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Gas chromatographic study of interaction between vinyl chloride and poly(vinyl chloride)

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ABSTRACT

A reversed-flow gas chromatographic method for studying the interactions between vinyl chloride monomer (VCM) and poly(vinyl chloride) (PVC) is described. The method permits the calculation of the VCM diffusion coefficient in the gas phase and the determination of the partition coefficient of VCM between PVC and the carrier gas (nitrogen). From the variation of the partition coefficients with temperature, differential thermodynamic parameters (enthalpy and entropy) of adsorption of VCM on PVC were calculated. These are discussed in comparison with the same parameters as determined by inverse gas chromatography.

INTRODUCTION

Considerable attention has been drawn recently to the possible migration of vinyl chloride monomer (VCM) from plasticized poly(vinyl chloride) (PVC) into the contacting food phase in PVC containers, since many workers have already indicated that VCM is a carcinogenic agent [1–3]. Gilbert [4] reviewed the general topic of the migration of minor constituents from food packaging materials. Whereas at first PVC bottles were widely used as containers for beverages, including alcoholic drinks, it was soon discovered that the alcoholic drinks tasted differently, as a result of contamination by VCM. Further tests showed that VCM migrated into most foods, *e.g.*, edible oils, fats, honey.

The phenomenon of desorption or migration of VCM from PVC into a contacting phase can be considered to be a function of polymer–migrant interaction and diffusion [5]. The thermodynamics of the interaction will determine the equilibrium distribution of the migrant, while the diffusion will affect the rate of attainment of equilibrium. The “active site” hypothesis, which limits the potential migration of the monomer from the polymer into a food contacting phase, has been supported by many workers [6,7]. At very low monomer concentrations the monomer molecules are sorbed onto the most active sites. Inverse gas chromatography has also been used to determine the diffusion coefficient of VCM in PVC plasticized with dioctyl phthalate [8].

In this work reversed-flow gas chromatography, which has been used previously in the determination of various physico-chemical parameters [9], was used for the

study of interactions between VCM and PVC. The method is based on reversing the direction of flow of the carrier gas at various time intervals. If the carrier gas contains other gases at concentrations recorded by the detector system, these flow reversals create perturbations on the chromatographic elution curve which form "extra peaks", such as those in Fig. 1.

If the concentration of a constituent in the flowing gas depends on a rate process taking place inside the chromatographic column, then, by reversing the flow, one performs a sampling of this process, for example the slow diffusion of the vapour of a liquid into the carrier gas. The equations necessary for the calculation of the rate coefficient of this slow process can be derived using suitable mathematical analysis [9]. Reversed-flow gas chromatography has been used to determine gas diffusion coefficients in binary and ternary mixtures [10–12], adsorption equilibrium constants [13], mass-transfer coefficients [14–19], activity coefficients [20,21] as well as solubility and interaction parameters [22]. An equation describing the height of the chromatographic sample peaks as a function of time was used to analyse the experimental data and calculate the values of the above coefficients. The physical separation of a rate or an equilibrium process under study from the chromatographic process itself is done keeping the former process to the diffusion column (section y in Fig. 2), while the latter occurs inside the sampling column. The flow reversals of the carrier gas at known

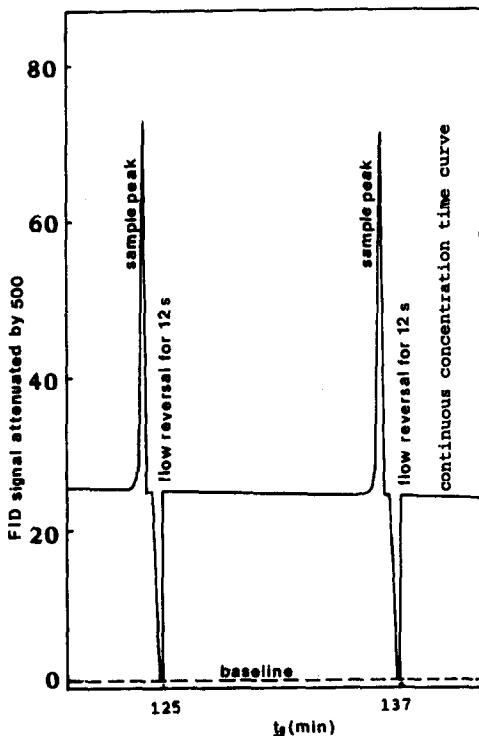


Fig. 1. Reversed-flow chromatogram showing two sample peaks for the adsorption of VCM on PVC from nitrogen at 314.2 K ($\dot{V} = 0.400 \text{ cm}^3 \text{ s}^{-1}$). FID = Flame ionization detection.

