Steady State Technique for Measuring Fluxes and Diffusivities in Binary Liquid Systems

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A steady state experimental technique for measuring fluxes of the components and diffusivities in binary liquid systems has been developed. Steady state diffusion is established through a sintered glass diaphragm of ultrafine porosity with a known concentration difference across the diaphragm. The concentrations are maintained by a flow of solution on one side of the diaphragm and an infinite sink on the other side. The fluxes and diffusivities are calculated from the measured flows and compositions. A syringe pump capable of delivering extremely small flow rates with good reproducibility is used to pump the solution past the sintered glass diaphragm. The diffusion cell design permits an accurate control of pressure drop across the diaphragm so that fluxes can be measured both with and without pressure gradients. The diffusion cell was calibrated by using the hydrochloric acid-water system.

Three binary systems, ethanol-benzene, aniline-benzene, and aniline-carbon tetrachloride were chosen for diffusion studies. Diffusivity-composition data for these systems at 25°C. were used to test the existing correlations for the concentration dependence of binary diffusivity. Of these, the empirical correlation of Vignes *(11)* represents the data satisfactorily. In addition, experimental molar diffusion flux ratio data for the above systems at 25°C. with no pressure gradients are reported and found to be essentially equal to the ratio of molar volumes of the components.

Molecular theory does not yet permit reliable prediction of liquid diffusivities, and experimental measurements continue to be necessary to develop the theory and to test existing methods. Concentrated solutions of dissimilar molecules are particularly difficult to handle. In the present work some new data for such systems have been obtained.

In gases and solids the bulk flow [Kirkendall (*1*) effect] which accompanies diffusion in a binary system is well known. For example, in gases the ratio of the molar fluxes in a porous material is inversely proportional to the square root of the ratio of the molecular weights, in the absence of any pressure gradient. Little information is available for the analogous effect in liquid systems, so the apparatus presented here has been designed to obtain diffusivities and component fluxes in the presence of a well-defined pressure gradient. This experimental method operates at steady state and thus differs from the recent work of Board and Spalding (2). The present design permits the use of a sintered glass diaphragm rather than the polymer film which was imposed by the design of Board and Spalding (2).

APPARATUS

The present design of the diffusion cell (Figure 1) differs from the conventional diaphragm cell in that it facilitates accurate control of pressure drop across the diaphragm, at the same time allowing continuous sampling of the liquid flowing out of the cell.

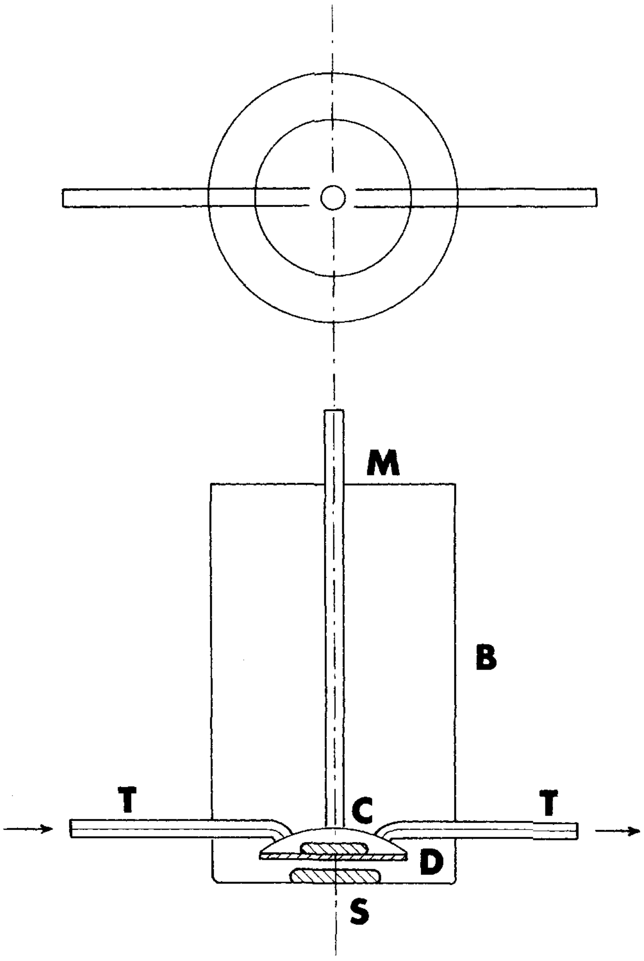

Fig. 1. Diffusion cell.

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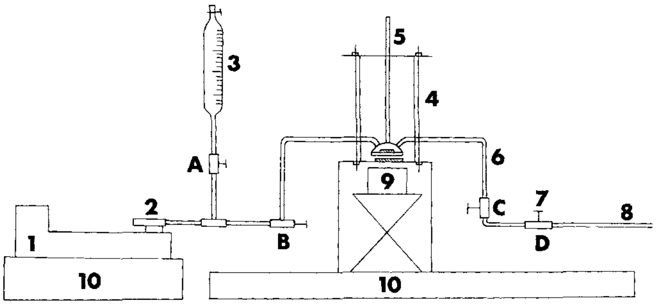

Fig. 2. Apparatus: 1. syringe pump, 2. syringe, 3. graduated cylinder, 4. diffusion cell, 5. manometer tube, 6. 1-mm. capillary tubing, 7. needle valve, 8. graduated capillary tubing, 9. magnetic stirrer, 10. support.

