Diffusivities and Densities for Binary Liquid Mixtures

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Measurement of liquid diffusivities over the complete range of composition for seven binary liquid systems at atmospheric pressure and at temperatures ranging from 25° to 60°C were carried out by use of a modified diaphragm cell technique. The systems studied were benzene–chloroform, cyclohexane–carbon tetrachloride, cyclohexane–toluene, benzene–*n*-heptane, all at 25°, 40°, and 55°C, respectively; benzene–cyclohexane at 25°, 40°, and 60°C; benzene–toluene at 20° and 40°C; and diethyl ether–chloroform at 25°C. Density measuments were made at these temperatures, covering the whole concentration range for all systems.

Liquid diffusivities have both practical and theoretical importance. Accurate experimental liquid-diffusion coefficients are of considerable use in checking various theories of the liquid state, as well as for studies on the mechanism of mass transfer. In addition, a knowledge of liquid-diffusion coefficients will increase the understanding of transport processes in liquids. Diffusion coefficients for ideal and nonideal binary liquid mixtures were measured in this laboratory to develop a theory to predict transport properties of the liquid state. Liquid diffusivities were measured in ideal and nonideal systems covering the entire concentration range.

Experimental

The major obstacle in the experimental study of transport properties of the liquid state is the lack of reliable experimental techniques for accurately measuring liquid diffusivities at temperatures other than room temperature. Since experimental techniques utilizing solutions of Fick's first law (2) offer an easier approach to measuring diffusion coefficients, considerable work has been done to improve this technique. The most successful method, which combines reasonable experimental simplicity with accuracy, is the diaphragm cell.

Diffusivity measurements were made with a modified three-compartment diaphragm cell. This new design eliminates the disadvantages inherent in the conventional two-compartment diaphragm cell. The new cell allows for the expansion of the test solution during temperature equilibration and also for volume changes on mixing during the diffusion process. A schematic diagram of the cell used by the authors is shown in Figure 1. The diaphragm was made from sintered glass and was about 40 mm in diameter. The whole cell was made of glass. The choice of the size of the pores in the diaphragm is critical. The effective diameter of the pores must be such that gross streaming through the diaphragm is avoided, but at the same time, the pores must be large in comparison with molecular dimensions so that the diffusion process will take place under conditions comparable to those in free diffusion. A diaphragm of porosity of 4 and pore diameter of 5–15 μm was used, which satisfies the above conditions (5).

Taps 1–4 were of high-vacuum quality and spring loaded. The bore diameter of each tap was 6 mm. A mercury U-tube attached to the cell at G allowed for expansion of the test solution during the heat-up period and for volume changes during the diffusion process. The volumes of the three compartments were: A, 29.10 cm^3; B, 60.52 cm^3; and C, 46.32 cm^3.

Use of the diaphragm cell as a quasi-steady state method for measuring liquid diffusivities assumes that the solutions in the upper and lower compartments are of uniform composition. In the absence of mechanical stirring, mixing owing to density variation could do the stirring automatically. But there remains the possibility of stagnant liquid layers existing immediately adjacent to the diaphragm as well as in the pores. The existence of such stagnant liquid layers was demonstrated by Hartley and Runnicles (5).

This new design was provided with two Teflon (PTEE) coated soft iron magnets, about 35 mm long and 5 mm in diameter, and a stirring mechanism. Because the concentration-measuring device was fixed on to the top of the cell, it was not practicable to use Stoke's horseshoe magnet stirring method (*14*). A stirring mechanism whereby two magnets were fixed on to a gear wheel which rotated on ball bearings was designed. The gear wheel was driven by a smaller gear wheel attached to a variable speed motor. The cell, together with the support plate for the larger gear wheel, was mounted on a Tufnol disk. The stirring mechanism is shown in detail in Figure 2.

Concentration of the solution in the top compartment of the diaphragm cell during a diffusion process was

