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Ternary Liquid Diffusion Coefficients Near Plait Points[1]

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Mutual diffusion coefficients were measured as a function of temperature above the 30°C plait point of the water + 2-propanol + cyclohexane system using a Gouy interferometer and a new temperature-jump procedure. The four independent diffusion coefficients were found to decrease rapidly along the constant plait-point line as the temperature approached the consolute or plait temperature. Effective critical exponents were found to be 0.55 for the individual diffusion coefficients and 1.31 for the determinant of the diffusion coefficient matrix. The measured diffusion coefficients satisfy all stability requirements, although cross diffusion coefficients were found to be as large as main diffusion coefficients and a negative value was obtained for the water main diffusion coefficient in the component representation utilized in this work.

KEY WORDS: critical exponents; diffusion coefficients; Gouy interferometry; plait points; ternary liquid systems.

1. INTRODUCTION

Nonequilibrium thermodynamics indicates that the driving force for isothermal molecular diffusion processes is a gradient of chemical potential [1–3]

$$\mathbf{J}_i = -\sum_{j=1}^{n} \Omega'_{ij} \nabla\mu_j; \qquad i = 1, 2, \ldots, n \tag{1}$$

where $\mathbf{J}_i$ is the molar flux of component i relative to the center of volume or Fickian reference frame, n is the number of components, μ_i is the

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chemical potential of component i, and Ω'_{ij} are Onsager coefficients. As discussed by Miller [1] neither the fluxes (usually constant-volume experiments) nor the chemical potential gradients (Gibbs-Duhem relation) are independent. Transformation to independent fluxes and forces is desirable so that the Onsager coefficients will satisfy reciprocity. In terms of independent fluxes and forces, Eq. (1) becomes

$$\mathbf{J}_i = -\sum_{j=1}^{n-1} \Omega_{ij} Y_j; \qquad i = 1, 2, \ldots, n-1 \tag{2}$$

where the Ω_{ij} constitute a set of Onsager coefficients which satisfy reciprocity, and the independent driving forces are given by

$$Y_j = \sum_{k=1}^{n-1} a_{jk} \nabla \mu_k \tag{3}$$

In the above equation,

$$a_{jk} = \delta_{jk} + \bar{v}_j c_k / \bar{v}_n c_n \tag{4}$$

δ_{ik} is the Kronecker delta, $\bar{v}_j$ is the partial molar volume, and c_k is the molarity.

Phenomenologically, the mole flux can be written in terms of diffusion coefficients, D_{ik}, as a generalized form of Fick's law

$$\mathbf{J}_i = -\sum_{k=1}^{n-1} D_{ik} \nabla c_k; \qquad i = 1, 2, \ldots, n-1 \tag{5}$$

While Eq. (5) is convenient, Eqs. (1) and (2) describe the true driving force; therefore, the interpretation of diffusion coefficients in multicomponent, highly nonideal systems must be done carefully. It is particularly enlightening to compare Eqs. (2) and (5) to obtain the relationship between diffusion and Onsager coefficients,

$$D_{ik} = \sum_{j=1}^{n-1} \sum_{l=1}^{n-1} \Omega_{ij} a_{jl} \mu_{lk}; \qquad i, k = 1, 2, \ldots, n-1 \tag{6}$$

where

$$\mu_{lk} = (\partial \mu_l / \partial c_k)_{T,P,c_{m \neq k}} \tag{7}$$

and μ_{lk} is the so-called thermodynamic factor [3].

As can be seen from Eq. (6), there are $(n-1)^2$ independent diffusion coefficients for an n-component mixture; they can be written more succinctly in matrix form:

$$\mathbf{D} = \boldsymbol{\Omega} \cdot \mathbf{a} \cdot \boldsymbol{\mu} = \mathbf{L} \cdot \boldsymbol{\mu} \tag{8}$$

where the second equality defines **L**.

