# Determination of Diffusion Coefficients of Glycols

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The holographic interferometric technique is used to determine the variation with concentration of the mutual diffusion coefficient at 25 °C. The systems studied were ethylene glycol + water, diethylene glycol + water, and triethylene glycol + water. Experimental results are compared with values reported in the literature.

## Introduction

Ethylene glycol mixtures with water are used as a common chemical. About 42% of the world production of ethylene glycol is used as antifreeze. It is becoming useful, together with other glycols, in the polyester market (Kirk-Othmer, 1994).

In spite of the industrial importance of glycols, the literature normally only refers to the mutual diffusion coefficient of ethylene glycol + water. For example, Rossi et al. (1958) reported a single value of the mutual diffusion coefficient at 15 °C, at high dilution in water, Garner and Marchant (1961) provided results at 20, 25, 30, and 40 °C in graphical form, Byers and King (1966) reported values over the entire range of composition at temperatures from 25 to 70 °C, and more recently, Bogacheva et al. (1982) reported values at 25 and 40 °C, although their results differed considerably from those reported previously. In the same paper, results from triethylene glycol + water were also reported. No results for mutual diffusion coefficients of diethylene glycol + water have been found in the literature.

Most of the reported data in the literature were obtained using either the diaphragm cell method or an interferometric technique. Among the wide variety of experimental methods to determine liquid diffusion coefficients, optical methods are one of the most reliable. In a previous paper (Ruiz et al., 1985a), the advantages of holographic interferometry over the classical interferometric methods were reported. The holographic interferometric technique was successfully used to determine diffusion coefficients both in liquid−liquid systems (Ruiz et al., 1985b, 1995) and in liquid−gel systems (Ruiz et al., 1989).

In order to resolve the disagreement in the literature concerning diffusion coefficients for ethylene glycol + water and to obtain additional information about other glycol + water systems, holographic interferometry was used to determine the variation with concentration of the mutual diffusion coefficient at 25 °C. The systems studied were ethylene glycol + water, diethylene glycol + water, and triethylene glycol + water.

## Experimental Section

Ethylene glycol, diethylene glycol, and triethylene glycol (all from Scharlau, pure grade, 99.5% or more) were used as supplied. Bidistilled water was prepared in the laboratory, and solutions were prepared by mass (accuracy 0.001 g). To study the diffusion process, two solutions with different concentrations were put in contact in a glass cell. Due to the strong dependence of the mutual diffusion coefficient on the concentration, the mass fractions of the two solutions were very similar, the difference in the mass

**Table 1. Mutual Diffusion Coefficients ($D_{12}$) at 25 °C and Their Sample Standard Deviations ($s$)**

| system | $w_1$ | $10^6 D_{12}/$ (cm$^2$ s$^{-1}$) | $10^6 s/$ (cm$^2$ s$^{-1}$) |
|---|---|---|---|
| ethylene glycol (1) + water (2) | 0.05 | 11.35 | 0.07 |
| | 0.225 | 9.33 | 0.08 |
| | 0.40 | 7.82 | 0.03 |
| | 0.627 | 5.59 | 0.10 |
| | 0.992 | 2.70 | 0.10 |
| diethylene glycol (1) + water (2) | 0.02 | 8.37 | 0.09 |
| | 0.10 | 7.71 | 0.12 |
| | 0.30 | 6.37 | 0.06 |
| | 0.50 | 4.89 | 0.11 |
| | 0.73 | 3.30 | 0.19 |
| | 0.95 | 1.96 | 0.13 |
| triethylene glycol (1) + water (2) | 0.02 | 7.31 | 0.09 |
| | 0.10 | 6.57 | 0.14 |
| | 0.25 | 5.68 | 0.14 |
| | 0.375 | 4.83 | 0.06 |
| | 0.50 | 4.17 | 0.06 |
| | 0.60 | 3.38 | 0.07 |
| | 0.73 | 2.73 | 0.19 |
| | 0.95 | 1.91 | 0.02 |

fractions between the two solutions being 0.03 or less. The diffusion coefficient was referred to the average mass fraction of the two solutions.

Diffusion coefficients at $(25.0 \pm 0.2)$ °C were measured by holographic interferometry. The optical system was the same as that used by Ruiz et al. (1989). The filling procedure of the diffusion cell has been described in previous papers (Ruiz et al., 1985b; Fernández et al., 1986). For the more viscous solutions, the filling procedure was different: first, the denser solution was introduced with a pipet, and then, very carefully, the lighter solution was added with a capillary tube over the denser solution, trying to keep the diffusion front unaffected. The experimental method to obtain interferograms is the same as described by Ruiz et al. (1985b): the diffusion cell was illuminated with a laser beam, and the state of the diffusion system was recorded on a holographic plate (hologram). Later, the hologram interfered with the state of the diffusion system at a different time and some interference fringes appeared on the image of the diffusion cell (interferogram). The mathematical treatment to obtain diffusion coefficients from the interference fringes was the same as described by Ruiz et al. (1985b).