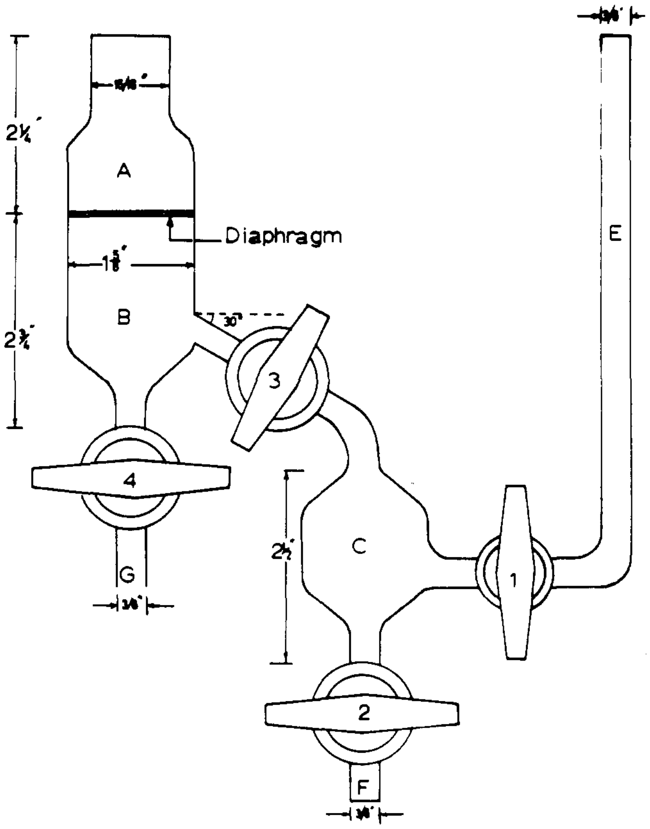

Figure 1. Diffusion cell

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measured continuously by automatically recording on paper tape, every quarter of an hour, either the conductivity or the capacitance of the solution. This was done by using a conductivity or a capacitance cell in conjunction with a continuous recording system (data logger). Solutions of known concentrations (of the binary system to be studied) were prepared and degassed by refluxing at total reflux for 4–6 hr. This was necessary especially when working above room temperature. The presence of dissolved air in the test solution affected the effective area and the diffusion path of the diaphragm.

Filling the cell with the test solutions requires a strict sequential procedure, the most important step in a diffusion run. The filling procedure is outlined below. One of the test solutions (of concentration C_1, for example) is drawn through the diaphragm via compartment A, to get rid of any trapped air bubbles, by applying suction at F. With taps 2–4 opened and tap 1 closed, compartment B is filled with clean mercury through tap 2. Enough mercury is used so that the bores of taps 3 and 4 are filled with mercury. Taps 3 and 4 are then closed.

A known volume of mercury is measured by a buret into compartment C so that when it expands at the operating temperature, the volume of the space left will be equal to the volume of compartment A with the capacitance cell inserted. This volume of mercury depends on the operating temperature. At 25°, 40°, and 55°C, the volumes of mercury used were 17.22, 17.15, and 17.10 cm^3, respectively. These complementary volumes of mercury were calculated from the coefficients of cubical expansion of mercury and the volumes of compartments A and C. Exact equality of the effective volumes simplifies the mathematics of computing the diffusion coeffi-

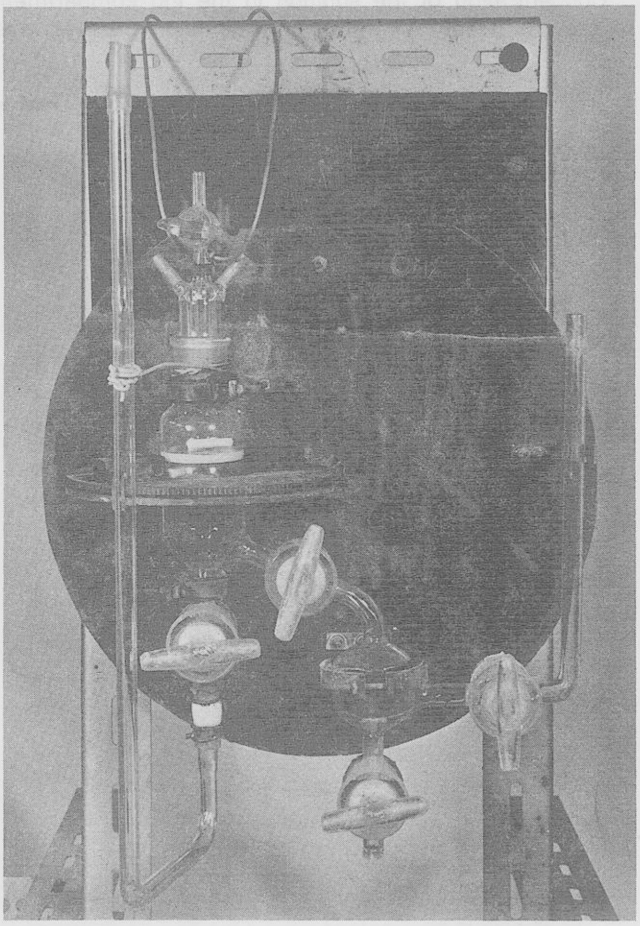

Figure 2. Cell assembly showing magnetic stirrers

Table I. Mutual Diffusion Coefficients and Densities for Benzene–Chloroform at 25°, 40°, and 55°C

