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Mutual Diffusivity of a Mixture of *n*-Hexane and Nitrobenzene Near Its Consolute Point

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It is demonstrated that the Taylor dispersion method can be used to measure the mutual diffusivity of liquid mixtures near a critical mixing point. For this purpose we have measured the mutual diffusivity of a liquid mixture of *n*-hexane and nitrobenzene at the critical composition at temperatures from 16 K down to 1 K above the critical temperature. The results are in agreement with the theoretically predicted behavior of the diffusivity near a critical point of mixing.

KEY WORDS: binary diffusion; critical phenomena; *n*-hexane; nitrobenzene; Taylor dispersion.

1. INTRODUCTION

As recently reviewed by Erkey and Akgerman [1], the Taylor dispersion method has become a versatile and reliable method for measuring mutual diffusivities in liquid mixtures. In our laboratory, we have developed an instrument based on the Taylor dispersion method and have used it to measure mutual diffusivities in various liquid mixtures [2–5]. Provided that the apparatus design and the operating conditions obey the constraints imposed by the theory [1, 6], the Taylor dispersion method is capable of yielding mutual diffusion coefficients with an accuracy of a few percent level as earlier demonstrated for mixtures of light and heavy water [3].

The purpose of the present paper is to demonstrate that the Taylor dispersion method can also be adapted to measure the mutual diffusivity in

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liquid mixtures in the vicinity of a critical mixing point, also known as consolute point. Specifically, we report experimental diffusivities obtained for the mixture *n*-hexane + nitrobenzene near its consolute point and show that these experimental data agree with the behavior predicted on the basis of the theory of the critical slowing down of the concentration fluctuations near a consolute point [7].

2. EXPERIMENTAL METHOD AND WORKING EQUATION

A description of the theory of the Taylor dispersion method is available in the literature [1, 6]. Ideally, the apparatus consists of an infinitely long straight tube with a uniform circular cross section in which a laminar flow with mean velocity $\bar{u}_0$ of a binary fluid mixture with uniform composition is established. A mixture of slightly different composition is injected in the tube as a δ-function pulse which is then dispersed by the combined action of molecular diffusion and parabolic velocity profile. Under suitable conditions, it is possible to determine the mutual diffusivity D_{12} of the binary mixture from the first two temporal moments of the Gaussian concentration distribution at a distance L from the injection point through [6]

$$D_{12} = \frac{a_0^2}{24\bar{t}_{\mathrm{id}}}\left[\frac{(1+4\sigma_{\mathrm{id}}^2/\bar{t}_{\mathrm{id}}^2)^{1/2}+3}{(1+4\sigma_{\mathrm{id}}^2/\bar{t}_{\mathrm{id}}^2)^{1/2}+2\sigma_{\mathrm{id}}^2/\bar{t}_{\mathrm{id}}^2-1}\right]\left[\frac{1}{2}+\frac{1}{2}(1-\delta_{\mathrm{a}})^{1/2}\right] \qquad (1)$$

In this working equation a_0 is the radius of the capillary tube, $\bar{t}_{\mathrm{id}}$ the first temporal moment, and σ_{id}^2 the second central temporal moment of the concentration distribution, while

$$\delta_{\mathrm{a}} = 12.7997\zeta_0 \qquad (2)$$

with

$$\zeta_0 = \bar{u}_0 a_0^2/48LD_{12} \qquad (3)$$

For the working equation to be applicable certain restrictions must be satisfied that affect the equipment design and the operating conditions. In addition, there are some effects that cannot be rendered negligible by proper design, such as the finite volume of the detector at the end of the capillary tube, the finite volume of the injected pulse, and the difference between the radius of the diffusion capillary and that of the tube connecting the diffusion capillary to the detector. These effects are accounted for by identifying the ideal first temporal moment $\bar{t}_{\mathrm{id}}$ and the ideal variance σ^2_{id} with

$$\bar{t}_{\mathrm{id}} = \bar{t} + \sum_i \delta t_i \tag{4}$$

$$\sigma^2_{\mathrm{id}} = \sigma^2 + \sum_i \delta\sigma^2_i \tag{5}$$

where $\bar{t}$ and σ^2 are the first moment and the variance measured experimentally and where δt_i and $\delta\sigma^2_i$ are corrections [6].

