

Thermodynamic Modeling of the Sorption of Organic Chemicals in Thermoplastics and Elastomers

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SYNOPSIS

The amount of solute sorbed per unit weight of sorbent, q_e , and the equilibrium solubility (partition) coefficient were measured using a gravimetric method for various types of organic chemicals in thermoplastics and elastomers. A thermodynamic model was derived to predict the activity-dependent partition coefficient and q_e for a wide range of organic chemicals. The thermodynamic model produced a better fit to the measured q_e values than did the Flory-Huggins equation. Partition coefficients and q_e increased with increase in activity. For nonpolar compounds, q_e increased logarithmically but decreased for polar compounds with an increase in the saturation organic chemical vapor concentration. Elastomers had 14–28 times greater q_e values than did thermoplastics. A structure-activity relationship was found to accurately predict the partition coefficient for lipophilic organic chemicals at a specific activity. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Plastic pipes and rubber gasket materials are widely used for potable water distribution. Polyethylene (PE), poly(vinyl chloride) (PVC), and polybutylene (PB) are the materials most predominantly used for smaller diameter pipes. Gasket materials are used to join larger diameter pipes. Styrene butadiene rubber (SBR) accounts for more than 95% of the water supply gasket market, while nitrile, neoprene (chlorinated rubbers), ethylene propylene diene monomer (EPDM), and the fluorinated rubbers (Viton[®]) share the rest of the market. Several recent studies have found that organic chemical contaminants in soil and groundwater may contaminate drinking water by penetrating the walls of buried plastic water pipes and gasket materials.^{1–4}

Geomembranes (or flexible membrane liners) are commonly used as barriers or covers of liquid or solid contaminant confinement systems. PE geomembranes are most widely used, followed by PVC and chlorinated polyethylene-chlorosulphonate poly-

ethylene (CPE-CSPE). The Environmental Protection Agency (EPA) requires a double-liner system for hazardous waste landfills and surface impoundments with a leachate collection system between these liners.⁵ In 1984, the EPA recommended a standard test method for chemical compatibility or resistance (EPA Method 9090) of geomembranes.⁶ Because of this test method, the number of geomembrane types used has been greatly reduced, particularly the number of those used for pollution control.⁷ PE geomembranes are the most common liners used for barriers or covers of the intended hazardous organic chemicals in the environment. Their range of applications is tremendous. Solely for civil engineering purposes, at least 30 individual applications have been developed,⁷ e.g., liquid containment liners, covers for reservoirs, canal liners, solid material (landfill) liners, caps and closure, underground storage tanks, and geotechnical applications such as earth dams, concrete dams, and tunnels. Although new applications of these polymers are regularly being developed, sorption and transport mechanisms of organic chemicals in polymers and elastomers are not well studied.

Many polymers and elastomers are used in the laboratory or field while investigating the physical/

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chemical properties and fate of organic chemicals in the environment. A lot of time and effort is being devoted to find a suitable plastic or elastomer in order to reduce the loss by sorption/permeation during experiments. Although the partition coefficients of organic chemicals in many materials are extensively studied, the partition coefficients of organic chemicals in plastics and elastomers are not.

Sorption is generally used to describe the initial penetration and dispersal of penetrant molecules into a polymer matrix. The term includes adsorption, absorption, incorporation into microvoids, and cluster formation. Sorption occurs on rigid internal surfaces adjacent to cavities and holes that have sufficient volume and proper shape to accommodate the penetrant molecules. Therefore, the magnitude of available sorption sites in a given solid can be expected to increase as the penetrant size and shape decrease.⁸ Additional factors affecting the sorption process are concentration, temperature, swelling-induced structural states, time of sorption to equilibrium, etc. In general, the partition coefficient follows an Arrhenius-type relationship.⁹⁻¹⁴ The partition coefficient of liquid penetrants in polymers generally increases with increasing temperature but may decrease depending on the nature of the penetrant-polymer interactions.^{9,14} The amount of the penetrant sorbed in a polymer at equilibrium and its mode of sorption are governed by the thermodynamics of the system.

Sorption of organic liquids and vapors in polymers generally follow a mass transfer behavior including concentration gradient-controlled diffusion and relaxation-controlled swelling. The physical phenomena that occur simultaneously are dissolution, diffusion, swelling, and relaxation. Permeation of organic chemicals through polymers has been the main subject of many recent contributions in the literature.¹⁵⁻¹⁹ Prediction of the rate of permeation is of primary interest and can only be achieved if the corresponding partition and diffusion coefficients are known.

