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Investigation into the effects of temperature and stirring rate on the solid-phase extraction of diuron from water using a C₁₈ extraction disk

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Abstract

A novel experimental method for determining the equilibrium constant, K_{eq} , and the uptake rate constant, k_{up} , for the solid-phase extraction (SPE) of diuron from water using a C₁₈ Empore extraction disk is reported. $\log K_{\text{eq}}$ and $\log k_{\text{up}}$ are determined at 7.0, 11.0, 18.0 and 23.0°C and for stirring rates of 100, 200 and 400 rpm. From a Van 't Hoff plot of $\log K_{\text{eq}}$ versus T^{-1} the enthalpy of sorption, ΔH^0 , is shown to be negative which indicates that the thermodynamic process of uptake is exothermic. The rate of stirring has no effect on $\log K_{\text{eq}}$ over the temperature range 7.0–23.0°C. The enthalpy of activation, ΔH^0 , calculated from Arrhenius plots of $\log k_{\text{up}}$ versus T^{-1} at 100, 200 and 400 rpm show that the kinetic process of uptake is endothermic. At 100 rpm the rate of uptake is limited by the aqueous diffusion of diuron. At 200 rpm or greater the aqueous diffusion layer around the disk is sufficiently small to prevent diffusion from being a limiting factor. The method described in this paper is limited to the analysis of analytes that contain a significant UV chromophore and are relatively soluble in water, but it can also be used to investigate pH and salinity effects on the SPE of diuron from water. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

The growing demand for clean water in the environment has encouraged new and more efficient methods for detecting aquatic pollutants to continually be developed. Solid-phase extraction (SPE) using particle loaded membranes has been used extensively to isolate pollutants in water since it was first introduced in 1990 [1–8]. The particle loaded membranes, or solid-phase extraction disks as they are more commonly known, consist of some type of sorbent embedded in an inert material [9]. The most

common types of disk contain octylsilica (C₈), octadecylsilica (C₁₈) or polystyrene–divinylbenzene (PS–DVB) sorbent particles embedded in a PTFE or glass fibre matrix.

What makes these SPE disks so attractive is that they are easy to handle, the homogeneous sorbent phase does not suffer from the same amount of channelling as earlier solid-phase cartridges and they boast many advantages over the traditional liquid–liquid extraction (LLE) used for monitoring pollutants in water [10–14]. The most important advantages of SPE over LLE are that (i) it is relatively fast, (ii) it has good accuracy and precision, (iii) relatively high recoveries are obtained, (iv) it requires much smaller volumes of hazardous organic solvent and (v) cleaner samples are obtained. All of

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these advantages translate to lower laboratory costs without the reduced quality of analytical data.

Due to the widespread popularity and use of the SPE technology considerable work has been carried out to explore their physical and chemical characteristics [15–22]. A knowledge of the principle factors that govern the extraction process has led to various predictive and optimisation methods for these SPE disks. This in turn means a greater ability to select the best type of extraction disk to give maximum extraction and recovery of the analyte under analysis.

Hennion et al. have shown how the retention factor of polar analytes can be predicted from a knowledge of the sample volume that is required to produce a recovery of at least 85% for SPE [15]. From these predicted retention factors it is possible to select the best type of disk to optimise the recovery process for either polar or non-polar analytes. Poole and co-workers have shown how it is possible to determine and characterise the physical and retention properties of SPE disks and cartridges using force-flow liquid chromatography. They have produced predictive models that can estimate the retention properties of the SPE disks and cartridges with a range of analytes [1,16–18]. An alternative use of the SPE disks has been developed by Hermens and co-workers, who used C_{18} SPE disks in an attempt to simulate the bioconcentration of pollutants in water [19,20]. This was done by determining the C_{18} –water disk partition coefficient for a set of chlorinated compounds and investigating the relationship between this coefficient and the well-established octanol–water partition coefficient ($\log P_{o/w}$). Other work carried out in this area includes the determination of capacity factors on C_{18} SPE cartridges [21]. These capacity factors were then used to predict recoveries for phenolic compounds at varying sample volumes on the SPE cartridges [22].

Numerous studies on modelling the parameters that govern partitioning of analytes in various systems have been carried out [23–30], particularly with regard to solid-phase microextraction (SPME) [26–30]. SPME is used to preconcentrate volatile organic compounds out of aqueous media and has been shown to be dependent on a whole range of physical and chemical parameters. The effects of salinity, humic acids, turbulence [28], temperature [29], and

fibre characteristics such as thickness and type of coating on SPME have all been reported [30].

