

Novel Correlation for Solubility of Gases in Polymers: Effect of Molecular Surface Area of Gases

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ABSTRACT: Novel correlations are proposed for the solubility coefficients of gases (S) as well as the parameters of the dual mode sorption isotherms k_D and b in polymers. They are based on the concept of molecular surface areas of dissolved species. Van der Waals surface areas (WSA) as estimated using UNIFAC group contributions and solvent accessible surface areas (SASA) were considered as possible parameters for correlations. Excellent dependencies with correlation coefficients R in the range 0.95–0.99 were obtained for the correlations of $\ln S$, $\ln k_D$, and $\ln b$ with surface area. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 76: 552–560, 2000

INTRODUCTION

Solubility of gases in polymers have been of continuous experimental and theoretical interest because gas and vapor separation membranes are based on the so-called solution–diffusion mechanism, according to which thermodynamic parameters of gas sorption determine the mass transfer driving force. Reliable solubility data have been reported for many gas–polymer systems and they can be used in various practical applications as well as for validating the results of theoretical studies.¹ There is currently a need for better correlations that will enable estimation of solubility coefficients for various gases on the basis of limited reported data. Better understanding of the sorption mechanism is required as well.

Three types of correlations have been used extensively for the solubility coefficient, S , of gases in polymers,^{2–6} namely:

$$\log S = \alpha_1 + \beta_1 T_c \quad (1)$$

$$\log S = \alpha_2 + \beta_2 T_b \quad (2)$$

$$\log S = \alpha_3 + \beta_3 (\varepsilon/k) \quad (3)$$

where T_c , T_b , and ε/k are critical temperature, boiling point, and Lennard–Jones energy parameter, respectively. Here S will be defined as the infinite dilution solubility coefficient or the initial slope of the sorption isotherms. As the parameters used in Eq. (1)–(3) are interrelated,⁷

$$T_b = 0.67 T_c \quad (4)$$

$$\varepsilon/k = 0.77 T_b \quad (5)$$

all of these correlations should be considered as a manifestation of the same behavior.

These types of correlations have proven useful for modelling the behavior of a large number of gas–polymer systems, including systems with both rubbers and glassy polymers as “solvents” and permanent gases and vapors as “solutes.” Correlated S values have been based on direct solubility measurements (using, for example, gravimetric or manometric methods) or on indirect estimation of S (determined via the ratio of

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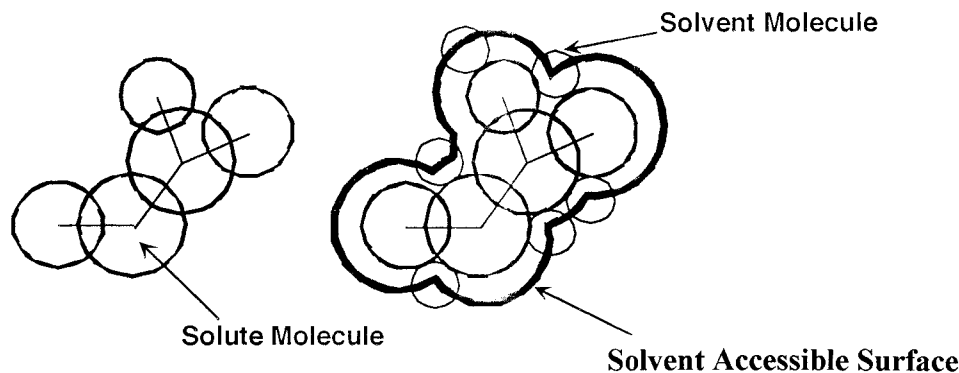


Figure 1 WSA (left) and ASURF (right) surface area models.

gas permeability and diffusion coefficients P/D). An improved ε/k scale which minimized the errors in prediction of S was also proposed⁸ based mainly on the latter method of the determination of the solubility coefficient.

Although practically applicable, eqs. (1)–(3) are not based on a rigorous theoretical treatment. Petropoulos showed⁹ that, for nonpolar or weakly polar systems, where van der Waals forces are responsible for gas-polymer intermolecular interactions, Flory–Huggins regular solution theory produces the following approximate equation:

$$\ln S = \ln k'_0 + \Delta H_v/RT \quad (6)$$

where ΔH_v is the molar enthalpy of vaporization. If it can be assumed that

$$\Delta H_v/R = \alpha T_b = \beta T_c = \gamma(\varepsilon/k) \quad (7)$$

then eqs. (1)–(3) should be obeyed at constant temperature. However, an analysis¹⁰ of vapor-liquid phase equilibrium data¹¹ indicates that the relationships between ΔH_v and critical temperatures or boiling point for numerous solutes can be nonlinear, so the latter assumption is rather suspect.

