Journal of Chromatography, 77 (1973) 406–409

CHROM. 6504

Note

Gas chromatographic measurement of the permeability of PTFE, PVC, polyethylene and nylon tubing towards oxygen and nitrogen

The permeability of PTFE towards a number of compounds is well known[1] and has been used in the generation of primary standard gas mixtures[2,3], the construction of a gas chromatograph–mass spectrometer interface[4] and the development of a selective polarographic oxygen sensor[5]. The permeability of PTFE towards oxygen and nitrogen has been measured by gas chromatography[6].

In view of the availability of the apparatus described in a previous paper[7], it was possible to use the same method as described by ROPER[6] to investigate the permeability towards oxygen and nitrogen of a number of polymeric tubing materials. In essence, the method consists of switching a sample loop, made of the polymeric material under investigation, by means of a six-port switching valve in and out of a carrier gas stream leading to a chromatographic separation column. The compounds that diffuse into the polymeric tubing from the surrounding atmosphere can, by switching the valve, thus be led into or withdrawn from the carrier gas stream, after which separation on the chromatographic column occurs and a frontal chromatogram is obtained.

The influence of the temperature and length of the tubing and the total pressure inside the tubing on the diffusion rate of oxygen and nitrogen into the tubing was investigated.

Materials

PTFE tubing of 4 mm I.D. × 6 mm O.D., PVC tubing of 4 × 6 mm, polyethylene tubing of 4 × 5.8 mm and nylon tubing of 4.9 × 6.22 mm were obtained from Technisch Handels- en Adviesbureau "Rubber" (Hilversum, The Netherlands) and used as sample loops[6,7]. Helium (Air Liquide) was used as carrier gas to flush the tubing. Oxygen and nitrogen were determined by frontal chromatography on a column containing a molecular sieve (Linde 4A) of 1 m length and 4 mm I.D.

TABLE I

DIFFUSION RATES FOR OXYGEN AND NITROGEN IN PTFE

P (bar)	$\varnothing^{25}_{O_2}\left(\frac{ml}{sec \cdot m}\right)$	$\varnothing^{25}_{N_2}\left(\frac{ml}{sec \cdot m}\right)$
1.098	$4.62 \cdot 10^{-4}$	$2.23 \cdot 10^{-4}$
1.67	$4.60 \cdot 10^{-4}$	$2.20 \cdot 10^{-4}$
1.68	$4.51 \cdot 10^{-4}$	$2.17 \cdot 10^{-4}$
2.56	$4.39 \cdot 10^{-4}$	$2.11 \cdot 10^{-4}$
3.39	$4.53 \cdot 10^{-4}$	$2.15 \cdot 10^{-4}$

TABLE II

FLOW-RATE ($\dot{V}$) AND SENSITIVITY (S) OF THE KATHAROMETER FOR NITROGEN

$\dot{V}\left(\frac{ml}{min}\right)$	$S\left(\frac{mV\cdot l}{mole}\right)$
6.65	$4.51\cdot 10^4$
7.35	$4.55\cdot 10^4$
15.6	$4.59\cdot 10^4$
20.3	$4.61\cdot 10^4$
35.3	$4.64\cdot 10^4$

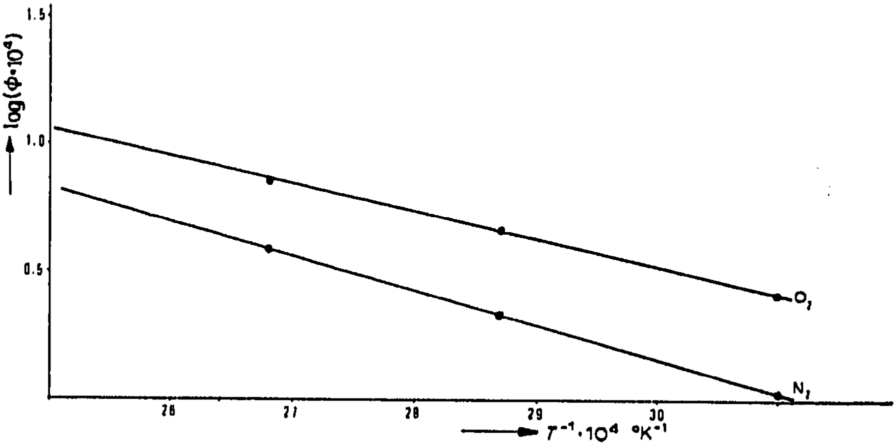

Fig. 1. Plot of the logarithm of the diffusion rate (∅ in millilitres of gas at 25° and 1 bar per second and per metre length of tubing) of O_2 and N_2 *versus* the inverse of the temperature (°K), for PTFE

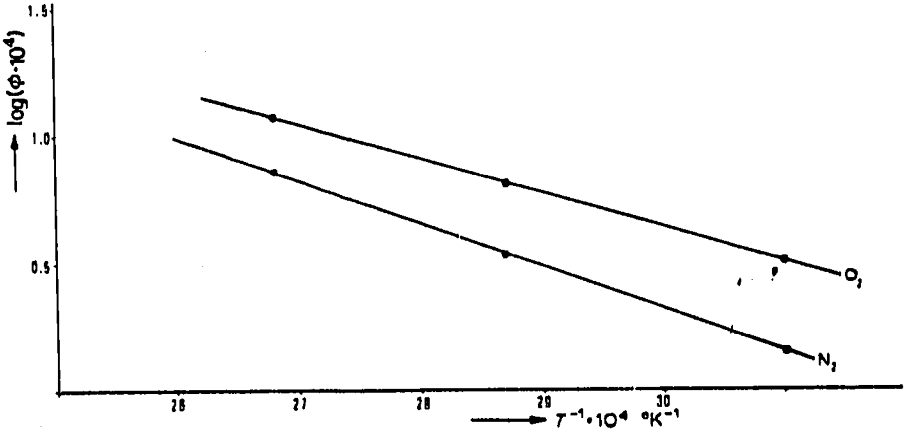

Fig. 2. Plot as in Fig. 1, for PVC.