An ultra fine* sintered glass diaphragm *D* (pore size 0.9 to 1.4 μ) of 6 cm. diameter is fitted to a bell shaped glass cell *C*, which contains a magnetic stirring bar sealed in glass S. This small cell is provided with 1-mm. capillary inlet and outlet tubes *T*, which are in turn ring sealed through the walls of glass jar *B* of 1-liter capacity. The volume of the cell is approximately 20 ml. A vertical graduated manometer tube *M* of 25 cm. length and 1 mm. I.D. is sealed to the top of the cell. The infinite sink, a glass jar of 10 cm. I.D., also serves as a consant temperature bath. It is protected from the atmosphere by a Teflon plate, positioned securely over the jar and held in place by ½-in. brass tie rods screwed to the wooden structure at the bottom (Figure 2).

A syringe pump is used to pump a liquid mixture of known composition through the diffusion cell. A reservoir of liquid mixture is available in the graduated cylinder of 120 ml. capacity to fill up the syringe when necessary. The pump can be operated with different combinations of 2,- 5,- 10,- 25,- and 50-ml. syringes at different flow rates; the range of nominal flow rates is 35 to 0.00017 ml./min. with a reproducibility of 1%.

A magnetic stirrer drives the stirring bars in the cell as well as in the bath and maintains the solutions homogeneous. In addition, an external stirrer in the bath driven by a small motor keeps the temperature variation to a minimum. A cooling coil and a Pyrex glass 100-w. heater are used as heat sink and source. The maximum variation of temperature in the bath was ±0.02°C.

A graduated 0.5-mm. capillary outlet tube 8 of 25 cm. length is used to measure the flow rates of the solutions. All the needle valves are made of glass and Teflon only, and inlet and outlet connections are through connector tubes made of Teflon. Solutions were analyzed by using a refractometer with a refractive index precision of 0.00005 in the range of 1.33 to 1.68. This uncertainty corresponds to a maximum absolute error of 0.1% of the concentration in the systems studied. A sample of 50 μliters is required.

EXPERIMENTAL TECHNIQUE

For each binary system studied, density and refractive index data of the mixtures were obtained at 25°C. Density measurements were made by weighing a 20-ml. pycnometer filled with a solution of known composition on a Mettler balance. The outlet tube used to measure flow rates was calibrated by delivering a carefully controlled amount of distilled water through the tube by a micrometer buret of precision of 0.0001 ml. To determine the height of the water (or mixture) level in the manometer tube corresponding to $\Delta P = 0$, the bath and the cell were filled with distilled water (or binary mixture under study) and the temperature was maintained at 25°C.; then the inlet and outlet valves were closed. When the level in the manometer had come to a stationary position, the height of the level above the liquid surface in the bath was measured with a cathetometer. Also, this height was checked against the measured value of capillary rise in a graduated capillary tube identical to the manometer tube in the diffusion cell. The calibration of the inlet flow rates delivered by the syringe pump was made by pumping the distilled water through the diffusion cell and measuring the outlet flow rate with no pressure gradient across the diaphragm. Running the glass stirrer bar had no visible effect on these measurements.

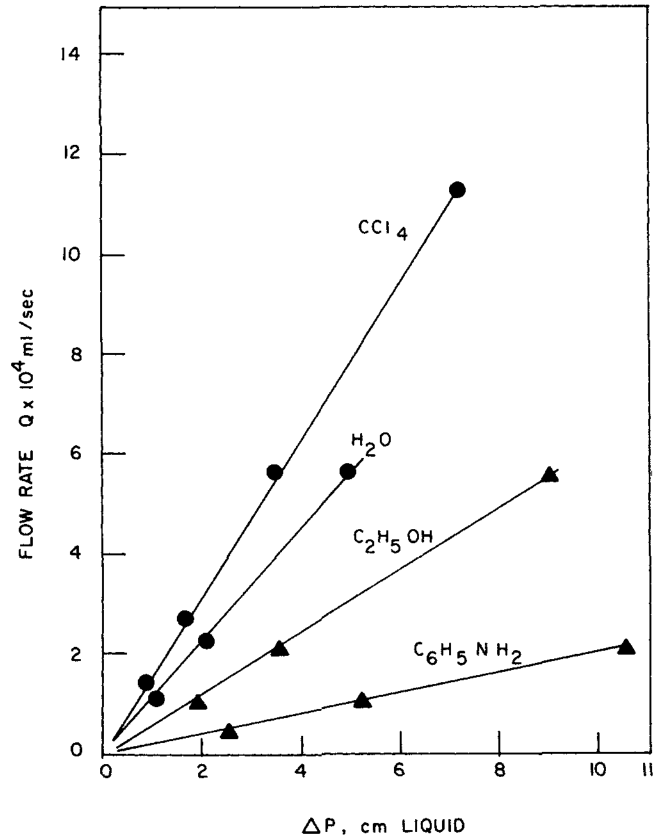

Fig. 3. Permeability rates through ultrafine diaphragm at 25°C.

