Diffusion Coefficients and Densities for Binary Organic Liquid Mixtures

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Experimental diffusion coefficients and densities are reported for the following binary systems at the temperatures indicated: benzene–cyclohexane, 25°, 40°, and 60°C; benzene–toluene, 25° and 40°C; benzene–*n*-heptane, cyclohexane–carbon tetrachloride and cyclohexane–toluene, all at 25°, 40°, and 55°C; and diethyl ether–chloroform at 25°C. The diffusion coefficients were determined by a modification of the conventional diaphragm cell technique.

Experimental liquid phase diffusion coefficients are of importance both for the testing of models for the liquid state and for predicting the mass transfer rates in those chemical engineering situations where the liquid phase diffusion is the rate limiting factor. Despite this, relatively few experimental measurements have been made, especially at elevated temperatures. Currently available experimental data are summarized in review articles such as that of Vignes (*13*).

The present article presents diffusional data over the whole of the concentration range and at elevated temperatures for six binary organic systems. The work is part of a continuing program to collect data on ideal and nonideal binary systems for evaluation of theoretical methods for predicting the concentration and temperature dependence of binary diffusion coefficients.

The diffusion coefficients reported are mutual diffusion coefficients ($D_{AB} = D_{BA}$) defined by the flux equation:

$$N_A = -cD_{AB}\nabla x_A + x_A \cdot (N_A + N_B) \qquad (1)$$

This definition, in terms of a concentration driving force, is the one most frequently used by experimentalists. Diffusion coefficients so defined can be related to the transport coefficients of statistical thermodynamics (defined in terms of a chemical potential driving force) using activity-concentration data (*2*).

EXPERIMENTAL

The diffusion coefficients were measured using a modified diaphragm cell fully described elsewhere (*3*, *11*, *12*). The design of the cell allowed for expansion of the test solutions during temperature equilibration and also for volume change on mixing during the diffusional process. The change in concentration in one compartment of the cell was continuously monitored during the diffusion run by an in situ capacitance probe which was calibrated to measure the true compartment concentration. By this means the need for handling of the test solutions during the diffusion process was eliminated.

The solvents used were all of Analar purity and were used without further purification. Densities of the pure materials are recorded in the density-concentration tables (Tables I to VI).

ANALYSIS OF EXPERIMENTAL DATA

The capacitance-time plot for each run was first converted into a concentration-time plot. Selected values from this curve were then processed to yield integral diffusion coefficients using the standard diaphragm cell integral equation (*9*). Differential diffusion coefficients were calculated from the integral values using either the method of Gordon (*4*) or that of Robinson et al. (*8*), depending on whether a significant volume change on mixing occurred.

Analysis of the experimental results for nonideal systems (with significant volume changes on mixing) required knowledge of the partial molar volumes. These were calculated

Table I Mutual Diffusion Coefficients and Densities for System Benzene–Cyclohexane

Mole fraction cyclohexane	Temp, 25° C		Temp, 40° C		Temp, 60° C	
	Density, g/cm³	$D \times 10^5$, cm²/sec	Density, g/cm³	$D \times 10^5$, cm²/sec	Density, g/cm³	$D \times 10^5$, cm²/sec
0.0	0.8734	2.090	0.8573	2.650	0.8356	3.445
0.1	0.8596	1.982	0.8439	2.550	0.8225	3.321
0.2	0.8465	1.905	0.8304	2.471	0.8091	3.225
0.3	0.8345	1.850	0.8187	2.410	0.7977	3.179
0.4	0.8230	1.815	0.8073	2.375	0.7865	3.120
0.5	0.8131	1.798	0.7981	2.360	0.7775	3.119
0.6	0.8035	1.797	0.7878	2.355	0.7675	3.119
0.7	0.7943	1.805	0.7797	2.365	0.7596	3.141
0.8	0.7861	1.825	0.7718	2.385	0.7519	3.170
0.9	0.7789	1.856	0.7653	2.415	0.7456	3.205
1.0	0.7743	1.896	0.7601	2.450	0.7406	3.285

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Table II. Mutual Diffusion Coefficients and Densities for System Benzene–Toluene

