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Study of the mechanism of the interaction of vinyl chloride with water by reversed-flow gas chromatography

Dimitrios Gavril, Khan Atta Rashid, George Karaiskakis*

Department of Chemistry, University of Patras, 26500 Patras, Greece

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Abstract

The investigation of the mechanism for the interaction of vinyl chloride (VC) with liquid foods is of great significance in food science. In the present work the model system VC–water was studied by using the relatively new technique of reversed-flow gas chromatography. Using suitable mathematical analysis the following physicochemical quantities were determined: (a) diffusion coefficients of VC into water, (b) overall mass transfer coefficients of VC in the water, and in the carrier gas nitrogen, (c) partition coefficients of VC between water and nitrogen, and (d) constants of Henry's law for the adsorption of VC by water. From the variation of the above parameters with temperature, and the stirring rate of the water, useful conclusions concerning the mechanism for the VC–water interaction were extracted. The experimental results for the transfer of VC into the bulk water suggest (i) a mechanism consisted of a fast equilibrium step between the VC in the gas phase and in the interface, followed by a slow adsorption of VC into the bulk of water, which is the rate-determining step, when the water is quiescent, and (ii) a mechanism consisted of a slow diffusion of VC from the gas phase to the interface, which is the rate-determining step, followed by a fast equilibrium step between the VC in the interface and in the water bulk, when the water is stirred. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Reversed-flow gas chromatography; Gas chromatography, reversed-flow; Vinyl chloride

1. Introduction

Vinyl chloride (VC) has received considerable attention both in terms of residual levels in the plastic [1] and as a consequent contaminant in foods [2–4]. VC is related to the primary group of toxic chemical carcinogens and its absence in poly(vinyl chloride) (PVC) is of great importance not only for polymer use and processing, but also for the food industry, as PVC is one of the most important food packaging materials [2–4]. The phenomenon of

desorption or migration of VC from a polymer (e.g. PVC) to a contacting phase (e.g. a liquid food) can be considered as a function of PVC–VC and VC–food interactions. Both these interactions have been already presented in previous works [5,6]. It is the purpose of our work to further investigate the mechanism of the interaction of VC with water by using the relatively new technique of reversed-flow gas chromatography.

Reversed-flow gas chromatography (RFGC) is based on reversing the direction of flow of the carrier gas at various time intervals. It uses a conventional gas chromatograph with any kind of detector, accommodating in its oven a sampling cell. This cell

*Corresponding author. Tel.: +30-61-997-144; fax: +30-61-997-144.

consists of a sampling column and a diffusion column connected to the carrier gas inlet and the detector via a four-port valve. If the carrier gas contains other gases at concentrations recorded by the detector system, the flow reversals create perturbations on the chromatographic elution curve in the form of extra peaks called “sample peaks”. If the concentration of a constituent in the flowing gas depends on a rate process, taking place within the sampling cell, then, by repeatedly reversing the flow, a repeated sampling of this rate process can be performed. By suitable mathematical analysis, equations can be derived that give the rate constant of the slow process responsible for the sample peaks.

RFGC has been used to determine adsorption equilibrium constants [7], gas diffusion coefficients in binary and ternary mixtures [8,9], activity coefficients [10,11], mass transfer coefficients on solids and liquids [12,13], solubility and interaction parameters in polymer-solvent systems [14], molecular diameters and critical volumes in gases [15], Lennard-Jones parameters [16], as well as rate constants and activation parameters [17,18]. Conversions of the reactants into products for various important surface-catalysed reactions, time distribution of adsorption energies, local monolayer capacities, local isotherms, and probability density functions for the adsorption energies on heterogeneous surfaces have also been measured by RFGC [19–21].

To investigate the detailed mechanism of the interaction of vinyl chloride with liquid foods, the RFGC technique was applied for the study of the VC interaction with quiescent and stirred water.

