2 \xi^2)/(q_c \xi)] \quad (6)$$

Analysis of the experimental dynamic light-scattering data in terms of these concepts requires knowledge of the value of the system-specific parameters  $Q_0$  and  $(q_d/q_c)$ , which can be obtained from viscosity measurements [10].

It is the aim of this study to determine the values of  $Q_0$  and  $(q_d/q_c)$  for a 2-butoxyethanol/water mixture of critical composition and to use this information to deduce the reduced diffusion coefficient  $D^*$   $[= (6\pi\eta\xi)/(k_B T)(D - D_b)]$  from experimental data obtained from dynamic light-scattering experiments for the same system. It is expected that  $D^*$  is a universal function of the scaling variable  $x (= q\xi)$ . The experimental data should collapse on a single curve given by  $\Omega(x) = R\Omega_K(x)[1 + (x/2)^2]^{-n/2}$ . A similar study has been carried out by Burstyn et al. [9] for the system nitroethane/3-methylpentane.

The system 2-butoxyethanol (2-C<sub>4</sub>E<sub>1</sub>)/water has a closed-loop miscibility gap. The experiments are carried out in the vicinity of the lower critical point. It is known that in a mixture of critical composition of these components, there exist aggregates of 2-C<sub>4</sub>E<sub>1</sub> molecules, reflecting the fact that 2-C<sub>4</sub>E<sub>1</sub> is the first member of a homologous series of nonionic tensides of the type C<sub>i</sub>E<sub>j</sub>.

For the data analysis the value of the system-specific critical amplitude  $\xi_0$  of the correlation length of local concentration fluctuations of this system determined by static light-scattering experiments has to be known. For the system 2-C<sub>4</sub>E<sub>1</sub>/water the critical amplitude  $\xi_0$  has a value of  $\xi_0 = 0.44$  nm [11]. Combining it with the critical amplitude  $\sigma_0$  of the liquid/liquid interfacial tensions and the critical amplitude  $A_0$  of the heat capacity of this system, respectively, leads to values of the universal amplitude ratios  $R_{\sigma,\xi}$  and  $R_{\sigma,A}$ , which are consistent with the theoretically predicted universal values [12, 13]. This finding is taken as evidence for the absence of systematic errors in the value of  $\xi_0$ . To check the reliability of the value of  $\xi_0$  of the system 2-C<sub>4</sub>E<sub>1</sub>/water, it was determined again in a new series of static light-scattering experiments (see Section 3.3). The experiments confirm the value of  $\xi_0$  given above within the uncertainty of the measurements.

## 2. METHOD OF DETERMINATION OF THE PARAMETER $Q_0$

To obtain the value of  $Q_0$  from viscosity data it is necessary to separate the experimentally determined shear viscosity of a mixture of critical composition into its regular and singular part.

## 2.1. Determination of the Regular Part of Viscosity

Two sets of viscosity measurements are carried out using an Ubbelohde capillary viscometer: set 1, experiments with 10 2-C<sub>4</sub>E<sub>1</sub>/H<sub>2</sub>O mixtures of noncritical composition  $y < y_c$  and  $y < y_c$  ( $y$ , mass fraction of 2-C<sub>4</sub>E<sub>1</sub>),  $T < T_P$  ( $T_P$ , temperature of phase separation); and set 2, experiments with a 2-C<sub>4</sub>E<sub>1</sub>/H<sub>2</sub>O mixture of critical composition.

### 2.1.1. Viscosity of 2-C<sub>4</sub>E<sub>1</sub>/H<sub>2</sub>O Mixtures of Different Compositions at Different Temperatures over a Wide Range of Temperatures and Compositions

The experimental data are used to calculate (a) the viscosity of the mixtures at a chosen set of identical temperatures using Eq. (7) (Vogel equation [14]; see Table III and Fig. 2b) and (b) the background viscosity  $\eta_b(y_c)$  of the mixture of critical composition at these temperatures by interpolation (interpolation of viscosity versus composition data at fixed temperatures to construct the viscosity of critical composition at these temperatures). The interpolations are carried out using the method of cubic spline approximation [15]. A fit of Eq. (7) to the interpolated (constructed)  $\eta_b(y_c)$  data (three-parameter fit) gives values of the parameters  $A_{c,sp}$ ,  $B_{c,sp}$ , and  $C_{c,sp}$  (sp, spline approximation; index  $c$  refers to the critical mixture). With these values the temperature dependence of  $\eta_b(y_c)$  (constructed) of a 2-C<sub>4</sub>E<sub>1</sub>/H<sub>2</sub>O mixture of critical composition is described (see Fig. 2a):

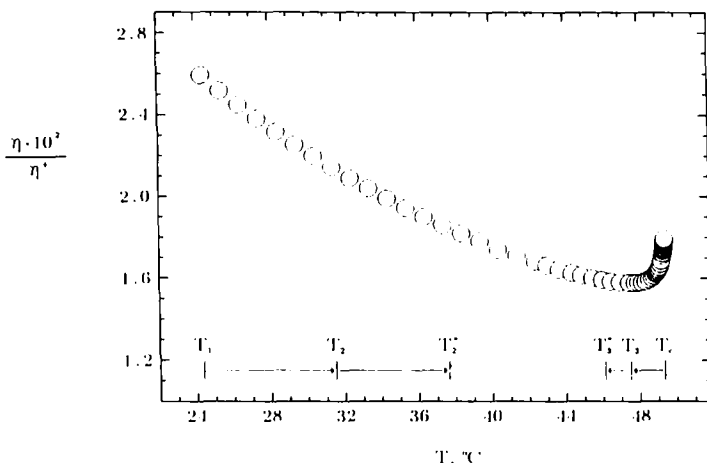
$$(\eta_b/\eta^+) = A \exp\{B/[(T/T^+) - C]\} \quad (7)$$

$\eta_b$  is the background viscosity of the mixture of critical composition;  $A$ ,  $B$ , and  $C$  are constants;  $T^+ = 1$  K; and  $\eta^+ = 1 \text{ g} \cdot \text{cm}^{-1} \cdot \text{s}^{-1}$  ( $= 1$  P).

Equation (7) is an empirical equation which has been used successfully to represent the temperature dependence of the viscosity of fluids in which hydrogen bonds act between the molecules.

### 2.1.2. Viscosity of a 2-C<sub>4</sub>E<sub>1</sub>/H<sub>2</sub>O Mixture of Critical Composition over a Wide Range of Temperatures Close to and Away from the Critical Temperature

Equation (7) is fitted to the experimental data (three-parameter fit with  $A_c$ ,  $B_c$ , and  $C_c$  as free parameters; index  $c$  refers to the critical mixture) at temperatures "sufficiently" far away from the critical temperature so that critical contributions can be neglected. To find this temperature range (see Fig. 1), only viscosity data obtained at temperatures



**Fig. 1.** Separation of regular (background) contribution from singular (critical) contributions of the shear viscosity  $\eta$  of a 2-C<sub>4</sub>E<sub>1</sub>/water mixture of critical composition ( $y_c = 0.2945$ ;  $y$ , mass fraction) in the vicinity of a lower critical point (schematically). Temperature range in which the viscosity data are not influenced by critical contributions,  $T_1 \Rightarrow T_2 \Rightarrow T_2^*$ ; crossover region,  $T_2^* \Rightarrow T_3^*$ ; critical region,  $T_3^* \Rightarrow T_3 \Rightarrow T_c$ .  $T$ , temperature. For details see text.  $\eta^* = 1 \text{ g} \cdot \text{cm}^{-1} \cdot \text{s}^{-1} (= 1 \text{ P})$ .

between  $T_2$  and  $T_1$  are used for the fit. The temperature difference ( $T_2 - T_1$ ) is increased step by step (keeping  $T_1$  constant and increasing  $T_2$ ). The standard deviation  $s$  of each fit is used as a criterion of the quality of the fit. It is expected that a plot of  $s$  versus  $T_2$  exhibits a "plateau" region away from the critical temperature extending up to a certain value  $T_2 = T_2^*$ . It is assumed that the temperature range ( $T_2^* - T_1$ ) of the "plateau" region of  $s$  represents the temperature range in which the viscosity of the critical mixtures is not influenced by critical contributions. It is expected that the values of the viscosity calculated from values of the parameter  $A_{sp,c}$ ,  $B_{sp,c}$ , and  $C_{sp,c}$  (obtained by the spline approximation procedure) are consistent with the values of the viscosity calculated from the values of the parameter  $A_c$ ,  $B_c$ , and  $C_c$  [obtained from viscosity data of a mixture of critical composition in the temperature range ( $T_2^* - T_1$ )]. It is assumed that the viscosity values calculated on the basis of Eq. (7) with the values of the parameters  $A_c$  ( $A_{sp,c}$ ),  $B_c$  ( $B_{sp,c}$ ), and  $C_c$  ( $C_{sp,c}$ ) represent the background viscosity of the mixture of critical composition away from the critical temperature as well as close to it.

## 2.2. Determination of the Singular Part

The determination of the singular part of the shear viscosity of a mixture of critical composition is based on Eq. (8), which is obtained by combining Eqs. (3), (7), and (10):

$$(\eta/\eta^+) = (\eta'/\eta^+) t^{-\nu} \quad (8)$$

with

$$(\eta'/\eta^+) = A'_c \exp\{B_c/[(T/T^+) - C_c]\}$$

and

$$A'_c = A_c(Q_0 \xi_0)^{-\nu} \quad (9)$$

$$\xi = \xi_0 t^{-\nu} \quad (10)$$

$\nu$  is the universal critical exponent, theoretical value  $\nu = 0.630$ ;  $t$ , the reduced temperature difference,  $t = (T_c - T)/T_c$ ;  $\eta$ , the shear viscosity; and  $\eta^+ = 1 \text{ g} \cdot \text{cm}^{-1} \cdot \text{s}^{-1}$  ( $= 1 \text{ P}$ ).