If van der Waals forces dominate in gas-polymer interactions during dissolution then equilibrium constants such as solubility coefficients should be proportional to appropriately defined surface areas of solute molecules. This approach for correlation of solubility coefficients in polymers, as well as the parameters of sorption isotherms, is examined in the present paper.

BACKGROUND

Langmuir¹² was the first to suggest that the superficial surface of a solute should be directly

proportional to the ability of the solute molecule to create a cavity in a solvent, and, hence, dissolve into it. However, the problem still remains of how to estimate the surface area around the dissolved molecule across which van der Waals interactions take place between the solute molecule and polymer matrix.

The calculation of molecular surface areas for a particular gas molecule has been attempted using several methods. The physical representation of the surface area is usually based on van der Waals radii given by Bondi.¹³ However, the approaches used,^{14–19} generally differ in the precise definition of the outside surface area of the molecules. Two-dimensional diagrams of some of the surface area representations are illustrated in Figure 1.

The van der Waals surface area is the external surface area of a molecule resulting from the substitution of each atom, or set of atoms, by spheres of known radii spaced at standard bond lengths. The intersection of such spheres is excluded. The surface areas of the molecules can be computed using the group contributions originally tabulated by Bondi.¹³ A development of these group contributions, called the UNIFAC method, by Abrams and Prausnitz²⁰ resulted in a correction factor being proposed for the calculation of activity coefficients in non-ideal liquids. Thus, the UNIFAC method allows the calculation of the van der Waals surface areas for a large number of organic molecules in addition to molecules of simple gases.

It is obvious that some parts of the solute molecules are inaccessible to surrounding solvent molecules or polymer chains in the process of gas dissolution in polymers. Therefore attempts have been made to define surface areas in other ways that account for the inaccessible area. It is easier to do this in relation to water solutions because the water molecule is small and has well-known dimensions.

With the development of computers in the last two decades, methods for calculating molecular surface areas have significantly improved. For instance, a program called GEPOL¹⁷⁻¹⁹ was developed by Silla et al. Surface areas calculated in this way resulted in correlations with thermodynamic parameters of gas dissolution in water.²¹ However, it is questionable whether Solvent accessible surface areas (SASA) computed for water-gas solutions will be representative of the van der Waals interactions of gases in polymers.

It is the aim of this work to examine possible correlations of the gas solubility coefficients and the parameters of the dual-mode sorption isotherm in polymers with molecular surface areas of gases defined in different ways.

RESULTS AND DISCUSSION

Two types of molecular surface areas were considered: van der Waals molecular surface area (WSA) and Solvent accessible surface area (SASA). Van der Waals surface areas were estimated using the UNIFAC method. The WSA and SASA parameters used for various gas molecules are given in Table I. The WSA parameters are based on the group contribution values reported by Gmehling et al.²² and Sander et al.²³ The SASA parameters are those reported by Scharlin et al.²¹

Numerous data for the solubility coefficients of gases in polymers can be found in the literature. They have been measured by direct methods including gravimetry and pressure decay. In these cases, the infinite dilution solubility coefficients S or C/p ratio, where C is the concentration of a solute when the pressure p is approaching zero, are expressed in $\text{cm}^3(\text{STP})$ per cm^3 of polymer. Often the solubility coefficients are estimated in an indirect manner as the ratio of P/D , where P is the gas permeability coefficient, and D is the diffusion coefficient. The latter values are considered to be less reliable and will be ignored in this work. Mainly amorphous glassy polymers will be considered. However, one rubber was also included for comparison.

For glassy polymers, either solubility coefficients S or the parameters of the dual-mode sorption (DMS) model are usually reported. In this model, the concentration of a solute C is represented by the equation

