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Molecular Diffusion Coefficients for the Triethylene Glycol–Water System

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Molecular diffusion coefficients for the triethylene glycol–water system have been determined as a function of composition at 30°, 45°, and 65° C. The diffusion coefficients were determined from photographically recorded interferograms made at various time intervals during diffusion experiments and compared to a number of frequently used correlations.

THEORY of molecular diffusion for the gaseous state is relatively well developed in comparison to that for the liquid state. This, in part, results from the fact that the kinetic theory of the gaseous state is relatively well defined, while there is as yet no workable kinetic theory for the liquid state (*18*). Even so, predicted values for molecular diffusion coefficients in binary gaseous systems, determined by correlations developed from theoretical considerations, contain significant uncertainties and typically deviate from experimentally determined values by 5 to 10% at ambient conditions. Often greater deviations are encountered and for pressures in excess of 20 atm., at or below normal temperatures; these correlations fail to yield even reasonable estimates for the binary molecular diffusion coefficients (*25*). No single correlation of gaseous diffusion coefficients has been found to be superior over other correlations for all gaseous systems.

Since there is no workable kinetic theory of the liquid state, much less has been accomplished theoretically for the liquid state than for the gaseous state. Even for simple binary liquid systems, no widely applicable molecular diffusion coefficient correlations have been derived from theoretical considerations. However, a large number of correlations have been presented in the literature, ranging from purely empirical to semitheoretical in nature.

There is a great need for accurate binary molecular diffusion data for use in design work and for testing these correlations under a variety of conditions so that the quality of the correlations can be improved. The data presented herein were determined for use in the latter cause.

EXPERIMENTAL EQUIPMENT AND PROCEDURES

Experimental Equipment. The experimental equipment consisted of a birefringent interferometer, a constant temperature air bath with controls and recorder, a flowing junction cell, and a 35-mm. camera with auxiliary attachments.

Among the available methods for determining liquid diffusivities, those which employ interferometric techniques of analysis are considered capable of the greatest accuracy (*11, 14, 18*). Several interferometric techniques have been developed and used for this purpose.

After an analysis of the various types of interferometers,

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the birefringence type, first introduced by Inglestam (*13, 14*), was selected for the present study.

The basic design of the interferometer used was that of Inglestam (*13, 14*) and Bryngdahl (*2*), and consisted of an optical bench, lens system, and polarized laser light source. A number of modifications were made to increase alignment sensitivity (*21*).

Many different types of diffusion test cells have been designed and employed in diffusion experiments in order to establish a sharp, flat initial boundary between two fluids of only slightly varying composition. Among these are the draw slide cell, the sliding solvent cell, the flowing junction cell, and the capillary withdrawal cell, all of which have been used by various experimentalists in determining diffusion coefficients (*1, 5, 6, 9, 11, 12, 15, 16, 17, 20, 23, 26, 27, 28*). In a detailed study of boundary formation Bryngdahl (*3*) found that good initial boundaries could be established in all these types of cells. For this work the flowing junction was used, so that the boundary formation could be observed visually during the formation process.

The test cell design, complete details of which are given by Merliss (*21*), was based on that of Svensson (*27*) and Skinner (*26*). The cell fluid cavity was ¼ inch wide by 3½ inches high by 3 inches thick, giving a geometrical light path of 3 inches through the cell. Cell windows were polished flat to 1000 A. or less, with surfaces parallel to within 15 seconds. Horizontal slits used to draw off liquid at the flowing junction were 0.0015 inch wide, centered vertically on each side wall.

The constant temperature air bath containing the diffusion cell consisted of a double-wall plywood box with a 3½-inch-thick annular space filled with Perlite insulation with an insulated, removable top. Optically flat windows were positioned with adjustable mounts in the wall of the bath in line with the optical path of the interferometer. The internal portion of the air bath was equipped with heater elements, baffles, an air-circulating fan, and temperature-sensing elements. Temperature control in the bath was within 0.01° C. from room temperature to 80° C.

Time measurements for the experiments were made using a precision tenth-second elapsed-time electric timer.

Procedures. DIFFUSION EXPERIMENTS. With the apparatus properly loaded with the test liquids, the lid to the constant temperature bath was closed and the air circulating fan in the bath started. The temperature controller was set at the desired control temperature, automatically starting heat-up of the bath. During heat-up the cell and lines were filled with the more dense test fluid through the bottom inlet to the cell.

After no difference in temperature could be determined on any of the thermocouples in the bath, fluid reservoirs, and cell, the temperature in the constant temperature bath was allowed to equilibrate for an hour longer. Some difficulty was experienced in exactly reproducing the set temperature for the various experiments, but with experience the control point could be set to within ±0.1° C.