The Flory-Huggins equation is commonly used to express sorption characteristics. This equation was developed for wide ranges of vapor activity and for polar polymer systems.²⁰ This theory expresses the activity of a solute as follows:

$$\ln a = \ln \nu_1 + (1 - \nu_1) + (1 - \nu_1)^2 \cdot \chi \quad (1)$$

where ν_1 is the volume fraction of the solute in the polymer-solute system and χ is the polymer-solute interaction parameter. The value of χ is regarded as a measure of the swelling power of an organic

chemical for a given polymer.¹ In general, when $\chi < 0.5$, the solute completely dissolves the polymer; as χ increases at values > 0.5 , the swelling power of the solute decreases gradually. The amount of solute sorbed on to the polymer per unit weight of the polymer, q_e , can be expressed in terms of ν_1 as follows:

$$q_e = \frac{\nu_1}{1 - \nu_1} \quad (2)$$

The objectives of this paper were to measure the partition coefficients of polymers and elastomers to various types of organic chemicals, to develop a thermodynamic model for the prediction of the partition coefficient over activity, and to find a structure-activity relationship for the prediction of the partition coefficient for an organic chemical of interest.

EXPERIMENTAL

PB, trade name for poly(1-butene), is a member of the polyolefin group of polymers made of straight-chain hydrocarbons. It can be represented by the formula $-\text{[CH}_2\text{CH(C}_2\text{H}_5\text{)]}-_n$, where n is the degree of polymerization.²¹ PB has a stiffness similar to low-density polyethylene (LDPE) but its strength is higher than that of high-density polyethylene (HDPE). Its most significant physical feature is its better retention of strength with increasing temperature: nearly 93°C for pressure uses and somewhat higher for nonpressure applications.²² For this experiment, several rolls of PB pipe were purchased on the open market. The LDPE pipes tested were obtained from the Netherlands Waterworks Testing and Research Institute Ltd. (KIWA). Thin strips of PB and LDPE were obtained from the water pipes with a lathe. PB and LDPE sample thicknesses ranged from 68 to 128 μm .

Representative finished gasket materials were obtained from manufacturers. Representative thin films of gasket materials were prepared by freezing the gasket to approximately -195°C in liquid nitrogen and then cutting slices from the frozen specimens with an electric food slicer. Gasket film thicknesses ranged from 100 to 400 μm . Density was determined by pycnometry according to the ASTM D 792-66 method. The densities of the materials tested are summarized in Table I.

The organic chemicals selected for study were toluene, *m*-xylene, *o*-xylene, *p*-xylene, ethyl benzene

Table I Densities of Polymers and Elastomers Used in the Experiments

Materials	PB	LDPE	SBR	Neoprene	Nitrile	EPDM	Viton
Density (g/cm ³)	0.93	0.92	1.13	1.29	1.27	1.09	1.32

(aromatic hydrocarbons); 1,2-dichlorobenzene, 1,3-dichlorobenzene (chlorinated aromatics); *n*-hexane, *n*-nonane (aliphatic hydrocarbons); dichloromethane, tetrachloroethylene, 1,1,1-trichloroethane, trichloroethylene (chlorinated aliphatics); *o*-chlorophenol (phenols); dichloropropane (fumigants); methanol (polar compound); and 2-butanone (methyl ethyl ketone) and ethyl acetate (other compounds). High-pressure liquid chromatography-grade organic chemicals were used without further purification.

The sorption isotherms were measured using two recording electrobalances (Cahn 1000) to measure the weight change. The apparatus was located in a cabinet in which temperature was controlled within $\pm 0.1^\circ\text{C}$. The temperature was measured with a thermocouple in the vertical tube of the electrobalance. The sensitivity of the electrobalance was 1 μg . Samples of approximately 100 g were used. All the organic chemicals were thoroughly degassed prior to use. Before starting a sorption run, the system containing the sample was completely evacuated. Then, the penetrant vapor was admitted into the system until the desired pressure was obtained. The equilibrium pressure and the weight gain of the sample were measured after no further increase in weight was observed in the electrobalance recorder. After that, more organic chemical vapor was admitted. This procedure was repeated until the maximum value of P/P_0 permitted by the experimental system was reached. All the experiments were conducted at $20 \pm 0.1^\circ\text{C}$. The detailed description of the experimental procedure can be found elsewhere.¹⁴

THEORY

Assuming that the solute is approaching the limit of infinite dilution in the polymer, the sorption isotherm will always be linear, or

$$C^* = K_v C_v \quad (3)$$

where C^* is the solute concentration in the polymer at equilibrium (mg/L); C_v , the solute concentration in the gas surrounding the polymer sample (mg/

L); and K_v , the vapor-polymer partition coefficient. The partition coefficient is then computed from the results of the electrobalance studies by

$$K_v = \frac{\Delta M^*}{M_0} \cdot \frac{\rho_0}{MW} \cdot \frac{RT}{p} 7.6 \times 10^8 \quad (4)$$

where ΔM^* is the gain in weight of the polymer sample at equilibrium (mg); ρ_0 , the density of the polymer at time zero (g/cm³); M_0 , the initial weight of polymer sample (mg); MW, the molecular weight of the solute (g/mol); R , the ideal gas constant ($8.206 \times 10^{-5} \text{ m}^3 \text{ atm/K mol}$); T , the absolute temperature (K); and p , the vapor pressure of the solute (mm Hg).

