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Diaphragm Cell Determination of the Interdiffusion Coefficient for Succinonitrile + Water[1]

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Using diaphragm cells, we have measured the interdiffusion coefficient for succinonitrile + water in the one-phase liquid region at a series of temperatures ranging form 25 to 60°C and compositions ranging from 34.5 to 96 mol% water. The diffusion coefficient was found to be a function of both temperature and concentration, varying from 1.66×10^{-6} to 16.6×10^{-6} $cm^2 \cdot s^{-1}$. Critical slowing down of diffusion was readily detected at 60°C (critical temperature, 56.17°C) over a broad range of composition on either side of the critical composition (82.7 mol% water).

KEY WORDS: diffusion; diaphragm cell; succinonitrile; water, consolute point; monotectic point.

1. INTRODUCTION

Above its melting point at 58.04°C, succinonitrile [$NC(CH_2)_2CN$] is miscible with water in all proportions and forms a single liquid phase. Roughly 2°C lower in temperature, however, as the phase diagram in Fig. 1 shows, the top of a wide miscibility gap is encountered with consolute point at the coordinates 82.7 mol% water and 56.17°C. For temperatures and compositions lying within the miscibility gap, the system stratifies into

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two liquid layers, L_1 and L_2. When the temperature of a liquid solution of any composition greater than 0 mol% water but less than 97.4 mol% water is lowered to 18.82°C, a monotectic point, *X*, is encountered, where liquids L_1 and L_2 are in equilibrium with solid succinonitrile (SS) [1].

The interdiffusion coefficient of the two components in the one-phase liquid region of a monotectic system can be expected to be a function of temperature and concentration, particularly so at points near the coexistence curve. Using the diaphragm cell technique, we have determined the concentration dependence of the interdiffusion coefficient for the system succinonitrile + water at 60°C for a number of compositions on either side of the critical composition, as well as for a number of temperatures and compositions approaching the monotectic point.

In Section 2, we review the theoretical method used to determine the concentration dependence of the diffusion coefficient from diaphragm cell measurements. In Section 3, we describe our experimental method. In Section 4, we summarize our results.

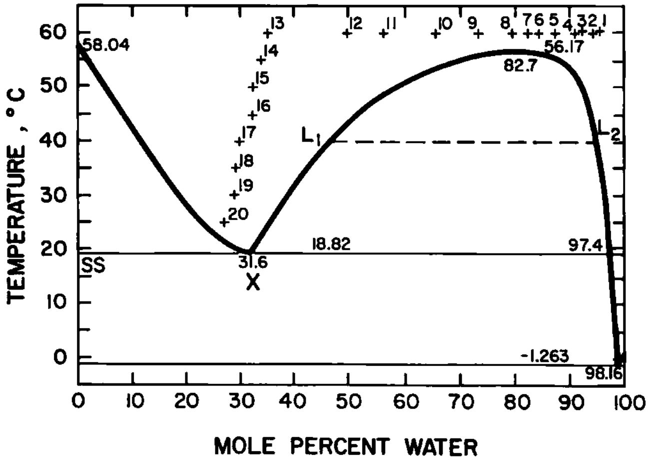

Fig. 1. Phase diagram for succinonitrile + water at 760-Torr pressure. The melting point of succinonitrile is 58.04°C, while that of water is 0°C. The one-phase liquid region consists of the area above the coexistence curve. The lowest freezing point in the system occurs at coordinates (98.16 mol% water, −1.263°C). The monotectic point (where liquids, L_1 and L_2, are in equilibrium with solid succinonitrile, SS) occurs at (31.6 mol% water, 18.82°C). The consolute (critical solution) point, where the distinction between L_1 and L_2 disappears, occurs at 82.7% and 56.17°C. The numbered crosses locate points in the one-phase liquid region where the interdiffusion coefficient was measured. The coexistence curve data, upon which this figure is based, were taken from Ref. 1.

2. THEORY

The diaphragm cell consists of two well-stirred solution compartments containing solutions of different composition on opposite sides of a membrane, which is usually a sintered glass disk. The stirring guarantees that the contents of each compartment are uniform, so that mixing is limited to transport through the frit. Because molecular diameters are small compared with the size of the interstitial spaces between the sintered glass beads, the diffusive transport within the frit is the same as in bulk solution.

The diaphragm cell is a relative device, since it involves a cell constant which must be calibrated by analyzing data for a solution whose diffusion coefficient is already known. Once calibrated, however, the cell may be used to determine an unknown diffusion coefficient by following the time relaxation of the concentration difference across the frit.

