

# Diffusion Coefficients of Aqueous Phenols determined by the Taylor Dispersion Technique

## Evidence for Solute Adsorption on the Walls of Teflon Tubing

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The Taylor dispersion technique has been used to determine the diffusion coefficients of the *m*-alkoxyphenol and alkyl *p*-hydroxybenzoate homologous series in aqueous  $5 \times 10^{-3}$  mol dm<sup>-3</sup> NaOH solutions and water–ethanol mixtures. The deviations from the expected behaviour for the higher homologues increase with the eluent water content and are attributed to solute adsorption on the walls of the Teflon dispersion tube. However, the adsorption corrections performed using Golay's equation for capillary chromatography do not account for all the diffusion coefficient deviations. The experimental solute hydrodynamic radii, calculated through the Stokes–Einstein equation, decrease as the eluent ethanol content is increased. These radii are smaller than those estimated by using atomic contributions or by adding the atomic van der Waals radii to the solute optimized geometry.

Diffusion is ubiquitous in several processes involving solute transport, such as mass transfer, chemical reactions and many biological processes. Knowledge of diffusion coefficients allows one to gain insight into the above cited processes and to obtain some useful information on solute–solvent interactions<sup>1–4</sup> and solute aggregation<sup>5,6</sup> or partitioning<sup>7–10</sup> processes.

A large number of techniques are used to measure diffusion coefficients. Some of the most common methods are Gouy interference,<sup>11</sup> diaphragm cell,<sup>12</sup> spin–echo NMR<sup>13</sup> and Taylor dispersion (or band broadening).<sup>14,15</sup> The Taylor dispersion technique is one of the most commonly used owing to the relative simplicity of the required apparatus and its well developed theoretical basis.<sup>14,16,17</sup>

This paper reports the application of this technique to the determination of diffusion coefficients of two homologous series of substituted phenols, the *m*-alkoxyphenols and the alkyl *p*-hydroxybenzoates (commonly known as parabens) in water and water–ethanol mixtures. Both series of compounds have well known bactericide and fungicide activities<sup>18,19</sup> and, for this reason, are widely used as preservatives in food and cosmetics.

### Experimental

In a Taylor dispersion experiment, a small amount of solute, a  $\delta$  peak, is injected into the solvent stream and suffers a combination of dispersion processes due to solute molecular diffusion and the eluent parabolic velocity profile. The Gaussian-like solute dispersion curve obtained allows determination of diffusion coefficients,  $D$ , through<sup>17</sup>

$$D = \frac{0.231 \times r^2 \times t_R}{(W_{1/2})^2} \quad (1)$$

where  $t_R$  is the solute retention time,  $r$  the tubing internal radius and  $W_{1/2}$ , the dispersion band's width at half height.

The diffusion apparatus was composed of a Varian 8500 HPLC pump operating at a flow rate of  $2.78 \text{ mm}^3 \text{ s}^{-1}$  and connected to an 8.5 m length Teflon tubing, which was coiled with a 50 cm diameter and placed in a temperature-

controlled bath. The tube was regularly cleaned with ethanol in order to avoid wall deposits. The solutes were injected directly into the solvent stream with sample volumes varying from 5 to 15 mm<sup>3</sup>. The solute concentrations were typically  $5 \times 10^{-4}$  mol dm<sup>-3</sup> for parabens and  $1 \times 10^{-3}$  mol dm<sup>-3</sup> for the *m*-alkoxyphenols. The solutes were detected with a UV detector and the dispersion curves registered with a chart recorder. The parameters of eqn. (1) were directly measured from the dispersion curves.

The Teflon tubing internal radius was calibrated by measurements with *p*-nitrophenol,  $\beta$ -naphthol and caffeine in water and diffusion coefficients from the literature.<sup>20,21</sup> The radii obtained using the phenols had a large uncertainty, ca. 10%, and their dispersion curves presented features which were attributed to solute adsorption (see Results and Discussion). In the case of caffeine, the close agreement of literature values measured using a glass diaphragm cell,<sup>21</sup> and the Taylor technique with stainless-steel<sup>5</sup> and Teflon tubings<sup>22</sup> rules out any significant deviation caused by caffeine adsorption and allows its use as a standard. The average radius obtained from six measurements was  $r = 0.418 \pm 0.014$  mm. A similar value,  $r = 0.38 \pm 0.02$  mm, was obtained from a transverse section of the tubing using a metallographic microscope. The Teflon tubing was purchased from LKB. FTIR analysis, performed in the ATR mode, confirmed its purity and did not detect surface chemical modification or hydrocarbon contamination.

