Fluid Phase Equilibria 301 (2011) 234–243

Contents lists available at ScienceDirect

Fluid Phase Equilibria

journal homepage: www.elsevier.com/locate/fluid

Binary diffusion coefficients of phenolic compounds in subcritical water using a chromatographic peak broadening technique

Keerthi Srinivas[a], Jerry W. King[a,*], Luke R. Howard[b], Jeana K. Monrad[b]

[a] Ralph E. Martin Department of Chemical Engineering, University of Arkansas, 3202 Bell Engineering Center, Fayetteville, AR 72701, United States
[b] Department of Food Science, University of Arkansas, 2650 North Young Avenue, Fayetteville, AR 72704, United States

ARTICLE INFO

Article history:
Received 16 July 2010
Received in revised form 3 December 2010
Accepted 8 December 2010
Available online 15 December 2010

Keywords:
Diffusion coefficient
Flavonoids
Phenolic compounds
Subcritical water
Taylor–Aris method

ABSTRACT

Infinite dilution diffusion coefficients of certain phenolic compounds were measured as a function of temperature in water slightly acidified with formic acid using the Taylor dispersion method. The diffusion coefficients calculated using the chromatographic peak broadening technique were found to increase exponentially with an increase in the temperature. The diffusion coefficients of the selected phenolic compounds did not vary as a function of their molecular weights and the diffusion coefficients of the phenolic compounds increased as a function of temperature (from 2.16×10^{-10} m^2 s^{-1} at 298 K to 5.79×10^{-10} m^2 s^{-1} at 413 K for malvidin-3,5-diglucoside). However, for some phenolic compounds such as gallic acid monohydrate, quercetin-3-β-D-glucoside, protocatechuic acid and (−)-epicatechin, there were difficulties in making measurements above temperatures of 352 K, 372 K, 392 K and 413 K, respectively, due to thermal degradation of the phenolic compounds in water above these temperatures. The experimentally measured diffusion coefficients of the phenolic compounds were correlated as a function of temperature and solvent viscosity and were compared with those predicted using theoretical models. The validity of the Stokes–Einstein diffusion model in predicting the diffusion coefficients of the phenolic compounds in hot pressurized water was also evaluated.

1. Introduction

Extraction of value-added products from natural matrices using pressurized fluids is gaining widespread application in the food and nutraceutical industries. Phenolic compounds are compounds present in natural products and are known for their benefits to human health due to their antioxidant, anti-microbial, anti-viral and anti-proliferative properties [1]. However, the knowledge of fundamental solution properties such as solute solubility and binary diffusion coefficients of polyphenolic compounds is required to optimize their extraction from natural products. Such data are limited in the literature and are also quite difficult to measure due to the molecular complexity of such compounds and their sensitivity to heat and light. Studies have indicated that the prediction of binary diffusion coefficients of various compounds using theoretical models such as the Stokes–Einstein model and hydrodynamic theory can show a deviation up to 20% from that measured experimentally [2]. In this study, we have measured the binary diffusion coefficients of certain phenolic compounds in water at temperatures above its boiling point.

Water is an environmentally benign solvent, and at higher temperatures, exhibits properties such as a higher diffusivity and lower viscosity [3]. Subcritical water, at temperatures above its boiling point and kept liquefied under pressure, can be used as a solvent to extract polar organic compounds from natural product matrices [4]. Hot pressurized water has been used for example to extract antioxidants from rosemary plants [5], canola meal [6], *Eucalyptus grandis* [7], citrus [8] and grape pomaces [9].

Knowledge of the thermodynamic and mass transfer properties of the phenolic compounds in subcritical water is important in predicting optimized conditions for maximum recovery from natural products. The Hansen solubility parameter concept has been used to predict the optimal temperature range for the extraction of phenolic compounds from natural products [10]. However, studies have indicated that the extraction rates of certain subcritical water extraction processes, especially at lower solvent flow rates, are mass-transfer limited [11]. Mass transport properties such as binary diffusion coefficients are dependent on the chosen processing conditions such as temperature, pressure, pH, residence time, particle size and solvent flow rate.

Studies have indicated that moderate pressures (>40 bar) are required to maintain water in its subcritical state, and that pressure has a negligible effect on the extraction of solutes from natural matrices [2]. However, a number of studies have been performed that indicate a significant effect of temperature and pH [12], particle

* Corresponding author. Tel.: +1 479 575 5979; fax: +1 479 575 7926.
E-mail address: jwking1@uark.edu (J.W. King).

0378-3812/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.fluid.2010.12.003

size [13] and solvent flow rate [14] on the subcritical water extraction of antioxidants from natural products. Studies performed by Cacae and Mazza [15] on the extraction of flavonoid compounds from milled frozen black currants using aqueous ethanol showed that the extraction rate was dependent on both temperature and ethanol concentrations. This study also indicated that thermal degradation of the phenolic compounds occurred at high temperatures resulting in lower flavonoid yield. Another study [16] by Palma et al. reported that phenolic compounds, especially aglycones, showed lower stabilities at temperatures greater than 372 K resulting in lower recoveries of flavonoids such as catechin and epicatechin, when methanol was used as solvent. Recent studies in our group have shown that even though the solubility of most flavonoids compounds increases exponentially with increasing temperature [17,18], it is also critical to determine physicochemical data which influence the mass transfer of solutes in this temperature range.

A number of methods have been used for measuring binary diffusion coefficients of organic compounds in solvents such as light scattering [19], nuclear magnetic resonance spectroscopy [20], the diaphragm-cell method [21], a membrane-based technique [22], interferometry [23], capillary evaporation [24] and the Taylor dispersion method [25] and its well known variant, the chromatographic impulse response method [26]. There are few studies on the measurement of diffusion coefficients of flavonoids in the literature. Mantell et al. [27] measured the infinite dilution binary diffusion coefficient of malvidin-3,5-diglucoside in supercritical carbon dioxide at different temperature, pressure and methanol (co-solvent) conditions using the Taylor dispersion method. Diffusion coefficients of catechin and epicatechin in water have also been measured using NMR pulsed-field gradient spin echo technique [28]. The diffusion coefficient of catechin at infinite dilution in water by this technique was found to be about 7.9×10^{-10} m^2 s^{-1}. The Taylor dispersion technique was also used to measure the diffusion coefficients of various flavonoids in alcoholic solvents at 298 K to study the effect of the hydrogen bonding between the solute and the solvent on mass transfer [29]. However, there are no data available in the literature on the diffusion coefficients of the phenolic compounds in water above its boiling point.

In this study, the binary diffusion coefficients at infinite dilution of the phenolic compounds in hot pressurized water were measured using a chromatographic peak-broadening method. The experimentally measured diffusion coefficients as a function of temperature were compared with those predicted using theoretical calculations based on the Stokes–Einstein model.

2. Theoretical background

The binary diffusion coefficient of the phenolic compounds can be measured using a method developed by Taylor [30] and extended by Aris [31]. The Taylor–Aris dispersion method involves the injection of a pulse of solute into a continuous flow of solvent. The solute flows through a capillary column placed in a constant temperature oven and the concentration profile of the solute is recorded at the outlet from the oven using an absorbance detector. The dispersion of the solute pulse through the capillary tubing is influenced by molecular diffusion and to a lesser extent, the axial bulk flow. The peak distribution obtained at the outlet of the Taylor diffusion apparatus is used to measure the diffusion coefficient of the solute in the solvent at a particular temperature. This procedure to measure the diffusion coefficient of a solute using the chromatographic peak broadening method has been reported previously [32–34].

