

Thermodynamics of Gas Solubilities in Molten Polymers

D. D. LIU and J. M. PRAUSNITZ, *Department of Chemical Engineering, University of California, Berkeley, California 94720*

Synopsis

Perturbed-hard-chain theory is extended to mixtures of polymers and volatile fluids, including supercritical gases. This extension is used to derive an expression for Henry's constant for a solute in a molten polymer. Theoretical calculations and data reduction are reported for a variety of solutes in polyethylene, polyisobutylene, and poly(dimethyl siloxane) in the temperature region 25–300°C. Calculated Henry's constants and their temperature dependence are generally in good agreement with the limited experimental data now available.

INTRODUCTION

While much attention has been given to the thermodynamics of mixtures containing polymers and ordinary liquids, relatively few studies have been reported on mixtures of polymers with gases. In this work we discuss the statistical thermodynamics of gas solubilities in liquid polymers at moderate pressures.

The thermodynamics of gas-polymer solutions is much more difficult than that of liquid-polymer solutions because in the former, the light component is supercritical, whereas in the latter it is subcritical. For liquid-polymer phase equilibria we need only to calculate the excess functions of mixing which lead directly to the desired activity coefficients; it is therefore sufficient to have a partition function applicable only to liquids. However, for gas-polymer phase equilibria, the usual excess functions are not useful because the light component cannot exist as a pure liquid at the system temperature. For such solutions, therefore, it is necessary to have a partition function which is applicable to the entire fluid density range, encompassing *both* gaseous and liquid states.

The solubility of a gas in a polymer at pressure P is conveniently expressed by the weight-fraction Henry's constant

$$H_{1,2}^{(P)} = \lim_{w_1 \rightarrow 0} \frac{f_1}{w_1} \quad (1)$$

where subscripts 1 and 2 represent solute and polymer, respectively; f stands for fugacity; and w is the weight fraction in the polymer phase. The following section shows how Henry's constants may be calculated from a perturbed-hard-chain theory for polysegmented fluids.^{1,2} In the final section we compare theoretical results with experimental data.

PARTITION FUNCTION

Using generalized Van der Waals theory, Beret and Prausnitz¹ proposed a partition function for pure fluids, applicable over the entire range of gas and liquid densities:

$$Q(N, V, T) = \frac{1}{N!} \left(\frac{V}{\Lambda^3} \right)^N \left(\frac{V_f}{V} \right)^N (\omega_{r,v})_{\text{int}}^N (\omega_{r,v})_{\text{ext}}^N \exp \left(- \frac{N\phi}{2kT} \right) \quad (2)$$

where N is the number of molecules at temperature T and volume V ; Λ is the thermal de Broglie wavelength; V_f is the free volume; ϕ is the potential field; k is Boltzmann's constant, and $\omega_{r,v}$ designates contributions from rotational and vibrational degrees of freedom. Following Prigogine,^{3a} the rotational and vibrational part of the partition function is factored into internal and external parts. The internal part depends only on temperature.

At liquid densities, the theories of Prigogine^{3a} and Flory^{3b} consider external vibrational and rotational degrees of freedom to be equivalent translational degrees of freedom. The total number of external degrees of freedom per molecule is $3c$, where c reflects the agility of the molecule. For argonlike molecules, c is unity, but for all others, c is larger. For the entire fluid-density range, Beret and Prausnitz proposed the approximation

$$(\omega_{r,v})_{\text{ext}} = (V_f/V)^{c-1} \quad (3)$$

Equations (2) and (3) yield a partition function that approaches the correct ideal-gas limit as the density approaches zero and a Prigogine-Flory-type partition function as the density becomes large.

For the free volume, Beret used the equation of Carnahan and Starling⁴ for hard-sphere fluids; for the potential field ϕ , he used the molecular-dynamics results of Alder et al.⁵ The equation of state, obtained from the partition function by

$$P = kT \left(\frac{\partial \ln Q}{\partial V} \right)_{N,T} \quad (4)$$

contains three characteristic parameters for a pure liquid; in addition to c , the parameters are molecular-core size v^* and characteristic temperature T^* . These three parameters can be obtained from data reduction, using experimental vapor-pressure and/or liquid-density data. Donohue² presented parameters for a variety of nonpolar fluids, including high-boiling hydrocarbons. Calculated vapor pressures and fluid densities agree with experiment to within about 3% over a wide range of temperature and pressure.