$$C = k_D p + C'_H b p / (1 + b p) \quad (8)$$

Table I Surface Area Parameters of Gases

| Gas | WSA ($\text{Å}^2/\text{molecule}$) | SASA ²¹ ($\text{Å}^2/\text{molecule}$) |
|--|---|--|
| He | 24.6 | 98.5 |
| Ne | 29.8 | 108.6 |
| Ar | 44.4 | 135.2 |
| Kr | 51.3 | 147 |
| Xe | 58.6 | 159.3 |
| H ₂ | 23.7 | 97.0 |
| O ₂ | 39.6 | 127.7 |
| N ₂ | 40.9 | 133.6 |
| CO | 44.0 | 135.1 |
| CO ₂ | 52.4 | 150.6 |
| CH ₄ | 48.0 | 143.8 |
| C ₂ H ₂ | 57.8 | 156.5 |
| C ₂ H ₄ | 61.6 | 168.1 |
| C ₂ H ₆ | 70.4 | 182.1 |
| C ₃ H ₆ | 84.0 | 202.7 |
| C ₃ H ₈ | 92.8 | 213.2 |
| <i>n</i> -C ₄ H ₁₀ | 115.2 | 244.4 |
| <i>i</i> -C ₄ H ₁₀ | 101.6 ^a | 238.2 |
| N ₂ O | 53.1 ^a | 152.9 |
| H ₂ S | | 143.6 |
| Cl ₂ | | 163.8 |
| SO ₂ | | 163.3 |
| NH ₃ | | 131.5 |
| CF ₄ | | |
| C ₂ F ₆ | 114.6 | 231.1 |
| Cyclo- C ₃ H ₆ | 67.3 | 177.4 |
| Neo- C ₅ H ₁₂ | 140.8 | 258.7 |

^a According to Scharlin et al.²¹

where k_D is the Henry's law solubility coefficient, b is the Langmuir affinity constant, and C'_H is the Langmuir capacity parameter. The parameters k_D and b are equilibrium constants as well as solubility coefficients because, at the low pressure limit, the solubility coefficient can be approximated by the formula

$$S = k_D + C'_H b \quad (9)$$

So the correlation of the values k_D and b with surface area were tested where the DMS model parameters were available.

The most abundant data were available for a group of light gases: Ar, O₂, N₂, CO₂, CH₄. For several polymers, the data was available for inert gases (He, Ne, Ar, Kr, Xe) and for gaseous hydrocarbons C₁-C₃. There were also several polymers for which the S values have been reported for much larger sets of solutes including light gases,

Table II Polymers Considered in Correlations of Solubility of Gases in Polymers

| Polymer | Abbreviation | Method (T, K) | Reference |
|--|--------------|---------------------|-----------|
| Polystyrene | PS | Volumetric, 298 | 24 |
| Poly(vinyltrimethyl silane) | PVTMS | — ^a | 25 |
| Natural rubber | NR | — | 2, 26–32 |
| Perfluorodioxole copolymer | AF2400 | Pressure decay, 308 | 33 |
| Polynorbornene | PNB | Gravimetric, 298 | 34 |
| Poly(trimethylsilyl norbornene) | PTMSNB | Idem | 34 |
| Poly(disilyl norbornene) | PDSNB | Idem | 34 |
| Poly(fluoromethyl norbornene) | PFMNB | Idem | 34 |
| Poly(oxyfluoropropyl norbornene) | POFPNB | Idem | 34 |
| Poly(trimethylsilyl propyne) | PTMSP | Idem | 34 |
| Poly(difluoro- <i>tert</i> -butyl acetylene) | PDFBA | Idem | 27 |
| Poly(ethylene terephthalate) | PET | Manometric, 298 | 35 |
| Poly(vinyl chloride) | PVC | Pressure decay, 308 | 36 |
| Poly(phenylene oxide) | PPO | Idem | 37 |
| Polysulfone | PSF | Idem | 38 |
| Poly(ether sulfone) | PES | Idem | 39 |
| Ethyl cellulose | EC | Volumetric, 298 | 40 |
| Nitrocellulose | NC | Idem | 40 |
| 6FDA-TADPO (polyimide) | 6FDA | Pressure decay, 308 | 41 |
| Polypyrrolone | PPR | Idem | 41 |

^a —, Different methods were used.

acidic gases and hydrocarbons of greater molecular mass. These systems were considered separately.

Different groups of researchers reported S values at either 298 K or 308 K. As the enthalpies of sorption of gases in polymers are not large (ca. 2–8 kcal/mol),¹ such variation of T should not have exerted a strong effect on the S values in comparison with other (systematic or random) errors in S . So this variation of temperature was ignored, and the data were compared independently of the actual temperature of measurement. The list of systems examined is given in Table II.