For the concentration profile to be considered Gaussian, the value of D_{eff}/u_aL should be very small ($\ll$0.1), and the variance of the concentration profile is given by

$$\sigma^2 = \frac{2D_{AB}L}{u_a} + \frac{r_o^2 u_a L}{24D_{AB}} \quad (1)$$

where r_o is the inner radius of the capillary column, L is the length of the column, D_{AB} is the diffusion coefficient of solute A in solvent B, u_a is the solvent flow velocity through the column. D_{eff} is the effective dispersion coefficient given by:

$$D_{eff} = D_{AB} + \frac{r_o^2 u_a^2}{48D_{AB}} \quad (2)$$

For diffusivity in liquid mixtures, the first term in Eq. (1) is considered negligible. The chromatographic plate height is then defined as the ratio of the variance in the concentration profile to the length of the column. In the case of a coiled column, there is a probability of secondary flow effects in the column. In such a situation, the following condition must be satisfied for the above equation to be valid [35].

$$DeSc^{0.5} < 10 \quad (3)$$

where De = Dean number and Sc = Schmidt number

$$De = \frac{\rho u_a d_{tube}}{\mu}\sqrt{\frac{d_{tube}}{d_{coil}}} \quad (4)$$

$$Sc = \frac{\mu}{\rho D_{AB}} \quad (5)$$

where d_{tube} and d_{coil} are the inner diameters of the capillary column and the coil, respectively, ρ is the density of the solvent and μ is the dynamic viscosity of the solvent. However, some studies have reported that the secondary flow effects can be neglected as long as $DeSc^{0.5}$ is less than 18 [36].

If the aforementioned conditions are satisfied, then the binary diffusion coefficient of the flavonoid solutes in water can be calculated from the following equation:

$$D_{AB} = \frac{u_a}{4}\left[H - \left(H^2 - \frac{r_o^2}{3}\right)^{0.5}\right] \quad (6)$$

The theoretical chromatographic plate height, HETP or H, can be calculated from the peak width at half height of the Gaussian peak using the following equation:

$$H = \frac{LW_{0.5}^2}{5.545t_R^2} \quad (7)$$

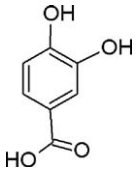
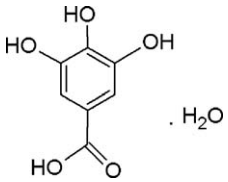
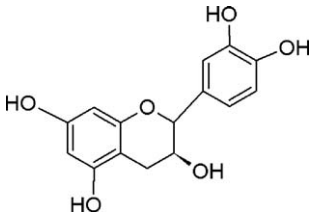
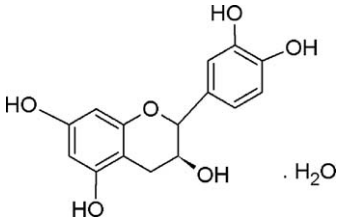
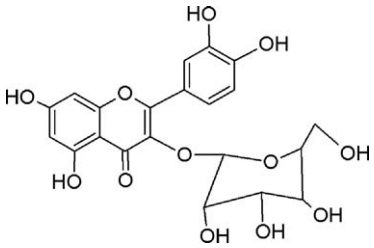
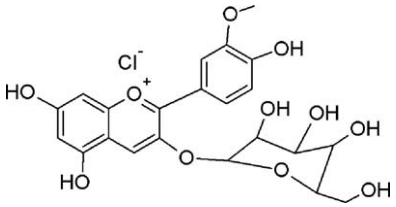
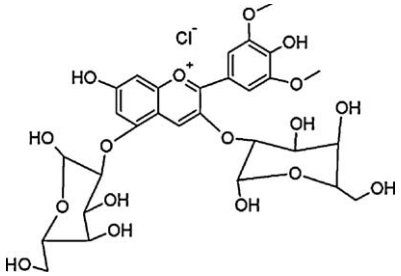
where $W_{0.5}$ is the peak width at half height of the Gaussian peak and t_R is the retention time of the solute in the column.

3. Materials and methods

3.1. Chemicals

The description and product information on the phenolic compounds used in this study are shown in Table 1. Ultrapure water (18.2 Ω cm; 1–5 ppb TOC and <0.001 EU/mL pyrogen levels) was obtained from a Milli-Q Synthesis A10 system (Millipore, Bellerica, MA, USA). Formic acid (CAS# 64-18-6; ACS grade) was purchased from VWR (Batavia, IL, USA). The solvent (0.5% (v/v) formic acid in water) was degassed using a nitrogen purge. For convenience, the molar volume at the boiling point of the phenolic compounds reported in Table 1 was calculated using Le Bas group contribution method [37], and these are utilized in Section 4 in predictive equations to estimate the diffusion coefficients of the phenolic compounds.

Table 1
Phenolic compounds used in this study.

Solute	Structure	Product information	Company	Wavelength (nm)	MW ($g\,mol^{-1}$)	$V_{b,m}$[a] ($cc\,mol^{-1}$)
Protocatechuic acid		CAS# 99-50-3; Lot# 0001400812; ≥98% powder	Sigma–Aldrich (St. Louis, MO)	280	154	163
Gallic acid monohydrate		CAS# 5995-86-8; Lot# CBEJB	VWR (Batavia, IL)	280	188	140
(−)-Epicatechin		CAS# 35323-91-2; Lot# 05125-550	Chromadex (Irvine, CA)	280	290	273
(+)-Catechin hydrate		CAS# 225937-10-0; Lot# 1386954; ≥97% purum	Sigma–Aldrich (St. Louis, MO)	280	308	288
Quercetin-3-β-D-glucoside		CAS# 21637-25-2; Lot# 1373210; Filling code: 11908159; ≥90% HPLC	Sigma–Aldrich (St. Louis, MO)	364	464	679
Peonidin-3-glucoside chloride		CAS# 6906-39-4; Lot# 16360-897	Chromadex (Irvine, CA)	510	499	1070
Malvidin-3,5-diglucoside chloride		CAS# 16727-30-3; Lot# 13076-315	Chromadex (Irvine, CA)	510	691	1650

[a] Molar volumes at boiling point ($V_{b,m}$) calculated using Le Bas [35] group contribution method.

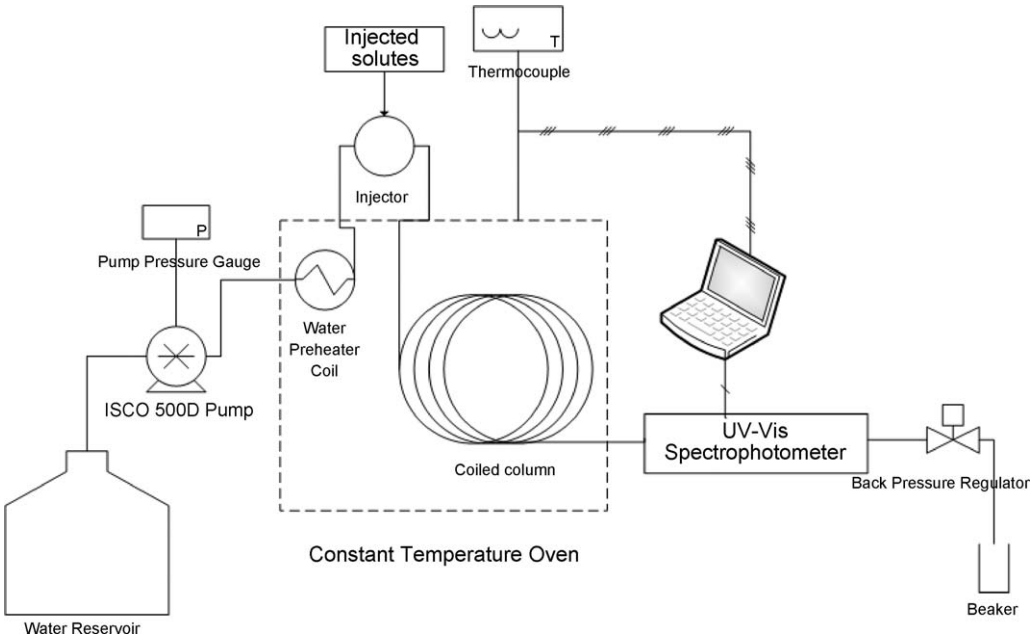


Fig. 1. Apparatus for measuring the diffusion coefficients of the phenolic compounds using the Taylor dispersion method.