The experimental conditions were chosen in order to satisfy the theoretical requirements of this method.<sup>17</sup> The following inequalities must apply

$$\frac{\bar{u}_0 r}{D} > 700 \quad (2)$$

where  $\bar{u}_0$  is the mean velocity of the fluid. In our experiments,  $\bar{u}_0$  is ca.  $6 \times 10^{-3} \text{ m s}^{-1}$  and the minimum value of  $D$  is ca.  $4 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ . These values lead to a value of ca. 2400 for the left-hand side of inequality (2).

$$\frac{Dt_R}{r^2} > 10 \quad (3)$$

This requirement is not fully satisfied under our experimental conditions since the values obtained range from 3 to 8. The failure to satisfy this condition is equivalent to neglecting a

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term in the flow equations for the diffusion process.<sup>17</sup> However, the maximum theoretical error caused by this assumption under our experimental conditions is smaller than 2%, which is within the reproducibility reported for this method.<sup>23</sup>

In order to ensure a laminar flow, the Reynolds number,  $Re$ , should satisfy

$$Re = 2\bar{u}_0 r \rho / \eta < 2000 \quad (4)$$

Using density,  $\rho$ , and viscosity,  $\eta$ , data for the eluents used, we obtain  $2 < Re < 5$ .

The effects of secondary flow caused by tube coiling can be neglected if the ratio of the coil radius to the internal radius,  $\omega$ , is larger than 100. According to our geometric parameters,  $\omega = 1300$ . Another requirement is that the product of the Dean ( $De$ ) and the Schmidt ( $Sc$ ) numbers satisfy

$$De^2 Sc \leq 20 \quad (5)$$

where  $De = Re\omega^{-1/2}$  and  $Sc = \eta/(\rho D)$ . According to our conditions, we obtain  $15 < De^2 Sc < 27$ . This theoretical requirement is needed in order to ensure an error of  $< 0.1\%$ . Therefore, slight violation of this requirement would not lead to a significant error in relation to our experimental reproducibility.

The alkyl *p*-hydroxybenzoates were a gift from Nipa Inc., with a stated purity of 99.9%, and were used as received. *m*-Methoxyphenol, p.a., was purchased from Eastman. The other *m*-alkoxyphenols were synthesized and purified as described elsewhere.<sup>24</sup> Ethanol (95% p.a., Merck) and doubly distilled water were used as solvents and the solutes were previously dissolved in the eluent solvent before injection. All experiments were performed at 298 K and each experiment was repeated at least four times.

## Results and Discussion

### Apparent Diffusion Coefficients

The measured diffusion coefficients, calculated using eqn. (1), are listed in Table 1. Examination of these data reveals that the decrease in the diffusion coefficients along the series is greater than that expected from the increase in the solute size. This deviation is especially large for the higher homologues in the high water content eluents, as can be seen in Fig. 1. Tominaga *et al.*,<sup>1-3</sup> in a study of the diffusion of some apolar

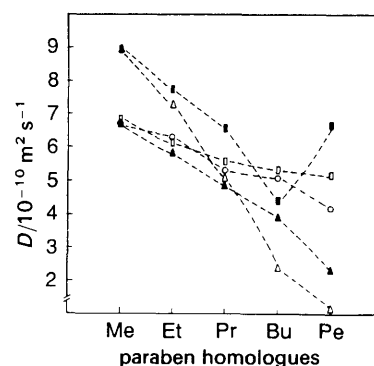


Fig. 1 Apparent and corrected diffusion coefficients for the parabens. Apparent diffusion coefficients in water ( $\Delta$ ), 10% ethanol ( $\blacktriangle$ ). Corrected coefficients in water ( $\blacksquare$ ), 10% ethanol ( $\circ$ ) and 95% ethanol ( $\square$ )