In this work we present a novel experimental technique utilising ultraviolet (UV) spectrometry for studying the effects of temperature and stirring rate on the equilibrium constant (K_{eq}) and the rate of uptake (k_{up}) for the solid-phase extraction of a typical pollutant, diuron, from water. The ability to estimate these two physical constants at various temperatures and stirring rates will aid in the optimisation of conditions required to achieve maximum uptake and recovery using SPE. The type of SPE disk used is a PTFE membrane with octadecyl (C_{18}) sorbent particles, commercially known as C_{18} Empore extraction disks. Diuron, a recognised herbicide, was used in this work as it is a relatively safe compound to work with, contains a UV active chromophore and is readily available at a high purity (+99%).

Previous studies on the processes involved in analyte uptake in a C_{18} –water system have been carried out using off-line procedures [15,17,19–22]. These usually involve two stages; extraction of the analyte onto the C_{18} phase by SPME, force flow liquid chromatography or by exposing the naked C_{18} disk to a sample solution. In the second stage the analyte has to be eluted from the disk, the eluent then being analysed by one of a number of analytical techniques including gas chromatography coupled with either mass spectrometry (MS), UV spectrometry, electron-capture detection or by vapour pressure osmometry. This whole procedure needs to be carried out at specified extraction times and over a long time-period to obtain the necessary equilibrium data. The disadvantage of this procedure is that it is time consuming, laborious and can be expensive if many repetitions are required.

In this work the extraction of the analyte from water onto the C_{18} disk is based on previously reported methods of exposing naked disks to the sample solution [19,20], but the change in diuron concentration in the aqueous sample solution is continuously monitored by on-line UV spectrometry. The relationship between the concentration of an analyte in solution (C) and its absorbance (A), is shown in Eq. (1):

$$A = \epsilon l C \quad (1)$$

where l is the path length of the absorbing solution in centimetres, 1 cm in this case, and ϵ is the molar absorption coefficient ($1000 \text{ cm}^2/\text{l}$) that is usually quoted without units. From the decrease in absorbance of the aqueous solution, the amount sorbed onto the disk can easily be calculated. Analysis of the absorbance versus time (or uptake versus time) yields both K_{eq} and k_{up} from the same set of data for each individual combination of temperature and stirring rate.

2. Experimental

2.1. Instrumentation

The arrangement of apparatus used to determine K_{eq} and k_{up} are shown in Fig. 1. The UV spectrophotometer is a Kontron, Uvikon 810 dual-beam spectrophotometer used with a quartz, flow-through 1-cm cell. The high-performance liquid chromatography (HPLC) pump produces a flow-rate of 2 ml/min. The sample solution is contained in a 2-l glass reservoir bottle with a PTFE-lined screw cap. The tubing throughout the system is PTFE tubing (this minimises leaching of the compound). The C_{18} Empore disks (47 mm diameter, 90% C_{18} , 10% PTFE fibres) were purchased from Phenomenex, Macclesfield, UK. The cage that suspends the 47 mm disk is based on a previous design [20]. It is constructed totally out of stainless steel and is suspended from the cap with a stainless steel wire.

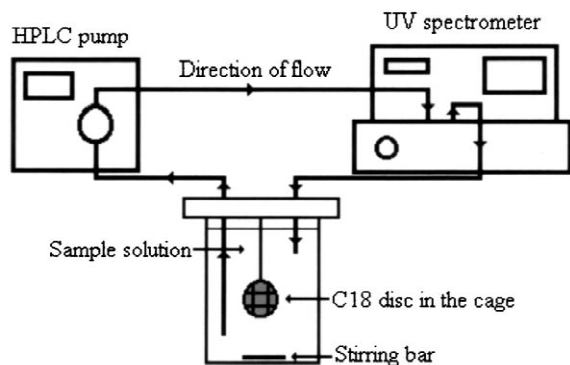


Fig. 1. A schematic diagram showing the on-line system used to measure K_{eq} and k_{up} .

The internal diameter is 48 mm and the breadth is 5 mm; this allows the disk to move around sufficiently so every part of it is exposed to the sample solution. The solution is stirred with a PTFE-coated magnetic stirring bar.

