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DETERMINATION OF THE SOLUBILITY OF VAPOURS IN POLYMERS BY AUTOMATED HEADSPACE GAS CHROMATOGRAPHY

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SUMMARY

An experimental procedure is described for measuring sorption equilibria between polymers and condensable vapours at temperatures above 40°C by headspace gas chromatography. From the results, the solubility coefficients, S, for 20°C were derived. Sorption isotherms and S values were determined for the systems polyethylene–bis(2-chloroethyl) sulphide, polyethylene–2-methoxyethanol, polyethylene–2-methoxyethyl acetate, FFAP–(Carbowax 20M–2-nitroterephthalic acid)–bis(2-chloroethyl) sulphide and Tenax TA–tetrachloroethene. From the sorption isotherms, it appears that in the polyethylene and FFAP systems merely absorption occurs (positive deviation from Henry's law), whereas with Tenax both adsorption and absorption take place.

INTRODUCTION

Headspace gas chromatography (HSGC) is a well known analytical application, in addition to a convenient technique for measuring vapour pressures and related physicochemical parameters[1,2]. In previous papers, we reported the determination of adsorption isotherms for hazardous chemicals[3] and Henry's law constants of aqueous solutions[4] by HSGC. It is now convenient to use this technique also for measuring the sorption–desorption equilibria between vapours and polymer matrices.

The need for information about the solubility of vapours in polymers arose in our laboratory from different routes of investigations, dealing with the permeation of vapours through polyethylene foils and the application limits of sorbent tubes for air sampling purposes. In both cases the solubility coefficient, $S = c_p/c_g$, where c_p and c_g are the equilibrium concentrations in the polymer and in the gas phase, respectively, is one of the important parameters governing the dynamic process. The HSGC technique provides an easy access to this interesting parameter so that it seemed worthwile to describe the general procedure and the results for some typical examples.

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TABLE I

HSGC CONDITIONS

Solute	*Carrier gas (helium) (bar)*	*Equilibr. time (min)*	*Sampl. pressure (bar)*	*Sampl. time (min)*	*Transfer temp. (°C)*	*Column temp. (°C)*	*Retention time (min)*
2-Methoxyethanol	0.4	120	1.5	1.2	120	80	2.58
2-Methoxyethyl acetate	0.4	120	1.5	1.2	120	80	3.87
Tetrachloroethene	0.4	120	1.5	3.0	120	75	3.48
Bis(2-chloroethyl) sulphide	0.85	180	2.2	3.0	150	110	4.75

EXPERIMENTAL

Materials and equipment

2-Methoxyethanol (99.9%), 2-methoxyethyl acetate (98%) and tetrachloroethene (99.9%) were obtained from Aldrich (Steinheim, F.R.G.), bis(2-chloroethyl) sulphide (97.5%) from Atlanta (Heidelberg, F.R.G.). Sorbent materials obtained from Macherey & Nagel (Düren, F.R.G.) were Tenax TA (60–80 mesh) and FFAP (Carbowax 20M–2-nitroterephthalic acid), 23.5% on Chromosorb W AW DMCS (60–80 mesh) (abbreviated as FFAPCHR), and polyethylene foil of thickness 73.1 μm and density 1.004 g/cm^3 was obtained from Wolff (Walsrode, F.R.G.).

The experiments were performed using the automatic HSGC instrument HS 100 from Bodenseewerk Perkin-Elmer (Überlingen, F.R.G.), equipped with a "Megabore" column (WCOT quartz, 30 m × 0.53 mm, DB-5, 1.5 μm). The test vials ("HS-flasks", 22.28 cm^3) were sealed with PTFE-coated septa from butyl rubber. The lowest operating temperature of the HS 100 is about 40°C. Sorption measurements were carried out with the following combinations: bis(2-chloroethyl) sulphide–FFAPCHR (system I); bis(2-chloroethyl) sulphide–polyethylene (II); 2-methoxyethyl acetate–polyethylene (III); 2-methoxyethanol–polyethylene (IV) and tetrachloroethene–Tenax (V).

Procedure

The HSGC system was calibrated in the usual way[5] by analyzing HS-flasks, thermostatted at 80°C and containing different amounts of the test substances (without sorbent). The test substances were dissolved in isooctane; the stock solutions were made up such that the aliquots introduced into the HS-flask would be vaporized completely at 80°C. The appropriate equilibration time was evaluated by analyzing series of HS-flasks, containing sorbent and test substances, after different times of storage at 41.5°C. With increasing storage time, the detector signals decreased to a minimum value, which then remained constant upon prolonged storage. The time which was necessary to achieve this minimum gas concentration in the headspace (corresponding to maximum uptake by the polymer) is given as the "equilibration time" in Table I.

