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Evaluation of Two Methods for Measuring Vapor Sorption in Polymers

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In this paper, two methods for measuring the equilibrium vapor sorption in polymers are critically compared and data on sorption of toluene, *p*-xylene, hexane, cyclohexane, and heptane in low density polyethylene are reported. The vapor phase calibration method (VPC) was used to measure vapor sorption at low vapor activities in air (below 0.01), and the gravimetric method was used to measure sorption over wide range of activities of pure vapors (0.1–0.9). The Flory-Huggins interaction parameter (in amorphous phase) varied between 1.00 for cyclohexane and 1.19 for toluene. The resulting confidence intervals are conjunctive, indicating that both methods provide consistent results.

Keywords gravimetric method; low density polyethylene; sorption; volatile organic compounds; VPC method

INTRODUCTION

In the recent papers, several methods for the measurement of single vapor sorption in polymers have been reported. Gravimetric methods (1,2), pressure decay methods (3), chromatographic methods (4) and headspace methods (5–7) allow to measure the equilibrium partitioning of a volatile compound between condensed and gaseous phases. Consequently, these methods imply specific experimental conditions, e.g., temperature, pressure, and concentration ranges. The static vapor phase calibration method (VPC) was reported (5–8) to be a reliable method for measuring the equilibrium sorption of volatile organic compounds in solids and liquids, particularly for measuring the sorption of diluted vapors in polymers. The gravimetric sorption method (2,9,10) is a classical method for measuring sorption of pure vapors, the uncertainty of which increases as the vapor becomes diluted. In this work, sorption of toluene, *p*-xylene, hexane, cyclohexane, and heptane vapors in low density polyethylene (LDPE) were determined at 25.0 °C, where the combination of the VPC method and the gravimetric method was used. The Flory-Huggins interaction parameters were evaluated from each method separately and compared to the literature data.

Both the gravimetric method and the VPC method allow to evaluate the equilibrium activity of a vapor in the headspace phase at the equilibrium, and the volume fraction of the sorbate in the polymer defined (1) as

$$\phi_1 = 1 - \phi_2 = \frac{1}{1 + \frac{m_2 \rho_1}{m_1 \rho_2}}, \tag{1}$$

where the subscripts 1 and 2 refer to the sorbate and to the polymer respectively, m means mass and ρ is density. The sorption isotherm of a solvent in polymer is assumed to be in the form of the Flory-Huggins (11) equation

$$\ln a_1 = \ln \phi_1 + (1 - \phi_1) + \chi (1 - \phi_1)^2, \tag{2}$$

where χ is the interaction parameter and a_1 represents activity, defined as the ratio of the partial pressure of the sorbate at sorption equilibrium and the saturated vapor pressure of the sorbate at the given temperature. The Flory-Huggins interaction parameter can be evaluated on the assumption that sorption occurs in the total volume of the semi-crystalline polymer. Alternatively, the interaction parameter can be evaluated on the widely accepted assumption that sorption occurs mainly in the amorphous phase (12,13) and that the crystalline phase is practically inert (14).

Constancy of the crystalline fraction content and reversibility of the sorption/desorption process were proved by Kim et al. (15) for sorption of hexane-*d*$_{14}$ vapor in semicrystalline linear low density polyethylene (LLDPE). Similarly, the invariant content of the crystalline phase was indicated by the negligibly different X-ray scattering spectra (16) of LDPE and of the same polymer swollen by toluene vapor.

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EXPERIMENTAL

Membrane and Chemicals

Low density polyethylene (17) Bralen FB2-30 (Slovnaft Bratislava, Slovakia, thickness 50 μm, density $919 \pm 2\,\mathrm{kg \cdot m^{-3}}$, volume fraction of crystalline phase 45.5%) was used. The following organic solvents were used for the gravimetric measurements: cyclohexane (min. 99.8%, Penta), *n*-heptane (min. 99.0%, Penta), *n*-hexane (min. 99.0%, Penta), toluene (min. 99.0%, Penta), *p*-xylene (99%, Aldrich). For the VPC method, the following solvents were used: cyclohexane (99.7%, Merck), *n*-heptane (99 + %, Sigma-Aldrich), *n*-hexane (97.58%, Acros), toluene (99.8%, Acros), *p*-xylene (99%, Acros). Vapor pressures and densities of the used chemicals are listed in Table 1.

