Diffusivities of Benzaldehyde in Methanol-Water Mixtures

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The axial dispersion of a tracer injected into a fluid in streamline flow in a tube was used to determine molecular diffusivities. Measurements for the benzene–methanol system, for which the diffusivity at low benzene concentrations was available, substantiated the method. Then the diffusivity of benzaldehyde at low concentrations was measured at 22°C in mixtures of water and methanol of varying methanol content.

The interpretation of adsorption rate measurements frequently requires diffusivities of the adsorbing component. Such information is scarce for multicomponent liquid systems. Experimental data are rare, and the few predictive correlations have not been tested for a variety of systems, particularly for nonideal mixtures. This report presents diffusivities of benzaldehyde in mixtures of methanol and water determined by measuring the axial dispersion of the mixture in streamline flow in a long tube. The method consists of injecting a concentration pulse of diffusing component (benzaldehyde, in our case) at one point in a tube containing the flowing mixture and measuring the Taylor axial dispersion at a downstream location. After completing the work, we learned that Ouano (*7*) had used a similar procedure for measuring diffusivities in other liquid systems.

Theory

The Taylor axial dispersion coefficient E is related to the molecular diffusivity D by the expression (*1, 3, 6–8, 11*):

$$E = \frac{(ur)^2}{48\,D} \tag{1}$$

The conditions for which Equation 1 is valid have been extensively studied (*1, 8*) and may be written as:

$$\frac{DL}{r^2u} > 0.8 \tag{2}$$

$$\frac{ru}{D} > 100 \tag{3}$$

When the reciprocal of the Peclet number (E/uL) is very small, as in a long tube, the concentration vs. time curve at a fixed axial location is well approximated by the normal distribution curve. Hence, the axial dispersion coefficient is related to the variance of the distribution:

$$\frac{E}{uL} = \frac{\sigma^2}{2} \tag{4}$$

The maximum fractional error in the approximation of Equation 4, which is exact only for $E/uL \rightarrow 0$, is $5(E/uL)$ when $E/uL < 0.01$ (*5*).

Eliminating E between Equations 1 and 4 gives the desired expression for the molecular diffusivity

$$D = \frac{ur^2}{24\,L\sigma^2} \tag{5}$$

In terms of the volumetric flow rate Q, this becomes

$$D = \frac{Q}{24\,\pi L\sigma^2} \tag{6}$$

Provided the conditions of Equations 2–4 are met, Equation 6 can be used to calculate the diffusivity from the variance of the concentration vs. time curve, the tube length, and the flow rate.

Apparatus and Procedure

The experiments were carried out in a room at a controlled temperature of 22° ± 1°C. A Cheminert metering pump (Model CMPL) was used to withdraw a methanol–water mixture of known composition from a reservoir at a constant flow rate of 2.4, 6, 12, or 24 cm^3/hr. To check the flow rate settings of the pump and constancy of the rate, the flow rate was calculated from the measured retention time of the pulses. These values were within 1% of the flow rates indicated by the pump settings.

The mixture was pumped in continuous streamline flow through a long Teflon tubing (i.d. = 0.936 mm). A solution containing 500 ppm of benzaldehyde was prepared from the same methanol–water mixture. A 2–10 μl sample of this solution was injected rapidly into the flowing stream with a microsyringe. The sample was injected into a 2-cm section of silicon rubber tubing which connected the exit of the pump to the long Teflon tube. The connection was made with stainless-steel fittings which provided a smooth connection between the silicon rubber and Teflon tubes.

At a location 8.30 m downstream from the injection point, the concentration of benzaldehyde was measured by connecting the Teflon tube to a Chromatronix uv photometer (Model 200) with a 2540 Å light source. At this wavelength benzaldehyde has a high absorptivity so that concentrations as low as 0.01 ppm could be detected. Calibration data showed that the photometer response was linear in concentration up to 12 ppm. All measured concentrations were less than 5 ppm. The retention time and dispersion in the photometer were negligible with respect to these quantities in the tubing since the photometer volume was only 17 μl.

The measured concentration-time data were plotted on probability paper as the total amount of benzaldehyde eluted at time t, divided by that eluted at infinite time vs. the dimensionless time $t/\bar{t}$ (Figure 1). The standard deviation σ_t was taken as one half of the time between when 84 and 16% of the benzaldehyde had been eluted (ordinate values in Figure 1). Then the variance is given by

$$\sigma^2 = \left(\frac{\sigma_t}{\bar{t}}\right)^2 \tag{7}$$

Values of σ^2 so determined were used in Equation 6 to establish the molecular diffusivity.

Results

In all the runs, $DL/r^2u \geq 7.0$, $ru/D \geq 470$, and $E/uL \leq 0.003$ so that the requirements of Equations 2 and 3 were satisfied, and Equation 4 should be a good approximation.