compounds in water and ethanol, observed that the diffusion in water is slower than expected, after viscosity corrections. They proposed that this effect was due to an increase in the apparent solvent microviscosity around the solute molecule as a consequence of an increase of the water organization caused by interaction with the solute hydrophobic moiety. However, their diffusion coefficients for an alkylbenzene series, benzene, toluene, ethylbenzene and butylbenzene, do not show any noticeable deviation with increase of the alkyl chain, as should be expected due to that hydrophobic effect. In addition, they were unable to detect any indication of an enhanced water structure in their diffusion experiments with temperature variation.<sup>2</sup> Those experiments were performed with the benzene derivatives in the concentration range  $(1-3) \times 10^{-4} \text{ mol dm}^{-3}$  and temperatures from 265 to 433 K. A similar non-deviating behaviour is observed with Frey and King's data<sup>25</sup> for the alkyl acetates, from ethyl to pentyl, in water at 298 K, with the solute concentration in the range  $(0.8-5) \times 10^{-3} \text{ mol dm}^{-3}$ .

Another possible explanation of this deviation is that the solutes might be undergoing hydrophobic aggregation. After injection, the solute dispersion inside the tube causes its dilution in a way that, when the solute band reaches the UV detector, the concentration profile is Gaussian-like, as revealed by the curve registered. Using the solute molar absorption coefficients, the maximum concentration at the detector was estimated to be *ca.* 1/50 of the initial value, *i.e.* *ca.*  $(1-2) \times 10^{-5} \text{ mol dm}^{-3}$ . The existence of hydrophobic aggregation in aqueous solutions is well known for more

Table 1 Apparent diffusion coefficients,  $D_{app}$ , and retention times,  $t_R$ , for the *m*-alkoxyphenols and alkyl *p*-hydroxybenzoates in aqueous,  $5 \times 10^{-3} \text{ mol dm}^{-3}$  NaOH solution and water-ethanol mixtures, at 298 K

solvent	methyl		ethyl		propyl		butyl		pentyl	
	$D_{app}$	$t_R$	$D_{app}$	$t_R$	$D_{app}$	$t_R$	$D_{app}$	$t_R$	$D_{app}$	$t_R$
parabens										
water	8.93	1544	7.25	1564	5.07	1630	2.37	1775	1.14	2566
NaOH solution	6.73	1500	7.84	1511	7.26	1529	6.79	1542	5.72	1563
10% EtOH <sup>a</sup>	5.24	1526	5.82	1551	4.84	1553	3.90	1614	2.30	1746
20% EtOH <sup>a</sup>	4.27	1525	5.01	1516	4.16	1534	3.78	1546	2.53	1643
30% EtOH <sup>a</sup>	4.27	1552	3.94	1544	3.69	1517	3.30	1520	2.93	1571
95% EtOH <sup>a</sup>	6.86	1541	6.13	1532	5.58	1554	5.35	1535	5.22	1551
<i>m</i> -alkoxyphenol										
water	10.4	1458	8.93	1470	6.81	1488	4.88	1528	—	—

<sup>a</sup> Ethanol volume fraction. Diffusion coefficients expressed as  $10^{-10} \text{ m}^2 \text{ s}^{-1}$ , these values were reproducible within 3%, and within 5% for the highly symmetric peaks. Retention times expressed in s, reproducible within 3% (the values for the *m*-alkoxyphenols were determined at a slightly higher pumping rate).

hydrophobic solutes, for instance surfactants at low concentrations. This phenomenon was also reported for molecules such as caffeine,<sup>5</sup>  $\alpha$ -phenylethylamine,<sup>26</sup> 2-butoxyethanol<sup>14</sup> and phenol<sup>27</sup> in water at higher concentration ranges or for alcohols and phenols in inert solvents.<sup>28</sup> However, to our knowledge, there is no report of the aggregation of molecules similar to phenols in aqueous solutions in the concentration range used. In addition, in this concentration range we did not detect any deviation than Beer's law for the parabens UV absorption, which would be expected in the case of solute association.

