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TECHNICAL NOTE

Solubilities of Carbon Dioxide and Methane in Polyetheretherketone and Polyethersulfone

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ABSTRACT

The solubilities of carbon dioxide and methane in polyethersulfone and polyetheretherketone have been measured at 298.2 K and pressures ranging from 2.7 to 5.1 MPa by using a weighing method. The solubility of carbon dioxide, in cm^3 (STP) cm^{-3}, is almost twice that of methane for both polymeric materials.

INTRODUCTION

Experimental measurements of solubilities of gases in commercially produced polymeric materials are available for very few of the possible systems. For the values which are published, many have been derived from permeability and rate of diffusion measurements rather than direct measurements, and others are for relatively low pressures. The purpose of this study was to provide simple procedures for direct determination of solubility at the relatively high pressures encountered in operational membrane separation processes.

EXPERIMENTAL

The procedure adopted involved containing the polymeric material sample as a membrane or in a finely divided form in a high-pressure vessel such that the mass of gas absorbed into the material could be determined by weighing.

The vessel was designed to be weighed on a Sartorius model R300S balance with a maximum load of 300 g and a weighing accuracy of ±0.1 mg. The vessel was constructed from 316 stainless steel and fitted with a Nupro JB series stainless steel valve and "Cajon VCR" aluminum gasketed connection fittings. No measurable change in the mass of the vessel resulted from repeated connection and disconnection of these fittings.

The volume was determined from the difference in mass between the evacuated vessel and the vessel filled with distilled water, repeated until a constant reading was obtained.

The mass of polymer was also determined from difference weighing, and the volume of polymeric material was estimated by using the density of 1.37 $g \cdot cm^{-3}$ supplied by the manufacturer.

Pressure was measured using a piezo electric pressure gauge (Digiquartz model 1001K-01) with a full scale reading of 7 MPa and a claimed accuracy of 0.0001 of the full scale. The gauge was calibrated using a Budenburg model 280L dead weight tester with a claimed accuracy of 0.0001 of reading.

The cell was immersed in a water-filled thermostat bath and was enclosed in polyethylene film to isolate it from the water so that subsequent weighing was not compromised.

The polymeric material was exposed to the high-pressure gas for at least 15 hours before measurements were taken.

Knowing the mass of the vessel and polymer when evacuated and also when loaded with the gas under pressure, and the volume of the gas phase in the vessel (being the difference between total volume and polymer volume), the mass of gas dissolved in the polymeric material could be determined. The compression factors of the gas needed to determine the small mass of gas in the gas phase were taken from the compilation of the Groupe Européen de Recherches Gazièrs Technical Monograph GERG TM2, 1988 (1).

Temperature was measured with a mercury in glass thermometer with a resolution of 0.05 K calibrated against a platinum resistance thermometer and a Rosemount A.C. resistance bridge (model VLF-51A).

RESULTS AND DISCUSSION

The results obtained are presented in Table 1. The solubility of gas in polymeric material has been reported in units of kg gas per kg of solid and also in the commonly employed units of cm^3 (STP) per cm^3. The results are plotted in Fig. 1, and straight lines with the solubility proportional to the pressure have been fitted to the data. While at low pressures

TABLE 1
Solubility of CO_2 and CH_4 in Polyetheretherketone and Polyethersulfone at 298.2 K

Pressure (MPa)	Absorbed mass (g)	Polymer mass (g)	Solubility	
			$kg \cdot kg^{-1} \cdot cm^3$	STP (cm^{-3})
CO_2 in PEEK				
4.723	0.341	2.280	0.150	52.8
4.660	0.328	2.280	0.144	50.7
4.471	0.330	2.280	0.145	51.0
4.227	0.312	2.280	0.137	48.2
3.868	0.271	2.280	0.119	41.9
3.681	0.268	2.280	0.118	41.5
3.571	0.260	2.280	0.114	40.1
CO_2 in PES				
5.081	0.491	3.384	0.145	69.8
4.921	0.442	3.384	0.130	62.7
4.820	0.430	3.384	0.127	61.3
4.650	0.402	3.384	0.119	57.3
3.764	0.351	3.384	0.103	49.9
3.659	0.342	3.384	0.102	48.7
3.516	0.340	3.384	0.101	48.4
CH_4 in PEEK				
4.890	0.066	2.280	0.029	28.1
4.687	0.064	2.280	0.028	27.2
4.418	0.057	2.280	0.025	24.2
4.185	0.056	2.280	0.025	23.8
3.726	0.051	2.280	0.022	21.7
3.220	0.032	2.280	0.014	13.6
CH_4 in PES				
4.899	0.066	3.384	0.020	25.9
4.257	0.062	3.384	0.018	24.3
4.101	0.050	3.384	0.015	19.6
3.922	0.063	3.384	0.018	24.5
3.134	0.041	3.384	0.012	16.1
2.739	0.034	3.384	0.010	13.3

a nonlinear relation might be expected, the linear approximation is expected to be valid at the pressures employed here.

The carbon dioxide solubility is greater than that of methane in both polymers, as might be expected from solubility in other polymers.

