Determination of the Trichloroethylene Diffusion Coefficient in Water

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Trichloroethylene (TCE) is a halogenated aliphatic organic compound frequently detected as pollutant in soils and ground water. To study the fate of TCE in water and to devise effective remediation strategies, a series of advection-diffusion (dispersion) models, where the diffusion coefficient of TCE (D_{TCE}) is an important parameter, have been developed. However, D_{TCE} in water has never been experimentally determined and only theoretical values ($\simeq 1\times10^{-5}$ cm^2 s^{-1} at 25°C) are present in the literature. A new method based on the Taylor dispersion technique, which allows to measure D_{TCE} in a broad range of temperature and, in principle, in any solvent is presented. At 25°C $D_{TCE} = 8.16\pm0.06\times10^{-6}$ cm^2 s^{-1} and the value increases almost linearly with the temperature, while, in the limit of the experimental error, is independent from [TCE] for dilute solutions. From the temperature dependence of D_{TCE}, it was possible to calculate the specific TCE fitting constant in the well-known Wilke and Chang theoretical relation and the activation energy of the diffusion process through the Arrhenius plot. © 2015 American Institute of Chemical Engineers *AIChE J*, 61: 3511–3515, 2015

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Introduction

Trichloroethylene (TCE) is a chlorinated solvent that belongs to the class of dense nonaqueous phase liquids (DNAPLs) pollutants.[1] The physical and chemical properties of DNAPLs, especially the low solubility in water, the high density ($\gg$ 1 g cm^{-3}) and the high affinity for organic compounds, cause a deep penetration of DNAPLs in the subsurface following accidental spills or intentional damping.[1,2] The high density also causes the stratification of DNAPLs at the bottom of the groundwater and aquifer reservoirs, often compromising their integrity and forming a permanent source of pollution.[3] TCE, in particular, is chemically stable and generally inert toward biological degradation in aquifers with half-lives measured in years, thus being a long-term source of contamination due to limited solubility and low mass-transfer rates.

In the last years, several remediation strategies were devised for the removal of DNAPLs from ground and surface waters, including: air stripping, adsorption processes, bioremediation, pump and treat and surfactant enhanced dissolution.[3–6] The numerical simulations for understanding the fate of DNAPLs before and during the remediation procedure are based on advection-dispersion models, where the dispersion coefficients are a function of the molecular diffusivity of the DNAPL in water and of the mechanical dispersion due to the water flows.[1,5,7,8] Moreover, the accurate evaluation of the mass-transfer coefficients associated with the dissolution of DNAPL pools and ganglia in the subsurface environment is also strongly dependent on the pollutants diffusion coefficients.[9,10]

In the specific case of TCE, the value of the diffusion coefficient used in models ($D_{\rm TCE} \simeq 1\times10^{-5}$ cm^2 s^{-1} at 25°C) is a theoretical estimation, generally derived from the well-known Wilke and Chang (W&C) equation

$$D = 7.4\times10^{-8}\frac{(xM)^{1/2}T}{\eta V^{0.6}} \qquad (1)$$

where the diffusion coefficient expressed in cm^2 s^{-1} is a function of the association parameter, x, of the molecular weight of the solvent, M (g mol^{-1}), of the temperature, T (K), of the viscosity of the solution, η (cP), and of the molal volume of the solute at normal boiling point, V (cm^3 mol^{-1}).[11] In addition to the W&C equation, another commonly used relation is the Hayduk e

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Laudie (H&L) equation. Hayduk e Laudie developed a specific relation for the diffusion of solutes in water; by eliminating the solvent-specific parameters and the explicit dependence on the absolute temperature from the W&C equation, they obtained

$$D = 1.326\times10^{-4}\frac{\mu_b^{-1.14}}{V_A^{0.589}} \tag{2}$$

In this case the diffusion coefficient D (cm^2 s^{-1}) is a function of the viscosity of the water μ_b (cP) and of the the LeBas molar volume V_A (cm^3 mol^{-1}) of the solute at the boiling point.[12,13]

At best of our knowledge, D_{TCE} has never been determined experimentally, probably because TCE is only slightly soluble in water and its volatility makes difficult the preparation of stable standard solutions. In this article, we present a method based on the Taylor dispersion technique (see section) to determine D_{TCE} in a broad range of temperatures and, in principle, in any solvent. The Taylor technique allows to overcome problems related to the low concentration of the solutions and problems related to the instrument calibration, moreover, we used silica chromatographic columns as dispersion capillaries in order to prevent TCE evaporation and/or adsorption on the capillary walls of teflon tubes generally used for this technique.