Gravimetric Method

We used a self-constructed sorption apparatus (9,10,16) equipped with McBain's quartz spiral balances. A sample of LDPE was suspended on the end of the quartz balances and degassed at an absolute pressure lower than 1 Pa until the mass of the sample remained constant over time. Prior to each measurement, the sample was degassed for approximately three times longer than the time needed for desorption to the initial mass of the degassed sample. At the start of each experiment, the vapor was released from the vapor container into the evacuated chamber with the membrane. The elongation of the calibrated quartz spiral and the absolute vapor pressure were measured continuously until reaching the sorption equilibrium. The whole apparatus was maintained at 25 °C for all experiments.

Vapor Phase Calibration Method

In the VPC method, the ambient air was saturated with the measured vapor in 100 ml glass bottles, each with 20 ml of the pure solvent (liquid). These bottles were placed in a water bath maintained at 9.0 °C until reaching the vapor-liquid equilibrium; the bottle with liquid *p*-xylene was inserted in the water bath maintained at 25.0 °C, because of its melting point. The same volume of the equilibrium vapor-air phase (0.5 ml) was injected into six 25 ml glass vials, closed with the Mininert valve (Valco Instruments Company, USA), and darkened with aluminum foil. Three of these vials contained the LDPE samples and the other three were empty. Three samples of the headspace phase were taken from each vial after reaching the sorption equilibrium and analyzed by means of GC-FID, calibrated for the appropriate compound. The amount of the sample of LDPE ranged from 0.10 to 0.12 g, all vials were incubated in the water bath at 25.0 °C.

TABLE 1
Vapor pressures and densities (18) at 25 °C

Compound	p^{sat} [kPa]	ρ [$\mathrm{g \cdot cm^{-3}}$]
Toluene	3.798	0.862
p-Xylene	1.179	0.857
Heptane	6.104	0.680
Cyclohexane	13.01	0.774
Hexane	20.17	0.655

All samples of the headspace phase were analyzed using a GC 8000 Top (CE Instruments, UK), equipped with a flame ionization detector maintained at 210 °C and a capillary column with the HP-5 stationary phase, length 30 m, inner diameter 0.320 mm (Agilent Technologies, USA). The column was maintained at 110 °C, helium was used as the carrier gas at the flow rate of $17.5\,\mathrm{ml \cdot min^{-1}}$. The Gastight #1750 (0.5 ml) and Gastight #1001 (1 ml) syringes (Hamilton-Bondauz, Switzerland) were used for injecting samples of the headspace phase into the GC (0.5 ml syringe, samples 0.2 ml) and for introducing the air saturated by the measured vapor into measuring vials (1 ml syringe).

RESULTS AND DISCUSSION

Sorption isotherms of the investigated compounds in LDPE are shown in Figs. 1–5, in which the sorption coefficient S is defined as the mass of the sorbate (in the polymer) per mass of the polymer and per equilibrium partial pressure of the sorbate above the surface of the sample ($\mathrm{g \cdot g^{-1} \cdot Pa^{-1}}$). The square points represent the measured values of the sorption coefficient evaluated on the assumption that sorption occurs in the whole volume of LDPE. The diamond points represent sorption coefficients related to the sorption of vapor in the amorphous phase of LDPE. The sorption isotherms, obtained gravimetrically, were

