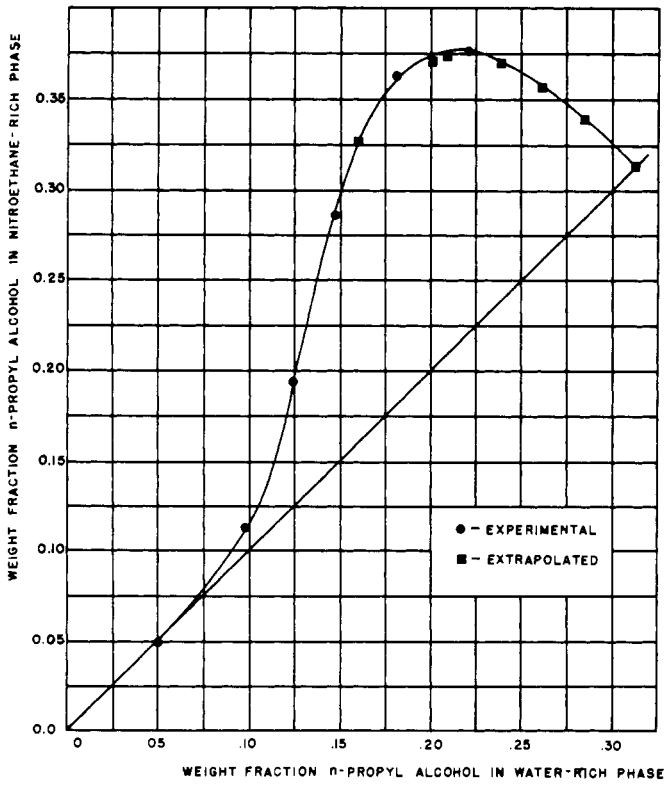

Figure 4. Distribution curve at 25° C.

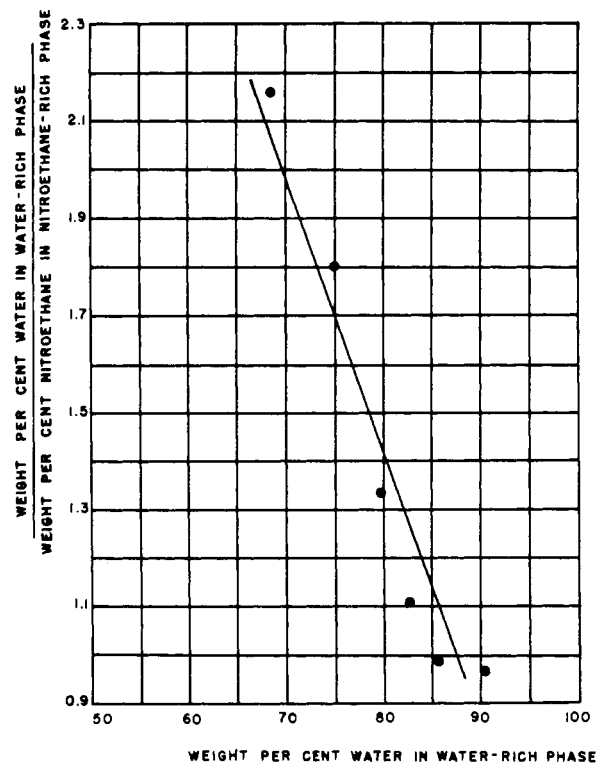

Figure 5. Bachman plot of tie line data

Tie Lines. The three components were added one at a time to a tared, 50-ml. Erlenmeyer flask fitted with a glass stopper until approximately equal volumes of the two liquid phases were obtained. The mixture was then agitated vigorously and allowed to stand. It was then again agitated and allowed to separate into phases. The two layers were removed by use of hypodermic assemblies. Density and refractive index determinations were then made as outlined previously. Densities were used to determine compositions of the equilibrium phases. Refractive index readings were used primarily to identify phases, particularly in the region near the isopycnic (*4*), and secondarily to check compositions from density measurements.

Figure 1 and Table I show the compositions at the binodal curve. Figure 2 presents the variation of density of the mixtures of the components as a function of the binodal curve compositions and Figure 3 is a similar plot of refractive index. Basic data for the distribution curve, Figure 4, and the Bachman plot (*2*), Figure 5, were experimental tie line data (Table II). Additional points to complete the distribution curve and define the plait point were extrapolated using Alders' method (*1*).

