Molecular Diffusion Coefficients of Organic Compounds in Water at Different Temperatures

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Molecular (or tracer) diffusion coefficient data were obtained for 2-naphthol, benzoic acid, salicylic acid, camphor, and cinnamic acid in water at temperatures that differ significantly from ambient value. Experimental values were determined for the dissolution of 2-naphthol in water at 283 to 368 K, of benzoic acid in water at 283 to 338 K, of salicylic acid in water at 283 to 343 K, of camphor in water at 283 to 318 K, and of cinnamic acid in water at 283 to 318 K. Empirical correlations are presented for the prediction of molecular diffusion coefficient over the entire range of temperatures studied, and they are shown to predict the obtained data with very good accuracy.

1. Introduction

Molecular diffusion is the basic physical mechanism undefsrlying mass-transfer processes, even when convection comes into play. As a result, values of the molecular (or tracer) diffusion coefficient (D_m) are required for mass-transfer calculations, and extensive tabulations of this parameter have been prepared in the past.[1,2] Equations for the prediction of D_m are also available, and, in general, they have reasonable accuracy.[3] Nevertheless, it is important to determine values D_m experimentally in atypical instances, such as temperatures above ambient.

The experimental technique described by Delgado et al.[4] has been successfully applied for determining diffusion coefficients in gas and liquid systems. This technique is based on the process of mass transfer from a soluble solid sphere buried in a packed bed of inert particles (sand or glass "ballotini") through which fluid is forced to flow continuously. When these processes are performed with very low fluid velocities, the rates of mass transfer are strongly determined by molecular diffusion, and the experiment may be used to provide an accurate method for the measurement of the diffusion coefficient.

2. Theory

Consider the situation of a soluble sphere (of diameter d_1) immersed in a packed bed of small inert particles (with diameter d and porosity ε) and exposed to a constant low fluid flow with average interstitial velocity u_0. The solute still diffuses away from the surface of the sphere, but the rate of mass transfer is now enhanced, since the solute is continuously swept away by the moving fluid. The surfaces of equal concentration are no longer spheres. For the conditions of interest in the present work, the expression[4]

$$\frac{Sh'}{\varepsilon} = \left[4 + \frac{4}{5} \left(\frac{u_0 d \, d_1}{D'_m \, d} \right)^{2/3} + \frac{4}{\pi} \left(\frac{u_0 d \, d_1}{D'_m \, d} \right) \right]^{1/2} \quad \text{(Eq 1)}$$

has been shown to give accurate values of Sh'/ε ($= kd_1/\varepsilon D'_m$), where k is the mass-transfer rate with accuracy attested by experimental values lying within 2% of the theoretical values over the range of $u_0 d/D'_m < 0.2$.

Weighing the sphere (with initial mass m_0) at the end of the time interval (mass m_t) gives the rate of dissolution as $(m_0 - m_t)/\Delta t$, and the mass-transfer coefficient may be calculated from

Nomenclature	
c^*	Saturation concentration of solute
c_{out}	Solute concentration in the outlet stream
d	Diameter of inert particles
d_1	Diameter of active sphere
D_m	Molecular diffusion coefficient
D'_m	Effective molecular diffusion coefficient ($= D_m/\sqrt{2}$)
k	Average mass-transfer coefficient
m_0	Initial weight of active sphere
m_t	Final weight of active sphere
Q	Volumetric flow rate of water
Sh'	Sherwood number ($= kd_1/D'_m$)
t	Time
T	Absolute temperature
u_0	Interstitial velocity (far from the active sphere)
ε	Bed voidage

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$$k = \frac{m_0 - m_t}{\Delta t \pi d_1^2 c^*} \qquad \text{(Eq 2)}$$

where is c^* the solubility of the organic compound in water.

In each experiment, measurement gives k (through Eq 2), d_1, u_0, and ε and the value of D_m' ($= D_m/\sqrt{2}$) has to be found solving the following equation

$$\frac{m_0 - m_t}{\Delta t} \frac{1}{\varepsilon \pi d_1 c^*} = D_m' \left[4 + \frac{4}{5} \left(\frac{u_0 d_1}{D_m'} \right)^{2/3} + \frac{4}{\pi} \left(\frac{u_0 d_1}{D_m'} \right) \right]^{1/2}$$

$$\text{(Eq 3)}$$

3. Experimental Section

A schematic diagram of the experimental setup used to measure diffusion coefficients is sketched in Fig. 1 and is discussed in detail elsewhere.[4] In experiments at temperatures differing from ambient, the test column has to be kept in a constant temperature bath maintained at ± 0.2 K. The experimental measurements of mass transfer were performed on the dissolution of individual spheres, buried in beds of sand through which a metered stream of distilled water (which had been previously deaerated under vacuum) was forced to flow steadily.