The form of Eq. (8) is interesting because the criteria for liquid–liquid phase stability can also be formulated in terms of $\boldsymbol{\mu}$. At a constant temperature and pressure, the propensity for phase splitting is governed by minimization of the Gibbs free energy, which can be shown, using variational calculus, to be a quadratic form [4] requiring [5]

$$\mu_{11}\mu_{22} - \mu_{12}\mu_{21} \geqslant 0; \qquad \mu_{11} > 0; \qquad \mu_{22} > 0 \tag{9}$$

for a stable single phase. The equality defines the spinodal curve or loci of incipient stability dividing stable from unstable states. For binary mixtures the stability requirements and Eq. (6) reduce to simple forms, both containing the thermodynamic factor, μ_{11}. In this case, the spinodal curve corresponds to $\mu_{11} = 0$, which is equivalent to zero difusivity [6]. Clark and Rowley [6] have recently shown that binary diffusion measurements as a function of composition can be used to determine the spinodal by extrapolation to zero diffusivity.

Noting that the ternary stability conditions of Eq. (9) apply at the plait point, some authors have immediately assumed that $\det|\mathbf{D}|$ will also vanish. Although this does not necessarily follow since $\det|\boldsymbol{\Omega}|$ may be infinite at the plait point, Kirkaldy and Purdy [7] have shown that since both $\boldsymbol{\Omega}$ and $\boldsymbol{\mu}$ are positive definite, **D** must have positive eigenvalues for stable solutions. In this manner the stability conditions can be expressed in terms of ternary diffusion coefficients as

$$\begin{gathered} D_{11} + D_{22} > 0; \qquad D_{11}D_{22} - D_{12}D_{21} > 0; \\ (D_{11} + D_{22})^2 > 4(D_{11}D_{22} - D_{12}D_{21}) \end{gathered} \tag{10}$$

There are no restrictions on the sign of any of the individual diffusion coefficients; any one of them may be negative provided there is sufficient coupling for the sums and differences expressed in Eqs. (10) to satisfy their respective inequalities.

To determine the behavior of **D** right at the plait point, Storonkin and Rusanov [8] considered the limiting slope of the tie lines at the plait point and showed that

$$\mathbf{D} = \mu_{11} \cdot \det \begin{pmatrix} L_{11} - L_{12}/\alpha & L_{12}/\alpha^2 - L_{11}/\alpha \\ L_{21} - L_{22}/\alpha & L_{22}/\alpha^2 - L_{21}/\alpha \end{pmatrix} \tag{11}$$

where α is the slope of the tie line at the critical point and is given by

$$\alpha = -\mu_{12}/\mu_{22}; \qquad \alpha^2 = \mu_{11}/\mu_{22} \tag{12}$$

from which it can be seen that $\det|\mathbf{D}| = 0$ or $D_{11}D_{22} = D_{12}D_{21}$. At the plait point the usually relatively small cross diffusion terms are equal in magnitude to the main diffusion terms. These coupled effects near the plait point and the manner in which $\det|\mathbf{D}|$ approaches zero in this region were experimentally investigated for the water + 2-propanol + cyclohexane system and the results are reported herein.

2. EXPERIMENTAL

Ternary diffusion coefficients were measured with a Gouy interferometer utilizing a new temperature-jump technique to initiate the diffusion process. We have previously reported on the use of the temperature-jump initiation technique in conjunction with Gouy interferometry [6] and report here only its adaptation to ternary mixtures. Measurements of the liquid–liquid equilibrium (LLE) surface for the water + 2-propanol + cyclohexane system [9] show it to be a type 1 system, containing a single nonconsolute pair, in which the immiscible region shrinks with increasing temperature. Thus the plait composition at a particular temperature will be in the homogeneous, single-phase region at a higher temperature. This temperature dependence of the solubility can be utilized for the formation of sharp, distinct initial interfaces in diffusion studies as schematically represented in Fig. 1. In this work, the 30°C plait point, labeled P, was investigated. The 30°C plait-point mixture was thermostated in the diffusion cell at a temperature below 30°C. The mixture was allowed to separate and reach equilibrium, the compositions of the two coexisting phases fixed by the ends of the tie line passing through the 30°C plait-point composition shown as L in Fig. 1. The initial composition difference between the two starting phases could be slightly altered from experiment to experiment by thermostating at different temperatures since the tie lines passing through the 30°C plait-point composition shift with temperature as shown in Fig. 2. This behavior is required for the use of the temperature-jump technique since a minimum of two diffusion experiments performed at the same overall composition with different initial composition gradients is required to obtain all four independent diffusion coefficients in ternary mixtures. A rapid (relative to the diffusional process) temperature jump was then performed which raised the temperature to some run temperature above 30°C. Above 30°C the system is now in the single-phase region, illustrated by point S in Fig. 1, and the diffusion process begins.

