

## Critical behavior of the self-diffusion coefficient in a binary fluid

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The method of the open-ended capillary tube has been used to determine the self-diffusion coefficient of the  $^{22}\text{Na}^+$  ion in an isobutyric acid, water, and a  $10^{-3}M$  NaCl critical mixture. The experimental range of temperature is  $0.360 \leq T - T_c \leq 9.860^\circ\text{C}$ . This study is a preliminary step in the investigation of ion-transport phenomena in binary fluids. We find that in the critical region the Arrhenius law has an important deviation and the self-diffusion coefficient  $D$  ( $\text{cm}^2/\text{s}$ ) can be governed by the mean-field theory.

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### I. INTRODUCTION

The determination of ion self-diffusion coefficients  $D$  ( $\text{cm}^2/\text{s}$ ) in electrolytes was developed in our laboratory for a critical mixture. Our experiments have been made on both, in the vicinity of and far away from the critical point. The open-ended capillary method has proved to be a powerful tool in the measurement of self-diffusion coefficients in a critical binary mixture.

In previous work [1,2] we studied extensively the variation of the self-diffusion coefficient  $D_+$  of labeled  $^{137}\text{Cs}^+$ , in the isobutyric acid, water, and  $10^{-3}M$  CsBr mixture as a function of mass fraction  $X$  of the acid for three different temperatures:  $T - T_c = 0.051, 8.051, \text{ and } 13.051$  K. The results of this work show that in the neighborhood of the critical composition  $X_c = 0.389$  in acid, the coefficient  $D_+$  does not show any anomaly, whereas the viscosity coefficient near the critical point shows a divergent behavior. This behavior reflects a tendency to desolvation of this  $\text{Cs}^+$  ions, as a result of strong correlation between the water and isobutyric acid molecules.

The self-diffusion depends on the properties of the diffusing particles and the medium. Therefore it can provide information concerning the properties of a critical mixture and dissolved substances. The variation of the self-diffusion coefficient was determined empirically as a function of temperature  $D(T)$  for the same system at the critical composition  $X_c$  [1]. This study reveals two variation regimes of the self-diffusion coefficient as a function of temperature  $T - T_c > 6.65^\circ\text{C}$ , i.e., far from the critical point, the logarithm of  $D$  is linear with the reciprocal of the absolute temperature, according to the Arrhenius and Eyring formula for the self-diffusion,

$$\ln(D) = \ln(D_0) - E_D/RT, \quad (1)$$

where  $E_D$  is the activation energy of diffusion and  $R$  is the gas constant. In Eq. (1)  $E_D$  remains constant, whereas in the domain of temperature  $T - T_c < 6.65^\circ\text{C}$ , i.e., near the critical point,  $\ln(D)$  is not linear with  $1/T$ . In order to interpret this critical behavior we have assumed that  $D$  varies in a similar way as the thermodynamical potential fluctuations. Accordingly, the activation energy of diffusion [3] is analytically represented by

$$\Delta E_D = -A|T_c - T|^{2\beta+1}, \quad (2)$$

where  $A$  is a constant and  $\beta$  is the universal exponent. The critical exponent  $\beta$  is predicted to be  $0.325 \pm 0.0015$  from renormalization-group theory [4],  $0.328 \pm 0.003$  from series expansion [5] and  $0.500$  from mean-field theory [6]. Equations (1) and (2) lead to

$$D = D_0 \exp[(A/T)(T_c - T)^{2\beta+1}]. \quad (3)$$

The purpose of this work is to clarify the relation between the temperature dependence on the activation energy in the vicinity of the critical region and the exponential form of the diffusion equation. Then it is interesting to test the relations (1) and (3) for an accurate determination of the self-diffusion coefficient of sodium (22) in the isobutyric acid + water +  $10^{-3}M$  NaCl critical mixture.

### II. EXPERIMENT

#### A. Sample preparation

The isobutyric acid was better than 99.5% pure and the water comes from a sophisticated purification setup. The critical mass fraction of the acid was 0.389 according to Ref. [7] and has been determined by weighing with a resolution of 0.1 mg.

We choose the mixture of isobutyric acid and water ( $I-W$ ) for the following reasons:

(i) Since their component densities are very close to each other, this mixture does not have density gradients induced by gravity.