The Taylor Dispersion Technique

The Taylor dispersion technique (TDT)[14–17] is a fast and reliable method for measuring the diffusion coefficients of solutes in one-component or multicomponent solutions.[18–26] Although less precise respect to other techniques (diaphragm technique, Gouy interferometer, etc.), the TDT presents several advantages like a simpler experimental apparatus (generally a High Performance Liquid Chromatography, HPLC), a small concentration difference between the sample and the solvent (1–4% M), the absence of a calibration procedure, and so forth.[27,28] The TDT is based on the diffusive spreading of a pulse of solution injected into a laminarly flowing stream of the same mixture but with slightly different concentrations. A small volume of the perturbing solution is injected into the flowing eluent at the entrance of a long capillary tube having a radius R_0. As it moves along the tube at a constant speed u_0 (cm s^{-1}), the injected sample is deformed by the shear flow, the rate of which has a parabolic shape across the capillary, and by radial diffusion. The drop spreads out into a shape that can be fitted by a combination of n Gaussian functions for an $(n+1)$-component system (n solutes + 1 solvent). The eluted peak, sometimes called the Taylor peak, is monitored by a suitable detector such as a flow-through spectrophotometer or a refractive index detector (RID). The diffusion coefficients are calculated from the parameters of the Gaussian functions that fit the eluted peak.

Taylor demonstrated that if the elution process is slow enough, the radial variation of the sample concentration is small relative to the axial variation and the concentration profile of the ith species (c_i) in a n-component system can be described with a one-dimensional (1-D) equation (c_i is averaged over the cross section of the tube) taking the form[14,21]

$$\frac{\partial c_i}{\partial t} = \sum_{j=1}^{n} F_{ij}\frac{\partial^2 c_j}{\partial z^2} \tag{3}$$

where

$$F_{ij} = \frac{R_0^2 u_0^2}{48\det(\mathbf{D})}\det(\mathbf{M}_{Dji})(-1)^{(i+j)} \tag{4}$$

$\det(\mathbf{D})$ is the determinant of the $n \times n$ diffusion matrix $\mathbf{D}$ and $\det(\mathbf{M}_{Dji})$ is the determinant of the minor associated with element D_{ji} of $\mathbf{D}$. The coefficients F_{ij} have the same dimensions as the diffusion coefficients D_{ij} (cm^2 s^{-1}), but they are inversely proportional to D_{ij}. In the simplest case, when all the off-diagonal elements of $\mathbf{D}$ are zero, Eq. 4 reduces to $F_{ii} = K_{FD}/D_{ii}$, where $K_{FD} = R_0^2 u_0^2/48$. The elements of matrix $\mathbf{D}$ can be finally retrieved by inverting the matrix $\mathbf{F}$. The F_{ij} can be obtained from the experimentally found parameters $P_{i,\mathrm{exp}}$, K_i, and σ_i through the following equations

$$l_0^{-1}\sum_{i=1}^{n} P_{i,\mathrm{exp}} = \sum_{i=1}^{n} K_i c_{i0} \tag{5}$$

$$l_0^{-1}\sum_{i=1}^{n} \sigma_i P_{i,\mathrm{exp}} = \sum_{j=1}^{n} c_{j0}\sum_{i=1}^{n} K_i F_{ij} \tag{6}$$

where l_0 (cm) is the length of the capillary occupied by the sample injected at the initial time ($l_0^{-1} = \pi R_0^2/V_0$, V_0 is the injected volume, R_0 is the inner radius of the tubing), $P_{i,\mathrm{exp}}$ are the pre-exponential parts of the Gaussian functions used to fit the experimental peaks, σ_i are the dispersions of the Gaussian functions, which are equal to the eigenvalues of the dispersion matrix $\mathbf{F}$, c_{i0} is the difference between the concentration of component i in the injected sample and in the carrier stream, K_i is the instrumental sensitivity respect to that component (typically linear in the concentration). The experimentally measurable quantities $P_{i,\mathrm{exp}}$, K_i, and σ_i can be found by fitting all the experimental peaks $v(t)$ (generated with injections of different compositions) according to

$$v(t) = \sum_{i=1}^{n} \frac{P_{i,\mathrm{exp}}}{\sqrt{4\pi\sigma_i t}}\exp\left[-\frac{u_0^2(t-t_0)^2}{4\sigma_i t}\right] \tag{7}$$

where u_0 is the mean velocity of the carrier stream and t_0 is the retention time. The coefficients K_i can be found by analyzing different experiments involving injections with only one $c_{i0} \neq 0$ as

$$K_i = l_0^{-1}\Big(\sum_{j=1}^{\mathrm{n}} P_{j,\mathrm{exp\_}i}\Big)/c_{i0} \qquad i = 1\ldots n \tag{8}$$

and $P_{j,\mathrm{exp\_}i}$ is the amplitude obtained for the jth Gaussian peak by fitting the experiment in which only $c_{i0} \neq 0$.