Finally, a correction needs to be made, since the physical properties of the mixture, specifically the diffusivity, in reality depend on concentration. As a consequence the measured diffusivity corresponds to a reference mole fraction x_{ref}, such that

$$x_{\mathrm{ref}} = x_{\mathrm{f}} + \delta x \tag{6}$$

where x_{f} is the mole fraction of component 1 of the flowing mixture and δx a correction. In normal circumstances all these corrections can be reduced to no more than ±1% by suitable instrument design. Near the critical point the diffusivity becomes more sensitive to changes in the concentration and the accuracy of the method needs to be checked experimentally.

3. INSTRUMENT DESIGN AND OPERATION

An instrument constructed according to the principles mentioned above was described in a previous publication [3]. To take measurements in the vicinity of a consolute point some improvements were made. A schematic representation of the experimental arrangement is shown in Fig. 1. The flow of the mixture is established with the aid of an infusion syringe pump (Harvard Instruments, Model 22) that pumps the fluid mixture directly into the diffusion tube. The solution with slightly different concentration is injected through a six-port injection valve (Rheodyne, Model 7010). The diffusion tube, as well as all fittings, are made of 316 stainless steel. The diffusion tube, 13 m long and with an inner radius of 0.4 mm, is wound around the inner wall of a U-shaped circular ring of stainless steel with a radius of 16 cm. The U-shaped ring was filled with molten lead to ensure good thermal contact and then covered with a stainless-steel cap. The entire block was suspended from a marble table to avoid any vibration of the tube which would induce enhanced dispersion. A differential refractometer (Waters Associates, Model R-401) was used as detector.

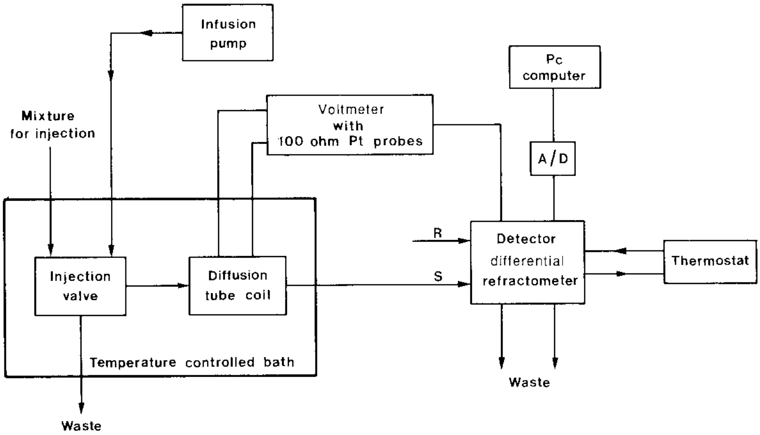

Fig. 1. Schematic representation of the experimental arrangement.

The temperature is measured with a resolution of 2.5 mK with the aid of platinum probes with a resistance of 100 Ω, embedded in the block containing the diffusion tube. This block, together with the injection valve, is immersed in an oil bath with a refrigerating coil as cold source and two incandescent bulbs as heating source. The temperature of the oil bath was regulated with a PID controller and maintained to within ±2.5 mK in the course of periods of 1 h, while the long-term drift in the temperature was kept within ±5 mK per day. The temperature of the refractometer was controlled to within ±10 mK with a separate thermostat (Haake, Model FE2).

The signal from the refractometer was amplified and digitized with a 12-bit analog-to-digital converter board in a microcomputer. The approximately 1000 data points characterizing the temporal concentration profile corresponding to each measurement were subsequently fitted to a Gaussian distribution yielding $\bar{t}$ and σ^2.