LITERATURE CITED

(1) Alders, L., "Liquid-Liquid Extraction," Elsevier, New York, 1955.
(2) Bachman, I., *Ind. Eng. Chem., Anal. Ed.* **12**, 38–9 (1940).
(3) Fowler, A.R., Hunt, H., *Ind. Eng. Chem.* **33**, 90–5 (1941).
(4) Francis, A.W., *Ibid.*, **45**, 2798 (1953).
(5) Francis, A.W., J. CHEM. ENG. DATA **11**, 234–7 (1966).
(6) Francis, A.W., "Liquid-Liquid Equilibriums," Wiley, New York, 1963.
(7) Hankinson, R.W., Thompson, D., J. CHEM. ENG. DATA **10**, 18 (1965).
(8) Schumacher, J.E., Hunt, H., *Ind. Eng. Chem.* **34**, 701 (1942).
(9) Seidell, A., "Solubilities of Organic Compounds," Van Nostrand, New York, 1941.

RECEIVED for review January 27, 1966. Accepted April 17, 1967.

Diffusivities of Some Binary Liquid Systems Using a Diaphragm Cell

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Diffusivity data on 25 binary systems were obtained by using a diaphragm cell at 30° C.

PRESENT UNDERSTANDING of diffusion is far from satisfactory, and reliable data are still scarce and fragmentary even for dilute binary solutions. The lack of a usable kinetic theory of liquids has resulted in dependence on simplified physical models and semiempirical correlations to predict diffusivities, and these can be used only with certain reservations. There is, therefore, need for accurate experimental measurements. Because of the simplicity in construction and fairly high accuracy, a diaphragm cell has been used in many investigations for measuring binary liquid diffusivities. The present investigation reports data for 25 binary systems using a diaphragm cell at 30° C.

DIAPHRAGM CELL EQUATION

Diaphragm cell equation for the measurement of diffusion coefficient may be expressed as follows, as indicated by Gordon (*2*), assuming unidirectional diffusion and quasi-steady state in the diaphragm:

$$D = \frac{1}{\beta t} \ln \frac{\Delta C_1^\circ}{\Delta C_1^F} \qquad (1)$$

Table I. Properties of Solvents Used

Reagents	Mol. Wt.	Density, G./Cc. at 30° C.	Viscosity, Cp. at 30° C.
Amyl acetate	130.18	0.876	0.8620
Amyl alcohol	88.15	0.813	3.3470
Benzene	78.11	0.779	0.5610
Butyl acetate	116.16	0.882	0.6880
Isobutyl alcohol	74.12	0.802	2.1223
n-Butyl alcohol	74.12	0.810	2.2710
Ethyl acetate	88.10	0.901	0.426
Hexane	86.17	0.662	0.2923
Kerosine	...	0.784	...
Methyl acetate	74.08	0.933	0.362
Methanol	32.04	0.792	0.5225
Isopropyl acetate	102.13	0.874	0.551
1-Propanol	60.09	0.804	0.2004
Toluene	92.13	0.866	0.5516

Table II. Solutes Used

Reagents	Mol. Wt.	Density	Mol. Vol., Cc./G. Mole
Methyl ethyl ketone	72.10	0.805	96.2
Adipic acid	146.14	1.360	173.8
Butyric acid	88.10	0.958	112.8
Cinnamic acid	148.15	1.284	181.8
Malic acid	134.09	1.601	141.4
Oleic acid	282.45	0.891	405.0
Tartaric acid	150.09	1.737	153.4

where

β = cell constant equal to $A_e/l_e\left[\frac{1}{V_A} + \frac{1}{V_B}\right]$

ΔC_1° = initial concentration difference, $C_{1A}^\circ - C_{1B}^\circ$

ΔC_1^F = final concentration difference, $C_{1A}^F - C_{1B}^F$

The diffusion coefficient as defined by Equation 1 is the time-averaged integral diffusion coefficient. Gordon (*3*) has shown that this coefficient can be treated without any serious error as the ordinary integral diffusion coefficient taken over the concentration range

$$C_{1AM} = \tfrac{1}{2}(C_{1A}^\circ + C_{1A}^F)$$

and

$$C_{1BM} = \tfrac{1}{2}(C_{1B}^\circ + C_{1B}^F)$$

The relationship between the integral diffusion coefficient and the true or differential diffusion coefficient may thus be expressed as

$$D = \frac{1}{C_{1AM} - C_{1BM}} \times \int_{C_{1BM}}^{C_{1AM}} \bar{D}\, dc \qquad (2)$$

where $\bar{D}$ is the true or differential diffusion coefficient. Gordon (*3*) has shown that if the original concentration is small, the integral diffusion coefficient calculated by using a diaphragm cell is approximately equal to the true or differential diffusion coefficient, if bulk transport due to volume changes or mixing can be neglected.

The use of Equation 1 is subject to the following conditions: quasi-steady state in the diaphragm, cell constant β remaining constant, solutions in the two compartments being homogeneous, and mechanism of transport only by diffusion and not by surface transport. These requirements were assumed to be met by the following considerations and the use of diaphragm cells of normal dimensions similar to the one used by Krishnan and Laddha (*4*).