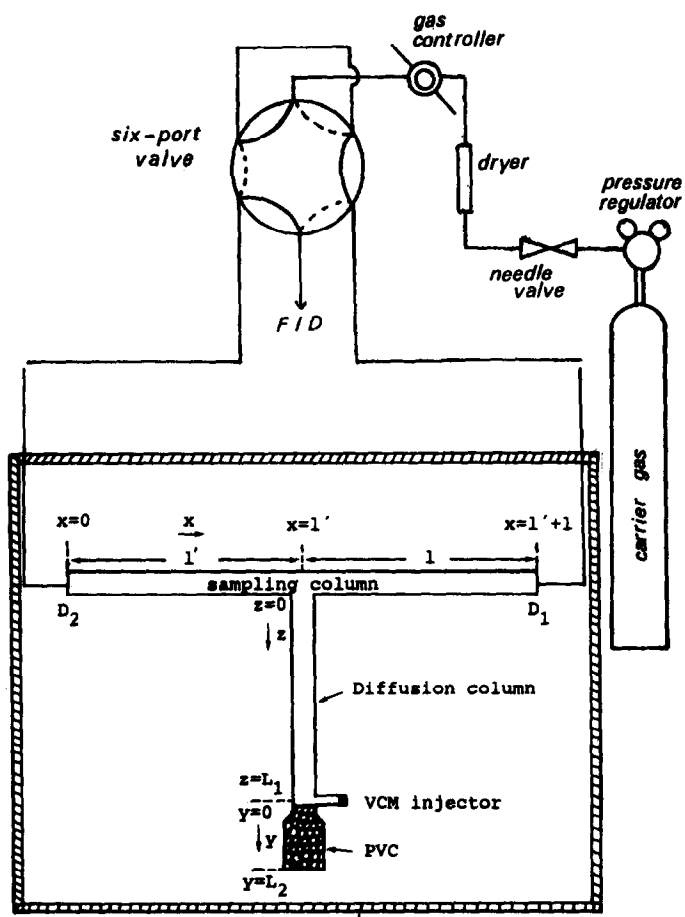


Fig. 2. Schematic representation of the reversed-flow gas chromatographic technique for studying the interactions between VCM and PVC.

times, t_0 , during the experiment sample the concentration $c(l', t_0)$ of a solute vapour at the junction $x = l'$ in the form of sample peaks. The height, h , of these peaks above the ending baseline is

$$h \approx 2c(l', t_0) \quad (1)$$

The current of the carrier gas in the diffusion column is used as a carrier and the rate or equilibrium processes are superimposed on it. In this work, the diffusion band is distorted by the adsorption of VCM on PVC.

EXPERIMENTAL

Prior to use the PVC sample was essentially denuded of residual VCM by placing a limited amount of it into a wide-mouth container and placing the container under

ventilation in a hood. The PVC sample, which was treated in this manner for 2 weeks, had a molecular weight of 110 000 and was supplied by Polysciences. Vinyl chloride gas (99.99% pure) was supplied by Matheson Gas Products.

A conventional gas chromatograph (Pye Unicam Series 104) with a flame ionization detector accommodated a sampling column made from stainless-steel (4 mm I.D.) and a total length of 2 m, empty from any packing material, was connected with the diffusion column at the middle point. This column has two sections, z and y (Fig. 2). Section z (L_1) was 89 cm long (11.18 cm³ volume) and of the same diameter as the sampling column, whilst section y (L_2) was shorter (4 cm) and with a larger diameter (18 mm I.D.). An injector between these two regions permits the introduction of a small gaseous volume (1 ml at atmospheric pressure) of solute (methane or VCM). The sampling and the diffusion columns form a "sampling cell" which must be connected to the carrier gas inlet and the detector in such a way that the direction of flow of the carrier gas (nitrogen of 99.99% purity from Linde) through the sampling column can be reversed at any time desired. This can be done using a four-port valve to connect the ends D_1 and D_2 of the sampling column to the carrier gas supply and the detector. To prevent the flame of the detector from being extinguished when the valve is turned from one position to the other, a restrictor is placed ahead of the detector.