It is well known that a partition function of the Van der Waals type is poor for second virial coefficients, especially at low temperatures. When pure-component parameters obtained from liquid-phase data are used to calculate second virial coefficients, an empirical correction term is required, as proposed by Kaul.⁶ The slightly modified partition function is

$$\ln Q = \ln Q^{\text{Beret}} + \ln Q^{\text{SV}} \quad (5)$$

where superscript SV refers to second virial coefficient.

In eq. (5), Q^{Beret} is given by eqs. (2) and (3) and

$$\ln Q^{\text{SV}} = \frac{1.7(3.65 - q/c)(q/c - 1.45)^4}{\bar{T}^4 \bar{v} (1 + 10/\bar{v})^4} \quad (6)$$

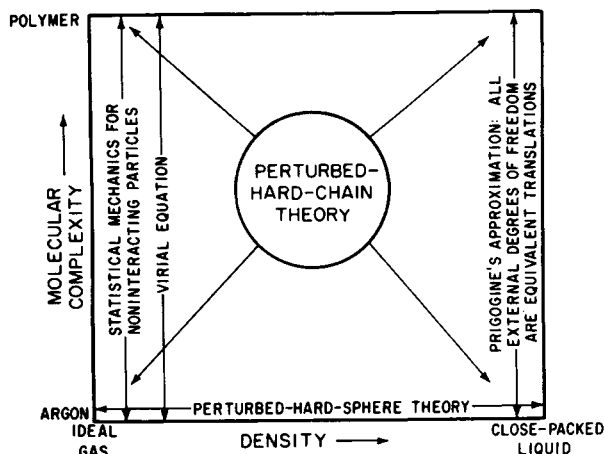


Fig. 1. Perturbed-hard-chain theory provides an equation of state for fluids containing simple or complex molecules, covering all fluid densities.

TABLE I
Pure-Component Parameters for Polymers^a

Polymer ^b	P^* , bars	v_{sp}^* , cm ³ /g	T^* , K	ϵ/k , K
Polyethylene	750	0.6717	503	135
Polyisobutylene	830	0.6216	518	80
Poly(dimethyl siloxane)	580	0.5641	408	80

^a Fit of data is within $\pm 1\%$ or better.

^b Parameters are fitted to PVT data of Beret (ref. 9).

where $\tilde{T} = T/T^*$, $\tilde{v} = v/v^*$, and $T^* = \epsilon q/c k$.

Parameter q is proportional to the molecular surface area and parameter ϵ/k characterizes the segment-segment interaction potential. For pure fluids, parameters ϵ/k and q always appear as a product. The correction term $\ln Q^{SV}$ is negligible at high (liquidlike) densities.

For polydispersed polymeric fluids, it is inconvenient to use molar quantities. It is customary to use a specific hard-core volume v_{sp}^* and a characteristic pressure P^* to replace the molar quantities v^* and c . The characteristic parameter P^* is related to the ratio of c and v^* ; therefore, P^* is not a molar quantity. It is defined by

$$P^* = cRT^*/v^* \quad (7)$$

Since vapor-pressure data are not available for polymers, P^* , v_{sp}^* , and T^* are determined from experimental PVT data only, as discussed previously.^{1,7}

The partition function given by eqs. (2), (3), and (6) is applied to simple and polysegmented fluids over the entire fluid-density range as illustrated in Figure 1.

