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Diffusion Coefficients of Aromatics in Aqueous Solution

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Diffusion coefficients of the 12 aromatic compounds phenol, aniline, pyridine, 2,2-bis(4-hydroxyphenyl)-propane (bisphenol A), 2-chlorophenol, 2-nitrophenol, 3-nitrophenol, 4-nitrophenol, *o*-cresol, *m*-cresol, *p*-cresol, and 3,5-dihydroxytoluol (orcinol) have been measured in aqueous solution at (277.15, 298.15, and 323.15) K using the Taylor dispersion technique. In addition, aqueous solutions of caffeine, benzene, tetraethylammonium perchlorate, and tetramethylammonium perchlorate have been studied where reliable diffusion data are available in the literature in order to test the apparatus. The method provides data with an accuracy to within ±1.5%. In the range of concentrations studied (0.2×10^{-4} to 5.8×10^{-4} mol L^{-1}) the diffusion coefficient depends on the concentration and values at infinite dilution can be obtained by extrapolation. A modified Wilke−Chang equation was found to correlate the data with respect to their dependence on temperature and molecular size of the aromatic compounds.

1. Introduction

Aromatic compounds play an important role in chemical production processes. In addition, because of their intensive use, aromatics often appear as undesired pollutants in process water from which they have to be removed before the water can be used again or delivered into the environment. Separation processes such as adsorption or reverse osmosis are used for that purpose. Modeling these processes requires a quantitative treatment of the diffusive transport of aromatics or other organic substances across the nonconvective aqueous boundary layer adjacent to the surface of the adsorbing material or the membrane material.[1−3] Therefore, accurate data of diffusion coefficients of aromatic compounds in aqueous solution are of interest. The Taylor dispersion technique is a reliable method for determining diffusion coefficients and has been successfully applied in liquid nonelectrolyte and electrolyte mixtures, particularly in dilute aqueous solutions.[4−14] Its design is comparatively simple and can provide data with an accuracy of (1−2)%. If certain precautions are taken into account, it is possible to use the Taylor dispersion technique as an absolute method for determining diffusion coefficients. The method was first described by Taylor,[15,16] later on treated theoretical in a more rigorous form by Aris,[17] and finally presented in a generalized version by Alizadeh et al.[18] It is based on the effect that a pulse of solution injected into a long and thin cylindric tube through which the pure solvent is flowing in a laminar fashion is spread out in an almost symmetrical manner from a point which moves at the mean velocity $\bar{\nu}$ of the solvent. Laminar flow exists if the Reynolds number $Re < 1800$. Under the ideal condition of injecting a δ-function-shaped pulse, the molar concentration distribution $c(l,t)$ observed at the end of the tube having the length l is given by[19,20]

$$c(l,t) = h\sqrt{\frac{\bar{t}}{t}}\,e^{-(\bar{t}/t)[(\bar{t}-t)^2/2\sigma^2]} \tag{1}$$

with the so-called retention time $\bar{t}$

$$\bar{t} = \frac{l}{\bar{\nu}} \tag{2}$$

The variance σ^2 is defined by

$$\sigma^2 = \frac{r^2\bar{t}}{24D} \tag{3}$$

D is the diffusion coefficient of the solute in the solvent, and r is the radius of the tube. Equation 1 can be used to determine D by adjusting eq 1 to the detector signal being proportional to $c(l,t)$. Equation 1 is applicable under the following condition

$$\frac{2\bar{\nu}r^2}{48Dl} < 5 \times 10^{-4} \tag{4}$$

Under real experimental conditions some corrections to eq 1 have to be applied.[18] The retention time $\bar{t}$ and variance σ^2 obtained from the experiment have to be corrected to the ideal values $\bar{t}_{id}$ and σ^2_{id} before eq 3 is used for determining D