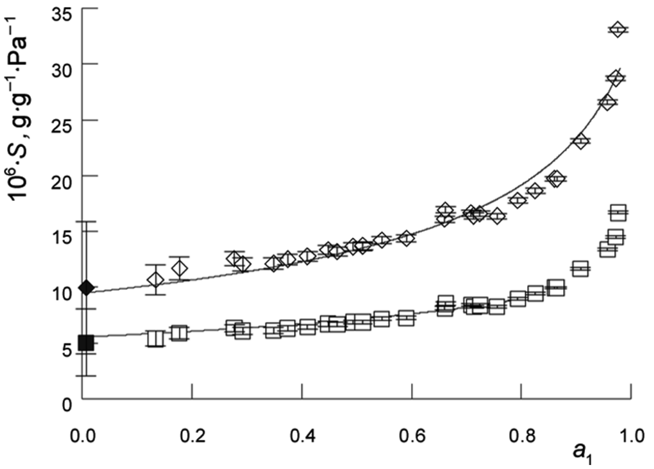

FIG. 1. Sorption coefficients of cyclohexane vapor in LDPE at 25 °C. Diamonds represent sorption in the amorphous phase; squares indicate sorption in the whole polymer. Empty points were measured using gravimetric method; filled points were measured using the VPC method. The 95% confidence intervals are shown.

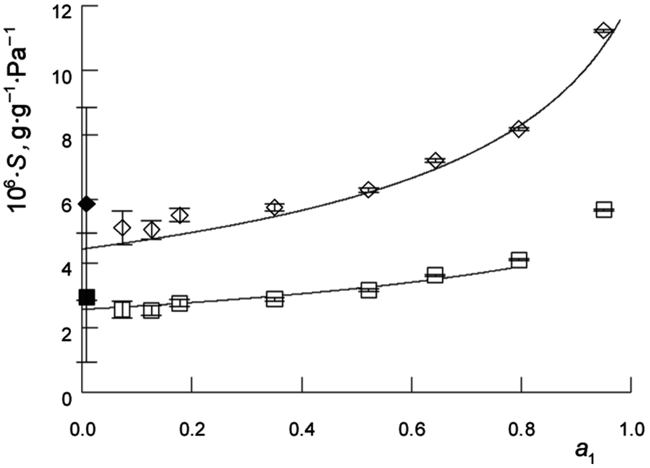

FIG. 2. Sorption coefficients of hexane vapor in LDPE at 25 °C. Diamonds represent sorption in the amorphous phase; squares indicate sorption in the whole polymer. Empty points were measured using gravimetric method; filled points were measured using the VPC method. The 95% confidence intervals are shown.

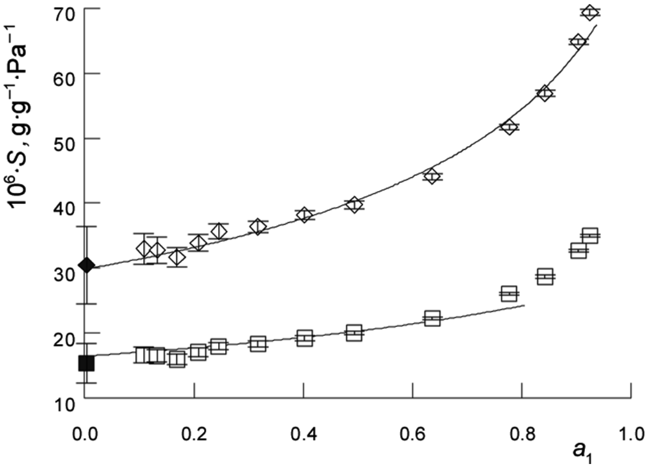

FIG. 4. Sorption coefficients of toluene vapor in LDPE at 25 °C. Diamonds represent sorption in the amorphous phase; squares indicate sorption in the whole polymer. Empty points were measured using gravimetric method; filled points were measured using the VPC method. The 95% confidence intervals are shown.

reproducible within the experimental error, which was checked (16) for toluene, heptane, and hexane, vapors.