To examine the reliability of the method, runs were made first for the diffusion of benzene (in low concentra-

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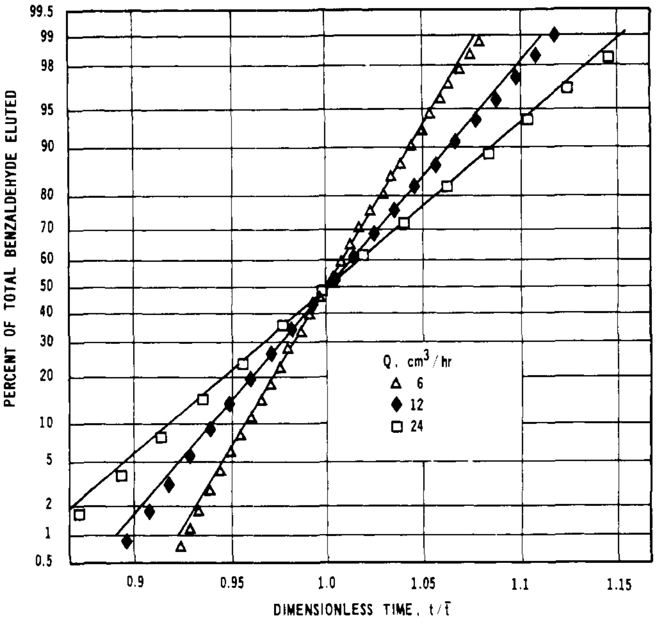

Figure 1. Elution data for benzene–methanol system at 22°C

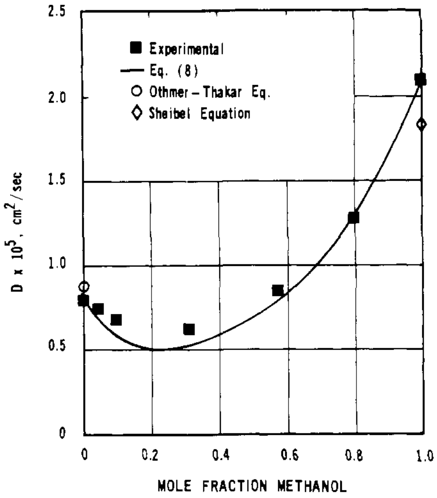

Figure 2. Diffusivity of benzaldehyde in methanol-water mixtures at 22°C

Table I. Diffusivities of Benzene in Methanol at 22°C

Flow rate Q, cm³/hr	$D \times 10^5$, cm²/sec Exptl	$D \times 10^5$, cm²/sec Lit (*4*)	Difference, %
6	2.44	2.47[a]	−1.2
12	2.42		−2.0
24	2.60		+5.2

[a] Literature value of 2.20 (±0.08) × 10^{-5} at 15°C was corrected to 22°C by the Sheibel equation ($\eta D/T$ = const.).

Table II. Diffusivities of Benzaldehyde in Methanol-Water Mixtures at 22°C

x, mole fraction methanol	η, viscosity[a] cP	$D \times 10^5$, cm²/sec Predicted, Equation 8	$D \times 10^5$, cm²/sec Exptl	Difference, %
0	0.958	0.816[b]	0.816 (0.873[c])	
0.0471	1.2	0.665	0.755	−13.5
0.1	1.425	0.574	0.685	−19.3
0.308	1.725	0.521	0.619	−18.8
0.572	1.315	0.769	0.845	−9.9
0.800	0.890	1.27	1.28	−0.8
1.0	0.585	2.09[b]	2.09 (1.83[d])	

[a] From refs. **2** and *10*. [b] Experimental value. [c] Predicted from the Othmer-Thakar equation (*9*). [d] Predicted from the Scheibel equation (*9*).

tions) in methanol, a system for which an experimental diffusivity at 15°C was available. Measurements were made at three flow rates and the results (Figure 1) agree well with the normal distribution curve, particularly between the 16 and 84 percentiles of eluted benzene. Diffusivities calculated from Equations 6 and 7 are compared with the literature (*4*) value in Table I. The results agreed with Bruins' value (*4*) within a few percent. A small increase in diffusivity with flow rate was observed, similar to that noted by Ouano (*7*).

Diffusivities were next determined in the same way for benzaldehyde in mixtures of methanol and water ranging from 0 to 100% methanol. The results are shown in Figure 2 by the experimental points. Also given in the figure are the diffusivities of benzaldehyde in pure water and in pure methanol, as predicted from the Othmer-Thakar and Scheibel equations, respectively. These equations have been recommended (*9*) for use in the absence of experimental data. The predicted values deviate about 7 and 12%, respectively, from our experimental results. These deviations are within the accuracy suggested by Reid and Sherwood (*9*) for these correlating equations.