2. Experimental

The apparatus used and the experimental procedure followed have been described elsewhere [6]; only slight modifications were made. A conventional gas chromatograph (Shimadzu GC-8A) with a flame ionization detector contained in its oven (cf. Fig. 1) two sections of lengths l' and l of a stainless-steel chromatographic column [(65+65) cm×5.3 mm I.D.] containing no chromatographic material. A stainless-steel diffusion column, consisted of the two sections z and y (cf Fig. 1), was connected perpendicularly at its upper end to the middle of the column

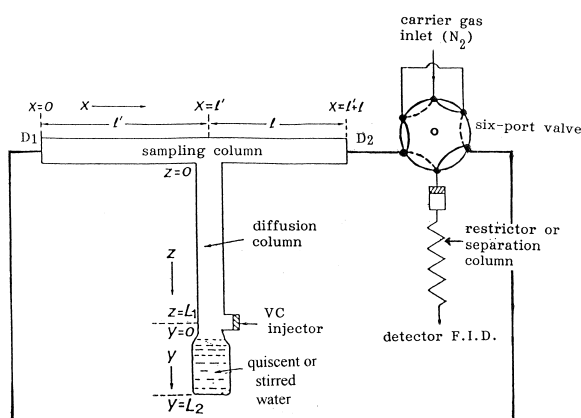


Fig. 1. Schematic representation of the reversed-flow gas chromatography method for studying the interaction of vinyl chloride with water.

$l'+l$. Section y , in which the water was contained, had a volume $V'_G = 4.52 \text{ cm}^3$, a length of 3 cm, and an internal diameter of 18 mm, whilst section z , which was empty of any material, had a volume $V_G = 9.10 \text{ cm}^3$, a length 42 cm, and an internal diameter of 5.3 mm. The volumes V'_G and V_G of the diffusion column were measured by filling it with water at a certain temperature, weighing it, and using the density of water at that temperature. The end D_1 of the sampling column $l'+l$ was connected, via a six-port valve, to the carrier gas (nitrogen) supply, while the other end D_2 was connected to the flame ionization detection (FID) system.

Through the injection port (cf. Fig. 1) 1 cm^3 of vinyl chloride (99.99% purity from Matheson Gas Products) was introduced into the system, at various temperatures and at atmospheric pressure. After waiting for the monotonously rising concentration-time curve to appear in the detector signal, we started the chromatographic sampling procedure by reversing the direction of the carrier gas flow for 6 s, which is a shorter time period than the gas hold-up time in both column sections l and l' . When the gas flow was restored to its original direction, sample peaks were recorded (cf. Fig. 2) corresponding to various times from the beginning. We performed two series of experiments: The first by filling the column section y with quiescent water, while the second by filling the same column section with water which was stirred throughout the whole experiment by a

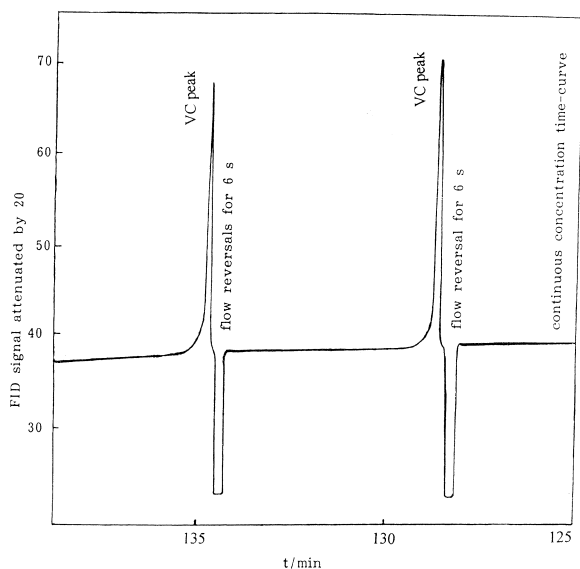


Fig. 2. Reversed-flow gas chromatogram showing two sample peaks for the adsorption of VC by stirred water at 312.15 K and 1 atm ($V=1.0 \text{ cm}^3 \text{ s}^{-1}$).

small magnetic stirrer using a glass-coated stirring bar.

The pressure drop along $l' + l$ was negligible and the pressure inside the whole cell was 1 atm. The carrier gas flow-rate was kept constant ($1.0 \text{ cm}^3 \text{ s}^{-1}$), and the working temperature was in the range $27.2\text{--}72.3^\circ\text{C}$.