Each sphere was weighed accurately (initial mass, m_0), in an analytical balance, before burying it (with some care, to avoid unwanted erosion) near the middle of the packed bed, which had been previously immersed in the constant temperature bath for a long enough period of time.

The soluble spheres were prepared from Pro analysis (*p.a.*) grade material, which was molten and then poured into molds made of silicone rubber. If any slight imperfections showed on the surface of the spheres, they were easily removed by rubbing with fine sand paper. The diameter of each sphere was measured, and it was typically about 20 mm.

The water flow rate was kept constant for a time Δt, following which the soluble sphere was removed for weighing (final mass, m_t). This requirement meant that

extremely low velocities of liquid had to be observed in the experiments (typically between 6×10^{-4} and 3×10^{-3} mm/s). As a result, the flow rate of liquid was so low (typically, 1 to 5 mm^3/s) that it was best measured by timing the amount discharged on a small beaker placed on the plate of an analytical balance. Also, it took several hours to reach the steady-state value of solute in the outlet stream, c_{out}. The c_{out} value was continuously measured to give the rate of dissolution, by means of a UV/VIS spectrophotometer or gas chromatography (camphor). When steady state was reached, the rate of dissolution of the solid could be found directly from $n = Qc_{out}$ where Q is the measured volumetric flow rate of water.

In the interpretation and correlation of the experimental data reported, it is important to know the solubility of the organic compounds in water in the range of temperatures studied. Data from a number of sources[5-11] are plotted in Fig. 2 to Fig. 6 for the systems used, and the latter also provide the fitted functions

$$c^* (\text{kg/m}^3) = 5.93 \times 10^{-6} \exp (0.0394 \, T(\text{K}))$$

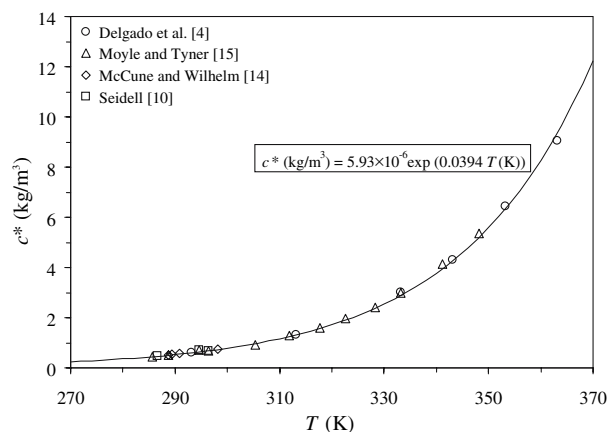$$(2 \text{ - naphthol in water}, R^2 = 0.998) \qquad \text{(Eq 4)}$$
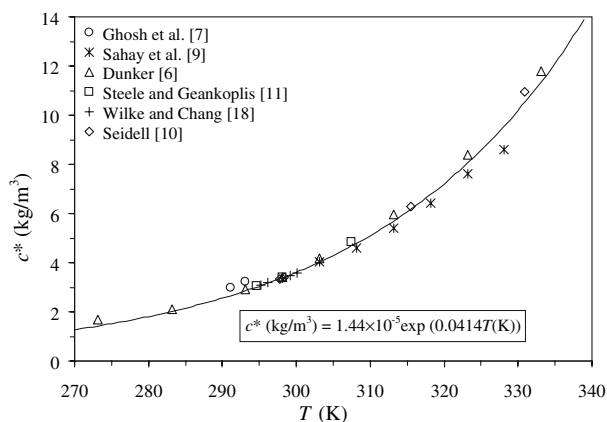