3.2. Procedure

The Taylor dispersion apparatus used to measure the diffusion coefficients of the phenolic compounds in subcritical water as a function of temperature is shown in Fig. 1. In this study, stainless steel 316 capillary tubing was placed in a constant temperature Hewlett Packard Model 5890 gas chromatograph oven. The temperature inside the oven was measured using iron–constantan J-type thermocouples. The signals from the thermocouples were transformed into digital signals using a Cole Parmer 18200-040 thermocouple module (Vernon Hills, IL, USA). The experimental temperature range was varied between 298 K and 413 K, and the deviation in the oven temperature during the time of experiments was found to vary within a range of ±0.5 K.

The capillary tubing (0.159 cm o.d. × 0.0228 cm i.d. × 3048 cm length; Waters Corporation, Milford, MA, USA) was placed in the oven, and coiled to form a column with a coil diameter of 25 cm. Solvent (0.5% (v/v) formic acid in water) is pumped into the tubing through a 1.5 m preheating coil placed in the oven, using an ISCO 500D syringe pump (Lincoln, NE, USA), and the flow rate of water maintained at 0.1 mL/min. The presence of formic acid in the eluent was to reduce the tailing of the concentration profile of the solute. This solute tailing reduces the adsorption of these highly hydroxylated compounds on the inner surface of the capillary column. The low concentration of formic acid in solution (pH = 2.75–3.00) would also help in maintaining the flavonoids in its most stable flavylium cation form [38]. An ISCO SFX 200 controller (Lincoln, NE, USA) was used to accurately control the flow rate of the solvent pump.

Solute solutions (corresponding to mole fractions from 10^{-4} to 5×10^{-5}) were made up with the solvent and injected into the apparatus using a Rheodyne 7725i injector (Upchurch Scientific, Oak Harbor, WA, USA) through a 20 μL sample loop. The injector and small amount of tubing that was outside the constant temperature oven were completely insulated to prevent any secondary dispersion. The solute exiting the empty column was detected using a Dionex AD-20 absorbance detector (Dionex Corporation, Sunnyvale, CA). The output signal from the absorbance detector is converted to digital signals using a Cole Parmer 18200-00 analog input module (Vernon Hills, IL, USA). The chromatographic peak from the translated digital signals from the absorbance detector is recorded using Tracer DAQ software (ver. 1.8.3; Cole Parmer Instrument Company, Vernon Hills, IL). The wavelengths at which the phenolic compound profiles were detected using the absorbance detector are given in Table 1. An adjustable back-pressure regulator (Upchurch Scientific P/N# P-880; Oak Harbor, WA, USA) rated to pressures between 2000 and 5000 psia, was attached to the exit of the absorbance detector to prevent the flashing of water to steam at high temperatures (≥373 K). The temperatures at the injector and on the column were also measured using the previously mentioned J-type thermocouples. Triplicate measurements of the diffusion coefficients of each flavonoid solute in hot pressurized water were made.

The system pressure was recorded by the ISCO SFX 200 controller. Studies have indicated that most processes using subcritical water as a solvent require pressures sufficient enough to maintain water in a liquid state above its boiling point [10,11,14]. The pump pressure recorded on the SFX 200 controller varied from 642 psia at 298 K to 605 psia at 413 K. It should be noted that the pump pressure refers to the total pressure recorded on the ISCO pump to provide a constant solvent flow rate through the preheat tubing, the coiled capillary tubing, tubing and UV-flow cell, and through a back-pressure regulator. The slight decrease in the pump pressure recorded at higher temperatures can be related to a decrease in the solvent viscosity and the adjustment of back-pressure regulator to maintain the water in its liquid state.

4. Results and discussion

4.1. Effect of temperature on the experimentally measured diffusion coefficients

The diffusion coefficient of the phenolic compounds as a function of temperature are reported in Table 2 and plotted in Fig. 2. It can be seen from Fig. 2 that the experimentally measured diffusion coefficients of the phenolic compounds in water increase exponentially with an increase in temperature. This is also shown in Fig. 2 by imposing an exponential trend line for the diffusion coefficient of malvidin-3,5-diglucoside chloride plotted as a function of temperature. This trend line shows qualitatively the increase of D_{AB} with an increase in temperature for all the phenolic compounds,

Table 2
Diffusion coefficients (D_{12}) of phenolic compounds in water along with η, $\eta D_{12}/T$ and Schmidt number (Sc) as a function of temperature.

Solute	T (K)	$10^{10} \times D_{12}$[a] (±SD) ($m^2\ s^{-1}$)	$10^4 \times \eta$ (Pa s)	$10^{17} \times \eta D_{12}/T$ ($kg\ m\ s^{-2}\ K^{-1}$)	Sc
Protocatechuic acid	298	2.46 (±0.1)	8.90	7.33	3630
	312	3.20 (±0.3)	6.53	6.67	2060
	332	3.84 (±0.2)	4.66	5.37	1240
	352	4.15 (±0.2)	3.54	4.16	879
	372	5.12 (±0.4)	2.82	3.87	574
	392	5.27 (±0.4)	2.32	3.11	467
Gallic acid monohydrate	298	2.50 (±0.1)	8.90	7.45	3580
	312	2.87 (±0.1)	6.53	5.98	2300
	332	3.30 (±0.1)	4.66	4.62	1430
	352	4.07 (±0.3)	3.54	4.08	894
(−)-Epicatechin	298	1.97 (±0.4)	8.90	5.88	4530
	312	2.66 (±0.4)	6.53	5.55	2470
	332	3.38 (±0.3)	4.66	4.73	1400
	352	3.89 (±0.0)	3.54	3.90	937
	372	4.06 (±0.2)	2.82	3.07	725
	392	5.19 (±0.3)	2.32	3.06	474
(±)-Catechin hydrate	298	2.33 (±0.1)	8.90	6.97	3830
	312	3.07 (±0.4)	6.53	6.40	2150
	332	3.76 (±0.4)	4.66	5.26	1260
	352	4.05 (±0.3)	3.54	4.06	900
	372	4.25 (±0.2)	2.82	3.21	692
	392	4.78 (±0.2)	2.32	2.82	514
	413	5.30 (±0.5)	1.97	2.53	402
Quercetin-3-β-D-glucoside	298	1.66 (±0.1)	8.90	4.95	5390
	312	2.19 (±0.2)	6.53	4.56	3010
	332	2.77 (±0.3)	4.66	3.88	1710
	352	3.07 (±0.1)	3.54	3.07	1190
	372	3.51 (±0.2)	2.82	2.65	839
Peonidin-3-glucoside chloride	298	2.19 (±0.1)	8.90	6.54	4020
	312	2.67 (±0.1)	6.53	5.58	2460
	332	3.65 (±0.2)	4.66	5.11	1300
	352	4.52 (±0.2)	3.54	4.53	807
	372	5.39 (±0.3)	2.82	4.07	546
	392	6.18 (±0.2)	2.32	3.65	398
	413	6.49 (±0.6)	1.97	3.09	328
Malvidin-3,5-diglucoside chloride	298	2.16 (±0.0)	8.90	6.45	4130
	312	2.71 (±0.1)	6.53	5.66	2430
	332	3.60 (±0.0)	4.66	5.03	1320
	352	4.41 (±0.1)	3.54	4.42	825
	372	5.15 (±0.3)	2.82	3.90	571
	392	5.30 (±0.5)	2.32	3.13	464
	413	5.79 (±0.3)	1.97	2.76	367

[a] The standard deviations (SD) for the diffusion coefficient data are calculated using Eq. (8).