The use of a unidirectional form of diffusion equation has been shown by Toor (*8*) to be rigorously valid, in the sense that A_e/l_e depends only upon the internal path of the diaphragm. The assumption of quasi- or pseudo-steady

Table III. Diffusivity Data at 30° C.

Solute	Solvent	Cell No.	Initial Concn., C_{1A}°	Concn. Difference ΔC_1°	Concn. Difference ΔC_1^F	$t \times 10^{-5}$, Sec.	$D \times 10^5$, Sq. Cm./Sec.	$D_v \times 10^5$, Sq. Cm./Sec.
Methyl ethyl ketone	Amyl acetate	1	0.2311	0.2311	0.0925	1.819	2.012	1.916
Methyl ethyl ketone	Amyl alcohol	1	0.2200	0.2200	0.1340	1.647	1.230	1.284
Methyl ethyl ketone	Benzene	1	0.2410	0.2400	0.1054	1.582	2.086	2.281
Methyl ethyl ketone	Butyl acetate	1	0.2271	0.2271	0.1072	1.625	1.852	2.216
Methyl ethyl ketone	Isobutyl alcohol	2	0.2355	0.2355	0.1753	1.626	0.5962	0.5873
Methyl ethyl ketone	*n*-Butyl alcohol	2	0.2436	0.2436	0.1819	1.652	0.5802	0.5488
Methyl ethyl ketone	Ethyl acetate	2	0.0481	0.0481	0.0106	1.692	2.932	3.190
Methyl ethyl ketone	Hexane	2	0.0596	0.0596	0.0102	1.560	3.740	4.595
Methyl ethyl ketone	Kerosine	1	0.2087	0.2087	0.1446	1.549	0.9478	...
Methyl ethyl ketone	Methanol	3	0.2659	0.2659	0.1007	1.616	1.870	2.127
Methyl ethyl ketone	Methyl acetate	2	0.0471	0.0471	0.01005	1.608	3.15	3.442
Methyl ethyl ketone	Isopropyl acetate	2	0.2995	0.2995	0.1015	1.605	2.211	2.655
Methyl ethyl ketone	Propyl alcohol	3	0.1636	0.1636	0.1234	1.592	0.552	0.5538
Methyl ethyl ketone	Toluene	1	0.2447	0.2447	0.1003	2.031	2.21	2.519
Adipic acid	Methanol	1	0.02343	0.02343	0.01328	1.640	1.382	1.492
Butyric acid	Methanol	1	0.03010	0.03010	0.01387	1.710	1.810	1.934
Cinnamic acid	Methanol	2	0.02721	0.02721	0.01003	1.642	2.52	2.711
Malic acid	Methanol	2	0.02469	0.02469	0.01030	1.732	1.712	1.689
Oleic acid	Methanol	3	0.0220	0.0220	0.01333	1.82	0.902	0.899
Tartaric acid	Methanol	3	0.03419	0.03419	0.01423	1.652	1.652	1.608
Adipic acid	1-Butanol	1	0.04679	0.04679	0.01014	1.514	0.3992	0.3849
Butyric acid	1-Butanol	3	0.02322	0.02322	0.01788	1.589	0.5120	0.4889
Cinnamic acid	1-Butanol	2	0.02040	0.02040	0.01591	1.568	0.4462	0.3746
Malic acid	1-Butanol	2	0.02040	0.02040	0.01591	1.830	0.4462	0.4356
Oleic acid	1-Butanol	1	0.03103	0.03103	0.01050	1.792	0.2513	0.2816
Tartaric acid	1-Butanol	3	0.02131	0.02131	0.01581	1.812	0.4050	0.4149

state condition in the pores—i.e., a linear concentration gradient—was proved to be valid by Barnes (*1*) as long as the following two conditions are met: The total pore volume is less than 1% of the total cell volume and the preliminary diffusion period has lasted long enough for the effect of the original constant cross section in the diaphragm to disappear, which takes about 4 to 5 hours with a D value of 2×10^{-5} sq. cm. per second. The first condition is usually met by using a diaphragm of normal dimensions and the second condition by proper experimentation. The constancy of the cell factor, β, was checked by a number of experiments with 0.1N HCl diffusing into pure water at a temperature of 30° C. The solutions in the two compartments were assumed to be homogeneous, since with the denser solution in the top chamber, the solutions in the two compartments tended to be density-stirred. It was, however, found necessary to have the diaphragm placed perfectly horizontal. The assumption of diffusion-controlled transport will be invalidated by a defective diaphragm having a relatively enormous area of the pores, which may permit streaming. The possibility of such transport can be neglected if a proper diaphragm is used.

