

## Chapter 7: Appendix

### Diffusion: A General Treatment of Molecules and Ions

We have seen that diffusion may be regarded as the net movement of solutes in solution (or in gas phase) due to a concentration gradient. We have also seen that ions move due to potential gradients. Hence, the unified treatment asserts that solutes in solution will move with the velocity proportional to the electrochemical potential gradient. This can be expressed as follows:

$$v_i = -u_i (\nabla \mu_i + z_i e \nabla \phi) \quad (1)$$

(ionic species  $i$  velocity) = (ionic mobility) (chemical forces + electrical forces)

where  $\mu_i$  is the molecular chemical potential of  $i$  (Gibbs free energy of  $i$  not accounting for the electrostatic contribution is  $G_i = \mu_i N_a$ ),  $z_i$  is the charge number on the ion,  $e$  is the Faraday constant (or charge on electrons) and  $\phi$  is the electrostatic potential.  $u_i$  - ion mobility is the physical property of the ion which must be measured. Often it is taken to be given by Einstein's equation  $1/6\pi\mu r_i$  where  $\mu$  is solvent viscosity and  $r_i$  is the effective ion radius (which we still do not know for most of the situations). Hence,  $u_i$  is a parameter to be determined from experiments. The *c g s.* units on  $u_i$  are (s/g)

Recall that the chemical potential of species  $i$

$$\mu_i = \mu_i^o + k_B T \ln a_i \quad (2)$$

so that

$$\nabla \mu_i = k_B T \nabla \ln a_i \quad (3)$$

where  $k_B$  is the Boltzmann constant. We will assume an ideal solution, then  $a_i = \left(\frac{C_i}{1M}\right)$  so that

$$\nabla \mu_i = \frac{k_B T}{C_i} \nabla C_i \quad (4)$$

where  $C_i$  is the concentration of ionic species  $i$  (in mole  $i$  per unit volume).

The molar flux of species  $i$  is given by  $J_i$  (in mol per unit area and second)

$$J_i = v_i C_i \quad (5)$$

Substitution of eq (4) and eq (1) into eq (5) yields upon reorganization:

$$J_i = -[u_i k_B T] \left( \nabla C_i + \frac{z_i e C_i}{k_B T} \nabla \phi \right) \quad (6)$$

By comparison with the situation when  $\nabla \phi = 0$  we recognize that diffusivity  $D_i$  is given by

$$D_i = u_i k_B T \quad (7)$$

If we take  $k_B = 1.381 \times 10^{-16}$  erg K<sup>-1</sup>,  $T$  in (°K), and  $u_i$  (s/g) we have  $D_i$  (cm<sup>2</sup>/s). If we take  $k_B = 1.381 \times 10^{-23}$  JK<sup>-1</sup>, we must take  $u_i$  (s/kg) to get  $D_i$  (m<sup>2</sup>/s).

It is customary to rewrite eq (6) as

$$J_i = -D_i \left( \nabla C_i + \frac{Z_i F}{RT} C_i \nabla \phi \right) \quad (8)$$

where  $F$  is the Faraday constant ( $F = 9.6485 \times 10^4$  C mol<sup>-1</sup>),  $R$  is the ideal gas constant. This is often called the Nernst-Planck equation.

### Strong electrolytes of charges $Z_1$ and $Z_2$

Since the condition of electro-neutrality has to be satisfied it can be shown that eq (8) can be rewritten for strong electrolytes as

$$J_T = -D \nabla C_T \quad (9)$$

where  $J_T = \frac{J_1}{|Z_2|} = \frac{J_2}{|Z_1|}$  and  $C_T$  is the equivalent concentration

$$C_T = \frac{C_1}{|Z_2|} = \frac{C_2}{|Z_1|} \quad (10)$$

and  $D$  is the composite diffusivity

$$D = \frac{\frac{|Z_1| + |Z_2|}{|Z_2| + |Z_1|}}{\frac{D_1}{D_2}} \quad (11)$$

### Weak 1-1 electrolytes

These often rapidly dimerize in solution. For example an aqueous-solution of acetic acid will contain hydrated protons [H<sub>3</sub>O<sup>+</sup>], acetate ions [CH<sub>3</sub>COO<sup>-</sup>], and acetic acid molecules [CH<sub>3</sub>COOH]. The cations and anions of this weak electrolyte diffuse at the same rate because of electrostatic interactions i.e they act as monomers of the same species. The electrolyte molecules i.e acid molecules, roughly equivalent to a dimer, diffuse at a different rate. As diffusion proceeds, the concentrations change and so do the fraction of monomer and dimer. Hence we have a concentration dependent diffusion process.

We assume the total solute concentration expressed in equivalents is:

$$C_T = C_1 + 2 C_2 \quad (12)$$

Furthermore the dimerization is much more rapid than diffusion so that

$$C_2 = KC_1^2 \quad (13)$$

where  $K$  is the equilibrium constant identical with the association constant for a weak electrolyte. Then one can show that

$$J_T = - \left( \frac{D_1 + D_2 \left[ \sqrt{1 + 8KC_T} - 1 \right]}{\sqrt{1 + 8KC_T}} \right) \nabla C_T = -D \nabla C_T \quad (14)$$

The quantity in parentheses is the apparent diffusivity of the dimerizing solute. At very low  $C_T$  this is equal to monomer diffusivity  $D_1$ . At high  $C_T$  it equals to the diffusivity of the dimer  $D_2$ . For the values of  $D/D_1$  see Figure 1.