Since the diaphragm cell can measure only relative diffusion coefficients, it is necessary to calibrate the cell with a system of known diffusivity. The hydrochloric acid-water system was selected mainly because its diffusivity (3) is high and is less concentration dependent than that of the potassium chloride-water system. Concentrations of hydrochloric acid were determined by titrating against standard sodium hydroxide solution, which was standardized by titrating against potassium hyrogen phthalate solution. The procedure for collecting the necessary data for calibration as well as for actual runs is described below.

For an experimental run, the graduated cylinder and the bath are filled with solutions of a binary mixture of

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* This diaphragm is finer than those used in conventional cells so as to increase the sensitivity of the use of the pressure drop across the frit as an indicator of hydrodynamic flow. See (2).

TABLE 1. DIFFUSION DATA OF ETHANOL(A)-BENZENE(B) SYSTEM WITH ZERO PRESSURE GRADIENT AT 25°C.

Capillary rise, cm.	$q_1 \times 10^4$, ml./sec.	$q_2 \times 10^4$, ml./sec.	x_{A0}	x_{A1}	x_{A2}	x_A, mean value	$\mathcal{D}_{AB} \times 10^5$, sq.cm./sec.
0.635	2.233	2.2284	0.00	0.1780	0.1517	0.0740	2.10
0.635	2.233	2.2235	0.0518	0.1800	0.1527	0.1022	1.42
0.635	2.233	2.2347	0.3885	0.4824	0.4716	0.4300	0.94
0.635	2.233	2.2372	0.4450	0.5515	0.5329	0.4890	1.13
0.635	2.233	2.2328	0.5320	0.6301	0.6172	0.5746	1.14
0.635	2.233	2.2142	0.6302	0.5320	0.5461	0.5881	1.17
0.635	2.233	2.2247	0.7788	0.6923	0.7081	0.7434	1.42
0.635	2.233	2.2322	0.8567	0.7788	0.7928	0.8248	1.45
0.635	2.233	2.2499	0.9730	0.9016	0.9136	0.9433	1.68
0.635	2.233	2.2284	0.9573	1.0004	0.9926	0.9749	1.80

different compositions. A 5-ml. syringe (10-ml. syringe for a few runs) is filled approximately to three-fourths of its capacity with the solution from the graduated cylinder. A small portion of the liquid in the syringe is pumped back into the graduated cylinder to eliminate the air bubbles in the connecting joints. After it is sure that there are no air bubbles in the glass tubing and in the connecting tubes, needle valves A and B are opened, and the liquid in the graduated cylinder slowly fills the cell because of the static head; depending on the solution, this takes approximately 10 to 30 min. The filling must often be repeated to remove all air bubbles from the diaphragm. Meanwhile, the temperature of the bath is maintained at 25°C., and the magnetic stirrer is set to drive the stirring bars in the bath and in the cell at about 100 rev./min. This speed is high enough for good mixing but low enough to avoid pumping effects. When the temperature is steady at 25°C. for about 15 min., the syringe pump is started on a suitable gear setting (8 or 9) to deliver the liquid into the cell. The inlet-liquid flow rates used are in the range of 0.06 to 0.013 ml./min. The composition should be uniform at every point in the inlet tubing within ½ hr. [estimated by using Taylor's model (4)]. The outlet needle valve C is adjusted so that the liquid level in the manometer tube remains at a predetermined position which corresponds to a fixed value of pressure drop between the cell and the bath. A sample is withdrawn occasionally (once every ½ hr. approximately) from the cell outlet line and is analyzed by using the refractometer (titration for hydrochloric acid solutions) until a steady state is attained. Valve D is then opened and at the same

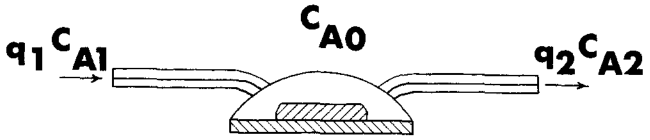

Fig. 4. Geometry of the diffusion cell.

