

Diffusion in Binary Nonelectrolyte Solutions

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For binary liquid mixtures of nonelectrolytes, we consider the dependence of the diffusion coefficient on composition and temperature, making use of an analytical expression for the kinematic diffusion coefficient (diffusion coefficient divided by thermodynamic factor). We present recent experimental data for the ideal liquid system chlorobenzene + bromobenzene and for the non-ideal liquid system water + methanol as well as literature data for other non-ideal mixtures.

The diffusion coefficient (interdiffusion coefficient) D of a binary liquid mixture is a function of composition and temperature while the dependence on pressure may usually be neglected.

For a binary nonelectrolyte solution it is expedient to write [1]

$$D = D^* B. \quad (1)$$

Here D^* is the kinematic diffusion coefficient and B a thermodynamic factor given by

$$B = 1 + \left(\partial \ln f_i / \partial \ln x_i \right)_{T,P}, \quad (2)$$

x_i denoting the mole fraction, f_i the activity coefficient (on the mole fraction scale) of component i ($i = 1, 2$), T the temperature, and P the pressure.

We now use an exponential expression for D^* (instead of that commonly applied to D):

$$D^* = D^0 \exp(-E^*/RT), \quad (3)$$

where D^0 and E^* are functions of the composition and R denotes the gas constant. E^* is analogous to, but not identical with, the activation energy in the exponential expression for D .

We derive from (1) and (2) for an *ideal mixture* ($f_i = 1$):

$$B = 1, \quad D = D^* \quad (\text{ideal mixture}). \quad (4)$$

Generalizing experimental results [2–5], referring mainly to the liquid system chlorobenzene + bromobenzene, we conclude that the following additional

relation holds for ideal mixtures:

$$D^0 = D_1^0 x_1 + D_2^0 x_2, \quad E^* = \text{const}(\text{ideal mixture}). \quad (5)$$

The constants D_1^0 and D_2^0 are the limiting values of D^0 for $x_1 = 1$ and $x_2 = 1$, respectively. The Eqs. (3), (4), and (5) imply that the diffusion coefficient varies linearly with the mole fraction x_2 or x_1 ($= 1 - x_2$).

For the ideal system chlorobenzene + bromobenzene, the available diffusion data [2, 3, 5] covering the whole range of compositions and the temperature range between 10 °C and 80 °C lead to the following values of the constants in (5):

$$\begin{aligned} D_1^0 &= 148.9 \cdot 10^{-5} \text{ cm}^2 \text{ s}^{-1}, \\ D_2^0 &= 117.8 \cdot 10^{-5} \text{ cm}^2 \text{ s}^{-1}, \\ E^* &= 11.15 \text{ kJ mol}^{-1}. \end{aligned}$$

They are only slightly different from those obtained previously [4].

For *non-ideal mixtures* ($f_i \neq 1$) the function $D(x_2)$ is no longer linear but usually exhibits a minimum or at least shows negative deviations from additivity. (Exceptions are rare.) An example for a case with a minimum is the liquid system water + methanol for which measurements of the diffusion coefficient have been carried out recently [5]. These experimental data (see Table 1) cover the whole range of compositions at 20 °C, 40 °C, and 60 °C. Unfortunately the activity coefficients given in the literature are not reliable enough for an evaluation of the diffusion data in the sense of the relations (1), (2), and (3).

Table 1. Diffusion coefficient D as a function of the mole fraction x_2 of methanol for the liquid system water + methanol at three different temperatures after Knopf [5] (a value in parenthesis refers to a second measurement).

x_2	D $10^{-5} \text{ cm}^2 \text{ s}^{-1}$		
	20 °C	40 °C	60 °C
0.007	1.38	2.23	3.22
0.100	1.08	1.76	2.54
0.200	0.89	1.37	—
0.400	0.87	1.38	2.13
0.499	0.94(0.91)	1.52	2.33
0.600	1.04	1.76	2.60
0.699	1.25	2.04	3.22
0.800	1.43	2.21	3.32
0.905	1.69	2.62	3.63
0.994	1.99(2.02)	2.84(2.87)	4.18(4.19)

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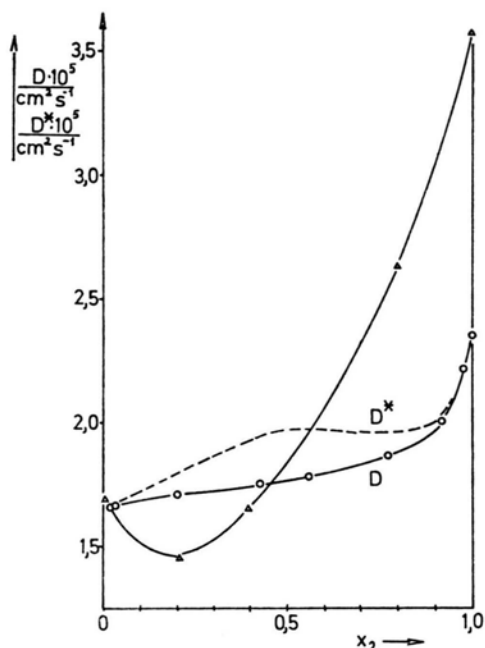


Fig. 1. Diffusion coefficient D and kinematic diffusion coefficient D^* as functions of the mole fraction x_2 of the second component at 25 °C for the liquid systems carbon tetrachloride + chloroform (O and ---) and carbon tetrachloride + acetone (Δ for D) after diffusion data due to Cordes and Steinmeier [6] and Anderson, Hall, and Babb [7], respectively, and after activity coefficients due to McGlashan, Prue, and Sainsbury [8].

We also checked published experimental results on other non-ideal liquid systems. We found that there is no binary nonelectrolyte solution where the experimental data for both the diffusion coefficients and the activity coefficients are unambiguous and self-consistent for several compositions and temper-

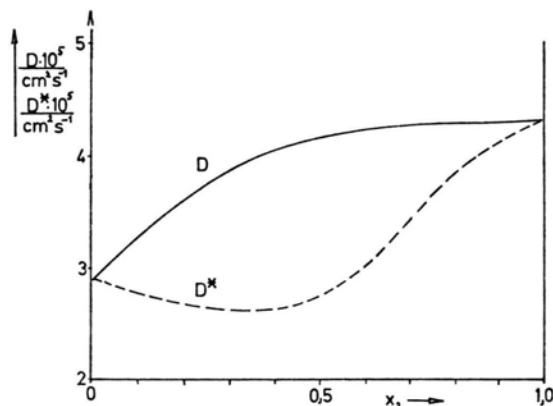


Fig. 2. Diffusion coefficient D and kinematic diffusion coefficient D^* as functions of the mole fraction x_2 of the second component for the liquid system chloroform + acetone after diffusion data (for ~ 40 °C) due to Anderson, Hall, and Babb [7] and activity coefficients (for ~ 35 °C) due to Zawadzki [9].

atures. Thus we are, at present, unable to derive the functions $D^0(x_2)$ and $E^*(x_2)$ for any non-ideal system. But we have met with some examples where, for one temperature, there are reliable data for both the diffusion coefficients and the activity coefficients, so that the functions $D(x_2)$ and $D^*(x_2)$ can be presented.

We restrict the presentation to the liquid systems carbon tetrachloride + chloroform (Fig. 1), carbon tetrachloride + acetone (Fig. 1), and chloroform + acetone (Fig. 2), where in the second case there are no reliable activity coefficients available for the temperature considered. It should be noted that in the last case the plot of $D(x_2)$ shows positive deviations from the straight line while $D^*(x_2)$ exhibits a minimum.

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