(ii) The critical temperature of this system varying from 299.20 to 299.94 K [8–10] is low. Moreover, since the use of isotopes as tracers was discovered, the self-diffusion coefficient measurements in various mediums were undertaken around  $T = 298.15$  K.

The method of radioactive tracer [11] was used for the accurate determination of self-diffusion coefficient  $D_+$  of labeled  $^{22}\text{Na}^+$  in the isobutyric acid + water +  $10^{-3}M$  NaCl critical mixture. Radioactive solution was supplied by the "Commissariat à l'Energie Atomique, France" and it was prepared by dissolving the  $^{22}\text{Na}$ -enriched sodium chloride in hydrochloric acid at 0.1N. The salt concentration  $C$  was maintained constant for all temperatures at 0.001 mol of salt-kg mixture. The (NaCl) salt (Merck

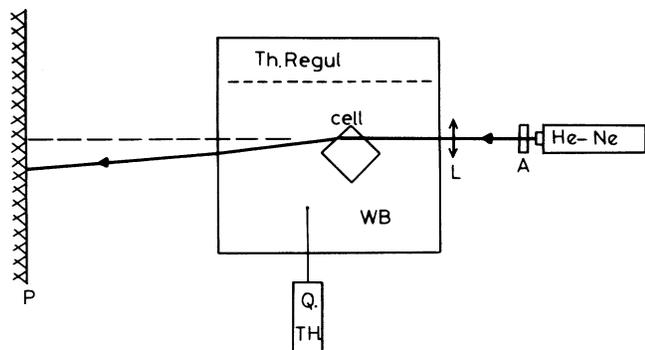


FIG. 1. Experimental setup for a critical temperature determination. He-Ne, helium-neon laser; A, attenuator; L, lens; th. Regul. thermal regulation; Q. Th., quartz thermometer; WB, water bath; P, plane where the beam laser was observed.

product) at the concentration  $0.001M$  constituted significant impurities and represented a third component. However, various investigators have reported not only substantial shifts in the critical temperature [12,13] but also changes in the critical composition [14] and critical exponents [15,16]. Investigators have also used impurities to move the critical point. Impurities have a significant impact on experimental and theoretical work in critical phenomena. In order to determine the critical temperature shift by  $(Na^+, Cl^-)$  salt, we have used a high-precision parallelepipedic cell filled with the electrolyte and immersed in a thermally stabilized water bath with an accuracy 2 mK. A slightly focused He-Ne laser beam ( $6328 \text{ \AA}$ , 5 mW power) is sent through the cell; the temperature was lowered by steps. The experimental set-up shown in Fig. 1 was already described in Ref. [16]. The critical temperature  $T_c$  was determined by the appearance of a ring of spinodal decomposition in the scattered light after a thermal quench of a few mK. The critical temperature was found to be  $T_c = 27.140 \pm 0.004 \text{ }^\circ\text{C}$ . We noticed a significant positive shift of the critical temperature  $T_c$ ,

$$\delta T_c(10^{-3}M \text{ NaCl}) = 0.192 \text{ K} .$$

### B. Self-diffusion coefficient

The diffusion coefficients determined are self-diffusion coefficients, i.e., it was ascertained that no concentration gradients of any species existed in the system.

The self-diffusion coefficient  $D(Na^+)$  is determined for each temperature  $T$  with the capillary method. The quartz capillary of length ( $l \approx 3 \text{ cm}$ ) was filled with a labeled electrolyte by means of a thin micropipette, operated with a medical syringe. A small drop of radioactive solution was left on top in order to prevent evaporation during the time necessary to reach thermal equilibrium, and also to avoid, as far as possible, convection disturbances when the capillary was immersed in the unlabeled electrolyte. The capillaries used had a small and uniform diameter (0.08 cm). In filling the capillaries the absence

of any air bubbles was carefully examined. The total radioactivity content in the capillaries was measured in the absence of diffusion (reference capillary) and after diffusion had taken place by means of a Packard Tri-Carb liquid scintillation spectrometer (model 33 200). The  $\gamma$  emitter ( $^{22}Na^+$ ) could be counted directly in the glass capillary. The number of counts was maintained to make the error in the radioactivity measurements negligible compared to the error due to the filling and emptying of the capillaries. The time for diffusion was 2.5–5 days. We denote by  $C(x,0)$  the total activity in the capillary at the time  $t=0$ . After a diffusion time  $t$  the final average activity will be  $C(x,t)$ . By solving Fick's equation with the proper limiting conditions, the ratio

$$\gamma = C(x,t)/C(x,0) \quad (4)$$

can be related to the self-diffusion coefficient  $D$  by solving the equation

$$\gamma = \sum_{n=0}^{\infty} (8/\pi^2)(2n+1)^2 \exp[\pi^2(2n+1)^2Dt/4l^2] . \quad (5)$$

