# Binary Mutual Diffusion Coefficients of Aqueous Alcohols. Methanol to 1-Heptanol

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Mutual diffusion coefficients, measured by Taylor dispersion at 25 °C, are reported for binary aqueous solutions of methanol, ethanol, isomeric propanols and butanols, 1-pentanol, 1-hexanol, and 1-heptanol. Limiting diffusion coefficients ($D^0$) for the 1-alkanols are found to decrease with alcohol molar volume $V$ approximately as $V^{-1/2}$. Although values of $D^0$ for aqueous 1-propanol and 2-propanol are nearly identical within experimental error, the limiting diffusion coefficients of the isomeric butanols differ by up to 10% and increase in the order $D^0$(2-methyl-2-propanol) < $D^0$(2-butanol) ≈ $D^0$(2-methyl-1-propanol)) < $D^0$(1-butanol). The butanol results illustrate the difficulty of predicting accurate diffusion coefficients for aqueous solutions.

## Introduction

Studies of the diffusion of alcohols in water can provide useful information about transport in associated liquid mixtures. For example, Taylor dispersion, diaphragm cells, and optical techniques have been used to measure accurate diffusion coefficients for binary aqueous solutions of methanol (Derlacki *et al.*, 1985; Easteal *et al.*, 1985; Easteal and Woolf, 1985; Lee and Li, 1991), ethanol (Dullein and Shemilt, 1961; Easteal and Woolf, 1985; Ghai *et al.*, 1973; Hammond and Stokes, 1953; Harris *et al.*, 1993; Pratt and Wakeham, 1974; Tominaga and Matsumoto, 1990), 1-propanol (Harris *et al.*, 1993; Leaist and Deng, 1992; Pratt and Wakeham, 1975; Tominaga and Matsumoto, 1990), 2-propanol (Pratt and Wakeham, 1975), 1-butanol (Lyons and Sandquist, 1953; Tominaga and Matsumoto, 1990), and 2-methyl-2-propanol (*tert*-butyl) (Harris and Lam, 1995; Tominaga and Matsumoto, 1990). Aqueous alcohol systems illustrate the dramatic consequences nonideal solution thermodynamics can have for diffusion (Ghai *et al.*, 1973; Harris *et al.*, 1993; Harris and Lam, 1995; Pratt and Wakeham, 1974, 1975).

In this paper mutual diffusion coefficients (interdiffusion coefficients) are reported for binary aqueous solutions of a series of 1-alcohols, from methanol up to heptanol. The results provide an internally consistent set of data for the change in the diffusion coefficient with alcohol chain length. Diffusion coefficients are also reported for aqueous solutions of isomeric propanols and butanols in order to study the effects of molecular shape on diffusion.

## Experimental Procedure

Solutions were prepared in calibrated volumetric flasks by dissolving weighed amounts of alcohol in distilled, deionized water. 1-Pentanol, 1-hexanol, and 1-heptanol were Sigma Chemical Co. products. The other alcohols were supplied by Caledon Laboratories. The methanol, ethanol, propanols, and 1-butanol were 99.5% pure. The other alcohols had minimum purities of 99%. Each alcohol contained <0.1% water.

Diffusion coefficients were measured by the Taylor dispersion (peak-broadening) method. At the start of each run a sample of solution containing alcohol at concentration $\bar{c} + \Delta c$ was injected into a laminar carrier stream at concentration $\bar{c}$. Dispersion of the sample in a long capillary tube generates the nearly-Gaussian concentration pulse (Aris, 1956; Taylor, 1953)

$$c(t) = \bar{c} + \frac{2\Delta c \Delta V}{\pi r^3 U}\left(\frac{3D}{\pi t}\right)^{1/2} \exp\left[-\frac{12D(t - t_R)^2}{r^2 t}\right] \quad (1)$$

at the tube outlet. $D$ is the mutual diffusion coefficient, $\Delta V$ the volume of the injected solution (20 mm$^3$), $r$ the inner radius of the dispersion tube (0.460 mm), $U$ the average flow speed (~4 mm s$^{-1}$), and $t_R$ the retention time (~7000 s). A liquid-chromatography differential refractometer detector monitored the dispersion of the eluted samples. Details of the equipment and procedure have been reported (Leaist, 1991, 1992).