For the determination of the sorption equilibria, known amounts of sorbent and pure test substance, m, were introduced into the HS flask in such a way that the liquid did not touch the solid material. After sealing and thermostatting at 41.5, 50.8 or 60.5°C for the respective equilibration time, the headspace analysis was done. From the calibration graph, the amount, m_g, of gaseous test substance in the headspace was derived, which, upon subtraction from m, yielded the amount, m_p, present in or at the sorbent. From the sorbents, the following amounts were applied: 5–100 mg FFAPCHR, 20–30 mg Tenax and 43.9 mg (= 6 cm^2) of the polyethylene foil. The respective ranges of the test substances were: 0.5–2 mg bis(2-chloroethyl) sulphide, 2-methoxyethyl acetate and 2-methoxyethanol and 0.5–6.5 mg tetrachloroethene. The test substances were injected by a dead volume-free syringe (Hamilton 7005).

For converting the mass m_g into the respective gas concentration, c_g, via the ideal gas law, the actual volume of the headspace must be known, *i.e.*, the volume of the HS-flask (22.28 cm^3) minus the volume of the sorbent. The latter were calculated from the densities, as determined by a "volumenometer"[6]: Tenax, 1.2 ± 0.1 g/cm^3; FFAPCHR, 1.75 ± 0.2 g/cm^3.

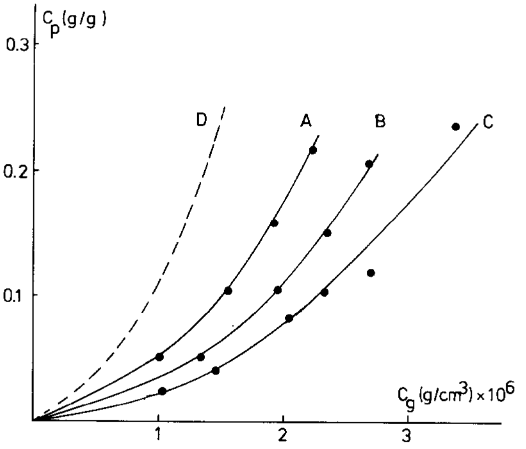

Fig. 1. Sorption isotherms of system I, bis(2-chloroethyl) sulphide–FFAPCHR, as measured at 41.5 (A), 50.8 (B), 60.5°C (C) and as calculated at 20.0°C (D); c_p = grams sorbed per gram pure FFAP.

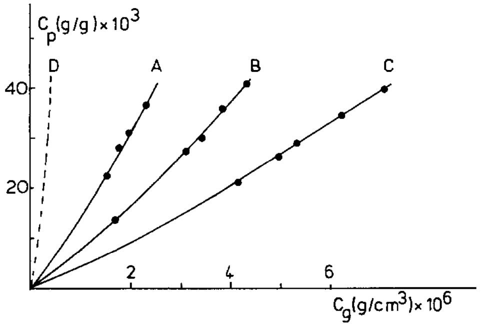

Fig. 2. Sorption isotherms of system II, bis(2-chloroethyl) sulphide–polyethylene, as measured at 41.5 (A), 50.8 (B), 60.5°C (C) and as calculated at 20.0°C (D).

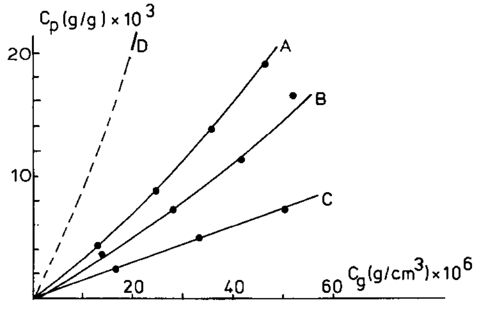

Fig. 3. Sorption isotherms of system III, 2-methoxyethyl acetate–polyethylene, as measured at 41.5 (A), 50.8 (B), 60.5°C (C) and as calculated at 20.0°C (D).

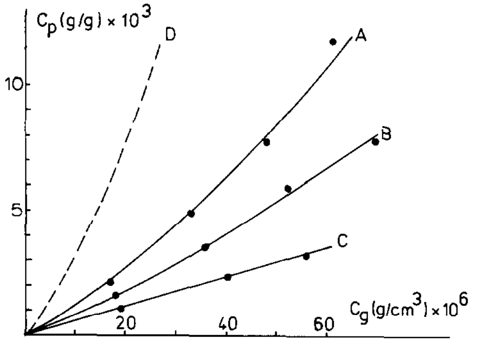

Fig. 4. Sorption isotherms of system IV, 2-methoxyethanol–polyethylene, as measured at 41.5 (A), 50.8 (B), 60.5°C (C) and as calculated at 20.0°C (D).