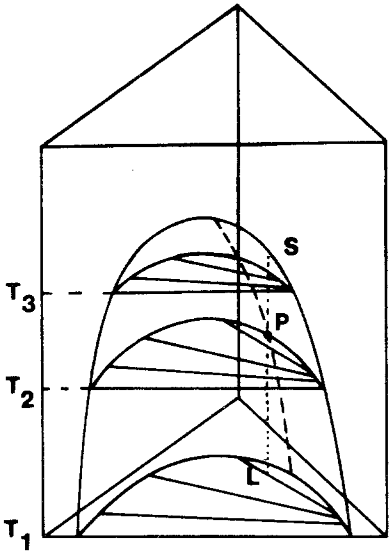

Fig. 1. Schematic representation of the temperature-jump procedure. The dotted line represents the temperature jump of a mixture of composition P (the plait point for T_2) from an initial temperature T_1 where two phases coexist (compositions shown by tie line L) to a final temperature T_3 for which this composition is in the single-phase region S.

The cyclohexane used in this study was Baker Analyzed reagent grade with a label-specified purity of better than 99.8%; the 2-propanol was Mallinkrodt lot KLAA with a water content of 0.004% by weight. Both were used without further purification. Water was distilled and deionized before use. Karl-Fischer titration was performed to verify the water content of the 2-propanol prior to gravimetric preparation of the mixtures. Densities, heats of mixing, and the entire LLE surface required for this study including multiple tie lines at several temperatures were measured in this laboratory and have been reported elsewhere [9]. Densities measured at 298.15 K in a Mettler-Paar 4.5-digit densitometer agreed to 0.1% with literature values and were therefore indicative of purity.

The Gouy interferometer used in this work has been described elsewhere [6, 10]. Initial testing of its performance on the aqueous sucrose system yielded better than 1% agreement with the diffusion coefficients measured by Gosting and Morris [11]. The cell was a Hellma model 221 optical Pyrex vacuum-sealed cell. The nominal 30°C plait point was chosen

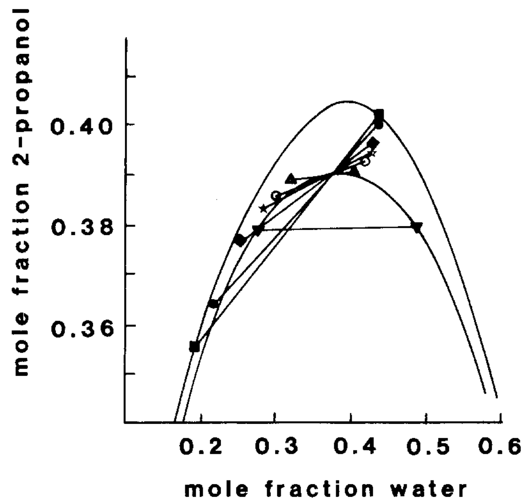

Fig. 2. Temperature dependence of several tie lines passing through the 30°C plait point. The upper curve is the 20°C equilibrium curve; the lower curve is the 30°C equilibrium curve; tie lines through the plait composition are at 29°C (△), 28°C (○), 27°C (☆), 25°C (◆), 22°C (●), and 20°C (■); and the horizontal line (▼) is a 30°C tie line.