The filled square points and filled diamond points represent the sorption coefficients related to the whole volume of LDPE and to the amorphous part of the LDPE respectively, which were measured using the VPC method. The 95% confidence intervals, calculated using the uncertainty distribution law, are shown in these figures. Such intervals include the uncertainty of the equilibrium volume fraction in the polymer and the uncertainty of the partial pressure of the sorbate. The Flory-Huggins model was fitted to the measured data on equilibrium vapor sorption, assuming either sorption in the whole volume of the polymer or sorption in the amorphous part of the polymer. If sorption in the whole volume was considered, the Flory-Huggins equation provided a good approximation of the sorption isotherms bellow the vapor activity of 0.8. On the contrary, the same equation provided a satisfactory approximation of the entire sorption isotherms, in which only sorption in the amorphous phase of LDPE was considered. The sorption isotherm of *n*-heptane vapor in the amorphous part of LDPE showed an exceptional

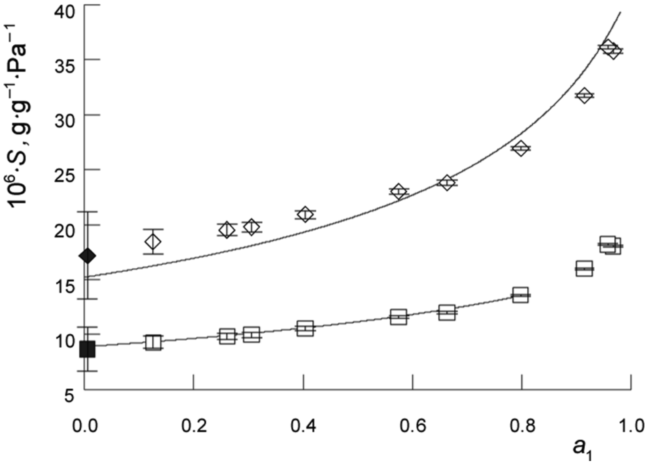

FIG. 3. Sorption coefficients of heptane vapor in LDPE at 25 °C. Diamonds represent sorption in the amorphous phase; squares indicate sorption in the whole polymer. Empty points were measured using gravimetric method; filled points were measured using the VPC method. The 95% confidence intervals are shown.

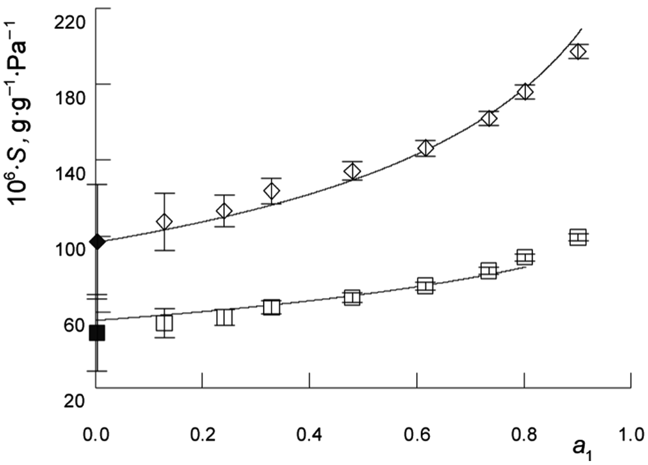

FIG. 5. Sorption coefficients of *p*-xylene vapor in LDPE at 25 °C. Diamonds represent sorption in the amorphous phase; squares indicate sorption in the whole polymer. Empty points were measured using gravimetric method; filled points were measured using the VPC method. The 95% confidence intervals are shown.

TABLE 2
The Flory Huggins interaction parameters obtained using the gravimetric method and the VPC method

Compound	χ^a	χ^b	χ^c	χ^{*a}	χ^{*b}	χ^{*c}
Toluene	1.71 ± 0.06	1.8 ± 0.2	1.58; 1.75^d	1.19 ± 0.06	1.2 ± 0.2	0.96; 1.23^d
p-Xylene	1.65 ± 0.04	1.8 ± 0.2	1.44	1.18 ± 0.05	1.2 ± 0.2	0.75
Heptane	1.62 ± 0.05	1.6 ± 0.2	1.40; 1.550^e	1.15 ± 0.05	1.1 ± 0.2	0.84; 1.065^e
Cyclohexane	1.47 ± 0.05	1.6 ± 0.4	1.32	1.00 ± 0.05	1.0 ± 0.4	0.64
Hexane	1.62 ± 0.06	1.5 ± 0.4	1.50; 1.569^e	1.13 ± 0.06	0.9 ± 0.4	0.88; 1.083^e

*sorption in the amorphous phase of the polymer; sorption in the whole volume of the polymer is calculated over the activity range 0–0.8.

