Aqueous Molecular Diffusivities of Carboxylic Acids

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Molecular diffusion coefficients in aqueous solution at 25.0° C. were measured for carboxylic acids—formic, acetic, propionic, butyric, valeric, and caproic—and at 9.7° C. for acetic acid. The diaphragm-cell method was used in the experiments. The data were compared with those of other recent investigators and were shown to be consistent. These data and the data of others on carboxylic acids and data on α-amino carboxylic acids of Longsworth were compared to the values predicted by the Wilke-Chang empirical correlation. The experimental values of the diffusion coefficients were lower on the average by 11% than the predicted values. Using a modified constant in the Wilke equation of 6.6 instead of 7.4, the data for acids were correlated by the following equation with an average deviation of ±3.7% and a maximum of 8.5%.

$$D = \frac{6.6 \times 10^{-8}\,(XM)^{1/2}T}{\eta\, V^{0.6}}$$

AT THE present time one of the most reliable semi-empirical equations available to predict the molecular diffusion coefficient of solutes in aqueous solution in the liquid state is that of Wilke and Chang (*21*). Other methods available are those by Scheibel (*14*) and Thakar and Othmer (*18*). Efforts to predict theoretically the diffusion coefficient of solutes in liquids have met with only limited success so far (*20*).

The equation of Wilke and Chang used to predict aqueous diffusion coefficients is based on 53 experimental points on 40 different solutes of which the majority are organic compounds. All of these experimental points are quite old data from the International Critical Tables (*5*) obtained prior to the year 1929. Only two experimental points for acids, one point for acetic acid and one for tartaric acid, were included in formulating this correlation.

There are many methods available to determine experimentally the diffusion coefficients in liquids. Johnson and Babb (*6*) give a comprehensive summary of the experimental methods used. The diaphragm-cell method has been shown to be quite accurate and rapid. The details of this method are discussed by Barnes (*1*), Gordon (*3*), Smith and Storrow (*15*). Stokes (*16, 17*), and Chang and Wilke (*2*). This cell consists of two compartments—one usually containing pure water and the other a dilute aqueous solution of the diffusing solute—separated by a porous, glass diaphragm through which molecular diffusion occurs. The diffusivities obtained are integral diffusion coefficients.

More experimental data on the diffusivity of organic acids in aqueous solution are needed to see if the diffusivities of these organics follow the same trend as that of other solutes. Also, a comparison is needed of more recent and modern experimental measurements of acids with the correlation of Wilke and Chang (*21*).

In the present research, experimental diffusion coefficients of the carboxylic acid series—formic, acetic, propionic, butyric, valeric, and caproic acids in water—were obtained using the diaphragm-cell method. The experimental data were then compared with data for acids from other recent investigations and a final correlation was obtained for carboxylic and α-amino carboxylic acids.

THEORY

The basic equations for the diaphragm-cell have been derived by Jost (*7*), Smith and Storrow (*15*), Barnes (*1*). and Gordon (*3*). If the volumes of the two compartments on either side of the diaphragm are equal, then the following equation relates the initial and final concentrations in the diaphragm cell and the diffusion coefficient, *D*.

$$\log\left[\frac{C_0'' - C_0'}{C'' - C'}\right] = \frac{(2.303)(2)ADt}{Lv} = \beta Dt \tag{1}$$

Smith and Storrow (*15*) and Barnes (*1*) show that if the value of λ (void volume of porous diaphragm/volume of one compartment) is less than 0.10, then the assumption of a linear gradient in the diaphragm is essentially correct and β is constant. Chang and Wilke (*2*) show that the cell constant does not vary with temperature.

To use Equation 1, the initial gradient in the diaphragm must be linear at time, *t*, is zero. Smith and Storrow (*15*), Barnes (*1*), and Gordon (*3*), set up this gradient by an initial preliminary run for 3 to 5 hours with initial concentrations of pure water in the top compartment and a concentration of solute of C_0' in the lower compartment. After the 3 to 5 hours have elapsed the solution in the lower compartment is withdrawn and replaced with fresh solution of concentration C_0' for the start of the diffusion run. The initial concentration C_0'' in the top at *t* is zero is solved for by a material balance neglecting the diaphragm pore volume.

$$C_0'' = C' + C'' - C_0' \tag{2}$$

The quantity β is determined experimentally using KCl of which the integral diffusion coefficient is well known. A value of 1.87 × 10^{-5} sq. cm./sec. at 25° C. has been recommended by Chang and Wilke (*2*), Harned and Nuttall (*4*), and Stokes (*16*). This value is used for an original concentration of 0.10*N* KCl in one side of the cell, water in the other side, and the diffusion proceeds to concentrations of 0.075*N* and 0.025*N* in the two sides. Prior to 1949 the value generally used was 1.83 to 1.84 × 10^{-5} sq. cm./sec. Gordon (*3*) shows that if the original concentration is less than 0.1*N*, the integral diffusion coefficient calculated from Equation 1 is approximately equal to the differential diffusion constant at an average concentration of $(C_0'' + C_0')/2$ with an error of less than 0.3%.