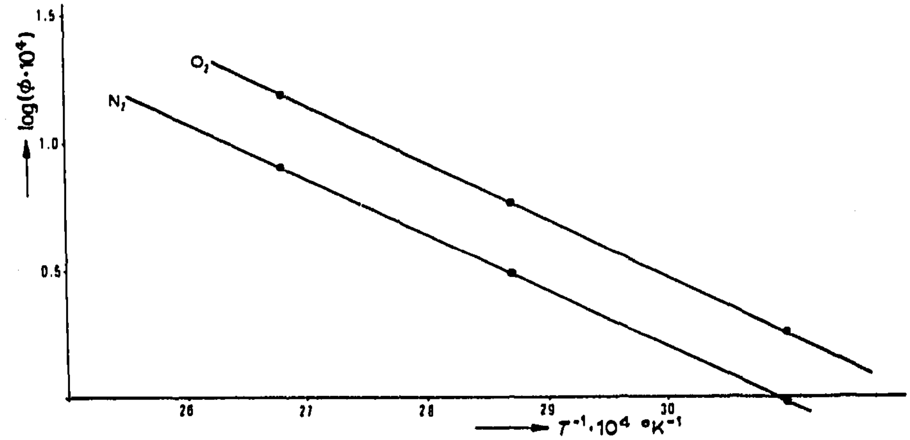

Fig. 3. Plot as in Fig. 1, for polyethylene.

The switching valves used (Valco VSV-6HT) were impermeable towards oxygen and nitrogen. This impermeability was tested by using copper sample loops. The detector was a katharometer (Servomex MK 158/GC 197).

Results

The temperature range used was 50–125 °C. The length of the tube used as sample loop varied from 25 to 100 cm and, as expected, was found to have no effect on the measured diffusion coefficient. The pressure of helium inside the tube also had no significant effect, as can be seen from Table I for PTFE at 75 °C. The diffusion rates, $\varnothing_i^T$, are given in millilitres of gas at 25 °C and 1 bar passing through the tube wall per second and per metre length at a pressure gradient across the tube of 1 bar for each compound (O_2 or N_2).

Averages of five measurements were taken. The resulting standard deviation in the diffusion rate was 2–3%.

In addition, Table II gives the corresponding flow-rates ($\dot{V}$) at 25 °C and 1 bar,

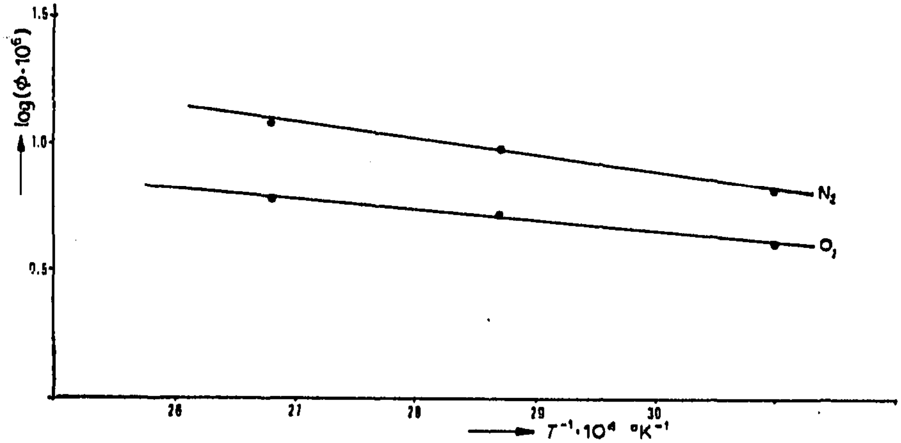

Fig. 4. Plot as in Fig. 1, for nylon.

together with the sensitivity (S) of the katharometer for nitrogen, which appeared to be practically independent of flow-rate.

The time required to obtain a constant diffusion rate varied from about 2 h at 50 °C to 30 min at 125 °C, because, when starting, the tubing material is saturated with oxygen and nitrogen and, due to the finite diffusion constant, time is required to establish a constant concentration gradient in the tube wall.

Figs. 1–4 show the results for the various polymers. It can by clearly seen that nylon is by far the least permeable polymer towards oxygen and nitrogen. Also, with nylon the diffusion rate for nitrogen is greater than that for oxygen. In all other instances, at least within the temperature range used, the opposite applies.

Laboratory of Analytical Chemistry,
University of Amsterdam,
Nieuwe Achtergracht 125,
Amsterdam (The Netherlands)

R. G. GERRITSE

1 R. A. PASTERNAK, M. V. CHRISTENSEN AND J. HELLER, *Macromolecules*, 3 (1970) 366.
2 A. E. O'KEEFFE AND G. C. ORTMANN, *Anal. Chem.*, 38 (1966) 760.
3 *Treatise on Analytical Chemistry*, Vol. 10, Part I, Wiley-Interscience, New York, 1972, p. 6003.
4 S. R. LIPSKY, C. G. HORVATH AND W. J. MCMURRAY, *Anal. Chem.*, 38 (1966) 1585.
5 *U.S. Pat.*, 2,913,386.
6 F. G. ROPER, *J. Chromatogr. Sci.*, 9 (1971) 697.
7 R. G. GERRITSE AND J. F. K. HUBER, *J. Chromatogr.*, 71 (1972) 173.

Received October 10th, 1972