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

LITERATURE CITED

(1) Anderson, D. K., Babb, A. L., *J. Phys. Chem.*, **65**, 1281 (1961).
(2) Bird, R. B., Stewart, W. E., Lightfoot, E. N., "Transport Phenomena," Wiley, New York, N. Y., 1960.
(3) Fell, C. J. D., PhD thesis, University of Cambridge, Cambridge, England, 1965.
(4) Gordon, A. R., *Ann. N. Y. Acad. Sci.*, **46**, 285 (1945).
(5) Hammond, B. R., Stokes, R. H., *Trans. Faraday Soc.*, **52**, 781 (1956).
(6) Kulkarni, M. V., 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, 1956.
(8) Robinson, R. L., Edmister, W. C., Dullien, F. A. L., *J. Phys. Chem.*, **69**, 258 (1965).
(9) Robinson, R., Stokes, R. H., "Electrolyte Solutions," Butterworths, London, 1955.
(10) Rodwin, L., Harpst, J. A., Lyons, P. A., *ibid.*, **69**, 2783 (1965).
(11) Sanni, S. A., Hutchison, H. P., *J. Sci. Instrum.*, *Ser.* **2**, **1**, 1101 (1968).
(12) Sanni, S. A., PhD thesis, University of Cambridge, Cambridge, England, 1967.
(13) Vignes, A., *Ind. Eng. Chem. Fundam.*, **5**, 189 (1966).

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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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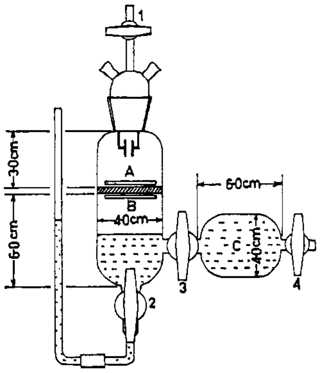

Figure 1. Experimental diaphragm cell

Conductivity Measurements. The immediate result of a run is a table of conductance measurements vs. time. Before diffusion coefficients can be calculated, this must be converted to a table of concentration measurements vs. time.

Experimental measurements of conductivity have not been reported with any accuracy at temperatures above 45°C (*8*). Owen (*7*) has given empirical equations of the form:

$$\lambda^\circ = \lambda_{25}^\circ + a(t - 25) + b(t - 25)^2 + c(t - 25)^3 \qquad (1)$$

where the values of a, b, c, and λ_{25}° are given as follows:

Ion	λ_{25}°	a	$b \times 10^2$	$c \times 10^4$
K^+	73.50	1.43262	0.40563	−0.3183
Cl^-	76.35	1.54037	0.46500	−0.1285
Na^+	50.15	1.09160	0.47150	−0.1150

For finite concentrations, the equivalent conductivity may be calculated from this empirical equation and from Stokes equation (*8*):

$$\Lambda = \Lambda_0 - \frac{(B_1\Lambda_0 + B_2)\sqrt{C_A}}{1 + B\mathring{a}\sqrt{C_A}} \qquad (2)$$

To ascertain the applicability of Owen's data (*7*) to the present study, measurements of the conductivity cell head constant were made using 0.1*N* KCl solution at temperatures to 80°C. The cell head constant was in fact constant to within 1%. Although not particularly accurate from the viewpoint of conductiometric studies, this result justifies our use of Owen's equations (*7*) at least to this precision in the current study.

Diffusion Cell Constant. The cell constant of the diffusion cell was determined by carrying out a number of runs at 25°C using water and 0.1*N* KCl solution in the respective cell compartments. The concentration-time curves were analyzed by the well-established method of Gordon (*3*) using the integral diffusion coefficient data of Stokes (*10*). The cell constants so found were consistent to 0.5%.

RESULTS

Diffusion coefficients for both systems were calculated from the concentration-time curves by making use of the unintegrated form of the diaphragm cell equation for the top surface of the diaphragm ($x = 0$):

$$V\frac{dC_A}{dT} = D_{AB}A\left(\frac{\partial C_A}{\partial x}\right)_{x=0} \qquad (3)$$

By numerical differentiation the term dC_A/dT may be evaluated directly. As a first approximation $(\partial C_A/\partial x)_{x=0}$ can be taken as equal to $\Delta C_A/l$. These, when combined with the cell constant give a first approximation to the differential diffusion coefficient at the top compartment concentration. The new diffusion coefficients can then be used to re-evaluate $(\partial C_A/\partial x)_{x=0}$ by making use of the constancy of flux within the diaphragm at any instant. The method requires three to four iterations to converge to the final values. Full details are separately available (*2*).