Stokes (*16*) found experimentally that if the initial solution is too dilute, erratic high values of the diffusion coefficient are obtained due to surface diffusion effects. At an initial concentration of 0.05*N* the error is +0.2% and increases as concentration drops. He also found that stirring rates in each solution of over 50 r.p.m. were needed to ensure complete mixing in the bulk compartments. Stokes (*17*) also found that the cell constant decreased by 0.5 to 1.0% after 1000 hours of use due to wearing away of the diaphragm by stirring.

The semi-empirical equation of Wilke and Chang (*21*) for diffusion of solutes in aqueous solution is

$$D = \frac{7.4 \times 10^{-8} (XM)^{1/2} T}{\eta V^{0.6}} \qquad (3)$$

The viscosity of the solution, η, is often assumed to be that of water for very dilute solutions.

The molar volume, V, of the solute at the normal boiling point is estimated by the method of LeBas (*8*). The tables of LeBas presented by Wilke and Chang (*21*) and others (*11, 12*) are condensed and do not give all the detailed values for the various elements as given in the original source (*8*). The pertinent values of LeBas for oxygen in carboxylic acids are 7.4 for oxygen in the —OH structure and 12.0 for oxygen in the =O structure. Using the condensed tables of others (*11, 12, 21*), the value of 12.0 should be used for each of the two oxygens in the carboxylic acids. However, LeBas definitely shows that the oxygen in the hydroxyl has a smaller value than the double-bonded oxygen.

Using the LeBas values of 7.4 and 12.0 for oxygen, the predicted values of V for acetic, propionic, butyric, valeric, and caproic acids are 63.8, 86.0, 108.2, 130.4, and 152.6, respectively. These values agree within 0.8% with the experimental values of the same acids of 64.1, 85.3, 107.8, 130.0, and 152.5 (*8, 12*), respectively. Using a value of 12.0 for both oxygens in the acids, the maximum error increases to 6.7% for the same compounds.

EXPERIMENTAL

The diaphragm-cell used in this work is similar to that used by Smith and Storrow (*15*) and is shown in Figure 1. The diaphragm was a porous, glass disk with pore sizes of 4.5 to 5.0 microns. Capillary vents for each compartment were used to equalize any pressure changes and stop any bulk flow of the solution through the diaphragm.

The magnetic stirrers were iron bars enclosed in polyethylene. The lower stirrer was lighter than water and floated, pressing against the diaphragm. The upper stirrer was heavier than water. Two permanent magnets were rotated outside of the cell and caused the stirrers inside the compartments to rotate at 100 r.p.m. The complete system was immersed in a constant-temperature water bath up to ½-inch from the top of the cell and the temperature of the bath was controlled to ±0.10° C. The stirring system was mounted separately from the cell and bolted to the floor to eliminate transmission of vibrations to the cell which would affect the diffusion coefficient.

Each chamber contained 25.00 cc. of solution. Assuming a per cent void fraction of 50% in the diaphragm, the ratio, λ, void volume of porous diaphragm/volume of one compartment, was 0.35/25.00 or 0.014. This is well below the value of 0.05 needed to keep β constant.

The 0.10N solutions of KCl were prepared by weighing amounts of KCl into a volumetric flask. The solutions, removed after the diffusion runs, were titrated in duplicate with 0.05N $AgNO_3$ solutions using a Fisher titrimeter with silver and silver–silver chloride electrodes. The carboxylic acid solutions were analyzed in duplicate by titration with 0.05N NaOH.

In making a diffusion run the cell was cleaned thoroughly with cleaning solution and rinsed repeatedly with degassed distilled water. The diaphragm was filled with water by placing the inner compartment in water and sucking the water through four times. Then the excess water was removed from outside the diaphragm. A volume of 25.00 cc. of water was added to the inner chamber and 25.00 cc. of the 0.10N solution to the outer or lower chamber. The inner compartment level was adjusted so that the levels in the two compartments were equal.