After temperature equilibrium was established in the system, the valves on the fluid reservoirs and on the drain through the cell slits were opened to establish the initial boundary in the cell. Effluent rate to the drain was set at about 10 to 12 drops per minute. After about 30 minutes an initial boundary could be seen in the cell with the naked eye.

Boundary sharpening was then followed visually through the lens of the camera. The relative rates of flow of the two fluids were manipulated by adjustment of needle valves on the lines to the fluid reservoirs to obtain the sharpest possible initial boundary. Formation of the desired initial boundary was delicate and required small adjustments in the relative rates of flow of the two fluids.

When the initial boundary was as sharp as could be obtained, the valves were closed to isolate the test cell and the timer was activated. A photographic recording of the interference was made every 25 seconds for about the first 300 seconds, then every 50 to 250 seconds, depending upon the visual observation of the rate of movement of the interference pattern. The faster the apparent movement of the interference pattern, the shorter was the time interval between exposures. In all, at least 36 recordings were made in each diffusion run over about 15,000 seconds.

INTERPRETATION OF DATA

The concentration difference between triethylene glycol-water solutions was held to 1 weight % or less. Under this condition it was assumed that Fick's second law held and that the diffusion coefficient was constant.

With an infinitely sharp initial boundary between the two solutions in the diffusion cell, a constant diffusion coefficient, and with a sufficiently long diffusion path above and below the initial boundary, the solution to Fick's second law equation (*7*) is

$$\frac{C_A(\xi, t) - C_{A0}}{C_{A1} - C_{A0}} = \tfrac{1}{2}\left\{1 + \operatorname{erf} \frac{\xi}{(4D_{AB}t)^{1/2}}\right\} \tag{1}$$

for one-dimensional diffusion. Equation 1 relates the concentration of component A for a binary solution at point ξ and time t to the original concentrations of the two solutions and the diffusion coefficient. Over small concentration intervals, the refractive index of the solutions may be considered to vary linearly with concentration. The product of the refractive index, n, and the geometrical length, α, through the test cell is defined as the length of the optical path, z, and is given by

$$z(\xi, t) = \alpha[k_0 + k_1\{C_A(\xi, t) - C_{A0}\}] \tag{2}$$

Solving Equation 2 explicitly for $C_A(\xi, t)$ and substituting the results into Equation 1 yields

$$\frac{z(\xi, t) - z_0}{z_1 - z_0} = \tfrac{1}{2}\left\{1 + \operatorname{erf} \frac{\xi}{(4D_{AB}t)^{1/2}}\right\} \tag{3}$$

The interference pattern provided by the birefringent interferometer was an optical path gradient, which was recorded on film at various constant times, t_i. For this condition, differentiating Equation 3 holding time constant yields

$$\left\{\frac{\partial z(\xi, t)}{\partial \xi}\right\}_t = \frac{z_1 - z_0}{2(\pi D_{AB}t)^{1/2}} \exp\left\{-\frac{\xi^2}{4D_{AB}t}\right\} \tag{4}$$

For two times, t_i and t_j, at constant values of the optical path gradient, Equation 4 may be solved for D_{AB} to obtain

$$D_{AB} = \frac{\dfrac{(2\xi_i)^2}{t_i} - \dfrac{(2\xi_j)^2}{t_j}}{8 \ln \dfrac{t_j}{t_i}} \tag{5}$$

where ξ_i and ξ_j refer to the cell coordinates at which the gradient is measured at t_i and t_j, respectively.

Through the use of Equation 5 and photographic recordings of the optical path gradient at a number of different times, the diffusion coefficients were determined.

It was not possible to establish an infinitely sharp initial boundary. However, it has been shown (*8, 19*) that the initial condition can be properly corrected mathematically. This involves determination of a zero time correction, Δt, to account for the imperfection in the initial boundary between the two solutions. Using the time correction, the expression for the diffusion coefficient becomes

$$D_{AB} = \frac{D'_{AB}}{(1 + \Delta t\, \theta)} \tag{6}$$

where D'_{AB}, the apparent diffusion coefficient, is given by Equation 6 and

$$\theta = \frac{t_i + t_j}{t_i t_j} - \frac{\frac{1}{t_i} - \frac{1}{t_j}}{\ln \frac{t_j}{t_i}} \tag{7}$$

By plotting D'_{AB} against θ and extrapolating the resultant straight line to $\theta = 0$—i.e., t_i and $t_j \rightarrow \infty$—the diffusion coefficient, D_{AB}, is determined. The slope of the resulting line determines the value of Δt.