It is a general experience in this laboratory that the effect of slowly stirring the solutions has a negligible effect on the measured diffusion coefficients under the conditions employed. The experiments were performed in a thermostated room within  $\pm 0.2 \text{ }^\circ\text{C}$ , in order to have one phase of the mixture, i.e., the temperature was around  $T_c$ .

The solution of Fick's law under the appropriate boundary conditions is given in Ref. [17]; the first term in the series expansion is

$$D = \frac{4l^2}{\pi^2 t} \ln \left[ \frac{8}{\pi^2 \gamma} \right] , \quad (6)$$

where  $D$  is the self-diffusion coefficient,  $l$  the capillary length, which was measured with a traveling microscope,  $t$  the diffusion time, and  $\gamma$  the ratio of Eq. (4).

If  $Dt/l^2 > 0.24$ , which was realized in most of our ex-

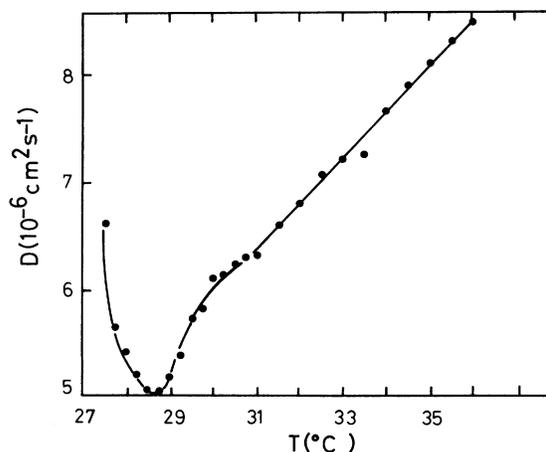


FIG. 2. Plot of the tracer diffusion coefficients for  $^{22}Na^+$  in the critical isobutyric acid + water +  $10^{-3}M \text{ NaCl}$  mixture as a function of  $T$  ( $^\circ\text{C}$ ).

TABLE I. Temperature dependence of self-diffusion coefficients of  $^{22}\text{Na}^+$  in the isobutyric acid + water +  $10^{-3}\text{M}$  NaCl mixture,  $T_c = 27.140^\circ\text{C}$ .

$T$ ( $^\circ\text{C}$ )	$D_+$ ( $10^6 \text{ cm}^2/\text{s}$ )	$t$ (s)	$\gamma = C(x,t)/C(x,0)$
27.50	$6.63 \pm 0.14$	337 350	$0.436 \pm 0.005$
27.75	$5.65 \pm 0.10$	354 270	$0.448 \pm 0.015$
28.00	$5.49 \pm 0.17$	232 530	$0.568 \pm 0.007$
28.25	$5.22 \pm 0.05$	228 360	$0.456 \pm 0.008$
28.50	$5.07 \pm 0.31$	323 070	$0.522 \pm 0.018$
28.75	$5.05 \pm 0.15$	315 250	$0.478 \pm 0.002$
29.00	$5.20 \pm 0.35$	300 765	$0.527 \pm 0.020$
29.25	$5.41 \pm 0.05$	357 375	$0.540 \pm 0.007$
29.50	$5.75 \pm 0.02$	400 000	$0.430 \pm 0.004$
29.75	$5.85 \pm 0.22$	361 205	$0.466 \pm 0.003$
30.00	$6.12 \pm 0.25$	230 300	$0.543 \pm 0.005$
30.25	$6.15 \pm 0.18$	234 856	$0.472 \pm 0.006$
30.50	$6.23 \pm 0.15$	238 540	$0.522 \pm 0.003$
30.75	$6.30 \pm 0.12$	339 024	$0.513 \pm 0.004$
31.00	$6.32 \pm 0.21$	312 320	$0.472 \pm 0.010$
31.50	$6.61 \pm 0.08$	310 450	$0.475 \pm 0.004$
32.00	$6.80 \pm 0.25$	311 840	$0.452 \pm 0.010$
32.50	$7.08 \pm 0.05$	287 530	$0.483 \pm 0.003$
33.00	$7.23 \pm 0.12$	243 770	$0.502 \pm 0.006$
33.50	$7.25 \pm 0.20$	249 550	$0.458 \pm 0.013$
34.00	$7.67 \pm 0.33$	259 000	$0.466 \pm 0.020$
34.50	$7.90 \pm 0.15$	245 109	$0.472 \pm 0.015$
35.00	$8.13 \pm 0.08$	220 518	$0.591 \pm 0.002$
35.50	$8.32 \pm 0.10$	212 425	$0.500 \pm 0.003$
36.00	$8.50 \pm 0.15$	207 350	$0.501 \pm 0.005$