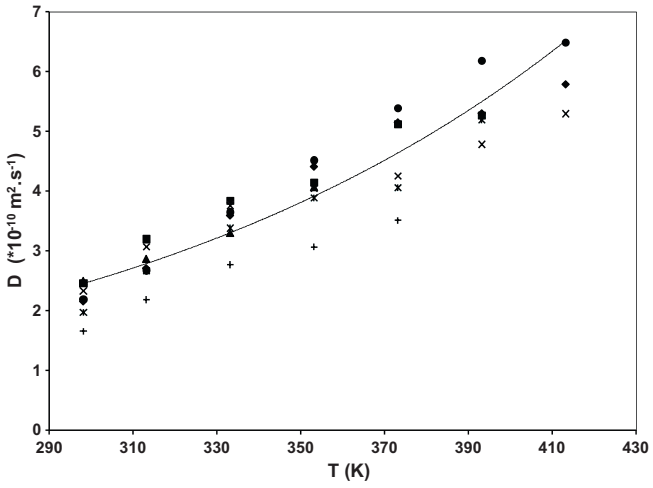


Fig. 2. Variation of experimentally measured diffusion coefficients of the phenolic compounds as a function of temperature. The solid trend line represents the regression of the experimental data for malvidin-3,5-diglucoside chloride (R^2 = 0.922); (■) protocatechuic acid, (▲) gallic acid monohydrate, (*) (−)-epicatechin, (×) (+)-catechin hydrate, (+) quercetin-3-β-D-glucoside, (●) peonidin-3-glucoside chloride, (♦) malvidin-3,5-diglucoside chloride.

though the slope of the linear regression for the other phenolic compounds would vary. It can also be seen from analyzing the data reported in Table 2 that the binary diffusion coefficients of the phenolic compounds in water at infinite dilution are very close to each other at the given particular temperatures. The condition for Gaussian peak profile: $D_{eff}/u_a L \ll 0.001$ and absence of secondary flow effects: $DeSc^{0.5} < 18$ as discussed previously were maintained throughout the experiments. The Reynolds number for the flow of solvent through the capillary varied between 6.8 and 35.5 over the selected temperature range (298–413 K).

Certain phenolic compounds such as protocatechuic acid, gallic acid monohydrate, (−)-epicatechin and quercetin-3-β-D-glucoside showed a distortion in the peak response at high temperatures. For example, the response curves for protocatechuic acid at 298 K, 352 K and 413 K are plotted as a function of residence time along the length of the column in Fig. 3. It can be seen from Fig. 3 that there is a broadening of the peak (peak height to width ratio) with an increase in temperature from 298 K to 352 K. However, at 413 K, there is a distortion in the response curve for protocatechuic acid in the hot water solvent. Madras et al. [39] have indicated that distortion in the response peak can occur due to strong solute polarity resulting in a tailing peak due to the adsorption isotherms on the inner wall of the stainless steel capillary column. However, this distortion in the response curve at temperatures greater than 373 K is primarily due to the thermal degradation of the phenolic com-

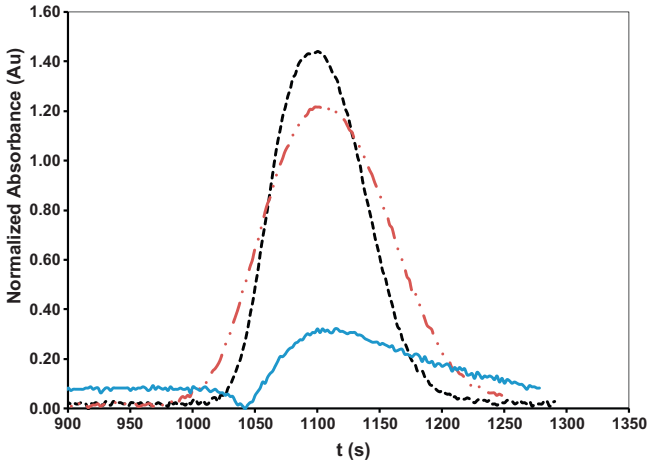


Fig. 3. The peak profile response curves for protocatechuic acid measured at 280 nm at three different temperatures 298 K, 352 K and 413 K using the Taylor dispersion method; (—) temperature = 298 K, (-·-) temperature = 352 K, (—) temperature = 413 K.

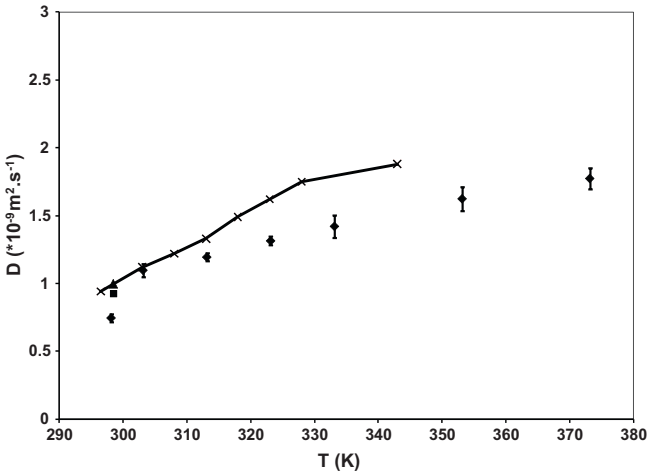


Fig. 4. Comparison of the experimentally measured diffusion coefficient of phenol in water as a function of temperature with that available in the literature; (♦) experimental values, (–) literature [41], (▲) literature [42], (×) literature [43].

pounds at this temperature. Tanchev et al. [40] have shown that there is significant thermal degradation of phenolic acid at higher temperatures and lower solvent flow rates and the extent of the degradation is dependent on both the solvent pH and the temperature. A further increase in the solvent flow rate would result in an increase in the value of $DeSc^{0.5}$ over the minimum value required to prevent secondary flows in the column.

Similar peak distortions were noticed for gallic acid monohydrate above 352 K, (−)-epicatechin above 392 K and quercetin-3-β-D-glucoside above 372 K. The calculation of the diffusion coefficients of the afore-mentioned phenolic compounds above these particular temperatures using Eq. (6) would not be correct and hence, is not reported in this study. Though such distortion in the response curves at high temperatures was not noticed in case of (+)-catechin hydrate, peonidin-3-glucoside and malvidin-3,5-diglucoside chloride, the effect of thermal degradation on the diffusion of these phenolic compounds in acidified water can be seen at temperatures equal to and above 372 K (as shown in Fig. 3). As discussed previously, there exist limited data in the literature on the diffusion coefficients of the selected phenolic compounds in water with which to compare the experimental data. The only known data point available in the literature relates to the diffusion coefficient of (+)-catechin as reported in Section 1 in this manuscript [28]. It can be seen that the diffusion coefficient of anhydrous catechin reported in the literature varies by around three fold when compared with the diffusion coefficient of catechin hydrate reported in Table 2.

In order to compare the diffusion coefficients of solutes in water measured using the experimental apparatus with those available in the literature, the D_{AB} for phenol was measured. The comparison between experimentally measured diffusion coefficients of phenol in water with those available in the literature [41–43] is shown in Fig. 4. It can be seen here that the measured diffusion coefficient values of phenol are only slightly lower than those reported in the literature lending evidence to the reliability of this measurement technique. The difference between the experimental and the literature values can be attributed to the slight tailing of the response peak due to strong solute polarity resulting in adsorption [39].

The standard deviations (SD) reported in Table 1 are calculated using the following equation:

$$\mathrm{SD} = \sqrt{\frac{\sum_{i=1}^{n}(D_{g,i} - \overline{D}_g)^2}{n-1}} \tag{8}$$

where $D_{g,i}$ = diffusion coefficient for ith sample at a particular temperature for a selected solute in water; $\overline{D}_g$ = average diffusion coefficient of the selected solute in water at a particular temperature and; n = number of replicates. All the data were reported to three significant digits based on the analysis of variances performed at $P < 0.005$ level.