MEASUREMENT OF RECORDED DATA

The films for the diffusion experiments were developed in fine-grain developer and printed on proof sheets. Each print was tested for clarity of the interference pattern, using a 60X precision magnifier. Enlargements, approximately three-times actual size, were made from all the negatives suitable for enlarging, usually 25 on each experimental run. A distinct image of the width of the cell cavity (actual size ¼ ± 0.001 inch) was recorded on each photograph, from which the actual magnification was determined.

The camera was focused at the beginning of each experimental run, so that there was no skewness in the recordings of the interference patterns. In the calculations of the diffusion coefficients using Equation 5, time-smoothed values of 2ξ were used. Seldom was a data point far enough off the smoothed curve to be discarded.

EXPERIMENTAL RESULTS AND COMPARISON WITH CORRELATIONS

To test the experimental apparatus and procedure, mutual diffusion coefficients were determined for 0.1 weight % sucrose in aqueous solution at 23° and 30° C. Duplicate experiments were performed at 23° C., one set with the air-circulating fan turned off and one with it on, to determine if the air-circulating fan caused sufficient vibration to affect the results significantly. Results of the duplicate experiments (Table I) were in agreement to within 1%.

The diffusion data of Akeley and Gosting (*1*) and Gosting and Morris (*12*) on aqueous sucrose solutions are reputed to be the most accurate data in the literature. They were determined using a Guoy interferometer and a capillary withdrawal cell. For determination of the mutual diffusion coefficient at 25° C., for sucrose concentrations below 0.05 mole per liter of solution, Akeley and Gosting present the equation

$$D_{AB} \times 10^5 = 0.5228 - 0.2648\bar{C}_A \tag{8}$$

where $\bar{C}_A$ is the mean concentration of sucrose between the diffusing solutions in moles per liter of aqueous solution. Using the Stokes-Einstein relationship, the data of Akeley and Gosting were corrected to the temperature of the experiments reported here. The results reported here agree within 2% with those reported by Akeley and Gosting (Table I).

Following the sucrose diffusion runs, mutual diffusion coefficients for the triethylene glycol-water system were determined as functions of composition at 30°, 45°, and 65° C. (Figure 1 and Table II).

The diffusion coefficient determined at 30° C. for the 0.005 weight fraction triethylene glycol solution was compared to the predicted diffusion coefficient calculated from the Othmer-Thakar correlation (*22*). The experimental value

Table I. Mutual Diffusion Coefficients for the Sucrose-Water System

Run No.	Temp., °C.	Sucrose Concn., Gram/Liter	$D_{AB} \times 10^6$, Sq. Cm./Sec. This study	$D_{AB} \times 10^6$, Sq. Cm./Sec. Akeley and Gosting (*1*)
1-S-2[a]	23	1.000	4.88	4.84
1-S-3	23	1.000	4.91	4.84
1-S-4[a]	30	1.000	6.20	6.12

[a] Air-circulating fan on.

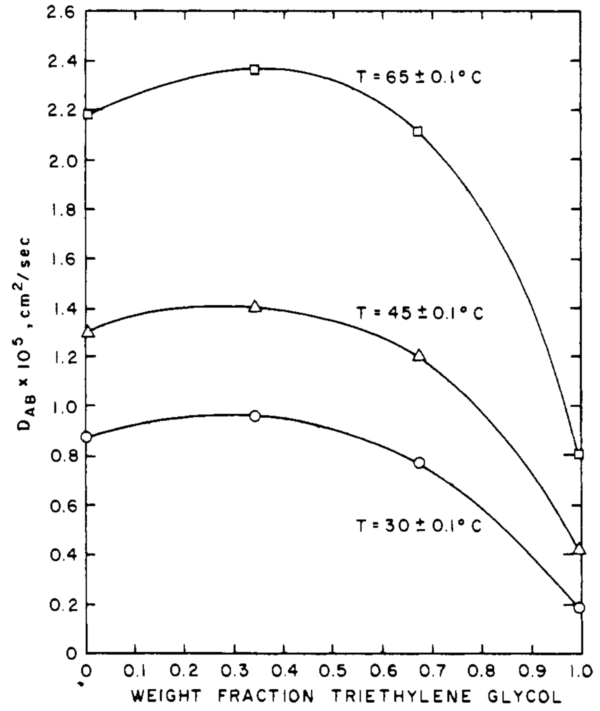

Figure 1. Molecular diffusion coefficients for triethylene glycol–water system as a function of composition and temperature