Fig. 2 Solubility of 2-naphtol in water
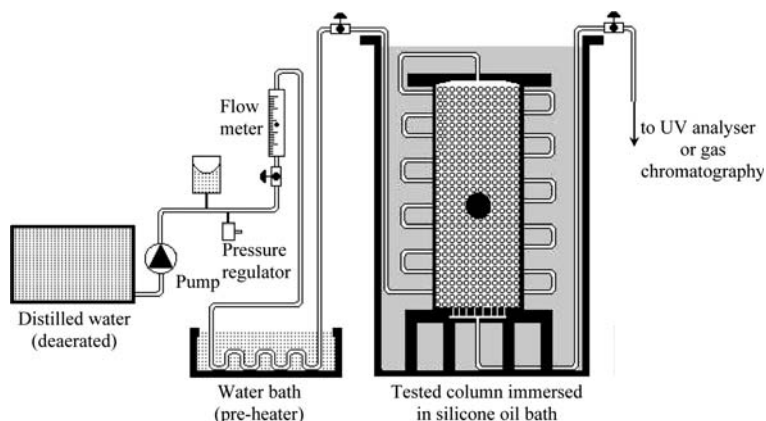
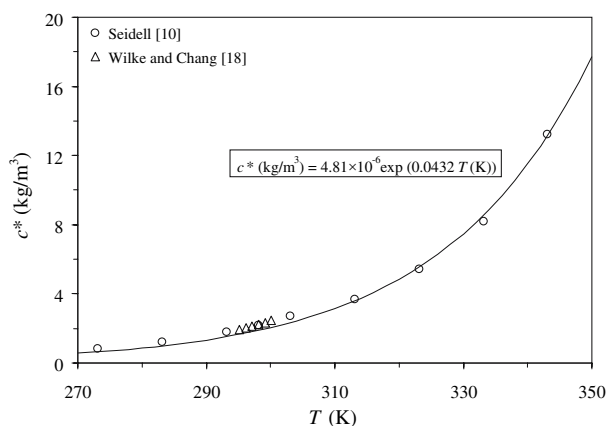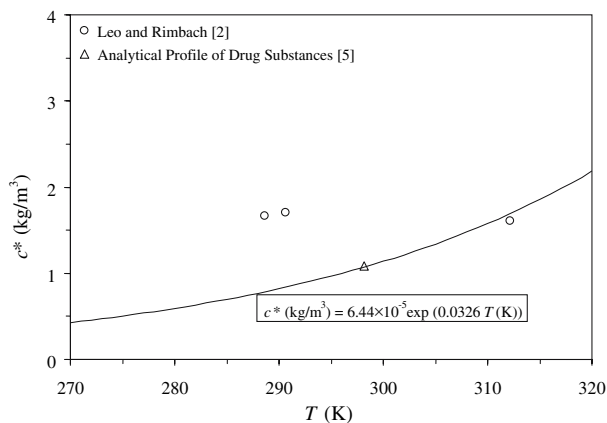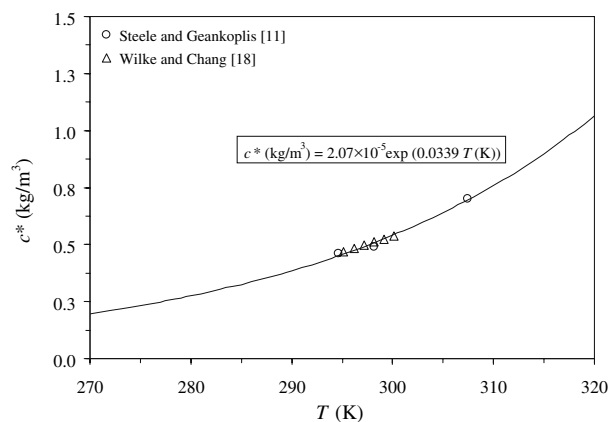**Fig. 1** Schematic diagram of the experimental setup

Fig. 3   Solubility of benzoic acid in water

Fig. 4   Solubility of salicylic acid in water

Fig. 5   Solubility of camphor in water

$$c^*(\text{kg/m}^3) = 1.44 \times 10^{-5} \exp (0.0414 \ T(\text{K}))$$
$$\text{(benzoic acid in water, } R^2 = 0.985) \qquad \text{(Eq 5)}$$

Fig. 6   Solubility of cinnamic acid in water

$$c^*(\text{kg/m}^3) = 4.81 \times 10^{-6} \exp (0.0432 \ T(\text{K}))$$
$$\text{(salicylic acid in water, } R^2 = 0.997) \qquad \text{(Eq 6)}$$

$$c^*(\text{kg/m}^3) = 6.44 \times 10^{-5} \exp (0.0326 \ T(\text{K}))$$
$$\text{(camphor in water)} \qquad \text{(Eq 7)}$$

$$c^*(\text{kg/m}^3) = 2.07 \times 10^{-5} \exp (0.0339 \ T(\text{K}))$$
$$\text{(cinnamic acid in water, } R^2 = 0.982) \qquad \text{(Eq 8)}$$

and these are drawn in the figures (R^2 is the symbol used to represent the correlation coefficient of the expressions proposed. R^2 is used as a measured of "goodness" of fit).