Equation (8) is fitted to the experimental data obtained with a mixture of critical composition (three-parameter fit,  $z_\eta$ ,  $T_c$ , and  $A'_c$ ; fixed parameter,  $\nu = 0.630$ ). The values of the constants  $B_c$  and  $C_c$  are fixed at values obtained by the procedure described above assuming that they are not influenced by critical contributions. The fitting procedure is started with viscosity data taken from the temperature range ( $T_c - T_3$ ) (see Fig. 1) close to  $T_c$ . The temperature difference ( $T_c - T_3$ ) is increased step by step (keeping  $T_c$  constant and decreasing  $T_3$ ). The standard deviation  $s$  of the fit is taken as a criterion of the quality of the fit. It is assumed that the temperature range ( $T_c - T_3^*$ ) leading to the "plateau" region of a  $s$  versus ( $T_c - T_3$ ) plot characterizes the "critical region." Since the value of  $A_c$  is known from the analysis of viscosity data of a mixture of critical composition taken at temperatures away from the critical temperature, the value of the system-specific critical amplitude of viscosity  $Q_0$  can be calculated from Eq. (9). The value of  $\xi_0$  of the system is known from static light-scattering experiments.

## 3. EXPERIMENTS

### 3.1. Materials

2-Butoxyethanol (2-C<sub>4</sub>E<sub>1</sub>) obtained from Merck (Darmstadt, Germany) was of synthetic quality (gas chromatographic purity >99%). It was purified by fractional distillation in a concentric-tube column of 75

theoretical plates at a reduced pressure of 33 mbar (boiling temperature at this pressure,  $T_s = 78^\circ\text{C}$ ). The main cut had a volume of  $10^3 \text{ cm}^3$  and was stored under  $\text{N}_2$  gas at  $T = -5^\circ\text{C}$ . Gas chromatographic analysis gave a purity of 99.99%. Water was double-distilled in a quartz distiller. Oxygen gas was removed from the water by treatment with argon gas.

### 3.2. Critical Data

The critical composition at the lower critical point determined on the basis of the equal volume criterion of liquid phases coexisting at temperatures above the critical ( $\lim T \Rightarrow T_c: (V'/V'')=1$ ) had a value  $y_c = 0.2945$  (mass fraction of  $2\text{-C}_4\text{E}_1$ , corresponding to a mole fraction of  $x_c = 0.0598$ ). The visually determined temperature of phase separation of a mixture with this composition had a value  $T_c(\text{visual}) = 49.365^\circ\text{C}$ . This value of  $T_c(\text{visual})$  refers to the critical mixture used for the viscosity measurements.

### 3.3. Static Light-Scattering Experiments

Measurements of the angular dependence of light intensity scattered by a  $2\text{-C}_4\text{E}_1/\text{water}$  mixture of critical composition were performed as function of the absolute value of the scattering vector  $q$  and the temperature difference ( $T_c - T$ ) [11]. The data were analyzed in terms of the Ornstein-Zernike correlation scaling function ( $q\xi < 4$ ). Data points near the critical temperature, which are influenced by double and multiple scattering, are excluded from the analysis [i.e.,  $(T_c(\text{visual}) - T) < 250 \text{ mK}$ ]. The scattering strength  $A_{\text{scat}}$  [16] has a value of about  $A_{\text{scat}} \approx 1 \times 10^{-3} \text{ m}^{-1}$ . This value of  $A_{\text{scat}}$  is deduced from measurements of turbidity of the mixture. The analysis of the  $\xi(T_c - T)$  data in terms of Eq. (10) (two-parameter fit:  $\xi_0$  and  $T_c$ , with  $\nu = 0.630$ ) gives the following result:  $\xi_0 = 0.42 \text{ nm}$ , and  $T_c(\text{fit}) = 49.189^\circ\text{C}$  (see Fig. 9). The value of  $\xi_0$  is consistent with that given in Ref. 11.

### 3.4. Viscometry

The construction of the viscometer used in this study was similar to that described in Ref. 17 (length of capillary,  $L = 9.8 \text{ cm}$ ; radius of capillary,  $r = 0.02286 \text{ cm}$ ; volume flowing through the capillary,  $V = 3.7 \text{ cm}^3$ ;  $\langle \Delta h \rangle$ , mean value of the height of the fluid meniscus during an experiment,  $\langle \Delta h \rangle = 11.55 \text{ cm}$ ). It was calibrated in the temperature range  $25^\circ\text{C} \leq T \leq 60^\circ\text{C}$  with water [18] ( $\eta/\rho = at - b/t$ ;  $a = 3.667 \times 10^{-5} \text{ cm}^2 \text{ s}^{-2}$ ,  $b = 1.127 \times 10^{-1} \text{ cm}^2$ ;  $\rho$ , density;  $t$ , time). The efflux time  $t_{\text{eff}}$  varied in the

range of  $400 \text{ s} < t_{\text{eff}} < 900 \text{ s}$  ( $\delta t_{\text{eff}} \approx 0.5 \text{ s}$ ). The viscometer, which could be rotated by  $360^\circ$  and positioned reproducibly in the vertical position, was immersed in a carefully insulated thermostat with a volume of  $150 \text{ dm}^3$  (long-time temperature stability  $\delta T = 1 \text{ mK}$ ). It was filled with filtered mixtures of  $2\text{-C}_4\text{E}_1/\text{H}_2\text{O}$  (Teflon filter, No. 11807-13; nominal pore size,  $0.2 \mu\text{m}$ ; Sartorius, Göttingen, Germany) in a glove box with a nitrogen atmosphere and flame-sealed thereafter. The compositions had the following values:  $y_1 = 0$ ;  $y_2 = 0.0400$ ;  $y_3 = 0.0800$ ;  $y_4 = 0.1000$ ;  $y_5 = 0.1900$ ;  $y_6 = 0.3511$ ;  $y_7 = 0.4700$ ;  $y_8 = 0.6000$ ;  $y_9 = 0.7300$ ; and  $y_{10} = 1$  ( $y$ , mass fraction of  $2\text{-C}_4\text{E}_1$ ).

The density of the mixtures was measured as a function of temperature using a vibrating-tube densitometer from Paar, Graz, Austria (Type DMA 601). It was calibrated with water [18] and cyclohexane [19]. The temperature dependence of the density of the  $2\text{-C}_4\text{E}_1/\text{H}_2\text{O}$  mixtures could be represented by a function of the form  $\rho = a + bT + cT^2 + dT^3$ . The constants  $a$ ,  $b$ ,  $c$ , and  $d$  had values given in Table I. The data for the mixture of critical composition are not accurate enough to look for the weak divergence of the density approaching the critical temperature. [The number of significant figures given for the parameters in Tables I and II and in the text are necessary to reproduce the experimental data within the uncertainty of the data.]

### 3.5. Dynamic Light-Scattering Experiments

The light-scattering photometer (light source, Ar ion laser; Spectra Physics, Model 162A, 15 mW at  $\lambda_0 = 488 \text{ nm}$ ) used for the dynamic light-

**Table I.** Density  $\rho$  of  $2\text{-C}_4\text{E}_1/\text{H}_2\text{O}$  Mixtures of Different Compositions ( $y$ , Mass Fraction of  $2\text{-C}_4\text{E}_1$ ) as a Function of Temperature ( $\rho/\rho^* = a + bT + cT^2 + dT^3$ ;  $a$ ,  $b$ ,  $c$ , and  $d$ , Constants;  $\rho^* = 1 \text{ g cm}^{-3}$ ;  $T$  in  $^\circ\text{C}$ )

$y$	$a$	$b$	$c$	$d$	Temp. range ( $^\circ\text{C}$ )
0.0400	0.99930	$1.323 \times 10^{-5}$	$-6.926 \times 10^{-6}$	$2.701 \times 10^{-8}$	20–50
0.0800	0.99884	$1.092 \times 10^{-5}$	$-8.217 \times 10^{-6}$	$3.835 \times 10^{-8}$	20–50
0.1000	1.00019	$-1.133 \times 10^{-4}$	$-6.442 \times 10^{-6}$	$2.750 \times 10^{-8}$	20–54
0.1900	0.99722	$-3.228 \times 10^{-4}$	$-4.094 \times 10^{-6}$	$1.493 \times 10^{-8}$	20–50.34
0.2945	0.99149	$-5.544 \times 10^{-4}$	$3.208 \times 10^{-6}$	$-1.883 \times 10^{-8}$	24.2–49.36
0.3511	0.98700	$-5.525 \times 10^{-4}$	$-1.291 \times 10^{-6}$	$-4.008 \times 10^{-9}$	20–49.47
0.4700	0.98531	$-9.999 \times 10^{-4}$	$1.821 \times 10^{-6}$	$-1.587 \times 10^{-8}$	25–53
0.6000	0.96625	$-6.988 \times 10^{-4}$	$-8.926 \times 10^{-7}$	$-1.728 \times 10^{-9}$	20–54
0.7300	0.95304	$-7.135 \times 10^{-4}$	$-1.578 \times 10^{-6}$	$5.330 \times 10^{-9}$	20–50
1.0000	0.91482	$-6.796 \times 10^{-4}$	$-3.610 \times 10^{-6}$	$2.394 \times 10^{-8}$	20–58



scattering experiments and the methods of data acquisition and data evaluation have been described in detail before [20, 21]. The normalized clipped second-order correlation function  $g_k^{(2)}(t)$  of the light intensity scattered by a mixture of critical composition at certain scattering angles was measured as a function of temperature  $\{0.005 \text{ K} < [T_c(\text{visual}) - T] < 2.0 \text{ K}\}$  and scattering angle ( $30^\circ \leq \theta \leq 135^\circ$ ) using a Malvern Correlator K 7023. From  $g_k^{(2)}(t)$  the first-order normalized electric field autocorrelation function  $g^{(1)}(t) = \sum A_i \exp\{-\Gamma_i(q, T)t\}$  was calculated ( $t$ , time). The reciprocal of the "linewidth"  $\Gamma(q, T)$  is the relaxation time of the electric field autocorrelation function. Provencher's program DISCRETE [22] was used for the analysis allowing for three exponential functions ( $i=1, 2, 3$ : "one-, two-, three-component solution"). It turned out that the one-component solution gave the best fit.