The cell was placed in the constant-temperature bath and stirring was started to set up a preliminary concentration gradient in the diaphragm. After 3 to 5 hours the solution in the outer compartment was removed and replaced with 25.00 cc. of fresh 0.10N solution. The actual diffusion experiment run was then started and continued for 50 to 60 hours.

DATA AND CALCULATIONS

The experimental data for the cell calibrations with KCl and the diffusivity data for the carboxylic acids are given in Table I. The values of C_0'' in Table I were calculated by Equation 2 and the values of the diffusivity for the carboxylic acids were calculated by Equation 1.

The cell constant, β, using KCl was determined three times at the start of the series of runs and calculated by Equation 1 using a value of 1.87 × 10^{-5} sq. cm./sec. for the diffusion coefficient of the KCl. The maximum deviation from the mean value of β of 0.0512 was 0.8% and the average deviation was ±0.5%. An analysis of the maximum expected analytical errors gave the result that because of

Table I. Experimental Diffusivity Data

Compound	Temp., ° C.	$t \times 10^{-5}$, Sec.	Normality C_0'	C'	C''	C_0''	β	$D \times 10^5$, sq. cm./sec.
			(Cell Calibration Data)					
KCl	25.0	2.229	0.1000	0.0805	0.0195	0.0000	0.0515	1.87
KCl	25.0	2.292	0.1000	0.0803	0.0198	0.0001	0.0508	1.87
KCl	25.0	2.160	0.1000	0.0811	0.0192	0.0003	0.0513	1.87
						Av. =	0.0512	
Acid			(Diffusivity Data)					
Acetic	25.0	2.133	0.0984	0.0851	0.0134	0.0002		1.250
Acetic	9.7	1.695	0.0978	0.0909	0.0077	0.0008		0.769
Formic	25.0	1.692	0.1235	0.1074	0.0163	0.0002		1.516
Acetic	25.0	1.968	0.0979	0.0855	0.0131	0.0007		1.271
Propionic	25.0	1.830	0.0996	0.0899	0.0099	0.0002		1.009
Butyric	25.0	1.800	0.0812	0.0741	0.0079	0.0008		0.918
Valeric	25.0	2.013	0.0646	0.0589	0.0057	0.0000		0.817
Caproic	25.0	2.007	0.0437	0.0400	0.0038	0.0001		0.784

these analytical errors the maximum expected deviation of the cell constant was ±2.5%. The experimental average error of ±0.5% was well within these limits.

To determine if the cell constant had changed during all the series of runs, a second run with acetic acid at 25° C. was made at the end of this series (Table I). The value of this diffusivity was 1.271×10^{-5} sq. cm./sec. as compared to 1.250×10^{-5} sq. cm./sec. at the start of the carboxylic acid runs. This error is 1.7% and within the limits due to the maximum expected analytical errors.

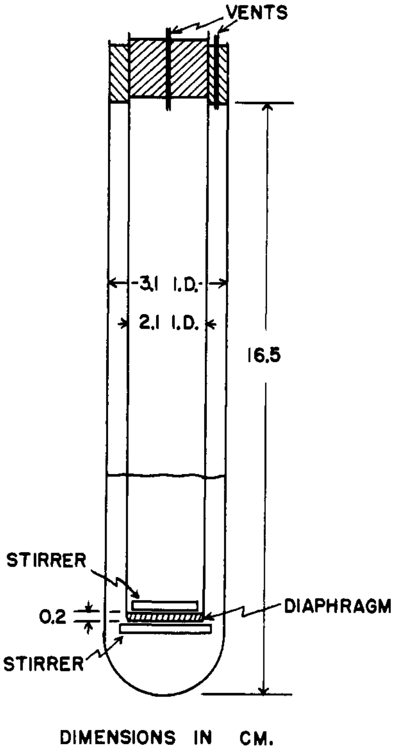

Figure 1. Diaphragm-Type Diffusion Cell Used in Experiments

To calculate the molar volume, V, of the carboxylic acids of this work and other investigators data (*5, 6, 13, 19*) on these acids and of the α-amino carboxylic acid data of Longsworth (*9, 10*), the values from LeBas (*8*) were used. The viscosities of the formic, acetic, propionic, and butyric acid solutions were obtained from the literature (*5*). The viscosity of the valeric acid solution was assumed the same as isovaleric acid (*5*). The viscosity of the caproic acid solution was estimated by plotting the viscosities of solutions of the homologous acid series, formic through valeric acids, *vs.* the number of carbon atoms in the acids and extrapolating to caproic acid.