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Example: The  $pK_a = 4.756$  for acetic acid. The diffusion coefficient for the acid molecules is  $D_2 = 1.80 \times 10^{-5} \text{ cm}^2/\text{s}$  at  $25^\circ\text{C}$ . What is  $D$  for a 1 M solution?

Recall

$$pK_a = -\log \frac{[H^+][A^-]}{[HA]}$$

so that

$$\frac{[HA]}{[H^+][A^-]} = 10^{pK_a}$$

but since  $[H^+] = [A^-]$  we get

$$K = 10^{pK_a} = 5.70 \times 10^4$$

Due to the high total concentration and the fact that  $K$  is so large, equation (14) reveals that  $D \approx D_2$  so that  $C_T \approx 1M$

$$J_T = -D_2 \nabla C_T \quad D = D_2 = 1.80 \times 10^{-5} \frac{\text{cm}^2}{\text{s}}$$

### Micelle Forming Solutions

In micelle formation, typical of detergent solutions,  $n$  monomers combine to make an  $n$ -mer. No other sizes are present. The diffusion coefficient in such detergent solutions represents an average over monomer and micelle present in solution.

The mass balance requires

$$C_T = C_1 + nC_m \quad (15)$$

and rapid equilibration is assumed

$$C_m = KC_1^n \quad (16)$$

Now we have

$$J_T = -D_1 \nabla C_1 - nD_m \nabla C_m \quad (17)$$

In order to get a workable equation one must experimentally determine the critical micelle concentration  $C_{CMC}$  at which the properties of the solution change dramatically. Approximately

$$C_{CMC} \approx C_1 \text{ so}$$

$$C_m = \frac{1}{m} (C_T - C_{CMC})$$

and

$$C_1 = \frac{1}{nK} (C_T - C_{CMC})^{1/n}$$

Finally, we get

$$J_T = -D \nabla C_T = - \left[ D_m + \frac{D_1 (nK)^{-1/n}}{n(C_T - C_{CMC})} \right] \nabla C_T \quad (18)$$

This works very well for non-ionic detergents. It does not work for ionic detergents at low ionic strength.

### Isodesmic Association

Here aggregation occurs 1 molecule at a time

$$C_i = KC_{i-1} C_1 \quad (19)$$

where  $K$  is equilibrium constant assumed independent of size

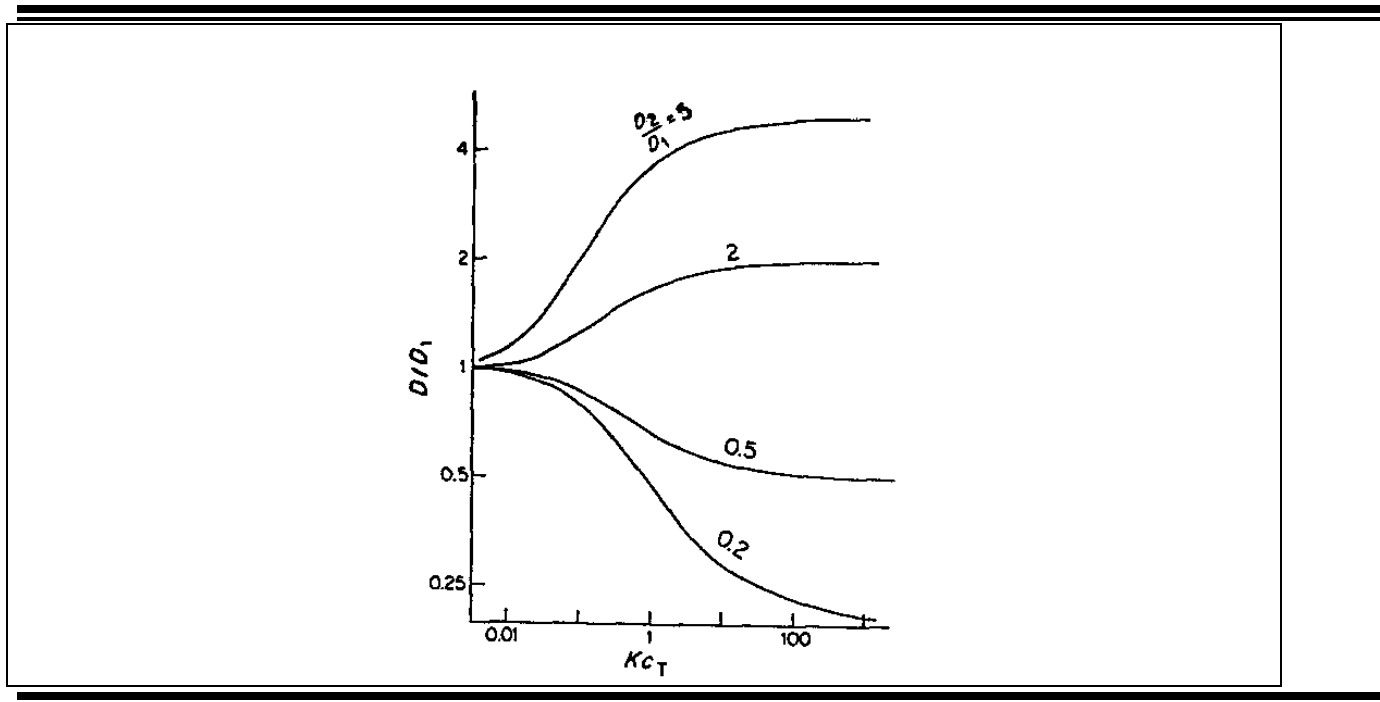
$$C_T = \sum_{i=1}^{\infty} i C_i = \frac{C_1}{(1 - KC_1)^2} \quad (20)$$