	25°C		40°C	
Mole fraction chloroform	Density, g/cc	$D \times 10^5$, cm^2/sec	Density, g/cc	$D \times 10^5$ cm^2/sec
0.02	0.8734	2.258	0.8573	2.881
0.10	0.9272	2.286	0.9098	2.941
0.20	0.9815	2.335	0.9634	2.963
0.30	1.0373	2.380	1.0179	3.010
0.40	1.0957	2.425	1.0744	3.067
0.50	1.1538	2.460	1.1320	3.118
0.60	1.2131	2.530	1.1899	3.163
0.70	1.2738	2.590	1.2491	3.226
0.80	1.3369	2.660	1.3110	3.290
0.90	1.4021	2.740	1.3743	3.371
1.00	1.4795	2.885	1.4508	3.550
	55°C			
0.02	0.8411	3.560		
0.10	0.8921	3.590		
0.20	0.9447	3.643		
0.30	0.9981	3.689		
0.40	1.0551	3.765		
0.50	1.1106	3.832		
0.60	1.1661	3.854		
0.70	1.2251	3.931		
0.80	1.2851	3.991		
0.90	1.3464	4.071		
1.00	1.4213	4.253		

Table II. Mutual Diffusion Coefficients and Densities for Cyclohexane–CCl_4 at 25°, 40°, and 55°C

	25°C			
Mole fraction CCl_4	Density, g/cc	$D \times 10^5$, cm^2/sec, Ref. *4*	$D \times 10^5$, cm^2/sec, Ref. *6*	$D \times 10^5$, cm^2/sec, Authors
0.02	0.7743	1.486	1.484	1.486
0.10	0.8467	1.474	1.468	1.470
0.20	0.9209	1.460	1.443	1.452
0.30	1.0024	1.444	1.417	1.432
0.40	1.0748	1.426	1.393	1.411
0.50	1.1533	1.405	1.371	1.391
0.60	1.2367	1.382	1.350	1.369
0.70	1.3220	1.357	1.330	1.347
0.80	1.4066	1.329	1.311	1.323
0.90	1.4954	1.298	1.296	1.298

	40°C		55°C	
Mole fraction CCl_4	Density, g/cc	$D \times 10^5$, cm^2/sec	Density, g/cc	$D \times 10^5$, cm^2/sec
0.02	0.7601	1.915	0.7456	2.415
0.10	0.8305	1.890	0.8143	2.369
0.20	0.9034	1.855	0.8861	2.331
0.30	0.9734	1.827	0.9506	2.278
0.40	1.0540	1.791	1.0352	2.237
0.50	1.1318	1.760	1.1108	2.192
0.60	1.2134	1.740	1.1900	2.154
0.70	1.2970	1.703	1.2727	2.111
0.80	1.3785	1.665	1.3542	2.065
0.90	1.4669	1.641	1.4376	2.020
1.00	1.5550	1.611	1.5254	1.979

Table III. Mutual Diffusion Coefficients and Densities for Cyclohexane–Toluene at 25°, 40°, and 55°C

	25°C		40°C	
Mole fraction toluene	Density, g/cc	$D \times 10^5$, cm^2/sec	Density, g/cc	$D \times 10^5$, cm^2/sec
0.02	0.7743	1.569	0.7601	1.913
0.10	0.7811	1.530	0.7664	1.985
0.20	0.7883	1.600	0.7737	2.075
0.30	0.7953	1.675	0.7816	2.170
0.40	0.8045	1.767	0.7889	2.255
0.50	0.8135	1.861	0.7988	2.380
0.60	0.8236	1.965	0.8072	2.505
0.70	0.8323	2.066	0.8171	2.631
0.80	0.8421	2.182	0.8287	2.789
0.90	0.8521	2.305	0.8375	2.923
1.00	0.8610	2.420	0.8469	3.069
	55°C			
0.02	0.7455	2.409		
0.10	0.7521	2.510		
0.20	0.7595	2.608		
0.30	0.7673	2.720		
0.40	0.7751	2.849		
0.50	0.7845	2.988		
0.60	0.7928	3.119		
0.70	0.8031	3.280		
0.80	0.8143	3.460		
0.90	0.8231	3.633		
1.00	0.8327	3.800		

cients when there is no volume change on mixing and is desirable as an initial condition when volume change on mixing is to be allowed for.