[a] Gravimetric method, this work, crystalline fraction content 0.455.

[b] VPC method, this work, crystalline fraction content 0.455.

[c] Gravimetric method, re-calculated from the correlations of Rogers et al. [12], polyethylene; 0.922 g · cm^{-3}; crystaline fraction content 0.60; 25°C.

[d] Value reported by Doong and Ho (19), polyethylene; 0.920 g · cm^{-3}; crystalline fraction content 0.45; 30°C.

[e] Values reported by Castro et al. [13], low density polyethylene; 0.9157 g · cm^{-3}; crystalline fraction content 0.43; 35 °C (hexane); 40 °C (heptane).

behavior, where the Flory-Huggins interaction coefficient became linearly dependent on its volume fraction, i.e., $\chi^* = 1.07 + 0.60 \cdot \phi_1$. Similarly, the Flory-Huggins interaction parameter of *p*-xylene in the amorphous phase of LDPE became concentration dependent ($\chi^* = 1.12 + 0.51 \cdot \phi_1$), while the proportional term was negligible for the other studied vapors. Similar behavior was described in the literature (13).

The Flory-Huggins interaction parameters were calculated by fitting Eq. (1) to the equilibrium sorption data obtained using the gravimetric method. The 95% confidence intervals $\chi \pm 2\sigma_{\text{fit}}(\chi)$ describing the quality of the fit were calculated with the Levenberg-Marquardt non-linear fitting procedure encapsulated in the Table Curve 2D 5.0 software package. The overall standard deviation of the Flory-Huggins interaction coefficient was calculated to cover the uncertainty of the fit, the uncertainty of the mass measuring system, the uncertainty of the pressure measuring system and the increase of pressure in the apparatus due to certain leaks (2). Hence, the uncertainty propagation law was used in form

$$\left(\frac{\sigma(\chi)}{\chi}\right)^2 = \left(\frac{\sigma_{\text{fit}}(\chi)}{\chi}\right)^2 + \left(\frac{\sigma_{\text{prop}}(\chi)}{\chi}\right)^2, \tag{3}$$

where

$$\sigma^2_{\text{prop}}(\chi) \approx \left(\frac{\partial \chi(a_1, \phi_1)}{\partial a_1}\right)^2 \cdot \sigma^2(a_1) + \left(\frac{\partial \chi(a_1, \phi_1)}{\partial \phi_1}\right)^2 \cdot \sigma^2(\phi_1). \tag{4}$$

The standard deviation of the sorbate volume fraction obtained from the VPC measurements was estimated from the variability of the GC responses to the samples taken from three vials with and without the polymer sample. This uncertainty can be reduced by increasing the number of simultaneously analyzed samples and by changing the volume of the polymer sample relatively to the volume of the headspace phase (5,7,8). The standard deviation of the activity of each vapor was estimated from the standard deviation of the proportionality factor of the GC calibration curve and from the variability of the GC responses to the headspace samples taken from the vials with the polymer samples. The values of the interaction parameters are listed in Table 2, indicating a relatively good agreement between our results and the literature data. The apparent discrepancy between our results and those of Rogers et al. (12) is most likely due to the two-step evaluation of such parameters, i.e., the calculation of the $\phi_1(a_1)$ dependencies from the reported empirical correlations and then fitting of Eq. (1) to these data.

CONCLUSION

The gravimetric method and the VPC method for vapor sorption measurements are shown to be compatible, so that both methods provide conjunctive confidence intervals of Flory-Huggins interaction coefficients. The sorption isotherms of toluene, *p*-xylene, hexane, cyclohexane, and heptane vapors in semi-crystalline LDPE are reported and the confidence intervals of the Flory-Huggins interaction coefficients at 25 °C are listed, extending the knowledge on the vapor sorption behavior of LDPE.

Finally, since the VPC measurements were conducted under ambient air and the gravimetric measurements were performed without any additional gas, no effect of the ambient air was proved, which corresponds to the observations reported by Dhoot and Freeman (20).

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