This yields

$$J_T = -D \nabla C_T = - \left\{ \begin{array}{l} D_1 - KC_T (4D_1 - 4D_2) + \\ K^2 C_T^2 (15D_1 - 24D_2 + 9D_3) \\ -K^3 C_T^3 (56D_1 - 112D_2 + 72D_3 + 16D_4) + \dots \end{array} \right\} \nabla C_T \quad (21)$$

$$J_T = -D_1 \nabla C_1 + nD_m \nabla C_m$$

**FIGURE 7A-1:** The diffusion coefficient of a dimerizing solute. As a solute dimerizes, its average diffusion coefficient changes from that of the monomer to that of the dimer. The concentration  $c_T$  at which this occurs is roughly the reciprocal of the association constant  $K$ .

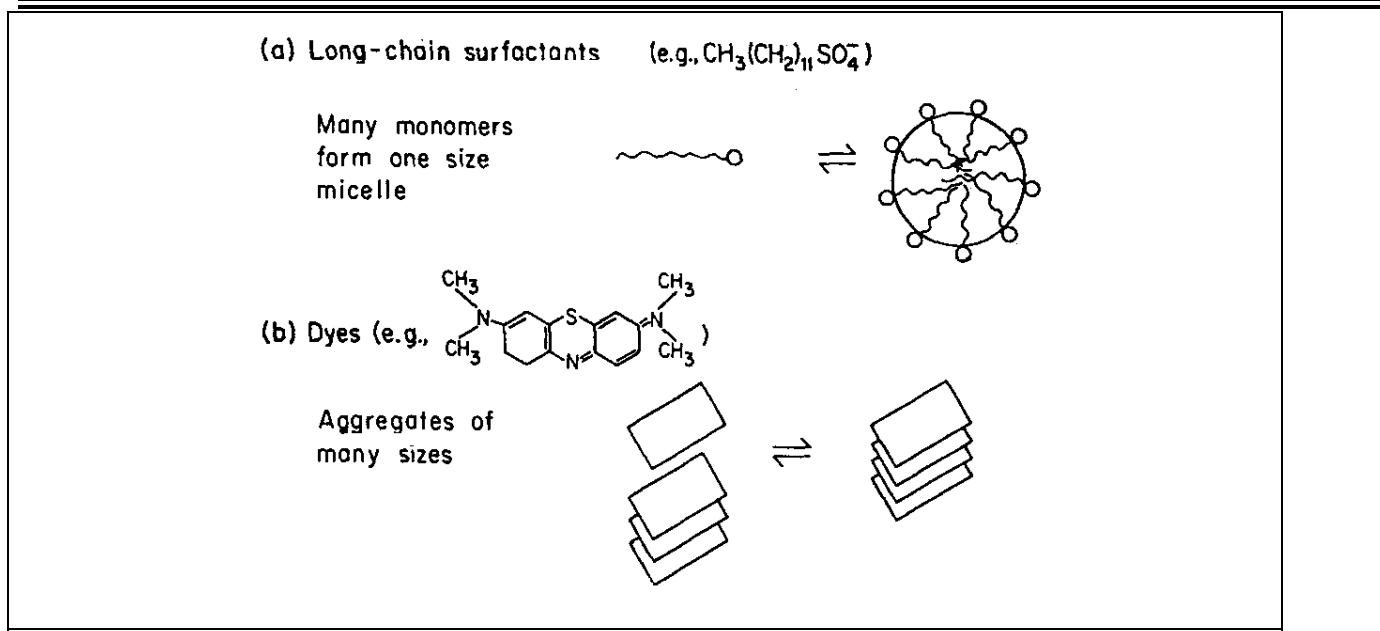


**TABLE 7-1:** Ionic diffusion coefficients in water at 25°C.

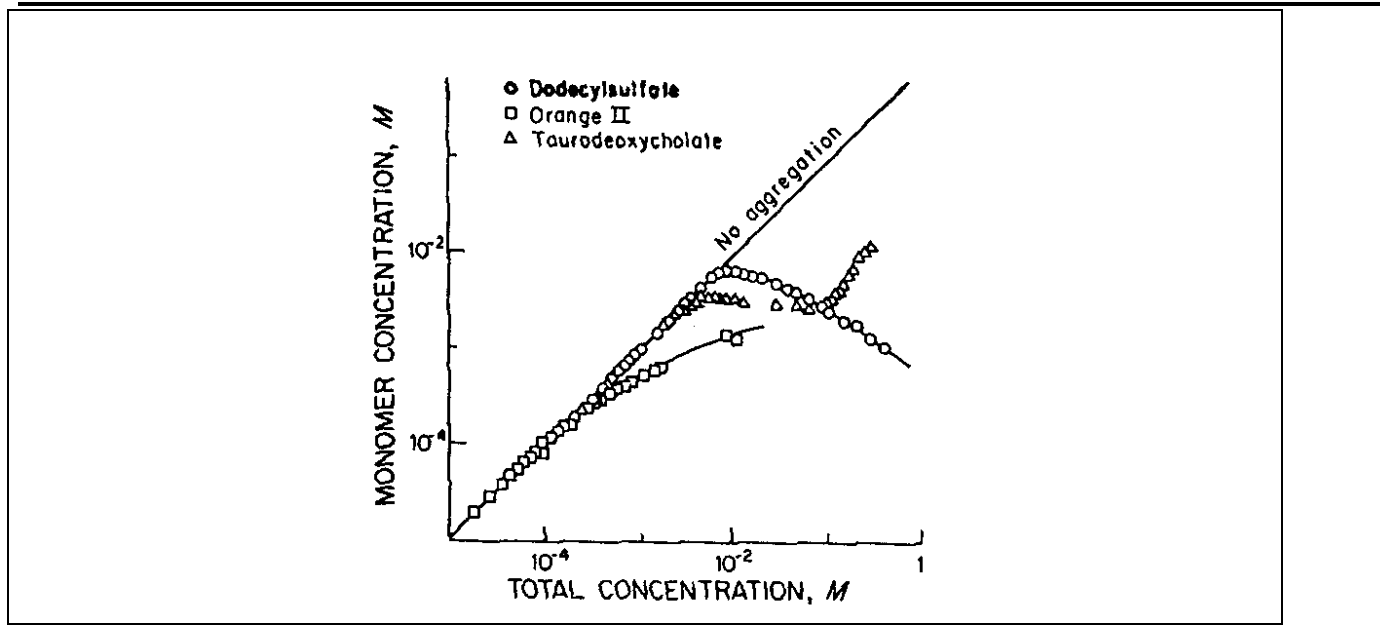
Cation <sub>i</sub>	$D_i$	Anion <sub>i</sub>	$D_i$
H <sup>+</sup>	9.31	OH <sup>-</sup>	5.28