The working temperature was in the range 29.8–52.3°C. The pressure drop along $l' + l$ was negligible and the pressure inside the whole cell was 1 atm. The carrier gas (nitrogen) flow-rate was 0.400 cm³ s⁻¹.

RESULTS AND DISCUSSION

If the diffusion column is empty and 1 ml of solute (VCM) is introduced through the injector of Fig. 2, while nitrogen flows through the sampling column $l' + l$, and fills the diffusion column, $L_1 + L_2$, a diffusion current into the carrier gas arises inside the latter column, creating a finite concentration of it at the junction $x = l'$. This is sampled as a function of time by reversing the direction of the carrier gas flow for a short interval, t' , as previously described, thus giving rise to sample peaks. In curve 1 in Fig. 3 the height of the sample peaks is plotted as a function of time, t_0 , of the flow reversal. This is called a "diffusion band" and is due to the longitudinal diffusion of the solute vapour into nitrogen along the diffusion column, $L_1 + L_2$. The mathematical equation describing a diffusion band as an analytical function of time has already been derived and is given by [18]

$$c(l', t_0) = \frac{\pi m D}{\dot{V} L_1^2 (1 + 1.801 V'_G/V_G)} \cdot \exp\left(-\frac{\pi^2 D/4 L_1^2}{1 + 1.801 V'_G/V_G} \cdot t_0\right) \quad (2)$$

where D is the diffusion coefficient of solute 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, m is the amount of solute injected and \dot{V} is the volumetric flow-rate of the carrier gas in the sampling column. As the height, h , of the sample peaks is approximately equal to

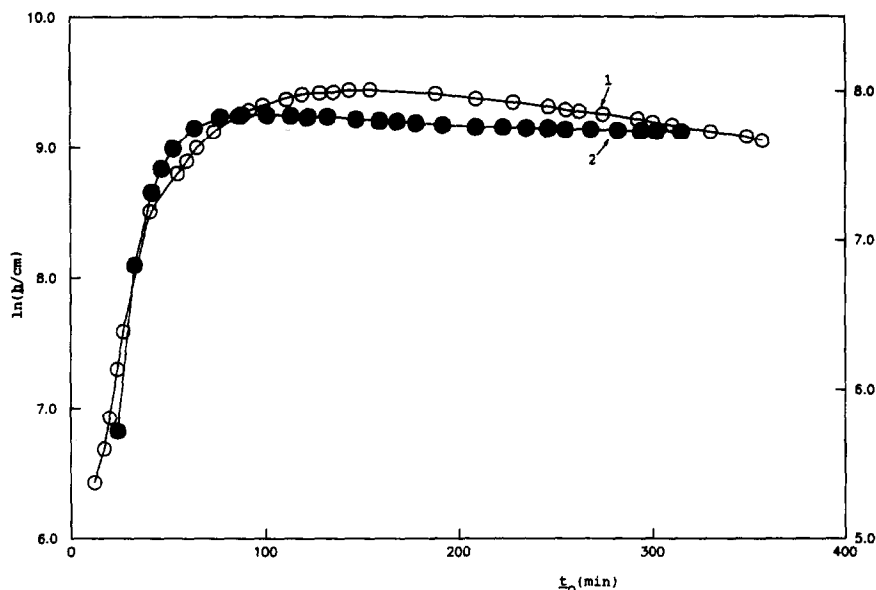


Fig. 3. Plots of $\ln h$ vs. t_0 for VCM and a vessel L_2 , (O) empty or (●) filled with 2.94 g of PVC with molecular weight = 110 000. $T = 314.2$ K; $\dot{V} = 0.400$ cm³ s⁻¹.