If V_1 and V_2 are the volumes of chemical solution below and above the frit, respectively, and $c_1(0)$, $c_2(0)$ and $c_1(t)$, $c_2(t)$ are the volume concentrations at time 0 and time t, the volume-average mean concentration defined by

$$\bar{c}=\frac{V_1 c_1(0)+V_2 c_2(0)}{V_1+V_2}=\frac{V_1 c_1(t)+V_2 c_2(t)}{V_1+V_2} \tag{1}$$

is time invariant while the concentration difference

$$\Delta c(t)=c_1(t)-c_2(t) \tag{2}$$

depends implicitly upon the time through the infinite series,

$$t=B_{\mathrm{O}}+B_{\mathrm{L}}\ln(\Delta c(t))+B_1(\Delta c(t))+B_2(\Delta c(t))^2+\cdots \tag{3}$$

The coefficient, B_{O}, is a constant of integration, whose value is determined by the initial conditions. The coefficient of $\ln(\Delta c(t))$ is given by

$$B_{\mathrm{L}}=-\frac{1}{\beta D(\bar{c})} \tag{4}$$

where $D(\bar{c})$ is the interdiffusion coefficient, $D(c)$, evaluated at the mean concentration, $c=\bar{c}$, while the cell constant is

$$\beta=\frac{A}{l}\left(\frac{1}{V_1}+\frac{1}{V_2}\right) \tag{5}$$

where A and l are the cross-sectional area and thickness, respectively, of the frit. Each of the coefficients, B_n $(n=1, 2, 3,\ldots)$ in Eq. (3) depends upon β, V_1, V_2, $D(\bar{c})$, and the concentration derivatives, $D^{(k)}(\bar{c}) = [d^kD(c)/dc^k]_{c=\bar{c}}$ $(k = 1, 2, \ldots, n)$ of $D(c)$ evaluated at $c = \bar{c}$[2][3].

In general, $D(\bar{c})$ and its derivatives, $D^{(k)}(\bar{c})$, are unknown at the outset; thus, the experimental strategy involves treating the coefficients, $B_O, B_L, B_1, B_2, \ldots$, as least-squares parameters and determining their values by fitting Eq. (3) to the points of a t vs $\Delta c(t)$ data set. Of course, the number of B coefficients evaluated cannot exceed the number of data points. From the values of the B's, $D(\bar{c})$ and its concentration derivatives can be obtained [3].

Since only the value of $D(\bar{c})$ is ordinarily sought, it is helpful if $\Delta c(t)$ can be made small enough that the sum of the terms, $B_1(\Delta c(t)) + B_2(\Delta c(t))^2 + \ldots$, is unimportant compared to $B_O + B_L \ln(\Delta c(t))$. As we shall see, this is not always possible, but when $V_1 = V_2$, all odd-order B_n are 0 [3], and Eq. (3) can be represented correctly to order $(\Delta c(t))^3$ by the three term truncation,

$$t = B_O + B_L \ln(\Delta c(t)) + B_2(\Delta c(t))^2 \tag{6}$$

By evaluating Eq. (6) of Ref. 2 for the special case $V_1 = V_2$, we find

$$B_2 = \frac{D^{(2)}(\bar{c})}{48\beta(D(\bar{c}))^2} \tag{7}$$

Now returning to this work, after substituting Eqs. (4) and (7) into Eq. (6) above and evaluating B_O by letting the concentration difference be $\Delta c(0)$ at $t = 0$, we obtain

$$t = \frac{1}{\beta D(\bar{c})} \ln\left(\frac{\Delta c(0)}{\Delta c(t)}\right) + \frac{D^{(2)}(\bar{c})}{48\beta(D(\bar{c}))^2}((\Delta c(t))^2 - (\Delta c(0))^2) \tag{8}$$

The relative importance of the term involving $D^{(2)}(\bar{c})$ is best assessed by introducing the integral diffusion coefficient, D', defined by

$$t = \frac{1}{\beta D'} \ln\left(\frac{\Delta c(0)}{\Delta c(t)}\right) \tag{9}$$

Equating Eqs. (8) and (9) leads to

$$\frac{1}{D'} = \frac{1}{D(\bar{c})} + \frac{D^{(2)}(\bar{c})}{48(D(\bar{c}))^2} \frac{((\Delta c(t))^2 - (\Delta c(0))^2)}{\ln(\Delta c(0)/\Delta c(t))} \tag{10}$$

After factoring $(\Delta c(0))^2$ from the second term on the right, Eq. (10) may be written as

$$\frac{1}{D'} = \frac{1}{D(\bar{c})} + \frac{D^{(2)}(\bar{c})(\Delta c(0))^2}{48(D(\bar{c}))^2} f(y) \tag{11}$$