4. APPLICATION TO A MIXTURE OF *n*-HEXANE AND NITROBENZENE

We have measured the mutual diffusivity of a mixture of *n*-hexane (component 1) and nitrobenzene (component 2) at the critical composition as a function of temperature at atmospheric pressure. The *n*-hexane and the nitrobenzene, obtained commercially from Fluka and Merck, respectively, with a stated purity of better than 99.5%, were distilled over calcium hydride at atmospheric pressure. The final purity of the two liquids was determined by gas–liquid chromatography and found to be 99.8 and

99.9%, respectively. The mixture was prepared gravimetrically and had a composition with mole fraction $x_1 = 0.5778 \pm 0.0001$ in agreement with the known critical composition $x_1 = 0.578 \pm 0.002$ of this mixture [8, 9]. The critical temperature of the mixture was not measured directly, but the value $T_c = 292.56$ K as measured by Wu et al. [8] was found to be consistent with our measurements.

To ensure that the instrument operated under the conditions required for the applicability of the working Eq. (1), the diffusion time $\bar{t}$ was chosen to be approximately 4 h at a temperature $T = 308$ K, increasing to 16 h at $T = 296$ K at which times the measured diffusivities are independent of $\bar{t}$, thus avoiding any buoyancy effects [6]. These measurement times are long because of the smaller values of the diffusivity in the vicinity of the consolute point. The apparatus had originally been designed for liquid mixtures under normal conditions, where times of 1 or 2 h is adequate. In principle, it is possible to reduce the required diffusion times by modifying the design of the apparatus. For instance, a reduction of the capillary radius by a factor n under suitable conditions will reduce the measurement time by a factor n^2 [6]. Such a modification may be made in the future.

We have measured the mutual diffusivity at temperatures from 308.6 K, which is 16 K above the critical temperature T_c down to $T = 293.7$ K, which is only 1.1 K above T_c. The experimental results are presented in Table I. As shown in a previous publication [3], for a liquid mixture under

Table I. Mutual Diffusivity of *n*-Hexane + Nitrobenzene at the Critical Composition ($T_c = 292.56$ K)

Temperature (K)	$10^{10} D_{12}$ ($m^2 \cdot s^{-1}$)
293.7	0.44
294.2	0.63
	0.54
295.2	0.73
297.2	1.12
	1.20
	1.16
	1.12
	1.18
	1.17
299.2	1.45
	1.31
	1.40
308.6	2.91

normal conditions it is possible to obtain with the instrument an accuracy of about 1 %. Operation of the instrument with a liquid mixture near the critical point is more difficult and leads to some reduction of the accuracy that can be obtained. As can be seen from the results in Table I, there is a spread in the data of up to ±5 % near the critical point. A major problem is that close the critical point increasingly longer measuring times are required. As mentioned earlier this situation can be improved in principle by reducing the radius of the capillary. We were not able to obtain reliable measurements at temperatures within 1 K from the critical temperature where the fluid mixtures becomes turbid, which is a problem generally encountered with optical techniques [10].

To check the accuracy of our Taylor dispersion method when applied in the critical region we compare our data with diffusivity data obtained by other investigators with other experimental methods. Haase and Siry [11, 12] have used interferometry to measure the binary diffusion coefficient of a mixture of *n*-hexane and nitrobenzene at the critical composition. More recently, Wu et al. [8] have determined the diffusion coefficient from dynamic light scattering with a claimed precision of 1 %. The experimental values obtained for D_{12} by us and by these previous investigators are plotted as a function of $T-T_c$ in Fig. 2a. Our data agree with those reported by Haase and Siry [11, 12] and by Wu et al. [8] within the spread of our measurements. Specifically, the good agreement with the accurate measurements of Wu et al. shows that the diffusivity near the critical mixing point can be measured with the Taylor dispersion method with an accuracy of about ±5 %.