Figure 2 gives examples of the correlation of S with surface area for light gases in several polymers (PVC, PS, PNB, PTMSNB). The data were treated using the equation:

$$\ln S = a_0 + a_1[SA] \quad (10)$$

where [SA] is either WSA or SASA. The regression coefficients, a_0 , and a_1 , and the correlation coefficient, R , for this equation are given in Tables III and IV for various polymers. It is difficult to recommend either the WSA surface area found using UNIFAC or the SASA in preference to the other for the correlation of solubility coefficient. Marginally better results are obtained using WSA. There is no obvious correlation between the

slopes of the lines and chemical structure or physical state of the polymers. Thus, NR, the single rubbery material included for comparison, shows no difference in a_0 and a_1 values compared with other, glassy polymers. However, the perfluorinated material Teflon AF2400, the polyimide 6FDA, and the polypyrrole PPR, all exhibit much weaker dependence of S on both WSA and SASA. The partially fluorinated polymers (PFMNB, POFPNB, PDFtBA) show no peculiarities. In contrast, the chlorinated polymer PVC shows a much stronger dependence of S on both WSA and SASA.

Correlation of the solubility coefficients versus WSA and SASA are shown in Figure 3 for inert gases in PS. Again both parameters give equally good correlations.

It is of interest to compare the correlations of S with the novel parameters (WSA and SASA) and the usual parameters (critical temperature, T_c , as proposed by Reid and Sherwood⁴² and the Lennard–Jones energy parameter, ϵ/k , as proposed by Svehla⁴³). As shown in Table V, all the parameters (except perhaps ϵ/k for hydrocarbons) give approximately equal and accurate correlations.

It has been shown⁴⁴ that the pressure range, over which the sorption isotherms have been measured can influence the parameters found in the

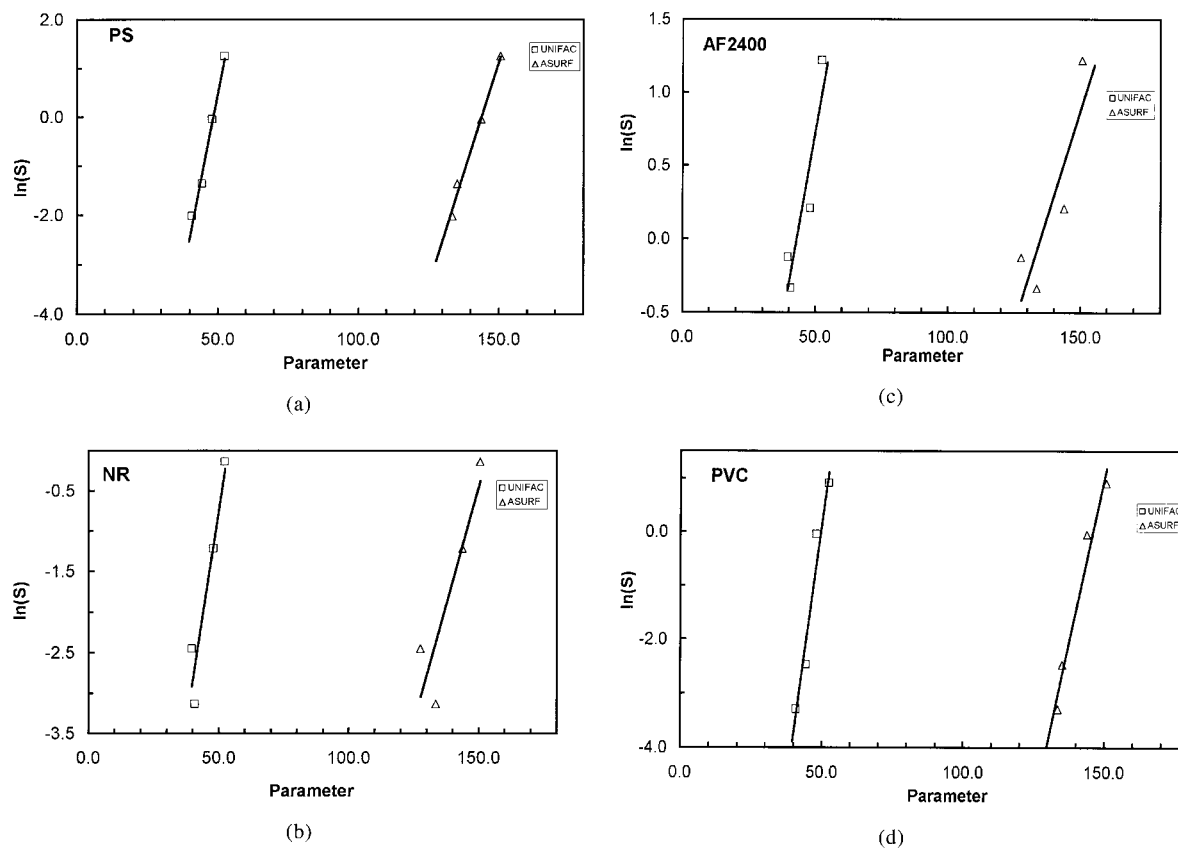


Figure 2 Correlations of $\ln S$ with surface area calculated using WSA and ASURF for light gases in various polymers. (a) Polystyrene; (b) natural rubber; (c) amorphous Teflon AF2400; (d) poly(vinyltrimethyl silane).