Mole fraction toluene	Temp, 25° C		Temp, 40° C	
	Density, g/cm³	$D \times 10^5$, cm²/sec	Density, g/cm³	$D \times 10^5$, cm²/sec
0.0	0.8734	1.847	0.8573	2.385
0.1	0.8718	1.897	0.8554	2.415
0.2	0.8687	1.950	0.8542	2.483
0.3	0.8688	1.992	0.8532	2.555
0.4	0.8670	2.090	0.8517	2.635
0.5	0.8661	2.135	0.8509	2.700
0.6	0.8649	2.224	0.8599	2.802
0.7	0.8638	2.298	0.8489	2.894
0.8	0.8628	2.380	0.8481	3.008
0.9	0.8627	2.460	0.8473	3.121
1.0	0.8610	2.545	0.8469	3.240

from density data (7). Density measurements were made for all of the systems at temperatures ranging from 25–60°C using a pycnometer.

RESULTS

Measurements of diffusion coefficients and densities were made over the whole of the concentration range for the following binary systems at the temperatures indicated:

	°C
Benzene–cyclohexane	25, 40, 60
Benzene–toluene	25, 40
Benzene-n-heptane	25, 40, 55
Cyclohexane–carbon tetrachloride	25, 40, 55
Cyclohexane–toluene	25, 40, 55
Diethyl ether–chloroform	25

Table III. Mutual Diffusion Coefficients and Densities for System Benzene–n-Heptane

Mole fraction n-Heptane	Temp, 25° C		Temp, 40° C		Temp, 55° C	
	Density, g/cm³	$D \times 10^5$, cm²/sec	Density, g/cm³	$D \times 10^5$, cm²/sec	Density, g/cm³	$D \times 10^5$, cm²/sec
0.0	0.8734	1.785	0.8573	2.279	0.8411	2.795
0.1	0.8418	1.785	0.8252	2.125	0.8079	2.660
0.2	0.8135	1.665	0.7985	2.150	0.7825	2.669
0.3	0.7891	1.742	0.7742	2.255	0.7591	2.845
0.4	0.7674	1.884	0.7529	2.430	0.7391	3.055
0.5	0.7485	2.085	0.7344	2.660	0.7204	3.304
0.6	0.7316	2.334	0.7179	2.952	0.7036	3.618
0.7	0.7166	2.630	0.7027	3.300	0.6896	4.083
0.8	0.7027	2.980	0.6894	3.714	0.6761	4.470
0.9	0.6905	3.399	0.6771	4.210	0.6636	4.990
1.0	0.6793	3.915	0.6665	4.744	0.6536	5.616

Table IV. Mutual Diffusion Coefficients and Densities for System Cyclohexane–Carbon Tetrachloride

Mole fraction CCl_4	Temp, 25° C		Temp, 40° C		Temp, 55° C	
	Density, g/cm³	$D \times 10^5$, cm²/sec	Density, g/cm³	$D \times 10^5$, cm²/sec	Density, g/cm³	$D \times 10^5$, cm²/sec
0.0	0.7743	1.486	0.7601	1.915	0.7456	2.415
0.1	0.8467	1.470	0.8305	1.890	0.8143	2.369
0.2	0.9209	1.452	0.9034	1.855	0.8861	2.331
0.3	1.0024	1.432	0.9734	1.827	0.9506	2.278
0.4	1.0748	1.411	1.0540	1.791	1.0352	2.237
0.5	1.1533	1.391	1.1318	1.760	1.1108	2.192
0.6	1.2367	1.382	1.2134	1.740	1.1900	2.154
0.7	1.3220	1.347	1.2970	1.703	1.2727	2.111
0.8	1.4066	1.323	1.3785	1.665	1.3542	2.065
0.9	1.4954	1.298	1.4669	1.641	1.4376	2.020
1.0	1.5843	1.275	1.5550	1.611	1.5254	1.979

Table V. Mutual Diffusion Coefficients and Densities for System Cyclohexane–Toluene