We also observed that, along with the diffusion coefficient deviations, there was an increase in the solute retention times, as shown in Table 1. In this technique the retention times should depend only on the fluid pumping rate. It was also observed that the increase in the retention times was, in some cases, associated with an asymmetry of the dispersion curves. In a Taylor experiment, the solute concentration profile is described by<sup>29</sup>

$$C(t) \propto (D/t)^{1/2} \exp[-12D(t - t_R)^2/r^2t] \quad (6)$$

Some theoretical dispersion curves are shown in Fig. 2 calculated for diffusion coefficients in the range  $(1-10) \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ . This figure shows that for slowly diffusing solutes, the pre-exponential factor produces an asymmetry on the upstream side of the peak. However, the asymmetry observed for the experimental curves is more pronounced, as can be seen in Fig. 3. The ratios of the widths at 10% height of the upstream to the downstream side of the peaks shown in Fig. 3 are 1.10, 1.23, 1.28 and 1.96, respectively, for methyl-, ethyl-, propyl- and butyl-paraben in water. At half height, these ratios are, respectively, 1.00, 1.08, 1.12 and 1.29. For the theoretical curves shown in Fig. 2, the ratios at 10% height are 1.11, 1.13, 1.15, 1.18 and 1.27 for diffusion coefficients equal to  $(10, 8, 6, 4 \text{ and } 2) \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ , respectively. At half height, the theoretical ratios are, respectively, 1.02, 1.02, 1.03, 1.03 and 1.05.

This comparison confirms that, although the theoretical dispersion curves also present an asymmetry, the tailing observed in the experimental curves is larger. Both features, the retention time increase and the curve tailing, may be interpreted as a consequence of solute adsorption on the Teflon dispersion tube. For the curves with higher asymmetries, the width-at-half-height method for data analysis may cause an additional error which could explain the higher experimental variance associated with the diffusion coefficients determined for butyl- and pentyl-paraben in water and 10% ethanol.

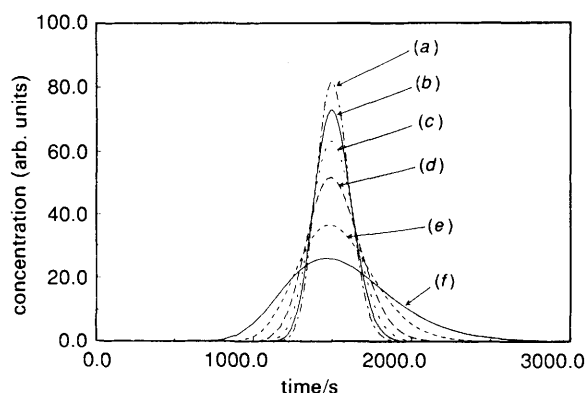


Fig. 2 Theoretical dispersion curves for Taylor experiments, calculated using eqn. (6), for diffusion coefficients in the range  $(1-10) \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ . Retention time,  $t_R = 1500 \text{ s}$  and tubing radius,  $r = 0.418 \text{ mm}$ .  $D/10^{-10} \text{ m}^2 \text{ s}^{-1} = 10$  (a), 8 (b), 6 (c), 4 (d), 2 (e) and 1 (f)

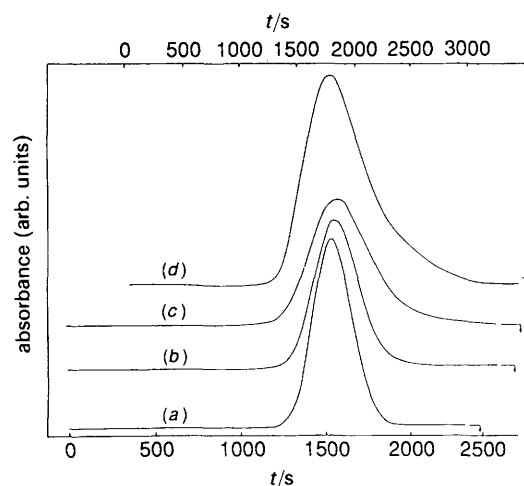


Fig. 3 Experimental dispersion curves for (a) methyl-, (b) ethyl-, (c) propyl- and (d) butyl-paraben in water

Teflon, a perfluorinated polymer, is believed to be relatively inert towards adsorption owing to its hydrophobic and lipophobic nature. For this reason, the use of Teflon instead of stainless-steel tubings was suggested<sup>30</sup> for Taylor experiments with the non-ionic surfactant Triton X-100 in order to minimize adsorption problems. Nevertheless, some evidence for the adsorption of compounds such as iron carbonyls, chloroform and acetic acid,<sup>31</sup> cationic surfactants<sup>32,33</sup> and inorganic acids<sup>34</sup> on Teflon has been reported.