DMS model. In order to exclude this effect, it is better to compare the DMS parameters for different gas/polymer systems over the same pressure range. The correlation of the dual mode sorption parameters was therefore performed using a series of polymers studied by Bondar³⁴ over the same pressure range using gravimetric method. The experimentally determined k_D and b values were reported for five light gases, namely argon, nitrogen, carbon dioxide, methane and ethane. As for the solubility coefficients, the data was fitted to equations of the type

$$\ln(k_D) = c_0 + c_1[\text{SA}] \quad (11)$$

$$\ln(b) = d_0 + d_1[\text{SA}] \quad (12)$$

where [SA] is the surface area found using either WSA or SASA. The parameters T_c and ε/k were also used for comparison. In Figure 4, examples of the dependencies for PTMSNB and PVTMS are shown. A deviation from the line of best fit for

WSA is obvious in the case of carbon dioxide. Similar deviations were also observed for other polymers.

The Henry's law solubility coefficient k_D represents the simple dissolution process in denser regions within a polymer matrix analogous to that in rubbers and low molecular weight solvents. In this case, it might be anticipated that the surface area would be an ideal parameter for the correlation of k_D . However, if carbon dioxide is included in the data set, the correlation coefficients based on the fitting of the data with SA are significantly lower than when the data is fitted with T_c or ε/k . The SA correlations are improved significantly by the removal of the CO_2 data point from the data set (Table VI). The same is true for the correlations with Langmuir affinity parameter b . Interestingly, as can be seen from Table VI, correlations of k_D and b with T_c and ε/k are also usually improved, although to a much lesser extent. It can be speculated that CO_2 is interacting with the polymer

Table III Regression coefficients of Eq. (10) for Sorption of Light Gases Involving WSA, Calculated by UNIFAC Method and Correlation Coefficients

| Polymer | a_0 | a_1 | R |
|---------|-------|-------|------|
| NR | -11.3 | 0.211 | 0.96 |
| PVTMS | -12.0 | 0.162 | 0.94 |
| PTMSP | -10.5 | 0.252 | 0.97 |
| PDFBA | -10.3 | 0.228 | 0.99 |
| PNB | -14.2 | 0.270 | 0.92 |
| PTMSNB | -11.4 | 0.233 | 0.99 |
| PDSNB | -13.0 | 0.246 | 1.00 |
| POFPNB | -11.4 | 0.234 | 0.95 |
| PFMNB | -10.2 | 0.230 | 0.95 |
| AF2400 | -4.53 | 0.106 | 0.92 |
| PET | -13.6 | 0.267 | 0.90 |
| PVC | -19.5 | 0.393 | 0.97 |
| PS | -14.2 | 0.294 | 0.99 |
| PSF | -13.7 | 0.290 | 0.96 |
| PPO | -11.8 | 0.264 | 1.00 |
| PES | -13.3 | 0.292 | 0.97 |
| 6FDA | -6.61 | 0.142 | 0.90 |
| PPR | -5.1 | 0.122 | 0.94 |
| EC | -9.38 | 0.184 | 0.95 |
| NC | -10.4 | 0.191 | 0.92 |

systems to a greater extent than is anticipated from WSA found via the UNIFAC method or SASA parameters.

Table IV Regression Coefficients of Eq. (10) for Sorption of Light Gases Involving SASA Parameters and Correlation Coefficients

| Polymer | a_0 | a_1 | R |
|---------|-------|--------|------|
| NR | -17.9 | 0.117 | 0.90 |
| PVTMS | -17.0 | 0.0891 | 0.88 |
| PTMSP | -21.1 | 0.158 | 0.98 |
| PDFBA | -19.6 | 0.141 | 0.99 |
| PNB | -25.0 | 0.165 | 0.97 |
| PTMSNB | -20.8 | 0.144 | 0.99 |
| PDSNB | -22.4 | 0.148 | 0.97 |
| POFPNB | -20.9 | 0.144 | 0.94 |
| PFMNB | -19.7 | 0.143 | 0.96 |
| AF2400 | -7.91 | 0.0587 | 0.87 |
| PET | -22.4 | 0.151 | 0.87 |
| PVC | -35.8 | 0.246 | 0.98 |
| PS | -26.2 | 0.182 | 0.99 |
| PSF | -25.7 | 0.181 | 0.97 |
| PPO | -22.6 | 0.163 | 0.99 |
| PES | -25.5 | 0.183 | 0.98 |
| 6FDA | -11.0 | 0.0774 | 0.84 |
| PPR | -8.9 | 0.0675 | 0.88 |
| EC | -15.8 | 0.106 | 0.94 |
| NC | -16.3 | 0.105 | 0.87 |