The pressure of the solute vapor may be expressed in terms of activity a , because the activity of a solute is constant within a multiphase system at equilibrium. If the solute vapor behaves as an ideal gas, the activity of the vapor at any pressure other than saturation vapor pressure p_s becomes

$$a = \frac{p}{p_s} \quad (5)$$

where p_s denotes the saturation vapor pressure of the solute (mmHg).

Equilibrium solubilities can be expressed in terms of the volume fraction of solute (v_1), the mass ratio of solute and PB (q), or the vapor-phase partition coefficient (K_v) for various types of organic chemicals. A relationship can be postulated based on chemical thermodynamics that relates q or K_v to activity over the whole range of activities. It can be assumed that a constant energy of adsorption is maintained regardless of surface coverage (i.e., a homogeneous surface) and there are no sorbed-phase molecular interactions. At equilibrium, the fugacity of the solute in the polymer phase is equal to its fugacity in the vapor phase. At low pressure and at ambient temperatures, it can be assumed that the vapor phase behaves like an ideal gas and thus the fugacity of the solute in the vapor phase is equal to the vapor pressure of the solute. The fugacity in the polymer phase can be expressed as a product of the mole fraction, the activity coefficient, and the sat-

uration vapor pressure of the solute. Therefore, the activity can be expressed as follows:

$$a = \frac{P}{p_s} = x_s^p \cdot \gamma_s^p \quad (6)$$

where x_s^p is the mole fraction of the solute in the polymer and γ_s^p is the activity coefficient of the solute dissolved in the polymer. In eq. (6), x_s^p can be expressed as follows:

$$x_s^p = \frac{m_s}{m_s + m_p} = \frac{M_t}{W_s \cdot \left(\frac{M_t}{W_s} + \frac{M_s}{W_p} \right)} \quad (7)$$

where m_s is the number of moles of solute in the polymer phase and m_p is the number of moles of the polymer; W_s , the molecular weight of solute; W_p , the molecular weight of the polymer; M_t , the total amount of solute that entered the polymer; and M_s , the initial weight of the polymer.

Defining q_e as the amount of solute sorbed (weight increase of the sample) per unit weight of the polymer (initial sample weight during a sorption test), i.e., M_t/M_s , and substituting in eq. (8) yields

$$x_s^p = \frac{1}{1 + \left(\frac{W_s}{W_p} \right) \cdot \frac{1}{q_e}} \quad (8)$$

Substituting eq. (8) in eq. (6) and rearranging gives

$$q_e = \frac{a}{\beta'(\gamma_s^p - a)} = \frac{a}{\beta a + \gamma} \quad (9)$$

where $\beta' = W_p/W_s$ and is a thermodynamic constant, and β and γ are constants. This equation resembles the Langmuir sorption isotherm equation. In eq. (9), q_e can be expressed in terms of K_v as follows:

$$q_e = \frac{\text{mass of solute in polymer (mg)}}{\text{mass of polymer}} = \frac{K_v \cdot C_s \cdot a}{\rho_0 \times 10^6} \quad (10)$$

where C_s is the solute saturation concentration in the vapor phase (mg/L) and ρ_0 is in g/cm³. Physically, this represents initial sorption in some kind of specific site or immobilization of penetrant molecules in microvoids in polymers. Using the relation in eq. (10), eq. (9) can be rearranged in terms of the partition coefficient in the vapor phase, K_v :