4. Results

The experimental results are in excellent agreement with the experimental values of the molecular (or tracer) diffusion coefficient measured by other authors,[12-18] and repeated measurements of D_m did not differ by more than 10%. Other experimental methods used to measure D_m, such as Taylor dispersion technique, diaphragm cells and interferometry,[19,20] give a precision higher than 1%; however, the experimental method presented has the added interest of easily providing data at temperatures that differ significantly from ambient values.

The experiments were performed with water and a sphere, of 20 mm internal diameter, placed in a bed of sand of 0.322 mm average diameter. The interstitial water velocities were in the range 5.7×10^{-4} to 3.5×10^{-3} mm/s, and the experimental values of D_m are given as a function of temperature in the plots of Fig. 7 and 11.

Table 1 contains the results of the molecular (or tracer) diffusion coefficients of five organic compounds at different temperatures in water. In all cases, diffusion coefficients increase with increasing temperature, as expected. Figures 7 to 11 show the very good agreement between the results
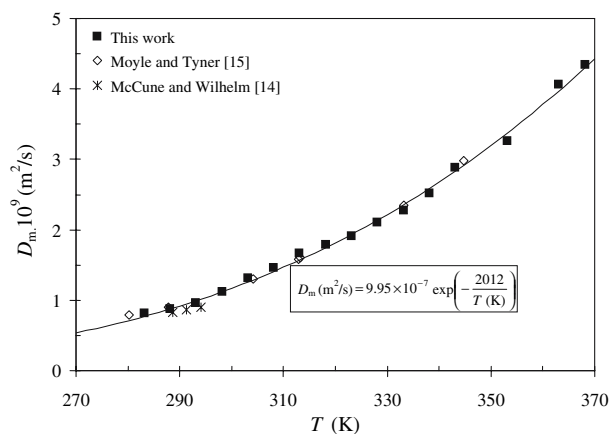
Fig. 7 Variation of D_m with T for 2-naphtol in water

Fig. 8 Variation of D_m with T for benzoic acid in water

Table 1 Experimental values of D_m of organic compounds in water, at different temperatures

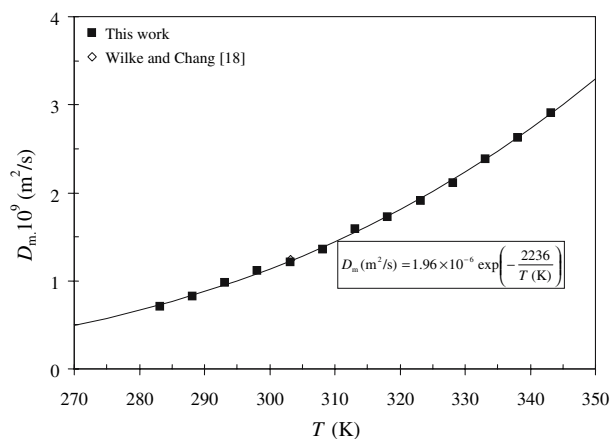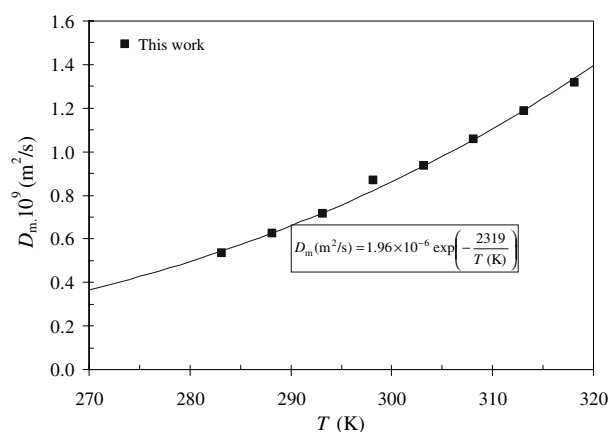|	D_m (m^2/s) $\times 10^9$				
T (K)	2-Naphthol	Benzoic acid	Salicylic acid	Camphor	Cinnamic acid
283.15	0.82	0.67	0.71	0.53	0.60
288.15	0.87	0.74	0.82	0.62	0.71
293.15	0.96	0.91	0.98	0.72	0.88
298.15	1.12	1.01	1.11	0.87	0.99
303.15	1.32	1.12	1.21	0.94	1.12
308.15	1.46	1.25	1.36	1.06	1.32
313.15	1.66	1.43	1.58	1.19	1.54
318.15	1.79	1.62	1.72	1.32	1.72
323.15	1.91	1.81	1.90	⋯	⋯
328.15	2.11	2.02	2.11	⋯	⋯
333.15	2.27	2.25	2.39	⋯	⋯
338.15	2.52	2.48	2.62	⋯	⋯
343.15	2.88	⋯	2.90	⋯	⋯
353.15	3.26	⋯	⋯	⋯	⋯
363.15	4.06	⋯	⋯	⋯	⋯
368.15	4.34	⋯	⋯	⋯	⋯