Fitting the equation

$$v(t) = A_0 + A_1 t + A_2 t^{-1/2} \exp[-A_3(t - A_4)^2/t] \quad (2)$$

to measured refractometer voltages gave least-squares values for parameters $A_0$ through $A_4$. $A_2$ is the peak height relative to the fitted baseline $A_0 + A_1 t$. Including the retention time as an adjustable parameter ($A_4$) allowed for small variations in the pumping rate. Diffusion coefficients were calcuated from the simple relation $D = A_3 r^2/12$.

A total of 5−10 injections were made into each carrier solution. The injected solutions contained ≤0.050 mol dm$^{-3}$ excess alcohol relative to the carrier solution. In this range $D$ was independent of $\Delta c$, indicating that the measured diffusion coefficients represented differential values at the carrier-stream composition. Check runs on 0.100 mol dm$^{-3}$ aqueous solutions of glycine and urea gave $D$ values within 1% of accurate values measured by Gouy interferometry (Gosting and Akeley, 1952; Lyons and Thomas, 1950).

## Results and Discussion

***Aqueous 1-Alkanols.*** Table 1 gives the average diffusion coefficient determined at each composition. Values of $D$ from replicate injections were usually reproducible within ±0.5%. For heptanol, however, the precision was ±2%. The low solubility of this alcohol (~0.016 mol dm$^{-3}$) resulted in smaller dispersion peaks and poorer signal-to-noise ratios.

The reported diffusion coefficients relate alcohol fluxes to concentration gradients. It is well known, however, that

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**Table 1. Binary Mutual Diffusion Coefficients of Aqueous Alcohols at 25 °C**

| $\bar{c}$/(mol dm$^{-3}$) | $D$/(10$^{-5}$ cm$^2$ s$^{-1}$) | $\bar{c}$/(mol dm$^{-3}$) | $D$/(10$^{-5}$ cm$^2$ s$^{-1}$) |
|---|---|---|---|
| Methanol | | Ethanol | |
| 0.000 | $(1.54_5)^a$ | 0.000 | $(1.22_7)^a$ |
| 0.010 | 1.543 | 0.010 | 1.228 |
| 0.050 | 1.549 | 0.050 | 1.219 |
| 0.100 | 1.545 | 0.100 | 1.207 |
| 0.300 | 1.548 | 0.300 | 1.170 |
| | | 0.500 | 1.136 |
| | | 0.700 | 1.104 |
| 1-Propanol | | 2-Propanol | |
| 0.000 | $(1.05_9)^a$ | 0.000 | $(1.02_9)^a$ |
| 0.010 | 1.062 | 0.010 | 1.029 |
| 0.050 | 1.046 | 0.050 | 1.014 |
| 0.100 | 1.031 | 0.100 | 1.016 |
| 0.300 | 0.980 | 0.300 | 0.954 |
| 0.500 | 0.933 | 0.500 | 0.915 |
| 0.700 | 0.889 | 0.700 | 0.881 |
| 1-Butanol | | 2-Butanol | |
| 0.000 | $(0.96_0)^a$ | 0.000 | $(0.94_1)^a$ |
| 0.050 | 0.949 | 0.050 | 0.932 |
| 0.100 | 0.926 | 0.100 | 0.914 |
| 0.300 | 0.883 | 0.300 | 0.851 |
| | | 0.500 | 0.800 |
| | | 0.700 | 0.754 |
| *2*-Methyl-1-propanol (Isobutanol) | | *2*-Methyl-*2*-propanol (*tert*-Butyl Alcohol) | |
| 0.000 | $(0.95_0)$ | 0.000 | $(0.87_6)$ |
| 0.025 | 0.941 | 0.010 | 0.880 |
| 0.050 | 0.939 | 0.025 | 0.871 |
| 0.100 | 0.921 | 0.050 | 0.863 |
| 0.300 | 0.871 | 0.100 | 0.855 |
| 0.500 | 0.802 | 0.300 | 0.801 |
| 0.700 | 0.746 | 0.500 | 0.771 |
| | | 0.700 | 0.728 |
| 1-Pentanol | | 1-Hexanol | |
| 0.000 | $(0.88_8)^a$ | 0.000 | $(0.83_0)^a$ |
| 0.025 | 0.875 | 0.010 | 0.829 |
| 0.050 | 0.875 | 0.020 | 0.828 |
| 0.100 | 0.852 | 0.030 | 0.810 |
| | | 0.125 | 0.840 |
| 1-Heptanol | | | |
| 0.000 | $(0.80)^a$ | | |
| 0.005 | 0.78 | | |
| 0.010 | 0.76 | | |