2.2. Materials and solutions

Diuron certified at 99.1% by HPLC, was purchased from Qm_x Labs., Halstead, UK and was used as received. A stock solution of approximately 85 mmol/l of compound in acetone (99.9+%, HPLC, Aldrich, UK) was prepared. Sample solutions of between 2.5 and $9.5 \cdot 10^{-5}$ mol/l were prepared by spiking 1.95 l of Milli-Q ultrapure water with the stock solution in 2-l glass bottles with PTFE-lined screw caps. Each solution was then allowed to equilibrate in the water bath for 24 h at the desired temperature and stirring rate.

2.3. Collection of partition data

The whole system is flushed through with ultrapure water to remove any contaminants from previous experiments and to zero the spectrophotometer. The sample solution is then circulated through the system and the absorbance at 249 nm when $t=0$, is recorded. The preconditioned C_{18} disk [17] is placed in the steel cage and immediately submerged in the sample solution, the absorbance of the sample solution is recorded every 30 min until there is no change in absorbance, i.e., equilibrium is reached. Fig. 2 shows the decrease of diuron concentration in water over time; it can be seen from the plot that equilibrium is reached after approximately 35 h. In an experiment carried out without the C_{18} disk, it was shown that the time-lag due to circulation through the pump was 1 min and 30 s, which when considered along side the total time for each experiment (approximately 35 h), can be assumed to be insignificant. Blank runs (without the C_{18} disk) were always carried out to ensure that the analytes were not absorbed by the apparatus, including the circulating pump.

2.4. Calculating the volume of the disk

In order to calculate the equilibrium constant it is

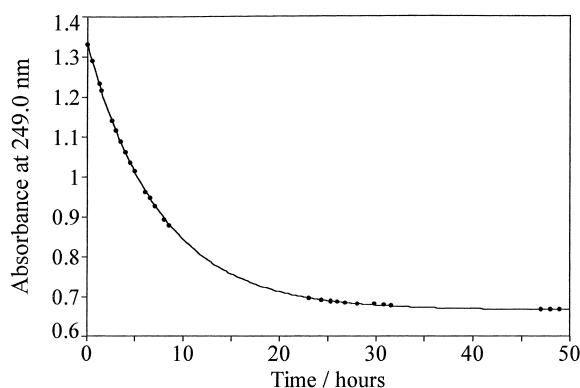


Fig. 2. An example of the decrease of diuron concentration in water as it is extracted onto the C_{18} disk over a period of 2 days. (●) Absorbance of diuron in water, (—) data fitted to Eq. (3).

necessary to know the volume of C_{18} material in the disk, i.e., the volume of the disk, V_D . According to the documentation accompanying the Empore disks, they consist of 10% (w/w) of PTFE fibres in which 90% (w/w) silica particles with chemically bonded C_{18} are contained. The organic carbon content of this silica- C_{18} material is 17% (w/w) [19], so 1 g of the silica- C_{18} material contains 0.20 g of C_{18} . Assuming the density of the bonded C_{18} is equal to that of octadecane, which is 0.78 g/ml, 1 g of the disk contains 0.25 ml of the C_{18} material. The 47 mm disk weighs 572 mg, so the volume of C_{18} in the whole disk is 144 μ l. The thickness of the disk is 0.5 mm.

3. Results and discussion

Partition data were gathered at four different temperatures and at three different stirring rates in order to determine the equilibrium constant, K_{eq} , and the rate of uptake, k_{up} and to observe how these physical conditions effect the two parameters. The temperatures studied are 7.0, 11.0, 18.0 and 23.0°C, the stirring rates are 100, 200 and 400 rpm. The initial concentration of diuron in water for each individual experiment varied from 2.5 to 9.5 $\cdot 10^{-5}$ mol/l.