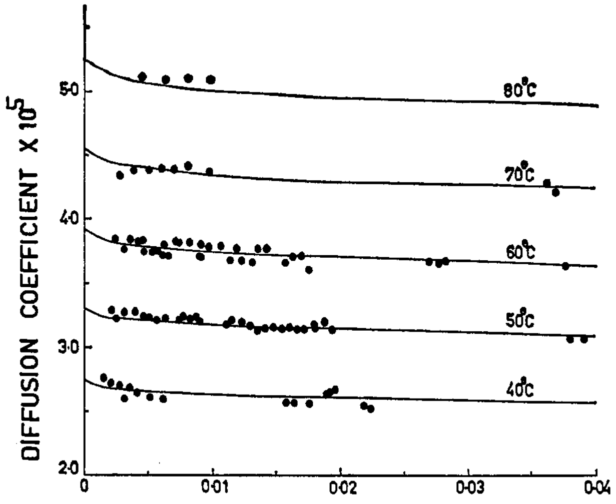

Figure 2. Experimental diffusion coefficients (cm²/sec) for KCl–water system

—— Calculated from Onsager-Fuoss equation

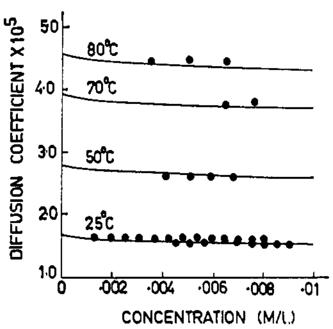

Figure 3. Experimental diffusion coefficients (cm²/sec) for NaCl–water system

—— Calculated from Onsager-Fuoss equation

The diffusion coefficients calculated using the above procedure are differential diffusion coefficients as defined by the flux equation:

$$N_A = -CD_{AB}\nabla x_A + x_A\cdot(N_A + N_B) \qquad (4)$$

or, in terms of the concentration C_A:

$$N_A = -D_{AB}\nabla C_A + C_A(N_AV_A + N_BV_B) \qquad (5)$$

The use of a definition incorporating a concentration driving force is common in experimental studies. Bird et al. (*1*) show how such diffusion coefficients relate to the transport coefficients of statistical thermodynamics.

The experimental diffusion coefficients are shown on Figures 2 and 3 and are given in Tables I and II. The values reported have been obtained using two separate diffusion cells. The solid lines on the figures give predicted values from the Onsager-Fuoss relationship discussed below. Although there is some scatter, the experimental diffusion coefficients agree quite closely with those predicted for NaCl at 25°C which involves a change of system.

The Onsager-Fuoss Equation. Both Stokes (*8*) and

Table I. Diffusion Coefficients for KCl–Water System

Concn $\times 10^2$, mol/l.	Diffusion coeff $\times 10^5$, cm²/sec	Concn $\times 10^2$, mol/l.	Diffusion coeff $\times 10^5$, cm²/sec	Concn $\times 10^2$, mol/l.	Diffusion coeff $\times 10^5$, cm²/sec
Temp, 40°C		Temp, 50°C		Temp, 60°C	
0.166	2.761	0.225	3.284	0.260	3.821
0.220	2.716	0.272	3.217	0.308	3.731
0.290	2.689	0.308	3.258	0.362	3.846
0.333	2.583	0.391	3.250	0.440	3.808
0.358	2.681	0.393	3.265	0.462	3.826
0.427	2.634	0.474	3.230	0.497	3.711
0.521	2.600	0.505	3.216	0.553	3.805
0.619	2.578	0.551	3.221	0.571	3.802
1.598	2.562	0.642	3.230	0.603	3.691
1.640	2.554	0.754	3.233	0.644	3.800
1.756	2.550	0.762	3.202	0.675	3.684
1.860	2.605	0.836	3.201	0.726	3.819
1.906	2.625	0.883	3.210	0.743	3.819
1.950	2.644	0.909	3.191	0.827	3.824
2.199	2.534	1.102	3.156	0.907	3.806
2.237	2.509	1.170	3.206	0.932	3.664
		1.237	3.197	0.996	3.798
Temp, 70 °C		1.302	3.152	1.077	3.797
0.296	4.311	1.366	3.102	1.154	3.644
0.413	4.356	1.428	3.123	1.194	3.765
0.517	4.372	1.490	3.131	1.228	3.648
0.627	4.384	1.550	3.129	1.304	3.649
0.727	4.386	1.610	3.146	1.369	3.757
0.815	4.403	1.668	3.120	1.417	3.755
0.978	4.380	1.725	3.121	1.572	3.634
3.620	4.270	1.815	3.176	1.642	3.688
3.680	4.170	1.819	3.122	1.708	3.684
		1.863	3.200	1.774	3.591
Temp, 80° C		1.946	3.124	2.702	3.671
0.454	5.129	3.807	3.027	2.795	3.656
0.644	5.104	3.915	3.043	2.816	3.666
0.837	5.122			3.770	3.638
1.004	5.105				