Table II. Mutual Diffusion Coefficients for the Triethylene Glycol–Water System

Run No.	Temp., °C.	Weight Fraction Triethylene Glycol	$D_{AB} \times 10^5$, Sq. Cm./Sec.
A-TEG-1	30	0.005	0.875
B-TEG-3	45	0.005	1.31
C-TEG-5	65	0.005	2.18
A-TEG-9	30	0.337	0.957
B-TEG-12	45	0.337	1.40
C-TEG-15	65	0.337	2.36
A-TEG-25	30	0.672	0.775
B-TEG-23	45	0.672	1.20
C-TEG-22	65	0.672	2.11
A-TEG-27	30	0.995	0.188
B-TEG-29	45	0.995	0.426
C-TEG-32	65	0.995	0.803

of 8.75×10^{-6} sq. cm. per second is 4% higher than the predicted value of 8.41×10^{-6} sq. cm. per second. At higher temperatures the correlation is greatly in error, so that its use is not recommended above 30° C.

The diffusion coefficient determined at 30° C. for the 0.995 weight fraction triethylene glycol solution was compared to values calculated from the Wilke-Chang (*31*) prediction divided by 2.3, as recommended (*25*). The experimental value of 1.91×10^{-6} sq. cm. per second is 24% higher than the predicted value of 1.53×10^{-6} sq. cm. per second.

Diffusion coefficients determined at 30° C. were tested using the Stokes-Einstein relationship (*10, 29*) to correct to the higher temperatures, 45° and 65° C. For the 0.005 weight fraction triethylene glycol solution, this relationship predicts a diffusion coefficient that is 6.5% low at 45° C. and 15.4% low at 65° C. The diffusion coefficients predicted for the 0.995 weight fraction triethylene glycol solution were low by 40.3 and 23.3% at 45° and 65° C., respectively. From a theoretical point of view, the Stokes-Einstein relationship applies only to the low concentration triethylene glycol solution, which accounts in part for the wide deviation at the high concentration level.

The data at each temperature were compared over a concentration range with the following correlation proposed by Rathbun and Babb (*24*);

$$D_{AB} = (D^{\infty}_{BA} X_A + D^{\infty}_{AB} X_B) \left(\frac{\partial \ln a_A}{\partial \ln X_A} \right)^{s}$$

where S has a value of 0.3 for systems exhibiting a negative deviation from Raoult's law and 0.6 for systems exhibiting a positive deviation from Raoult's law. Use of the correlation requires activity data as a function of composition. No such data could be found in the literature for the triethylene glycol–water system, but data on the vapor pressures of triethylene glycol–water solutions as a function of composition and temperature were available (*30*). These data were used with the following assumptions: Because of the extremely low vapor pressure of triethylene glycol at the experimental temperatures of this study, the total vapor pressure of the solution is the vapor pressure of the water over the solution, and at the low vapor pressure of the solutions, less than ⅓ atm. at most, the vapor over the solution obeys the ideal gas law. Activities of the water were calculated as a function of mole fraction of water in the solution. The best least squares fit of the data was an equation relating activity of the water to a fifth degree polynomial in water mole fraction. Infinite dilution diffusion coefficients were determined by extrapolating to zero water concentration and to zero triethylene glycol concentration. Triethylene glycol-water solutions deviate negatively from Raoult's law; therefore, exponent S in Rathbun's correlation was taken to be 0.3.

The solid line in Figure 2 represents the Rathbun correlation over the range of concentrations for which activity data could be calculated. The diffusion coefficients determined experimentally are correlated to within about 5% over this concentration range, the predicted diffusion coefficients being generally higher than those determined experimentally.

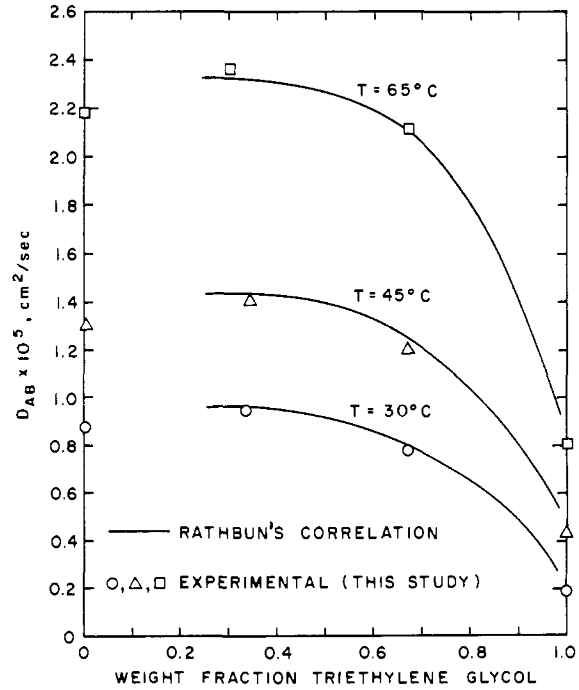

Figure 2. Comparison of experimental values of diffusion coefficients for triethylene glycol–water system to predicted values by Rathbun correlation