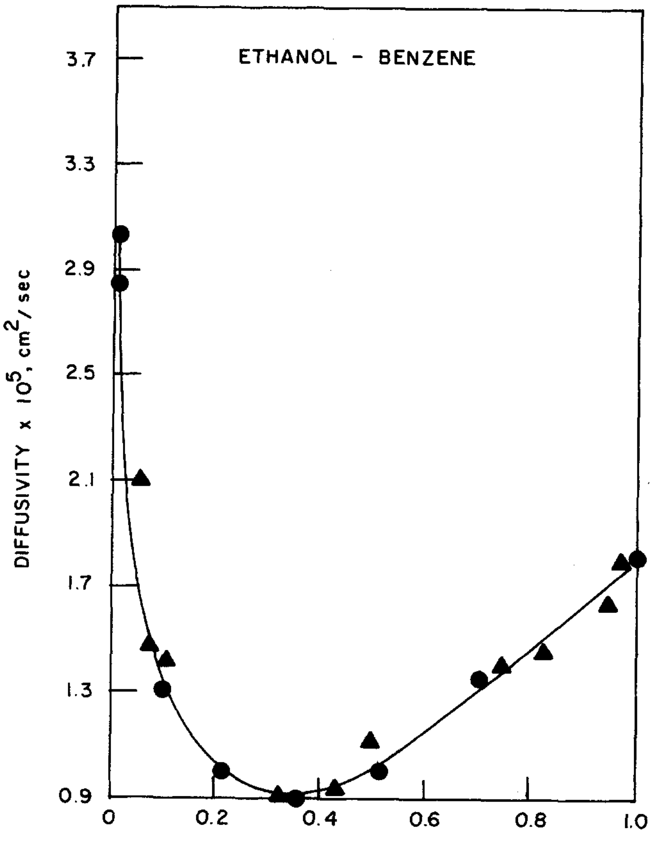

Fig. 5. Ethanol (A)-benzene (B) system at 25°C. ●—literature (6), ▲—present work.

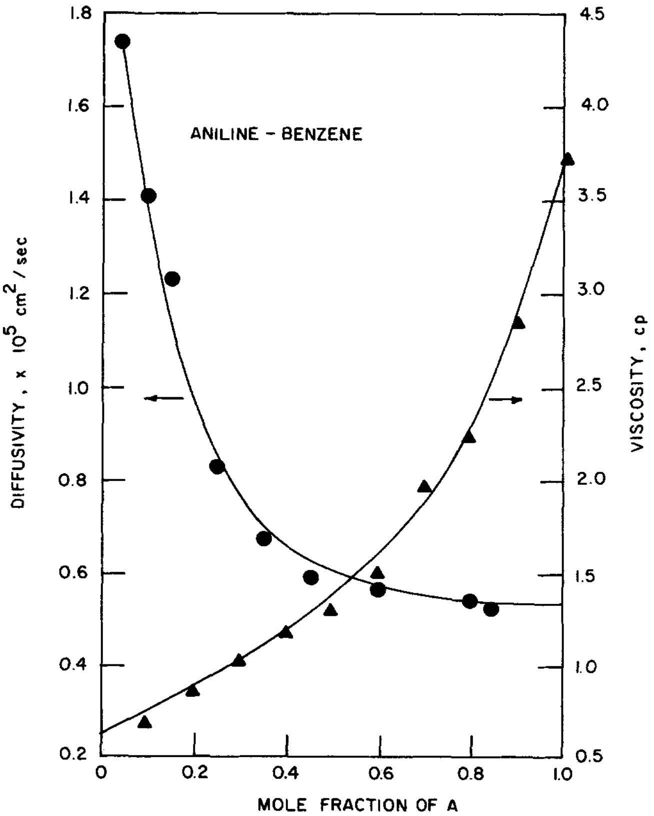

Fig. 6. Aniline(A)-benzene(B) system at 25°C.

Table 2. Concentration Dependence of Diffusivity Aniline(A)-Benzene(B) System at 25°C.

Average mole fraction	$\mathcal{D}_{AB} \times 10^5$, sq.cm./sec.	η_{AB}, centipoise	α_{AB}	$\mathcal{D}_{AB}\eta_{AB} \times 10^5$	$\frac{\mathcal{D}_{AB}\eta_{AB}}{\alpha_{AB}} \times 10^5$	$\ln\left(\frac{\mathcal{D}_{AB}}{\alpha_{AB}}\right)$
0.0360	1.76	0.665	0.935	1.17	1.25	−10.88
0.0945	1.41	0.733	0.834	1.03	1.24	−10.99
0.1457	1.22	0.800	0.757	0.98	1.29	−11.04
0.1703	1.09	0.825	0.724	0.90	1.24	−11.10
0.2448	0.82	0.925	0.643	0.76	1.18	−11.27
0.3410	0.67	1.050	0.591	0.70	1.19	−11.39
0.4511	0.66	1.215	0.606	0.80	1.32	−11.43
0.5929	0.60	1.525	0.725	0.92	1.26	−11.70
0.7944	0.56	2.275	0.970	1.27	1.31	−12.06
0.8431	0.53	2.538	1.013	1.35	1.33	−12.16

time the sampling outlet is closed with a syringe tip; the time for the liquid to fill the graduated capillary tube is measured with a stopwatch. A typical run for zero pressure drop lasts 10 hr. However, depending on the initial compositions, inlet flow rate, and pressure drop, the time for the runs ranges from 4 to 15 hr.

Permeability rates of distilled water, ethanol, benzene, carbon tetrachloride, and aniline through the diaphragm were measured at different pressure drops (Figure 3). These data were used to calculate the cell constant and compare it with the value from hydrochloric acid-water diffusion data. For example, for water this method gave β' equal to 3.28 ± 0.15 cm. Since ethanol absorbs moisture from air and aniline is oxidized on exposure to air, for diffusion runs on these chemicals it is necessary to pass nitrogen slowly over the bath to minimize the exposure of these chemicals to air. All the chemicals used were of Fischer certified reagent grade; aniline was pale yellow in color even after distillation and other chemicals were used without further purification. Analysis by gas chromatography did not indicate the presence of any impurities in these chemicals; also, density and refractive index values agreed very well with those of the literature. Diffusion studies were conducted for hydrochloric acid-water, ethanol benzene, aniline-benzene, and aniline-carbon tetrachloride, and the results are discussed below.