## Results and Discussion

Table 1 summarizes the experimental diffusion coefficients ($D_{12}$) as well as the corresponding sample standard deviations ($s$). Several interferograms (3−8) were made for each concentration, and from each interferogram, several diffusion coefficients (4−12) were measured. In this
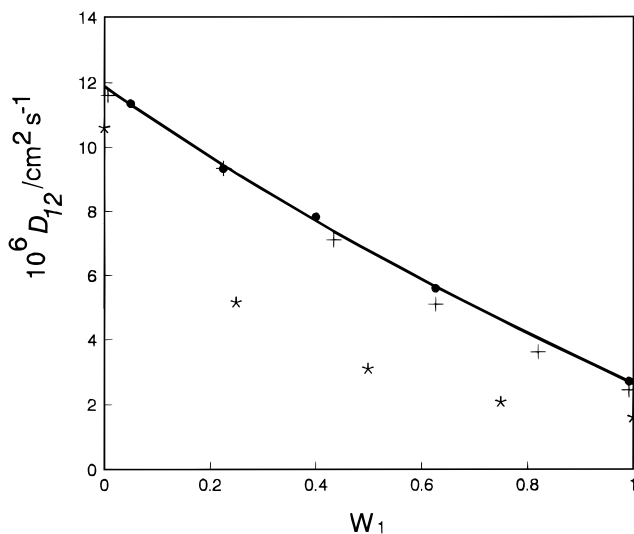
**Figure 1.** Variation of the diffusion coefficient $D_{12}$ at 25 °C as a function of the mass fraction of ethylene glycol ($w_1$): (●) this study, (+) Byers and King (1966), (*) Bogacheva et al. (1982), (−) best fit of the data.
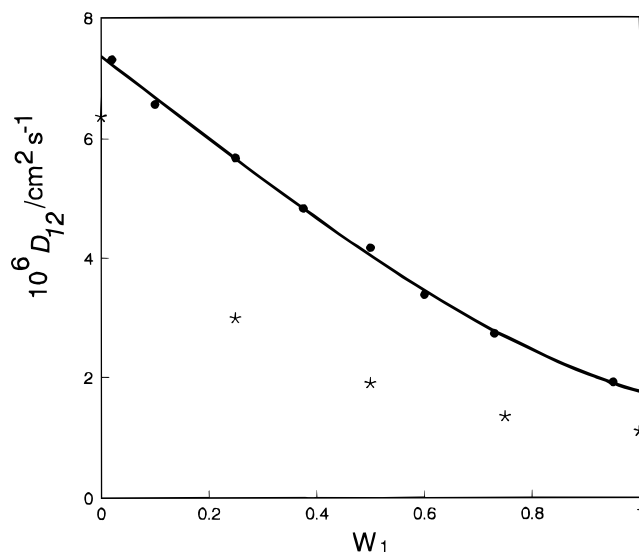


**Figure 2.** Variation of the diffusion coefficient $D_{12}$ at 25 °C as a function of the mass fraction of triethylene glycol ($w_1$): (●) this study, (*) Bogacheva et al. (1982), (−) best fit of the data.

way, the diffusion coefficients presented are the mean values of a reasonable number of experimental determinations.

In the case of ethylene glycol (1) + water (2), the results obtained in this paper are very similar to those reported by Byers and King (1966) (Figure 1). In this figure, the disagreement with results reported by Bogacheva et al. (1982) can be observed. Their values are lower than the other two series of results. Values reported by Garner and Marchant (1961) are not represented, but their values are also higher than Bogacheva's, although lower than Byers and King's, as the authors indicate in their paper (Byers and King, 1966). Our results were fitted to the polynomial equation

$$D_{12} = 1.189 \times 10^{-5} - 1.152 \times 10^{-5} w_1 + 2.837 \times 10^{-6} w_1{}^2 - 5.773 \times 10^{-7} w_1{}^3 \quad (1)$$

where $D_{12}$ is the mutual diffusion coefficient (cm² s⁻¹) and $w_1$ is the mass fraction.

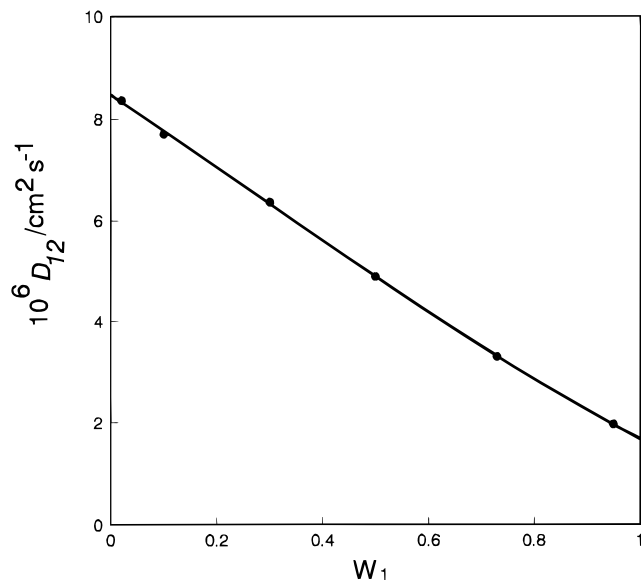A similar disagreement with Bogacheva's data can be observed in triethylene glycol (1) + water (2) (Figure 2).



**Figure 3.** Variation of the diffusion coefficient $D_{12}$ at 25 °C as a function of the mass fraction of diethylene glycol ($w_1$): (●) this study, (−) best fit of the data.

Our values of the diffusion coefficient are higher than Bogacheva's. Our results were fitted to the polynomial equation

$$D_{12} = 7.367 \times 10^{-6} - 6.690 \times 10^{-6} w_1 - 9.208 \times 10^{-7} w_1{}^2 + 1.998 \times 10^{-6} w_1{}^3 \quad (2)$$

In Figure 3, experimental results for diethylene glycol (1) + water (2) are presented. Results were fitted to the polynomial equation

$$D_{12} = 8.472 \times 10^{-6} - 6.890 \times 10^{-6} w_1 - 1.173 \times 10^{-6} w_1{}^2 + 1.268 \times 10^{-6} w_1{}^3 \quad (3)$$

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