3. Theoretical

Previous work [13] has shown that the height, H , of the sample peaks produced by a short flow reversal, due to the injection into the system of a small quantity of VC, when the lower part L_2 of the diffusion column is empty, is given by the relation:

$$H^{1/M} \approx gc(l', t) = N \exp\left(-\frac{3D_g/L_1^2}{1 + 3V'_G/V_G} \cdot t\right) \quad (1)$$

where M is the response factor of the detector, which can be determined as described elsewhere [22], g is the proportionality constant (usually assumed unity for convenience), $c(l', t)$ is the concentration of VC at $x = l'$ (cf. Fig. 1), the time t is measured from the

moment of injecting the VC into the diffusion column, D_g is the diffusion coefficient of VC into the carrier gas nitrogen, V_G and V'_G are the gaseous volumes in sections L_1 and L_2 of the diffusion column, respectively, and N is given by:

$$N = \frac{6mD_g}{\dot{V} L_1^2 (1 + 3V'_G/V_G)} \quad (2)$$

m being the amount of VC injected, and \dot{V} is the volumetric flow-rate. Eq. (1) shows that a plot of $\ln H$ vs. t (after the maximum) is linear during the whole experiment, from the slope of which the diffusion coefficient of VC into nitrogen can be determined, as the V_G and V'_G values are known.

When the lower part L_2 of the diffusion column is filled with quiescent water and the equilibrium distribution of VC between water and nitrogen is rapidly established, the plot of $\ln H$ vs. t (after the maximum) remains linear, as in the situation when the vessel L_2 is empty, but its slope changes, so as the partition ratio, k , to be included in the exponential term of Eq. (1), which is transformed to [13]:

$$H^{1/M} = N \exp\left(-\frac{3D_g/L_1^2}{1 + 3(1+k)V'_G/V_G} \cdot t\right) \quad (3)$$

From the slope of the last equation the partition ratio, k , of VC between the quiescent water and nitrogen can be determined, when the equilibrium distribution is established rapidly.

On the other hand, when the equilibrium distribution of VC between the quiescent water and nitrogen is established slowly, the equation describing the height of the sample peaks is [13]:

$$\begin{aligned} H^{1/M} &= gc(l', t) \\ &= N \cdot \left[\left(1 + \frac{Z}{Y}\right) \cdot \exp\left(-\frac{X+Y}{2} \cdot t\right) \right. \\ &\quad \left. + \left(1 - \frac{Z}{Y}\right) \cdot \exp\left(-\frac{X-Y}{2} \cdot t\right) \right] \end{aligned} \quad (4)$$

where

$$X = \frac{3\beta + 72KaV_L/V_G}{\pi^2(1 + 3V'_G/V_G)} + 25a \quad (5)$$

$$\frac{X^2 - Y^2}{4} = \frac{75a(\beta + 16KaV_L/V_G)}{\pi^2(1 + 3V'_G/V_G)} \quad (6)$$

$$Z = X - 50a \quad (7)$$

$$a = \frac{\pi^2 D_L}{4L_2^2} \quad (8)$$

$$\beta = \frac{\pi^2 D_g}{L_1^2} \quad (9)$$

K is the partition coefficient expressed as the ratio of the VC concentration at the interface to that in the gas phase, V_L is the volume of the water, and D_L is the diffusion coefficient of VC into the water.

The sum of the two exponential coefficients of Eq. (4) $(X + Y)/2$ and $(X - Y)/2$ gives the value of X , while their difference gives the Y value. From the ratio of the two exponential factors of the same equation:

$$\rho = \frac{1 - Z/Y}{1 + Z/Y} \quad (10)$$

the value of Z can be found:

$$Z = \frac{1 - \rho}{1 + \rho} \cdot Y \quad (11)$$

Combination of Eq. (11) with Eq. (7) gives the value of a as:

$$a = \frac{1}{50} \left(X - \frac{1 - \rho}{1 + \rho} \cdot Y \right) \quad (12)$$

from which the D_L value is computed via the Eq. (8).

Solving Eq. (5) for β and substituting it in Eq. (6) we can find the value of K :

$$K = \frac{X - 25a - (X^2 - Y^2)/100a}{24aV_L/V_G} \cdot \pi^2(1 + 3V'_G/V_G) \quad (13)$$

It is also computed from K , the Henry's law constant H^+ , by using the approximation:

$$H^+ = \frac{P}{x} \approx \frac{RTd}{KM} \quad (14)$$

where P is the partial pressure of VC in the gas phase, x its mole fraction in the liquid, d is the density of the water and M its molar mass.