3.1. Calculating the equilibrium constant, K_{eq}

The equilibrium constant, K_{eq} for each experiment is calculated from Eq. (2):

$$K_{eq} = C_D / C_W = f(C_W^0 - C_W) / C_W \quad (2)$$

where C_D is the concentration of diuron in the disk at equilibrium, C_W^0 is the initial concentration of diuron in the water and C_W is the final concentration of diuron in the water at equilibrium, all in mol/l. f is the phase ratio ($f = V_W / V_D$, where V_W and V_D are the volume of water and disk in litres). It is important to note that the value of K_{eq} depends on the calculated value of V_D , other methods used to calculate the disk volume may result in slightly different values of K_{eq} . The absorbances are converted into concentrations using Eq. (1). Given in Table 1 are the logarithms of the experimental C_{18} -water equilibrium constants ($\log K_{eq}$) for diuron at 7.0, 11.0, 18.0 and 23.0°C. The standard deviation is given for each $\log K_{eq}$ value; the mean value of at least three repetitions. This data is also depicted in Fig. 3, this shows a plot of the concentration of diuron in the disk and water at equilibrium for all four temperatures. The precision in K_{eq} varies between 2.5 and 5.5% depending on the experimental temperature.

Table 1

C_{18} -water equilibrium and uptake rate constants, with corresponding standard deviations, for diuron (parentheses indicate values from Van 't Hoff or Arrhenius equations)

Temperature (°C)	Log K_{eq} ^a	Log k_{up} (100) ^b (s ⁻¹)	Log k_{up} (200) ^d (s ⁻¹)
7.0	4.14 ± 0.01	(-5.49)	-5.08 ± 0.05
11.0	4.13 ± 0.02	-5.35	-4.94 ± 0.05
15.0 ^e	(4.10)	(-5.16)	(-4.87)
18.0	4.08 ± 0.02	-5.03 ± 0.01 ^c	-4.82 ± 0.03
23.0	4.03 ± 0.02	-4.89	-4.68 ± 0.04
25.0 ^e	(4.03)	(-4.78)	(-4.64)

^a Mean value of at least three repetitions, stirring rate 100, 200 or 400 rpm.

^b Single value when stirring rate is 100 rpm.

^c Mean value of two repetitions, stirring rate 100 rpm.

^d Mean value of at least two repetitions, stirring rate 200 rpm.

^e Values given at this temperature are from Van 't Hoff or Arrhenius equations.

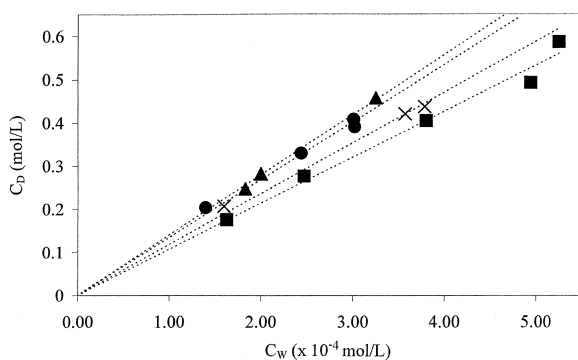


Fig. 3. A plot showing the concentration of diuron in the disk (C_D) and water (C_W) at equilibrium. (\blacktriangle) 7.0°C, (\bullet) 11.0°C, (\times) 18.0°C, (\blacksquare) 23.0°C.

The stirring rate varies for each repetition since it has no effect on the value of K_{eq} at a known temperature, see below for details.

3.2. Effect of concentration on $\log K_{eq}$

Shown in Fig. 3 are plots of the concentration of diuron, given in mol/l, in the disk and water when equilibrium has been reached at 7.0, 11.0, 18.0 and 23.0°C. At each temperature the relationship between C_D and C_W is linear through the origin with correlation coefficients of 1.00, 0.98, 0.99 and 0.98, respectively. Since K_{eq} is given by the ratio of C_D over C_W at equilibrium, see Eq. (2), it can be concluded that the values of K_{eq} given in this paper are constant over the initial concentration range of $0\text{--}9.5 \cdot 10^{-5}$ mol/l at a given temperature. This is useful to know as most analytical techniques such as gas chromatography (GC)–MS or HPLC, used to analyse environmental waters, are applicable for pollutant concentrations at very much lower concentrations than those detected by UV spectrometry. This does highlight a limitation with the method for determining K_{eq} and k_{up} described in this paper. Working with UV spectrometry requires the concentration of analyte to be approximately $1 \cdot 10^{-4}$ mol/l, depending on the size of the absorption coefficient, ϵ , in order to achieve reliable and reproducible absorbance readings. This limits the application of this method to those analytes that are sufficiently soluble and

stable in water at this concentration and those with significant chromophores.