Fig. 9 Variation of D_m with T for salicylic acid in water

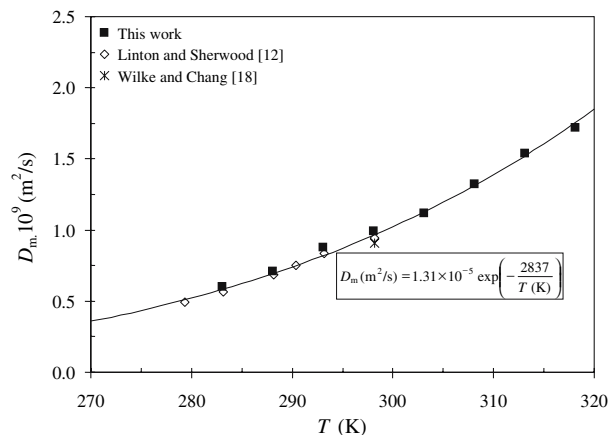**Fig. 10** Variation of D_m with T for camphor in water

Fig. 11 Variation of D_m with T for cinnamic acid in water

obtained by the present technique and the experimental values of the diffusion coefficient measured by other researchers[12-17] at different temperatures, and this is an indication of the accuracy of the proposed method.

Moyle and Tyner[15] propose the following equation to represent their data for 2-naphthol in water (see Fig. 7)

$$D_m(\text{m}^2/\text{s}) = 9.95 \times 10^{-7} \exp\left(-\frac{2012}{T\,(\text{K})}\right) \qquad \text{(Eq 9)}$$

and the data are within 8% of this line.

For benzoic acid in water, Lozar et al.[13] propose (see Fig. 8)

$$D_m(\text{m}^2/\text{s}) = 2.20 \times 10^{-6} \exp\left(-\frac{2295}{T\,(\text{K})}\right) \qquad \text{(Eq 10)}$$

and the data are within 5% of this equation.

For salicylic acid, camphor, and cinnamic acid with water, the expressions proposed are based on the experimental values obtained and some values reported in literature.[12,18] The regression equations were programmed using Microcal Origin software (version 7.0). For salicylic acid in water (see Fig. 9) we propose the following equation ($R^2 = 0.998$ and $p < 0.0001$), $p = p$ value used in statistical hypothesis testing to known the probability of obtaining a result at least as extreme as a given data point.

$$D_m(\text{m}^2/\text{s}) = 1.96 \times 10^{-6} \exp\left(-\frac{2236}{T\,(\text{K})}\right) \qquad \text{(Eq 11)}$$

for camphor in water, see Fig. 10, ($R^2 = 0.994$ and $p < 0.0001$)

$$D_m(\text{m}^2/\text{s}) = 1.96 \times 10^{-6} \exp\left(-\frac{2319}{T\,(\text{K})}\right) \qquad \text{(Eq 12)}$$

and for cinnamic acid in water ($R^2 = 0.992$ and $p < 0.0001$), the following regression is proposed (see Fig. 11)

$$D_m(\text{m}^2/\text{s}) = 1.31 \times 10^{-5} \exp\left(-\frac{2837}{T\,(\text{K})}\right) \qquad \text{(Eq 13)}$$

5. Conclusions

The results show that it is possible to obtain good results for the value of the diffusion coefficient, over a range of temperatures above ambient, with a simple procedure.

The experimental values obtained for the molecular diffusion coefficient of 2-naphtol and benzoic acid in water are in good agreement with the values of Moyle and Tyner[15] and Lozar et al.,[13] respectively, and those for salicylic acid and camphor in water are in good agreement with the values proposed by Wilke and Chang[18] and Linton and Sherwood,[12] respectively.