## 4. RESULTS AND DISCUSSION

### 4.1. Viscosity Data

The curves shown in Figs. 2a and b demonstrate the temperature and composition dependence of the viscosity of the system  $2\text{-C}_4\text{E}_1/\text{H}_2\text{O}$ . In Fig. 2b the data influenced by critical contributions are marked with filled circles. The experimental data are compiled in Table II.

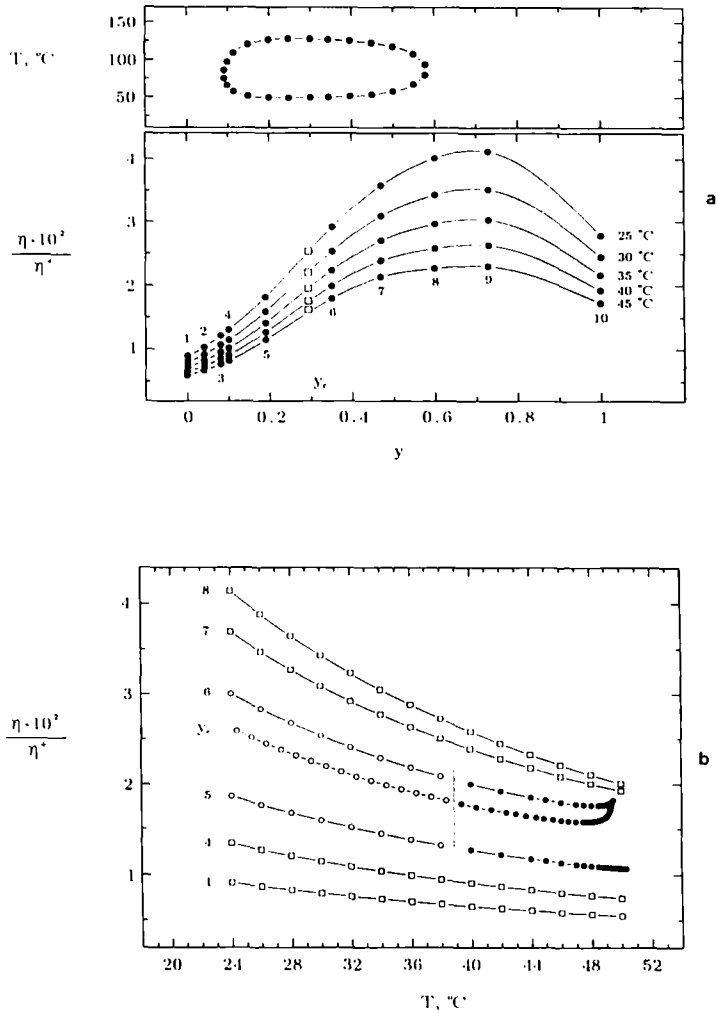
#### 4.1.1. Determination of the Regular Part (See Section 2.1.1)

The background viscosity of a mixture of critical composition at different temperatures is extracted from the viscosity data of mixtures of noncritical composition (i.e., mixtures with compositions  $y_1$  to  $y_{10}$ ; see Table II) in three steps as follows.

(a) Equation (7) is fit to viscosity data of the mixtures with compositions  $y_1$  to  $y_{10}$  (see Table III). This is a three-parameter fit giving, for each mixture, values of the constants  $A$ ,  $B$ , and  $C$ . The viscosity for each mixture is calculated at 25 temperatures in the range  $25^\circ\text{C} \leq T \leq 49^\circ\text{C}$ .

(b) Viscosity data of a mixture of critical composition ( $y_c = 0.2945$ ) at these temperatures are constructed using the method of cubic spline approximation (maximum allowed deviation between spline curve and constructed data points, about 0.7%). Two sets of spline approximations are carried out: set I, using  $y_1$  to  $y_{10}$ ; and set II, using  $y_1$  to  $y_{10}$  without  $y_5$  and  $y_6$  (see Fig. 2a).

(c) Equation (7) is fit (three-parameter fit:  $A_{\text{sp,c}}$ ,  $B_{\text{sp,c}}$ ,  $C_{\text{sp,c}}$ ) to the viscosity data constructed in this way (two sets of fits: data of set I and



**Fig. 2.** Temperature and composition dependence of the viscosity  $\eta$  of the system 2-C<sub>4</sub>E<sub>1</sub>/H<sub>2</sub>O in the vicinity of its lower critical point.  $y$ , mass fraction of 2-C<sub>4</sub>E<sub>1</sub>;  $\eta^* = 1 \text{ g} \cdot \text{cm}^{-1} \cdot \text{s}^{-1}$  ( $= 1 \text{ P}$ ). (a) Isotherms calculated from the experimental data compiled in Table II using Eq. (7) (see Table III). The open squares refer to experimental data obtained with a mixture of critical composition (separate data set, not included in Table II). In the upper part an overview of the isobaric phase diagram of the system is given (data from Ref. 30). (b) Temperature dependence of the viscosity of mixtures of different composition. The filled circles mark viscosity data influenced by critical contributions.  $y_1 = 0$ ;  $y_2 = 0.0400$ ;  $y_3 = 0.0800$ ;  $y_4 = 0.1000$ ;  $y_5 = 0.1900$ ;  $y_6 = 0.3511$ ;  $y_7 = 0.4700$ ;  $y_8 = 0.6000$ ;  $y_9 = 0.7300$ ;  $y_{10} = 1$ .

**Table II.** Shear Viscosity  $\eta$  of 2-C<sub>4</sub>E<sub>1</sub>/H<sub>2</sub>O Mixtures of Different Compositions at Different Temperatures [ $y$ , Mass Fraction of 2-C<sub>4</sub>E<sub>1</sub>;  $\eta^+ = 1 \text{ g} \cdot \text{cm}^{-1} \cdot \text{s}^{-1} (= 1 \text{ P})$ ]

No.	$y_1 = 0^a$		$y_2 = 0.0400$		$y_3 = 0.0800$		$y_4 = 0.1000$	
	$T (^{\circ}\text{C})$	$\eta \times 10^2/\eta^+$	$T (^{\circ}\text{C})$	$\eta \times 10^2/\eta^+$	$T (^{\circ}\text{C})$	$\eta \times 10^2/\eta^+$	$T (^{\circ}\text{C})$	$\eta \times 10^2/\eta^+$
1	20	1.002	20	1.1659	20	1.3914	20	1.5070
2	22	0.9548	21	1.1363	21	1.3523	22	1.4210
3	24	0.9111	22	1.1065	22	1.3150	24	1.3420
4	26	0.8705	23	1.0785	23	1.2790	26	1.2707
5	28	0.8327	24	1.0522	24	1.2446	28	1.2052
6	30	0.7975	25	1.0261	25	1.2116	30	1.1443
7	32	0.7647	26	1.0012	26	1.1802	32	1.0891
8	34	0.7340	27	0.9782	27	1.1499	34	1.0380
9	36	0.7052	28	0.9547	28	1.1206	36	0.9913
10	38	0.6783	29	0.9328	29	1.0924	38	0.9476
11	40	0.6529	30	0.9113	30	1.0660	40	0.9070
12	42	0.6291	31	0.8910	31	1.0401	42	0.8696
13	44	0.6067	32	0.8711	32	1.0154	44	0.8346
14	46	0.5856	33	0.8521	33	0.9916	46	0.8021
15	48	0.5656	34	0.8342	34	0.9686	48	0.7716
16	50	0.5468	35	0.8158	35	0.9465	50	0.7430
17			36	0.7990	36	0.9251	52	0.7160
18			37	0.7823	37	0.9045	54	0.6913
19			38	0.7663	38	0.8847		
20			39	0.7507	39	0.8657		
21			40	0.7357	40	0.8474		
22			41	0.7211	41	0.8294		
23			42	0.7073	42	0.8121		
24			43	0.6935	43	0.7957		
25			44	0.6799	44	0.7795		
26			45	0.6676	45	0.7640		
27			46	0.6552	46	0.7487		
28			47	0.6431	47	0.7347		
29			48	0.6313	48	0.7202		
30			49	0.6205	49	0.7065		
31			50	0.6094	50	0.6934		

<sup>a</sup>Viscosity data taken from Ref. 18.

Table II. (Continued)

No.	$y_5 = 0.1900$		$y_6 = 0.3511$		$y_7 = 0.4700$		$y_8 = 0.6000$	
	$T (^{\circ}\text{C})$	$\eta \times 10^2/\eta^+$	$T (^{\circ}\text{C})$	$\eta \times 10^2/\eta^+$	$T (^{\circ}\text{C})$	$\eta \times 10^2/\eta^+$	$T (^{\circ}\text{C})$	$\eta \times 10^2/\eta^+$
1	20	2.1017	20	3.4003	25	3.5759	20	4.7458
2	22	1.9786	22	3.1918	27	3.3654	22	4.4308
3	24	1.8680	24	3.0043	29	3.1836	24	4.1440
4	26	1.7665	26	2.8332	30	3.0923	26	3.8835
5	28	1.6754	28	2.6788	30.8	3.0227	28	3.6465
6	30	1.5916	30	2.5366	32	2.9227	30	3.4321
7	32	1.5151	32	2.4084	33	2.8424	32	3.2332
8	34	1.4452	34	2.2915	34	2.7731	34	3.0507
9	36	1.3809	36	2.1849	35	2.7041	36	2.8827
10	38	1.3217	38	2.0885	36	2.6374	38	2.7256
11	40	1.2681	40	2.0000	37	2.5723	40	2.5823
12	42	1.2183	42	1.9221	38	2.5056	42	2.4489
13	44	1.1725	44	1.8520	39	2.4469	44	2.3262
14	45	1.1515	45	1.8222	40	2.3848	46	2.2116
15	46	1.1314	46	1.7952	41	2.3291	48	2.1055
16	47	1.1129	47	1.7732	42	2.2772	50	2.0066
17	47.5	1.1040	47.5	1.7658	43	2.2298		
18	48	1.0961	48	1.7602	44	2.1828		
19	48.5	1.0877	48.5	1.7609	45.5	2.1112		
20	48.8	1.0833	48.8	1.7642	46	2.0836		
21	49	1.0806	49	1.7705	47	2.0452		
22	49.3	1.0763	49.1	1.7748	48	2.0020		
23	49.5	1.0737	49.2	1.7833	49	1.9615		
24	49.8	1.0702	49.3	1.7915	50	1.9213		
25	50	1.0686	49.4	1.8039	51	1.8849		
26	50.3	1.0663	49.45	1.8126	52	1.8557		
27	50.34	1.0655	49.47	1.8172	53	1.8231		
28			49.474	1.8181				