Compartment C and manometer E are then filled with the second solution, concentration C_2, leaving approximately a 25-mm air space in the manometer for expansion. Tap 1 is opened, allowing the bore to be filled with the solution, and the manometer is corked. The U-tube attached to compartments B and G (Figure 2) is filled with mercury, the level being about 5 mm below that in compartment B, i.e., just below the diaphragm.

Compartment A is now filled with the first solution (concentration C_1), and the capacitance cell is placed in position.

The mercury used in all experimental runs was initially triply distilled and then cleaned after each run by passing it through a small orifice into a column of 25% nitric acid solution and washing six times with distilled water. The mercury was redistilled after about 27 runs or at the completion of a system, whichever occurred first.

After the filling operation, the cell is positioned in a conventional water-filled constant-temperature bath with a constant-level device. Temperature equilibrium is usually reached 1 hr after the cell is positioned in the bath. To start a run, tap 1 is closed and tap 3 opened. Because of the relatively high density of mercury, the solution in compartment C will be displaced into compartment B by the inflow of mercury from compartment B. If there is no gross streaming through the diaphragm, the capacitance of solution in compartment A, before and immediately after the displacement of the solution in compartment C, should be the same.

Table IV. Mutual Diffusion Coefficients and Densities for Benzene–*n*-Heptane at 25°, 40°, and 55°C

	25°C		40°C	
Mole fraction toluene	Density, g/cc	$D \times 10^5$, cm^2/sec	Density, g/cc	$D \times 10^5$, cm^2/sec
0.02	0.8734	1.785	0.8573	2.279
0.10	0.8418	1.660	0.8252	2.125
0.20	0.9135	1.665	0.7985	2.150
0.30	0.7891	1.742	0.7742	2.255
0.40	0.7674	1.884	0.7529	2.430
0.50	0.7485	2.085	0.7344	2.660
0.60	0.7316	2.334	0.7179	2.952
0.70	0.7166	2.630	0.7027	3.300
0.80	0.7027	2.980	0.6894	3.714
0.90	0.6905	3.399	0.6771	4.210
1.00	0.6793	3.915	0.6665	4.744

	55°C	
Mole fraction *n*-heptane	$D \times 10^5$, cm^2/sec	Density, g/cc
0.02	2.795	0.8411
0.10	2.660	0.8097
0.20	2.669	0.7825
0.30	2.845	0.7591
0.40	3.055	0.7391
0.50	3.304	0.7204
0.60	3.618	0.7036
0.70	4.083	0.6896
0.80	4.470	0.6761
0.90	4.990	0.6636
1.00	5.616	0.6536

Table V. Mutual Diffusion Coefficients and Densities for Benzene–Cyclohexane at 25°, 40°, and 60°C

	25°C		
Mole fraction cyclohexane	Density, g/cc	$D \times 10^5$, cm^2/sec, Ref. *11*	$D \times 10^5$, cm^2/sec, Authors
0.02	0.8734	2.104	2.090
0.10	0.8596	1.988	1.982
0.20	0.8465	1.903	1.905
0.30	0.8345	1.846	1.850
0.40	0.8230	1.813	1.815
0.50	0.8131	1.798	1.798
0.60	0.8035	1.796	1.797
0.70	0.7943	1.810	1.805
0.80	0.7861	1.834	1.825
0.90	0.7789	1.859	1.856
1.00	0.7743	1.880	1.896

	40°C		60°C	
Mole fraction cyclohexane	Density, g/cc	$D \times 10^5$, cm^2/sec, Authors	Density, g/cc	$D \times 10^5$, cm^2/sec, Authors
0.02	0.8573	2.650	0.8356	3.445
0.10	0.8439	2.550	0.8225	3.321
0.20	0.8304	2.471	0.8091	3.225
0.30	0.8187	2.410	0.7977	3.179
0.40	0.8073	2.375	0.7865	3.129
0.50	0.7981	2.360	0.7775	3.120
0.60	0.7878	2.355	0.7675	3.119
0.70	0.7797	2.365	0.7596	3.141
0.80	0.7718	2.385	0.7519	3.170
0.90	0.7653	2.415	0.7456	3.205
1.00	0.7601	2.450	0.7406	3.285

The main diffusion process is allowed to proceed for 2-4 days with tap G open to allow for volume changes on mixing.