3.3. Effect of temperature on $\log K_{eq}$

A Van 't Hoff plot of $\log K_{eq}$ versus the reciprocal of the temperature, shown in Fig. 4, exhibits approximate linearity over the temperature range 7.0–23.0°C with a correlation coefficient of 0.95. The enthalpy of sorption, ΔH^0 , is calculated as -11.2 kJ/mol for the SPE of diuron from water. The negative value of the sorption enthalpy indicates that the uptake of diuron from water onto the C_{18} disk is an exothermic process. This explains why the equilibrium constants given in Table 1 decrease with increasing temperature. The value of $\log K_{eq}$ at 15.0 and 25.0°C have been calculated from the assumed linear expression given by the Van 't Hoff plot shown in Fig. 4, these values are given in Table 1 as those in parentheses. The enthalpy of sorption along with the calculated Gibbs free energy of sorption, ΔG^0 , and the entropy of sorption, ΔS^0 , corresponding to K_{eq} at 15.0°C are given in Table 2.

The thermodynamic parameters for the SPE of diuron have never been published before which makes a direct comparison with existing data rather difficult. It has been found that the SPME of 60 volatile organic compounds (VOCs) from drinking water with a polydimethylsiloxane (PDMS) fibre is an exothermic process [27]. This is also true for the partitioning of chlorobenzenes between water and

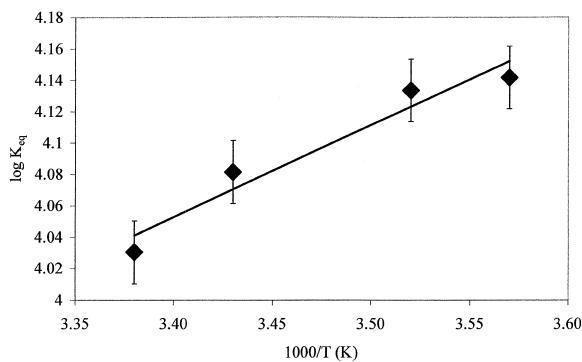


Fig. 4. A Van 't Hoff plot of $\log K_{eq}$ versus reciprocal temperature for the SPE of diuron from water.

Table 2
Thermodynamic and activation parameters for the SPE of diuron by a C₁₈ disk at 15.0°C

	Parameter value	ΔH^0 (kJ/mol)	ΔG^0 (kJ/mol)	ΔS^0 (J K ⁻¹ /mol)
Log K_{eq}	4.10	-11.2	-22.6	40
Log k_{up} (100) ^a	-5.16	60.4 ^c	98.9	-133.6
Log k_{up} (200+) ^b	-4.87	36.1 ^d	97.4	-212.7

^a Parameters when the stirring rate is 100 rpm.

^b Parameters when the stirring rate is 200 rpm or greater.

^c $E_a = 62.8$ kJ.

^d $E_a = 38.5$ kJ.

octanol [23]. The numerical values of ΔH^0 , ΔG^0 and ΔS^0 for various analytes in the two systems mentioned above are similar to those for the C₁₈-SPE of diuron from water. Thus the value of ΔH^0 reported in this paper compares favourably to other reported values even though they are for different systems.

3.4. Effect of stirring rate on log K_{eq}

Given in Table 3 are five values of log K_{eq} all measured at 23.0°C but with varying stirring rates. It

Table 3
C₁₈-water equilibrium and uptake rate constants for diuron in the stirring rate range 100–400 rpm

Stirring rate (rpm)	Log K_{eq} ^a	Log k_{up} (s ⁻¹)
100	4.00	-4.89 ^a
		-5.03 ^b
		-5.04 ^b
		-5.35 ^c
200	4.05	-4.71 ^a
		-4.66 ^a
		-4.84 ^b
		-4.80 ^b
		-4.92 ^c
		-4.96 ^c
400	4.03	-5.05 ^d
		-5.12 ^d
		-4.67 ^a
		-4.82 ^b
		-4.77 ^b

^a Experimental value for a single experiment at 23.0°C.

^b Experimental value for a single experiment at 18.0°C.

^c Experimental value for a single experiment at 11.0°C.

^d Experimental value for a single experiment at 7.0°C.

is evident that log K_{eq} does not vary significantly with stirring rate. The mean value of all five log K_{eq} values at 23.0°C is 4.03 with a standard deviation of 0.02 log units. The average relative standard deviation (RSD) for K_{eq} is 4%. It is therefore acceptable to say that with such a low standard deviation and RSD, the effects of stirring rate on the equilibrium constant are negligible over the range 100–400 rpm. At other temperatures similar standard deviations for the mean log K_{eq} values are observed so the same negligible stirring rate effect can be assumed for the temperature range studied in this work.