Li <sup>+</sup>	1.03	F <sup>-</sup>	1.47
Na <sup>+</sup>	1.33	Cl <sup>-</sup>	2.03
K <sup>+</sup>	1.96	Br <sup>-</sup>	2.08
Rb <sup>+</sup>	2.07	I <sup>-</sup>	2.05
Cs <sup>+</sup>	2.06	NO <sub>3</sub> <sup>-</sup>	1.90
Ag <sup>+</sup>	1.65	CH <sub>3</sub> COO <sup>-</sup>	1.09
NH <sub>4</sub> <sup>+</sup>	1.96	CH <sub>3</sub> CH <sub>2</sub> COO <sup>-</sup>	0.95
N(C <sub>2</sub> H <sub>5</sub> ) <sub>4</sub> <sup>+</sup>	0.52	B(C <sub>6</sub> H <sub>5</sub> ) <sub>4</sub> <sup>-</sup>	0.53
Ca <sup>2+</sup>	0.79	SO <sub>4</sub> <sup>2-</sup>	1.06
Mg <sup>2+</sup>	0.71	CO <sub>3</sub> <sup>2-</sup>	0.92
La <sup>3+</sup>	0.62	Fe(CN) <sub>6</sub> <sup>4-</sup>	0.98

<sup>a</sup> Values at infinite dilution in 10<sup>-5</sup> cm<sup>2</sup>/sec. Calculated from data of Robinson and Stokes (1960).