5. COMPARISON WITH THEORY

The diffusivity D_{12} can be written as the ratio λ/χ, where λ is a mass conductivity and χ the derivative of the concentration with respect to the chemical potential of one of the components [13]. In the critical region, the conductivity λ and the viscosity η can be written as $\lambda = \Delta_c\lambda + \bar{\lambda}$ and $\eta = \Delta_c\eta + \bar{\eta}$, where $\Delta_c\lambda$ and $\Delta_c\eta$ are singular critical contributions and $\bar{\lambda}$ and $\bar{\eta}$ nonsingular background contributions [7]. The separation of the conductivity λ into a singular and a background contribution implies a resulting separation for the diffusivity

$$D_{12} = \Delta_c D + \bar{D} \tag{7}$$

where $\bar{D} = \bar{\lambda}/\chi$. The theory of critical dynamics predicts that near the critical point $\Delta_c D$ satisfies a Stokes–Einstein law of the form

$$\Delta_c D = \frac{R k_B T}{6\pi\eta\xi} \tag{8}$$

where k_B is Boltzmann's constant, ξ the correlation length, and R a universal dynamic amplitude close to unity [7]. At the critical concentration the correlation length ξ and the response function χ diverge as

$$\xi = \xi_0(\Delta T^*)^{-\nu}, \qquad \chi = \Gamma(\Delta T^*)^{-\gamma} \tag{9}$$

where $\Delta T^* = (T - T_c)/T_c$, ξ_0, and Γ are system-dependent amplitudes and

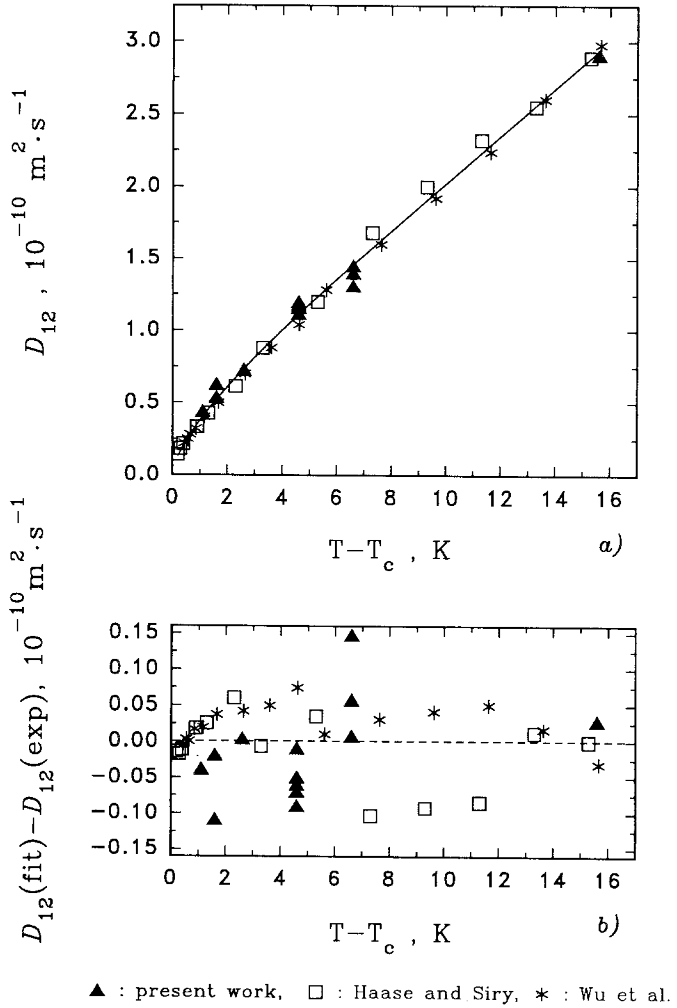

Fig. 2. (a) Mutual diffusivity D_{12} of a mixture of n-hexane + nitrobenzene at the critical composition as a function of $T - T_c$. The curve represents the values calculated from Eq. (13). (b) Difference between experimental diffusivities and those calculated from Eq. (13).