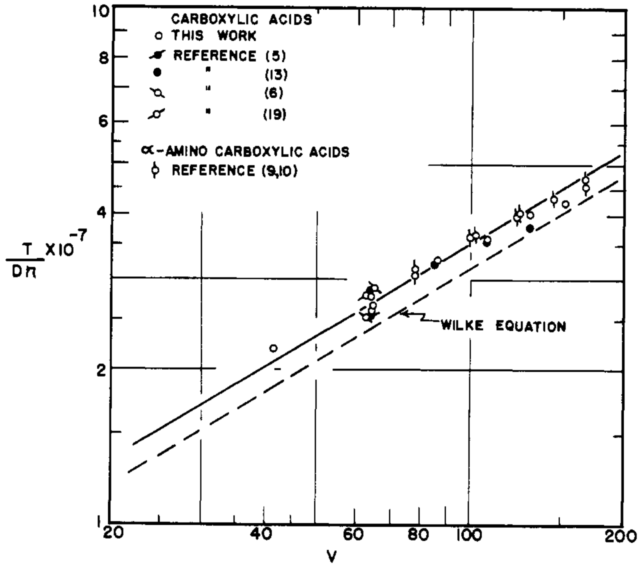

Figure 2. Diffusivity of Organic Acids in Water

Table II. Diffusivity Data for Acids

Compound	Investigator	Av. Conc.	Temp., ° C.	$D \times 10^5$, sq. cm./sec.	LeBas V	η_w	(η/η_w)	$(T/D\eta)10^{-7}$
			(Carboxylic Acids)					
Formic	This work	0.06*N*	25.0	1.516	41.6	0.894	1.002	2.20
Acetic	(*5*)	0.01*N*	12.5	0.91	63.8	1.223	1.001	2.56
Acetic	(*13*)	0	20.0	1.012	63.8	1.005	1.000	2.87
Acetic	This work	0.05*N*	9.7	0.769	63.8	1.310	1.006	2.78
Acetic	This work	0.05*N*	25.0	1.250	63.8	0.894	1.0056	2.66
Acetic	This work	0.05*N*	25.0	1.271	63.8	0.894	1.0056	2.61
Acetic	(*6*)	0.5*N*	14.0	0.90	63.8	1.1709	1.059	2.58
Acetic	(*6*)	$1.0\%^b$	15.0	0.88	63.8	1.1404	1.028	2.80
Acetic	(*19*)	0.05*N*	25.0	1.210	63.8	0.894	1.0056	2.74
Propionic	This work	0.05*N*	25.0	1.009	86.0	0.894	1.0095	3.27
Propionic	(*13*)	0^a	20.0	0.898	86.0	1.005	1.000	3.25
Butyric	This work	0.04*N*	25.0	0.918	108.2	0.894	1.010	3.59
Butyric	(*13*)	0^a	20.0	0.824	108.2	1.005	1.000	3.54
Valeric	This work	0.032*N*	25.0	0.817	130.4	0.894	1.010	4.03
Valeric	(*13*)	0^a	20.0	0.767	130.4	1.005	1.000	3.80
Caproic	This work	0.022*N*	25.0	0.784	152.6	0.894	1.008	4.21
			(α-Amino Carboxylic Acids)					
Acetic	(*10*)	$0.3\%^b$	25.0	1.055	78.0	0.894	1.0068	3.14
Acetic	(9)	$0.29\%^b$	1.0	0.515	78.0	1.7313	1.0068	3.06
Propionic	(*10*)	$0.32\%^b$	25.0	0.910	100.2	0.894	1.0087	3.63
Propionic	(9)	$0.31\%^b$	1.0	0.432	100.2	1.7313	1.0087	3.64
Butyric	(*10*)	$0.31\%^b$	25.0	0.829	122.4	0.894	1.009	3.98
Butyric	(9)	$0.30\%^b$	1.0	0.389	122.4	1.7313	1.009	4.03
Valeric	(*10*)	$0.32\%^b$	25.0	0.768	144.6	0.894	1.0096	4.30
Caproic	(*10*)	$0.32\%^b$	25.0	0.725	166.8	0.894	1.0096	4.55
Caproic	(9)	$0.31\%^b$	1.0	0.333	166.8	1.7313	1.0096	4.71

[a] Assumed. [b] By Wt.

The viscosity of the α-amino propionic acid solution was obtained from the literature (*5*). The viscosities of the other α-amino carboxylic acid solutions were estimated by plotting a line through the α-amino propionic acid viscosity point parallel to the line for the carboxylic acids.