Viscosity data of aniline-benzene and aniline-carbon tetrachloride systems were obtained through the use of a falling ball viscosimeter. It was calibrated with distilled water by using a glass ball of density 2.53 g./ml. at 20° and 25°C.

WORKING EQUATIONS

The geometry of the diffusion is shown in Figure 4; q_1 and q_2 are the volumetric inlet and outlet flow rates, respectively, and c_{A0}, c_{A1}, and c_{A2} are the concentrations of the component A in the bath, in the pumping liquid, and in the cell (steady state value) respectively. The basic equation is, on the volume centered basis

$$N_A = -\mathcal{D}_{AB}\frac{dc_A}{dx} + \frac{q}{A_e}c_A \tag{1}$$

where x is the distance in the direction of diffusion, and

$$q = q_1 - q_2 \tag{2}$$

A mass balance on component A leads to the following relations:

$$q_1c_{A1} - q_2c_{A2} = A_e N_A \tag{3}$$

Case 1: $q = 0$

Equation (1) simplifies to

$$N_A = \mathcal{D}_{AB}\frac{c_{A2} - c_{A0}}{l_e} \tag{4}$$

Combining Equations (3) and (4), we have

$$q_1(c_{A1} - c_{A2}) = \frac{A_e}{l_e}\mathcal{D}_{AB}(c_{A2} - c_{A0}) \tag{5}$$

In Equations (4) and (5), $x_{A2} - x_{A0}$ is less than 0.10, so $\mathcal{D}_{AB}$ is the rate at the mean concentration of the two solutions. Therefore

$$\mathcal{D}_{AB} = \frac{q_1}{\beta'}\frac{c_{A1} - c_{A2}}{c_{A2} - c_{A0}} \tag{6}$$

where $\beta' = \frac{A_e}{l_e}$ (cell constant).

Case 2: $q \# 0$

From Equations (1) and (3)

$$q_1c_{A1} - q_2c_{A2} - qc_A = -A_e\mathcal{D}_{AB}\frac{dc_A}{dx} \tag{7}$$

Table 3. Concentration Dependence of Diffusivity Aniline(A)-Carbon Tetrachloride(b) System at 25°C.

Average mole fraction	$\mathcal{D}_{AB} \times 10^5$, sq.cm./sec.	η_{AB}, centipoise	α_{AB}	$\mathcal{D}_{AB}\eta_{AB} \times 10^5$	$\frac{\mathcal{D}_{AB}\eta_{AB}}{\alpha_{AB}} \times 10^5$	$\ln\left(\frac{\mathcal{D}_{AB}}{\alpha_{AB}}\right)$
0.0378	1.37	0.913	0.812	1.25	1.54	−10.99
0.0999	0.86	1.000	0.576	0.86	1.49	−11.11
0.1378	0.75	1.050	0.472	0.79	1.67	−11.05
0.1752	0.57	1.100	0.393	0.63	1.60	−11.14
0.2535	0.43	1.210	0.294	0.52	1.77	−11.13
0.3557	0.37	1.340	0.265	0.50	1.87	−11.18
0.4459	0.35	1.475	0.300	0.52	1.72	−11.36
0.6107	0.39	1.830	0.441	0.71	1.62	−11.64
0.7656	0.42	2.380	0.616	1.00	1.62	−11.90
0.8732	0.46	2.875	0.764	1.32	1.73	−12.02

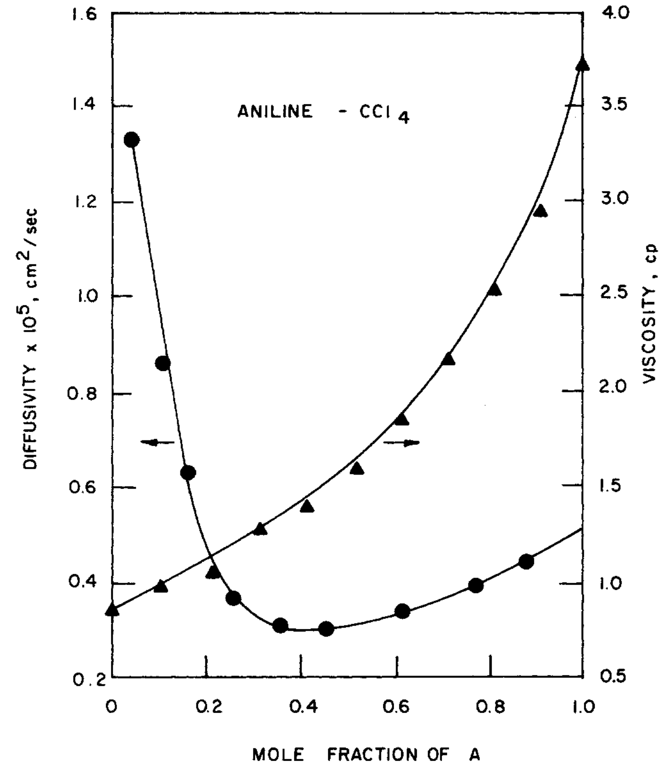

Fig. 7. Aniline(*A*)-carbon tetrachloride(*B*) system at 25°C.