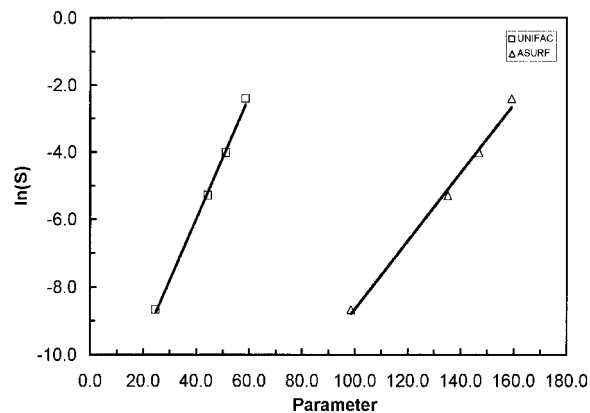


Figure 3 Correlation of $\ln S$ with surface area calculated using WSA and ASURF for inert gases in polysulfone.

The exclusion of the CO_2 data point exerts the strongest effect for polymers containing C–F bonds in addition to C–H bonds, that is, for partly fluorinated norbornene polymers. Such anomalies in the CO_2 sorption isotherms for these polymers have been noted previously.⁴⁵ Some anomalies can also be noted in the absolute values of k_D . In PFMNB and POFPNB k_D values are larger for carbon dioxide than for ethane, a tendency opposite to what is observed in common hydrogen-containing polymers. Hence, some other interactions between carbon dioxide molecules and C–F and C–H bonds in addition to pure van der Waals interactions appears to be occurring in these polymers.

The regression coefficients for eq. (11) and (12) are shown in Tables VII and VIII for a number of polymers with the CO_2 data points omitted. It is seen that excellent correlations are observed both with WSA and SASA. It is noteworthy that both partly fluorinated polymers show weaker dependencies of dual mode sorption parameters on surface area than other polymers examined. This fact can be related to weaker interchain interactions in fluorinated materials, where the work of chain displacement is smaller than those in common organic solvents or polymers.⁴⁶

Sorption in several polymers has been studied for larger sets of gases. It was of interest to test new correlations for solubility coefficients in such cases without artificial grouping of gases. Figure 5 shows such correlations for glassy PVTMS. It is seen that reasonably good correlations are obtained over a wide range of variation of molecular surface area.

Table V Summary of Modeling Results for Various Parameters

| Gas Series | WSA | SASA | T_c | ε/k |
|--------------------|-------------------|-------------------|-------------------|-------------------|
| Noble gases | 0.993 ± 0.005 | 0.991 ± 0.007 | 0.995 ± 0.005 | 0.983 ± 0.003 |
| Light gases | 0.961 ± 0.065 | 0.944 ± 0.108 | 0.981 ± 0.073 | 0.980 ± 0.036 |
| Light hydrocarbons | 0.988 ± 0.003 | 0.987 ± 0.002 | 0.940 ± 0.003 | 0.815 ± 0.009 |

CONCLUSIONS

A novel method was investigated for correlation of solubility coefficients (S) and sorption isotherm parameters (k_D , b) of gases in polymers. It uses molecular surface areas as represented by van der Waals surface areas (estimated using UNIFAC method) and SASA parameters (calculated for gas dissolution in water). Although both approaches can be considered as highly approximate (because the whole van der Waals surface area is not accessible to surrounding polymer chains in the first case and because there is only a weak resemblance between dissolution in water and in polymers in the second case) both parameters provided quite satis-

factory correlations of the S , k_D , and b values for various gas/polymer systems. Equally good correlations with S were obtained for glassy polymers and rubbers. This implies that molecular surface area of simple mono- and di-atomic molecules and light hydrocarbons can serve as a measure of energy of the van der Waals interactions between a solute molecule and a polymer matrix. It also indicates that intermolecular interaction per unit of surface area is constant for the dissolution of simple molecules in polymers. Systematic deviations were observed for carbon dioxide and other molecules capable of donor-acceptor interactions, such as SO_2 , H_2S and NH_3 . As these deviations are observed for polymers containing no groups that can interact specif-