Leffler and Cullinan (*5*) proposed a method for predicting the effect of composition of the solvent on the diffusivity of a component (at low concentrations) in a solvent consisting of two components. Required data include diffusivities of the two binaries formed by the component and each of the solvent components. Also required are the viscosities of the solvents and their mixtures. The predictive equation may be written:

$$D = \frac{(D_1^\circ\,\eta_1)^{x_1}\,(D_2^\circ\,\eta_2)^{x_2}}{\eta} \qquad (8)$$

Viscosity data for methanol-water mixtures are available (*2, 10*) at different compositions and temperatures. Since the concentration of benzaldehyde was very low, these values may be employed for η. Similarly, η_1 and η_2 may be taken as the viscosities of pure water and pure methanol. The diffusivities predicted from Equation 8 and the viscosities of the mixture are summarized in Table II. Comparison with the experimental results we have determined shows a maximum deviation of 19.3%. The values of D_1° and D_2° used in Equation 8 were our experimental values for benzaldehyde in pure water and in pure methanol. The curve in Figure 2 represents the predicted results.

In summary, the method originally developed by Ouano (*7*) appears to be reliable for obtaining diffusivities accurate to within a few percent. It is easily adaptable to multicomponent systems for which there is a scarcity of data. Although Ouano found that the diffusivities were a function of flow rate in the tube, our measurements did not suggest such a dependency as long as the conditions of Equations 2–4 were met.

Nomenclature

D = molecular diffusivity, cm^2/sec
D_i° = molecular diffusivity of the limiting component in a dilute solution of solvent i, cm^2/sec
E = Taylor axial dispersion coefficient, cm^2/sec
L = length of tubing between sample injection and photometer, cm
Q = volumetric flow rate, cm^3/sec
r = radius of tubing, cm
t = time after injection, sec
$\bar{t}$ = average residence time, L/u, sec
u = average linear velocity of fluid in tube, cm/sec
x_i = mole fraction of component i

Greek Letters

σ^2 = variance of concentration vs. time curve at photometer
σ_t = standard deviation of concentration vs. time curve, sec
η = viscosity of liquid mixture, P
η_i = viscosity of solvent i, P

Subscript

i = refers to solvent i

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Enthalpy of Dilution of Aqueous Na_2SO_4 and Li_2SO_4

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The enthalpies of dilution of aqueous solutions of Na_2SO_4 and Li_2SO_4 were measured at 25°C for molalities from 3.0 to 0.09 mol/kg. Values of the excess enthalpy (H^{ex} or ϕ_L) at molalities from 0 to 3 mol/kg were derived by combining the results with the low-concentration data of Lange and Streeck and Wallace and Robinson.

Lange and Streeck (*11*) reported values for the enthalpies of dilution of aqueous solutions of Na_2SO_4 and Li_2SO_4 at 25°C at concentrations from 0.1 to 0.00016 mol/l. Wallace and Robinson (*14*) measured Na_2SO_4 enthalpies of dilution from 0.4 to 0.0006 mol/l. Results at higher concentrations are limited to two measurements by Greyson and Snell (*6*) (Na_2SO_4 from 1.25 to 0.0135 mol/kg) and some results of Gritsus et al. (*7*) of low accuracy. In the course of an investigation into the heats of mixing solutions of these two electrolytes, a need for excess enthalpies arose; hence, this study was undertaken.

Experimental

Preparation and analysis of solutions. The solutions were prepared from reagent-grade salts and deionized distilled water. All impurities reported by the manufacturer were less than 0.1%. The sodium sulfate was dried for 24 hr at 200°C (*2*). Solutions were prepared by weight.

The solubility of Na_2SO_4 in H_2O is reported to be 1.96 mol/kg at 25°C (*12*). Hence, a $3m$ Na_2SO_4 solution is supersaturated. It was necessary to load this solution, warmed slightly above room temperature to prevent crystallization, in the syringe and the mixing vessel.

The Li_2SO_4 was dried at 500°C in a muffle furnace for 15 hr (*1, 2, 10*). For some runs the pH was adjusted to eight or nine by the addition of a negligible amount ($<<$0.1%) of LiOH or NaOH. No difference was detected in these runs. Both salts were prepared and measured by two different investigators (D. E. S. and P. T. T.) working independently.

The calorimeter used for these experiments, an LKB batch microcalorimeter (LKB-Produkter AB, Fack, 161 25 Bromma 1, Sweden, Model 10700-2), has been described previously (*3, 4, 13*). At the beginning of a run, the cell was rinsed with water and dried with a stream of nitrogen. One of the calorimeter compartments (compartment A) was loaded with a solution containing n_A moles of solute at a molality m_A. The other calorimeter compartment (B) was loaded with water. The two solutions were then mixed in the calorimeter, resulting in q calories of heat being released and a final molality m_F. For each of the succeeding experiments, the calorimeter was not rinsed and dried, but compartment B was emptied (by weight) with a 5-ml plastic syringe. This process left behind 10 ± 2 mg of solution if compartment B was the 2-ml side of the calorimeter and 15 ± 2 mg if compartment B was the 4-ml side of the calorimeter.

A known weight of solvent was added to compartment B, and this, when mixed with the small amount of solution left behind produced a solution containing n_B moles of solute at concentration m_B. The moles of solute (n_A)

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