Since the effective area and the length of the diffusion path in a diaphragm cell cannot be determined by direct measurement, it is necessary to calibrate the cell by use of a system of known diffusivity. A 0.1*N* KCl water system was used for the calibration. The integral diffusion coefficient for this system was measured by Stokes (*14*). The experimental procedure for the calibration run was the same as outlined above, except that the conductivity cell was used instead of the capacitance cell. More detailed descriptions of experimental equipment and procedures are given elsewhere (*12*).

The following equations were used in calculating the cell constant β from experimental data:

$$-\beta D_i t = \ln\left(\Delta C_f / \Delta C_o\right) \qquad (1)$$

where

$$\beta = (a/l)\left(\frac{1}{V'} + \frac{1}{V''}\right) \qquad (2)$$

$$\Delta C_f = C_f' - C_f'' \qquad (3)$$

and

$$\Delta C_o = C_o' - C_o'' \qquad (4)$$

The derivation of Equation 1 was based on the assumptions that quasi-steady state is achieved in the diaphragm; there are negligible volume changes on mixing; the cell constant β is constant; and there is homogeneity of the test solution and no streaming in the diaphragm. The cell constant β was calculated from Equation 1 by use of known values of D_i for the KCl-water system and measured values of t, ΔC_f, and ΔC_o. The cell constant for the diaphragm was 0.501.

Analysis of Experimental Data

The diffusion coefficients which have theoretical and practical significance are the differential values. What results from the diaphragm cell measurements, however, are the time-averaged (integral) diffusion coefficients. The experimental capacitance time data were converted to concentration time data by use of a calibration curve of capacitance vs. concentration. The integral diffusion coefficients were then calculated by use of Equation 1.

Table VI. Mutual Diffusion Coefficients and Densities for Benzene–Toluene at 25° and 40°C

	20°C		40°C	
Mole fraction toluene	Density, g/cc	$D \times 10^5$, cm²/sec	Density, g/cc	$D \times 10^5$, cm²/sec
0.02	0.8734	1.847	0.8573	2.385
0.10	0.8718	1.897	0.8554	2.415
0.20	0.8687	1.950	0.8542	2.483
0.30	0.8688	1.992	0.8532	2.555
0.40	0.8670	2.090	0.8517	2.635
0.50	0.8661	2.135	0.8509	2.700
0.60	0.8649	2.224	0.8599	2.802
0.70	0.8638	2.298	0.8489	2.894
0.80	0.8628	2.380	0.8481	3.008
0.90	0.8627	2.460	0.8473	3.121
1.00	0.8610	2.545	0.8469	3.240

Table VII. Mutual Diffusion Coefficients and Densities for Diethyl Ether–Chloroform at 25°C

Mole fraction diethyl ether	Density, g/cc	$D \times 10^5$, cm²/sec, Ref. *1*	$D \times 10^5$, cm²/sec, Authors
0.02	1.4796	2.140	2.131
0.10	1.3835	2.542	2.550
0.20	1.2983	2.909	2.930
0.30	1.2130	3.311	3.331
0.40	1.1314	3.661	3.685
0.50	1.0530	3.982	4.001
0.60	0.9785	4.210	4.212
0.70	0.9079	4.361	4.353
0.80	0.8376	4.443	4.380
0.90	0.7713	4.491	4.420
1.00	0.7077	4.510	4.475

