15. Appendix D.

Molecular diffusivity of electrolytes can be calculated from Nernst equation

$$D = \frac{2 \cdot R \cdot T}{F^2} \cdot \frac{\lambda_+ \cdot \lambda_-}{\lambda_+ + \lambda_-}, \qquad \textbf{(D.1)}$$

where λ_+ and λ_- are equivalent conductivity of monovalent cation and anion respectively, **R** is a universal gas constant equal to 8.314 J/mol/K and **F** is Faraday's constant equal to 96500 C/mol. Equation (D.1) is valid for diluted solutions of electrolytes.

The equivalent conductivity of hydrogen ions equals 349.8 S/(cm·mol), whereas the equivalent conductivity of chlorine ions equals 76.3 S/(cm·mol) in aqueous solutions at 298.15 K. Thus molecular diffusivity of hydrochloric acid computed from equation (D.1) is $D_{HCl}=3.33 \cdot 10^{-9}$ m^2/s.

The equivalent conductivity of sodium ions equals 50.1 S/(cm·mol), whereas the equivalent conductivity of hydroxyl ions equals 197.6 S/(cm·mol) at 298.15 K and finaly from equation (D.1) one receives $D=2.13 \cdot 10^{-9}$ m^2/s.

Wilke-Chang method was used to compute molecular diffusivity of ethyl chloroacetate. Wilke-Chang relation is given by:

$$D_A = 7.4 \cdot 10^{-15} \cdot \frac{T \cdot (\chi_B \cdot M_B)^{0.5}}{\mu_B \cdot V_{SA}^{0.6}}, \qquad \textbf{(D.2)}$$

where subscripts **A** and **B** reffer to solute and solvent respectively. According to Le Bass rule molar volume of boiling ethyl chroactetate, $\mathbf{V_{SA}}$, equals 126.5 cm^3/mol. Association coefficient for water, $\boldsymbol{\chi_B}$, equals 2.6, water viscosity, $\boldsymbol{\mu_B}$, at 298.15 K equals $0.8913 \cdot 10^{-3}$ Pa·s and its molecular weight, $\mathbf{M_B}$, is equal to 18 g/mol. In this case equation (D.2) yields $D_{ester}=0.928 \cdot 10^{-9}$ m^2/s.

Physical and chemical data used in the calculations, and expressions (D.1) and (D.2) were taken from Reid et al. [81].