periments, the second term in the series expansion is less than  $10^{-3}$  of the first term and the other terms are still smaller. Only in a few cases was it necessary to include the second term. From the measured radioactivities and the measured diffusion times,  $D$  is directly obtained. It was experimentally checked that  $D$  was not dependent on the choice of  $l$  or  $t$ . In most cases  $t$  was chosen to give  $\gamma = C(x,t)/C_0(x,0)$  between 0.45 and 0.55.

The thermal stabilization was  $\pm 0.2\%$   $^\circ\text{C}$  over more than one day; we estimate the precision of our diffusion results to be  $\pm 1\%$ . The experimental self-diffusion coefficient of  $^{22}\text{Na}^+$  in the critical isobutyric acid + water +  $10^{-3}\text{M}$  NaCl mixture for various temperatures  $T$  ( $^\circ\text{C}$ ) are given in Fig. 2 and Table I, ranging between  $27.50$  and  $36^\circ\text{C}$ .

The reported self-diffusion coefficients are the average values of  $8 \times 2$  separate measurements.

### C. Viscosity

According to the Einstein-Stokes law the shear viscosity of critical mixture is an important factor in the interpretation of the self-diffusion process. It is necessary to know the shear viscosity  $\eta$  of the electrolyte. The coefficient  $\eta$  (cP) =  $\nu$  (cSt)  $\rho$  ( $\text{g}/\text{cm}^3$ ) of the mixture at different temperatures was determined by measuring the density  $\rho$  and the kinematic viscosity  $\nu$ .

The densities were measured in a digital precision densimeter, DMA 46 (PAAR, Graz, Austria). The density of a solution was calculated from the electronically mea-

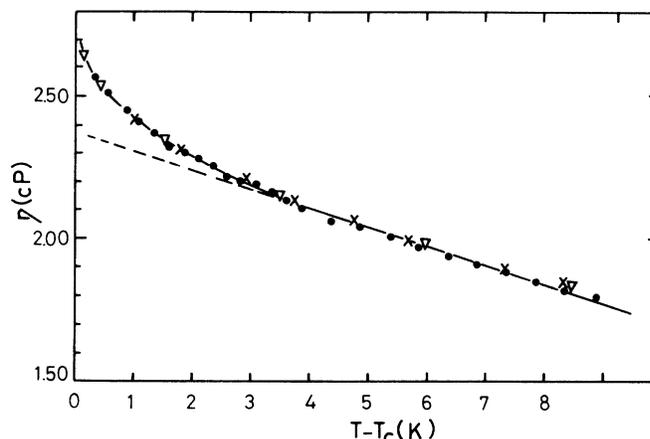


FIG. 3. Shear viscosity vs  $T - T_c$  for the  $I + W + 10^{-3}\text{M}$  NaCl: (●) our data; (▽) the data of Ref. [18]; (×) from Ref. [9].

sured frequency of a mechanical oscillator filled with the solution. The oscillator was  $U$  shaped glass tubing (volume  $0.7 \text{ cm}^3$ ) placed in a metal block which was controlled temperature to about  $\pm 10^{-3}\text{C}$ . The temperature was measured by a quartz thermometer. The precision of the density measurement was about  $\pm 0.1 \text{ mg}/\text{cm}^3$ .