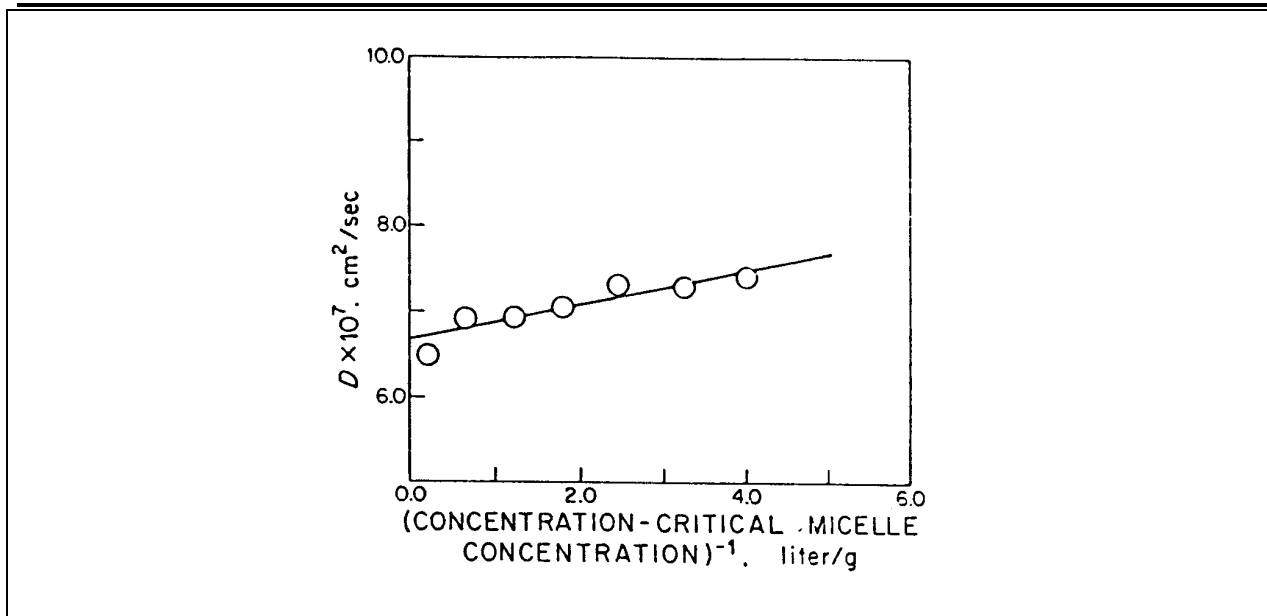
**FIGURE 7A-2: Micelle formulation and isodesmic aggregation.** In the type of micelle formation discussed here,  $n$  monomers combine to form an  $n$ -mer. No other sizes are present. In isodesmic association, monomers add with equal facility to monomers or aggregates of any size.



**FIGURE 7A-3: Types of solute aggregation.** The detergent sodium dodecylsulfate aggregates abruptly to form micelles, and the dye Orange II has isodesmic aggregates (see Fig. 6.2-4). The bile salt sodium taurodeoxycholate falls between these two limits. These results were obtained using ion-selective electrodes. [Data from Kale et al. (1980).]



**FIGURE 7A.4:** Diffusion of the detergent Triton X-100 at 25°C. The variation with concentration is predicted by Eq. ????. The intercept is the micelle's diffusion coefficient, and the slope is related to the monomer's diffusion coefficient. [From Weinheimer et al., (1981), with permission]



**FIGURE 7A.5:** Diffusion of sodium dodecylsulfate (SDS) at 25°C. The diffusion coefficients in this case increase as SDS concentration and solution viscosity rise. This increase is the result of aggregation and electrostatic interaction. [Data from Weinheimer et al. (1981)].