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NOMENCLATURE

a = activity
A = component of binary solution
C = total concentration, moles per unit volume of solution
C_i = concentration of component i, moles of i per unit volume of solution
$\overline{C}_A$ = average concentration of A
C_{A0} = concentration of component A in less dense solution
C_{A1} = concentration of component A in more dense solution
D_{AB} = Fick's mutual diffusion coefficient
D'_{AB} = pseudo-diffusion coefficient defined by Equation 6
D^{∞}_{ij} = mutual diffusivity at infinite dilution of component i
k_0 = constant defined by Equation 2
k_1 = constant defined by Equation 2
S = exponent
t = time variable
X_i = mole fraction of component i in solution
z = optical path length
α = cell thickness in line of optical path
θ = time factor defined by Equation 7
ξ = distance coordinate in one-dimensional linear diffusion systems

Subscripts

0 = less dense solution
1 = more dense solution
i = component i
j = component j

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Specific Conductance of Ammonium Nitrate Solutions

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Specific conductances at about 10° intervals between 30° and 100° C. are reported for ammonium nitrate solutions ranging in concentration from 30 to 80 weight %. Measurements were made with alternating current at a frequency of 2000 c.p.s. using a modified version of the method previously used.

THE SPECIFIC conductance data of concentrated ammonium nitrate solution have been reported by only Campbell (*1-6*) and a few others (*10, 11, 12*). Ammonium nitrate is an explosive that is not easily detonated. Occasionally it may explode for unknown reasons; hence, it should be handled with this fact in mind. Many data have been obtained at pressures above 1 atm., but, in general, there is a lack of values at temperatures between 35° and 95° C. at atmospheric pressure and at concentrations between 40 and 65 weight % ammonium nitrate. In this investigation specific conductance was measured for aqueous solutions containing from 30 to 82 weight % ammonium nitrate at temperatures varying from 28° to 99° C.

EXPERIMENTAL

The determination of the electric conductivity of concentrated salt solutions at high temperature presents difficulties which often lead to results of limited accuracy. These difficulties pertain generally to the temperature-controlling and the conductivity-measuring systems.

Even with the most elaborate temperature-controlling systems, cyclic variations of bath temperature are observed which lead to corresponding variations in the resistance of the conductivity cell. However, by recording such variations of temperature and resistance balance on a graph and then applying statistical analysis to the data so obtained, specific conductance values of high accuracy can be obtained.

Temperature Control. Since the specific conductance is influenced by slight variations in temperature, particular care was given to the temperature control of the cell. The related system used is schematized in Figure 1.

It consists essentially of three paraffin oil (*7, 8*) baths, B_1, B_2, and B_3. The temperature of bath B_2, in which the cell is immersed, is controlled by paraffin oil pumped by P_3 from bath B_3 through copper coils S_2. The temperature of B_3 is held at 10° C. above that of B_2. Stirring is effected by pump P_2 connected in series with heat exchanger E to compensate for mechanical heat transfer. In turn, the temperature of the cooling liquid flowing through E is thermostatically controlled in B_1, which is at 2° to 5° C. lower than liquid in B_2. Also, the temperature of B_1 is fixed by balancing cooling unit M with heater C_1.

A thermal balance is obtained by opposing heat input and heat removal by a proper coordination of heaters C_1, C_2, and C_3 with thermoregulators T_1, T_2, and T_3. This arrangement permits a stabilization of the temperature in B_2 within such narrow limits that the variation in the temperature of cell CE can be reduced to $\pm 0.004°$ C. if necessary.

Cell. After having tested several commercial cells, authors believe that none of these had characteristics permitting a valuable determination of the conductivity of ammonium nitrate solutions at high temperatures. The authors therefore designed and built several cells, the last being shown in Figure 2. It has two arms, A, filled with mercury to provide electrical contact with the circular platinized platinum electrodes. The three 3-pronged branches have other functions. Prongs B are closed with mercury safety valves to maintain the pressure relatively constant during heating. Prongs C serve as thermocouple wells filled with paraffin oil. The bottom parts of the wells dip into the cell solution and, because of their positions and number (fore, aft, and center), permit a close evaluation of the average solution temperature. Prongs D serve only to fill the cell with the solution.

The body of the cell is cylindrical, with a concave shape between the branches to eliminate all gas bubbles that would form during heating and would render the resistance measurements imprecise.

Temperature. Nine iron-constantan thermocouples