Table II. (Continued)

$\gamma_9 = 0.7300$			$\gamma_{10} = 1$		
No.	$T (^{\circ}\text{C})$	$\eta \times 10^2/\eta^+$	$T (^{\circ}\text{C})$	$\eta \times 10^2/\eta^+$	
1	20	4.8792	20	3.1872	
2	22	4.5536	22	3.0154	
3	24	4.2564	24	2.8570	
4	26	3.9873	26	2.7091	
5	28	3.7420	28	2.5758	
6	30	3.5139	30	2.4459	
7	32	3.3065	32	2.3273	
8	34	3.1166	34	2.2168	
9	36	2.9403	36	2.1180	
10	38	2.7777	38	2.0168	
11	40	2.6283	40	1.9298	
12	42	2.4894	42	1.8440	
13	44	2.3621	44	1.7643	
14	46	2.2427	46	1.6882	
15	48	2.1315	48	1.6179	
16	50	2.0281	50	1.5516	

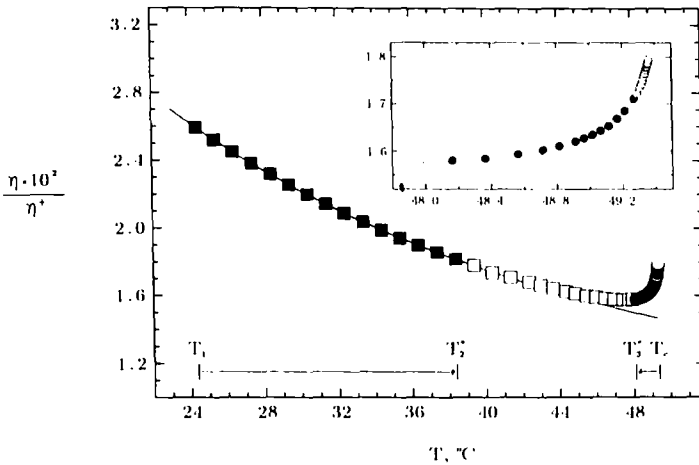
  

$\gamma_c = 0.2945$								
No.	$T (^{\circ}\text{C})$	$\eta \times 10^2/\eta^+$	No.	$T (^{\circ}\text{C})$	$\eta \times 10^2/\eta^+$	No.	$T (^{\circ}\text{C})$	$\eta \times 10^2/\eta^+$
1	24.365	2.5924	21	43.665	1.6419	41	49.167	1.6689
2	25.365	2.5176	22	44.365	1.6246	42	49.215	1.6856
3	26.365	2.4491	23	44.865	1.6126	43	49.271	1.7113
4	27.365	2.3809	24	45.465	1.5997	44	49.289	1.7220 <sup>b</sup>
5	28.365	2.3168	25	45.992	1.5912	45	49.306	1.7337 <sup>b</sup>
6	29.365	2.2545	26	46.474	1.5835	46	49.317	1.7412 <sup>b</sup>
7	30.365	2.1980	27	46.965	1.5794	47	49.324	1.7491 <sup>b</sup>
8	31.365	2.1423	28	47.465	1.5777	48	49.335	1.7580 <sup>b</sup>
9	32.365	2.0884	29	47.765	1.5774	49	49.341	1.7640 <sup>b</sup>
10	33.365	2.0389	30	47.965	1.5797	50	49.346	1.7715 <sup>b</sup>
11	34.365	1.9887	31	48.165	1.5798	51	49.35	1.7765 <sup>b</sup>
12	35.365	1.9428	32	48.365	1.5850	52	49.353	1.7797 <sup>b</sup>
13	36.365	1.8995	33	48.565	1.5937	53	49.355	1.7837 <sup>b</sup>
14	37.365	1.8591	34	48.715	1.6021	54	49.358	1.7858 <sup>b</sup>
15	38.365	1.8187	35	48.815	1.6110	55	49.36	1.7865 <sup>b</sup>
16	39.365	1.7809	36	48.914	1.6209	56	49.361	1.7926 <sup>b</sup>
17	40.365	1.7384	37	48.965	1.6280			
18	41.365	1.7110	38	49.015	1.6343			
19	42.365	1.6811	39	49.065	1.6432			
20	42.984	1.6621	40	49.115	1.6535			

<sup>b</sup> Influenced by shear.

**Table III.** Results of Fits of Eq. (7) to Experimental Viscosity Data [Measured in Units of  $\eta^* = 1 \text{ g} \cdot \text{cm}^{-1} \cdot \text{s}^{-1}$  ( $= 1 \text{ P}$ )]  
 ( $A$ ,  $B$ , and  $C$ , Constants;  $\Delta\eta = \eta_{\text{exp}} - \eta_{\text{fit}}$ ;  $\eta = \eta_{\text{exp}}$ ; Index "max," Maximum Value; and  $y$ , Mass Fraction of 2-C<sub>4</sub>E<sub>1</sub>)

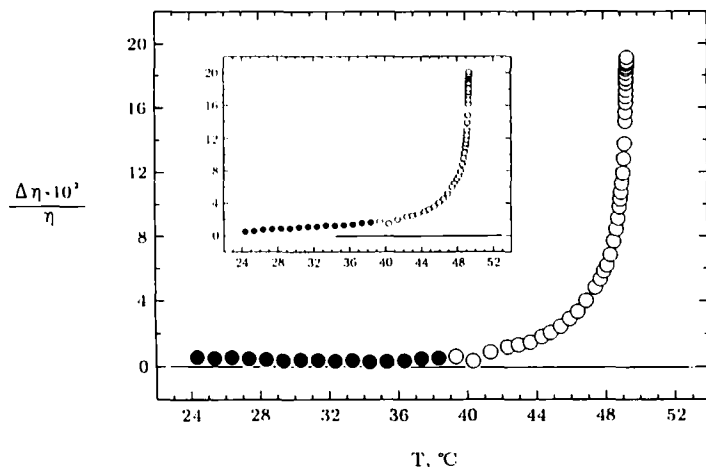
	$y$									
	0	0.0400	0.0800	0.1000	0.1900	0.3511	0.4700	0.6000	0.7300	1
$A \times 10^2$	0.030158 $\pm 0.000238$	0.033070 $\pm 0.000526$	0.037828 $\pm 0.000258$	0.055573 $\pm 0.000489$	0.12376 $\pm 0.00191$	0.16136 $\pm 0.00739$	0.15295 $\pm 0.00953$	0.03228 $\pm 0.00123$	0.021922 $\pm 0.000440$	0.01750 $\pm 0.00165$
$B$	503.04 $\pm 2.47$	479.98 $\pm 4.69$	451.77 $\pm 1.88$	363.02 $\pm 2.18$	260.22 $\pm 3.08$	286.88 $\pm 9.27$	321.51 $\pm 14.23$	718.91 $\pm 11.90$	836.59 $\pm 6.71$	974.20 $\pm 37.74$
$C$	149.555 $\pm 0.383$	158.422 $\pm 0.720$	167.833 $\pm 0.286$	183.151 $\pm 0.370$	201.271 $\pm 0.589$	199.033 $\pm 1.631$	196.176 $\pm 2.518$	149.087 $\pm 1.290$	138.372 $\pm 0.668$	105.971 $\pm 3.866$
$[\Delta\eta \times 10^2/\eta]_{\text{max}}$	0.016	0.058	0.040	0.050	0.023	0.046	0.453	0.069	0.038	0.15
Data points	1-16	1-31	1-31	1-18	1-10	1-9	1-27	1-16	1-16	1-16
Temp. range (°C)	20-50	20-50	20-50	20-54	20-38	20-36	25-53	20-50	20-50	20-50



**Fig. 3.** Temperature dependence of the viscosity  $\eta$  of a 2-C<sub>4</sub>E<sub>1</sub>/H<sub>2</sub>O mixture of critical composition [ $y_c = 0.2945$ ;  $T_c(\text{visual}) = 49.365^\circ\text{C}$ ].  $\eta^* = 1 \text{ g} \cdot \text{cm}^{-1} \cdot \text{s}^{-1}$  ( $= 1 \text{ P}$ ). Filled squares, viscosity data not influenced by singular contributions; filled circles, viscosity data dominated by singular contributions; open circles, viscosity data influenced by singular contributions and influenced by shear; open squares, viscosity data in the transition region. Drawn-out curve: Eq. (7) with  $A_c = 0.20961 \times 10^{-2}$ ;  $B_c = 214.011$ ;  $C_c = 212.434$ . Inset, drawn-out curve: Eq. (8) with  $A'_c = 0.17532 \times 10^{-2}$ ;  $B'_c = 214.011$ ;  $C'_c = 212.434$ ;  $T'_c = 322.528 \text{ K}$ ;  $z_\eta = 0.066$ .

data of set II). The two three-parameter fits give the following results: set I,  $A_{\text{sp,c}} = 0.15122 \times 10^{-2}$ ;  $B_{\text{sp,c}} = 278.377$ ; and  $C_{\text{sp,c}} = 199.350$ ; and set II,  $A_{\text{sp,c}} = 0.19109 \times 10^{-2}$ ;  $B_{\text{sp,c}} = 222.947$ ; and  $C_{\text{sp,c}} = 211.858$ . The maximum relative deviation ( $\Delta\eta_{\text{sp}} 10^2 / \eta_{\text{sp}}$ ) is smaller than  $1 \times 10^{-2}$  ( $\Delta\eta_{\text{sp}} = \eta_{\text{sp,constr.}} - \eta_{\text{sp,fit}}$ ;  $\eta_{\text{sp}} = \eta_{\text{sp,constr.}}$ ;  $\eta_{\text{sp,constr.}}$ , viscosity data of a mixture of critical composition constructed by spline approximation).