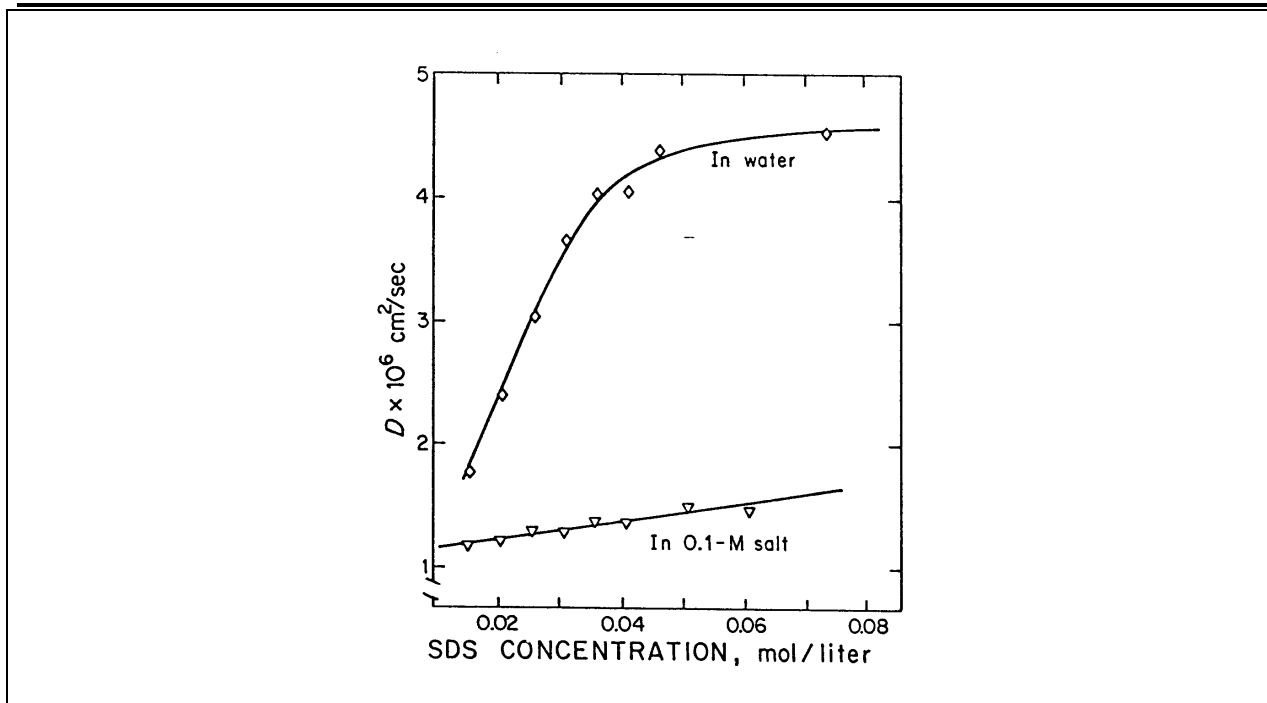


TABLE 7.1.2: Lennard-Jones potential parameters found from viscosities

Substance		$\sigma$ (Å)	$\epsilon/k$ (°K)
Ar	Argon	3.542	93.3
He	Helium	2.551	10.22
Kr	Krypton	3.655	178.9
Ne	Neon	2.820	32.8
Xe	Xenon	4.047	231.0
Air	Air	3.711	78.6
Br <sub>2</sub>	Bromine	4.296	507.9
CCl <sub>4</sub>	Carbon tetrachloride	5.947	322.7
CF <sub>4</sub>	Carbon tetrafluoride	4.662	134.0
CHCl <sub>3</sub>	Chloroform	5.389	340.2
CH <sub>2</sub> Cl <sub>2</sub>	Methylene chloride	4.898	356.3
CH <sub>3</sub> Br	Methyl bromide	4.118	449.2
CH <sub>3</sub> Cl	Methyl chloride	4.182	350
CH <sub>3</sub> OH	Methanol	3.626	481.8
CH <sub>4</sub>	Methane	3.758	148.6
CO	Carbon monoxide	3.690	91.7
CO <sub>2</sub>	Carbon dioxide	3.941	195.2
CS <sub>2</sub>	Carbon disulfide	4.483	467
C <sub>2</sub> H <sub>2</sub>	Acetylene	4.033	231.8
C <sub>2</sub> H <sub>4</sub>	Ethylene	4.163	224.7
C <sub>2</sub> H <sub>6</sub>	Ethane	4.443	215.7
C <sub>2</sub> H <sub>5</sub> Cl	Ethyl chloride	4.898	300
C <sub>2</sub> H <sub>5</sub> OH	Ethanol	4.530	362.6
CH <sub>3</sub> OCH <sub>3</sub>	Methyl ether	4.307	395.0
CH <sub>3</sub> CHCH <sub>3</sub>	Propylene	4.678	298.9
CH <sub>3</sub> CCH	Methylacetylene	4.761	251.8
C <sub>3</sub> H <sub>6</sub>	Cyclopropane	4.807	248.9
C <sub>3</sub> H <sub>8</sub>	Propane	5.118	237.1
<i>n</i> -C <sub>3</sub> H <sub>7</sub> OH	<i>n</i> -Propyl alcohol	4.549	576.7
CH <sub>3</sub> COCH <sub>3</sub>	Acetone	4.600	560.2
CH <sub>3</sub> COOCH <sub>3</sub>	Methyl acetate	4.936	469.8
<i>n</i> -C <sub>4</sub> H <sub>10</sub>	<i>n</i> -Butane	4.687	531.4
iso-C <sub>4</sub> H <sub>10</sub>	Isobutane	5.278	330.1
C <sub>2</sub> H <sub>5</sub> OC <sub>2</sub> H <sub>5</sub>	Ethyl ether	5.678	313.8
CH <sub>3</sub> COOC <sub>2</sub> H <sub>5</sub>	Ethyl acetate	5.205	521.3
<i>n</i> -C <sub>5</sub> H <sub>12</sub>	<i>n</i> -Pentane	5.784	341.1
C(CH <sub>3</sub> ) <sub>4</sub>	2,2-Dimethylpropane	6.464	193.4
C <sub>6</sub> H <sub>6</sub>	Benzene	5.349	412.3
C <sub>6</sub> H <sub>12</sub>	Cyclohexane	6.182	297.1
<i>n</i> -C <sub>6</sub> H <sub>14</sub>	<i>n</i> -Hexane	5.949	399.3
Cl <sub>2</sub>	Chlorine	4.217	316.0
F <sub>2</sub>	Fluorine	3.357	112.6
HBr	Hydrogen bromide	3.353	449
HCN	Hydrogen cyanide	3.630	569.1
HCl	Hydrogen chloride	3.339	344.7
HF	Hydrogen fluoride	3.148	330
HI	Hydrogen iodide	4.211	288.7
H <sub>2</sub>	Hydrogen	2.827	59.7
H <sub>2</sub> O	Water	2.641	809.1
H <sub>2</sub> O <sub>2</sub>	Hydrogen peroxide	4.196	289.3
H <sub>2</sub> S	Hydrogen sulfide	3.623	301.1
Hg	Mercury	2.969	750
I <sub>2</sub>	Iodine	5.160	474.2
NH <sub>3</sub>	Ammonia	2.900	558.3
NO	Nitric oxide	3.492	116.7
N <sub>2</sub>	Nitrogen	3.798	71.4
N <sub>2</sub> O	Nitrous oxide	3.828	232.4
O <sub>2</sub>	Oxygen	3.467	106.7
PH <sub>3</sub>	Phosphine	3.981	251.5
SO <sub>2</sub>	Sulfur dioxide	4.112	335.4
UF <sub>6</sub>	Uranium hexafluoride	5.967	236.8

Source: Data from Hirschfelder et al. (1954).