In a two-component system, one solute and solvent, the eigenvalue of the 1-D dispersion matrix, σ, obviously coincides with the self-dispersion coefficient F. Equation 7 can be rewritten as

$$v(t) = \frac{P_{\mathrm{exp}}}{\sqrt{4\pi F t}}\exp\left[-\frac{u_0^2(t-t_0)^2}{4Ft}\right] \tag{9}$$

In the two-component case, the knowledge of the instrumental sensitivity to calculate D is not necessary. In principle, F can be retrieved by fitting just one experimental peak through Eq. 9, however, the simultaneous fitting of multiple experimental peaks improve the confidence on the value of F. Finally, D can be easily calculated through the formula

$$D = \frac{R_0^2 u_0^2}{48F} \tag{10}$$

Materials and Methods

Our experimental setup for the measurement of diffusion coefficients consists of a high pressure liquid chromatography apparatus (Agilent 1260 series), which ensures suitable experimental conditions for the Taylor dispersion measurement.

The length of silica glass capillary used in all the experiments was 15 m between the injector and the cell of the differential flow-through thermostated refraction index detector, RID. The inner radius R_0 (= 0.016 ± 0.002 cm) of the tubing was checked by gravimetry, that is, from the mass of water required to fill the tube and it was found to be consistent with the value declared by the manufacturer. Both untreated and deactivated silica capillaries (SUPELCO Analytical) were employed. To adapt the small bore silica tubings to the standard 1/16″ connection ports of the HPLC apparatus, a specifically designed microtight fittings (IDEX UP-CHURCH) were used. The tubing was coiled in a 30-cm diameter helix and immersed in a thermostated water-bath (Julabo ME-16G). For all the experiments, the temperature of the water-bath was set as to match that of the RID cell (Agilent G1362A).

An isocratic pump (Agilent G1310B), which maintained a steady flow, was placed between the eluent reservoir and the injector. A 2-μL sample loop was used for injection. The detector was connected to a personal computer for data acquisition. An inline ion exchange resin-based degasser (Agilent G1322A) was also placed between the eluent reservoir and the pump.

Solutions were prepared using bidistilled water, TCE (Sigma-Aldrich analytical grade), mannitol (Sigma analytical grade), and sodium chloride (Sigma analytical grade). TCE was handled only with glass tools and syringes.

Samples were injected every 20 min to avoid the overlapping of the peaks. Experimental peaks generated with different injections were simultaneously fitted, using the Levenberg–Marquardt algorithm,[29] to Eq. 9. F and t_0 were fitted as shared parameters among the multiple peaks, P_{exp} was fitted as single parameter for each peak, while u_0, calculated from the instrumental flow rate, f (cm^3 min^{-1}) and from the capillary radius, R_0, was taken as a constant input parameter. A baseline of the form $(a+bt)$ was previously subtracted from the recorded signals with the help of a suitable software.

Results and Discussion

Generally, the most used capillaries for the implementation of the Taylor method are made in teflon. Teflon is chemically inert toward most of the solvents and analytes and 1/16″ teflon tubings, suitable for HPLC instruments, are cheap and can be found in any desired lengths. However, TCE is known to have a great affinity for this material[30] and its sorption on the tubing walls during the dispersion process alters the measurement of the diffusion coefficients. The physicochemical properties of TCE, in particular its high volatility and its affinity for polymeric materials, make difficult the choice of an alternative material. Silica tubings used as columns for gas chromatography seemed to be a valid alternative and we successfully used them for the measurement of D_{TCE} in water.