Rearranging and integrating, we get

$$\frac{l_e}{A_e} = \mathcal{D}_{AB}\int_{x_{A0}}^{x_{A2}} \frac{dc_A}{q_1c_{A1} - q_2c_{A2} - qc_A} \qquad (8)$$

Integration of Equation (8) gives

$$\mathcal{D}_{AB} = \frac{q_1/\beta'}{\ln\left[\dfrac{c_{A1} - c_{A2}}{c_{A1} - c_{A0} - \left(\dfrac{q_2}{q_1}\right)(c_{A2} - c_{A0})}\right]} \qquad (9)$$

From equations (1) and (3), it follows that

$$\frac{N_A}{N_B} = \frac{c_{A1} - \left(\dfrac{q_2}{q_1}\right)c_{A2}}{(c_1 - c_{A1}) - \left(\dfrac{q_2}{q_1}\right)(c_2 - c_{A2})} \qquad (10)$$

and the net volumetric flux, V_T is given by

$$V_T = q = q_1 - q_2 \qquad (11)$$

RESULTS AND DISCUSSION

Three binary systems, ethanol-benzene, aniline-benzene, and aniline-carbon tetrachloride, were studied in detail. The results of the measurements at 25°C. without pressure gradient are given in Tables 1, 2, and 3. The concentration difference used was always about 0.1 mole fraction. The results are plotted in Figures 5, 6, and 7. The viscosity measurements are also shown on these figures.

Some determinations of $\mathcal{D}_{AB}$ were made with small pressure gradients across the diaphragm; Equation (9) was used to calculate the values. The total volumetric flow q has been found to be zero when Δp is zero. The results for $\mathcal{D}_{AB}$ found with Δp (or q) not zero have more scatter than do those for $\Delta p = 0$ and have not been incorporated into the results presented here.

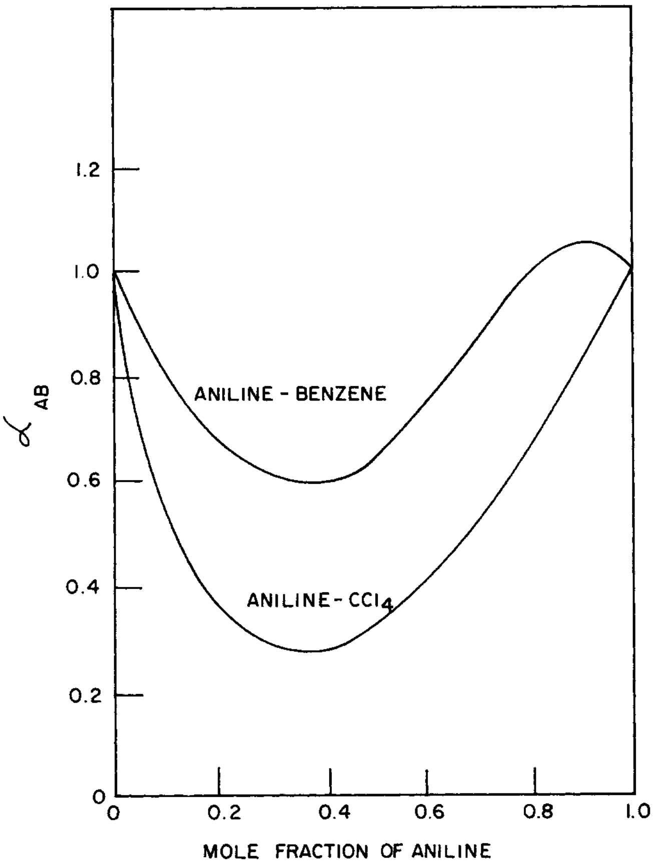

Fig. 8. Thermodynamic factor curves.

Diffusivity data of the ethanol-benzene system with zero pressure gradient (Figure 5) are compared with the values reported in the literature (5). Although there is some scatter, the agreement is quite satisfactory, within the estimated 5% error of the method.

The shapes of the experimentally obtained diffusivity curves (Figures 5, 6, and 7) clearly show the nonideal behavior of these systems. The ethanol-benzene system is an associated system and has been studied extensively. Aniline is a polar molecule and can be expected to have some degree of association with benzene and carbon tetrachloride molecules. The aniline-carbon tetrachloride system like the ethanol-benzene system has a minimum in its diffusivity curve (Figure 7). Extrapolated values of diffusivities for aniline-benzene and aniline-carbon-tetrachloride systems are compared to the predicted values of Wilke-Chang (6), Scheibel (7), and Othmer-Thakar (8) correlations in Table 4. The agreement is poor for benzene and carbon tetrachloride diffusing in aniline. This could be caused by association effects and the relatively high viscosity of aniline.