Figure 4 shows a plot of relative deviations ( $\Delta\eta \cdot 10^2 / \eta$ ) of viscosity data of a mixture of critical composition constructed by spline approximation [Eq. (7) with  $A_{\text{sp,c}} = 0.15122 \times 10^{-2}$ ,  $B_{\text{sp,c}} = 278.377$ , and  $C_{\text{sp,c}} = 199.35$  for set I] from experimental data obtained with a mixture of critical composition away from the critical temperature ( $\Delta\eta = \eta_{\text{exp}} - \eta_{\text{sp}}$ ;  $\eta = \eta_{\text{exp}}$ ). The insert in Figure 4 refers to data calculated with values of  $A_{\text{sp,c}}$ ,  $B_{\text{sp,c}}$ , and  $C_{\text{sp,c}}$  taken from set II. The experimental values are slightly larger than those obtained by interpolation (parameter values of set I,  $(\Delta\eta \times 10^2 / \eta) \approx 0.5$ ; set II,  $(\Delta\eta \times 10^2 / \eta) \approx 1$ ). From these data it is concluded that in the temperature range  $T \leq 38.365^\circ\text{C}$ , corresponding to  $(T_c - T) \geq 11 \text{ K}$ , the critical contributions to the measured viscosity can be neglected.



**Fig. 4.** Determination of the temperature range in which the viscosity data of a 2-C<sub>4</sub>E<sub>1</sub>/H<sub>2</sub>O mixture of critical composition are not influenced by critical contributions. Plot of the relative deviations ( $\Delta\eta \times 10^3/\eta$ ) of viscosity data of a mixture of critical composition constructed by spline approximation from viscosity data of a mixture of critical composition measured at temperatures away from the critical temperature (Table II,  $y_c$ ) as a function of temperature  $T$  ( $=T_2$ ; see Fig. 1). Calculation of  $\eta_{sp,c}$ : Eq. (7) with  $A_{sp,c} = 0.15122 \times 10^{-2}$ ,  $B_{sp,c} = 278.377$ , and  $C_{sp,c} = 199.350$  (set I). Viscosity data not influenced by critical contributions are indicated by filled circles. The inset shows a corresponding plot for the data in set II, i.e., calculation of  $\eta_{sp,c}$ : Eq. (7) with  $A_{sp,c} = 0.19109 \times 10^{-2}$ ,  $B_{sp,c} = 222.947$ , and  $C_{sp,c} = 211.858$ .

#### 4.1.2. Determination of the Regular Part (See Section 2.1.2)

Analysis of the experimental viscosity data of a mixture of critical composition also shows that at temperatures  $(T_c - T) \geq 11$  K, critical contributions are absent. Figure 5 shows a plot of the standard deviation  $s$  of the fits of Eq. (7) to experimental data (see Table II,  $y_c$ ) as function of the temperature  $T_2$  (see Figs. 1 and 2).

In summary, it is found that the temperature dependence of the background viscosity  $\eta_b$  of a 2-C<sub>4</sub>E<sub>1</sub>/H<sub>2</sub>O mixture of critical composition can be calculated using Eq. (7) with the following parameter values:  $A_c = (0.20961 \pm 0.01400) \times 10^{-2}$ ,  $B_c = 214.011 \pm 12.300$ , and  $C_c = 212.434 \pm 2.600$  (see Fig. 3). In analyzing experimental data it is observed that the values of the parameters in Eq. (7) are highly correlated. Therefore it is not surprising to find that the values of  $\eta_b$  calculated with the parameter values for  $A_{sp,c}$ ,  $B_{sp,c}$ , and  $C_{sp,c}$  given in the preceding paragraph agree with the values of  $\eta_b$  calculated with the values of  $A_c$ ,  $B_c$ , and  $C_c$  using Eq. (7).



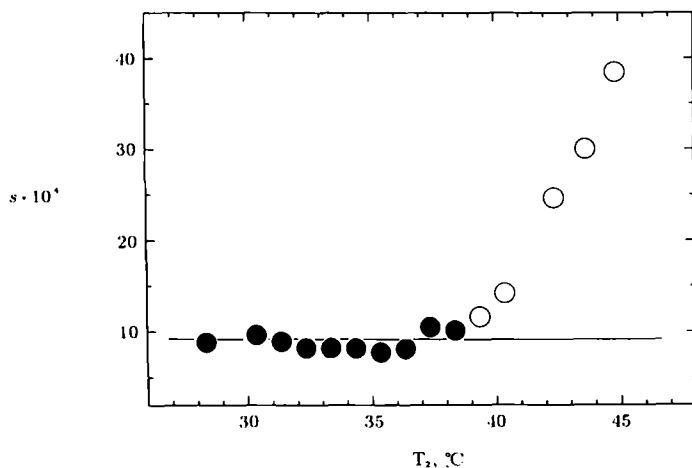


Fig. 5. Determination of the temperature range in which the viscosity data of a 2-C<sub>4</sub>E<sub>1</sub>/H<sub>2</sub>O mixtures are not influenced by critical contributions. Plot of the standard deviation  $s$  of the fit of Eq. (7) to experimental viscosity data of a mixture of critical composition (see Table II,  $y_c$ ) as a function of temperature  $T$  ( $= T_2$ ; see Fig. 1). The temperatures at which the viscosity data are not influenced by critical contributions are marked by filled circles.

#### 4.1.3. Determination of the Singular Part (See Section 2.2)

The viscosity data of a mixture of critical composition determined at temperatures close to the critical are corrected for the influence of shear. An influence of shear is expected when the product of the relaxation time  $\tau$  of the dynamics of the local concentration fluctuations and the rate of shear  $S$  is comparable with or larger than 1 (i.e.,  $\tau S > 1$ ). Approaching  $T_c$  the relaxation time  $\tau$  diverges strongly [ $\tau \approx (6\eta\xi^3)/(k_B T)$ ; “critical slowing down”], whereas the rate of shear increases only slightly. As a consequence, the rate of shear produces two effects when approaching  $T_c$ : a decrease in the shear viscosity and a change in the critical temperature (enlargement of the one-fluid phase region of the phase diagram). Following considerations of Oxtoby [23, 24], the change in viscosity with shear of a mixture of critical composition is given by

$$\eta(S=0) = \eta(S)/[1 - \Delta(\lambda)] \quad (11)$$

with

$$\lambda_S = (\eta\xi^3 S)/(k_B T)$$

and

$$\Delta(\lambda_s) = \begin{cases} 0.0214 + 0.0266 \log \lambda + 0.0078 (\log \lambda)^2 & \text{for } 0.1 < \lambda < 20 \\ [8/(45\pi^2)] \ln(\lambda/0.45) & \text{for } \lambda > 20 \end{cases}$$

$S$  is the rate of shear.

In a capillary viscometer the rate of shear changes during the experiment and an effective shear  $S_{\text{eff}}$  is used for the calculations:

$$S_{\text{eff}} = (4/15)(\rho g \langle \Delta h \rangle r)/(\eta L) \quad (12)$$

$\rho$  is the density of the mixture;  $r$ , the radius of the capillary;  $L$ , the length of the capillary;  $g$ , the acceleration due to gravity; and  $\langle \Delta h \rangle$ , the mean value of the height of the fluid meniscus during an experiment.

The change in the critical temperature with the rate of shear is considered by Onuki et al. [25–27] with the result given by Eq. (12):

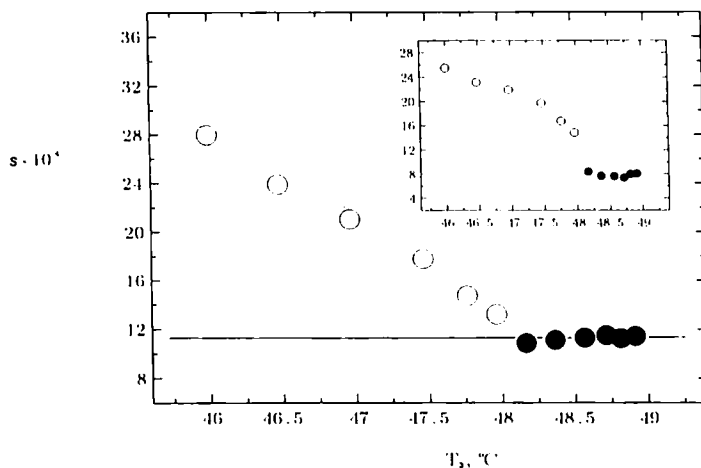
$$T_c(S) = T_c(S=0)[1 + 0.0832[(16\eta\xi_0^3 S)/(k_B T)]^{0.53}] \quad (13)$$

$T$  is the temperature at which the viscosity  $\eta$  is measured. [Equation (13) refers to a system with a lower critical point.]

The change in  $T_c$  with  $S$  has an influence on the temperature dependence of  $\xi$ , which in turn influences  $\lambda_s$  [see Eq. (11)]. In the following, a correction of the experimental data on the basis of Eq. (11) is called an Oxtoby correction. A correction on the basis of Eq. (13) in combination with Eq. (11) is called an Oxtoby–Onuki correction.