#### Diffusion Coefficient Correction for Solute Adsorption

Golay<sup>35</sup> has derived equations to describe the solute diffusion and partitioning processes which occur in capillary chromatography columns. According to this approach, when the diffusion process occurs with solute adsorption and the adsorption process is sufficiently fast, the real diffusion coefficient can be related to the apparent value, calculated from the dispersion parameters through eqn. (1), as follows

$$D = D_{\text{app}} \frac{(1 + 6k + 11k^2)}{(1 + k)} \quad (7)$$

The capacity factor,  $k$ , is

$$k = \frac{t_a - t_0}{t_0} \quad (8)$$

where  $t_a$  and  $t_0$  are, respectively, the retention times of the adsorbed and unretained solute.

The retention times for the first homologues do not change, within experimental error, for all of the solvents used, ruling out any significant adsorption. Therefore, the methyl-paraben retention time was used as  $t_0$  in eqn. (8), for each solvent, and the capacity factors obtained are listed in Table 2. The diffusion coefficients corrected for solute adsorption through eqn. (7) are also shown in Table 2.

The corrected solute diffusion coefficients in water and 10% ethanol solutions still present a more pronounced decrease along the series than the values with higher ethanol content, with larger deviation for the higher homologues, as can be observed in Fig. 1. In addition, the corrected value for pentylparaben, which is the most influenced by the adsorption, falls out of the normal trend. This behaviour indicates that eqn. (7) does not fully account for the solute adsorption and that the solvation process suggested by Tominaga *et al.*,<sup>1-3</sup> another type of solute hydrophobic association or even

**Table 2** Corrected diffusion coefficients,  $D_{\text{corr}}$ , capacity factors,  $k$ , for the solute adsorption on Teflon, eqn. (8), and the solute hydrodynamic radii,  $r$ , calculated using eqn. (9) and (10), with  $C = 6$ 

solvent	methyl			ethyl			propyl			butyl			pentyl		
	$D_{\text{corr}}$	$k$	$r$	$D_{\text{corr}}$	$k$	$r$	$D_{\text{corr}}$	$k$	$r$	$D_{\text{corr}}$	$k$	$r$	$D_{\text{corr}}$	$k$	$r$
	parabens														
water	8.93	<sup>a</sup>	2.74	7.76	0.013	3.16	6.59	0.056	3.72	4.44	0.15	5.52	6.70	0.66	3.65
NaOH solution	8.63	<sup>a</sup>	2.83	8.16	0.007	3.01	7.99	0.019	3.07	7.74	0.028	3.16	6.98	0.042	3.50
10% EtOH <sup>b</sup>	6.73	<sup>a</sup>	2.63	6.29	0.016	2.81	5.28	0.018	3.36	5.11	0.058	3.46	4.21	0.14	4.20
20% EtOH <sup>b</sup>	5.24	<sup>a</sup>	2.48	5.01	<sup>a</sup>	2.60	4.33	0.006	3.00	4.04	0.014	3.21	3.59	0.077	3.61
30% EtOH <sup>b</sup>	4.72	<sup>a</sup>	2.42	3.94	<sup>a</sup>	2.62	3.69	<sup>a</sup>	2.80	3.30	<sup>a</sup>	3.13	3.11	0.012	3.32
95% EtOH <sup>b</sup>	6.86	<sup>a</sup>	2.42	6.13	<sup>a</sup>	2.71	5.58	<sup>a</sup>	2.98	5.35	<sup>a</sup>	3.11	5.22	<sup>a</sup>	3.18
	<i>m</i> -alkoxyphenol														
water	10.14	<sup>a</sup>	2.36	9.28	0.008	2.64	7.56	0.021	3.24	6.10	0.048	4.02	—	—	—

<sup>a</sup> Adsorption negligible. <sup>b</sup> Ethanol volume fraction. Diffusion coefficients expressed in  $10^{-10} \text{ m}^2 \text{ s}^{-1}$  and hydrodynamic radii expressed in  $10^{-10} \text{ m}$ .

a combination of these processes may be occurring. However, our results at the moment do not allow discrimination of the reasons for these deviations.