It should be noted that the presence of the ionic components in hot water has a tendency to create its own small electric field which can influence the diffusion of ionisable solutes in water. In this study, it can influence the diffusion coefficient of two solutes peonidin-3-glucoside chloride and malvidin-3,5-diglucoside chloride in aqueous solution. To account for this phenomenon, the Nernst equation is used to explain the ionic migration of the chloride salts of phenolic compound ($D_{\text{ph-Cl}}$), we obtain the following equation [44]:

$$D_{\text{ph-Cl}} = \frac{2D_{\text{ph}}D_{\text{Cl}}}{D_{\text{ph}} + D_{\text{Cl}}} \tag{9}$$

where D_{ph} and D_{Cl} refer to the ionic migration of the phenolate (peonidin-3-glucoside and malvidin-3,5-diglucoside) and chloride ions, respectively. The infinite dilution diffusion coefficient of chloride ion in aqueous solutions as a function of temperature can be calculated using the Nernst Hartley equation [45] as given by the equation below:

$$D_{\text{Cl}} = \frac{RT\lambda^{o}_{\text{Cl}}}{z_{\text{Cl}}F^2} \tag{10}$$

where R is the universal gas constant, λ^{o}_{Cl} is the limiting conductance of chloride ion in aqueous solution at temperature (T) given by Quist and Marshall [46], z_{Cl} is the valency of chloride ion in solution (=1) and F is the Faraday's constant. The diffusion coefficient of the chloride ion in aqueous solution calculated as a function of temperature by Eq. (10) is given in Table 3. Miller [47] and Oelkers and Helgeson [48] have indicated that the error in estimating the aqueous tracer diffusion coefficients of chloride ions as a function of temperature using Eq. (10) was of the order of not more than 5–10%. From Eqs. (9) and (10), it is possible to calculate the diffusion coefficient of the phenolic compound (or phenolate) in water as a function of temperature. It can be seen from comparing the diffusion coefficients of the chloride salts of phenolic compounds ($D_{\text{ph-Cl}}$) and the phenolate ions (D_{ph}) that there is a significant effect of the chloride ions on the diffusion of the phenolic compound in water. The diffusion coefficient of the chloride salts of phenolic compounds in water was found to be approximately 1.5–2

Table 3
Effective diffusion coefficients of some phenolic compounds (D_{ph}) and their chloride salts ($D_{ph\text{-}Cl}$) as a function of temperature.

Solute	T (K)	$10^{10} \times D_{ph\text{-}Cl}$ ($m^2\ s^{-1}$)	$10^9 \times D_{Cl}$ ($m^2\ s^{-1}$)	$10^{10} \times D_{ph}$ ($m^2\ s^{-1}$)
Peonidin-3-glucoside	298	2.19	2.13	1.15
	312	2.67	2.98	1.40
	332	3.65	4.22	1.91
	352	4.52	5.59	2.35
	372	5.39	7.09	2.80
	392	6.18	8.71	3.21
	413	6.49	10.5	3.35
Malvidin-3,5-diglucoside	298	2.16	2.13	1.14
	312	2.71	2.98	1.42
	332	3.60	4.22	1.88
	352	4.41	5.59	2.30
	372	5.15	7.09	2.67
	392	5.30	8.71	2.73
	413	5.79	10.5	2.98

times more than that of the corresponding phenolate ion. Similar trend was observed by Leaist [49] where the diffusion coefficient of bovine serum albumin in water was found to increase on addition of chloride ions. This increase in the diffusion coefficient of the protein in an aqueous electrolyte solution was found to be due to the binding of chloride ion with the protein.

A number of studies have been performed to study the migration of chloride [50] ion in water but there exist no studies on its effect on the diffusion of the phenolic compound in water. The effect of chloride (and similar) ions on the diffusion of a compound was found to be relatively low at infinite dilutions and increased with its increasing concentration in solution [51]. This is because the diffusion of the chloride salts of the phenolic compound is dependent on the ionic strength of the solution given by the following equation [50]:

$$I = \frac{1}{2}\sum_{i=1}^{n} C_i Z_i^2 \tag{11}$$

where Z is the coulombic charge on the ion, and n is the total number of ionic components in the compound. The ionic migrations in an electric field can be minimized and/or eliminated using a high concentration of an electrolyte in the solvent. Studies have shown that addition of 0.1 N HCl to water can result in an increase in the solvent viscosity by 3%, thereby, the reported diffusion coefficients of chloride in water may exhibit a 3% variation from the effective diffusion coefficient in pure water at a particular temperature [50]. Although formic acid is a weaker electrolyte even at higher concentrations in water, it would be expected to slightly exhibit small electric field effects, thereby, reducing the effect of chloride ions on the diffusion coefficient of the phenolic compound in solution.

From the afore-mentioned discussions, it can be seen that even though there is a significant effect of chloride ion on the diffusion of the phenolic compounds in water, this effect is dependent on various sources. The effect of formic acid as an electrolyte in water to prevent any ionic migration has not been studied in detail and the actual diffusion of the phenolic compounds in absence of its chloride salts cannot be estimated accurately due to the lack of knowledge of their physical and thermal properties in the literature. Even though, it is not possible to maintain physical and thermal stability of these phenolic compounds in the absence of their chloride salts, the data presented in Table 3 can be of great importance when optimizing industrial extraction systems. However, in order to prevent any error propagation, further studies in this manuscript on the diffusion coefficients of these phenolic compounds (peonidin-3-glucoside and malvidin-3,5-diglucoside) in subcritical water would be as their chloride salts (which are experimentally measured) instead of their phenolate forms.

4.2. Correlation with temperature

As discussed previously, the measured diffusion coefficients of the phenolic compounds in water increased exponentially as a function of temperature. This temperature dependence for the diffusion coefficients of the phenolic compounds in water can then be expressed as follows [52]:

$$\ln(D_{AB}) = a_T + \frac{b_T}{T} \tag{12}$$

where a_T and b_T are empirical constants that can be obtained from the plot of the natural logarithm of the diffusion coefficient (D_{AB}) as a function of the inverse of the temperature, as shown in Fig. 5. It can be seen from Fig. 5 that there is a linear relationship between the natural logarithm of the diffusion coefficient of the phenolic compounds and temperature. As discussed previously, this is represented in Fig. 5 as a trend line obtained by plotting natural logarithm of the diffusion coefficient of malvidin-3,5-diglucoside chloride as a function of inverse of temperature. The empirical constants a_T and b_T for the diffusion of the individual phenolic compounds in water are given in Table 4. The relative deviations (*RD*s) between the experimentally measured diffusion coefficients ($D_{AB,exp}$) and

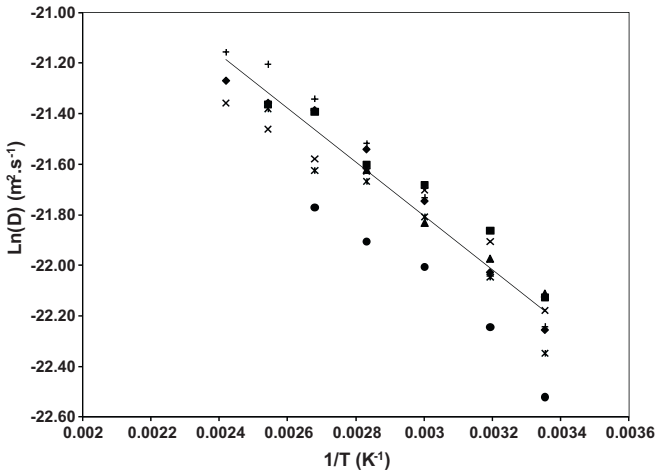


Fig. 5. Variation of the natural logarithm of diffusion coefficient of the phenolic compounds as a function of inverse of temperature. The solid trend line represents the regression of the experimental data for malvidin-3,5-diglucoside chloride to Eq. (9) (R^2 = 0.963); (■) protocatechuic acid, (▲) gallic acid monohydrate, (*) (−)-epicatechin, (×) (+)-catechin hydrate, (+) quercetin-3-β-D-glucoside, (●) peonidin-3-glucoside chloride, (♦) malvidin-3,5-diglucoside chloride.