Polyethersulfone (PES) is an amorphous polymer while polyetheretherketone (PEEK) is partially crystalline with a maximum crystallinity of 48% reported (2). As a general rule, a given solute is more soluble in

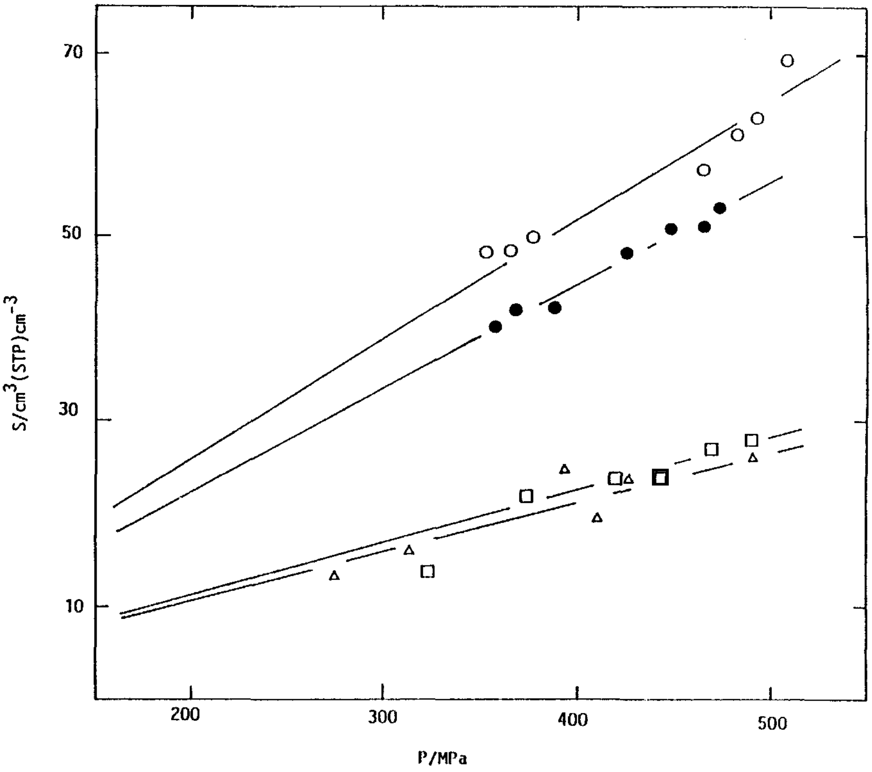

FIG. 1 Solubility of gases in polymers: (○) CO_2 in PES, (●) CO_2 in PEEK, (△) CH_4 in PES, (□) CH_4 in PEEK.

amorphous than in crystalline polymers, and while the results obtained for CO_2 are consistent with this, the difference is slight. The methane solubility as indicated in Fig. 1 is perhaps a little greater in PES, but given the experimental uncertainty, the difference is negligible.

The reduction in solubility expected due to greater crystallinity is apparently overcome by other factors in polyetheretherketone. The effect of reducing the crystallinity by rapid quenching will be investigated in future work.

The densities of the polymers at atmospheric pressure were used for the conversion of units from kg per kg to cm^3 (STP) cm^{-3}. Another possibility would be to determine any change in volume of polymer due to gas absorption and to report results in terms of the volume under pressure. Measurements of this type would be difficult to conduct and have not been attempted here.

DIFFUSION COEFFICIENT DETERMINATION

When the results are coupled with measurements of permeability P of the polymeric materials and the solubility S, the mean diffusion coefficients $\bar{D}$ may be determined using the standard relation

$$\bar{D} = P/S \qquad (1)$$

Ellig and coworkers (3) measured the permeability of PES to mixtures of CO_2 and CH_4, and from their results the permeabilities of the individual gases can be estimated.

For binary gas mixture permeation of a membrane, the separation factor α is defined as

$$\alpha = y(1 - x)/x(1 - y) \qquad (2)$$

where x and y are mole fractions of one component (CO_2 in this case) in the feed gas phase and the permeate gas phase, respectively.

For a $CO_2 + CH_4$ feed gas at a pressure of 2068 kP, a mole fraction of CO_2 of 0.6, and a permeate stream at 101.35 kPa, the separation factor recorded was $\alpha = 40$ for PES membrane of thickness 0.025 mm. This α value corresponds to y (CO_2) = 0.984. The permeate flux found was 1.1×10^{-4} cm^3 (at STP) $cm^{-2} \cdot s^{-1}$.

Assuming that the fluxes of the two gases can be considered independent and equating the gas phase partial pressures to the fugacities of the components, the permeability P of the membrane to the two components can be calculated. The values for P are 2.15×10^{-13} cm^3 (STP) $cm^{-1} \cdot Pa^{-1} \cdot s^{-1}$ for CO_2 in PES and 4.96×10^{-9} cm^3 (STP) $cm^{-1} \cdot Pa^{-1} \cdot s^{-1}$ for CH_4 in PES.

Using the simple Eq. (2) and the solubilities of CO_2 and CH_4 in PES, the mean diffusion coefficients ($\bar{D}$) are calculated to be 2.9×10^{-8} $cm^2 \cdot s^{-1}$ for CO_2 in PES and 1.25×10^{-8} $cm^2 \cdot s^{-1}$ for CH_4 in PES. The magnitudes are of the order expected for small molecule diffusion in an organic solid, and the relative magnitudes mirror quite closely the relative solubilities.

NOTATION

$\bar{D}$	mean diffusion coefficient
P	permeability
S	solubility
α	separation factor
y	mole fraction feed
x	mole fraction permeate

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