



Binary mutual diffusion coefficient of aqueous solutions of propylene glycol and dipropylene glycol

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ABSTRACT

Binary mutual diffusion coefficient data for aqueous solutions of propylene and dipropylene glycols were measured using the Taylor dispersion technique for each aqueous binary system at different concentrations ($x_1 = 0.2$ – 0.80) and temperatures (303.2 – 323.2 K). The measured data were fit to different empirical and semi-theoretical models and compared with the values predicted from such models. The measured mutual diffusion coefficient data are well represented by either rough hard-sphere or UNIDIF model. On the side, the infinite dilution diffusion coefficient has been found greater at lower glycol molecular weight, an observation that corroborates with the property's dependence on free volume.

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1. Introduction

Diffusion in liquid phase is often encountered as a limiting mechanism in systems involving mass transfer; therefore, it assumes an important role in many chemical engineering processes and equipment design undertakings for systems involving mass transport. An important property that is indispensable in process and equipment design for diffusion systems is the diffusivity or diffusion coefficient. Present molecular theories are not always adept to predict diffusion coefficients accurately. In addition, only little experimental measurements are available even for (the most common) diffusion in aqueous media and that the measurement methodology tends to be intricate and tedious (Cussler, 1976, 1984; Ren *et al.*, 2005; Tyrell and Harris, 1984). To calculate accurately mass transfer coefficients, extensive measurement of diffusivity over the whole range of concentrations is necessary (Ren *et al.*, 2005).

In this work, mutual diffusion coefficient data for aqueous solutions of propylene glycol (PG) and dipropylene glycol (DPG) were measured using the Taylor dispersion method for each aqueous binary system at different concentrations and temperatures. The measured values were fit to models based on: (a) the three-parameter empirical model proposed by Snijder *et al.* (1993); (b) modified Darken equation (Li *et al.*, 2001); (c) group

contribution concept (UNIDIF) (Hsu and Chen, 1998); and, (d) free volume (rough hard-sphere theory) (Dymond, 1974).

Snijder *et al.* (1993) explicitly expresses the functional dependence of the diffusion coefficient D_{12} on temperature and concentration:

$$\ln D_{12} \text{ (m}^2\text{/s)} = A_1 + \frac{A_2}{T/K} + A_3 \times C \text{ (kmol/m}^3\text{)} \quad (1)$$

where A_i 's are empirical parameters determined from both infinite dilution diffusion coefficient and mutual diffusion coefficient data, T the absolute temperature, and C the molar concentration of solution. In Eq. (1), the concentration is in terms of molar concentration of solution, thus, density data are necessary. The density equations for the considered glycols systems, PG + H₂O and DPG + H₂O, obtained from our previous works (Chen *et al.*, 2009; Tsai *et al.*, 2009) were applied in this work.

There are two modified Darken equations used in this work. One is the form as modified and subsequently used in Li *et al.* (2001). The other is the form of the Darken equation that has been modified from the original in the manner presented in Appendix A of this paper.

UNIDIF is based on the absolute reaction rate theory and local composition model (Hsu and Chen, 1998). The UNIDIF equation has been proposed and used satisfactorily for calculation of mutual diffusion coefficients of various polar and non-polar binary systems. A brief description of the UNIDIF model has been presented in our previous work (Chang *et al.*, 2005).

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Nomenclature

A_i	empirical parameters of Eq. (1) where $i = 1, 2,$ and 3
b	constant in Eq. (3)
C	molar concentration of solution (kmol/m^3)
D	diffusion coefficient (m^2/s)
F	added empirical constant of the modified Darken equation from this work
n	association degree
N	Avogadro's number
r_c	internal radius of the capillary tube (mm)
R	gas constant
R_c	radius of the coil tube (mm)
Re	Reynolds number
Sc	Schmidt number
T	absolute system temperature (K)
V_0	close-packed hard-sphere volume (m^3/kmol)
V	molar volume (m^3/kmol)
$[V - V_D]$	free volume of the solution (m^3/kmol)
x	mole fraction