We adapted silica capillaries (O.D. 430 μm) to the standard conic 10–32 HPLC ports using nanotight adapters and we carefully conducted calibration procedures and tests in several experimental conditions. To separate the contribution of diffusion and convection to the dispersion process, we first ensured that the length and the radius of the capillary and the flow rate satisfied the condition $l/u \gg 0.14r^2/D$, where D was assumed to be of the order of 10^{-5} cm^2 s^{-1}. Moreover, in order to avoid the development of secondary flows, we also checked that the coiling radius of the capillary matched the condition $De^2Sc \le 20$, where De and Sc are the Dean and Schmidt numbers, respectively.[14,16] The experimental apparatus was finally tested by measuring the diffusion coefficient of a strong electrolyte, NaCl, and a sugar, mannitol, in water. Both the chemicals were tested in deactivated and untreated columns to check whether the polarity of the capillary could have an influence on the dispersion processes. The two diffusion coefficients were found to differ less than 1% with respect to those determined by diffractometer methods[28,31] in all the experimental conditions.

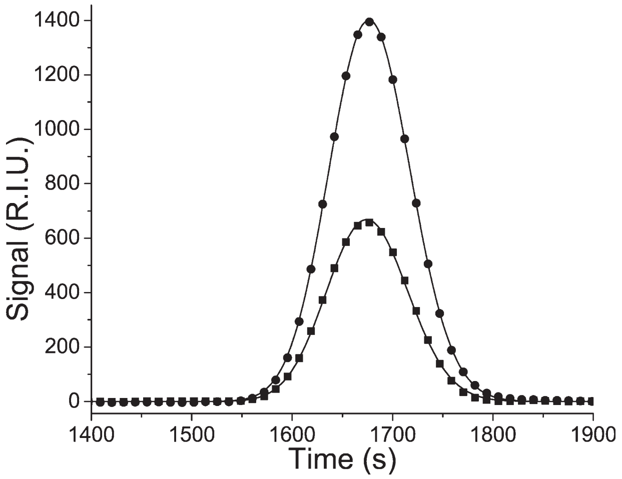

Figure 1. Dispersion peaks obtained by injecting a solution with Δ[TCE] = 1×10^{-3} M (■) and with Δ[TCE] = 2×10^{-3} M (•), in a flowing solution with [TCE] = 1×10^{-4} M.

Solid lines are the best fitting curves.

Figure 1 shows the dispersion peaks of TCE obtained for two different initial concentrations of the samples injected in a flowing solution of [TCE] = 1×10^{-4} M in water at 30°C. Solid lines represent the best fitting curves of the experimental data obtained by means of Eq. 9, after the subtraction of the signal baseline. The two peaks were fitted simultaneously and the integration confirmed a linear dependence of the instrument response on the concentration of the injected samples; in fact, the pre-exponential term P_{exp} is 7.0×10^3 R.I.U. × cm when Δ[TCE] = 1×10^{-3} M and 14.7×10^3 R.I.U. × cm when Δ[TCE] = 2×10^{-3} M, with a sensitivity $K = 2.90\times10^7$ R.I.U./M, as calculated through Eq. 8. Peaks generated by injection at various Δ[TCE] were simultaneously fitted in order to minimize the experimental errors and results for different experimental temperatures are reported in Table 1 and in Figure 2. The concentration of TCE in the eluent solution was varied in the range 1×10^{-5}–1×10^{-4} M without finding any appreciable difference among the diffusion coefficients measured at different temperatures, this means that for diluted solutions D_{TCE} is independent from the concentration of TCE.

Table 1. Dependence of D_{TCE} from the Temperature for a Dilute Solution of TCE in Water

T (°C)	D_{TCE} (cm^2 s^{-1})
25	$8.16 \pm 0.06 \times 10^{-6}$
30	$9.48 \pm 0.06 \times 10^{-6}$
35	$1.08 \pm 0.02 \times 10^{-5}$
45	$1.27 \pm 0.08 \times 10^{-5}$
55	$1.54 \pm 0.01 \times 10^{-5}$

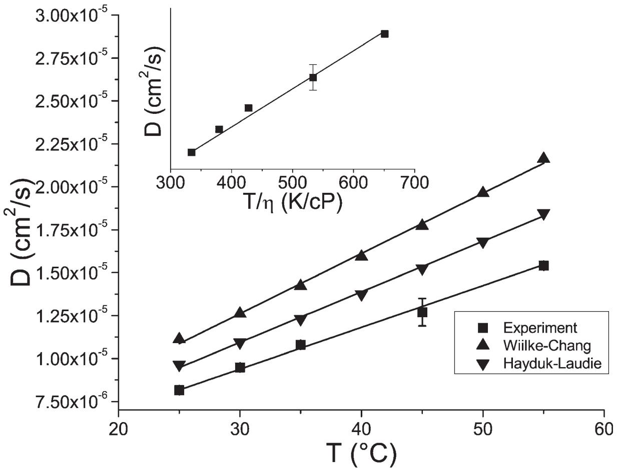

Figure 2. Comparision of D_{TCE} among experimental and theoretical data.