MIXTURES

As discussed by Donohue,⁵ when extended to mixtures, it is necessary that the partition function meet the following boundary conditions: (i) The second virial coefficient of any mixture must be a quadratic function of the mole frac-

TABLE II
 Pure-Component Parameters for Solutes from Data Reduction^a

Solute	$100v^*$, liter/mole	T^* , K	c	ϵ/k , K
Saturated hydrocarbons				
Methane	1.984	152.2	1.000	60
Ethane	2.753	224.4	1.274	105
<i>n</i> -Butane	4.619	228.7	1.625	105
<i>n</i> -Pentane	5.511	309.1	1.815	105
<i>n</i> -Hexane	6.467	326.5	1.972	105
<i>n</i> -Heptane	7.344	339.4	2.158	105
<i>n</i> -Octane	8.377	351.0	2.299	105
<i>n</i> -Nonane	9.267	354.9	2.558	105
2-Methyl hexane	7.381	330.9	2.137	105
2-Methyl heptane	8.320	342.6	2.307	105
3-Methyl hexane	7.279	328.4	2.198	105
2,2,4-Trimethyl pentane	8.355	342.2	2.050	105
Unsaturated hydrocarbons				
Ethylene	2.426	209.8	1.246	108
Cyclopentane	4.729	338.8	1.697	125
Cyclohexane	5.669	373.4	1.658	125
Benzene	4.683	381.3	1.648	134
Toluene	5.587	385.4	1.867	130
<i>o</i> -Xylene	6.398	399.0	2.080	127
<i>m</i> -Xylene	6.456	391.2	2.071	127
<i>p</i> -Xylene	6.513	392.2	2.040	127
Ethyl benzene	6.448	388.5	2.064	127
<i>t</i> -Butyl benzene	8.264	394.4	2.282	124
Others				
Nitrogen	1.770	96.72	1.104	50
Methyl chloride	2.483	292.7	1.475	108
Acetone ^b	3.693	340.0	1.847	110
Vinyl acetate ^c	4.601	325.8	2.173	108
Carbon dioxide	1.680	204.5	1.670	80
Hexamethyl disiloxane ^d	10.53	305.6	2.538	80

^a Data sources listed in ref. 2.

^b Fitted to vapor-pressure and PVT data from API Project 44 Tables (1945) and International Critical Tables, Vol. 3 (1933).

^c Fitted to vapor-pressure and density data from Union Carbide Corporation.

^d Fitted to vapor-pressure and PVT data in refs. 7 and 10.

tions. (ii) At liquidlike densities, when the reduced volume of the pure components and solution are identical, the athermal entropy of mixing must reduce to the well-known Flory-Huggins entropy of mixing. (iii) We define an excess quantity as that relative to the ideal gas at the same volume, temperature, and composition. The excess chemical potential of a volatile solute at infinite dilution in a polymer solution must remain finite when the polymer chain length becomes infinitely large. (iv) For a mixture, nonrandom mixing due to microscopic clustering becomes important whenever there is a large difference in solute-solute and polymer segment-segment potential energies. In the limit, for mixtures of spherical molecules, the partition function must agree with the nonrandom-mixing theory of Henderson.⁸

To meet these conditions, we follow a procedure similar to that presented by Donohue. First, following Alder et al.,⁵ we expand the Helmholtz energy A in

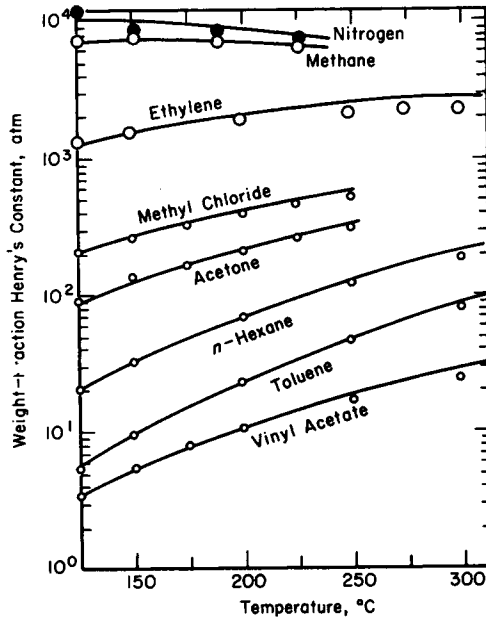


Fig. 2. Weight-fraction Henry's constants in low-density polyethylene. —, Calculated; O, experimental.