After correcting the viscosity data measured close to the critical temperature for the influence of the rate of shear (see Table III), the corrected  $\eta(T_c - T)$  data set is analyzed in the manner described in Section 2.2. The results of the analysis are discussed on the basis of Figs. 4 and 5. In the temperature range  $(T_c - T) > 11$  K, the influence of singular contributions to the viscosity of a critical mixture can be neglected and the temperature dependence of the viscosity can be represented by Eq. (6) with  $A_c = 0.20961 \times 10^{-2}$ ,  $B_c = 214.011$ , and  $C_c = 212.434$  (see drawn-out line in Fig. 3 and filled-square data points). Close to the critical temperature [ $(T_c - T) \leq 1.2$  K] the viscosity is dominated by singular contributions. This temperature range is surprisingly small (see “plateau” regions in Fig. 6). Figure 6 shows a plot of the standard deviation  $s$  of the fit of Eq. (14) (three free parameters,  $A'_c$ ,  $z_\eta$ , and  $T_c$ ; fixed parameters,  $B_c = 214.011$ ,  $C_c = 212.434$ , and  $\nu = 0.630$ ) to viscosity data corrected for the change in the critical temperature caused by shear (see Table IV) as function of  $T_3$  (see Figs. 1 and 3):

$$(\eta/\eta^+) = A'_c \exp\{B_c/[(T/T^+) - C_c] t^{-z_\eta \nu}\} \quad (14)$$



**Fig. 6.** Analysis of the singular contributions to the viscosity of a 2-C<sub>4</sub>E<sub>1</sub>/H<sub>2</sub>O mixture of critical composition: plot of the standard deviation  $s$  of the fit of Eq. (14) with three free parameters,  $A'_c$ ,  $z_\eta$ , and  $T_c$ , and fixed parameters  $B_c = 214.011$ ,  $C_c = 212.434$ , and  $\nu = 0.630$  to experimental viscosity data corrected for the change of the critical temperature caused by shear (see Table IV, Oxtoby-Onuki correction) as a function of  $T$  ( $=T_3$ ; see Fig. 1). The filled circles indicate the temperature range in which the viscosity data are dominated by critical contributions. The inset refers to a similar fit neglecting the data influenced by shear.

The inset in Fig. 6 refers to a similar fit neglecting the data influenced by shear.

The analysis of the data not influenced by shear gives the following values of the free parameters:  $A'_c = (0.17532 \pm 0.00059) \times 10^{-2}$ , and  $z_\eta = 0.066 \pm 0.001$ ,  $T_c = (322.528 \pm 0.004)$  K [i.e.,  $T_c(\text{fit}) - T_c(\text{vis}) = 13$  mK; maximum relative deviation  $(\Delta\eta \cdot 10^2/\eta) < 0.1$ ;  $\Delta\eta = \eta_{\text{exp}} - \eta_{\text{fit}}$ ;  $\eta = \eta_{\text{fit}}$ ].

The value of the critical exponent  $z_\eta$  obtained in this way is close to the theoretically predicted value ( $z_\eta \approx 0.065$ ) and experimental values reported in the literature [2–4].  $T_c(\text{fit})$  and  $T_c(\text{vis})$  agree with each other satisfactorily.  $A'_c$  and  $Q_0$  are related by Eq. (9). With  $A_c = 0.20961 \times 10^{-2}$ ,  $\xi_0 = 0.44$  nm, and  $z_\eta = 0.066$ , a value of  $Q_0 = (1.52 \pm 0.60) \times 10^6 \text{ cm}^{-1}$  is obtained. Similar values of  $Q_0$  for the same system have been reported by Hamano et al. [28] ( $Q_0 = 1.63 \times 10^6 \text{ cm}^{-1}$ ) and Izumi et al. [29] ( $Q_0 = 1.7 \times 10^6 \text{ cm}^{-1}$ ) using other methods of data analysis. They are of the same order of magnitude as that reported for nitrogen ( $Q_0 = 4.5 \times 10^6 \text{ cm}^{-1}$  [2]). However, they are an order of magnitude smaller than that reported by Burstyn et al. [9] for the binary mixture nitroethane/3-methylpentane ( $Q_0 = 14.0 \times 10^6 \text{ cm}^{-1}$ ), which has an upper critical point. The small value

**Table IV.** Shear Viscosity  $\eta_{\text{cor}}$  of a 2-C<sub>4</sub>E<sub>1</sub>/H<sub>2</sub>O Mixture of Critical Composition ( $y_c = 0.2945$ ;  $T_c(\text{vis}) = 49.365^\circ\text{C}$ ) Corrected for the Influence of Shear (Oxtoby Correction,  $[\eta_{\text{cor}} \times 10^2/\eta^+]_{\text{Ox}}$ ; Oxtoby-Onuki Correction,  $[\eta_{\text{cor}} \times 10^2/\eta^+]_{\text{On}}$ ; See Text)<sup>a</sup>

No.	$T_c(\text{vis}) - T_c$ (K)	$S_{\text{eff}}$ (s <sup>-1</sup> )	$\lambda$	$\Delta(\lambda)$	$[\eta_{\text{cor}} \times 10^2/\eta^+]_{\text{Ox}}$
Oxtoby correction					
44	0.076	393	0.0935	0.0023	1.7301
45	0.059	391	0.1504	0.0048	1.7421
46	0.048	389	0.2221	0.0073	1.7541
47	0.041	388	0.2992	0.0096	1.7661
48	0.030	387	0.5400	0.0148	1.7845
49	0.024	384	0.8232	0.0192	1.7985
50	0.019	383	1.2802	0.0243	1.8156
51	0.015	382	2.0012	0.0301	1.8317
52	0.012	381	3.0509	0.0361	1.8464
53	0.010	380	4.3064	0.0414	1.8606
54	0.007	380	8.4504	0.0528	1.8853
55	0.005	380	15.961	0.0647	1.9101
56	0.003	378	41.913	0.0817	1.9520
No.	$T_c(\text{vis}) - T_c$ (K)	$S_{\text{eff}}$ (s <sup>-1</sup> )	$\lambda$	$\Delta(\lambda)$	$[\eta_{\text{cor}} \times 10^2/\eta^+]_{\text{On}}$
Oxtoby-Onuki correction					
44	0.076	393	0.0791	0.0016	1.7247
45	0.059	391	0.1217	0.0036	1.7400
46	0.048	389	0.1718	0.0056	1.7511
47	0.041	388	0.2222	0.0074	1.7620
48	0.030	387	0.3038	0.0097	1.7752
49	0.024	384	0.4259	0.0126	1.7865
50	0.019	383	0.7078	0.0176	1.8032
51	0.015	382	0.9704	0.0211	1.8147
52	0.012	381	1.2774	0.0243	1.8241
53	0.010	380	1.5797	0.0270	1.8331
54	0.007	380	2.2801	0.0319	1.8447
55	0.005	380	3.0512	0.0361	1.8534
56	0.003	378	4.3065	0.0414	1.8701

<sup>a</sup> The uncorrected data are given in Table II using the same numbers.  $\eta^+ = 1 \text{ g} \cdot \text{cm}^{-1} \cdot \text{s}^{-1}$  ( $= 1 \text{ P}$ ).  $L$ , length of capillary,  $L = 9.8 \text{ cm}$ ;  $r$ , radius of capillary,  $r = 0.02286 \text{ cm}$ ;  $\langle h \rangle$ , mean value of the height of the meniscus of the fluid,  $\langle h \rangle = 11.55 \text{ cm}$ .

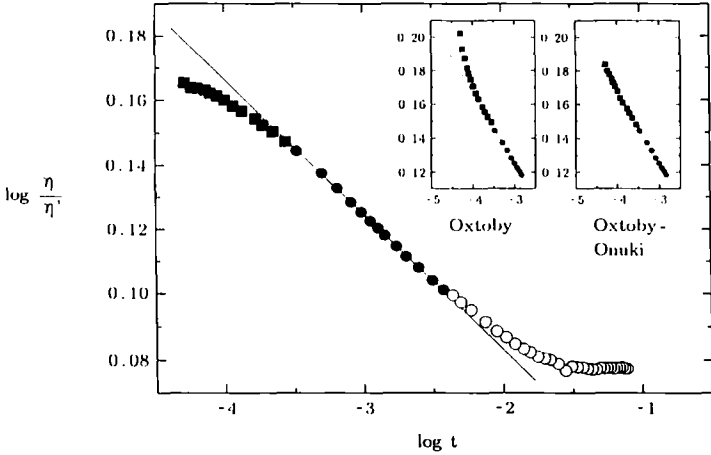


Fig. 7. Analysis of singular contributions to the viscosity of a 2-C<sub>4</sub>E<sub>1</sub>/H<sub>2</sub>O mixture of critical composition at temperatures  $(T_c - T) \leq 1.2$  K: plot of  $\log(\eta/\eta')$  as a function of  $\log t$  (decadic logarithm) ( $\log(\eta/\eta') = -\nu z_\eta \log t$ ;  $\eta' = A'_c \exp\{B_c/[(T/T^+) - C_c]\}$ ;  $t = (T_c - T)/T_c$ ;  $T_c = 322.528$  K;  $A'_c = 0.17532 \times 10^{-2}$ ;  $B_c = 214.011$ ;  $C_c = 212.434$ ). The drawn-out line has a slope of  $(\nu z_\eta) = -0.042$ .  $\eta'$  is proportional to the background viscosity of a mixture of critical composition in the temperature range in which the measured viscosity is influenced by contributions of composition fluctuations with long-range correlations. The data points indicated by filled squares are influenced by shear. The data points indicated by filled circles are not influenced by shear. The data points indicated by open circles belong to the transition region or represent regular viscosity data. The two insets show the influence of the Oxtoby and the Oxtoby-Onuki corrections, respectively (see text).

of  $Q_0$  of the system 2-C<sub>4</sub>E<sub>1</sub>/H<sub>2</sub>O reflects the fact that the temperature range in which the viscosity is dominated by singular contributions is rather narrow ( $(T_c - T) \leq 1.2$  K).