for study and the cell was filled with the solution prepared at 13.06 wt% water, 46.23 wt% 2-propanol, and 40.71 wt% cyclohexane, the plait-point composition determined from Treybal's method [12] applied to previously measured tie lines. The plait-point uncertainty is ±0.25 wt% and the actual separation temperature of this mixture was measured in the diffusion cell to be 30.52°C. The cell was gravimetrically filled at a temperature above 31°C, a Teflon-coated magnetic stir bar was added, the contents were frozen by immersion of the cell in liquid nitrogen, and the cell was evacuated and flame sealed.

A water jacket surrounding the cell contained quartz optical windows cemented into the planes perpendicular to the optical axis. A quartz thermometer probe was cemented into the lid of the water jacket. A description of the Gouy interferometer, the operation of the cell, and the design and use of the two temperature-control baths used to perform the temperature jump can be found elsewhere [6, 10]. The control baths were of large enough capacity that very little effect was observed when the valve was switched to allow the run-temperature bath to sweep out the entire jacket containing water at the initial temperature. Compared to the diffusion time scale, the temperature-change time was extremely short; thermal

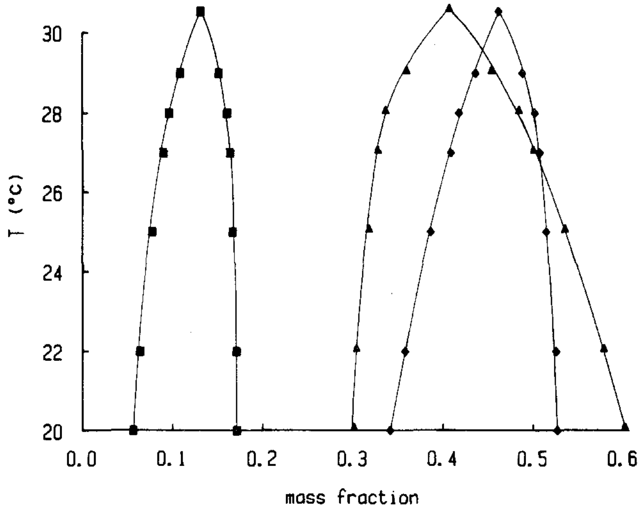

Fig. 3. Tie-line end compositions for water (■), 2-propanol (◆), and cyclohexane (▲).

equilibration was complete on the order of minutes, while several hours was required before sufficient decay of the initial concentration gradient had occurred to allow photography of the entire fringe pattern on a single film, and 5 to 6 h more was required for completion of the experiment.

Four diffusion experiments were performed for each run temperature to provide unique determination of the diffusion coefficients from the Gouy analysis. Starting compositions for diffusion experiments were determined from plots of the tie-line end composition of each component versus the temperature, greatly reduced versions of which are shown in Fig. 3.

3. RESULTS

The results of the ternary temperature-jump diffusion studies are presented in Table I. The rather suprising negative main diffusion coefficient for water, D_{11}, concerned us. As previously mentioned, Kirkaldy and Purdy [7] suggested that a negative main diffusion coefficient would not violate the stability conditions of Eqs. (10). Castleman [13] has examined in detail the theoretical possibility that individual main diffusion coefficient elements of a realistic diffusion coefficient matrix can be negative and found not only that one of the diagonal elements of the matrix may be negative but that several systems have been measured previously with one negative main diffusion coefficient. Similarly, Vitagliano et al. [14] found that when water was chosen as the solvent, the main diffusion coefficient

Table I. Diffusion Coefficient Results for the Water (1)–2-Propanol (2)–Cyclohexane (3) 30.52°C Plait-Point Composition

$(T-T_c)^a$ (°C)	$10^{-10}\,m^2 \cdot s^{-1}$				
	D_{11}	D_{12}	D_{21}	D_{22}	D_A
6.54	−1.071	1.064	−2.120	1.984	0.2075
2.98	−0.467	0.547	−0.997	1.064	0.1114
0.98	−0.309	0.328	−0.566	0.571	0.0638
0.48	−0.257	0.267	−0.440	0.439	0.0487
0.08	−0.347	0.323	−0.559	0.510	0.0383

[a] $T_c = 30.52$°C.

for chloroform was negative near the plait point of the water + chloroform + acetic acid system. Vitagliano and co-workers explained their findings as an interesting case of incongruent diffusion in which diffusion occurs against a concentration gradient.