Table 4
Parameters a_T and b_T in Eq. (12), Arrhenius constant (A) and activation energy (E_a) for the phenolic compounds in water.

Solute	a_T	b_T	$10^9 \times$ A ($m^2\ s^{-1}$)	E_a (kJ mol)	100*ARD*[a]	100*MRD*[a]
Protocatechuic acid	−18.962	−923.67	5.82	7.68	0.817	1.16
Gallic acid monohydrate	−19.053	−914.16	5.31	7.60	0.395	0.863
(−)-Epicatechin	−18.919	−991.23	6.08	8.24	1.10	1.83
(±)-Catechin hydrate	−19.427	−790.29	3.66	6.57	0.730	1.52
Quercetin-3-β-D-glucoside	−18.842	−1078.0	6.56	8.96	0.899	1.37
Peonidin-3-glucoside chloride	−18.130	−1214.7	1.34	10.1	0.643	1.28
Malvidin-3,5-diglucoside chloride	−18.602	−1067.2	8.35	8.87	0.889	1.26

[a] Average relative deviation (*ARD*) and maximum relative deviation (*MRD*) are expressed in % units.

that predicted using Eq. (12) ($D_{AB,theo}$) are calculated as follows:

$$RD = \left[\frac{(D_{AB,exp} - D_{AB,theo})}{D_{AB,theo}}\right] \quad (13)$$

The average relative deviations (*ARD*s) and the maximum relative deviations (*MRD*s) for the phenolic compounds over the entire temperature range are also given in Table 3. Since the parameters a_T and b_T were calculated from the experimental values, it is expected that the *RD* values between the experimental and predicted values calculated using Eq. (13) would provide a quantitative value for the regression of the trend line equations for the different phenolic compounds specified in Fig. 5. It can be seen from the table that the average absolute deviation between the experimental and predicted values for the diffusion coefficients of the phenolic compounds in water over the set temperature range is about 1%.

The diffusion coefficients of the phenolic compounds as a function of temperature can also be correlated using an Arrhenius-type equation as given below:

$$D_{AB} = A \times \exp\left(\frac{-E_a}{RT}\right) \quad (14)$$

where A is the Arrhenius constant, E_a is the activation energy (kJ mol^{-1}) of the phenolic compounds in water and T is the temperature in K. The values for the Arrhenius constant and the activation energy of the phenolic compounds in water can then be calculated from a plot of the natural logarithm of the diffusion coefficient of the phenolic compounds versus reciprocal of temperature, as given in Fig. 5. The values of the Arrhenius constant and the activation energy of the phenolic compounds in water are given in Table 4. The activation energy of the phenolic compounds in water did not show any specific trend as a function of their molecular weight, and their values varied from 6.57 kJ mol^{-1} for (+)-catechin hydrate to 10.1 kJ mol^{-1} for peonidin-3-glucoside.

4.3. Correlation with solvent viscosity

Apart from the temperature, the diffusion coefficient of a solute in water can also be correlated in terms of solvent viscosity [53] as given below:

$$\frac{D_{AB}}{T} = \alpha(\eta)^{\beta} \quad (15)$$

where η is the dynamic viscosity of the solvent; α and β are empirical constants. The values for dynamic viscosity and the density of the solvent as a function of temperature were obtained from the NIST Refprop database [54]. It can be seen from Eq. (15) that the value of diffusion coefficient of the phenolic compounds at a particular temperature is proportional to the solvent viscosity. The natural logarithm of the ratio of the diffusion coefficient of the phenolic compounds with temperature is plotted as a function of the natural logarithm of the solvent viscosity in Fig. 6. As discussed previously, a trend line was plotted for malvidin-3,5-diglucoside chloride as a function of natural logarithm of viscosity to qualitatively indicate the trends for the different phenolic compounds

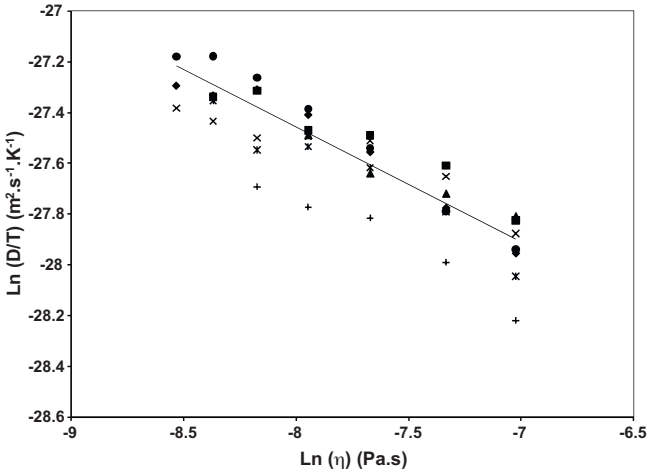


Fig. 6. Natural logarithm of diffusion coefficient of the phenolic compounds measured as a function of temperature plotted versus the natural logarithm of the solvent viscosity. The solid trend line represents the regression of the experimental data for malvidin-3,5-diglucoside chloride to Eq. (11) (R^2 = 0.940); (■) protocatechuic acid, (▲) gallic acid monohydrate, (*) (−)-epicatechin, (×) (+)-catechin hydrate, (+) quercetin-3-β-D-glucoside, (●) peonidin-3-glucoside chloride, (♦) malvidin-3,5-diglucoside chloride.

given in Fig. 6. It can be seen from the trend line in Fig. 6 that the natural logarithm of D_{AB}/T of the phenolic compounds in water increases linearly with an increase in the natural logarithm of the solvent viscosity.

The parameters α and β for the various phenolic compounds in water were calculated from the linear trends which are shown in Fig. 6 and presented in Table 5. The *ARD* and *MRD* values between the measured diffusion coefficients and the predicted values are calculated using Eq. (13) and the values are also given in Table 5. On comparing the *ARD* and *MRD* values for the phenolic compounds in water between Tables 4 and 5, we can see that the correlation of the measured diffusion coefficients of the phenolic compounds in water using Eq. (15) than those predicted using Eq. (12) were marginally different. The *ARD* values as given in Table 5 are less than 1% for all the phenolic compounds in water.

Table 5
Parameters α and β in Eq. (15) for the flavonoids in water.

Solute	α	β	100*ARD*[a]	100*MRD*[a]
Protocatechuic acid	−30.266	−0.3558	0.772	0.993
Gallic acid monohydrate	−30.159	−0.3329	0.462	0.872
(−)-Epicatechin	−31.169	−0.4541	0.873	1.57
(±)-Catechin hydrate	−29.745	−0.2791	0.705	1.37
Quercetin-3-β-D-glucoside	−31.221	−0.4421	0.815	1.24
Peonidin-3-glucoside chloride	−31.725	−0.5413	0.513	1.09
Malvidin-3,5-diglucoside chloride	−31.075	−0.4523	0.785	1.15

[a] Average relative deviation (*ARD*) and maximum relative deviation (*MRD*) are expressed in % units.

Table 6
Accuracy in the prediction of the diffusion coefficients of the phenolic compounds in water using various theoretical equations.