The kinematic viscosity was calculated from the flow times using the following equation:

$$v = k(t - \theta), \quad (7)$$

where  $t$  is the flow time,  $k$  is a constant for a given viscosimeter (AVS/N-Chott-Gerate), and  $\theta$  is the correction time. The viscosimeter was calibrated with fluids of known density and viscosity.

The temperature dependence on the shear viscosity of isobutyric acid +  $10^{-3}\text{M}$  (NaCl), was determined from  $27.50$  to  $36^\circ\text{C}$ . The coefficient  $\eta$  versus  $T - T_c$  is plotted in Fig. 3. In Fig. 3 it appears that  $\eta$  changes more slowly in the region very close to  $T_c$  than in the region far away from  $T_c$ . The usual increase of  $\eta$  near  $T_c$  is observed; this effect is well known. Our results are in conformity with those of [9,18]. The salt NaCl at a concentration  $10^{-3}\text{M}$  has an important effect of the shear viscosity for this study and a comparison with already published [9,18] data for the same system (isobutyric acid–water critical mixture).

## III. RESULTS AND DISCUSSION

### A. Evaluation of viscosity activation energy

In the neighborhood of the critical point the variation of the viscosity coefficient  $\eta$  as a function of temperature  $T$  is given by the following formula [19] which reflects the divergent behavior of  $\eta$  when  $T \rightarrow T_c$ :

$$\eta = \eta_0 t^{-Y_n}, \quad (8)$$

where  $t$  is the reduced temperature  $t = (T - T_c)/T_c$  and  $Y_n$  a small coefficient of about 0.04 [19].  $\eta_0$  also changes with temperature according to the following relation:

$$\eta_0 = \eta_s \exp(\Delta E_v / RT) . \quad (9)$$

Here  $\eta_s$  is a constant,  $\Delta E_v$  is the viscosity activation energy, and  $R$  is the gas constant. The relations (8) and (9) lead to the following equation:

$$\ln(\eta) = \ln(\eta_s) + \Delta E_v / RT - Y_n \ln(t) . \quad (10)$$

In order to interpolate the viscosity of isobutyric acid + water +  $10^{-3}M$  NaCl to any given temperature a least-squares method was used to find an equation which would fit the viscosity data. For an estimation of the quality of the fit, we considered the deviation between calculated and measured values. The distribution of the errors are measured by a quality coefficient  $Q$ . This parameter equals one if the errors are randomly distributed, but is drastically lowered if a systematical distortion occurs. The following equation was found to agree with known viscosities at given temperatures within  $\pm 0.003$  cp:

$$\ln \eta = 2995/T - 9.100 , \quad (11)$$

where  $\eta$  is viscosity ( $10^{-2}$  g/cm s) and  $T$  is temperature (in K).

This result is in agreement with Eq. (10) because of the low value of  $Y_n = 0.04$  and the small variation of  $\ln(t)$ . The activation energy  $\Delta E_v$  resulting from this fitting is 6 kcal/mol. The statistical quality of the fit was very good (factor of  $Q = 0.98$ ).

### B. Critical behavior of $D_+$

Table I lists the experimental self-diffusion data, showing the effects of the various temperatures. These data are plotted in Fig. 2. However, this study distinguishes two  $D_+$  behaviors in the critical isobutyric acid + water +  $10^{-3}M$  NaCl mixture.

(i) In the domain of temperature  $T - T_c > 4.36$  K, i.e., far away from the critical region. The plot of  $\ln(D_+)$  versus  $1/T$  yields a straight line. The self-diffusion coefficient is compatible with the generally used form of the diffusion equation (1). The normal behavior is characterized by the relation (1).

The best fitting of our experimental data considering the variation of  $\ln(D_+)$  with  $1/T$  shows that  $\Delta E_D$  remains constant, and in this region of temperature the fitting gives the expression

$$\ln(10^6 D_+) = 19.4973 - 5.365 \times 10^3 / T \quad (Q = 0.99) . \quad (12)$$

Here  $10^6 D_+$  is expressed in  $\text{cm}^2/\text{s}$ .