$$K_v(a) = \frac{\omega}{\beta \cdot a + \gamma} \quad (11)$$

where

$$\omega = \frac{\rho_0}{p_s} \cdot \frac{RT}{MW} \quad (12)$$

Note that γ in eqs. (9) and (11) must always be greater than βa and that

$$\lim_{a \rightarrow 0} K_v(a) = \frac{\omega}{\gamma} \quad (13)$$

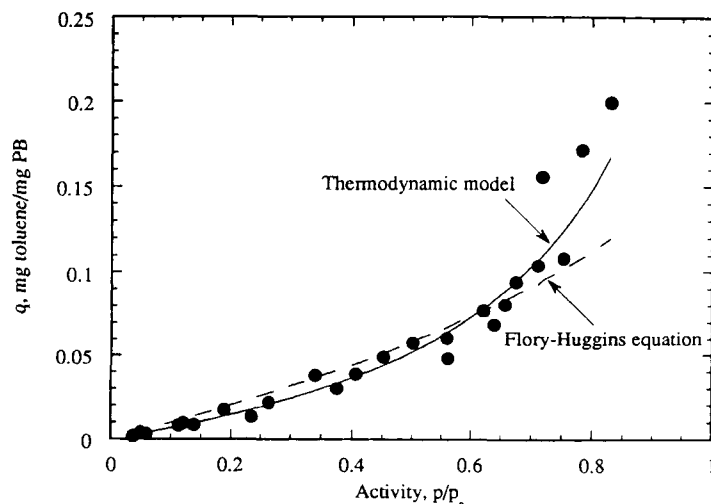


Figure 1 Sorption isotherm curves for toluene in PB along with the curves predicted from the thermodynamic model and the Flory-Huggins equation.

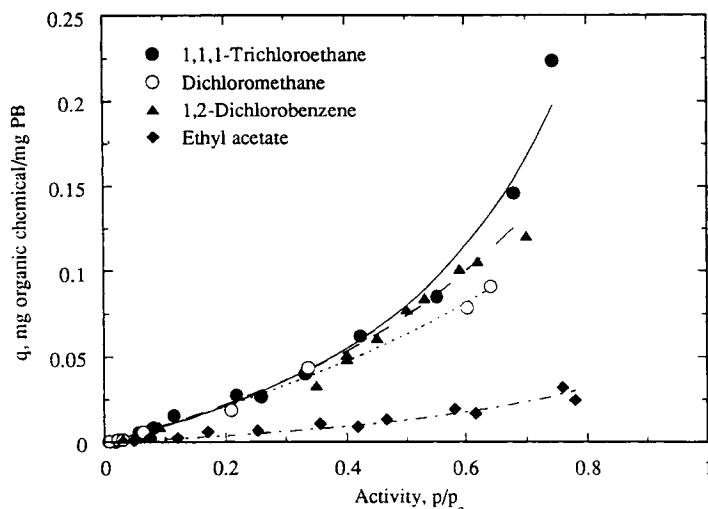


Figure 2 Sorption isotherm curves for selected organic chemicals in PB along with the curves predicted from the thermodynamic model.

RESULTS AND DISCUSSION

The sorption data for toluene in PB are shown in Figure 1 as a plot of q_e vs. toluene activity. Figure 1 also includes the isotherm curves obtained from the Flory-Huggins relationship [eqs. (1) and (2)] and the thermodynamic relationship derived herein [eq. (9)]. At different χ values, ν_1 values for each activity were estimated using a Newton-Rapson iteration method and the absolute values of the differences between measured and calculated ν_1 values were summed. The χ value, having the smallest sum, was

considered to be the best value. In the case of toluene, the χ value was found to be 1.36. PB did not swell significantly by toluene up to activities of 0.7 but suddenly and markedly did at activities >0.7 . Because of this, the Flory-Huggins equation was not able to predict equilibrium solubilities especially at higher activities. To improve the prediction at higher activities, an empirical exponential increase of χ values as a function of activity was determined. The relationship $\chi = 1.98e^{0.56a}$ gave a fit almost identical to that obtained from the thermodynamic model. However, parameter estimation of the Flory-Hug-

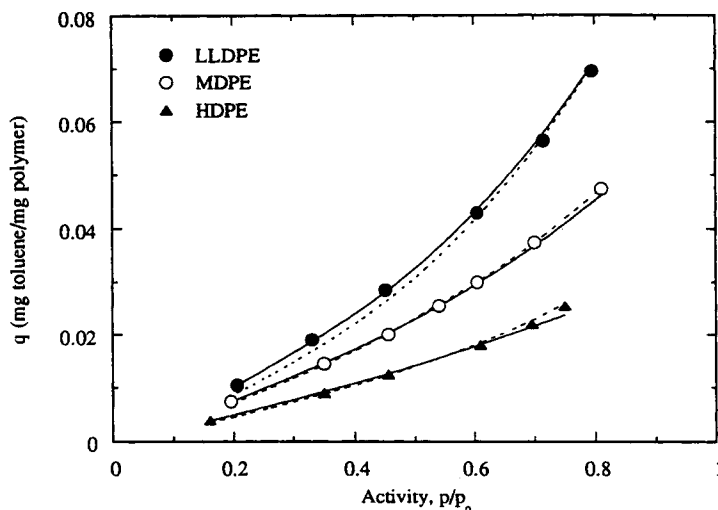


Figure 3 Sorption isotherm curves in toluene for HDPE, MDPE, and LLDPE at draw ratio of 1.0. The solid lines are predicted from the thermodynamic model and the dotted lines from the Flory-Huggins equation.