It has been shown previously [23], that the height of the sample peaks produced by short flow reversals, when the vessel L_2 of the diffusion column is filled with stirred water, is given by an equation

similar to Eq. (4), but with the auxiliary parameters N , X , Y and Z expressed by different relations [23]:

$$N = \frac{\pi m D_g}{2V L_1^2} \quad (15)$$

$$X = \frac{\pi^2 D_g}{4L_1^2} + \frac{2K_G a_L}{V_G} + \frac{K_L a_L}{V_L} \quad (16)$$

$$Y = \left[\left(\frac{\pi^2 D_g}{4L_1^2} + \frac{2K_G a_L}{V_G} + \frac{K_L a_L}{V_L} \right)^2 - \frac{\pi^2 D_g}{L_1^2} \cdot \frac{K_L a_L}{V_L} \right]^{1/2} \quad (17)$$

$$Z = \frac{\pi^2 D_g}{4L_1^2} + \frac{2K_G a_L}{V_G} - \frac{K_L a_L}{V_L} \quad (18)$$

where V_G is the gaseous volume in column L_1 , V_L is the volume of the liquid in column L_2 , K_G and K_L are the overall mass transfer coefficients in the gas and the liquid phase, respectively, and a_L is the free surface area of the liquid.

By multiplying the two exponential coefficients $(X + Y)/2$ and $(X - Y)/2$ of Eq. (4) we can find:

$$\left(\frac{X + Y}{2} \right) \cdot \left(\frac{X - Y}{2} \right) = \frac{\pi^2 D_g}{4L_1^2} \cdot \frac{K_L a_L}{V_L} \quad (19)$$

Dividing this product by the factor $\pi^2 D_g / 4L_1^2$ we can find the value of $K_L a_L / V_L$, from which we calculate K_L , as a_L and V_L are known. The K_G value is found by adding the two exponential coefficients $(X + Y)/2$ and $(X - Y)/2$ as follows: Their sum equals X , which is given by Eq. (16). Then, subtracting $\pi^2 D_g / 4L_1^2$ and $K_L a_L / V_L$ previously found, the K_G value can be calculated. Finally, the partition coefficients K are calculated from the ratio K_L / K_G , while the Henry's law constants H^+ are computed from Eq. (14).

4. Results and discussion

When the vessel L_2 is empty (cf Fig. 1), the plot of $\ln H$ vs. t (cf. Fig. 3a of ref [6].) is linear according to Eq. (1), from which the diffusion coefficient of VC into nitrogen can be determined [6], as the V_G and V'_G values are known. In the

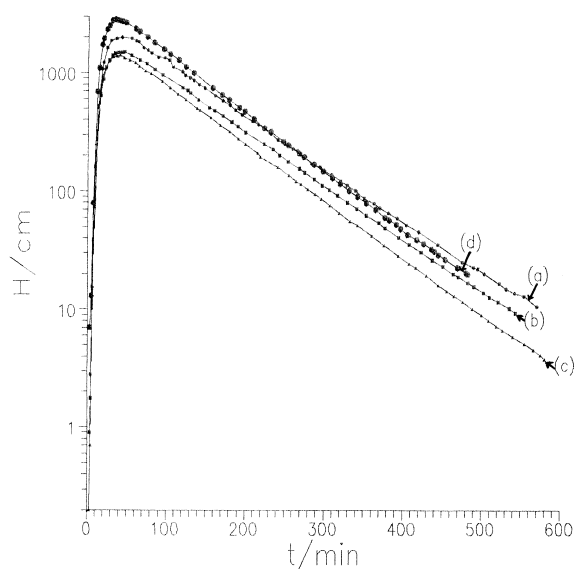


Fig. 3. Plot of H (in logarithmic scale) vs. t for the adsorption of VC by quiescent water at various temperatures lower than 317.15 K. (a) $T=300.35$ K; (b) $T=305.05$ K; (c) $T=312.45$ K; (d) $T=317.15$ K.