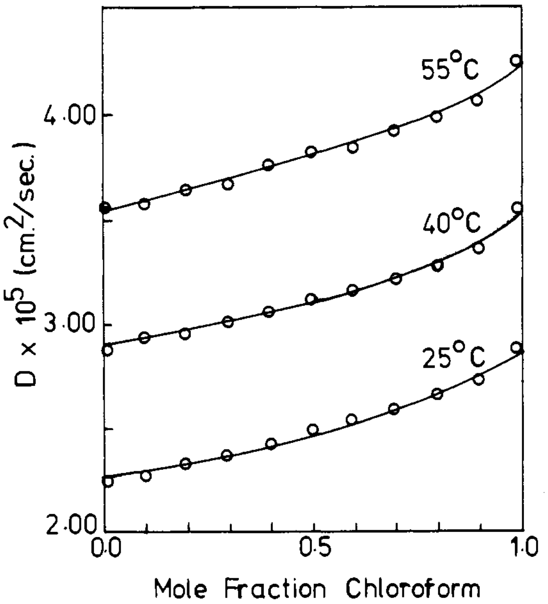

Figure 3. Diffusion of coefficient for benzene-chloroform

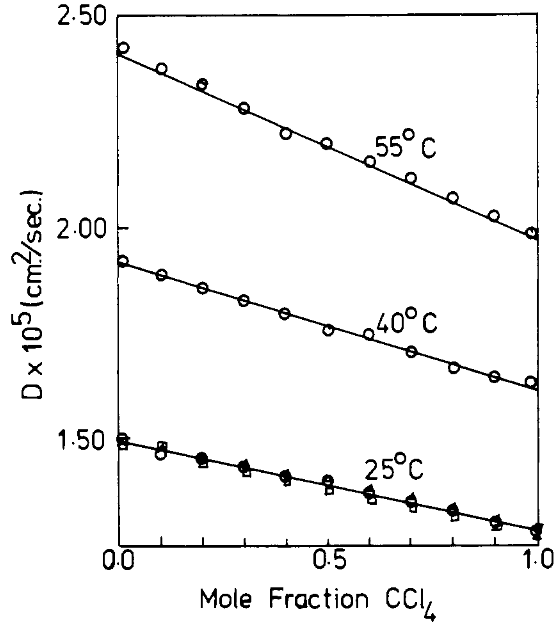

Figure 4. Diffusion coefficient for cyclohexane-CCl_4

□ Ref. *6*
△ Ref. *4*
○ Authors

For systems where there were no volume changes on mixing, differential diffusion coefficients were calculated with Gordon's (*3*) equation. The calculation of differential diffusion coefficients from the diaphragm integral data was discussed extensively by Gordon (*3*).

Methods of computing differential diffusion coefficients from the diaphragm cell integral data for systems with significant volume changes on mixing were discussed by Olander (*8*), Prager (*9*), and Robinson et al. (*10*). The assumptions made in solving Olander's equation are only applicable to runs with small initial concentration differences or in systems where volume changes are small. These assumptions are not valid for this investigation in which maximum initial concentration differences and long diffusion times were used. For systems with significant volume changes on mixing, differential diffusion coefficients were calculated with the equation of Robinson et al. (*10*). Analysis of the experimental data for systems with significant volume changes on mixing requires the