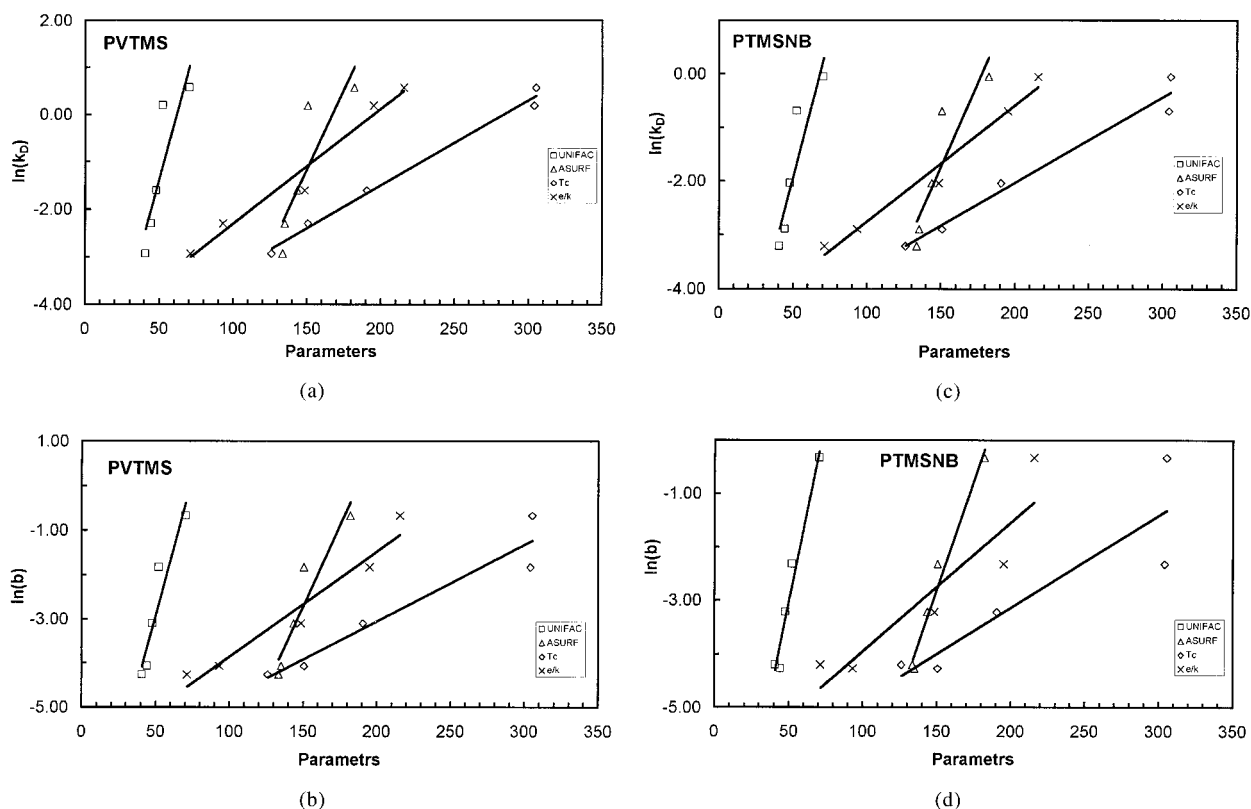


Figure 4 Correlations of k_D and b with T_c , ε/k and surface area calculated using WSA or ASURF for selected polymers. (a, b) Poly(vinyltrimethyl silane); (c, d) poly(trimethylsilyl norbornene).

Table VI Correlation Coefficients R of Different Models for the Data Including CO_2 and Without CO_2

| Polymer | DMS Model Parameter | SA Model | Including CO_2 | | Without CO_2 | |
|---------|---------------------|-----------------|-------------------------|-------|-----------------------|--|
| | | | | | | |
| PTMSNB | k_D | WSA | 0.909 | 0.988 | | |
| | | SASA | 0.904 | 0.987 | | |
| | | T_c | 0.985 | 0.999 | | |
| | b | ε/k | 0.988 | 0.985 | | |
| | | WSA | 0.981 | 0.990 | | |
| | | SASA | 0.986 | 0.997 | | |
| PFMNB | k_D | T_c | 0.897 | 0.988 | | |
| | | ε/k | 0.924 | 0.958 | | |
| | | WSA | 0.741 | 0.992 | | |
| | b | SASA | 0.724 | 0.974 | | |
| | | T_c | 0.977 | 0.982 | | |
| | | ε/k | 0.908 | 0.934 | | |
| | b | WSA | 0.906 | 0.992 | | |
| | | SASA | 0.904 | 0.996 | | |
| | | T_c | 0.985 | 0.995 | | |
| | | ε/k | 0.976 | 0.969 | | |

ically with these solutes, it would appear that these gases start to interact with the polymer matrix at the distances markedly larger than those that can be expected for hard spheres of the size estimated by the UNIFAC and SASA approximations. Bearing in mind these limitations, the correlations with WSA and SASA parameters can be used in the prediction of the thermodynamic properties of gas-polymer systems.