$2c(l', t_0)$ according to eqn. 1, eqn. 2 describes the diffusion band ($\ln h$ vs. t_0) as a linear function with slope

$$b = -\frac{\pi^2 D / 4L_1^2}{1 + 1.801 V'_G / V_G} \quad (3)$$

This is valid only for the descending part of the plot after the maximum (*cf.*, Fig. 3). Knowing all the other quantities, D is easily determined from the slope of this straight line. Table I gives the experimental values of the diffusion coefficient, D^{exp} , for VCM and methane into the carrier gas (nitrogen) at various temperatures. For comparison purposes Table I also gives the respective theoretical values of diffusion coefficient, D^{theor} , as they were calculated from the equation of Fuller *et al.* [23]. The

TABLE I

EXPERIMENTAL DIFFUSION COEFFICIENTS, D^{exp} , OF VCM VAPOUR AND METHANE, INTO THE CARRIER GAS (NITROGEN) AND THEORETICAL VALUES, D^{theor} , AS CALCULATED FROM THE EQUATION OF FULLER *ET AL.* [23], AT VARIOUS TEMPERATURES

T (K)	VCM		CH ₄	
	D^{exp} . (cm ² s ⁻¹)	D^{theor} . (cm ² s ⁻¹)	D^{exp} . (cm ² s ⁻¹)	D^{theor} . (cm ² s ⁻¹)
303.0	0.150	0.147	0.307	0.283
308.2	0.157	0.153	0.317	0.292
314.2	0.149	0.158	0.322	0.302
318.2	0.181	0.161	0.336	0.308
325.5	0.191	0.168	0.351	0.321

TABLE II

APPARENT DIFFUSION COEFFICIENT, D^{app} , OF VCM VAPOUR AND METHANE INTO NITROGEN, IN THE PRESENCE OF PVC, AT VARIOUS TEMPERATURES

T (K)	$D_{\text{VCM}}^{\text{app}}$ ($\text{cm}^2 \text{s}^{-1}$)	$D_{\text{CH}_4}^{\text{app}}$ ($\text{cm}^2 \text{s}^{-1}$)
298.2	0.103	—
308.2	0.177	0.313
314.2	0.157	0.322
318.2	0.145	0.334
325.5	0.065	0.351

experimentally determined diffusion coefficients are in most instances very close to those calculated theoretically, and increase with increasing temperature, as the theory predicts.

If we now repeat the same experiments, but with the lower part L_2 of the diffusion column filled with solid particles of PVC (2.94 g), and we assume that the solute (VCM and methane) is not adsorbed on the solid PVC, then the descending part of the diffusion band is again described by eqn. 2, the only difference being that V'_G is now the gaseous volume of the void space in L_2 , filled with the solid PVC. An example is given by curve 2 in Fig. 3. Therefore, knowing again all the other quantities in eqn. 3, one can determine the apparent diffusion coefficients, D^{app} , of VCM and methane into nitrogen (*cf.*, Table II). Table II shows that, whereas the apparent diffusion coefficients of methane into nitrogen are almost identical with the true values, D^{exp} , given in Table I, the apparent diffusion coefficients of VCM into nitrogen deviate significantly from the true values and, except for the D^{app} value at 298.2 K, decrease with increasing temperature, contrary to theory. This is probably due to the fact that, whereas methane is not adsorbed on the PVC particles, as is well known, VCM is adsorbed on the same particles, making possible the determination of the partition ratio, k , of the solute (VCM) between the two phases (solid and gaseous) from the relationship [24]

$$c(l', t_0) = \frac{\pi m D}{\dot{V} L_1^2 (1 + 1.801 V'_G/V_G)} \cdot \exp \left[- \frac{\pi^2 D / 4 L_1^2}{1 + 1.801 (1 + k) V'_G/V_G} \cdot t_0 \right] \quad (4)$$

TABLE III

PARTITION RATIOS, k , PARTITION COEFFICIENTS, K , AND ENTHALPY AND ENTROPY OF ADSORPTION OF VCM ON PVC FROM NITROGEN

T (K)	k	K	ΔH^0 (kJ mol^{-1})	ΔS^0 ($\text{J K}^{-1} \text{mol}^{-1}$)
298.2	1.55	1.83		
314.2	0.95	1.12	-26.1 ± 0.4^a	-148 ± 1^a
318.2	0.85	1.01		

^a These values are independent of temperature; derived from eqn. 8.