[a] Extrapolated value.

chemical potential gradients are the driving forces for diffusion (Tyrrell and Harris, 1984). $D$ is therefore a product of a mobility factor as well as an equilibrium thermodynamic factor for the change in chemical potential with concentration. To compare the mobilities of different alcohols in water, it is helpful to extrapolate measured diffusion coefficients to infinite dilution where the thermodynamic factors of the alcohols are identical. In this limit interactions between alcohol molecules, such as alcohol association, are negligible.

In Figure 1 the diffusion coefficients measured for the 1-alkanols are plotted against the alcohol concentration. Limiting diffusion coefficients ($D^0$) calculated by linear least-squares extrapolation to zero alcohol concentration are summarized in Table 2. Table 2 includes for comparison limiting alcohol diffusion coefficients reported in previous studies. Agreement with the present results is good, usually within the accuracy of the different experimental techniques: ~0.2% for Gouy interferometry; ~(0.5 to 1)% for the diaphragm-cell method; (1 to 2)% for Taylor dispersion.

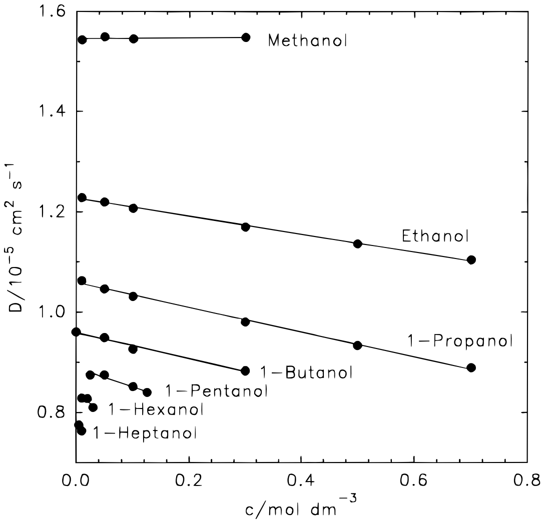

**Figure 1.** Binary mutual diffusion coefficients of aqueous 1-alkanols plotted against alcohol concentration.

According to the Stokes law (Tyrrell and Harris, 1984), the limiting diffusion coefficient of a spherical molecule is inversely proportional to the effective molecular radius, and hence the approximate result $D^0 \propto V^{-1/3}$ for compact solutes, where $V$ is the solute molar volume. The diffusion of long, flexible molecules, on the other hand, is qualitatively different because transport is governed by the motion of molecular segments. In this case $D^0$ is predicted to be inversely proportional to the number of segments (Van Geet and Adamson, 1964), and hence $D^0 \propto V^{-1}$. Figure 2 is a plot of $\ln D^0$ against $\ln V$ for the 1-alkanols. The slope $-0.49 \pm 0.03$ suggests behavior intermediate between Stokes-law (slope $-1/3$) and segmental diffusion (slope $-1$). Longer-chain alcohols might conform more closely to segmental diffusion, but the solubility of these compounds is too low to test this possibility. (Longsworth has measured the diffusion of unbranched alkanes, up to $C_{32}H_{66}$, in carbon tetrachloride (Longsworth, 1966). For $C_{12}H_{26}$ and the heavier alkanes the slope of $\ln D^0$ against $\ln V$ is about $-0.80$, in closer agreement with the segmental diffusion limit.)