$$\bar{t}_{id} = \bar{t} + \sum_{i=1}^{3}\Delta\bar{t}_i \tag{5}$$

$$\sigma^2_{id} = \sigma^2 + \sum_{i=1}^{3}\Delta\sigma^2_i \tag{6}$$

The terms $\Delta\bar{t}_1$ and $\Delta\sigma^2_1$ are responsible for the influence of the finite volume of the injected pulse V_I, $\Delta\bar{t}_2$ and $\Delta\sigma^2_2$ are the corrections for the influence of the finite detector volume V_D, and $\Delta\bar{t}_3$ and $\Delta\sigma^2_3$ are those for the influence of the length l_v of the tubing (inner radius r_v) connecting the long dispersion tube with the detector. Detailed formulas for $\Delta\bar{t}_i$ and $\Delta\sigma^2_i$ are given in ref 18. A further correction which has to be considered arises from coiling the tube in the apparatus,[21] which has also been accounted for.

2. Experimental Section

2.1. Taylor Dispersion Apparatus. A piston pump (model 260D, ISCO) delivers continuously the carrier liquid at a constant flow rate through a tube which consists of two parts: the tube connecting the pump and the injection

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Table 1. Process Parameters of the Taylor Dispersion Apparatus

$\bar{v}/10^{-3}$ m s^{-1}	r(eq 8)/μm	r(microscope)/μm	l/m	$2\bar{v}r^2/48Dl$	Re
16.2 ± 0.1	154.4 ± 1.6	156.5 ± 4.3	61.91 ± 0.01	2.3×10^{-4}	6

Table 2. Input Data and Results for the Correction to $\bar{t}$ and σ^2 Using the UV-Detector (UV) or the Refractive Index Detector (RI)

	V_I/μL	V_D/μL	l_V/m	r_V/μm	$\Delta\bar{t}_1/t$	$\Delta\sigma_1^2/\sigma^2$	$\Delta\bar{t}_2/t$	$\Delta\sigma_2^2/\sigma^2$	$\Delta\bar{t}_3/t$	$\Delta\sigma_3^2/\sigma^2$
UV	5.0	0.8	0.08	125	-5×10^{-4}	-2×10^{-4}	-8×10^{-5}	-7×10^{-5}	1×10^{-3}	9×10^{-4}
RI	5.0	8.0	0.40	125	-5×10^{-4}	-2×10^{-4}	-7×10^{-4}	-6×10^{-4}	4×10^{-3}	4×10^{-3}

valve (six port valve, model 7725, Rheodyne), having a length of ~5 m, and the dispersion tube connecting the injection valve with the detector, having a length of 61.91 m which is coiled around a cylindric aluminum block having a diameter $2r_c = 0.40$ m and a height of 0.25 m. All tubings are made of stainless steel (Cr 16.8%, Ni 11.1%, Mo 2.1%, Mn 1.5%, Fe ~68.5%). The major part of the 5-m tubing and practically the total length of the dispersion tube including the injection valve and the aluminum block are immersed into a water bath whose temperature is controlled to within ±0.01 K using a thermostat (Haake F6C40) circulating water through the bath. The temperature of the bath is measured by the internal thermometer of the thermostat. Either a UV-detector (Lambda 1010, Bischoff) or a differential refractometer (Wat410, Waters) can be used as a detector, which is connected to a PC to receive the detector signals in a digitalized form. The UV-detector has preferentially been used in our experiments. Since it requires no special temperature control, it is located as close as possible to the outlet of the tube from the water bath to keep the length between the wall of the bath and the detector as small as possible (~0.15 m). The disturbing effect of an uncontrolled temperature over this length is minimized by thermal insulation and can be neglected.

2.2. Chemicals. Phenol, aniline, and pyridine were obtained from Merck, the nitrophenoles were obtained from Fluka, and the cresols, bisphenol A, 2-chlorophenol, and orcinol were obtained from Aldrich. In all cases the purities were better than 99%, stated by the manufacters and checked by the GC analysis. The chemicals were used without further purification, with the exception of aniline. Aniline was distilled under reduced pressure before using it. Bidistilled and degassed water was used as solvent.