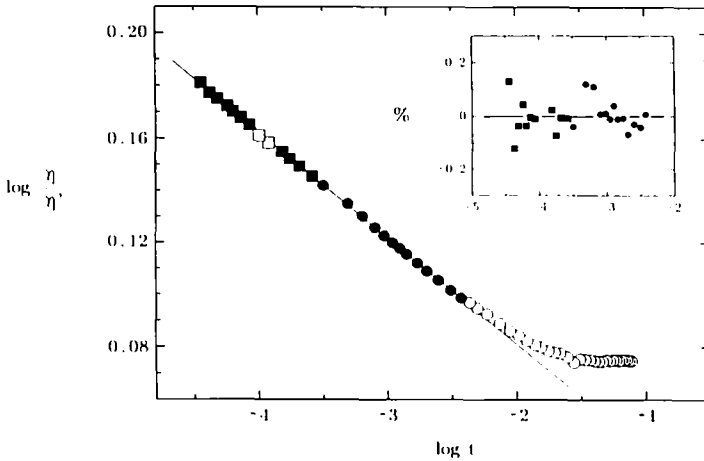
In Fig. 7 a plot of  $\log(\eta/\eta')$  versus  $\log t$  is shown, demonstrating the influence of shear on the viscosity data at temperatures close to the critical temperature ( $\log(\eta/\eta') = -(\nu z_\eta) \log t$ ;  $\eta' = A'_c \exp\{B_c/[(T/T^+) - C_c]\}$ ). The uncorrected data points characterized by filled squares are influenced by shear. The drawn-out line has a negative slope of  $(\nu z_\eta) = 0.042$  (theoretically expected value,  $\nu z_\eta \approx 0.041$ ). The two insets show the influence of the Oxtoby and Oxtoby-Onuki corrections. The Oxtoby correction seems to "overcorrect" the data. The Oxtoby-Onuki correction appears to bring the viscosity data back to the theoretically expected curve.

A fit of Eq. (14) to the viscosity data of a mixture of critical composition obtained close to  $T_c$  ( $(T_c - T) \leq 1.2$  K) including the data points corrected by the Oxtoby-Onuki method with the three free parameters  $A'_c$ ,

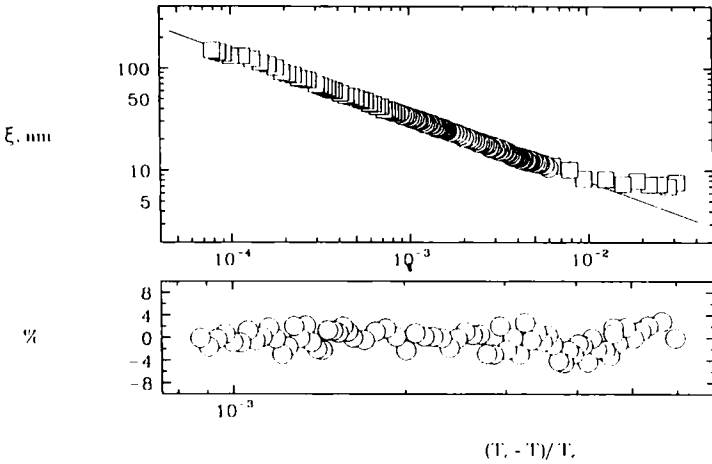
$T_c$ , and  $z_\eta$  and three fixed parameters ( $B_c = 214.011$ ,  $C_c = 212.434$ , and  $\nu = 0.630$ ) gives the following result:  $A'_c = (0.1764 \pm 0.0024) \times 10^{-2}$ ,  $z_\eta = 0.064 \pm 0.001$ ,  $T_c = (322.524 \pm 0.001)$  K [i.e.,  $T_c(\text{fit}) - T_c(\text{vis}) = 9$  mK; maximum relative deviation  $(\Delta\eta \times 10^2/\eta) = 0.13$  ( $\Delta\eta = \eta_{\text{exp}} - \eta_{\text{fit}}$ ;  $\eta = \eta_{\text{fit}}$ )]. This leads to a value of the parameter  $Q_0$  of  $Q_0 = (1.56 \pm 0.60) \times 10^6 \text{ cm}^{-1}$ . This value agrees with that calculated from the data neglecting the values influenced by shear within the uncertainty of the measurements [ $Q_0 = (1.52 \pm 0.60) \times 10^6 \text{ cm}^{-1}$ ].

The corresponding plot of  $\log(\eta/\eta')$  as a function of  $\log t$  is shown in Fig. 8. The negative slope of this curve has a value of  $(\nu z_\eta) = 0.040$  (theoretically expected value,  $\nu z_\eta \approx 0.041$ ).

The complete data set of the temperature dependence of the viscosity obtained with a 2-C<sub>4</sub>E<sub>1</sub>/water mixture of critical composition (with data points influenced by shear and corrected by the Oxtoby–Onuki method) is analyzed using Eq. (4). The background viscosity  $\eta_b$  is calculated from the expression  $(\eta_b/\eta^+) = A_c \exp\{B_c/[(T/T^+) - C_c]\}$  with  $A_c = 0.20961 \times 10^{-2}$ ,



**Fig. 8.** Analysis of singular contributions to the viscosity of a 2-C<sub>4</sub>E<sub>1</sub>/H<sub>2</sub>O mixture of critical composition at temperatures  $(T_c - T) \leq 1.2$  K. The viscosity data close to the critical temperature are corrected for the influence of shear (Oxtoby–Onuki correction; see text) and are included in the analysis (see Table IV): plot of  $\log(\eta/\eta')$  as a function of  $\log t$  (decadic logarithm) ( $\log(\eta/\eta') = -\nu z_\eta \log t$ ;  $\eta' = A'_c \exp\{B_c/[(T/T^+) - C_c]\}$ ;  $t = (T_c - T)/T_c$ ;  $T_c = 322.524$  K;  $A'_c = 0.17638 \times 10^{-2}$ ;  $B_c = 214.011$ ;  $C_c = 212.434$ ). The drawn-out line has a slope of  $(\nu z_\eta) = -0.040$ . Filled squares, data points corrected for shear; filled circles, data points in the critical region; open squares, data points corrected for the influence of shear but excluded from the fitting procedure. The inset shows the deviations.

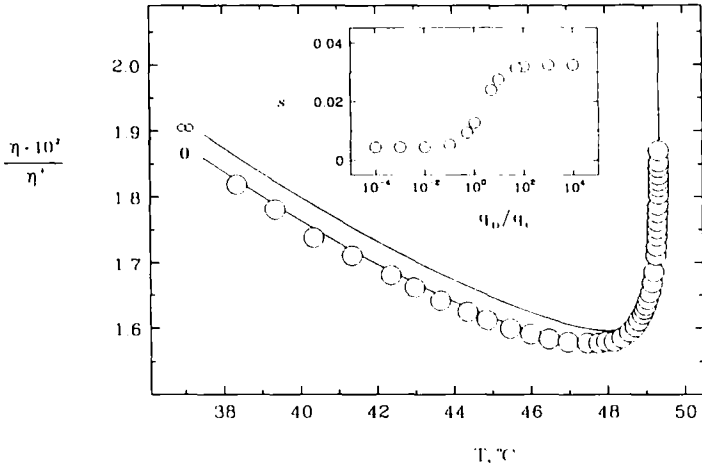


**Fig. 9.** Double-logarithmic plot of the correlation length  $\xi$  as a function of the reduced temperature difference  $t = (T_c - T)/T_c$  of the system 2-C<sub>4</sub>E<sub>1</sub>/water of critical composition. The drawn-out line represents the function  $\xi = \xi_0 t^{-\nu}$ , with  $\xi_0 = 0.42$  nm,  $T_c(\text{fit}) = 322.339$  K, and  $\nu(\text{theory}) = 0.630$ . A plot of the deviation of the data points from the function is given. Data points represented by open squares are excluded from the fitting procedure.

$B_c = 214.011$ , and  $C_c = 212.434$ . For the calculation of values of function  $H$ , three forms of  $H$  are used. They are given in Ref. 8:

- (a) the complete  $H$  function [see Ref. 8, Eq. (2.18)];
- (b) the asymptotic form of  $H$  for  $(q_d/q_c) \rightarrow 0$  [i.e.,  $Q_0 = 2/(\exp\{4/3\}) q_d$ ; see Ref. 8, Eq. (2.25)]; and
- (c) the asymptotic form of  $H$  for  $(q_d/q_c) \rightarrow \infty$  [i.e.,  $Q_0 = 2/(\exp\{4/3\}) q_c$ ; see Ref. 8, Eqs. (2.23) and (2.24)].

Equation (4) is fitted to the entire data set [temperature range,  $3 \text{ mK} \leq (T_c - T) \leq 25 \text{ K}$ ] with fixed values of the parameters  $A_c$ ,  $B_c$ , and  $C_c$  (see above),  $z_\eta = 0.064$ ,  $T_c = 322.524 \text{ K}$ , and  $\xi_0 = 0.44 \text{ nm}$ . Using the complete  $H$  function the ratio  $(q_d/q_c)$  is fixed at different values. The parameter  $q_c$  is the only free parameter. Using the two asymptotic forms of  $H$ , only  $Q_0$  is allowed to be an adjustable parameter. Figure 10 shows corresponding results of the data analysis. It turns out that Eq. (4) with the asymptotic form of  $H$  in the limit  $(q_d/q_c) \rightarrow 0$  represents best the viscosity data set, with a maximum deviation of experimental data points from the calculated curve of less than 0.5%. For the parameter  $Q_0$  a value of  $Q_0 = 1.52 \times 10^6 \text{ cm}^{-1}$  is found. It is in very good agreement with the value of  $Q_0 = 1.56 \times 10^6 \text{ cm}^{-1}$  determined independently (see Section 2). The



**Fig. 10.** Fit of Eq. (4) to experimental viscosity data of the 2-C<sub>4</sub>E<sub>1</sub>/water mixture of critical composition in the temperature range 3 mK ≤ (T<sub>c</sub> - T) ≤ 25 K. The two drawn-out lines represent the function  $\eta = \eta_b \exp\{z_\eta H\}$  (see Ref. 8) using two limiting forms of function  $H$  with  $Q_0$  as the only free parameter. The curve marked “∞” refers to function  $H$  in the limit  $(q_d/q_c) \rightarrow \infty$ ; the curve marked “0” refers to function  $H$  in the limit  $(q_d/q_c) \rightarrow 0$ . The inset shows a plot of the standard deviation  $s$  of fits of Eq. (4) to the experimental data for different fixed values of  $(q_d/q_c)$  with  $q_c$  as the only adjustable parameter.

limit  $(q_d/q_c) \rightarrow 0$  corresponds to the case in which the background diffusion coefficient  $D_b$  can be neglected.