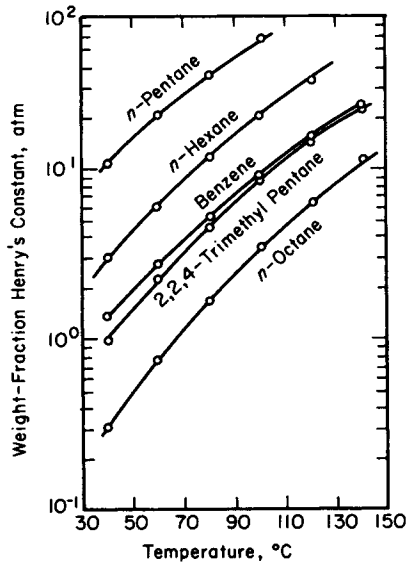


Fig. 3. Weight-fraction Henry's constants in polyisobutylene. —, Calculated; O, experimental.

reciprocal temperature:

$$A - A(\text{ideal gas}) = A^{(0)} + \frac{A^{(1)}}{T} + \frac{A^{(2)}}{T^2} + \frac{A^{(3)}}{T^3} + \frac{A^{(4)}}{T^4} \quad (8)$$

The leading term $A^{(0)}$ is the hard-chain repulsive-force term. It is given by a function of the form

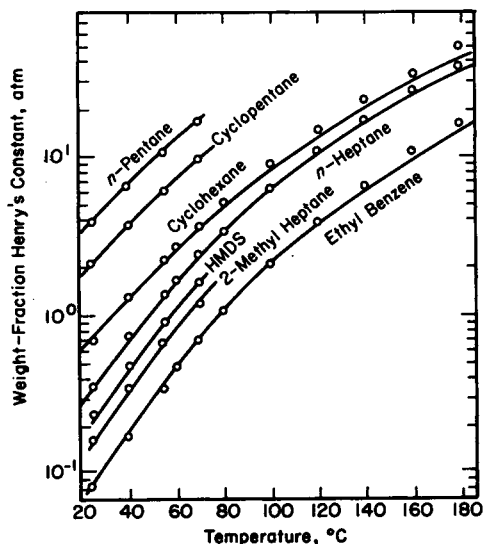


Fig. 4. Weight-fraction Henry's constants in poly(dimethyl siloxane). —, Calculated; O, experimental.

$$A^{(0)}/NRT = \mathcal{f}^{(0)}(\bar{\rho}, \langle c \rangle) \quad (9)$$

The angular brackets in eq. (9) indicate a composition average. The function $\mathcal{f}^{(0)}$ is based on the hard-sphere fluid equation of Carnahan and Starling:

$$\mathcal{f}^{(0)} = -N\langle c \rangle(3\tau\bar{\rho} - 4)\tau\bar{\rho}/(1 - \tau\bar{\rho})^2 \quad (10)$$

where $\tau = 0.7405$, and $\bar{\rho}$ is the reduced density.

Higher-order terms in eq. (8) represent contributions from attractive forces. They have the form

$$A^{(i)}/NRT = \mathcal{f}^{(i)}(\bar{\rho}, \langle T^{*i} \rangle, \langle c \rangle), \quad i = 1, 2, 3, 4 \quad (11)$$

The functions $\mathcal{f}^{(i)}$ are primarily extensions of those given by Alder et al.² Second, we must decide on appropriate composition averages for reduced density and reduced temperature. The composition average for $\langle T^{*i} \rangle$ in eq. (11) depends on i . The purpose of these separate average procedures is to eliminate the approximation that the mixture is random. Details of the derivation are given elsewhere.²

HENRY'S CONSTANT FROM PARTITION FUNCTION

The weight-fraction Henry's constant of solute 1 in polymer 2 is

$$H_{1,2}^{(P)} = (RT)/(v_{2,\text{sp}}M_1) \exp(\mu_1^E/RT) \quad (12)$$

where $v_{2,\text{sp}}$ is the specific volume of polymer at system temperature T and pressure P ; M_1 stands for the molecular weight of solute and μ_1^E is the excess chemical potential of the solute dissolved in the polymer. The weight-fraction Henry's constant is independent of polymer chain length when polymer molecular weight is high.