$\nu = 0.63$ and $\gamma = 1.24$ are universal critical exponents [14]. The viscosity η is expected to diverge as

$$\eta = \bar{\eta}(Q\xi)^z = \bar{\eta}Q'(\Delta T^*)^{-z\nu} \tag{10}$$

where Q and $Q' = (Q\xi_0)^z$ are system-dependent amplitudes and $z = 0.065$ [15–18]. It thus follows from Eq. (7) that the diffusivity in the vicinity of the critical point should behave as

$$D_{12} = \frac{Rk_B T}{6\pi\eta\xi_0}(\Delta T^*)^\nu + D_0(\Delta T^*)^\gamma \tag{11}$$

where $D_0 = \bar{\lambda}/\Gamma$ can be treated as a system-dependent constant.

In order to compare the experimental diffusivity data with the predicted behavior given by Eq. (11), we need reliable information for the correlation-length amplitude ξ_0 and the viscosity η. These properties have indeed been measured by several investigators for a mixture of *n*-hexane and nitrobenzene at the critical concentration, but the results reported in the literature illustrate the difficulty of obtaining accurate data in the critical region.

The experimental values reported from light-scattering or turbidity measurements for the correlation-length amplitude ξ_0 are summarized in Table II. It can be seen that these values vary by as much as 30%. We have accepted the value

$$\xi_0 = (2.65 \pm 0.07)\ \text{Å} \tag{12}$$

most recently reported, since it seems to satisfy the theoretically predicted amplitude combinations [21].

In Fig. 3, we show the viscosity η as a function of temperature as measured by Miyake et al. [22], Beysens et al. [23, 24], and Dega-Dalkowska [25]. The measurements originally obtained by Beysens et al.

Table II. Values reported for ξ_0 of *n*-Hexane + Nitrobenzene at the Critical Concentration

Year	ξ_0 (Å)	Reference
1972	3.64 ± 0.22	Lai and Chen [19]
1980	3.14 ± 0.06	Beysens [20]
1983	3.54 ± 0.15	Chen et al. [9]
1983	2.65 ± 0.07	Zalczer et al. [21]

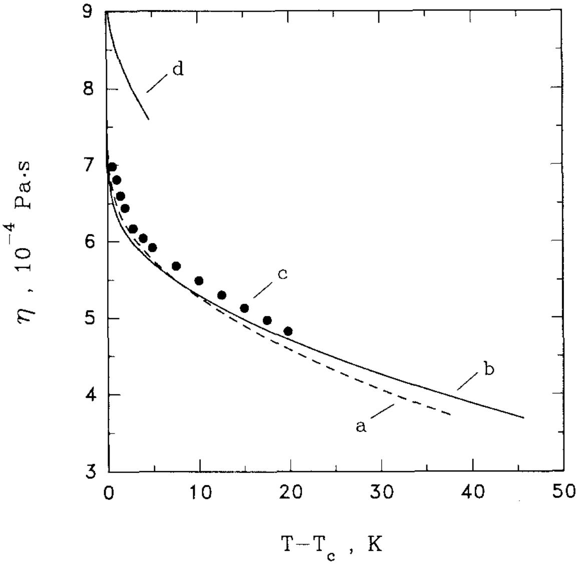

Fig. 3. Viscosity η of a mixture of *n*-hexane + nitrobenzene at the critical concentrations. (a) Beysens et al. [9, 23]; (b) Beysens et al. [24]; (c) Dega-Dalkowska [25]; (d) Miyake et al. [22].

[23] appeared to be affected by a calibration error and were revised subsequently [24]. The measurements of Dega-Dalkowska, taken in a very small temperature interval, appear to be grossly inconsistent with those of all other investigators, leaving only the measurements of Miyake et al. [22] and the revised data of Beysens et al. [24] as the more reliable. The latter two sets of data still show differences of up to 3 to 5%. For this paper we have accepted the revised data of Beysens et al. [24], since they have provided an explicit equation to represent the viscosity data as given by Eq. (12) with

$$\bar{\eta}Q' = A\exp[B/(1+\Delta T^*)] \qquad (13)$$

and with the parameter values $A = 2.696 \times 10^{-3}$ Pa · s, $B = 2.941$, and $z\nu = 0.0398$.