present work we repeat the same experiments, but with the lower part L_2 of the diffusion column filled with quiescent and stirred water. In the first case the variation of $\ln H$ vs. t (after the maximum) is linear at temperatures lower than 44°C (cf Fig. 3, curves a–d), and the slope of the straight line after the maximum differs little from that obtained with no liquid in the diffusion column. Therefore, the partition ratio k in Eq. (3) is approximately zero indicating that mass transfer phenomena across the boundary VC–water are negligible, as expected from the very low solubility of VC in water at temperatures lower than 44°C . Applying again Eq. (1) we can find the D_g^{app} values of VC into nitrogen in the presence of quiescent water at temperatures lower than 44°C (cf. Table 1), which are in good agreement with those found previously [6] in the absence of water (D_g^{exp}). In the same Table are compiled the theoretical diffusion coefficients, D_g^{theor} , as they were calculated from the equation of Fuller–Shettler–Giddings [24]. The D_g^{app} and D_g^{exp} values are in most cases close to the D_g^{theor} values, and increase with increasing temperature, as the theory predicts.

It is shown experimentally that a resolution of each curve in the plot of $\ln H$ vs. t (alter the

Table 1

Apparent diffusion coefficients, D_g^{app} , of VC into nitrogen in the presence of quiescent water, as well as experimental diffusion coefficients, D_g^{exp} , of VC into nitrogen in the absence of water [6], and theoretical values, D_g^{theor} , as calculated from the equation of Fuller–Shettler–Giddings [25] at temperatures lower than 317.15 K

$T(\text{K})$	$D_g^{\text{app.}} (\text{cm}^2 \text{s}^{-1})$	$D_g^{\text{exp.}} (\text{cm}^2 \text{s}^{-1})$	$D_g^{\text{theor.}} (\text{cm}^2 \text{s}^{-1})$
300.35	0.100	0.123	0.114
305.05	0.104	0.126	0.117
312.45	0.110	0.131	0.122
317.15	0.112	0.136	0.125

maximum) into two straight lines is achieved at temperatures higher than 51°C (cf. Fig. 4). Following the treatment presented in the theoretical section the D_L , K and H^+ parameters were calculated. The apparent diffusion coefficients of VC into quiescent water, D_L^{app} , together with those calculated theoretically from the Wilke–Chang equation [25] are listed in Table 2, in which the partition coefficients, K , and the Henry's law constants, H^+ , of VC between quiescent water and nitrogen are also included. In the same Table the apparent overall mass transfer coefficients of VC into the quiescent water, K_1^{app} , which were determined from the ratio $K_1^{\text{app}} = D_L^{\text{app}} /$

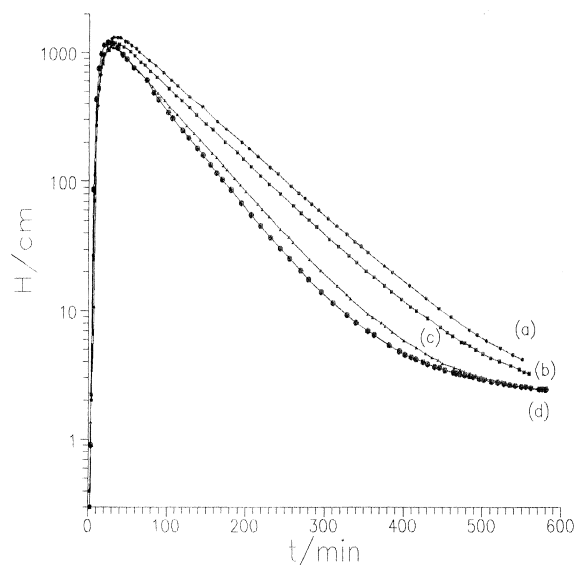


Fig. 4. Plot of H (in logarithmic scale) vs. t for the adsorption of VC by quiescent water at various temperatures higher than 324.15 K (a) $T=324.15$ K; (b) $T=329.05$ K; (c) $T=339.55$ K; (d) $T=345.45$ K.