Mole fraction toluene	Temp, 25° C		Temp, 40° C		Temp, 55° C	
	Density, g/cm³	$D \times 10^5$, cm²/sec	Density, g/cm³	$D \times 10^5$, cm²/sec	Density, g/cm³	$D \times 10^5$, cm²/sec
0.0	0.7743	1.569	0.7601	1.913	0.7455	2.409
0.1	0.7811	1.530	0.7664	1.985	0.7521	2.510
0.2	0.7883	1.600	0.7737	2.075	0.7595	2.608
0.3	0.7953	1.675	0.7816	2.170	0.7673	2.720
0.4	0.8045	1.767	0.7889	2.255	0.7751	2.849
0.5	0.8135	1.861	0.7988	2.380	0.7845	2.988
0.6	0.8236	1.965	0.8072	2.505	0.7928	3.119
0.7	0.8323	2.066	0.8171	2.631	0.8031	3.280
0.8	0.8421	2.182	0.8287	2.789	0.8143	3.460
0.9	0.8521	2.305	0.8375	2.923	0.8231	3.633
1.0	0.8610	2.420	0.8469	3.069	0.8327	3.800

Table VI. Mutual Diffusion Coefficients and Densities for System Diethyl Ether–Chloroform

Mole fraction diethyl ether	Temp, 25° C	
	Density, g/cm³	$D \times 10^5$, cm²/sec
0.0	1.4796	2.131
0.1	1.3835	2.550
0.2	1.2983	2.930
0.3	1.2130	3.331
0.4	1.1314	3.685
0.5	1.0530	4.001
0.6	0.9785	4.212
0.7	0.9079	4.353
0.8	0.8376	4.380
0.9	0.7718	4.420
1.0	0.7077	4.475

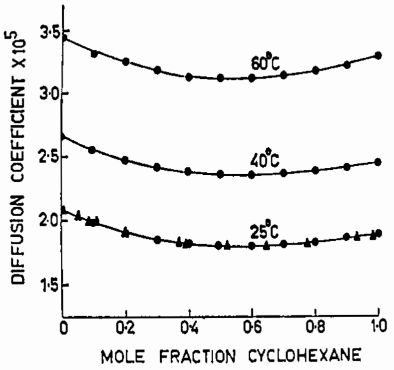

Figure 1. Diffusion coefficients for benzene–cyclohexane system, cm²/sec

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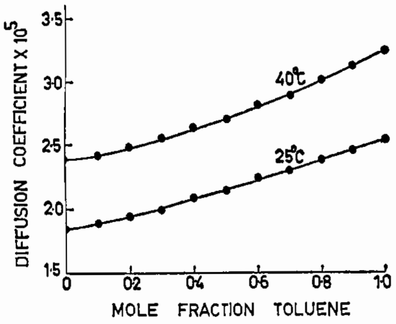

Figure 2. Diffusion coefficients for benzene–toluene system, cm²/sec

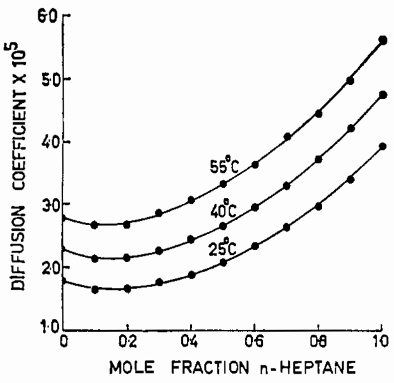

Figure 3. Diffusion coefficients for benzene–*n*-heptane system, cm²/sec

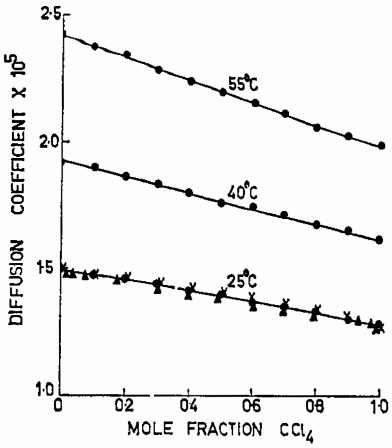

Figure 4. Diffusion coefficients for cyclohexane–carbon tetrachloride system, cm²/sec

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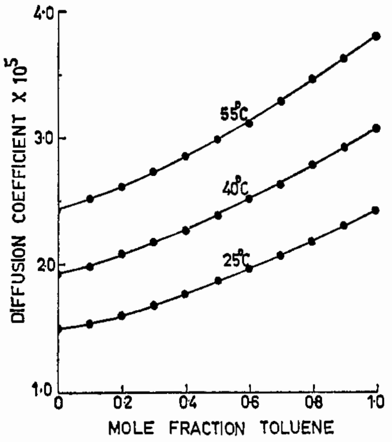