Table II. Diffusion Coefficients for NaCl–Water System

Concn $\times 10^3$, mol/l.	Diffusion coeff $\times 10^5$, cm²/sec	Concn $\times 10^3$, mol/l.	Diffusion coeff $\times 10^5$, cm²/sec
Temp, 25°C		Temp, 50°C	
1.377	1.628	4.210	2.566
1.962	1.634	5.124	2.589
2.550	1.633	5.951	2.588
3.140	1.631	6.869	2.515
3.703	1.620		
4.267	1.622		
4.616	1.534	Temp, 70°C	
4.824	1.620	6.442	3.751
5.104	1.538	7.631	3.802
5.374	1.614		
5.656	1.537		
5.933	1.606	Temp, 80°C	
6.448	1.600	3.609	4.394
6.522	1.523	5.109	4.434
6.971	1.587	6.595	4.419
7.013	1.518		
7.508	1.594		
7.521	1.516		
8.004	1.605		
8.091	1.522		
8.564	1.522		
9.058	1.524		

Harned and Owen (*5*) and other textbooks discuss the derivation of the Onsager-Fuoss relationship which relates the diffusion coefficient to ionic parameters and to the limiting ionic equivalent conductivities of the solute. It need not be presented here. For the higher temperatures, it was necessary to calculate the limiting ionic conductivities by extrapolating Owen's empirical equations discussed above. With this in mind, the agreement between the measured diffusion coefficients and the predicted values is very good. From this it would appear that the estimation of diffusion coefficients at elevated temperatures and for other electrolytes from measured ionic conductivities by means of the Onsager-Fuoss relationship can be undertaken with some reliability.

NOMENCLATURE

a, b, c = empirical constants, Equation 1
$\mathring{a}$ = ion size parameter, Equation 2
A = effective cross-sectional area of diaphragm, cm²
B, B_1, B_2 = parameters in Stokes conductivity equation, Equation 2
C = molar density of solution, g-mol/cm³
C_A = molar concentration of solute, g-mol/cm³
D_{AB} = mututal diffusion coefficient as defined by Equations 4 and 5, cm²/sec
l = thickness of diaphragm, cm
N_A, N_B = molar flux of solute, solvent with respect to stationary coordinates, g-mol cm^{-2} sec^{-1}
t = temp, °C
T = time, sec
V = volume of top compartment of diaphragm cell, cm³
V_A, V_B = partial molar volumes of solute, solvent, cm³/g-mol
x = distance from top surface of diaphragm measured downward, cm
x_A = mole fraction of solute

GREEK LETTERS

λ° = equivalent ionic conductivity at infinite dilution, cm²/Ω
$\Lambda(\Lambda_0)$ = equivalent conductivity (at infinite dilution), cm²/Ω

LITERATURE CITED

(1) Bird, R. B., Stewart, W. E., Lightfoot, E. N., "Transport Phenomena," Wiley, New York, N. Y., 1960.
(2) Fell, C. J. D., PhD thesis, University of Cambridge, Cambridge, England, 1965.
(3) Gordon, A. R., *Ann. N. Y. Acad. Sci.*, **46**, 285 (1945).
(4) Harned, H. S., Nuttall, R., *J. Amer. Chem. Soc.*, **69**, 736 (1947).
(5) Harned, H. S., Owen, B. B., "The Physical Chemistry of Electrolyte Solutions," Reinhold, New York, N. Y., 1943.
(6) Mysels, K. J., McBain, J. W., *J. Colloid Sci.*, **3**, 45 (1948).
(7) Owen, B. B., *J. Chim. Phys.* **49**, C72 (1952).
(8) Robinson, R., Stokes, R. H., "Electrolyte Solutions," Butterworths, London, 1955.
(9) Sanni, S. A., Hutchison, H. P., *J. Sci. Instrum., Ser. 2*, **1**, 1101 (1968).
(10) Stokes, R. H., *J. Amer. Chem. Soc.*, **72**, 763 (1950).

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