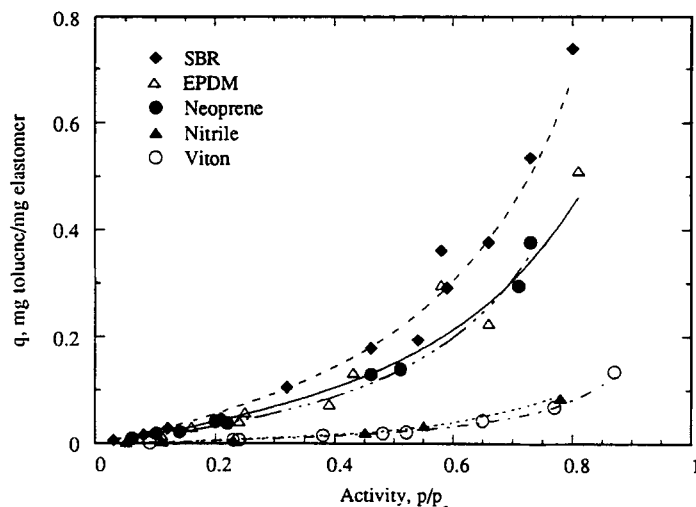


Figure 4 Sorption isotherm curves for SBR, EPDM, neoprene, nitrile, and Viton in toluene along with the curves predicted from the thermodynamic model.

gins equation is complex and there is no theoretical basis for the exponential variation of χ . Castro et al.²³ also found that the value of χ varied with activity in PE for temperatures lower than 27°C. It is clear that the thermodynamic model predicted equilibrium solubilities more accurately than did the Flory–Huggins equation over a wide range of activities.

Isotherm curves for trichloroethane, dichloromethane, ethyl acetate, and 1,2-dichlorobenzene in

PB are shown in Figure 2 together with the curves predicted from the thermodynamic model [eq. (9)]. Ethyl acetate gave the smallest increase in q_e with increase in activity. With decrease in polarity and increase in the number of chlorine atom, q_e increased drastically, especially for activities >0.6. For all the organic chemicals tested, the equilibrium sorptions were well described by a thermodynamic curve of appropriate β and γ values. These results demonstrated that complete sorption isotherms for poly-

Table II Parameters ω , β , and γ in eq. (9) Obtained from Electrobalance Data for the Prediction of K_s between PB and LDPE and Organic Chemicals at 20°C

Organic Chemical	ω	β	γ
2-Butanone (MEK)	2,704.7	-23.71	30.74
<i>o</i> -Chlorophenol (<i>o</i> -CP)	63,356.2	-334.42	393.18
1,2-Dichlorobenzene (1,2-DCB)	115,625.0	-7.32	10.39
1,3-Dichlorobenzene (1,3-DCB)	54,411.8	-11.30	11.82
Dichloromethane (DCM)	127.8	-5.21	10.50
1,2-Dichloropropane (1,2-DCP)	3,585.3	-12.80	16.82
Ethyl acetate (EA)	2,643.7	-44.22	60.27
Ethylbenzene (EB)	21,412.0	-9.00	14.70
<i>n</i> -Hexane	1,549.4	-15.32	20.70
Methanol	5,572.3	-46.84	116.38
<i>n</i> -Nonane	33,035.7	-9.55	13.00
Tetrachloroethylene (PCE)	6,801.5	-5.60	6.96
Toluene	8,186.8	-12.68	15.70
Toluene (LDPE)	8,141.6	-18.87	28.88
1,1,1-Trichloroethane (TCA)	1,267.1	-15.89	23.45
Trichloroethylene (TCE)	2,146.2	-6.20	7.71
<i>m</i> -Xylene	25,000.0	-11.97	17.50
<i>o</i> -Xylene	31,896.6	-11.78	15.83
<i>p</i> -Xylene	23,125.0	-8.22	12.71

Table III Regression Parameters Used for the Prediction of q_e Values of Various Organic Chemicals at 20°C in SBR

Organic Chemical	ω	β	γ
2-Butanone (MEK)	3,304.1	-10.50	10.51
1,2-Dichlorobenzene (1,2-DCB)	141,250.0	-2.62	2.68
n-Hexane	1,892.8	-7.88	9.84
Tetrachloroethylene (PCE)	8,308.8	-2.35	2.56
Toluene	10,000.0	-4.01	4.38
1,1,1-Trichloroethane (TCA)	1,547.9	-4.60	4.67
o-Xylene	39,965.5	-2.15	3.24

mers and elastomers could be predicted with sufficient accuracy from a few equilibrium sorption values.

The thermodynamic model developed worked best when the energies of sorption were high or when the absorbed molecules were quite large. At low temperature or high concentrations, this model may underestimate the amount of the penetrant sorbed. This error may be caused by surface heterogeneities, nonlocalized sites, or the formation multilayers rather than monolayers.