Figure 5. Diffusion coefficients for cyclohexane–toluene system, cm²/sec

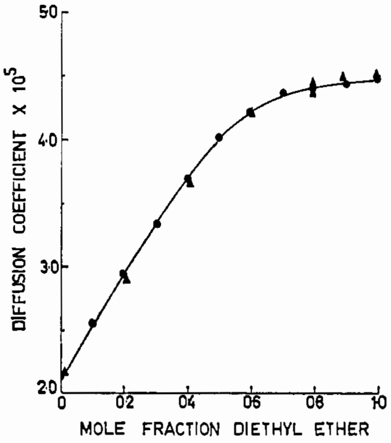

Figure 6. Diffusion coefficients for diethyl ether–chloroform system, cm²/sec

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The experimental results are given in Tables I–VI and the diffusion coefficients are plotted on Figures 1–6. Because, by use of the continuous recording technique, it was possible to calculate a large number of diffusion coefficients from each run, only smoothed data at equal concentration increments are reported here. The average deviation of individual data points from the smoothed curve amounted to no more than 1–2% for all experimental systems.

The experimental diffusion coefficients for benzene–cyclohexane and cyclohexane–carbon tetrachloride systems at 25°C agree well with those previously determined (*5*, *6*, *10*). So also do those for the diethyl ether–chloroform system (*1*).

CONCLUSION

A modified diaphragm cell technique has been used successfully to measure diffusion coefficients in six binary organic liquid mixtures covering the whole concentration range and over a wide range of temperatures. No attempt has been made to interpret the results theoretically. This will be done in a later publication.

NOMENCLATURE

c = molar density of solution, g-mol/cm^3

D_{AB}, D_{BA} = mutual diffusion coefficient as defined by Equation 1

N_A, N_B = molar flux of component A, B with respect to stationary coordinates, g-mol cm^{-2} sec^{-1}

x_A = mole fraction of component A

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Diffusion Coefficients for Sodium and Potassium Chlorides in Water at Elevated Temperatures

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Experimental measurements of diffusion coefficients in the systems KCl–water and NaCl–water have been carried out over a moderate concentration range and at temperatures to 80°C. Good agreement with the Onsager-Fuoss equation is obtained.

Experimental measurements of diffusion coefficients in the systems KCl–water and NaCl–water at low to moderate solute concentrations have not previously been reported at temperatures above 30°C. Harned and Nuttall's values (*4*) obtained at 25°C have been shown by Harned and Owen (*5*) to agree closely with the extended Onsager-Fuoss theory. The current work has been carried out to test the Onsager-Fuoss theory at higher temperatures.

The method used was a modification of the normal diaphragm cell technique in which the conductivity in the upper compartment was continuously monitored. The experimental cell used is shown in Figure 1 (*2*). It is the prototype of that already described elsewhere (*9*) and was operated in an identical fashion.

All runs had for initial conditions pure water in the top compartment of the cell and through the diaphragm, and 0.1*N* solution in the bottom compartment. During a run, the concentration in the top compartment changed from 0–0.04*N*, but the continuous measurement system permitted evaluation of the diffusion coefficients at selected concentrations between 0 and 0.04*N*. Mysels and McBain (*6*) have indicated a source of error due to the adsorption of salt onto the glass of the diaphragm. However, with the continuous measurement technique, it is not necessary to rely on the period when the upper part of the diaphragm is at concentrations substantially lower than that for which the diffusion coefficient is calculated.

EXPERIMENTAL

The water used in all experimental work was purified by ion exchange and had a specific conductivity of approximately 1.5×10^{-6} Mho cm^{-1}. The potassium and sodium chlorides were of Analar quality and were carefully dried before use. The concentration in the upper compartment was measured by determining the conductance of the electrode system as described below. As a check, the solutions in both top and bottom compartments were titrated with silver nitrate solution using a potentiometric technique.

Before charging the cell, the respective solutions were warmed and degassed under vacuum until cool to remove dissolved air. This was particularly important before the high temperature runs.

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