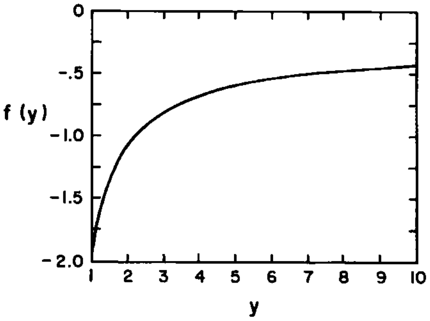

Fig. 2. A plot of $f(y) = (y^{-2} - 1)/\ln y$.

where $y = \Delta c(0)/\Delta c(t)$ and $f(y) = (y^{-2} - 1)/\ln y$. A plot of $f(y)$ is shown in Fig. 2. Since $\Delta c(t)$ decreases monotonically with time, it is clear from Fig. 2 and the definition of y that $f(y)$ approaches zero as t increases. Thus the second term on the right-hand side of Eq. (11) is made small when $(D^{(2)}(\bar{c})(\Delta c(0))^2/48(D(\bar{c}))) \ll 1$ and in all cases when $y \gg 1$.

In the two-component system succinonitrile + water, we let c, $\bar{c}$, $c_1(t)$, $c_2(t)$, $c_1(0)$, and, $c_2(0)$ refer to the molar concentration of succinonitrile. For diffusion with respect to a center-of-volume-fixed frame of reference, as occurs in the case of the diaphragm cell, the Fick's law diffusion coefficient, $D(c)$, is the same for both components, however [2].

3. EXPERIMENT

3.1. Diaphragm Cell Calibration

Four standard Stokes diaphragm cells [4] with disks sintered from 10- to 16-μm-diameter glass beads were operated with $V_1 = V_2$ and with stirring at 1 Hz in thermostated baths. A mixture of ethylene glycol and water served as the thermostating fluid so that the bath could be used at temperatures up to 60°C without excessive evaporation. The bath temperature was stable to ±0.05°C at 60°C and ±0.005°C at 25°C.

Each cell constant was calibrated with aqueous KCl at 25°C. Initial KCl concentration values for each run were $c_1(0) = 0.5\ M$ and $c_2(0) = 0$. The final concentrations, $c_2(t)$, were determined using a calibrated Radiometer (Copenhagen) Model CDM 83 conductivity meter. As the cell was operated with $V_1 = V_2$, then according to Eq. (1), $\bar{c} = (1/2)(c_1(t) + c_2(t)) = 0.25\ M$, and the value $c_1(t)$ could be obtained by subtraction. The value of β was calculated from $\Delta c(0)$ and $\Delta c(t)$ using Eq. (9) with $D' = 1.840 \times 10^{-5}\ \text{cm}^2 \cdot \text{s}^{-1}$ [5]. Repeat determinations of β differed by 0.5 to 1.5%.

3.2. Materials

Succinonitrile labeled 99% pure was obtained from Aldrich Chemical Company. Although succinonitrile is colorless and odorless, this Aldrich material was slightly yellow and had a pungent odor. The principle impurity identifiable by GC/MS proved to be $NC(CH_2)_3CN$. This impurity, as well as those responsible for the color and the odor, was readily removed by distillation.

Aqueous solutions of the purified succinonitrile were prepared with water once distilled from a glass system. The water, which had a residual conductivity of 1.5 $\mu S \cdot cm^{-1}$ at 25°C, was deaerated by boiling before use so as to prevent the formation of bubbles in the diaphragm cells.

3.3. Analytical Procedures

Solutions of succinonitrile in water were prepared by weighing the two components. The density data of Frazier and Facemire [6] were used to convert the weight fractions to molar concentrations, $c_1(0)$ and $c_2(0)$. The density data were interpolated as required to obtain concentration values at our various operating temperatures.

To determine $c_2(t)$ at the end of each diffusion run, a 7- to 12-g sample from the top compartment of the cell was removed. This sample was mixed with toluene and distilled azeotropically into a calibrated Dean and Stark flask [7]. The mass of water in the original sample could be obtained by determining the change in weight of the flask. This distillation method was calibrated using succinonitrile + water solutions of known composition. The actual weight-percentages and the measured weight-percentages as obtained by distillation agreed to better than 1 part in 100.