	100*ARD*[a]						
	Protocatechuic acid	Gallic acid monohydrate	(−)-Epicatechin	(±)-Catechin hydrate	Quercetin-3-β-D-glucoside	Peonidin-3-glucoside chloride	Malvidin-3,5-diglucoside chloride
Wilke and Chang (1955) [55]	19.2	13.4	10.5	12.5	14.4	9.11	8.22
Hayduk and Laudie (1974) [56]	18.8	13.2	10.3	12.2	14.0	8.74	7.78
Hayduk and Minhas (1982) [57]	19.1	13.6	9.81	11.8	9.70	4.68	5.25
Scheibel (1982) [58]	18.8	13.2	10.4	12.4	14.5	9.28	8.69
Lusis and Ratcliffe (1968) [59]	19.6	13.6	11.1	13.1	15.6	10.3	9.97
Reddy and Doraiswamy (1967) [60]	19.5	13.4	11.2	13.2	15.8	10.5	10.3

[a] Average relative deviation (*ARD*) is expressed in % units.

4.4. Stokes–Einstein model and the comparison of the experimental values with those predicted using theoretical equations

As indicated in Section 1, the diffusion coefficient of phenolic compounds in water as a function of temperature is necessary to optimize conditions for their extraction from natural products. Since the value of the diffusion coefficient of phenolic compounds in water is not available in the literature, especially at higher temperatures (≥373 K), theoretical models such as the Stokes–Einstein model were predominantly used. In Eq. (15), if the value of $\beta = (-1)$ and the value of $\alpha = k_B/6\pi r$, where k_B is the Boltzmann constant and r is the radius of the solute molecule, assuming that the solute molecule is spherical and its radius does not vary as a function of temperature, the Stokes–Einstein model can be expressed as follows:

$$\frac{D_{AB}\eta}{T} = \frac{k_B}{6\pi r} \tag{16}$$

In order to compare the measured diffusion coefficients of the phenolic compounds with those predicted using the Stokes–Einstein model, the first step is to compare the β values of the phenolic compounds given in Table 5. It can be seen that the values of β for the phenolic compounds in water are greater than (-1) and tend towards zero. This indicates that theoretical equations based on the Stokes–Einstein model cannot be used to predict the diffusion coefficients of the phenolic compounds in water as a function of temperature. Studies performed by Umecky et al. [53] and Funazukuri and Nishio [2] for the diffusion coefficients of solutes in water at temperatures (<333 K) have shown good agreement with those predicted using the Stokes–Einstein model and their calculated β-values varied between −1.005 and −1.009. However in this study, the β-values for the phenolic compounds in water, varied between −0.2791 and −0.5413.

The Stokes–Einstein model is based on the assumption that the solute molecule is spherical in nature and the hydrodynamic radius of the solute molecule does not vary as a function of temperature. According to this model, if $D\eta/T$ was plotted as a function of temperature, then a linear trend of zero slope should be obtained. However, when this is done for the phenolic compound data (Fig. 7), a decrease in $D\eta/T$ was observed for all the phenolic compounds in water as a function of increasing temperature. This decreasing trend for $D\eta/T$ as a function of temperature is shown for malvidin-3,5-diglucoside chloride in Fig. 7. This decreasing trend seen in Fig. 7 could be caused by a change in the molecular radii of the phenolic compounds as a function of temperature.

Theoretical equations based on the Stokes–Einstein model are those of Wilke–Chang [55], Hayduk and Laudie [56], Hayduk and Minhas [57], Scheibel [58], Lusis and Ratcliffe [59], and Reddy and Doraiswamy [60]. Solute molar volumes that are used in these theoretical equations are given in Table 1 as indicated previously. The *ARD* values between the measured diffusion coefficients of the phenolic compounds and those predicted using the aforementioned equations were calculated using Eq. (13) and are presented in Table 6. The *ARD* values for most phenolic compounds in water were found to be varying between 10 and 20%. However, the theoretical models showed a very good agreement with the experimentally measured diffusion coefficients of certain flavonoids in water in some cases. For example, the *ARD* values between the measured diffusion coefficients of peonidin-3-glucoside chloride and malvidin-3,5-diglucoside chloride as a function of temperature with those predicted using the Wilke–Chang equation were only about 9.11% and 8.22%, respectively. It should be noted that the association factor, φ in the Wilke–Chang [55] equation is given as 2.6, when water is used as a solvent, though an φ value of 2.26 was used by Hayduk and Laudie [56]. This correction used by Hayduk and Laudie was found to improve the prediction of the diffusion coefficients of phenolic compounds in water as a function of temperature. However, even with the different correction factors, the diffusion coefficient of the flavonoids in water predicted using the aforementioned theoretical models did not show as good an agreement with the experimental values.

It was also seen that the relative deviation between the predicted and experimental diffusion coefficient values increased with an increase in temperature indicating that the accuracy of prediction using these theoretical models decreases with an increase in temperature. This can also be due to the decrease in the molecular radii of the flavonoid with an increase in temperature as discussed previously. The variation in the radii of the solute molecule as a function of temperature, and subsequently disagreement with the

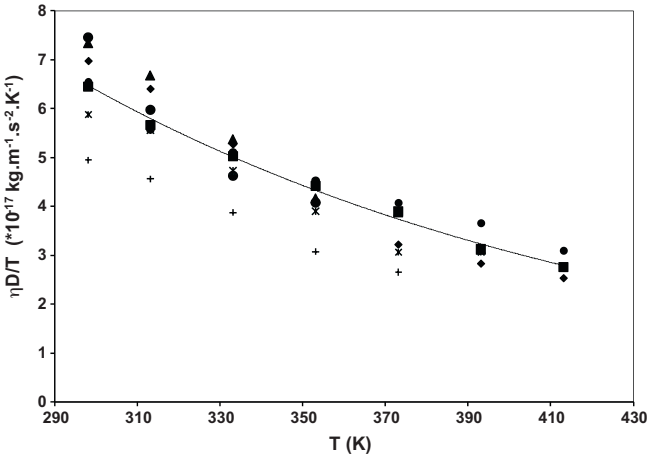


Fig. 7. Variation of $\eta D/T$ as a function of temperature used to check the validity of a Stokes–Einstein diffusion coefficient model. The solid trend line represents the regression of the $\eta D/T$ of malvidin-3,5-diglucoside chloride as a function of temperature ($R^2 = 0.993$); (■) protocatechuic acid, (▲) gallic acid monohydrate, (*) (−)-epicatechin, (×) (+)-catechin hydrate, (+) quercetin-3-β-D-glucoside, (●) peonidin-3-glucoside chloride, (♦) malvidin-3,5-diglucoside chloride.

Stokes–Einstein model can be attributed to intermolecular association or cluster formation between the solute and solvent molecule [61].

5. Conclusions

The binary diffusion coefficients of the phenolic compounds in water at infinite dilution were measured using Taylor dispersion method between 298 K and 413 K. The measured diffusion coefficients of the phenolic compounds increased exponentially with an increase in temperature. The measured diffusion coefficients of the phenolic compounds in water were correlated as a function of temperature and solvent viscosity. It was found that the values of $D\eta/T$ did not remain constant as a function of temperature but rather decreased with an increase in temperature. This could be due to the change in the hydrodynamic radius of the phenolic compounds (assumed spherical in shape) as a function of temperature. The measured diffusion coefficients were also compared with those predicted using the theoretical equations based on the Stokes–Einstein model. It was found that the diffusion coefficients of the phenolic compounds predicted using the theoretical equations showed good agreement with the experimental values but they were not as accurate as those predicted using empirical Eqs. (12), (14) and (15). The diffusion coefficients of the phenolic compounds in water were also correlated as a function of temperature using an Arrhenius-type equation and the activation energy of the flavonoids (used in this study) in water was found to vary between 6.57 and 10.1 kJ mol. The effect of chloride ions on the diffusion of flavonoids such as malvidin-3,5-diglucoside and peonidin-3,O-glucoside in water was estimated and it was found that the diffusion coefficient of these flavonoids was found to be about 1.5–2 times lesser than that of their chloride salts at different temperatures.

Acknowledgment

This study was supported by the United States Department of Agriculture (grant number 2006-35503-17618) under the CSREES National Research Initiative (NRI).