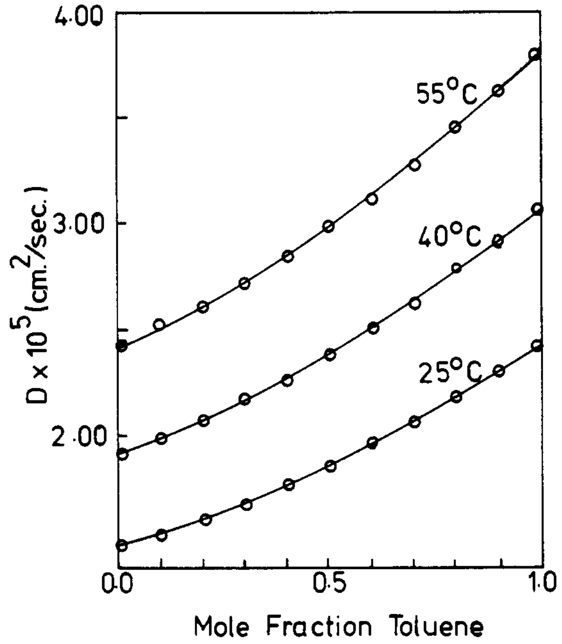

Figure 5. Diffusion coefficient for cyclohexane-toluene

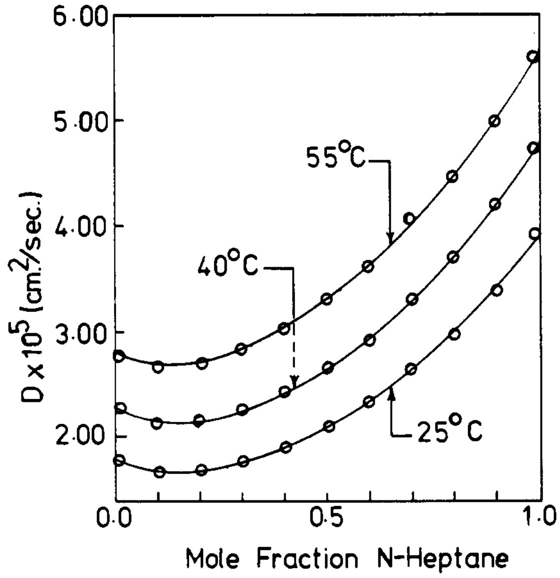

Figure 6. Diffusion coefficient for benzene-*n*-heptane

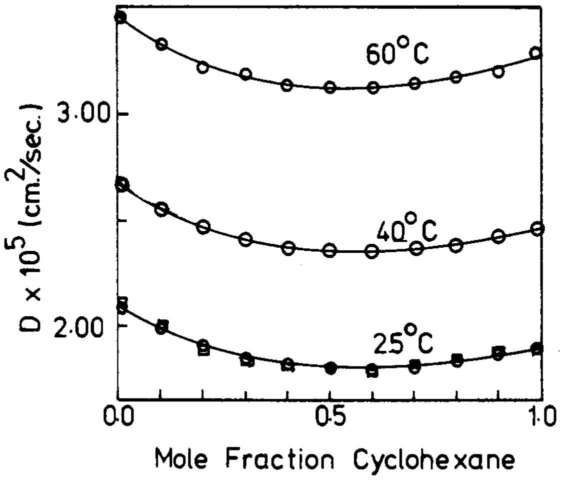

Figure 7. Diffusion coefficient for benzene-cyclohexane

□ Ref. *11*
○ Authors

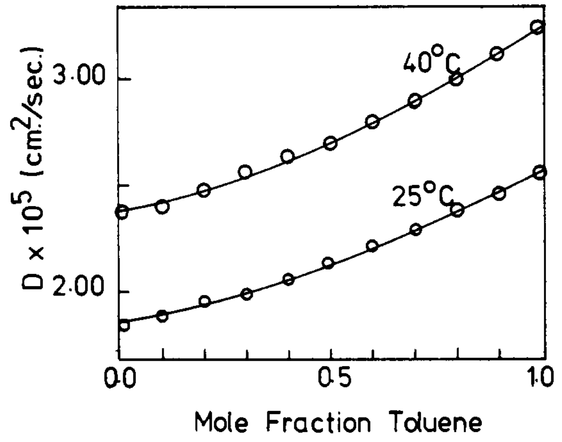

Figure 8. Diffusion coefficient for benzene-toluene

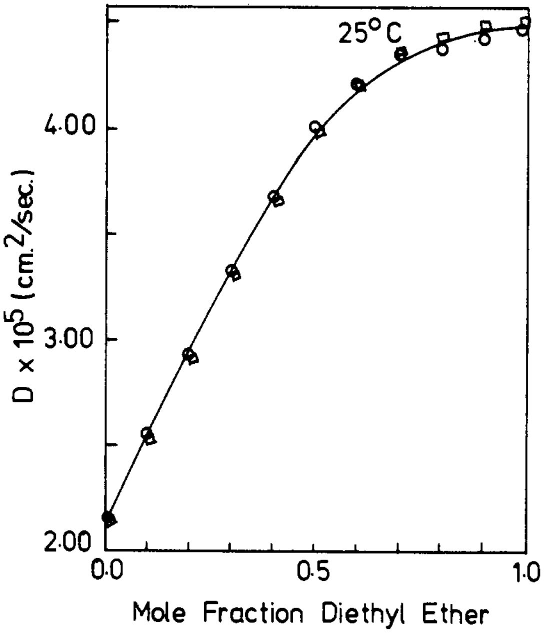

Figure 9. Diffusion coefficient for diethyl ether-chloroform

□ Ref. *7*
○ Authors

knowledge of partial molar volumes as a function of concentration. These were calculated from density data (*7*). Density measurements were made for all systems at temperatures ranging from 25° to 60°C and covering the whole concentration range (*13*).

Results and Discussion

Tables I–VII show the experimental differential diffusion coefficients and densities for the systems benzene–chloroform (at 25°, 40°, and 55°C); cyclohexane–carbon tetrachloride (at 25°, 40°, and 55°C); benzene-*n*-heptane (at 25°, 40°, and 55°C); benzene–cyclohexane (at 25°, 40°, and 60°C); benzene–toluene (at 25° and 40°C); and diethyl ether–chloroform (at 25°C). These results are shown graphically in Figures 3–9 as differential diffusivities vs. mole fraction.

The accuracy of the experimental results obtained with the modified diaphragm cell is of the order of 1 to 2% and depends largely on the error involved in reproducing the calibration curves for the capacitance or conductivity measuring cell. The diffusion coefficients for cyclohexane–carbon tetrachloride, benzene–cyclohexane, and diethyl ether–chloroform at 25°C agree with those of other workers (*4, 6, 11*). The agreement is well within the experimental accuracy of 1 to 2%.