Chen and co-workers [9, 26] have tried to estimate the magnitude of the background diffusivity $\bar{D}$, and hence of the coefficient D_0 in (13), from the amplitude Q in the power law given by Eq. (10) for the experimentally observed viscosity. However, there are a number of difficulties with this procedure. First, Chen et al. use the viscosity measurements reported originally by Beysens et al. [23], which are subject to a calibration error as mentioned above, while it is also not clear how well the background viscosity $\bar{\eta}$ can be separated in practice from the observed total viscosity η. More fundamentally, there is a theoretically difficulty with the procedure. The critical contributions to the transport properties arise from the long-range critical fluctuations up to a maximum cutoff wave number q_D [27, 28]. To estimate the diffusivity background from the amplitude Q, Chen et al. identify an expression for the coefficient Q, obtained originally by Perl and Ferrell [29], neglecting any diffusivity background, with another expression derived by Oxtoby and Gelbart [30], in which the finite cutoff wave number q_D was neglected. However, as pointed out by Bhattacharjee et al. [27], the amplitude Q depends both on the background diffusivity and the cutoff wavenumber q_D. As a consequence, as also discussed by Beysens et al. [24], one cannot calculate the background diffusivity from the amplitude Q without knowing q_D. Hence, we have no other choice than to treat the coefficient D_0 in Eq. (11) as an adjustable parameter.

In practice, we have fitted Eq. (11) with Eqs. (10), (12) and (13) to the combined set of our diffusivity data and those of the previous investigators [8, 11, 12], treating both the universal amplitude R and the system-dependent coefficient D_0 as adjustable parameters with the result

$$R = 1.04 \pm 0.06, \qquad D_0 = 0.40 \pm 0.68 \tag{14}$$

The values thus calculated from Eq. (11) for D_{12} are represented by the curve in Fig. 2a, while the differences between experimental and calculated diffusivities are shown in Fig. 2b. The equation represents the experimental diffusivities within experimental accuracy. The error in the value R incorporates the errors in D_{12} and ξ_0, but not in η. The value found for the amplitude is in good agreement with the value $R = 1.03$ predicted theoretically [31, 32] and with the value $R = 1.01 \pm 0.04$ measured by Burstyn et al. [32, 33]. In practice we find that the asymptotic Eq. (13) represents the diffusivity data in the experimental temperature range, while any background effects are small.

For temperatures up to 10 K above the critical temperature one should, in principle, also consider a possible correction-to-scaling term in the asymptotic power laws given by Eq. (9) for ξ and χ [14, 24, 34, 35]. However, the limited accuracy of the data does not warrant inclusion of such correction terms at this stage.

6. CONCLUSION

We have measured the mutual diffusivity of a mixture of *n*-hexane and nitrobenzene at the critical concentration at temperatures close to the critical mixing temperature. The experimental results are in good agreement with the diffusion coefficients determined by Wu et al. [8] from dynamic light-scattering measurements. The measurements also show that the diffusivity decreases upon approaching the critical temperature as predicted by the theory of critical dynamics. We conclude that the Taylor dispersion indeed can be used to investigate the behavior of the diffusivity of liquid mixtures in the region near the critical mixing point. In the temperature range covered by the present experiments the diffusivity can be represented by an asymptotic Stokes–Einstein law. Since the Taylor dispersion method is also suitable for measuring diffusivities in liquid mixtures far away from the critical temperature, it may be a possible method for studying any crossover from singular diffusive behavior close to the critical mixing point to regular diffusive behavior far away from the critical mixing point. This crossover phenomenon has been investigated for one-component fluids near the vapor–liquid critical point [28], but not yet for liquid mixtures near the critical point of mixing.

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