4. RESULTS AND CONCLUSIONS

4.1. Diffusion at 60°C Near the Critical Concentration

To check for the applicability of Eq. (10) at 60°C and $\bar{c} = 5.9\,M$ (critical concentration), 10 repeat determinations of D' were carried out using a range of values for $\Delta c(0)$ and $\Delta c(t)$. These results are shown in Fig. 3, where they are plotted in accordance with Eq. (10). After fitting the data by least squares to the straight line predicted by Eq. (10), we found $D(5.9\,M) = 2.09 \times 10^{-6}\,cm^2 \cdot s^{-1}$ and $D^{(2)}(5.9\,M) = 4.86 \times 10^{-7}\,cm^2 \cdot s^{-1} \cdot M^{-2}$. The positive value for $D^{(2)}(5.9\,M)$ is consistent with a minimum in $D(c)$ at $c = 5.9\,M$. We estimate the accuracy of $D(c)$ and $D^{(2)}(c)$ to be about 5%.

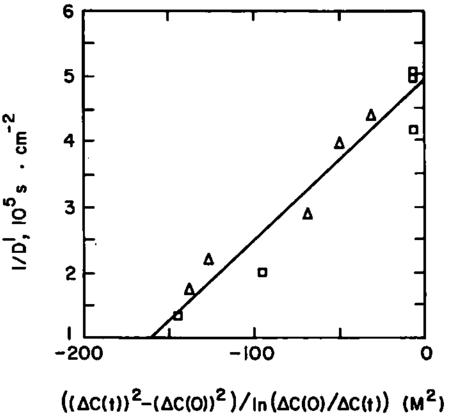

Fig. 3. Experimental values of D', $\Delta c(0)$, and $\Delta c(t)$ plotted according to Eq. (10) for succinonitrile + water at 60.0°C and $\bar{c} = 5.9\,M$ (critical concentration for succinonitrile). Data taken with different cells are distinguished by the plotting symbols: (□) $\beta = 0.200\ \text{cm}^{-2}$ and (△) $\beta = 0.278\ \text{cm}^{-2}$, where β is the cell constant defined by Eq. (5). The line, which was drawn by setting $D(\bar{c}) = 2.09 \times 10^{-6}\ \text{cm}^2 \cdot \text{s}^{-1}$ and $D^{(2)}(\bar{c}) = 4.86 \times 10^{-7}\ \text{cm}^2 \cdot \text{s}^{-1}\ M^{-2}$, represents a least-squares fit of Eq. (10) to the data.

The least-squares procedure illustrated in Fig. 3 for determining $D(\bar{c})$ could have been repeated at each value of $\bar{c}$ of interest, although it would have proved costly in both time and effort. As our objective was to study the diffusivity in the system succinonitrile + water at 60°C over a wide range of compositions, we subsequently limited ourselves to the determination of D' alone. To minimize the variation of D' with $\Delta c(0)$ and $\Delta c(t)$, however, each run was started with $\Delta c(0) = 4.0\,M$ and ended after an elapsed time of exactly 4 days. The factor, $((\Delta c(t))^2 - (\Delta c(0))^2)/\ln(\Delta c(0)/\Delta c(t))$, in Eq. (10) was thus rendered nearly constant from run to run.

The results obtained for D' at 60°C as a function of $\bar{c}$ are listed in Table I and are plotted in Fig. 4 as a function of $z = (c - c^{\text{crit}})/c^{\text{crit}}$, where c^{crit} is the critical value of the succinonitrile concentration. The data were fitted to the function $10^6 D'(z) = D_0 + A\,|z - b|^{1.9}$, where $D_0 = 1.61$, $A = 21.3$, and $b = 0.115$. The exponent of $|z - b|$ was given the value, 1.9, which is required by the theory of critical slowing down of diffusion [8]. The minimum value of the curve in Fig. 4 occurs at $z = b = 0.115$, which is a bit to the right of $z = 0$. As noted by Sengers, however, some assymetry

Table I. D' as a Function of $\bar{c}$ at $\Delta c(0)=4.0\ M$ and 60.0°C[a]

Point No. in Fig. 1	Cell No.	$\bar{c}\,(M)$	$D'\ (10^{-6}\,\mathrm{cm}^2\cdot\mathrm{s}^{-1})$
1	1	2.00	16.6
2	1	2.50	13.4
3	3	3.00	8.00
4	3	3.50	5.46
5	1	4.50	3.99
6	3	5.50	2.89
7	2	6.00	2.63
8	1	6.50	1.66
9	3	7.50	3.04
10	1	8.48	5.06
11	3	9.50	6.64
12	3	10.0	8.44

[a] First column refers to the numbered points in Fig. 1. The second column identifies the diaphragm cell used to measure D'. Cell 1 had $\beta=0.200\ \mathrm{cm}^{-2}$, cell 2 had $\beta=0.252\ \mathrm{cm}^{-2}$, and cell 3 had $\beta=0.278\ \mathrm{cm}^{-2}$. Diaphragm cell runs lasted 4 days.