A question can be asked as to which surface area parameters should be preferred for the correlations of solubility: WSA or SASA. We believe that the UNIFAC method has some advantages because it is used in the thermodynamic model-

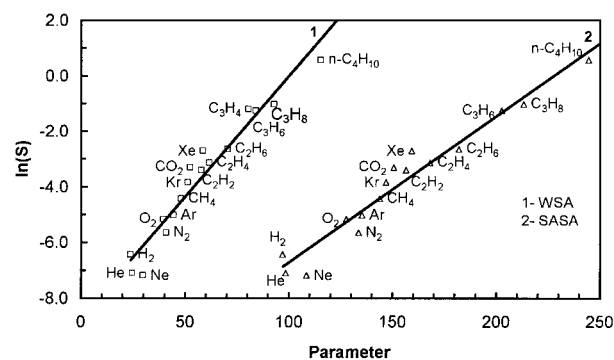
Table VII Regression Coefficients of the Correlations for Henry's Law Solubility Coefficients k_D [$\text{cm}^3(\text{STP})/\text{cm}^3 \text{atm}$] at 298 K

| Polymer | Model | $-c_0$ | c_1 | R |
|---------|-------|--------|-------|-------|
| PVTMS | WSA | 7.35 | 0.11 | 0.989 |
| | SASA | 11.4 | 0.066 | 0.982 |
| PTMSNB | WSA | 7.44 | 0.106 | 0.988 |
| | SASA | 11.2 | 0.062 | 0.987 |
| PTMSP | WSA | 7.96 | 0.128 | 0.997 |
| | SASA | 12.6 | 0.075 | 0.994 |
| PFMNB | WSA | 4.84 | 0.067 | 0.992 |
| | SASA | 7.17 | 0.038 | 0.980 |
| POFPNB | WSA | 5.32 | 0.073 | 0.989 |
| | SASA | 7.86 | 0.042 | 0.974 |

Table VIII Regression Coefficients of the Correlations for Langmuir Affinity Constant b (atm^{-1}) at 298 K

| Polymer | Model | $-d_0$ | d_1 | R |
|---------|-------|--------|-------|-------|
| PVTMS | WSA | 9.29 | 0.123 | 0.991 |
| | SASA | 13.8 | 0.072 | 0.999 |
| PTMSNB | WSA | 10.0 | 0.134 | 0.990 |
| | SASA | 15.0 | 0.081 | 0.997 |
| PTMSP | WSA | 9.09 | 0.118 | 0.986 |
| | SASA | 13.5 | 0.070 | 0.994 |
| PFMNB | WSA | 7.9 | 0.095 | 0.992 |
| | SASA | 11.4 | 0.056 | 0.996 |
| POFPNB | WSA | 8.09 | 0.092 | 0.996 |
| | SASA | 11.4 | 0.054 | 0.999 |

ling of other systems, e.g., vapor/liquid equilibrium, liquid/liquid equilibrium and even in supercritical extractions and in the modelling of mass transfer phenomena. Second, WSA (UNIFAC) parameters are readily available in a number of standard commercial design packages, such as ASPEN, which also now incorporates the design of some membrane systems. Although the SASA parameters tabulated in the present work can be applied for other vapor/polymer systems, it is a rather extensive computational problem to find them for the solutes that have not been reported by Scharlin et al.²¹ So if the eventual aim is to model permeability, then the effect of activity coefficients will need to be included and this paper would provide some useful first insights into the overall applicability of UNIFAC for modelling of gas separation membrane systems. The suggestion to use SASA at all is not unreasonable, but it is not unexpected that these surface areas based on water solutions do not translate well to gas polymer systems. What is surprising is how well

**Figure 5** Correlation of $\ln S$ with surface area calculated using WSA and ASURF for a wide range of gases in poly(vinyl trimethyl silane).

these values are able to correlate the effects. In conclusion, a success of using WSA and other molecular surface area parameters in correlations of the thermodynamic parameters of gas sorption suggests that further and deeper investigation of the UNIFAC method for the modelling of permeation is both desirable and warranted.

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