

Diffusion Coefficients of CO, CO₂, N₂O, and N₂ in Ethanol and Toluene

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The Taylor dispersion technique was applied for the measurement of diffusion coefficients of dissolved gases in ethanol and toluene. Experiments with the system CO₂ in H₂O have been made to evaluate the accuracy of the method. The experimental procedure as described provides a fast and highly reproducible method for the determination of diffusion coefficients of dissolved gases in liquids. The diffusion coefficients of CO, CO₂, and N₂O have been determined in the temperature range of 298–333 K in ethanol and 298–348 K in toluene and of N₂ in toluene at 298 K. There is a good agreement between the values as determined in the present work and available literature results at 298 K.

1. Introduction

The Taylor–Aris dispersion method (1–4) is a very convenient method for the determination of diffusion coefficients, especially of dissolved salts and liquids in liquids (5–8). This method is less often applied for the determination of dissolved gases in liquids (9). In the present work the Taylor–Aris method has been used for the determination of the diffusion coefficients of CO₂, CO, and N₂O in ethanol and toluene.

Data on the CO + toluene system are required for modeling the so-called Cosorb process, where CO is selectively absorbed by a CuAlCl₄ complex dissolved in toluene (10). The results on CO₂ or N₂O + ethanol can be applied as reference values for the determination of porosity–tortuosity factors (ϵ/τ , where ϵ is porosity and τ is the tortuosity of the diaphragm) for the diffusion of gases through porous media filled with ethanol or toluene. Knowledge on the porosity–tortuosity values are required when a diaphragm cell is used for the determination of diffusion coefficients (11, 12).

2. Experimental Section

2.1. Theory. In the case where a pulse of solute is injected into a solvent showing laminar flow through a capillary tube, the combined action of axial convection and radial molecular diffusion will eventually change the square pulse into a Gaussian curve at the end of the tube. Taylor and Aris (1–3) have been able to describe this phenomenon, and they provided an approximate solution of the complete diffusion equation. This solution is only applicable under certain experimental conditions (4). A complete overview of the required theory and the solution methods as applied in the present work has been given elsewhere (7, 8). More extended information is given in refs 4 and 13.

2.2. Experimental Procedure. The apparatus has previously been used for the determination of diffusion coefficients of alkanolamine solutions in aqueous alkanolamine solutions (7) and is shown schematically in Figure 1. The two liquids are stored in two glass storage vessels; one is kept under a constant helium pressure of 5 bar. In the other vessel, the liquid is saturated with the desired tracer gas by bubbling the gas through the liquid for a certain time after which it is stored under a tracer gas

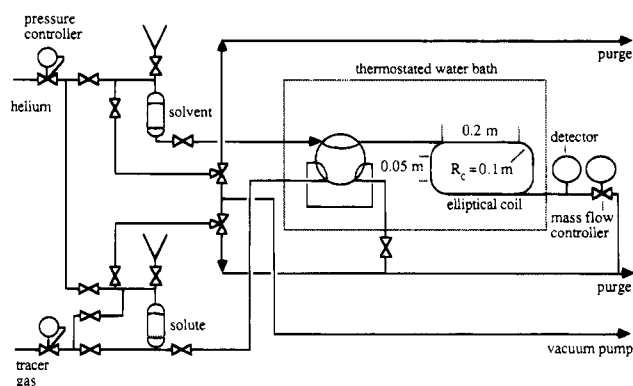


Figure 1. Schematic diagram of the apparatus.

Table 1. Dimensions of the Setup and Experimental Conditions, with L_c = Tube Length, R = Tube Radius, R_c = Coil Radius, V_c = Coil Volume, V_{inj} = Injector Volume, V_{det} = Detector Volume, u = Average Velocity, and T = Temperature