**TABLE 7.1.3: The collision integral  $\Omega$**

$kT/\epsilon$	$\Omega$	$kT/\epsilon$	$\Omega$	$kT/\epsilon$	$\Omega$
0.30	2.662	1.65	1.153	4.0	0.8836
0.35	2.476	1.70	1.140	4.1	0.8788
0.40	2.318	1.75	1.128	4.2	0.8740
0.45	2.184	1.80	1.116	4.3	0.8694
0.50	2.066	1.85	1.105	4.4	0.8652
0.55	1.966	1.90	1.094	4.5	0.8610
0.60	1.877	1.95	1.084	4.6	0.8568
0.65	1.798	2.00	1.075	4.7	0.8530
0.70	1.729	2.1	1.057	4.8	0.8492
0.75	1.667	2.2	1.041	4.9	0.8456
0.80	1.612	2.3	1.026	5.0	0.8422
0.85	1.562	2.4	1.012	6	0.8124
0.90	1.517	2.5	0.9996	7	0.7896
0.95	1.476	2.6	0.9878	8	0.7712
1.00	1.439	2.7	0.9770	9	0.7556
1.05	1.406	2.8	0.9672	10	0.7424
1.10	1.375	2.9	0.9576	20	0.6640
1.15	1.346	3.0	0.9490	30	0.6232
1.20	1.320	3.1	0.9406	40	0.5960
1.25	1.296	3.2	0.9328	50	0.5756
1.30	1.273	3.3	0.9256	60	0.5596
1.35	1.253	3.4	0.9186	70	0.5464
1.40	1.233	3.5	0.9120	80	0.5352
1.45	1.215	3.6	0.9058	90	0.5256
1.50	1.198	3.7	0.8998	100	0.5130
1.55	1.182	3.8	0.8942	200	0.4644
1.60	1.167	3.9	0.8888	300	0.4360

Source: Data from Hirschfelder et al. (1954).

**TABLE 7.1.4: Atomic diffusion volumes for use in Eq. ???**

<i>Atomic and structural diffusion-volume increments <math>V_{ij}</math></i>		<i>Diffusion volumes for simple molecules <math>\Sigma V_{ij}</math></i>	
C	16.5	H <sub>2</sub>	7.07
H	1.98	He	2.88
O	5.48	N <sub>2</sub>	17.9
(N) <sup>a</sup>	5.69	O <sub>2</sub>	16.6
(Cl)	19.5	Air	20.1
(S)	17.0	Ar	16.1
Aromatic ring	-20.2	Kr	22.8
Heterocyclic ring	-20.2	CO	18.9
		CO <sub>2</sub>	26.9
		N <sub>2</sub> O	35.9
		NH <sub>3</sub>	14.9
		H <sub>2</sub> O	12.7
		(Cl <sub>2</sub> )	37.7
		(SO <sub>2</sub> )	41.1

<sup>a</sup> Parentheses indicate that the value is uncertain.

Source: Adapted from Fuller et al. (1966).

TABLE 7.2.1: Diffusion coefficients at infinite dilution in water at 25°C

Solute	$D$ ( $\cdot 10^{-5}$ cm <sup>2</sup> /sec)
Argon	2.00
Air	2.00
Bromine	1.18
Carbon dioxide	1.92
Carbon monoxide	2.03
Chlorine	1.25
Ethane	1.20
Ethylene	1.87
Helium	6.28
Hydrogen	4.50
Methane	1.49
Nitric oxide	2.60
Nitrogen	1.88
Oxygen	2.10
Propane	0.97
Ammonia	1.64
Benzene	1.02
Hydrogen sulfide	1.41
Sulfuric acid	1.73
Nitric acid	2.60
Acetylene	0.88
Methanol	0.84
Ethanol	0.84
1-Propanol	0.87
2-Propanol	0.87
<i>n</i> -Butanol	0.77
Benzyl alcohol	0.821
Formic acid	1.50
Acetic acid	1.21
Propionic acid	1.06
Benzoic acid	1.00
Glycine	1.06
Valine	0.83
Acetone	1.16
Urea	$(1.380 - 0.0782c_1 + 0.00464c_1^2)^a$
Sucrose	$(0.5228 - 0.265c_1)^a$
Ovalbumin	0.078
Hemoglobin	0.069
Urease	0.035
Fibrinogen	0.020

<sup>a</sup> Known to very high accuracy, and so often used for calibration;  $c_1$  is in moles per liter.

Source: Data from Cussler (1976) and Sherwood et al. (1975).