3.5. Calculating the rate of uptake, k_{up}

Eq. (3) given below can be rearranged into Eq. (4) so that the data for the uptake of diuron from water onto the C₁₈ disk may be fitted to Eq. (4) using the graphical package Table Curve 2D, Jandel Scientific, CA, USA. This package uses a simple least-squares method to fit the data to the equation and provides a rate constant that is applicable over the whole data range, not just the linear portion of the data that is often used to determine rate constants. k_{up} is a first-order rate constant so it does not depend on the initial concentration of diuron in water:

$$(\epsilon M - ZK_{eq}V_D A_t) / (\epsilon M - ZK_{eq}V_D A_0) = \exp^{-k_{up}Zt} \quad (3)$$

$$A_t = (\epsilon M / ZK_{eq}V_D) + [A_0 - (\epsilon M / ZK_{eq}V_D)] \exp^{-k_{up}Zt} \quad (4)$$

where A_0 is the initial absorbance of diuron in water, A_t is the absorbance after time t , ϵ is the molar absorption coefficient, log $\epsilon = 4.34$ for diuron in water, M is the total number of moles of diuron in

the system, k_{up} is the uptake rate constant (s^{-1}), t is exposure time of experiment (s) and Z is equal to $(K_{eq}V_D + V_W)/K_{eq}V_D$, where V_D and V_W are the volumes of the disk and water (l); K_{eq} is the equilibrium constant determined from Eq. (2) using the initial and final absorbances of diuron. Eq. (4) takes the form $y = b + (a - b) \exp(-cx)$, where coefficients a , b and c are calculated. All the data of absorbance against time for the SPE of diuron were fitted to Eq. (4); an example is shown in Fig. 2. The correlation coefficients for these plots varied from 0.97 to 0.99. The rate of uptake, with units of s^{-1} , is calculated automatically in a Microsoft Excel spreadsheet from coefficient c since:

$$c = -k_{up}Z \quad (5)$$

By rearranging Eq. (3) to give Eq. (6):

$$\left\{ \ln \left[\frac{(\epsilon M - ZK_{eq}V_D A_t)}{(\epsilon M - ZK_{eq}V_D A_0)} \right] \right\} / Z = -k_{up}t \quad (6)$$

it is possible to determine both k_{up} and K_{eq} from a single data set using simple linear regression. We denote the left hand side of Eq. (6) as LHS. All the quantities on LHS are known except for K_{eq} , so if a value for K_{eq} is assumed, a plot of LHS against t will yield a straight line of slope $-k_{up}$. This process is repeated with different values of K_{eq} until the best straight line, as judged by the coefficient of determination R^2 , is obtained. The value of K_{eq} and k_{up} corresponding to those for the best straight line are taken as the final values.

The problem with this method is that when the inserted value of K_{eq} is below a certain value, the equation breaks down. It is therefore difficult to examine a wide range of values for K_{eq} and to know with certainty that the K_{eq} value taken as the optimum is in fact correct. Although the use of Eq. (6) gives results quite comparable to those obtained through Eqs. (2) and (4), it is much more cumbersome to use than the direct procedure. We strongly suggest that the best method of obtaining K_{eq} and k_{up} is to determine K_{eq} directly through Eq. (2), and then to calculate k_{up} through fitting the data to Eq. (4). All the values of $\log K_{eq}$ and $\log k_{up}$ in this paper have been determined in this way.

3.6. Effect of temperature on $\log k_{up}$

Given in Table 1 are the logarithms of the uptake rate constant ($\log k_{up}$) when the temperature is 7.0, 11.0, 18.0 and 23.0°C and when the stirring rate is 100 and 200 rpm, along with the corresponding standard deviations. The individual $\log k_{up}$ values used to determine the mean values in Table 1 are given in Table 3 along with those when the stirring rate is 400 rpm at varying temperatures. This data are depicted in Fig. 5; which shows Arrhenius plots of $\log k_{up}$ against reciprocal temperature at 100, 200 and 400 rpm. The average RSD for k_{up} is 8.5%. There is a linear relationship between $\log k_{up}$ and T^{-1} when the stirring rate is 100, 200 and 400 rpm with correlation coefficients of 0.98, 0.95 and 0.91, respectively. The linear expressions for $\log k_{up}$ versus T^{-1} have been used to calculate $\log k_{up}$ at 15.0 and 25.0°C for 100 and 200 rpm, these values are given in parentheses in Table 1.