RESULTS AND DISCUSSION

Figs. 1–5 show the sorption isotherms obtained at the three experimental temperatures and, as dashed lines, the isotherms as calculated for 20°C.

In the systems I–IV (Figs. 1–4) the solubility coefficient, $S = c_p/c_g$ (cm³), increases with increasing c_g. As has been shown by other authors[7–9], this behaviour can be described by

$$\log S = ac_g + \log S_0 \tag{1}$$

From c_p and c_g (Figs. 1–4) the individual solubility coefficients, S, were calculated and subjected to linear regression according to eqn. 1. The results are given in Table II. As a typical example a plot of log S *vs.* c_g for system I is shown in Fig. 6. The respective data are related to the 23.5% portion of pure FFAP; separate measurements revealed

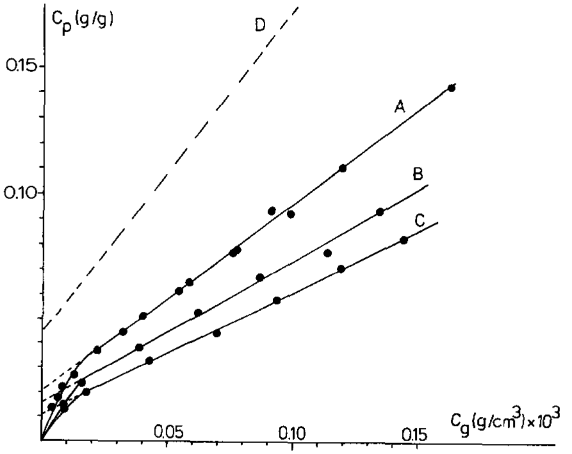

Fig. 5. Sorption isotherms of system V, tetrachloroethene–Tenax, as measured at 41.5 (A), 50.8 (B) and 60.5°C (C); from the linear parts of curves A–C the corresponding line D for 20.0°C was calculated.

TABLE II

LINEAR REGRESSION DATA FOR EQN. 1

$\log S = ac_g + \log S_0$ (cm^3/g)

Temp. (°C)	*System**											
	I			*II*			*III*			*IV*		
	$a \cdot 10^{-5}$	*$\log S_0$***	*r*	*$a \cdot 10^{-4}$*	*$\log S_0$*	*r*	*$a \cdot 10^{-3}$*	*$\log S_0$*	*r*	*$a \cdot 10^{-3}$*	*$\log S_0$*	*r*
41.5	2.64	4.40	0.998	4.12	4.11	0.89	3.37	2.46	0.990	4.05	2.03	0.98
50.8	2.20	4.29	0.999	2.81	3.86	0.97	2.15	2.37	0.81	2.03	1.92	0.93
60.5	1.94	4.17	0.98	1.42	3.65	0.95	0.00	2.16		0.00	1.75	
20.0***	3.46	4.70		7.60	4.70		7.18	2.87		9.33	2.39	

* I = Bis(chloroethyl) sulphide–FFAPCHR; II = bis(chloroethyl) sulphide–polyethylene; III = 2-methoxyethyl acetate–polyethylene; IV = 2-methoxyethanol–polyethylene.

** S and S_0 in cm^3 per g pure FFAP.

*** Calculated using eqns. 2 and 3.

TABLE III

LINEAR REGRESSION DATA FOR EQNS. 2 AND 3, S_0 AND S_c CALCULATED AT 20°C AND THE SLOPE, a^{20}, OF EQN. 1 FOR 20°C

System	*Eqn. 2*				*Eqn. 3*			*Eqn. 1 for 20°C*	
	$a' \cdot 10^{-3}$	*b'*	*r*	*$\log S_0^{20}$*	*c ($g/cm^3 \cdot 10^6$)*	*$a'' \cdot 10^{-3}$*	*b''*	*$\log S_c^{20}$*	*a^{20}*
I*	1.27	0.384	0.999	4.70	1	1.65	−0.570	5.05	$3.03 \cdot 10^5$
II	2.54	−3.96	0.998	4.70	4	3.13	−5.69	5.00	$7.60 \cdot 10^4$
III	1.68	−2.87	0.98	2.87	40	2.43	−5.13	3.16	$7.18 \cdot 10^3$
IV	1.53	−2.82	0.97	2.39	40	2.43	−5.51	2.76	$9.33 \cdot 10^3$

* Related to the content in pure FFAP.