It is important to realize that the diffusion coefficient is a proportionality factor between a component's flux and its composition gradient, whereas the actual driving force is a chemical potential gradient, as shown in Eq. (1), which depends upon the gradients of all three compositions. Thus, in very nonideal solutions, such as near the plait point, it is not suprising that diffusion may occur up the composition gradient while still moving down the actual driving force. In fact the only criteria that must be satisfied by the diffusion coefficients are those of Eqs. (10), which are shown in Table II to be satisfied by these experimental results.

Table II. Test of the Thermodynamic Consistency of Measured Diffusion Coefficients for the Water (1)–2-Propanol (2)–Cyclohexane (3) System

$(T-T_c)^a$ (°C)	$D_{11}+D_{22}$ $(10^{-10}\,m^2 \cdot s^{-1})$	$\det\lvert\mathbf{D}\rvert$ $(10^{-18}\,m^4 \cdot s^{-2})$	Diff^b $(10^{-17}\,m^4 \cdot s^{-2})$
6.54	0.913	13.082	3.103
2.98	0.597	4.847	1.625
0.98	0.262	0.921	0.318
0.48	0.182	0.466	0.145
0.08	0.163	0.359	0.122

[a] $T_c = 30.52$°C.

[b] $\text{Diff} = (D_{11}+D_{22})^2 - 4(\det\lvert\mathbf{D}\rvert)$.

Table I also shows that all the diffusion coefficients approach zero as the consolute temperature is approached. The cross diffusion terms are of a magnitude comparable to that of the main terms as also observed by Ziebold and Ogilvie [15]. In this region there is a strong coupling between the flux of one component and the concentration gradient of another.

The determinant of the diffusion coefficient matrix, shown in Table II, is seen to approach zero as the plait point is approached from higher temperatures along a path of constant composition. In analogy to a binary critical exponent, the slope of $\ln|D|$ vs $\ln\varepsilon$ is a constant, where ε is defined as $(T-T_c)/T_c$. Figure 4 shows a log–log plot of both $(\det|\mathbf{D}|)/2$ vs ε and the individual diffusion coefficients obtained from this study. The slope of these lines represents the effective critical exponent; the values obtained are tabulated in Table III. While the average critical exponent for the individual diffusion coefficients is 0.55 ± 0.20, the value obtained for $\det|\mathbf{D}|$ is, as expected, roughly twice that, 1.31. It appears that the individual diffusion coefficients are still slightly coupled; i.e., although $\det|\mathbf{D}|$ is reasonably well known, the actual values for D_{ij} are less reliable. This coupling is due primarily to the small differences in initial compositions obtainable between replicate runs due to the proximity to the plait point and the temperature-jump procedure.

Errors associated with the determination of ternary diffusion coefficients using Gouy interferometry subject to the constraints of the plait-point proximity and temperature-jump procedures are considerably larger