Figure 3 shows the isotherm curves for toluene in HDPE, medium density PE (MDPE), and linear LDPE (LLDPE) at a draw ratio of 1.0 obtained by Ng et al.²⁴ Also included are the curves predicted from the thermodynamic model and the Flory-Huggins equation. Both the thermodynamic model and the Flory-Huggins equation equally predicted q_e well. However, it appears that when a polymer swells

by absorption of an organic chemical the thermodynamic model tends to give a better prediction than does the Flory-Huggins equation.

A wide range of organic chemicals was studied on SBR gasket materials. On the other gasket materials, two organic chemicals (toluene and 2-butanone) were studied. These were selected because (1) extensive data were available for polymer pipe material on toluene and (2) toluene and 2-butanone represented the organic chemicals found in two of the major contaminants involved in pipe permeation incidents—gasoline and paint thinner, respectively.

Isotherm curves for toluene in SBR, neoprene, EPDM, nitrile, and Viton are shown in Figure 4 together with the curves predicted from the thermodynamic model. It can be seen that toluene permeated least in Viton, followed by nitrile, SBR, neoprene, and EPDM. In the case of 2-butanone, nitrile performed best, followed by SBR, neoprene, Viton, and EPDM. When both polar and nonpolar organic compounds are used, nitrile appears to be the best material. When nonpolar organic compounds are used, Viton should be selected although nitrile performs almost equally. It should be noted, however, that Viton does not provide a good seal unless the joints are mechanically fixed.

Parameters β , γ , and ω in eqs. (9) and (11) for PB and elastomers are summarized in Tables II and III, respectively. Those for toluene in LDPE are also included in Table II.

A structure-activity relationship was applied to predict q_e from known chemical properties. It was found that q_e had a logarithmic relationship with

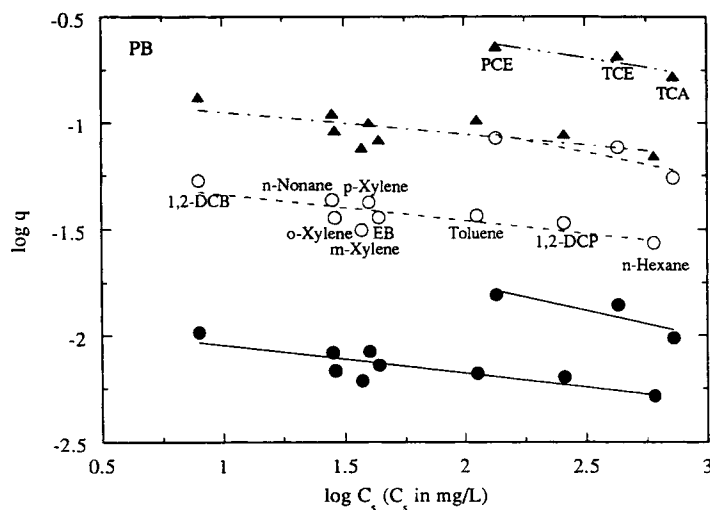


Figure 5 Structure-activity relationships for nonpolar compounds in PB at activities of 0.1, 0.4, and 0.7.

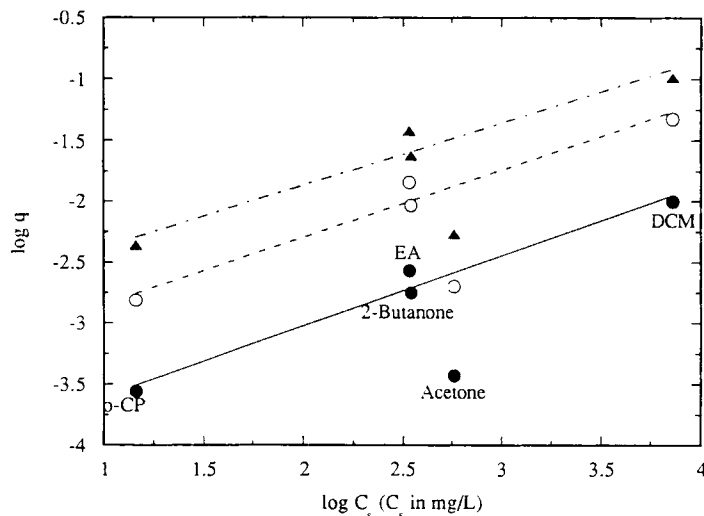


Figure 6 Structure-activity relationships for polar compounds in PB at activities of 0.1, 0.4, and 0.7.

the saturation vapor pressure, C_s . For a better fit, the organic chemicals tested for PB were divided into three groups as follows:

- Group 1: aromatics, chlorinated aromatics, and alkanes.
- Group 2: chlorinated alkanes and alkenes.
- Group 3: polar compounds.