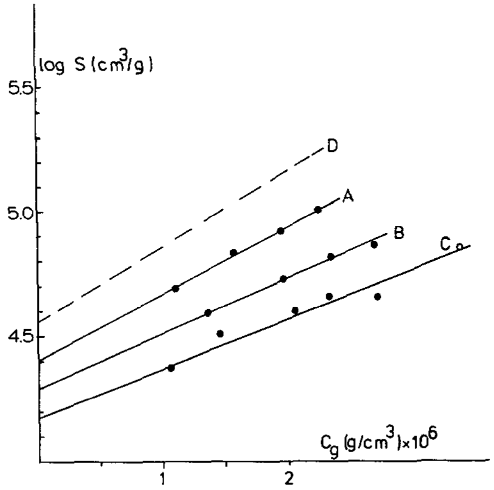

Fig. 6. Logarithm of the solubility coefficient, S, as a function of the equilibrium gas concentration, c_g, according to eqn. 1, for System I, as measured at 41.5 (A), 50.8 (B), 60.5°C (C) and as calculated at 20.0°C (D). The S values are related to the content in pure FFAP.

that the Chromosorb carrier made a negligible contribution to the sorptive capacity.

The temperature dependence of the solubility over small ranges of temperature can be represented by Arrhenius-type equations[7–9]:

$$\log S_0 = a' \cdot 1/T + b' \tag{2}$$

$$\log S_c = a'' \cdot 1/T + b'' \tag{3}$$

In Table III, the linear regression data for the four systems are given, using throughout the respective S_0 from Table II and, additionally, one appropriate S_c within the experimental range of c_g. Fig. 7 shows as an example the graph obtained for system

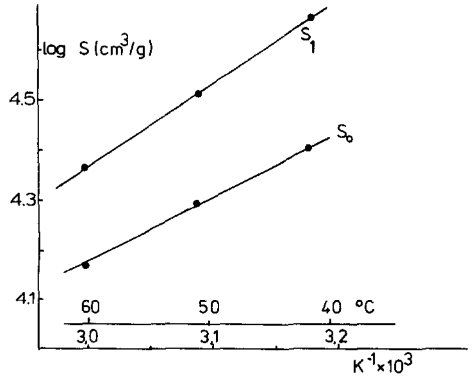

Fig. 7. Temperature dependence of the solubility coefficients at the equilibrium gas concentrations $c_g = 0$ (S_0) and $c_g = 1 \cdot 10^{-6}$ g/cm³ (S_1), as calculated for system I according to eqn. 1.

TABLE IV

LINEAR REGRESSION DATA OF EQN. 5 FOR SYSTEM V

Temp. (°C)	*S* (cm^3/g)	α ($g/g \cdot 10^2$)	*r*
41.5	759	2.07	0.998
50.8	575	1.58	0.997
60.5	495	1.14	0.999

I with S_0, *i.e.*, S for $c_g = 0$ and S_c for $c_g = 1$ µg/cm³ (indicated in Fig. 7 as S_1). These S_c values were calculated by inserting $c_g = 1 \cdot 10^{-6}$ g/cm³ into each of the respective regression equations 1 for the three experimental temperatures. Linear regression according to eqn. 3 resulted in the values of a'' and b'' given in Table III, from which log S_c^{20} was calculated.

Hence, with log S_0^{20} and S_c^{20} two values of eqn. 1 for 20°C are obtained, which allow a plot of the dashed line D in Fig. 6 (assuming eqn. 1 to be valid also at 20°C), according to:

$$\log S_c^{20} = a^{20} c_g + \log S_0^{20} \tag{4}$$

The respective data are included in Table III. From these, using the relationship $c_p = S_c c_g$, the dashed curve D in Fig. 1 was constructed. The curves D in Figs. 2–4 were obtained in the same way.

The isotherms found for system V, Tenax–tetrachloroethene, exhibit a biphasic shape: at low c_g, c_p ascends like an adsorption-type isotherm whereas at higher vapour concentrations, so far as were measured, the sorption behaviour follows Henry's law according to:

$$c_p = S c_g + \alpha \tag{5}$$

The parameters S and α, resulting from linear regression, are given in Table IV. From these data, the temperature dependences of S and α are:

$$\log S = 1024 \cdot 1/T - 0.383 \qquad (r = 0.990) \tag{6}$$

$$\log \alpha = 1426 \cdot 1/T - 6.211 \qquad (r = 0.998) \tag{7}$$

With eqns. 6 and 7 the linear regression parameters according to eqn. 5 for 20°C were calculated (included in Table IV), from which line D in Fig. 5 was constructed.

The positive deviation from Henry's law in systems I–IV may either be a consequence of structural changes in the polymer matrix or result from the fact that the solute–solute interactions are stronger than those between the solute and the polymer[10]. Negative deviation from Henry's law as in system V represents "initial sorption on some kind of specific sites"[10]. The value of α gives an estimate of this initial sorptive capacity, which was found to be in a similar range also with other compounds. This behaviour of Tenax, favouring sorption at low gas concentrations, will be the subject of further studies.

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