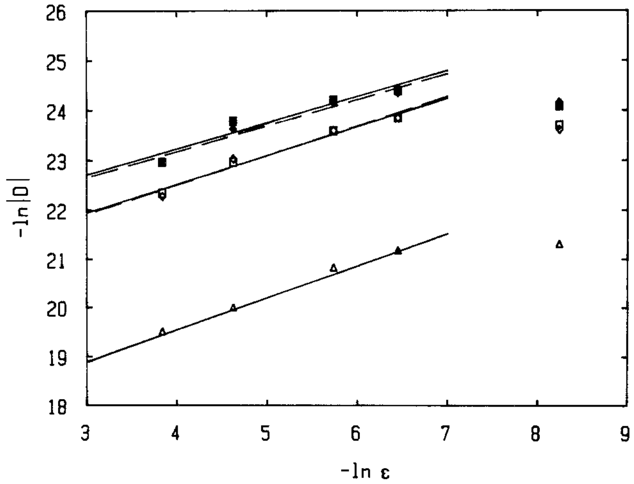

Fig. 4. Critical exponent determination from $-\ln|D|$ vs $-\ln\varepsilon$ for D_{11} (■), D_{12} (◆), D_{21} (◇), D_{22} (□), and $(\det|\mathbf{D}|)/2$ (△).

Table III. Results of Critical Exponent Determinations for Measured Diffusion Coefficients in Water (1)–2-Propanol (2)–Cyclohexane (3) Mixtures

Coefficient	Exponent
D_{12}	0.521
D_{11}	0.522
D_{22}	0.577
D_{21}	0.590
Average D_{ij}	0.552
$\det\lvert\mathbf{D}\rvert$	1.31

than those reported for binary systems. A detailed error analysis of the apparatus and technique is available [10], but it is important to realize here that analysis of ternary diffusion coefficients assumes composition-independent diffusivities over the range employed in the experiment. This assumption is quite poor near the consolute point [6]. Cross diffusion coefficients are usually somewhat unreliable because the analysis requires obtaining fringe deviations, which involves taking the difference between two numbers to obtain a small one. This effect is minimized in this work since the relative size of the cross diffusion coefficients is enlarged in the plait-point region. Nevertheless, we estimate the uncertainty in the actual values of the diffusion coefficients to be 40–50%.

As can be inferred from Fig. 4, the point nearest the consolute temperature was not used to obtain the critical exponents. The reliability of this point is suspect for the following reasons: (i) the temperature is close enough to the consolute point that temperature variability and uncertainty in the consolute temperature become very significant in $\ln \varepsilon$; (ii) the time required for the fringe pattern to shrink to a measurable size was substantially longer for this point than the next closest one, yet if the analyzed value were correct, the required time would have been about the same; and (iii) the results are clearly inconsistent with the known linear behavior shown by the other points in Fig. 4.

In spite of the above-mentioned uncertainties in the absolute values of the diffusivities, the critical exponents, trends, and behaviors are accurate. The decrease in the diffusivities as the consolute temperature is approached and the negative main diffusion coefficient are significant. Their reliability is further attested to by the values obtained for the effective binary diffusivity, an intermediate value obtained in the Fujita and Gosting method of analysis [16, 17]. This effective diffusivity does not suffer from any of the coupling and analysis uncertainty problems associated with the final analysis of the four independent diffusion coefficients and should be as reliable as binary mutual diffusion coefficients, i.e., better than 1%. Values of the effective binary diffusivity are shown in Table I and are seen to have the same general behavior as the individual diffusivities. Moreover, the effective critical exponent obtained from these data is 0.55, in agreement with the average critical exponent obtained for the individual diffusivities.

4. CONCLUSIONS

Ternary diffusion coefficients were measured for the water + 2-propanol + cyclohexane, 30°C plait-point composition as a function of temperature above the consolute point. It was found that the four individual diffusion coefficients all rapidly go to zero in this region with critical exponents identical (within experimental error) to each other and equal to 0.55. The determinant of the diffusion coefficient matrix goes to zero along this constant composition line with a critical exponent of 1.31. In this system, the cross diffusion coefficients are about as large as the main diffusion terms and large coupling occurs due to the large nonidealities of the system. This leads to a negative water diffusion coefficient in the component numbering system used in this work (cyclohexane treated as the solvent). The large cross terms and negative main term at first seem anomalous because they are not observed in systems far from phase separation, but other experimentalists studying diffusion near phase boundaries in alloy systems have also found similar behavior. The observed coefficients do obey all known requirements including stability conditions.

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