Figure 5 shows the relationships for Groups 1 and 2 at activities of 0.1, 0.4, and 0.7 for PB. It can be seen that q_e decreased logarithmically with the increase in C_s for these groups. Chlorinated alkanes and alkenes had much higher q_e values than those

of other nonpolar compounds. For polar compounds, the trend was reverse, as seen in Figure 6. Polar compounds appear to be absorbed less than nonpolar compounds in nonpolar thermoplastics such as PB and PE. The regression equations for the three groups are summarized in Table IV.

Figure 7 shows the relationship between q_e and C_s for organic chemicals in SBR. Unlike PB, 2-butanone, a polar compound, was right on the regression line for nonpolar compounds. Again, chlorinated alkanes and alkenes had higher q_e than those of other compounds. The regression equations are summarized in Table V. SBR had approximately 14–28 times greater q_e values or three to six times greater K_p values than that of PB.

Table IV Regression Equations Relating q_e to the Saturation Vapor Concentration (C_s) of Various Groups of Organic Chemicals for PB

Group	Equation	r
Activity 0.1		
Aromatics and chlorinated aromatics	$\log q_e = -0.131 \log C_s - 1.916$.836
Chlorinated alkanes and alkenes	$\log q_e = -0.253 \log C_s - 1.249$.877
Polar compounds	$\log q_e = 0.587 \log C_s - 4.230$.988
Activity 0.4		
Aromatics and chlorinated aromatics	$\log q_e = -0.122 \log C_s - 1.215$.806
Chlorinated alkanes and alkenes	$\log q_e = -0.228 \log C_s - 0.570$.876
Polar compounds	$\log q_e = 0.566 \log C_s - 3.473$.985
Activity 0.7		
Aromatics and chlorinated aromatics	$\log q_e = -0.104 \log C_s - 0.844$.692
Chlorinated alkanes and alkenes	$\log q_e = -0.253 \log C_s - 0.176$.914
Polar compounds	$\log q_e = 0.528 \log C_s - 2.993$.979

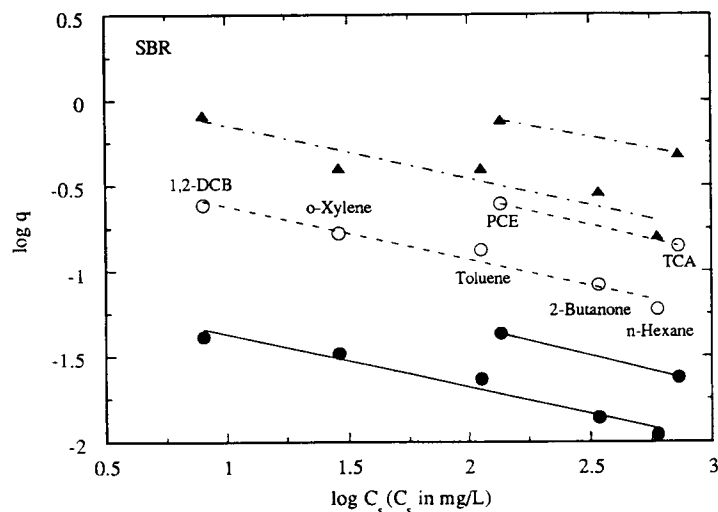


Figure 7 Structure-activity relationships for organic compounds in SBR at activities of 0.1, 0.4, and 0.7.

It is possible to predict q_e values at the three activities using the relationships shown in Tables IV and V. These values can then be used to determine the parameters α , β , and γ of the thermodynamic equation [eq. (11)] derived herein. This will allow the prediction of q_e values at any activity for various organic chemicals.

CONCLUSIONS

A gravimetric method was used to determine the partition coefficient and the amount of solute sorbed to the sorbent, q_e , at various activities for a wide range of organic chemicals in polymers and elastomers. The partition coefficients of various organic

chemicals in PB, PE, and elastomers increased with activity (or concentration). This variation was successfully fitted with the thermodynamic model.

For both polar and nonpolar organic compounds, nitrile appeared to be the most resistant elastomer to permeation, although Viton performed slightly better for nonpolar organic compounds.

It was found that q_e had a logarithmic relationship with the saturation vapor pressure. For nonpolar compounds, q_e decreased logarithmically with the increase in C_s . For polar compounds, the reverse trend was found. PB absorbed polar compounds less than did nonpolar compounds because PB is a nonpolar thermoplastic. Chlorinated alkanes and alkenes tended to have significantly higher q_e values than those of other nonpolar compounds.