References

[1] N.C. Cook, S.J. Sammon, Nutr. Biochem. 7 (1996) 66–76.
[2] T. Funazukuri, M. Nishio, J. Chem. Eng. Data 44 (1999) 73–76.
[3] M.S.S. Curren, J.W. King, Anal. Chem. 73 (2001) 740–745.
[4] G.E. Sultan, K. Saliha, K.D. Alpaslan, T. Murat, S. Ozgur, I. Memet, Talanta 74 (2008) 930–935.
[5] E. Ibanez, A. Kubatova, F.J. Senorans, S. Cavero, G. Reglero, S.B. Hawthorne, J. Agric. Food Chem. 51 (2003) 375–382.
[6] M. Hassas-Roudsari, P.R. Chang, R.B. Pegg, R.T. Tyler, Food Chem. 114 (2009) 717–726.
[7] A. Kulkarni, S. Suzuki, H. Etoh, J. Wood Sci. 54 (2008) 153–157.
[8] J.-W. Kim, T. Nagaoka, Y. Ishida, T. Hasegawa, K. Kitagawa, S.-C. Lee, Sep. Sci. Technol. 44 (2009) 2569–2608.
[9] M. Garcia-Marino, J.C. Rivas-Gonzalo, E. Ibanez, C. Garcia-Moreno, Anal. Chim. Acta 563 (2006) 44–50.
[10] K. Srinivas, J.W. King, J.K. Monrad, L.R. Howard, C.M. Hansen, J. Food Sci. 74 (2009) E342–E354.
[11] A. Shotipruk, J. Kiatsongserm, P. Pavasant, M. Goto, M. Sasaki, Biotechnol. Prog. 20 (2004) 1872–1875.
[12] N. Turner, F. Erdogdu, J. Food Eng. 76 (2006) 579–583.
[13] Y. Chalermchat, M. Fincan, P. Dejmek, J. Food Eng. 64 (2004) 229–236.
[14] J.E. Cacae, G. Mazza, J. Food Eng. 77 (2006) 1087–1095.
[15] J.E. Cacae, G. Mazza, J. Food Eng. 68 (2003) 240–248.
[16] M. Palma, Z. Pineio, C.G. Barroso, J. Chromatogr. A 921 (2001) 169–174.
[17] K. Srinivas, J.W. King, L.R. Howard, J.K. Monrad, J. Food Eng. 100 (2010) 208–218.
[18] K. Srinivas, J.W. King, L.R. Howard, J.K. Monrad, J. Chem. Eng. Data, in press.
[19] C. Yang, W. Li, C. Wu, J. Phys. Chem. B 108 (2004) 11866–11870.
[20] M.E. Komlosh, P.T. Callaghan, Macromolecules 33 (2004) 6824–6827.
[21] R.H. Stokes, J. Am. Chem. Soc. 72 (1950) 763–767.
[22] B. Bettens, S. Dekeyzer, B.V. der Bruggen, J. Degreve, J. Vandecasteele, J. Phys. Chem. B 109 (2005) 5216–5222.
[23] E.L. Cussler, Diffusion Mass Transfer in Fluid Systems, Cambridge University Press, London, UK, 1984.
[24] H. Higashi, Y. Iwai, Y. Nakamura, S. Yamamoto, Y. Arai, Fluid Phase Equilibr. 166 (1999) 101–110.
[25] T. Funazukuri, C.Y. Kong, S. Kagei, Int. J. Thermophys. 22 (2001) 1643–1660.
[26] C.Y. Kong, T. Funazukuri, S. Kagei, J. Chromatogr. A 1035 (2004) 177–193.
[27] C. Mantell, M. Rodriguez, M. de la Ossa, J. Supercrit. Fluids 25 (2003) 165–173.
[28] C. Monteiro, C. Maechling, C.H. du Penhoat, Magn. Reson. Chem. 40 (2002) S110–S114.
[29] C. Sandoral, M.C. Rezende, F. Gonzalez-Nilo, J. Solution Chem. 32 (2003) 781–790.
[30] G. Taylor, Proc. R. Lond. Soc. A219 (1953) 186–203.
[31] R. Aris, Proc. R. Lond. Soc. A235 (1956) 67–77.
[32] E. Grushka, E.J. Kikita Jr., J. Phys. Chem. 78 (1974) 2297–2301.
[33] A. Alizadeh, C.A.N. de Castro, W.A. Wakeham, Int. J. Thermophys. 1 (1980) 243–284.
[34] J.C. Giddings, Dynamics of Chromatography: Part 1. Principles and Theory, Marcel Dekker, New York, NY, 1965.
[35] K.K. Liong, P.A. Wells, N.R. Foster, J. Supercrit. Fluids 4 (1991) 91–108.
[36] T. Funazukuri, C.Y. Kong, S. Kagei, J. Supercrit. Fluids 38 (2006) 201–210.
[37] G. Le Bas, Molar Volumes of Liquid Chemical Compounds, Longman, New York, USA, 1915.
[38] M.N. Clifford, J. Sci. Food Agric. 80 (2000) 1063–1072.
[39] G. Madras, B.L. Hamilton, M.A. Matthews, Int. J. Thermophys. 17 (1996) 373–389.
[40] S. Tanchev, N. Ioncheva, N. Genov, E. Malchev, Mol. Nutr. Food Res. 23 (1979) 863–866.
[41] R. Castillo, C. Garza, J. Orozco, J. Phys. Chem. 96 (1992) 1475–1478.
[42] R. Niesner, A. Heintz, J. Chem. Eng. Data 45 (2000) 1121–1124.
[43] X.-N. Yang, M.A. Matthews, J. Colloid Interface Sci. 229 (2000) 53–61.
[44] J.R. Vinograd, J.W. McBain, J. Am. Chem. Soc. 63 (1941) 2008–2015.
[45] D.G. Miller, J. Phys. Chem. 71 (1967) 3588–3592.
[46] A.S. Quist, W.L. Marshall, J. Phys. Chem. 69 (1965) 2984–2987.
[47] D.G. Miller, Estimation of tracer diffusion coefficients of ions in aqueous solution, Lawrence Livermore National Laboratory, Livermore, CA, 1982 (UCRL – 53319).
[48] E.H. Oelkers, H.C. Helgeson, Geochim. Cosmochim. Acta 52 (1988) 63–85.
[49] D.G. Leaist, J. Phys. Chem. 93 (1989) 474–479.
[50] J.L. Anderson, F. Rauh, A. Morales, J. Phys. Chem. 82 (1978) 608–616.
[51] L. Tang, Cement Concrete Res. 29 (1999) 1463–1468.
[52] V. Sanchez, H. Ofladeh, C. Durou, J. Hot, J. Chem. Eng. Data 22 (1977) 123–125.
[53] T. Umecky, T. Kuga, T. Funuzukari, J. Chem. Eng. Data 51 (2006) 1705–1710.
[54] NIST Standard Reference Database (REFPROP), vol. 23, 2007 (Gaithersburg, MD), CD. Available from: www.nist.gov.
[55] C.R. Wilke, P. Chang, AIChE J. 1 (1955) 264–270.
[56] W. Hayduk, H. Laudie, AIChE J. 20 (1974) 611–615.
[57] W. Hayduk, B.S. Minhas, Can. J. Chem. Eng. 60 (1982) 295–299.
[58] E.G. Scheibel, Ind. Eng. Chem. Res. 46 (1954) 2007–2008.
[59] M.A. Lusis, G.A. Ratcliffe, Can. J. Chem. Eng. 46 (1968) 385–387.
[60] K.A. Reddy, L.K. Doraiswamy, Ind. Eng. Chem. Fund. 6 (1967) 77–79.
[61] C. Mantell, M. Rodriguez, E.M. de la Ossa, J. Supercrit. Fluids 29 (2004) 165–173.