L_c	15.085 m	V_{inj}	$8.76 \times 10^{-8} \text{ m}^3$
R	$5.565 \times 10^{-4} \text{ m}$	V_{det}	$8 \times 10^{-9} \text{ m}^3$
R_c	0.1 m	u	$(5-9) \times 10^{-3} \text{ m/s}$
V_c	$1.47 \times 10^{-5} \text{ m}^3$	T	288–348 K

pressure of 5 bar. At this pressure the solubility of all gases in the solvents was high enough to give a measurable response at the end of the tube, while it was assumed that at this pressure the influence on the diffusion coefficients in the liquid phase is negligible. The capillary tube is held in a thermostated water bath (Tamson), which provides a thermal stability within 0.1 K. The tube length L_c is 15 m; the diameter has been determined by filling and weighing the tube with a solvent with known density. The dimensions of the tube and the experimental conditions are given in Table 1. Control of the liquid is carried out with a liquid mass flow controller (Rosemount Flowmega 5881), which is placed at the end of the tube after the detector. This yields a constant and pulseless flow throughout the experiment. The detector is a differential refractometer (Varian, RI-4), which can be operated till a pressure of 7 bar. The complete apparatus is controlled (temperature, flow rate, injection of solute) with a computer, which also stores the measured data from the refractometer and calculates the diffusion coefficient and average flow rate. The gases N₂, CO, CO₂, N₂O, and He were obtained from

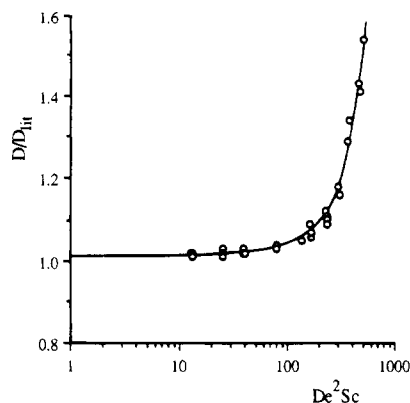


Figure 2. Influence of $(De)^2(Sc)$ on the diffusion coefficient of CO_2 in water at 298 K.

Hoekloos and the solvents ethanol and toluene from Merck. More information on the experimental procedure is provided by Snijder *et al.* (7).

3. Results

The first experiments were conducted on the system CO_2 + water at 298 K to evaluate whether the method provides results of adequate accuracy. Since a coiled tube is used in the experiment, the average velocity has to be below a certain value. Above that velocity the calculated diffusion coefficients start to increase due to centrifugal forces, which develop secondary flow. The value of the dimensionless $(De)^2(Sc)$ number (where $De = Re(R/R_c)^{1/2}$, $Re = 2\rho u_1 R/\eta$, $Sc = \eta/(\rho D)$, R and R_c are the tube and coil diameters, respectively, and u_1 is the average liquid velocity) gives an indication of the influence of secondary flow. Below a critical value, the effect is negligible (4). For CO_2 + water diffusion coefficients have been determined at various liquid velocities and compared with available literature data (14–18, summarized in Table 3), the results are shown in Figure 2. Below a $(De)^2(Sc)$ number of 20 the measured diffusion coefficient equals the literature value. All other experiments were carried out at velocities below this critical value. For the determination of the diffusion coefficients of dissolved salts + liquids, a maximum value for $(De)^2(Sc)$ of about 100 has been reported in earlier work in the same apparatus (7). In the case of dissolved gases, small gas bubbles are most likely formed at the entrance of the tube, due to supersaturation of the solvent and pressure fluctuations after injection of the solute pulse. These small bubbles will initially disturb the flow in the capillary tube and dissolve after a period of flow. If the total residence time in the tube is long enough, the initial disturbances will become negligibly small. Consequently, more accurate results will be obtained at low flow velocities (i.e., low $(De)^2(Sc)$ numbers).

Table 2 gives an overview of the diffusion coefficients (average of 3–4 measurements) for CO_2 , CO , and N_2O in toluene and ethanol at various temperatures and nitrogen in toluene at 298 K. The reproducibility between the different measurements is $(0.02\text{--}0.05) \times 10^{-9} \text{ m}^2/\text{s}$. Literature data are presented in Table 3. There exists a rather good agreement between the present results and previous results (mainly available at 298 K). The literature values are obtained using various experimental methods, which might be the reason for the discrepancies for some systems (especially N_2O + toluene).