TABLE 7.2.2: Diffusion coefficients at infinite dilution in nonaqueous liquids

Solute <sup>a</sup>	Solvent	$D$ ( $\cdot 10^{-5}$ cm <sup>2</sup> /sec)
Acetone	Chloroform	2.35
Benzene		2.89
<i>n</i> -Butyl acetate		1.71
Ethyl alcohol (15°)		2.20
Ethyl ether		2.14
Ethyl acetate		2.02
Methyl ethyl ketone		2.13
Acetic acid	Benzene	2.09
Aniline		1.96
Benzoic acid		1.38
Cyclohexane		2.09
Ethyl alcohol (15°)		2.25
<i>n</i> -Heptane		2.10
Methyl ethyl ketone (30°)		2.09
Oxygen (29.6°)		2.89
Toluene		1.85
Acetic acid	Acetone	3.31
Benzoic acid		2.62
Nitrobenzene (20°)		2.94
Water		4.56
Carbon tetrachloride	<i>n</i> -Hexane	3.70
Dodecane		2.73
<i>n</i> -Hexane		4.21
Methyl ethyl ketone (30°)		3.74
Propane		4.87
Toluene		4.21
Benzene	Ethyl alcohol	1.81
Camphor (20°)		0.70
Iodine		1.32
Iodobenzene (20°)		1.00
Oxygen (29.6°)		2.64
Water		1.24
Carbon tetrachloride		1.50
Benzene	<i>n</i> -Butyl alcohol	0.988
Biphenyl		0.627
<i>p</i> -Dichlorobenzene		0.817
Propane		1.57
Water		0.56
Acetone (20°)	Ethyl acetate	3.18
Methyl ethyl ketone (30°)		2.93
Nitrobenzene (20°)		2.25
Water		3.20
Benzene	<i>n</i> -Heptane	3.40

<sup>a</sup> Temperature 25°C except as indicated.  
 Source: Data from Reid et al. (1977).

FIGURE 7A.5: Alternatives to Stokes-Einstein equation for diffusion in liquids <sup>a,b</sup>

Authors	Origin	Basic equation	Viscosity variation	Solute size variation	Remarks
Sutherland (1905)	Parallel to Stokes-Einstein, but "no stick" at sphere's surface	$D = \frac{k_B T}{4\pi\mu R_0}$	$\mu^{-1}$	$R_0^{-1}$	Always mentioned but rarely used
Glasstone et al. (1941)	Diffusion as a rate process	$D = \frac{k_B T}{2\mu R_0}$	$\mu^{-1}$	$R_0^{-1}$	Smaller coefficient; closer to some experimental results
Scheibel (1954) <sup>c,d</sup>	Empirical	$D = \frac{AT}{\mu(\bar{V}_1)^{1/3}} \left[ 1 + \left( \frac{3\bar{V}_2}{\bar{V}_1} \right)^{2/3} \right]$	$\mu^{-1}$	Equivalent to $R_0^{-1}$ for large solutes and $R_0^{-3}$ for small ones	Variation with solute size is the interesting feature of this equation
Wilke & Chang (1955) <sup>c,e</sup>	Empirical	$D = \frac{7.4 \cdot 10^{-8} (\phi \bar{M}_2)^{1/2} T}{\mu_2 \bar{V}_1^{0.6}}$	$\mu^{-1}$	Equivalent to $R_0^{-1.8}$	Factor $\phi$ for solute-solvent interaction
King et al. (1965) <sup>e</sup>	Empirical	$D = 4.4 \cdot 10^{-8} \frac{T}{\mu_2} \cdot \left( \frac{\bar{V}_2}{\bar{V}_1} \right)^{1/6} \left( \frac{\Delta H_{vap,2}}{\Delta H_{vap,1}} \right)$		$R_0$	Not suitable for viscous solvents or aqueous systems

<sup>a</sup> The subscripts 1 and 2 indicate the solute and solvent, respectively.

<sup>b</sup> These relations are accurate within about 10% for water and 20% for most organics, but they are often inaccurate for alcohols and other hydrogen-bonded solvents.

<sup>c</sup> Specific units implied are  $D$  [=] cm<sup>2</sup>/sec;  $T$  [=] °K;  $\mu$  [=] 10<sup>-2</sup> g/cm-sec;  $V_i$  [=] cm<sup>3</sup>/g-mol.

<sup>d</sup> The  $\bar{V}$  are the molar volumes at the boiling points. The constant  $A$  equals  $8.2 \cdot 10^{-8}$ , except as follows:  $25.2 \cdot 10^{-8}$  for water if  $\bar{V}_1 < \bar{V}_2$ ;  $18.9 \cdot 10^{-8}$  for benzene when  $\bar{V}_1 < 2\bar{V}_2$ ;  $17.5 \cdot 10^{-8}$  for others if  $\bar{V}_1 < 2.5\bar{V}_2$ .

<sup>e</sup> The factor  $\phi$  has the following values: 2.26 for water, 1.9 for methanol, 1.5 for ethanol, and 1.0 for non-hydrogen-bonded solvents.