EXPERIMENTAL

The cells consisted of two equal compartments separated by a No. 4 sintered glass diaphragm (porosity 5 to 10 microns) about 30 mm. in diameter and 2 to 3 mm. thick. Each compartment was provided with a filling and draining capillary tube with stopcocks. In order to measure the diffusion coefficient, the lower chamber of the vertical cell and the diaphragm were filled with the denser solution and the upper chamber with the less dense solution. The cell was then placed in the constant temperature bath in an inverted vertical position so as to have the dense solution in the top chamber. The initial concentration of the solute in the chamber from which diffusion occurred was C°_{1A}. The initial concentration of the solute in the other compartment, C°_{1B}, was taken to be zero. Diffusion was then allowed to occur for a preliminary period of 4 to 5 hours to establish the concentration gradient across the diaphragm. Then the cells were emptied and refilled with fresh solutions to begin the experiment. It was assumed that the solutions in the compartments were density-stirred, so that the concentration was uniform throughout each compartment. After a known time the solutions from each compartment were drained and analyzed.

The cell constant, β, was found by calibrating the cells with 0.1N HCl diffusing into pure water at a temperature of 30° C. in a constant temperature bath. The value of 3.078×10^{-5} sq. cm. per second from Stokes' data (*7*) was used for the diffusion coefficient in the diaphragm cell equation. The average values of the cell constants thus determined are

β (cell 1) 0.2496

β (cell 2) 0.3049

β (cell 3) 0.3209

The 95% confidence limit values obtained by the analysis of independent experimental runs for each cell using the procedure suggested by Mickley, Sherwood, and Reed (*5*) were ± 0.000765, ± 0.000089, and ± 0.0004, respectively.

Ketone was determined by the method suggested by Morasco (*6*). Carboxylic acid in solution was estimated by titration with 0.02N potassium hydroxide using phenolphthalein as an indicator.

RESULTS

Diffusion coefficients were measured for 25 binary systems involving methyl ethyl ketone, adipic acid, butyric acid, cinnamic acid, malic acid, oleic acid, and tartaric acid as diffusing solutes. The properties of the solvents and the solutes are given in Tables I and II, respectively. Experimental data on binary diffusivities are recorded in Table III and compared with the predicted values according to the following empirical correlation of Wilke and Chang (*9*).

$$D_w = \frac{7.4 \times 10^{-8} (\bar{x} M_s)^{0.5} T}{\eta (V_m)^{0.6}} \qquad (3)$$

The agreement between the experimental and predicted values is satisfactory.

NOMENCLATURE

A_e = effective cross-sectional area of all pores
C_{1A} = concentration of component 1 in A, compartment from which component 1 diffuses, g. mole/liter
C_{1B} = concentration of component 1 in B, compartment to which component 1 diffuses, g. mole/liter
C_{1AM} = mean concentration of component 1 in compartment A
C_{1BM} = mean concentration of component 1 in compartment B
ΔC_1 = molar concentration difference of component 1
D = binary diffusivity as defined by Equation 1, sq. cm./sec.
D_w = diffusivity as calculated by Wilke and Chang's equation
l_e = effective pore length
M_s = molecular weight of solvent
T = absolute temperature, ° K.
t = time, sec.
V_A = volume of compartment A, cc.
V_B = volume of compartment B, cc.
V_m = molar volume of solute
$\bar{x}$ = association parameter

Greek Letters

β = cell factor
η = viscosity of solvent, centipoises

Superscripts

° = initial condition
F = final condition

LITERATURE CITED

(1) Barnes, C., *Physics* **5**, 4 (1934).
(2) Gordon, A.R., *Ann. N. Y. Acad. Sci.* **46**, 285 (1945).
(3) Gordon, A.R., *J. Chem. Phys.* **5**, 522 (1937).
(4) Krishnan, K.S., Laddha, G.S., *Indian Chem. Engr.* **7**, *Trans.* 83 (1965).
(5) Mickley, H.S., Sherwood, T.K., Reed, C.E., "Applied Mathematics in Chemical Engineering," 2nd ed., p. 66, McGraw-Hill, New York, 1957.
(6) Morasco, M., *Ind. Eng. Chem.* **18**, 701 (1926).
(7) Stokes, R.H., Dunlop, P.J., Hall, J.R., *Trans. Faraday Soc.* **49**, 886 (1953).
(8) Toor, H.L., *J. Phys. Chem.* **64**, 1580 (1960).
(9) Wilke, C.R., Chang, P., *A.I.Ch.E. J.* **1**, 264 (1955).

RECEIVED for review February 24, 1966. Accepted December 17, 1966.