Table V Regression Equations Relating q_e to the Saturation Vapor Concentration (C_s) of Various Groups of Organic Chemicals for SBR

Group	Equation	r
Activity 0.1		
Aromatics and chlorinated aromatics	$\log q_e = -1.058 \log C_s - 0.311$.983
Chlorinated alkanes and alkenes	$\log q_e = -0.355 \log C_s - 0.609$	—
Activity 0.4		
Aromatics and chlorinated aromatics	$\log q_e = -0.228 \log C_s - 0.310$.982
Chlorinated alkanes and alkenes	$\log q_e = -0.333 \log C_s + 0.105$	—
Activity 0.7		
Aromatics and chlorinated aromatics	$\log q_e = -0.253 \log C_s - 0.167$.934
Chlorinated alkanes and alkenes	$\log q_e = -0.275 \log C_s + 0.473$	—

REFERENCES

1. A. R. Berens, *J. Am. Water Works Assoc.*, **77**(11), 57-64 (1985).
2. M. W. Vonk, *Permeation of Organic Compounds through Pipe Materials*, Publication No. 85, KIWA, Neuwegein, The Netherlands, 1985.
3. J. K. Park, T. M. Holsen, L. Bontoux, D. Jenkins, and R. E. Selleck, *Permeation of Plastic Pipes by Organic Chemicals*, Sanitary Engineering and Environmental Health Research Laboratory, University of California, Berkeley, 1989.
4. T. M. Holsen, J. K. Park, D. Jenkins, and R. E. Selleck, *J. Am. Water Works Assoc.*, **83**(8), 53-56 (1991).
5. Environmental Protection Agency, *Lining of Waste Containment and Other Impoundment Facilities*, EPA/600/2-88/052, U.S. EPA Risk Reduction Laboratory, Office of Research and Development, Cincinnati, OH, 1988.
6. Environmental Protection Agency, in *Proposed Sampling and Analytical Methodologies for Addition to Test Methods for Evaluating Solid Wastes: Physical/Chemical Methods*, 3rd ed., SW-846, U.S. EPA, Washington, DC, 1984.
7. R. M. Koerner, *Designing with Geosynthetic*, 2nd ed., Prentice-Hall, Englewood Cliffs, NJ, 1990.
8. C. E. Rogers, in *Engineering Design for Plastics*, E. Baer, Ed., Reinhold, New York, 1964.
9. E. Sacher and J. R. Susko, *J. Appl. Polym. Sci.*, **30**, 1393-1398 (1985).
10. M. A. Parker and D. Vesely, *J. Polym. Sci. Part B Polym. Phys.*, **24**, 1869-1878 (1986).
11. K. A. Peppas and K. G. Urdahl, *Polym. Bull.*, **26**, 201-207 (1986).
12. C. Mensitieri, M. A. Del Nobile, A. Apicella, and L. Nicolais, *Polym. Eng. Sci.*, **29**(24), 1786-1975 (1989).
13. E. F. Castro, E. E. Gonzo, and J. C. Gottifredi, *J. Membr. Sci.*, **31**, 235-248 (1987).
14. J. K. Park and L. Bontoux, *J. Appl. Polym. Sci.*, **42**, 2989-2995 (1991).
15. H. August, R. Tatzky, G. Pastuska, and T. Win, *Study of the Permeation Behavior of Commercial Plastic Sealing Sheets as a Bottom Liner for Dumps against Leachate, Organic Solvents, and Their Aqueous Solutions*, Environmental Research Plan of the Federal Minister of the Interior, Germany, Research Report No. 103-02-208, 1984.
16. H. E. Haxo, J. A. Miedema, and N. A. Nelson, in *Proceedings of the Education Symposium on Migration of Gas, Liquid, and Solids in Elastomers*, Denver, CO, sponsored by Rubber Division, American Chemical Society, October 23-26, 1984.
17. J. Koszinowski, *J. Appl. Polym. Sci.*, **32**, 4765-4786 (1986).
18. L. N. Britton, R. B. Ashman, T. M. Aminabhavi, and P. E. Cassidy, *J. Appl. Polym. Sci.*, **38**, 227-236 (1989).
19. G. W. Reynolds, J. T. Hoff, and R. W. Gillham, *Environ. Sci. Technol.*, **24**, 135-142 (1990).
20. P. J. Flory, *Principles of Polymer Chemistry*, 8th ed., Cornell University Press, Ithaca, NY, 1953.
21. I. D. Rubin, *Poly(1-Butene)—Its Preparation and Properties*, Gordon and Breach, New York, 1968.
22. S. A. Mruk, in *Plumbing Materials and Drinking Water Quality*, T. J. Sorg and F. A. Bell, Jr., Eds., Park Ridge, NJ, 1986, pp. 10-26.
23. E. F. Castro, E. E. Gonzo, and J. C. Gottifredi, *J. Membr. Sci.*, **31**, 235-248 (1987).
24. H. C. Ng, W. P. Leung, and C. L. Choy, *J. Polym. Sci. Polym. Phys. Ed.*, **23**, 973-989 (1985).

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