2.3. Determination of Process Parameters. For sufficiently long retention times $\bar{t}$, $\bar{v}$ can be obtained from the time at which the peak maximum of the concentration distribution of an injected solution appears at the detector, which is identical with $\bar{t}$. The mean velocity $\bar{v}$ is then simply calculated by

$$\bar{v} = \frac{l}{\bar{t}} \tag{7}$$

The length l can be determined with high accuracy. A more critical point is an exact determination of the inner radius r of the dispersion tube. Two independent methods have been used. The flow rate u of the pump was measured gravimetrically by weighing the amount of water collected within a certain time interval in a glass vessel which was sealed properly to avoid losses of water by vaporization during the collection time. Several series of measurements for each volume rate have been made. Using the known value of $\bar{v}$, the radius r can be obtained from

$$r = \sqrt{\frac{u}{\pi\bar{v}}} \tag{8}$$

with $\bar{v}$ from eq 7.

Alternatively, the radius r was determined using a direct method. Seventy-seven small pieces cut from the sample from which the dispersion tube in the apparatus was made were immersed in parallel orientation into a liquid viscous resin material (Varidur 10). After its solidification, the resin block was cut perpendicular to the length direction of the imbedded bundle of tubes. The cut surface was polished carefully by an emulsion of argillaceous earth, and each area of the open capillary end pieces was measured using a microscope (Axiovert 405, Zeiss). By means of software (KS 300, Kontron Electronic), the area πr^2 can be determined with a resolution of 2.6 μm^2 and r can be calculated.

All results obtained for l, $\bar{v}$, and r are listed in Table 1 including the standard deviations and the estimated error for l. The results obtained for r using the two independent methods show satisfactory agreement. Table 1 also contains figures calculated from the process parameters of the apparatus which show that its operation fulfills all the limiting conditions under which the theory is applicable.

In Table 2 values of V_I, V_D, l_v, and r_v are listed which are needed for calculating the correction terms according to eqs 5 and 6. The results reveal that the corrections to be made for t as well as those for σ^2 are very small and can be neglected.

2.4. Measurements of Test Systems. Experimental data of the diffusion coefficient D of some aromatic compounds and other UV-light-absorbing organic substances such as caffeine in diluted aqueous solution exist in the literature. More recently data of aqueous solutions of tetramethylammonium perchlorate and tetraethylammonium perchlorate have been published. These data have been obtained using the Taylor dispersion technique[7,8,22,23] or other experimental techniques such as the diaphragm cell method[24] or a modified open end elution method[25] and can be used for comparison.

We have performed measurements with dilute solutions of benzene, caffeine, tetramethylammonium perchlorate, and tetraethylammonium perchlorate at 298.15 K. Double-distilled and degassed water were used as solvent. Benzene and caffeine solutions have been studied using an UV-detector. Figure 1 shows a typical example obtained for the concentration distribution registered by the UV-detector expressed as extinction E

$$E = \epsilon d c(l,t) \tag{9}$$

where ϵ is the molar extinction coefficient, d *is* the optical path length of the cuvette, and $c(l,t)$ is the concentration of the solute. The UV-detector was used at the wavelengths $\lambda = 203.0$ nm for benzene and $\lambda = 274.0$ nm for caffeine. We have tested the linear relationship between E and c by independent measurements of E as a function of c in the concentration range 1.3×10^{-4} to 2.6×10^{-3} mol L^{-1} for aqueous solutions of benzene and all other aromatic compounds studied here using a special UV–vis spectrometer (Lambda 12, Perkin-Elmer). The validity of eq 9 was confirmed by the results.[26] It is obvious from Figure 1 that

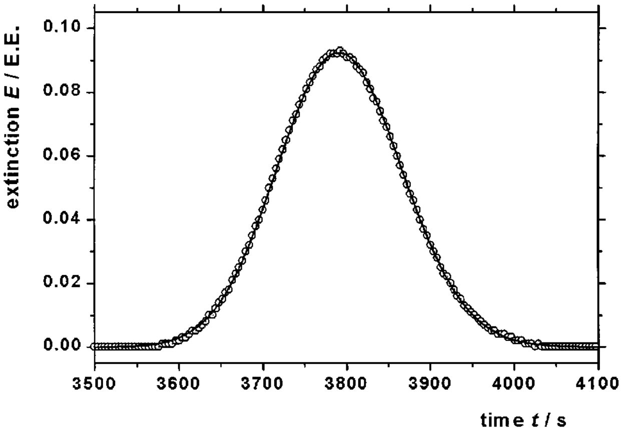

Figure 1. Dispersion peak for the extinction E using the UV-detector. Example: caffeine solution at 298.15 K, $c_{\mathrm{eff}} = 2 \times 10^{-5}$ mol L^{-1}; ○, data points; —, eq 1.