***Aqueous Propanol and Butanol Isomers.*** Diffusion coefficients measured for the aqueous propanols are plotted in Figure 3. In view of the identical chemical compositions and similar structures, it is not surprising that the propanol isomers have nearly identical $D^0$ values: $1.06 \times 10^{-5}$ and $1.03 \times 10^{-5}$ cm$^2$ s$^{-1}$ for 1-propanol and 2-propanol, respectively.

On the basis of the 1-propanol and 2-propanol results, nearly identical diffusion coefficients could be anticipated for the aqueous butanol isomers, although the compact structure of 2-methyl-2-propanol (*tert*-butyl alcohol) might be expected to give this isomer a slightly larger diffusion coefficient relative to the other butanols. Figure 3 shows, however, that the diffusion of 2-methyl-2-propanol is significantly slower than that the other butanols. The limiting diffusion coefficients increase in the order $D^0$(2-methyl-2-propanol) < $D^0$(*2*-butanol) < $D^0$(2-methyl-1-propanol) < $D^0$(1-butanol), and $D^0$ for 2-methyl-2-propanol is about 10% smaller than $D^0$ for 1-butanol. There is evidence (Bender and Pecora, 1986) that aqueous 2-methyl-2-propanol molecules are of the correct size and shape to be "encaged" or "clathrated" by surrounding water molecules. Clathration might account for the relatively slow diffusion of 2-methyl-2-propanol.

The results summarized in Table 2 show that limiting alcohol diffusion coefficients from the literature are in good agreement with the present results. After this work was completed, a reviewer (K. R. Harris) kindly brought to our

**Table 2. Limiting Diffusion Coefficients of Aqueous Alcohols at 25 °C**

| alcohol | $D^0/(10^{-5}\ \mathrm{cm^2\ s^{-1}})$ |
|---|---|
| methanol | $1.54_5$ [Taylor dispersion (this work)] |
| | $1.56_3$ diaphragm cell (Derlacki *et al.*, 1985)] |
| ethanol | $1.22_7$ [Taylor dispersion (this work)] |
| | $1.22_4$ diaphragm cell (Easteal and Woolf, 1985)] |
| | 1.22 diaphragm cell (Ghai *et al.*, 1973; Dullein and Shemilt, 1961)] |
| | 1.24 diaphragm cell (Hammond and Stokes, 1953)] |
| | 1.23 [Taylor dispersion (Harris *et al.*, 1993)] |
| | $1.23_5$ [Taylor dispersion (Pratt and Wakeham, 1974)] |
| | 1.24 [Taylor dispersion (Tominaga and Matsumoto, 1990)] |
| 1-propanol | $1.05_9$ [Taylor dispersion (this work)] |
| | 1.064 [Taylor dispersion (Harris *et al.*, 1993)] |
| | 1.02 [Taylor dispersion (Pratt and Wakeham, 1975)] |
| 2-propanol | $1.02_9$ [Taylor dispersion (this work)] |
| | 0.99 [Taylor dispersion (Pratt and Wakeham, 1975)] |
| 1-butanol | $0.96_0$ [Taylor dispersion (this work)] |
| | 0.972 Gouy interferometry (Lyons and Sandquist, 1953)] |
| | 0.933 [Taylor dispersion (Tominaga and Matsumoto, 1990)] |
| 2-butanol | $0.94_1$ [Taylor dispersion (this work)] |
| 2-methyl-1-propanol | $0.95_0$ [Taylor dispersion (this work)] |
| 2-methyl-2-propanol | $0.87_6$ [Taylor dispersion (this work)] |
| | 0.93 [Taylor Dispersion (Harris and Lam, 1995)] |
| | 0.874 [Taylor dispersion (Tominaga and Matsumoto, 1990)] |
| 1-pentanol | $0.88_8$ [Taylor dispersion (this work)] |
| 1-hexanol | $0.83_0$ [Taylor dispersion (this work)] |
| 1-heptanol | 0.80 [Taylor dispersion (this work)] |