Table 2

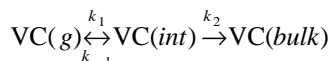
Apparent diffusion coefficients, D_L^{app} , of VC into quiescent water, theoretical values, D_L^{theor} , of VC into water, as calculated from the equation of Wilke–Chang [26], partition coefficients, K , and Henry's law constants, H^+ , for the distribution of VC between quiescent water and nitrogen, as well as apparent overall mass transfer coefficients of VC into quiescent water, K_1^{app} , at various temperatures

$T(\text{K})$	$10^5 \times D_L^{\text{app}}$ ($\text{cm}^2 \text{ s}^{-1}$)	$10^5 \times D_L^{\text{theor}}$ ($\text{cm}^2 \text{ s}^{-1}$)	K	H^+ (atm)	$10^5 \times K_1^{\text{app}}$ (s^{-1})
324.15	2.11	6.76	3.94	36.98	9.33
329.05	1.75	7.37	4.37	33.81	7.74
339.55	0.84	8.71	5.70	26.59	3.72
345.45	0.66	9.54	8.15	18.87	2.97

a_L , are also compiled. From the variation of the parameters D_L^{app} , K , H^+ and K_1^{app} , with temperature the following conclusions can be drawn:

1. The D_L^{app} values decrease with temperature, contrary to theory, indicating that other than the liquid diffusion is the rate-determining step for the adsorption of VC by quiescent water.
2. The partition coefficients K increase with temperature indicating that the distribution of VC to the nitrogen/water interface increases with temperature. As a consequence, the Henry's law constants decrease with temperature, due to the increasing solubility of VC into the water with temperature.
3. The apparent overall mass transfer coefficients of VC into the quiescent water, K_1^{app} , decrease with temperature, indicating that the resistance, k_1^{app} , of VC to the water phase increase with temperature, as K_1^{app} and k_1^{app} are quantities inversely proportional. The fact that the transfer rate of VC into the quiescent water decreases with temperature, and the resistance offered by the liquid (water) phase increases with temperature can be explained as follows: while the diffusion in the liquid phase, according to Wilke–Chang equation, is proportional to temperature T , the diffusion in the gas phase, according to the Fuller–Schettler–Giddings equation, is proportional to $T^{1.75}$, so the injected VC follows two competed processes from which by increasing temperature the diffusion in the gas phase is favoured.
4. The resolution of the plot of $\ln H$ vs. t (after the maximum) into two straight lines indicates a resistance offered by the gas or/and the liquid phase for the transfer of VC into the bulk water. The bigger the difference between the slopes of these two straight lines the stronger the resistance

offered by the two phases. As the distortion of the plot of $\ln H$ vs. t (after the maximum) increases with temperature (cf. Fig. 4), the resistance offered by the quiescent water for the transfer of VC into the bulk water increases with temperature. Thus the **rate-determining step** for the transfer of VC into quiescent water is the slow (irreversible) transfer of VC from the interface to the water bulk, and the mechanism for the adsorption of VC by quiescent water would be:



where k_1 and k_{-1} are the rate constants for the adsorption and desorption of VC by and from quiescent water in the interface nitrogen/water, respectively, and k_2 is the rate constant for the process representing the rate-determining step of the VC transfer from the interface to the quiescent water bulk.

The overall mass transfer coefficients of VC in the gas (nitrogen), K_G , and the liquid phase (stirred water), K_L , across the nitrogen–water boundary, as well as the partition coefficients, K , of VC between the water and nitrogen, and the Henry's law constants, H^+ , for the dissolution of VC into the stirred water at various temperatures (cf. Fig. 5) are compiled in Table 3 from which the following conclusions can be drawn:

1. The K_G values decrease with temperature, thus leading to an increase of the resistance offered by the gas phase, k_G , with temperature, as K_G is inversely proportional to k_G , according to the relation of Blackadder and Nedderman [26]:

$$\frac{1}{K_L} = \frac{1}{k_L} + \frac{K}{k_G} = \frac{K}{K_G} \quad (20)$$

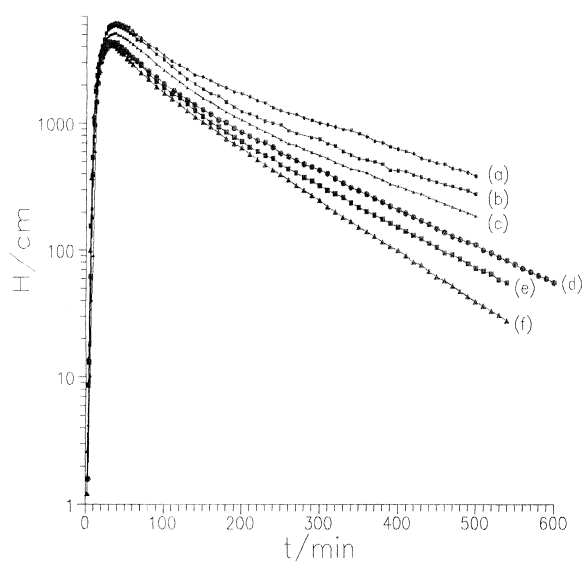


Fig. 5. Plot of H (in logarithmic scale) vs. t for the adsorption of VC by stirred water at various temperatures. (a) $T=305.45$ K; (b) $T=312.15$ K; (c) $T=318.45$ K; (d) $T=328.95$ K; (e) $T=334.85$ K; (f) $T=340.65$ K.

In the last equation k_G and k_L are the gas and liquid film transfer coefficients or the resistances in the gas and the liquid film, respectively, according to the two-film theory of Whitman.

- As the K_L values increase with temperature, the resistance offered by the liquid phase, k_L , for the transfer of VC into the stirred water decreases with temperature.
- The values of the partition coefficients, K , of VC between stirred water and nitrogen increase with temperature, as the solubility of VC into water increases with temperature. The relatively high values of the partition coefficients, K , found in the

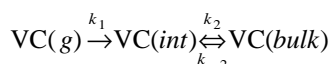
Table 3

Overall mass transfer coefficients of VC in stirred water (K_L) and nitrogen (K_G), as well as partition coefficients (K) and Henry's law constants (H^+) for the distribution of VC between stirred water and nitrogen at various temperatures

T (K)	$10^3 K_G$ (s ⁻¹)	$10^3 K_L$ (s ⁻¹)	K	H^+ (atm)
305.45	1.62	4.46	2.76	44.90
312.15	1.25	4.07	3.25	45.52
318.45	1.08	4.28	3.95	35.63
328.95	1.05	4.83	4.61	31.49
334.85	0.86	5.22	6.07	24.18
340.65	0.97	7.99	8.27	18.05

present work, compared to those given in the literature for other systems [27], can be attributed to the fact that by definition, K gives the ratio of the liquid concentration of the VC at the interface to that in the gas phase and not the ratio of the bulk liquid concentration of VC to that in the gas phase. Thus, K is not an ordinary distribution coefficient of VC between water and nitrogen, but a coefficient probably pertaining to the interface layers of the liquid and the gas.

- The H^+ values, which are immediately related to the K values, as $H^+ = RT/K$, decrease with temperature, due to the fact that the dissolution of VC into stirred water increases with temperature.
- As the K_L values in all temperatures are higher than the K_G values, the resistance offered by the gas phase for the transfer of VC into stirred water is higher than the corresponding resistance in the liquid phase. Because the decrease of k_L with temperature follows a faster rate compared to that for the increase of k_G with temperature, the transfer rate of VC into the stirred water increases with temperature. Thus, the **rate-determining step** for the adsorption of VC by stirred water is the transfer of VC from the gas phase to the interface, followed by the fast equilibrium step between the VC in the interface and in the water bulk, and the mechanism for the adsorption of VC by stirred water would be:



where k_1 is the rate constant for the process representing the rate-determining step (e.g. the transfer of VC from the gas phase to the interface) for the transfer of VC into stirred water, while k_2 and k_{-2} are the rate constants for the adsorption and desorption of VC by and from the bulk phase to the interface, respectively.

- The experimental observation that better resolution of each curve into two straight lines is achieved at the lower temperatures (cf Fig. 5) can be attributed to the fact that the resistance to the liquid phase which is measured by the k_L values is higher at the lower temperatures.
- The values of the partition coefficients, K , of VC between nitrogen and water are independent of the stirring of water (cf. Tables 2 and 3), as they

express the ratio of the VC concentration in the interface to that in the gas phase, and the VC concentration in the interface, according to the theory of Eyring, depends on the number of the vacant sites of the interface, and not on the stirring of the water bulk. The fact that two different mathematical analysis, for both the quiescent and the stirring water, give the same values of the partition coefficients, verifies the consequence and the accuracy of the reversed-flow gas chromatography technique for studying mass transfer phenomena.

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