Nevertheless, the corrected diffusion coefficients are close to those reported for similar compounds, some of them obtained by using other techniques. The values of some diffusion coefficients, in water at 298 K, expressed as  $10^{-10} \text{ m}^2 \text{ s}^{-1}$ , are as follows: 9.40 for phenol,<sup>14</sup> 8.43 for *p*-aminobenzoic acid,<sup>36</sup> 9.0 for benzoic acid<sup>37</sup> and 7.18 for the diffusion of *o*-ethoxyphenol in 0.1 mol  $\text{dm}^{-3}$   $\text{H}_2\text{SO}_4$  solution.<sup>38</sup>

The capacity factor can be used as a measure of the solute affinity for the tubing walls, in relation to its affinity for the solvent. Ethanol addition and solute ionization in NaOH solution reduce paraben adsorption. These features indicate that the adsorption process has a hydrophobic nature. This behaviour is confirmed by preliminary results from batch adsorption experiments from aqueous solutions of the alkyl *p*-hydroxybenzoates on Teflon, which confirmed a higher adsorption for the more hydrophobic homologues. It is known that hydrocarbons and fluorocarbons have an overall unfavourable interaction<sup>39</sup> and any attractive interactions between them are often disregarded. However, these adsorption results point out that this interaction cannot be neglected, especially when it occurs associated with hydrophobic interactions, as in the case of these aqueous solutions.

Therefore, in order to avoid errors due to solute adsorption on the dispersion tube, other tube materials should be used, rather than Teflon. Although there is no confirmation, some possibilities are stainless steel, or other metals and glass. Another alternative procedure to avoid such deviations is to inject the solute into a dilute carrier solution of the solute.

### Estimates of the Solute Hydrodynamic Radii

The relationship between the diffusion coefficients and the solute hydrodynamic radius can be described by the Stokes–Einstein relation:

$$D = k_{\text{B}} T / f \quad (9)$$

where  $k_{\text{B}}$  is the Boltzmann constant,  $T$  the temperature and  $f$  a frictional factor. For the case of a spherical diffusing entity in a continuum solvent, the frictional factor can be expressed as

$$f = C \pi \eta r \quad (10)$$

where  $\eta$  is the solvent viscosity,  $r$  the solute hydrodynamic radius and  $C$ , in this case, is equal to 6.

For the case of asymmetric solutes, if the flow rate is low enough to allow the Brownian motion to randomize the solute orientations, the frictional factor becomes<sup>40</sup>

$$f_{\text{asy}} = \frac{6\pi\eta a_s}{x(p)} \quad (11)$$

where  $a_s$  is the radius of a sphere with the same volume on the solute and  $x(p)$ , where  $p$  is the ratio of the revolution to the equatorial semiaxes of the ellipsoid, is defined as

$$x(p) = \frac{p^{1/3}}{(p^2 - 1)^{1/2}} \ln[p + (p^2 - 1)^{1/2}] \quad (12)$$

Using scale molecular models, we estimate the  $p$  values for the two extreme paraben conformations, when the alkyl chain is fully extended and when it is folded over the aromatic ring. The benzene ring and the carbonyl group were kept coplanar as indicated by molecular orbital calculations (which are in agreement with our AM1 calculations).<sup>41</sup> According to this approach, the maximum difference between the cases of the spherical approximation and of the fully extended conformation is 8%, as shown in Table 3. The fully extended conformation reduces the repulsion due to the *gauche* conformations in the alkyl chain, but the folded one should be favoured in aqueous solutions owing to its smaller hydrophobic surface. Beezer *et al.*<sup>42</sup> observed that the paraben solubility changes due to a methylene increment are smaller for chain lengths greater than hexyl. They suggested that this behaviour is due to a greater freedom of movement, which allows the alkyl chain to fold, thus facilitating solute accommodation within the solvent structure. Since we do not know the actual solute conformation, we chose to use the

**Table 3** Asymmetry parameter,  $p$ , and the relative difference caused by the asymmetry in relation to the assumption of spherical solutes [eqn. (11) and (12)], calculated for the alkyl *p*-hydroxybenzoates

solute	conformation	$p$	$1/x(p)$
methyl	extended	1.7	1.03
	folded	1.6	1.02
ethyl	extended	1.9	1.04
	folded	1.6	1.02
propyl	extended	2.1	1.05
	folded	1.6	1.02
butyl	extended	2.3	1.06
	folded	1.6	1.02
pentyl	extended	2.6	1.08
	folded	1.6	1.02



spherical approximation, assuming that any deviation caused by different conformations could be neglected.