Table 4. Comparison of Experimental Diffusivities with Predicted Values in Dilute Solutions

	$\mathcal{D}^0_{AB} \times 10^5$, sq.cm./sec.			
System	Experimental	Wilke-Chang	Scheibel	Othmer-Thakar
Aniline(*A*)-benzene(*B*)	1.96	2.03	2.03	1.34
Benzene(*A*)-aniline(*B*)	0.54	0.37	0.31	0.24
Aniline(*A*)-Carbon tetrachloride(*B*)	1.58	1.90	1.24	0.97
Carbon tetrachloride(*A*)-aniline(*B*)	0.52	0.36	0.31	0.23

Diffusivity data of aniline-benzene and aniline-carbon tetrachloride are used to test the existing correlations for the concentration dependence of diffusivity: Bearman's (9) prediction that the product of $\mathcal{D}_{AB}\ \eta_{AB}$ is constant, Hartley and Crank's (*10*) prediction that $\mathcal{D}_{AB}\ \eta_{AB}/\alpha_{AB}$ should vary linearly with composition, and the correlation of Vignes (*11*) and of Cullinan (*12*):

$$\mathcal{D}_{AB} = (\mathcal{D}_{AB}^0)^{x_B}\ (\mathcal{D}_{BA}^0)^{x_A}\ \alpha_{AB} \tag{12}$$

The thermodynamic factors for the aniline-benzene and aniline-carbon tetrachloride systems were calculated (Figure 8) by using the following equations suggested by Deshpande and Pandya (13) based on their vapor-liquid equilibrium data:

$$\alpha_{AB} = 1.0 + 48D\,x_A^4 + (12C - 96D)\,x_A^3 + (58D - 18C + 2B)\,x_A^2 + (6C - 2B - 10D)\,x_A \tag{13}$$

where B, C, and D are constants characteristic of the systems (*13*).

Variations of the product $\mathcal{D}_{AB}\ \eta_{AB}$ with mole fraction for aniline-benzene and aniline-carbon tetrachloride systems are shown in Figures 9 and 10. It can be seen that these curves have a minimum, and they are nowhere near a straight line relationship. Values of $\mathcal{D}_{AB}\ \eta_{AB}/\alpha_{AB}$ are listed in Tables 2 and 3, no definite trend with mole fraction can be seen. Figures 9 and 10 also show the variation of log $(\mathcal{D}_{AB}/\alpha_{AB})$ with mole fraction, and the points lie on a straight line with some scatter. The scatter is well within the combined experimental errors of diffusivity and thermodynamic factor. Therefore, the correlation of Vignes [Equation (12)] does represent the data satisfactorily. However, Vignes' correlation requires two experimental diffusivity values to calculate the diffusivity at any other composition.

Attempts were made to measure the flux ratios at different concentrations for these three systems with an approximate initial mole fraction difference of 0.1. The inaccuracies in the measurements of flow rate differences become very significant in comparison with diffusion fluxes, consequently reproducibility of the values is poor. Therefore, it is necessary to use the pure components in the bath and in the cell and thus increase the fluxes manyfold. Flux ratio measurements, calculated by Equation (10), for ethanol-benzene, aniline-benzene, and aniline-carbon tetrachloride were measured, and in all these systems essentially equivolume diffusion prevailed for zero pressure gradients.

The present technique seems to be capable of measuring liquid diffusivities in binary systems with a maximum absolute error not exceeding 5%. The principal advantage of this method over the conventional diaphragm cell is that it requires less time (usually less than 10 hr.) in contrast to longer times (2 or 3 days) required by the latter method. Also it offers the advantages inherent in a steady state method. Because of the accurate pressure control, diffusion flux ratios of the species could be measured, and ambiguities regarding hydraulic flow do not exist. Further, no special computations are required for those systems with considerable volume change on mixing. Optical Schlieren methods, although they are more accurate than the present technique, are not suitable for measuring flux ratios of the diffusing species.

In ternary systems, optical methods are less convenient, and the present apparatus can be used to obtain the matrix of multicomponent diffusion coefficients in a relatively direct way.

NOTATION

A_e = effective area, sq.cm.
c = total molar concentration, g.-mole/ml.
c_A = molar concentration of component A, g.-mole/ml.
$\mathcal{D}_{AB}$ = binary diffusivity, sq.cm.
$\mathcal{D}_{AB}^0$ = binary diffusivity at infinite dilution of A
l_e = effective diffusion length, cm.

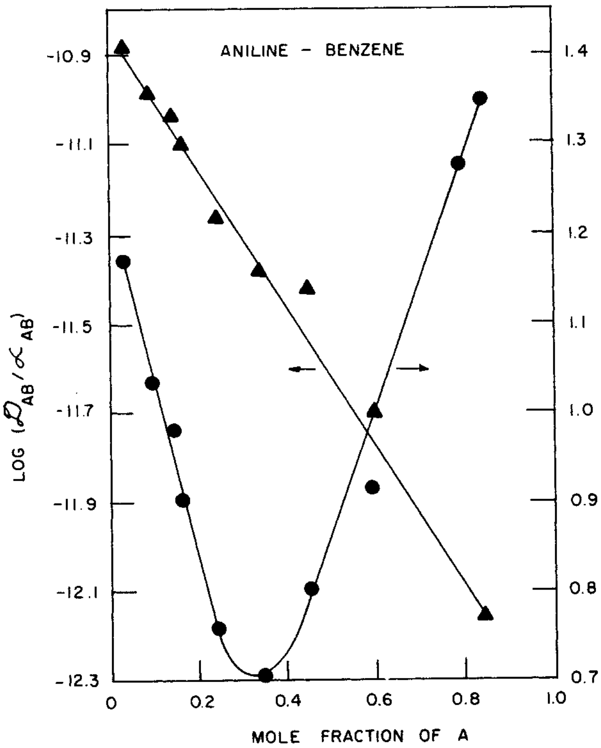

Fig. 9. Aniline(*A*)-benzene(*B*) system at 25°C.