The results are presented as a function of the temperature according to an Arrhenius relation in Figure 3 (CO_2 and N_2O in ethanol). From the straight line plot, the

Table 2. Diffusion Coefficients of Several Dissolved Gases in Ethanol and Toluene

solvent	T/K	$10^9 D/(\text{m}^2\text{s}^{-1})$			
		CO_2	N_2O	CO	N_2
toluene	298.0	4.89	5.02	5.70	
	298.1				5.80
	307.9		5.70		
	308.0	5.58		6.28	
	317.7		6.36		
	318.0	6.24		7.04	
	333.0	7.54	7.49	8.45	
	348.0	8.82	8.70	9.85	
ethanol	298.1	4.11	4.26		
	308.0	4.70	4.92		
	313.0	5.05			
	318.0		5.62		
	323.1	5.77	5.97		
	333.0	6.51	6.76		

Table 3. Literature Data on Various Diffusion Coefficients at 298 K

system	$10^9 D/(\text{m}^2\text{s}^{-1})$	method	ref
CO_2 + water	1.93	diaphragm cell	14
	1.85	laminar jet	15
	2.00	diaphragm cell	16
	1.98	laminar jet	17
	1.94	wetted wall column	18
	1.98	Taylor dispersion	present work
CO_2 + ethanol	4.04	diaphragm cell	14
	4.5	wetted wall column	18
CO_2 + toluene	4.11	Taylor dispersion	present work
	4.33/4.61	diaphragm cell	14
	4.60	capillary cell	19
	4.02	diaphragm cell	12
N_2 + toluene	4.89	Taylor dispersion	present work
	6.13	diaphragm cell	12
N_2O + toluene	5.80	Taylor dispersion	present work
	3.79	diaphragm cell	12
	5.02	Taylor dispersion	present work

temperature dependence for the diffusion coefficients in toluene can be obtained:

$$D_{\text{CO}_2}/(\text{m}^2\text{s}^{-1}) = 277.0 \times 10^{-9} \exp\left(\frac{-1164.2}{T/\text{K}}\right)$$

$$D_{\text{N}_2\text{O}}/(\text{m}^2\text{s}^{-1}) = 228.1 \times 10^{-9} \exp\left(\frac{-1137.4}{T/\text{K}}\right)$$

$$D_{\text{CO}_2}/(\text{m}^2\text{s}^{-1}) = 296.1 \times 10^{-9} \exp\left(\frac{-1224.5}{T/\text{K}}\right)$$

For the diffusion coefficients in ethanol the following relations were found:

$$D_{\text{CO}_2}/(\text{m}^2\text{s}^{-1}) = 336.5 \times 10^{-9} \exp\left(\frac{-1314.7}{T/\text{K}}\right)$$

$$D_{\text{N}_2\text{O}}/(\text{m}^2\text{s}^{-1}) = 345.0 \times 10^{-9} \exp\left(\frac{1310.4}{T/\text{K}}\right)$$

These equations can be applied in the temperature range 298–348 K for toluene and 298–333 K for ethanol.

4. Conclusions

It has been demonstrated that the Taylor–Aris dispersion technique is an accurate method for the determination of diffusion coefficients of dissolved gases in liquids provided that the maximum $(De)^2(Sc)$ number is lower than 20. The advantage of the experimental procedure as described in this work (and previous work: 7, 8) is that diffusion measurements of all type of solutes (gases, liquids,

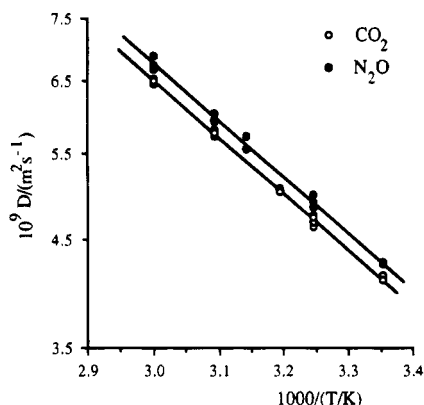


Figure 3. Diffusion coefficients of CO₂ and N₂O in ethanol.

salts) in liquids can be carried out in a single setup. Moreover, the setup can be fully automatized, resulting in a 24 h a day availability.

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