in the physical properties of fluids near the critical point is not uncommon [9]. The wide extent of the minimum is similar to that found by Haase and Siry for diffusion in the case of *n*-hexane + nitrobenzene [10]. Although the values of D' plotted in Fig. 4 were measured at a temperature nearly 4° above the critical temperature, it is interesting to note that the

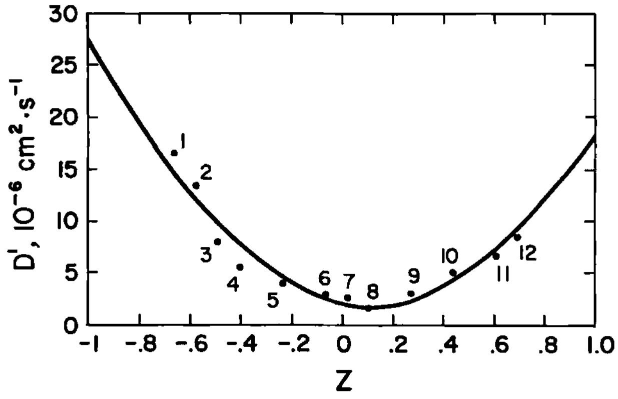

Fig. 4. D' at 60.0°C as a function of z. Here $z=(c-c^{\mathrm{crit}})/c^{\mathrm{crit}}$ is the critical value of the succinonitrile concentration, c. Each measurement of D' started from $\Delta c(0)=4.0\ M$ and lasted 4 days. The number associated with each point identifies its location in the phase diagram in Fig. 1. The solid curve is a least-squares fit of the data to the function $10^6 D'(z)=1.61+21.3\,|z-0.115|^{1.9}$.

phenomenon of critical slowing down is still readily apparent. This is consistent with the results of Matos Lopes et al. for *n*-hexane + nitrobenzene [11]. They observed slowing down of diffusion at the critical composition and at temperatures several degrees above critical.

4.2. Diffusion in the Vicinity of the Monotectic Point

In the one-phase liquid region above the monotectic point, experiments showed that the second term in Eq. (10) was less than 5% of D', so that D' was a measure of $D(\bar{c})$. Our results for $D(\bar{c})$, which decrease with decreasing temperature, are summarized in Table II. It is remarkable, however, that at $c = 5.9\ M$ and 60°C, $D = 2.09 \times 10^{-6}\ \mathrm{cm}^2 \cdot \mathrm{s}^{-1}$, while 35°C lower, at $c = 11.6\ M$ and 25°C, $D = 5.50 \times 10^{-6}\ \mathrm{cm}^2 \cdot \mathrm{s}^{-1}$, which is more than twice as great. Near $c = 5.9\ M$ and 60°C the critical slowing down is the dominant process in depressing the diffusion coefficient. In contrast, away from the critical point, diffusion coefficients ordinarily decrease with decreasing temperature and often also with increasing concentration [12].

Chopra et al. employed the diaphragm cell technique to measure D for succinonitrile + acetone at 58°C and 0.5 to 18 mol% acetone. They found $D = 12.7 \times 10^{-6}\ \mathrm{cm}^2 \cdot \mathrm{s}^{-1}$, independent of concentration [13]. We have no data for succinonitrile + water which directly compare. However, our point No. 13 at 60°C and 34.5 mol% water, where we found $D = 12.0 \times 10^{-6}\ \mathrm{cm}^2 \cdot \mathrm{s}^{-1}$, comes the closest.

Table II. Interdiffusion Coefficient as a Function of Concentration, c, and Temperature, in the One-Phase Liquid Region Above the Monotectic Point[a]

Point No. in Fig. 1	Cell No.	c (M)	Temp. (°C)	D ($10^{-6}\ \mathrm{cm}^2 \cdot \mathrm{s}^{-1}$)
13	1	11.0	60.0	12.0
14	1	11.0	55.0	10.5
15	3	11.1	50.0	9.08
16	1	11.2	45.0	8.33
17	3	11.3	40.0	7.95
18	4	11.3	35.0	7.35
19	3	11.4	30.0	6.70
20	4	11.6	25.0	5.50

[a] First column identifies the numbered point in Fig. 1. The second identifies the diaphragm cell used to measure D. Cell 1 had $\beta = 0.200\ \mathrm{cm}^{-2}$, cell 3 had $\beta = 0.278\ \mathrm{cm}^{-2}$, and cell 4 had $\beta = 0.279\ \mathrm{cm}^{-2}$.

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