Nomenclature

ΔC_o, ΔC_f = initial and final concentration differences between the two compartments of the diffusion cell, g/cc
C_f', C_f'' = final concentrations in the top and lower compartments of the cell
C_o', C_o'' = initial concentrations in the top and lower compartments of the cell
Di = integral diffusion coefficient, cm^2/sec
a = effective area of the diffusion path
l = length of the diffusion path
t = total diffusion time, sec
V', V'' = volumes of the top and lower compartments of the cell, cm^3

Greek Letter

β = diaphragm cell constant, cm^2

Literature Cited

(1) Anderson, D. K., Babb, A. L., *J. Phys. Chem.*, **65**, 1281 (1961).
(2) Fick, A., *Ann. Phys. Leipzig*, **94**, 59 (1855).
(3) Gordon, A. R., *Ann. N.Y. Acad. Sci.*, **46**, 285 (1945).
(4) Hammond, R. H., Stokes, H., *Trans. Faraday Soc.*, **52**, 781 (1956).
(5) Hartley, G. S., Runnicles, D. F., *Proc. Roy. Soc.*, **A168**, 401 (1938).
(6) Kulkarni, M. F., Allen, G. F., Lyons, P. A., *J. Phys. Chem.*, **69**, 2491 (1965).
(7) Moore, W. J., "Physical Chemistry," 2nd ed., Longmans Green and Co., London, England, 1956.
(8) Olander, D. R., *J. Phys. Chem.*, **67**, 1011 (1963).
(9) Prager, S., *J. Chem. Phys.*, **21**, 1344 (1953).
(10) Robinson, R. L., Edminster, W. C., Dullien, F. A. L., *J. Phys. Chem.*, **69**, 258 (1965).
(11) Rodwin, L., Harpst, J. A., Lyons, P. A., *ibid.*, p 2783.
(12) Sanni, S. A., Hutchison, H. P., *J. Sci. Inst.*, **1**, 1101 (1968).
(13) Sanni, S. A., PhD thesis, University of Cambridge, Cambridge, England, 1967.
(14) Stokes, R. H., *J. Amer. Chem. Soc.*, **73**, 3527 (1951).

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Vapor-Liquid Equilibria of Binary Systems Containing Selected Hydrocarbons with Perfluorobenzene

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Isobaric vapor-liquid equilibria were determined for the binary systems benzene–perfluorobenzene, perfluorobenzene–toluene, perfluorobenzene–methylcyclohexane, and *n*-hexane–perfluorobenzene. All measurements were made in a modified Hipkin-Meyers apparatus at 760 mm Hg pressure. Two azeotropes were observed in the benzene–perfluorobenzene system. These occurred at temperatures of 79.3° and 80.3°C and concentrations of 20.8 and 81.3 mol % perfluorobenzene. The system perfluorobenzene–toluene followed Raoult's Law, although the system exhibits a significant heat of mixing. A minimum boiling azeotrope was observed in the perfluorobenzene–methylcyclohexane system at a temperature of 79.9°C and concentration of 94.9 mol % perfluorobenzene. A minimum boiling azeotrope was observed in the *n*-hexane–perfluorobenzene system at a temperature of 67.9°C and composition of 75.6 mol % *n*-hexane.

The physical and thermodynamic properties of perfluorobenzene were reported by Patrick and Prosser (*12*) and Counsell et al. (*3*). Duncan and Swinton (*6*) reported solid-liquid phase diagrams for perfluorobenzene with benzene, toluene, and several other hydrocarbons. The excess volumes of mixing for perfluorobenzene with benzene, toluene, and several other hydrocarbons were reported by Duncan et al. (*5*). They also reported the dipole moments of perfluorobenzene in benzene and other hydrocarbons. The enthalpies of perfluorobenzene with hydrocarbons were reported by several investigators (*2, 7, 8*). Gaw and Swinton (*9*) reported vapor-liquid equilibrium data for the system benzene–perfluorobenzene at 70°C and also at 500 mm Hg total pressure.

Apparatus

The equilibrium still was based upon the design of Hipkin and Myers (*11*) as modified by Yen and Reed (*14*). The sampling valves were replaced by septums, and samples were withdrawn with a syringe and injected directly into the chromatograph or refractometer. This eliminated errors owing to liquid holdup in the sampling lines and valves. A schematic is shown in Figure 1.

The temperature was measured with copper–constantan thermocouples and potentiometer. The thermocouples were calibrated at the ice point, steam point, and boiling point of *n*-hexane. The calibration results were fit to a second-order polynominal for interpolation. The temperature was obtained with an accuracy of ±0.1°C. The pressure was maintained constant at 760.0 ± 0.1 mm Hg by a Cartesian manostat with compressed dry nitrogen

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