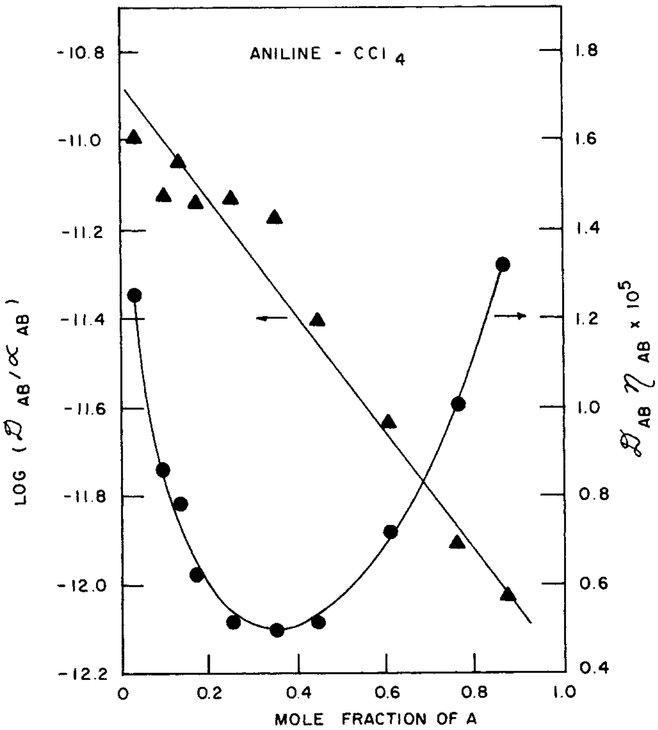

Fig. 10. Aniline(*A*)-carbon tetrachloride(*B*) system at 25°C.

N_A = molar flux of A with respect to a stationary frame, g.-mole/(sq.cm.)(sec.)
P = pressure
ΔP = pressure drop across the diaphragm
q_1 = inlet flow rate, ml./sec.
q_2 = outlet flow rate, ml./sec.
t = time, sec.
T = absolute temperature, °K.
V_A = molar volume of A at normal boiling point, ml./b.-mole
x = distance coordinate, cm.
x_A = mole fraction of A

Greek Letters

α_{AB} = thermodynamic factor $= 1 + \dfrac{d\ln\gamma_A}{d\ln x_A}$
β' = cell constant, cm.
γ_A = activity coefficient of A
η_A = viscosity of A, centipoise
η_{AB} = viscosity of the mixture of components A and B, centipoise

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Ultrafiltration of Proteins in Stagnation Flow

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The effect of viscosity and diffusivity variations on concentration polarization during the ultrafiltration of protein solutions in two-dimensional stagnation flows is investigated by numerical integration of the equations of continuity and motion. It is found that these effects are surprisingly small and insensitive to the forms of concentration dependence postulated. The high Schmidt numbers and low permeation rates characteristic of these systems result in considerable simplification of the analysis and permit use of a modified Chilton-Colburn relation for predicting the onset of sludge formation at the membrane-solution interface. The predicted dependence on Schmidt number agrees with published experimental data for other boundary-layer flows and suggests the possibility of improved prediction of equipment performance.

Ultrafiltration of proteinaceous solutions is of current interest in the purification of proteins, the processing of fluid food products, and a number of biomedical applications. Ultrafiltration is formally similar to reverse osmosis but is normally characterized by much smaller osmotic pressures, more efficient solute rejection, and much larger changes in transport properties. The high viscosity and low diffusivity of concentrated protein solutions are particularly troublesome and frequently result in the formation of thick sludge layers on the upstream faces of ultrafiltration membranes.

These sludges can be very complex in nature, but they appear to consist basically of protein gels. They tend to thicken with time, and they can reduce ultrafiltration rates so markedly that they provide the chief obstacle to higher productivity of presently available ultrafiltration equipment. At the same time they have interesting permeability characteristics of their own which on occasion can dominate membrane behavior and which suggest the possibility of self-renewing permselective membranes. They are therefore doubly interesting to process engineers.

Protein sludges have their origin in concentration polarization which has already been described for constant-property mixtures in a number of flow systems. These analyses include both papers in the reverse-osmosis literature (*2, 4, 8, 12, 13*) and more general treatments of boundary-layer flows (*5, 6, 9* to *11*). It is our purpose here to assess the importance of viscosity and diffusivity variations on concentration polarization of protein solutions by boundary-layer analysis of a simple flow system suitable for experimental study.

In this preliminary paper we consider only two-dimensional stagnation flow and rather simple expressions for