Calculation of Henry's constant requires pure-component parameters and one binary constant k_{12} defined by

$$\epsilon_{12} = (\epsilon_1\epsilon_2)^{1/2}(1 - k_{12}) \quad (13)$$

where ϵ_{12} is the characteristic potential energy of interaction between an average segment in molecule 1 and an average segment in molecule 2. Binary parameter k_{12} depends only on the nature of molecules 1 and 2; it is independent of temperature, density and composition. Equations for excess Helmholtz energy and excess chemical potential are shown in the supplementary material.

RESULTS

Tables I and II give pure-component properties for three polymers and 26 solutes. For the solutes, there are four parameters (c , T^* , v^* , and ϵ/k) for each component in the mixture. However, only three of them (c , T^* , and v^*) are obtained from reduction of PVT and vapor-pressure data. Following Donohue,⁵ the segment-segment parameter ϵ/k for a normal alkane is set equal to 105 K; this follows from arbitrarily setting $q = 0.724$ for one $-\text{CH}_2-$ segment. For other fluids, optimal values for ϵ/k are shown as determined from an overall study of the experimental data. A segment is defined as a part of a molecule whose size is equal to that of a $-\text{CH}_2-$ unit.

Weight-fraction Henry's constants were calculated for several solutes in polyethylene, polyisobutylene, and poly(dimethyl siloxane); these are compared with experimental data. Tables III, IV, and V summarize the binary parameters k_{12} for various systems. Some typical calculated results are shown in Figures 2, 3, and 4.

TABLE III
Interaction Parameters for Binary Systems Containing Low-Density Polyethylene

Solute	Temperature range (°C)	$100k_{12}$	Ref.
Methane	125.6–227.2	9.92	11
Nitrogen	125 –250	7.72	11, 12
Carbon dioxide	125 –250	13.05	13
Methyl chloride	125 –250	4.97	13
Ethane	124 –250	1.33	13
Ethylene	124 –300	0.92	12, 13
<i>n</i> -Butane	124 –300	0.60	12
<i>n</i> -Hexane	124 –300	0.70	12
<i>n</i> -Octane	124 –300	0.69	12
Benzene	124 –300	0.79	12
Toluene	124 –300	0.44	12
Vinyl acetate	124 –300	5.14	13
Acetone	125 –250	7.77	13

TABLE IV
Interaction Parameters for Binary Systems Containing Polyisobutylene. Data from ref. 16^a

Solute	Temperature range (°C)	$100k_{12}$
<i>n</i> -Pentane	40–100	4.6
<i>n</i> -Hexane	40–120	4.1
<i>n</i> -Heptane	40–120	3.7
<i>n</i> -Octane	40–120	3.6
2,2,4-Trimethyl pentane	40–120	4.7
Benzene	40–120	4.9
Cyclohexane	40–120	5.1

^a To reduce the data, it is necessary to use equations given in Appendix A of ref. 14.

TABLE V
Interaction Parameters for Binary Systems Containing Poly(Dimethyl Siloxane)

Solute	Temperature range (°C)	$100k_{12}$	Ref.
<i>n</i> -Pentane	25-70	0.8	10
<i>n</i> -Hexane	25-180	0.9	10
<i>n</i> -Heptane	25-180	0.7	10, 15
<i>n</i> -Octane	25-180	0.7	10
Cyclopentane	25-170	0	10
Cyclohexane	25-180	1.1	10, 15
2-Methyl heptane	25-70	0.7	10
2-Methyl hexane	25-70	0.7	10
2,2,4-Trimethyl pentane	25-70	1.4	10
3-Methyl hexane	25-70	0.5	10
Benzene	25-180	0.2	10, 15
Toluene	25-180	0.7	10, 15
<i>o</i> -Xylene	25-70	0	10
<i>m</i> -Xylene	25-70	0	10
<i>p</i> -Xylene	25-70	0	10
Ethyl benzene	25-180	0.2	10, 15
<i>t</i> -Butyl benzene	25-70	0.8	10, 15
Hexamethyl disiloxane	25-70	0	10

For most solutes, the interaction energy parameters reported here agree with those reported by Donohue⁵ and Kaul⁶ in their studies of mixtures containing ordinary gases and liquids. However, for the light gases (methane, nitrogen, and carbon dioxide) the parameters found in this work are systematically lower.