Eqn. (9) and (10) were originally developed to describe the diffusion of spheres in a continuum fluid, but it has also been successfully applied to the diffusion of macromolecules<sup>40</sup> and large aggregates such as micelles.<sup>43</sup> Nevertheless, there are some doubts as to its applicability when the solute and the solvent have similar sizes.<sup>44–46</sup>

In general, it was found that the Stokes–Einstein equation describes the solute diffusion well with  $C$  values between 4, for a slipping condition, and 6, for a sticking condition. Loh and Volpe<sup>47</sup> have shown that this equation fits a large number of literature diffusion coefficients well, by using  $C = 6$  for diffusion in water and  $C = 4$  for organic aprotic solvents.

Edward pointed out<sup>46</sup> that an adequate measure for the solute hydrodynamic radius is obtained through its van der Waals volume. For this reason, we estimated this data through two different approaches: one using the sum of the atomic group contributions<sup>46</sup> and the other through calculations using the approach developed by Higo and Go<sup>48</sup> which required the optimized molecular geometries, in this case obtained by the AM1 semi-empirical method. The solvated radius was estimated by adding a water monolayer to the solute-optimized conformation. Both calculations were performed by a program elaborated by Gaudio.<sup>49</sup> As can be seen in Table 4, both methods lead to the same van der Waals radii. The experimental molar volume reported for methylparaben in aqueous solutions,<sup>50</sup>  $V_m = 117.5 \text{ cm}^3 \text{ mol}^{-1}$ , leads to a solute radius  $r = 3.60 \times 10^{-10} \text{ m}$ , which is larger than the calculated one.

In the present study, we estimate the parabens and  $m$ -alkoxyphenol hydrodynamic radii from the diffusion coefficients using eqn. (9) and (10) and  $C = 6$ . The results are shown in Table 2. The experimental hydrodynamic radii are smaller than the calculated ones. The assumption of  $C = 4$ , would lead to 50% higher radii values, which are still smaller than those calculated assuming a complete water solvation shell. This supports the idea that these solutes diffuse at the most, partially solvated.

Despite the fact that the Stokes–Einstein approach has been used to evaluate the number of solute and solvent molecules in a diffusing entity,<sup>51</sup> the above discussed limitations of this equation require caution in the interpretation of the absolute values obtained for the solute hydrodynamic radii. However, one important conclusion of that study<sup>51</sup> is that solute and solvent diffusion are strongly correlated. For this reason, we prefer to compare the variation of the solute hydrodynamic radii with the eluent composition changes in order to determine the solute–solvent interactions.

Analysis of the experimental paraben hydrodynamic radii reveals a slight decrease in the solute Stokes–Einstein radius

as the ethanol content increases. It is expected that ethanol addition would lead to the replacement of the water by ethanol molecules in the solvation shell. This preferential ethanol solvation is supported by the higher solubility of these compounds in alcohol than in water. Therefore, these results indicate that, although ethanol preferentially interacts with these solutes in relation to water, the alcohol has a smaller effect on the solute diffusion.

## Conclusion

This paper demonstrates that the Taylor dispersion technique requires careful use owing to the possibility of systematic deviations caused by solute adsorption on the tubing walls, even when using supposedly inert materials such as Teflon. For the solutes studied in this paper, this adsorption has a hydrophobic nature and decreases with phenol ionization and with the addition of ethanol to the eluent. The diffusion coefficients were corrected for adsorption, but some deviations still remain for the higher homologues, indicating that the correction performed is not complete. The experimental hydrodynamic radii are smaller than the calculated solute van der Waals radii. These values decrease slightly with ethanol addition to the solvent, suggesting that this solvent has a smaller effect on the paraben diffusion in comparison to water.

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**Table 4** Estimates of the solute van der Waals radii, expressed in  $10^{-10} \text{ m}$ , for the  $m$ -alkoxyphenols and the alkyl  $p$ -hydroxybenzoates, for details, see text

homologue	parabens			$m$ -alkoxyphenols
	$r^a$	$r^b$	solvated radius <sup>c</sup>	$r^a$
methyl	3.15	3.15	4.97	2.99
ethyl	3.29	3.29	5.16	3.14
propyl	3.41	3.40	5.33	3.27
butyl	3.52	3.52	5.48	3.39
pentyl	3.62	3.62	5.63	—

<sup>a</sup> Obtained using atomic contributions. <sup>b</sup> Obtained through the AM1 optimized solute geometry. <sup>c</sup> AM1 values with a water monolayer.

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