From the Arrhenius plots in Fig. 5, it is possible to calculate the activation energy, E_a , for the kinetic process involved in the SPE of diuron from water. The activation energies when the stirring rate is 100 rpm and 200 or greater rpm (the k_{up} values at 200 and 400 rpm have been combined in the same linear relationship against T^{-1}) are 62.8 and 38.5 kJ, respectively. These activation energies were then used to calculate the enthalpy of activation, ΔH^0 , Gibbs function of activation, ΔG^0 and the entropy of activation, ΔS^0 , all are given in Table 2. The two positive values of ΔH^0 ; 60.4 and 36.1 kJ/mol for the rate constant at 100 rpm and 200 rpm or greater,

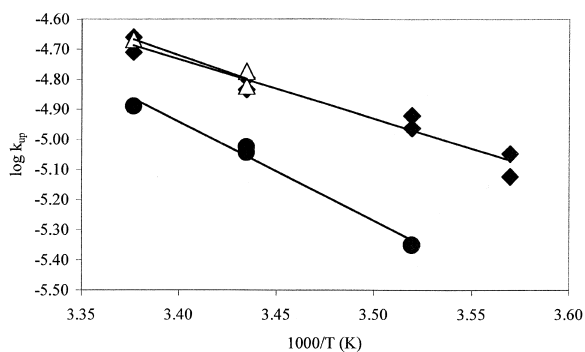


Fig. 5. An Arrhenius plot of $\log k_{up}$ versus reciprocal temperature at 100 (●), 200 (◆) and 400 (△) rpm.

respectively, indicate that the kinetic process involved in the SPE of diuron from water is endothermic. It is concluded that an increase in experimental temperature will bring about an increase in the rate of uptake which is reflected in the values of $\log k_{up}$ given in Table 1.

3.7. Effect of stirring rate on $\log k_{up}$

The rate of uptake is effected by the stirring rate as can be seen in Fig. 5. When the stirring rate is 100 rpm compared to 200 rpm at the same temperature, $\log k_{up}$ is lower, i.e., the rate of uptake is slower when the rate of stirring is slower. Interestingly, when the stirring rate is increased to 400 rpm, $\log k_{up}$ is the same as that for 200 rpm at the same temperature. This would indicate that at 100 rpm the aqueous diffusion of diuron is acting as a limiting factor. When the stirring rate is increased to 200 rpm or greater the aqueous diffusion layer around the disk is sufficiently small to prevent diffusion from being a limiting factor in the extraction process.

4. Conclusions

A novel experimental method for the determination of the equilibrium and uptake rate constants for the solid-phase extraction of pollutants from water is reported. In practice this method is straightforward and time efficient as a value for both constants can be determined from a single experiment. The applications of this method are limited to analysis of analytes that are sufficiently soluble and stable in water and those that contain a significant chromophore in order to achieve a reliable and reproducible UV absorbance. In addition, the method is limited to the study of single analytes, and could not be used easily to investigate a mixture of analytes. It is worth noting that this method would also be applicable for the study of pH and salinity effects on equilibrium and rate constants, although when studying salinity, the stainless steel cage and HPLC pump lining should be replaced by some other material that is inert to salt corrosion.

The equilibrium constant, K_{eq} , and the rate of uptake, k_{up} , have been determined for diuron at four different temperatures and three different stirring

rates in order to investigate the effects these conditions have on the two parameters. The precision in the experimental values for K_{eq} and k_{up} is in the region of ± 2.5 –8.5%. The present method is devised for passive sampling systems. It should be noted that K_{eq} will be independent of dimensions and configuration of the system. However, this will not be the case for k_{up} . In particular, values of k_{up} found by our method will not necessarily be the same as those obtained in experiments in which a sample solution flows through the C_{18} disk, which is the more traditional procedure for solid-phase extraction of analytes from water.

It is hoped that the observations reported in this paper will aid in the optimisation of solid-phase extraction of pollutants from water using a C_{18} Empore disk. Taking into consideration the effects of temperature and stirring rate on two key parameters involved in SPE could help to achieve more precise and accurate detection and analysis techniques essential in meeting the ever increasing demand for clean water.

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