### 4.2. Dynamic Light-Scattering Experiments

The results of the viscosity measurements discussed in Section 4.1 suggest that the measured value  $\Gamma$  of the reciprocal of the time constant of the autocorrelation function of light intensity scattered by a 2-C<sub>4</sub>E<sub>1</sub>/water mixture of critical composition can be identified with the singular contribution  $\Gamma_c$  of  $\Gamma$  [i.e.,  $(\Gamma/q^2) = D = D_c$ ]. Therefore the data set of the dynamic light-scattering experiments is analyzed in terms of the scaled diffusion coefficient  $D^*$  defined by Eq. (15):

$$D^* = (6\pi\eta\xi)/(k_B T) D \tag{15}$$

The corresponding approximant of the scaling function proposed by Burstyn et al. [9] has the form:

$$D^* = R\Omega_K(x)[1 + (x/2)^2]^{-\eta/2} \tag{16}$$



with

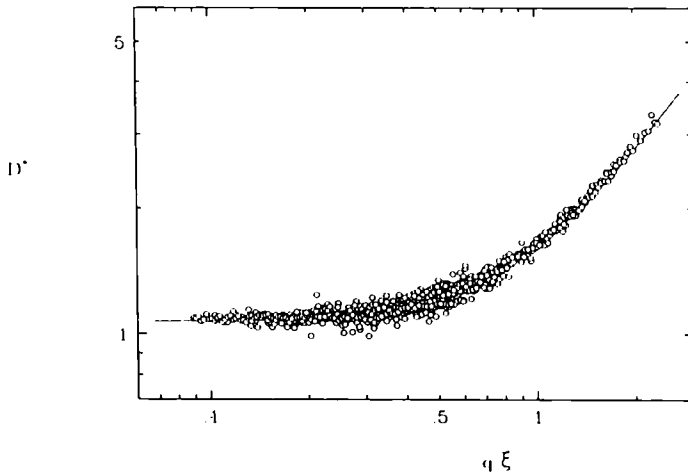
$$\Omega_{\kappa}(x) = [3/(4x^2)][1 + x^2 + (x^3 - 1/x) \arctan(x)]$$

and

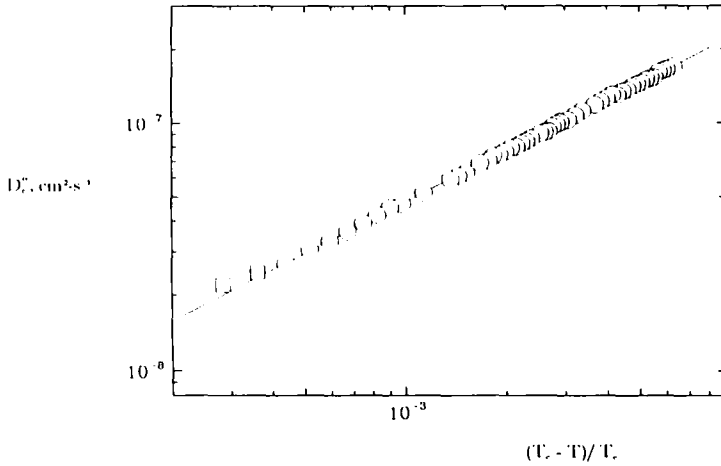
$$x = q\xi$$

The information to calculate  $D^*$  from Eq. (15) is available: (a) the measured values of  $D (= \Gamma/q^2)$  as a function of temperature and (b) the viscosity  $\eta$  of the critical mixture as a function of temperature, which is calculated from Eq. (14) with  $A'_c = 0.17532 \times 10^{-2}$ ,  $B_c = 214.011$ ,  $C_c = 212.434$ ,  $z_\eta = 0.066$ , and  $\nu = 0.630$ . The values of  $t$  are calculated from the critical temperature of the sample used for the light-scattering experiments.

A double-logarithmic plot of  $D^*$  calculated from the experimental data on the basis of Eq. (15) as function of the scaling variable  $x (= q\xi)$  reveals that the  $D^*(x)$  data collapse on a single curve as expected. For the calculation of  $\xi(T_c - T)$  a value of  $\xi_0 = 0.44$  nm is used. But the data are not represented by Eq. (16) with  $R = 1.03$ . The manner in which the experimental data deviate from the theoretical curve suggests an uncertainty in  $\xi_0$ .



**Fig. 11.** Double-logarithmic plot of the reduced diffusion coefficient  $D^*$  [see Eq. (15)] of a 2-C<sub>4</sub>E<sub>1</sub>/water mixture of critical composition as a function of the scaling variable  $x = q\xi$ . The values of  $\xi$  are calculated with  $\xi_0 = 0.39$  nm and  $\nu = 0.630$ . The drawn-out line represents Eq. (15) with  $R = 1.07$  and  $z_\eta = 0.065$ .



**Fig. 12.** Temperature dependence of the singular contribution  $D^0$  [double-logarithmic plot:  $D^0 = \lim(q \rightarrow 0)(\Gamma_c/q^2)$ ]. The drawn-out line represents the function  $D^0 = D_0 t^{v^*}$ , with  $T_c = 322.447$  K,  $v^* = 0.692$ , and  $D_0 = 5.68 \times 10^{-6} \text{ cm}^2 \cdot \text{s}^{-1}$ . Data points represented by open squares are excluded from the fitting procedure.

Using  $R$  and  $\xi_0$  as free parameters in a fit of Eq. (16) to the experimental data, the best fit is obtained with  $R = 1.07$  and  $\xi_0 = 0.39$  nm (see Fig. 11). From this finding it is concluded that we underestimated the uncertainty in the value of  $\xi_0$  of the system 2-butoxyethanol/water using static light-scattering experiments. The quality of the fit is reduced slightly if

- (a)  $\xi_0$  is fixed at  $\xi_0 = 0.42$  nm (value of  $\xi_0$  obtained from a new set of static light-scattering data; see Section 3.3 and Fig. 9), leaving  $R$  as the only free parameter of the fit [ $R(\text{fit}) = 1.15$ ], and
- (b)  $R$  is fixed at  $R = 1.03$ , leaving  $\xi_0$  as the only free parameter of the fit [ $\xi_0(\text{fit}) = 0.37$  nm].

In case a, the theoretically calculated  $D^*(x)$  curve lies only very slightly above the experimental data for  $x > 1$ . In case b, the opposite is true.

The temperature dependence of the singular contribution  $D^0 [= \lim(q \rightarrow 0)(\Gamma_c/q^2)]$  is shown in Fig. 12. The drawn-out line represents the function  $D^0 = D_0 t^{v^*}$ , with  $T_c = 322.447$  K,  $v^* = 0.692$ , and  $D_0 = 5.68 \times 10^{-6} \text{ cm}^2 \cdot \text{s}^{-1}$  (three-parameter fit). With  $v^*$  fixed at its theoretical value ( $v^* = 0.671$ ), the critical amplitude  $D_0$  has a value  $D_0 = 5.11 \times 10^{-6} \text{ cm}^2 \cdot \text{s}^{-1}$ , and the critical temperature  $T_c$  a value of  $T_c = 322.429$  K (two-parameter fit). The knowledge of  $D^0$  is required in an analysis of the kinetics of the liquid/liquid phase separation in studies of spinodal decomposition.

## 5. CONCLUSIONS

The following conclusions can be drawn from the results of this study.

(a) The crossover function for the critical viscosity of a classical fluid developed by Bhattacharjee et al. [8] connecting the asymptotic behavior near the critical point with the normal behavior away from the critical point describes well the shear viscosity data of the binary liquid mixture 2-butoxyethanol/water of critical composition over a wide range of temperatures [ $3 \text{ mK} \leq (T_c - T) \leq 25 \text{ K}$ ] using the limiting form of the crossover function for  $(q_d/q_c) \rightarrow 0$ . This limit corresponds to the case in which the background contribution  $D_b$  to the mutual diffusion coefficient can be neglected. Under this condition the critical amplitude of the viscosity  $Q_0$  is related to the parameter  $q_d$  by  $Q_0 = 2/(\exp\{4/3\}) q_d$ .

(b) A procedure is worked out to obtain the value of the critical amplitude of the viscosity  $Q_0$  from viscosity data by separating the experimentally determined shear viscosity of a mixture of critical composition into its regular and singular part. This procedure is applied to the viscosity data of the system 2-butoxyethanol/water. A value of  $Q_0 = (1.54 \pm 0.60) \times 10^6 \text{ cm}^{-1}$  is found, which is small for a binary mixture of components of small molar mass.

(c) Taking into account that the background contribution of the mutual diffusion coefficient in the system 2-butoxyethanol/water can be neglected with respect to the critical contribution, the reduced diffusion coefficient  $D^*$  is calculated from the experimental viscosity and dynamic light-scattering data. The  $D^*(x)$  data ( $x$ , scaling variable;  $x = q\xi$ ) are represented well by the approximation of the dynamic scaling function proposed by Burstyn et al. [9] with  $R = 1.07$  and  $\xi_0 = 0.39 \text{ nm}$ . This value of  $\xi_0$  is smaller by 10% than the mean value of  $\xi_0$  determined by static light-scattering experiments [ $\xi_0 = (0.43 \pm 0.1) \text{ nm}$ ].

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