The data for average concentration, diffusivity, temperature, molar volume, viscosity of water, viscosity ratio of the aqueous solution to that of water, and the factor $(T/D\eta)$ are tabulated in Table II for all the acid data.

DISCUSSION OF RESULTS

The data from Table II are plotted in Figure 2 and for comparison the Wilke and Chang Equation 3 is plotted on the same graph. The best solid line through all the data on carboxylic acids and α-amino carboxylic acids was drawn with a slope of 0.6 since this slope has been quite well established by Wilke and Chang (*21*).

This solid line is drawn much higher than the dashed line of Equation 3 and gives lower values of diffusivity on the average by approximately 11%. The new recommended empirical equation for organic carboxylic acids is given below with a constant of 6.6 instead of 7.4.

$$D = \frac{6.6 \times 10^{-8} (XM)^{1/2} T}{\eta V^{0.6}} \tag{4}$$

The average deviation of all 25 experimental points from the solid line in Figure 2 is ±3.7% and the maximum is only 8.5%. The average deviation of the data from the dashed line of Wilke and Chang is ±13.1% and the maximum is 19.8%. These deviations from the Wilke and Chang line are not unexpected since only two of the 53 points used in their correlation were acids and all of the data were obtained prior to 1929.

As noted in Table II most of the aqueous solutions are quite dilute. The maximum increase in viscosity of the solution over that of pure water for the α-amino carboxylic acids is 1% and 5.9% for the carboxylic acids with the majority less than 1%. This cannot account for the difference between the two lines in Figure 2. Wilke and Chang (*21*) state that they corrected the viscosities of the solutions because of the solute present but do not give the actual values used.

If the value for the atomic volume of oxygen is used erroneously as 12.0 for both oxygens in the acid radical, then a higher molar volume, V, for formic acid of 46.2 is obtained instead of the correct value of 41.6. For caproic acid 157.2 is obtained instead of 152.6. This would change the position of the experimental points in Figure 2 and bring them closer to the Wilke line by about 6% for the formic acid and 1.5% for the caproic acid. These changes cannot account for the 11% difference in the two lines.

In Figure 2 the values of the diffusivities for acetic acid in this work are found to fall between the values of the other investigators. Also, a reasonable check is obtained between this work and that of Rossi and Bianchi (*13*) for the experimental diffusivity values of propionic, butyric, and valeric acids.

As pointed out earlier, the correlation of Wilke was developed for a large number of compounds of which only a few were as polar as the carboxylic acids. Molecules such as the carboxylic acids which form strong hydrogen bonds with water would be expected to provide a larger effective volume for diffusion than the molecular volume of other solutes. Hence, the experimental diffusivity values for carboxylic acids would be smaller as is shown in Figure 2.

The incremental volume for the COOH group in water is constant so that the correlating line for the acid compounds would approach the Wilke correlation at very high molecular volumes (Figure 2). Also, at very large molar volumes the slope of the line should decrease to a value of ⅓ for spherical molecules according to the Stokes-Einstein relation (*21*).

The shape of the molecule affects the diffusion coefficient (*20*). The derivation of the Stokes-Einstein equation using hydrodynamic assumptions shows theoretically that for the same size solute volume the cylindrical molecules diffuse at a greater rate than spherical molecules. This might be another explanation for the decreasing deviation of the diffusivity from the Wilke correlation at large molecular volumes.

Much information could be obtained by determining experimentally the diffusion coefficients with different solutes in nonpolar solvents which cannot form hydrogen bonds. Data of this nature could lead to an accurate evaluation of the true molecular volume, and the larger effective molecular volume obtained in solvents forming hydrogen bonds might lead to a better understanding of this important phenomenon in liquid solutions.

NOMENCLATURE

A = Effective area of pores perpendicular to diffusion, sq. cm.
C_0'' = Initial concentration in dilute side, g. moles/cc.
C'' = Final concentration in dilute side g. moles/cc.
C_0' = Initial concentration in concentrated side, g. moles/cc.
C' = Final concentration in concentrated side, g. moles/cc.
D = Diffusivity of solute, sq. cm./sec.
L = Effective length of pores, cm.
M = Molecular weight of solvent
t = Time, sec.
T = °K.
V = Molar volume of solute at normal boiling point, cc./g. mole
v = Volume of compartment, cc.
X = Constant = 2.6 for water
β = Cell constant
η = Viscosity of solution, centipoises
η_w = Viscosity of water, centipoises
λ = Void volume of porous diaphragm/volume of one compartment

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