Eqn. 4 shows that the slope of the plot of $\ln h$ vs. t_0 for the VCM, in the presence of PVC particles in vessel L_2 , is not that given by eqn. 3, but is equals to

$$b' = -\frac{\pi^2 D/4L_1^2}{1 + 1.801(1+k)V'_G/V_G} \quad (5)$$

The partition ratios, k , for the adsorption of VCM on PVC from nitrogen at three temperatures, as they were determined from eqn. 5, are given in Table III. Table III also gives the partition coefficients, K , as determined from the relationship

$$K = \frac{k\varepsilon}{1 - \varepsilon} \quad (6)$$

where ε is the external porosity (void fraction) of the PVC solid bed, which can be found from [24]

$$\varepsilon = \frac{b}{b'} + \frac{b/b' - 1}{1.801} \cdot \frac{V_G}{V'_G} \quad (7)$$

where V'_G is the gaseous volume of the empty vessel L_2 .

From the variation of the partition coefficients with temperature, the differential enthalpy, ΔH^0 , and entropy, ΔS^0 , of adsorption can be determined via the equation [13]

$$\ln(K/T) = \ln R + \frac{\Delta S^0}{R} - \frac{\Delta H^0}{R} \cdot \frac{1}{T} \quad (8)$$

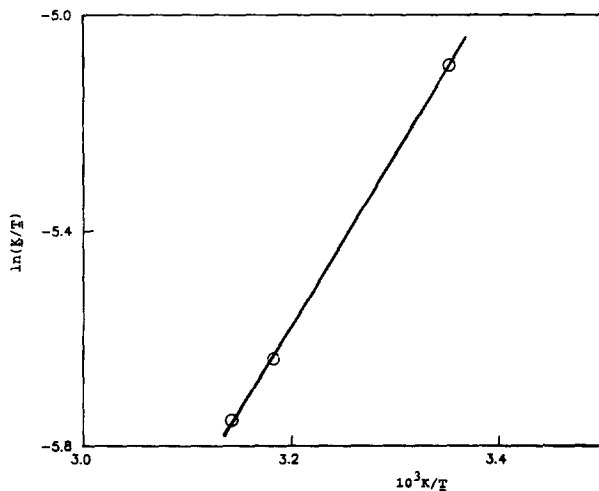


Fig. 4. Plot of $\ln(K/T)$ vs. $1/T$ for the adsorption of VCM on PVC.

Table III lists the enthalpies and entropies of adsorption determined by this method, and Fig. 4 gives an example of plotting the experimental results according to eqn. 8. It must be pointed out that the ΔS^0 value is a relative one, as it depends on the selected standard state for the adsorbed solute. The ΔS^0 value is negative, indicating that the polymer-monomer interaction leads to a more ordered system (binding of monomer molecules on active sites). ΔH^0 is also negative and is a measure of the exothermic nature of the interaction.

The values of ΔH^0 and ΔS^0 found in this work by the reversed-flow gas chromatographic technique are very close to those determined by other workers [6,25] using inverse gas chromatography ($-55.6 < \Delta H^0 < -29.8 \text{ kJ mol}^{-1}$; $-164.9 < \Delta S^0 < -71.5 \text{ J K}^{-1} \text{ mol}^{-1}$).

For the experimental verification of eqns. 2 and 4, experiments were performed with a second vessel L_2 , having a different volume, and thus containing a different amount (4.91 g) of PVC from that used previously. The experimental data for the diffusion coefficients and partition ratios in both cases are almost identical.

If the equilibrium state of the interaction between VCM and solid PVC is established slowly, there is a finite value for the overall mass-transfer coefficient of VCM between the gas and solid phases, and the diffusion band is no longer linear after the maximum, but distorted, as shown in Fig. 3 in ref. 18. In all of our experiments the plots of $\ln h$ vs. t_0 are linear (after the maximum), indicating that the monomer is either reversibly sorbed onto the polymer's "active sites" or reversibly distributed in the polymer entanglements or random coils, thus limiting the potential migration of the monomer from the polymer into a food contacting phase. Further, the thermodynamic data provide additional support for the second hypothesis, as the heat and entropy of adsorption found correspond approximately to an isosteric region of zero coverage, because the total amount of solute injected into the system was of the order of 10^{-5} mol.

It is concluded that reversed-flow gas chromatography can be used successfully for the study of interaction between VCM and PVC with obvious advantages over inverse gas chromatography, owing to the fact that the former method is a pulse technique under steady-state conditions.

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