(ii) We now examine the coefficient  $D_+$  in the vicinity of  $T_c$ . In the domain of temperature  $0.360 < T - T_c < 4.36$  K, the Arrhenius plot was characterized by a significant curvature, as shown in the Fig. 4(b). In order to interpret this anomaly of Arrhenius law, we have developed recently a new method [1,3]. The self-diffusion coefficient presented a critical behavior. The activation energy due to the diffusion process depended well on the temperature. We are led to suppose a critical behavior in agreement with a relative thermo-

dynamic potential fluctuation. The Landau free energy  $E(T, M)$  close to critical temperature  $T_c$  is written as an expansion in order parameter  $M$  [20]:

$$E(T, M) = E_0(T, 0) + \frac{A(T)}{2} M^2 + \frac{B(T)}{4} M^4 + \dots . \quad (13)$$

For symmetry reasons, only the even power of  $M$  are retained. The minimum of  $E$  provides the values of  $M$  in both regions (when  $T < T_c$ ),

$$\frac{\partial E}{\partial M} = 0 \implies M [A(T) + B(T)M] = 0 , \quad (14)$$

$$T > T_c \implies E \text{ should be minimum for } M = 0 , \quad (15)$$

$$T < T_c \implies E \text{ should be minimum for } M^+ \text{ or } M^- , \quad (16)$$

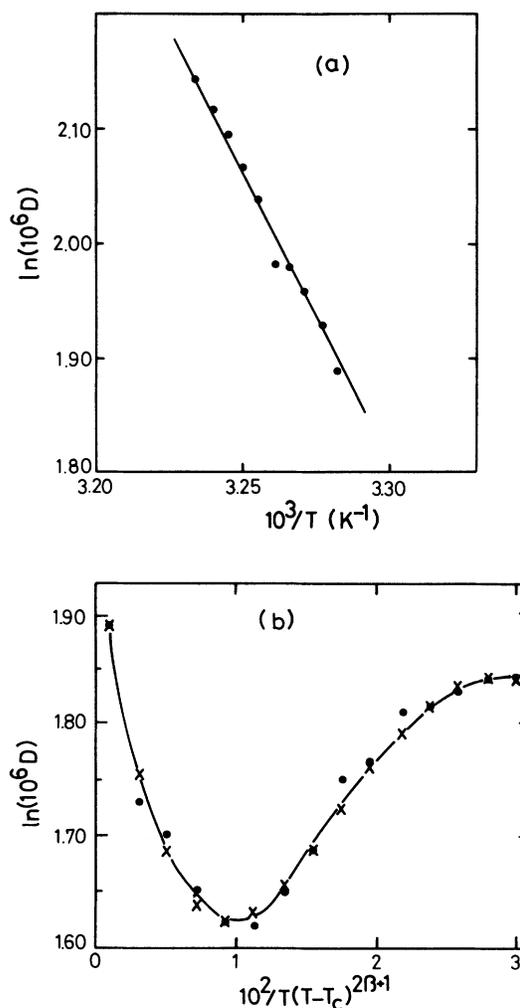


FIG. 4. (a) Arrhenius region. The logarithm of the tracer diffusion coefficient or  $^{22}\text{Na}^+$  in the critical isobutyric acid + water +  $10^{-3}M$  NaCl vs the reciprocal of the absolute temperature. (b) Critical region. Variation of the  $\ln(10^6 D_+)$  with  $(T - T_c)^{2\beta+1}/T$ . The values represented by  $\times$  are calculated from Eq. (26).

where  $M^+ = M > 0$  and  $M^- = M < 0$ . Equations (15) and (16) are satisfied if  $A(T)$  is an odd function of  $(T - T_c)$  and  $B(T)$  an even function,

$$A(T) = a(T - T_c) + \dots, \quad (17)$$

$$B(T) = b + \dots. \quad (18)$$

Therefore (13) becomes

$$\Delta E = E(T, M) - E_0(T, 0) = \frac{a}{2}(T - T_c)M^2 + \frac{b}{4}M^4 + \dots. \quad (19)$$