Greek symbols

ϕ_{11}, ϕ_{22}	Wilson parameters in modified Darken equation
γ	constant of Eq. (2) and is a function of the average collision diameter (σ_{AB}) and molecular mass of solute and solvent
γ_2	activity factor for component 2 in Eq. (A.1)
η	dynamic viscosity of component i
Λ_{12} or $\lambda_{12} - \lambda_{11}$	interaction parameters of modified Darken equation
Λ_{21} or $\lambda_{21} - \lambda_{22}$	interaction parameters of modified Darken equation
σ	hard-sphere diameter of the component
σ_{AB}	average collision diameter of components A (glycol) and B (water)
σ_{vdW}	van der Waals diameter
ω	defined as R_c/r_c

Subscript

12	binary mutual diffusivity
A	pertains to glycol component
B	pertains to solvent (water) component
c	critical parameter
D	diffusion coefficient approaches zero
i	component in the system such as 1 (glycol) and 2 (water)

Superscript

0	pure component or self-diffusion
*	intra-diffusion
∞	infinite dilution

used in previous works (Chang *et al.*, 2005; Chen *et al.*, 1982; Matthews and Akgerman, 1987; Wong and Hayduk, 1990):

$$\frac{D_{12}}{\sqrt{T}} = \gamma[V - V_D] \quad (2)$$

where V is the molar volume of the solution, V_D the molar volume of the solution at which the diffusion coefficient approaches zero, and $[V - V_D]$ the free volume of the solution. The constant γ is a function of the average collision diameter (σ_{AB}) and molecular mass of solute and solvent (Matthews and Akgerman, 1987). In Eq. (2), the molar volumes of the solution were obtained from the density equations mentioned previously in Eq. (1).

2. Experimental

2.1. Chemicals

The propylene glycol and dipropylene glycol were both supplied by ACROS and have a minimum purity of 99%. The glycols were used without further purification. In preparing all solutions we used Type I reagent grade water (resistivity, 18.3 M Ω cm); total organic carbon less <15 ppb, purified using our in-house water purification system (Barnstead Thermodyne, Easy Pure 1052). A digital balance with an accuracy of $\pm 1 \times 10^{-4}$ g was used to weigh the glycols and the water during preparation of the solutions.

2.2. Measurement of diffusion coefficient

A Taylor dispersion apparatus was used to measure the diffusion coefficient the considered aqueous glycol solutions. The experimental setup had been described in our previous works (Chang *et al.*, 2005; Su *et al.*, 2007). In this work, however, we describe some important details of the measurement/setup as follows:

The diffusion tube (Valco Instruments Inc.) was 50.218 m long, having an inside radius (R_c) of 0.254 mm. Arranged in helical stack of horizontal coils of radius (r_c) of 300 mm, the tube was placed in a constant-temperature bath equipped with a thermometer (Hart Scientific, model 1502) having a reading accuracy of ± 0.01 K. A metering pump provided the constant (laminar) flow of 0.08–0.2 mL/min. The carrier fluid was made to flow in a six-point injection valve (Rheodyne, model 7725i) into a diffusion tube.

To prevent the secondary flows in the helical coil, a flow rate of 0.18 mL/min was maintained, as suggested by Alizadeh *et al.* (1980), to ensure that $Re^2\omega^{-1}Sc \leq 100$, where Re and Sc are Reynolds and Schmidt numbers, respectively, and $\omega = R_c/r_c$. Through the six-way injection valve, 1–1.5 μL of glycol solution was introduced into the carrier liquid. The concentration gradient was then determined using a differential refractometer (Precision Instruments, model IOTA 2) at the capillary exit. The analog output was transmitted to a computer system via an integrating converter INT5 (DataApex Chromatography Station, CSW 1.7).

3. Results and discussion

We checked the validity of the method used in the work (the Taylor dispersion setup described in Section 2.2) by measuring mutual diffusion coefficient data for the system EG (1) + H₂O (2) at 298.2 K and atmospheric pressure using the present method and compared the measurements against the data for the EG (1) + H₂O (2) system (Byers and King, 1966; Fernández-Sempere *et al.*, 1996) that are available in literature. The comparison, shown in Fig. 1, suggests that the measured data agree well with the data reported in literature. The smoothed line in the figure was determined from

The rough hard-sphere theory (Dymond, 1974) is an accurate representation of self-diffusion coefficients of hard-sphere molecules. An equivalent equation for the diffusion in terms of the molar volume of the solution, Eq. (2), was introduced and had been

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