When these processes are performed with very low fluid velocities ($u_0 d/D_m' < 0.2$), the rates of mass transfer are strongly determined by molecular diffusion, and the method presented proves to be accurate for the measurement of diffusion coefficients of low solubility solutes in water, so

that it does not correspond to a significant variation in the diameter of the sphere. It is important to remember that for higher-solubility solutes, natural convection near the surface of the dissolving solids may become significant, thus invalidating the method.

Acknowledgment

References

1. R.H. Perry and D. Green, *Perry's Chemical Engineer's Handbook*, 6th ed., McGraw-Hill International Editions, 1984
2. National Research Council, *International Critical Tables*, Vol 5, McGraw-Hill International Editions, 1929
3. R.C. Reid, J.M. Prausnitz, and B.E. Poling, *The Properties of Gases and Liquids*, 4th ed., McGraw-Hill International Editions, 1988
4. J.M.P.Q. Delgado, M.A. Alves, and J.R.F. Guedes de Carvalho, A Simple and Inexpensive Technique to Measure Molecular Diffusion Coefficients, *J. Phase Equilib. Diff.*, 2005, **26**(5), p 447-451
5. G. Clarke, *Analytical Profile of Drug Substances*, Vol 9, K. Florey, Ed., Academic Press, 1990
6. C. Dunker, *Benzoic Acid*, in *Kirk-Othmer Encyclopedia of Chemical Technology*, Vol 3, 2nd ed., Interscience Publishers, 1964, p 422
7. U.K. Ghosh, S. Kumar, and S.N. Upadhyay, Diffusion Coefficient in Aqueous Polymer Solutions, *J. Chem. Eng. Data*, 1991, **36**(4), p 413-417
8. H. Leo and G.J. Rimbach, *Soc. Chem. Ind.-London*, 1919, **38**(2), p 738A-740A (referenced in Ref 2)
9. H. Sahay, S. Kumar, S.N. Upadhyay, and Y. Upadhyay, Solubility of Benzoic Acid in Aqueous Polymeric Solutions, *J. Chem. Eng. Data*, 1981, **26**(2), p 181-183
10. A. Seidell, *Solubilities of Organic Compounds*, 3rd ed., D. Van Nostrand Co., 1941
11. L.R. Steele and C.J. Geankoplis, Mass Transfer from a Solid Sphere to Water in Highly Turbulent Flow, *AIChE J.*, 1959, **5**(2), p 178-181
12. W.H. Linton and T.K. Sherwood, Mass Transfer from Solid Shapes to Water in Streamline and Turbulent Flow, *Chem. Eng. Prog.*, 1950, **46**(5), p 258-264
13. J. Lozar, C. Laguerie, and J.P. Couderc, Diffusivité de L'acide Benzoique dans L'eau: Influence de la Temperature, *Can. J. Chem. Eng.*, 1975, **53**(2), p 200-203, in French
14. L.K. McCune and R.H. Wilhelm, Mass and Momentum Transfer in Solid-Liquid System, *Ind. Eng. Chem. Res.*, 1949, **41**(4), p 1124-1134
15. M.P. Moyle and M. Tyner, Solubility and Diffusivity of 2-Naphtol in Water, *Ind. Eng. Chem. Res.*, 1953, **45**(8), p 1794-1797
16. R.A. Noulty and D.G. Leaist, Diffusion Coefficient of Aqueous Benzoic Acid at 25 °C, *J. Chem. Eng. Data*, 1987, **32**(4), p 418-420
17. V. Vanadurongwan, C. Laguerie, and J.P. Couderc, Diffusivité Moienne de L'acide Benzoique dans L'eau entre la Dilution Infinie et la Saturation—Influence de la Temperature, *Can. J. Chem. Eng.*, 1976, **54**(4), p 460-463, in French
18. C.R. Wilke and P. Chang, Correlation of Diffusion Coefficients in Dilute Solutions, *AIChE J.*, 1955, **1**(2), p 264-270

19. H.J.V. Tyrrell and K.R. Harris, *Diffusion in Liquids*. Butterworth, London, 1984

20. P.J. Dunlop, K.R. Harris, and D.J. Young, Experimental Methods for Studying Diffusion in Gases, Liquids and Solids, in B.W. Rossiter and R.C. Baetzold, Ed., *Physical Methods of Chemistry*, Vol 6, 2nd ed., *Determination of Thermodynamic Properties*, John Wiley & Sons 1992, Chapter 3, p 175-282