The inset shows the dependence of D_{TCE} upon the ratio T/η from the W&C equation.

These results suggest that over the range of concentrations studied, the TCE molecules move through water more or less independently of each other.

When the concentration of TCE in the flowing solution is rather small and does not contribute significantly to the viscosity of the eluent, diffusion coefficients increase linearly with the temperature as predicted by the semiempirical relation of Wilke and Chang (Eq. 1) and Hayduk e Laudie (Eq. 2). The comparison among experimental and theoretical values is reported in Figure 2. The up-pointing triangles represent the theoretical values for D_{TCE} calculated by the W&C relation, where the typical values for the water as the solvent (M, η, and $x = 2.6$[11,32]) were used and the molar volume for TCE, $V = 96.3$ cm^3 mol^{-1}, was calculated using the incremental method of Le Bas corrected by a factor 0.9.[13,33] The down-pointing triangles were calculated through the H&L relation with $V_A = 107$ cm^3 mol^{-1}. Both the theoretical series resulted overestimated (20–40%) respect to the experimental diffusion coefficients determined in this work (black squares in Figure 2). The inset in Figure 2 shows the dependence of D_{TCE} respect to the ratio T/η, the linear fitting of the plotted data, scaled by the ratio $(xM)^{0.5}/V^{0.6}$, yielded the numeric constant of the W&C relation for the specific case of TCE (5.1×10^{-8} in the place of 7.4×10^{-8}), so that theoretical values can be extrapolated for every temperature.

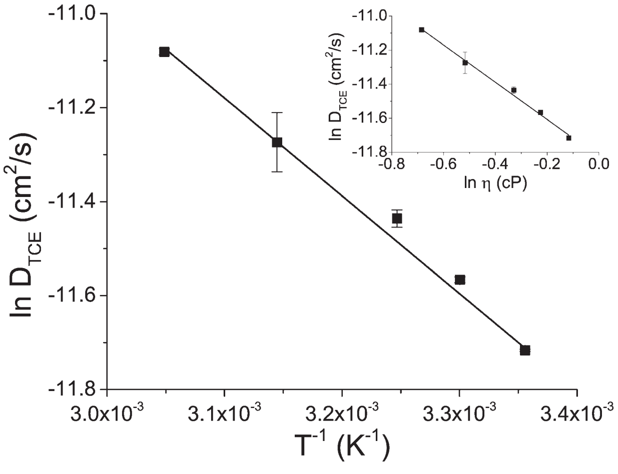

Figure 3. Arrhenius plot of D_{TCE} vs. 1/T.

The inset reports the dependence of D_{TCE} on the shear viscosity of solutions different temperatures.

The dependence of D_{TCE} upon the temperature (Figure 3), allowed to calculate the activation energy for the diffusion process E_a (Kcal mol^{-1}) of TCE in water, through the Arrhenius relation

$$\ln D = \ln D_0 - \frac{E_a}{RT} \tag{11}$$

where D_0 (cm^2 s^{-1}) is the diffusion coefficient for infinite temperature, R is measured in j mol^{-1} K^{-1} and T in K. The result (4.1 ± 0.1 Kcal mol^{-1} with $D_0 = 8.9\times10^{-3}$ cm^2 s^{-1}) was found to be in line with the literature data and lies in between the value for hydrocarbons[34] and aromatic compounds.[35] The inset in Figure 3 also reports the linear dependence of D_{TCE} on the shear viscosity of the solutions at different temperatures.

Conclusions

In this article, we presented a fast and convenient method based on the TDT, which allowed to measure for the first time D_{TCE} in a broad range of temperature and, if necessary, in any solvent. In principle, this method could be applied to all those chemicals which present experimental difficulties, such as high volatility or high affinity for commonly used polymeric materials, such as teflon. In the specific case of TCE, we found that at 25°C $D_{TCE} = 8.16\pm0.06 \times 10^{-6}$ cm^2 s^{-1} and the value was found to increase linearly with the temperature, while, in the limit of the experimental error, was independent from [TCE] for dilute solutions. Moreover, from the temperature dependence of the diffusion coefficients we could modify the Wilke and Chang equation to adapt it to the specific case of TCE, thus providing a suitable tool to extrapolate D_{TCE} for any desired experimental temperature. Our results are potentially useful for increasing the reliability of the advection-dispersion models commonly used to predict the fate of TCE in the environment.

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