Table 3. Diffusion Coefficients *D* of Benzene, Caffeine, Tetramethylammonium Perchlorate (TMAP), and Tetraethylammonium Perchlorate (TEAP) in Aqueous Solution at 298.15 K

			$D/10^{-9}$ m^2 s^{-1}		
	$c_I/10^{-4}$ mol L^{-1}	$c_{\mathrm{eff}}/10^{-4}$ mol L^{-1}	this work (absolute)	lit.	this work (corrected)
benzene	26	0.4	0.96 ± 0.02	1.10 [8]	1.07
	53	0.8	0.97 ± 0.02		1.08
	105	1.7	1.03 ± 0.02		1.15
caffeine	6	0.1	0.704 ± 0.013	0.776 [22]	0.782
	8	0.1	0.704 ± 0.016		0.782
	14	0.2	0.695 ± 0.011		0.786
	17	0.2	0.706 ± 0.018		0.785
	32	0.4	0.729 ± 0.017		0.810
TMAP	83	1.4	1.22 ± 0.02	1.351 [23]	1.35
TEAP	69	1.1	1.01 ± 0.02	1.097 [23]	1.12

an almost perfect adjustment to the experimental detector signal is possible. Tetramethylammonium perchlorate and tetraethylammonium perchlorate solutions have been studied using a differential refractive detector. Since D can depend on concentration, it is necessary to determine the effective concentration c_{eff} to which the measured diffusion coefficient is related and which is obtained by the relation[18]

$$c_{\mathrm{eff}} = \frac{c_{\mathrm{I}} V_{\mathrm{I}}}{\pi r^3}\sqrt{\frac{24D\bar{t}}{l^2}}\left(\frac{5}{16} - \frac{1}{8\sqrt{\pi}}\right) \qquad (10)$$

where c_{I} is the concentration of the injected solution. Table 3 shows the results obtained for benzene, caffeine, tetramethylammonium perchlorate, and tetraethylammonium perchlorate at the different concentrations, and a comparison is made with the literature. Even at these low concentrations a distinct dependence of D on concentration is observed. Single measurements have been repeated several times, revealing that this dependence is significant. It is obvious that our data obtained by the absolute method are lower than the results found in the literature in all cases. The deviations are distinctly outside the experimental error limits of our method, which results from the error propagation of the uncertainties of $\bar{v}$, r, and l. Even though we are not aware of any systematic error sources of our procedure, we adjusted the effective capillary radius r so that minimal deviation from the literature data of the benzene, caffeine, tetramethylammonium perchlorate, and tetraethylammonium perchlorate solutions was obtained. This value of r is (165 ± 2) μm. The data obtained for the diffusion coefficients with this adjusted value of r are also listed in Table 3 and are denoted as corrected values of D.

3. Results and Data Reduction

Table 4 contains the results of the diffusion coefficients of 12 aromatic compounds obtained at different concentrations at three temperatures in aqueous solution determined by using the effective capillary radius. The concentrations c_{eff} are calculated according to eq 10. In all cases D decreases slightly at 298.15 K with decreasing concentration within the concentration range, with the exception of 2-chlorophenol.