In binary mixture the order parameter  $M$  is the difference  $M^{u,l} = x^{u,l} - x_c$  of the concentration  $x^{u,l}$  of one component and its critical value  $x_c$ .  $u$  or  $l$  refers to the phase above or below the meniscus, in a gravity field. If we consider only the first term of the coexistence curve amplitude,

$$M = Bt^{\beta}(1 + a_n t^{\Delta}) + \dots, \quad (20)$$

where  $a_n$  is the first-order correction to scaling amplitude,  $\beta = 0.325$ , and  $\Delta = 0.50$  are the universal exponents, the order-parameter behavior can be written as

$$M = Bt^{\beta}. \quad (21)$$

In Equation (13) the  $M^4$  term can be negligible; therefore,  $\Delta E$  can be written in the following form:

$$\Delta E = \frac{a}{2}(T - T_c)M^2. \quad (22)$$

Equations (21) and (22) lead to

$$\Delta E = \frac{a}{2}B^2(T - T_c)t^{2\beta} \quad (23)$$

$$= aB^2(T - T_c)(T_c - T)^{2\beta}/2T_c^{2\beta}. \quad (24)$$

Accordingly, the activation energy of diffusion is analytically represented by

$$\Delta E = -A|T_c - T|^{2\beta+1}, \quad (25)$$

where  $A = (a/2)b^2/T_c^{2\beta}$ . With this approximation of  $\Delta E$  in the critical region Eq. (1) takes the following form:

$$\ln(D) = \ln(D_0) + (A/RT)|T_c - T|^{2\beta+1}. \quad (26)$$

The values of  $D_+$  calculated from Eq. (26) were plotted in Fig. 4(b) in order to compare them visually with the experimental data. From Fig. 4(b) it appears that the calculated data coincide with the experimental data very well (with a maximum error of 1%). In order to get more precision about the  $D_+$  variation with temperature, the self-diffusion coefficient  $D_+$  can be related to  $T - T_c$  through the relationship

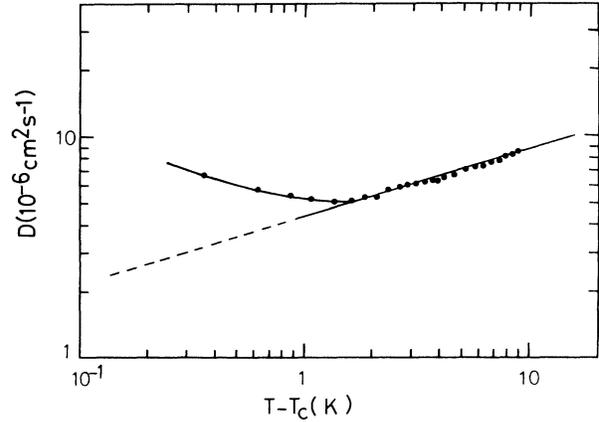


FIG. 5. Log-log plot for  $D_+$  vs  $T - T_c$ , allowing the exponent  $\beta$  to be measured.

$$D = D_0(T - T_c)^\beta. \quad (27)$$

Then a log-log plot of  $D_+$  versus  $T - T_c$  should be a straight line of slope  $\beta$ . Figure 5 illustrates our self-diffusion coefficient data on such a plot. The coefficient  $D_0$  and the critical exponent  $\beta$  of Eq. (27) have been solved by the least-squares method. The best fit gave  $D_0 = 4.368 \times 10^{-6} \text{ cm}^2/\text{s}$  and  $\beta = 0.304 \pm 0.090$  with the quality coefficient  $Q = 0.95$ .

#### IV. CONCLUSION

The self-diffusion coefficient of  $^{22}\text{Na}^+$  in the critical mixture isobutyric acid + water +  $10^{-3}M$  NaCl has been determined in a large domain of temperature from

$$T - T_c = 0.360^\circ\text{C} \text{ up to } T - T_c = 9.860^\circ\text{C}.$$

At high temperature  $T - T_c > 4.360^\circ\text{C}$ , the coefficient  $D_+(T)$  behaves according to a simple Arrhenius law. In the critical region  $T - T_c < 4.360^\circ\text{C}$ , we have detected an important deviation of this law, the self-diffusion coefficient can be governed by the mean-field theory and the activation energy of diffusion depends well on the temperature. It now possible to form an explicit expression for the self-diffusion coefficient in the neighborhood of critical point of binary fluid.

The anomalous increase in the shear viscosity coefficient in the critical region has been well established in binary liquid mixture with ions.

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