Henry's constant for a gas dissolved in a polymer depends strongly on the binary parameter k_{12} and on the ratio ϵ_1/ϵ_2 ; in particular, the effect of temperature on Henry's constant is a strong function of ϵ_1/ϵ_2 . For light gases in polymers, Henry's constants have a weaker temperature dependence than do those of heavier solutes; we find that low values for ϵ/k are necessary to reproduce the experimental results for light gases. However, since the solubilities of light gases in polymers are very small, they are difficult to measure with high accuracy. Measurements for heavier solutes tend to be more accurate.

Agreement between calculated and experimental Henry's constants is satisfactory if we consider the probable accuracy of experimental data. Although some experimentalists reported accuracies of about (1-3)% for most of the volatile organic solvents and (8-15)% for light gases, measurements for a given polymer-gas pair performed in different laboratories often disagree with each other. [See, for example, solubility data for poly(dimethyl siloxane) systems given in refs. 10, 15-18]. For a given polymer, we choose from the literature those measurements that were obtained over the widest temperature range and that contain a large variety of solutes. Our examination of these solubility data suggests that the experimental uncertainties are $\pm(8-15)\%$ for ordinary volatile organic solvents and $\pm(10-40)\%$ for light gases.

CONCLUSION

The perturbed-hard-chain theory is extended to mixtures including polymers and supercritical fluids. Using only one adjustable binary parameter, calculated Henry's constants and their temperature dependence generally show good agreement with the limited reliable experimental data now available.

The authors are grateful to M. D. Donohue, B. K. Kaul, and R. N. Lichtenthaler for helpful discussions, to T. F. Anderson for extensive assistance in numerical analysis, and to the Donors of the Petroleum Research Fund, administered by the American Chemical Society, for financial support.

References

1. S. Beret and J. M. Prausnitz, *Macromolecules*, **8**, 878 (1975); *AIChE J.*, **21**, 1123 (1975).
2. M. D. Donohue and J. M. Prausnitz, *AIChE J.*, **24**, 848 (1978).
3. (a) I. Prigogine, *The Molecular Theory of Solutions*, North-Holland, Amsterdam, 1957; (b) P. J. Flory, *J. Am. Chem. Soc.*, **87**, 1833 (1965).
4. N. F. Carnahan and K. E. Starling, *J. Chem. Phys.*, **51**, 635 (1969).
5. B. J. Alder, D. A. Young, and M. A. Mark, *J. Chem. Phys.*, **57**, 3013 (1969).
6. B. K. Kaul, PhD thesis, University of California, Berkeley, 1977.
7. R. N. Lichtenthaler, D. D. Liu, and J. M. Prausnitz, *Macromolecules*, **11**, 192 (1978).
8. D. Henderson, *J. Chem. Phys.*, **61**, 926 (1974).
9. S. Beret, PhD thesis, University of California, Berkeley, 1974, Appendix II.
10. R. N. Lichtenthaler, D. D. Liu, and J. M. Prausnitz, *Ber. Bunsenges. Phys. Chem.*, **78**, 470 (1974).
11. J. L. Lunberg and E. J. Mooney, *J. Polym. Sci., A-2*, **7**, 458, (1969), Table II.
12. D. P. Maloney and J. M. Prausnitz, *AIChE*, **22**, 74 (1976).
13. D. D. Liu and J. M. Prausnitz, *Ind. Eng. Chem. Fundam.*, **15**, 330 (1976).
14. D. D. Liu, PhD thesis, University of California, Berkeley, 1978, Appendices.
15. M. Galin, *Macromolecules*, **10**, 1239 (1977).
16. W. E. Hammers and C. L. DeLigny, *Rec. Trav. Chim.*, **90**, 912 (1971).
17. R. N. Lichtenthaler, J. M. Prausnitz, C. S. Su, H. P. Schreiber, and D. Patterson, *Macromolecules*, **7**, 136 (1974).
18. W. R. Summers, Y. B. Tewari, and H. P. Schreiber, *Macromolecules*, **5**, 12 (1972).

Received October 31, 1978