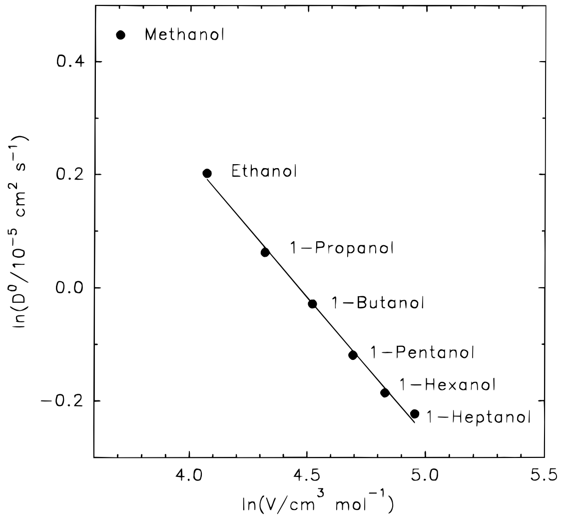

**Figure 2.** Logarithm of the limiting diffusion coefficients for the aqueous 1-alkanols plotted against the logarithm of the molar volume of the pure alcohol. Excluding methanol, the first member of the series, the least-squares slope is (−0.49 ± 0.03). Molar volumes were calculated from published densities (Landolt-Börnstein, 1974).

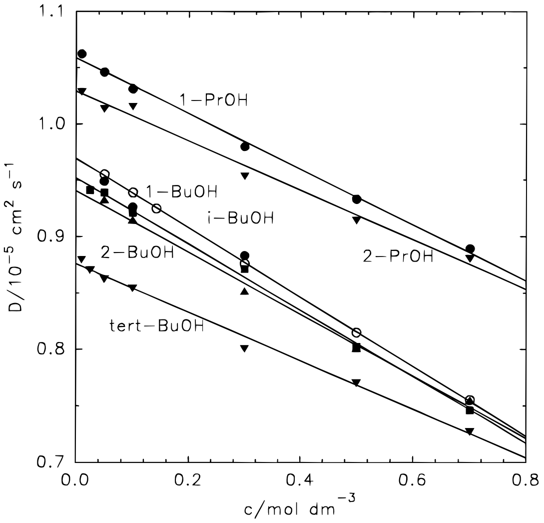

**Figure 3.** Binary mutual diffusion coefficients of aqueous propanols and butanols plotted against alcohol concentration: solid symbols, this work; ○, optical data for 1-butanol (Lyons and Sandquist, 1953).

attention additional Taylor dispersion data indicating a limiting diffusion coefficient of 0.93 × $10^{-5}$ cm$^2$ s$^{-1}$ for aqueous 2-methyl-2-propanol solutions (Harris and Lam, 1995), which is 6% higher than our value and the value reported by Tominaga and Matsumota (1990). This discrepancy prompted us to remeasure diffusion coefficients for aqueous 2-methyl-2-propanol. Several different dispersion tubes were used, and some of the solutions were prepared with a better grade of the alcohol (Fluka puriss, >99.7% pure). However, the remeasured diffusion coefficients were identical within experimental precision with our previous results for 2-methyl-2-propanol in Table 1. Additional check runs made with aqueous solutions of sucrose or potassium chloride indicated an accuracy of (1 to 2)% for diffusion measurements with our Taylor equipment, so we cannot explain the more rapid diffusion of 2-methyl-2-propanol reported by Harris and Lam.

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