It is worthwhile to note that the three nitrophenols and phenol are weak acids which are dissociated to some extent at low concentrations. With decreasing concentration, an

Table 4. Diffusion Coefficients, *D*, Activation Energies, E_A, and Hard Core Volumes, V^*, of Aromatics in Aqueous Solution

			$D/10^{-9}$ m^2 s^{-1}				
substance	$c_I/10^{-4}$ mol L^{-1}	$c_{\mathrm{eff}}/10^{-4}$ mol L^{-1}	277.2 K	298.2 K	323.2 K	E_A/kJ mol^{-1}	V^*/cm^3 mol^{-1}
aniline	24	0.4	0.576	1.050	1.840	18.8	74.3
	48	0.9		1.061			
	96	1.8		1.175			
bisphenol A	12	0.2	0.220	0.508	0.958	23.8	174.7
2-chlorophenol	41	0.7	0.503	0.929	1.654	19.3	96.4
	81	1.4		0.923			
	162	2.7		0.924			
o-cresol	93	1.6	0.497	0.926	1.608	19.0	86.1
	187	3.2		0.942			
m-cresol	49	0.8	0.489	0.889	1.578	19.0	97.5
	245	4.2		0.944			
p-cresol	87	1.5	0.499	0.914	1.611	19.0	87.8
2-nitrophenol	12	0.2	0.536	0.977	1.663	18.3	91.4
	62	1.1		1.000			
3-nitrophenol	13	0.2	0.510	0.917	1.589	18.4	96.3
	64	1.1		0.936			
4-nitrophenol	69	1.2	0.474	0.919	1.518	18.8	81.1
	344	5.8		0.930			
orcinol	54	0.8	0.451	0.798	1.407	18.4	89.7
phenol	72	1.3	0.543	0.998	1.788	19.3	76.3
	144	2.5		1.018			
pyridine	33	0.6	0.602	1.125	1.951	19.0	66.8
	66	1.2		1.117			
	165	3.1		1.154			

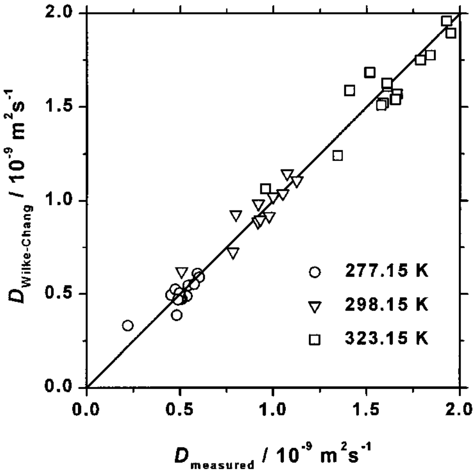

Figure 2. Wilke−Chang correlation according to eq 12.

increasing degree of dissociation is expected, possibly associated with an increase of the effective diffusion coefficient. However, this is not confirmed by the experiment.

The values obtained at the lowest concentrations can be assumed to be close to the diffusion coefficients at infinite dilution. At 277.15 K and 323.15 K, only data at the lowest concentration have been obtained, from which formal activation energies E_A were calculated according to

$$D = D_0 e^{-E_A/RT} \tag{11}$$

by a linear regression fitted to experimental values of ln D as a function of $1/T$. E_A has approximately the same value for all the compounds. Table 4 shows also values of the molar hard core volumes V^* which were calculated using an ab initio quantum mechanical procedure provided by the GAUSSIAN 94 software which calculates V^* of each molecule in its lowest electronic energy configuration using the basis set 6-31g(d′,p′).[27] In view of a quantitative use of V^*, the tight-option was used to calculate the volume.

The results in Table 4 show that D decreases with increasing molecular size and increases with increasing temperature. We have used the well-known Wilke−Chang correlation formula[28] to represent the data by

$$D = 7.4 \times 10^{-12} \frac{T\sqrt{\Phi_W M_W}}{\eta_W V^{*0.6}} \tag{12}$$

where M_W is the molar mass of water (18.015 g mol^{-1}) and η_W is the viscosity of water at temperature T in Kelvin with the values $\eta_{W,277} = 1.568$ mPa s, $\eta_{W,298} = 0.890$ mPa s, and $\Phi_{W,323} = 0.547$ mPa s taken from the literature.[29] The association factor Φ_W is a dimensionless empirical parameter which is characteristic for the solvent water. Φ_W was obtained by fitting its value to all data of D obtained for the 12 aromatics at the lowest concentrations and the three temperatures simultaneously. With $\Phi_W = 1.61$ a satisfying correlation was obtained, as illustrated in Figure 2.

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