Applying lattice-hole theory to gas solubility in polymers

Robert Simha[1], Hankun Xie[2]

[1] Department of Macromolecular Science, Case Western Reserve University,
Cleveland, OH 44106-7202, USA
[2] Department of Basic Sciences, China Textile University, Shanghai 200051, China

Summary

A recent theory based on the Simha-Somcynsky theory is applied to the solubility of the 1,1,1,2 tetrafluoroethane vapor in polystyrene. The requisite chemical potentials of the vapor and of its condensate in contact with the polymer involve the equations of state (eos) of the 3 species and are evaluated by means of literature information. Good agreement with experiment ensues at 120ºC and pressures up to 35 bar. At 90ºC systematic differences, increasing with pressure, result above 10 bar. These may be caused by the use of melt theory in the glass transition region and/or an inadequacy of the eos of the vapor at lower temperatures and elevated pressures. Extensions to further pairs, gaseous mixtures and the glassy state are indicated.

Introduction

We have recently developed a theory of gas solubility in amorphous polymers (1) which rests on the lattice-hole model of Simha-Somcynsky (SS) (2). Application to several polymer-vapor pairs has demonstrated consistency with empirical relationships proposed in the literature, and involving the critical temperature of the gas and the heat of solution. The purpose of this paper is to investigate solubility relations for a particular vapor with technological importance, namely 1,1,1,2 tetrafluoroethane (HFC). The polymer is to be polystyrene. The next section summarizes the requisite results of the theory. In the third section, comparisons of computations with experiment and further predictions are presented.

Theory

What is required are the chemical potential of the gas μ_1 to be balanced by the chemical potential μ_2 of the condensed gas in contact with the polymer. The requisite inputs to the theory are

        a)   The equation of state (eos) of the gas.
        b)   The eos of the polymer.
        c)   The eos of the condensed vapor.

Vapor: Chemical potential and eos

For μ_1 we have simply the Gibbs free energy $G = F + PV$ per mole, with F the Helmholtz free energy and

$$F = -\int_{V}^{\infty} P\,dV + f(T) \tag{1}$$

where f(T) is the corresponding function for the ideal gas. Given the eos of the gas

$$P = P(V, T) \tag{2}$$

the integral is evaluated as function of volume and temperature. Since ultimately results as functions of pressure and temperature are desired, an inversion of eq. (2) is required, either analytically when eq. 2 appears in the form of a virial expansion, or otherwise numerically (see the next Section).

Polymers and Condensed Vapor: eos

The two eos are obtained by means of the SS theory (2) which models the system as a mixture of lattice sites occupied by a polymer segment or a small molecule, and empty sites. The latter may be taken as a measure of free volume. The scaled eos takes the form

$$\tilde{P}\tilde{V}/\tilde{T} = (1-\eta)^{-1} + 2y\,Q^2(1.011Q^2 - 1.2045)/\tilde{T} \tag{3}$$

where $Q = (y\tilde{V})^{-1}$, $\eta = 2^{-1/6}\,y\,Q^{1/3}$, and y represents the fraction of occupied sites. Its dependencence on volume and temperature is determined by a minimization of the configurational free energy which yields the following condition:

$$s[(s-1)/s + y^{-1}\ln(1-y)]/(3c) = (1-\eta)^{-1}(\eta - 1/3)$$

$$+ y\,Q^2(2.409 - 3.033Q^2)/(6\tilde{T}) \tag{4}$$

Here s is the number of constituent segments per chain. The characteristic parameters of the system are the maximum intersegmental attraction energy ε^*, the intersegmental repulsion volume v^*, and the "flexibility" parameter c, i.e. 3c being the number of volume dependent, external degrees of freedom. For a large s-mer 3c will be of the order of s. For the condensed gas we set c = 1. Finally, the scaling parameters in eqs. 3 and 4 are

$$T^* = [s(z-2) + 2]\varepsilon^*/(ck); \quad P^* = [s(z-2) + 2]\varepsilon^*/(sv^*) \tag{5}$$

and the volume $V^* = v^*/m_o$, where m_o is the molecular segmental mass, and z the coordination number of the lattice.

The Mixture: eos and Free Energy

Provided the assumption of random mixing is adopted, the generalization to multiconstituent systems proceeds as follows (3): The scaled eqs. 3 and 4 retain their validity and the scaling parameters become explicitly defined functions of composition. For a binary system of mole fraction x_1, the averaged functions are:

$$< s > = x_1 s_1 + (1 - x_1) s_2; \; < c > = x_1 c_1 + (1 - x_1) c_2 \tag{6}$$

To define the scaling parameters, see eq. 5, averages of ε^* and v^* are obtained in terms of self and cross interactions, by means of the following equations:

$$< v^* >^2 = B_4 / B_2; \; < \varepsilon^* > = B_2^2 / B_4 \tag{7}$$

with $B_2 = X_1^2 \varepsilon_{11}^* v_{11}^{*2} + 2 X_1 (1 - X_1) \varepsilon_{12}^* v_{12}^{*2} + (1 - X_1)^2 \varepsilon_{22}^* v_{22}^{*2}$, B_4 the analogous expression with v_{ij}^{*4}, and the site fraction

$$X_1 = [s_1 x_1 (z - 2) + 2] / [s_1 x_1 (z - 2) + 2 + s_2 x_2 [z - 2] + 2]$$

Thus, given the eos of the constituents and hence their interaction parameters, the cross-interactions are extracted, once the eos of the mixture has been obtained. In the absence of the latter, as in our instance, averaging assumptions are required, viz:

$$\varepsilon_{12}^* = \delta_e (\varepsilon_{11}^* \varepsilon_{22}^*)^{1/2}; \; v_{12}^* = \delta_v (v_{11}^{*1/3} + v_{22}^{*1/3})^3 \tag{8}$$

with the δ's adjustable parameters. The first relation generalizes the familiar geometric mean rule. The second expresses an averaging of characteristic lengths rather than volumes, considering the asymmetry of the chain (2,3).

With the above information at hand, the Gibbs free energy G_m of the mixture can be evaluated as a function of T, P and x_1 (1,3), i.e., omitting the averaging symbol

$$G_m / RT = x_1 \ln x_1 + (1 - x_1) \ln (1 - x_1) + \ln(y / s) +$$

$$s(1 - y) \ln(1 - y) / y + (s - 1) \ln[e / (z - 1)] - c[\ln(v^* / N_a)$$

$$\times (1 - \eta)^3 / Q] + c y Q^2 (1.011 Q^2 - 2.409) / 2 \tilde{T} \tag{9}$$

$$- \frac{3}{2} c_1 x_1 \ln[2 \pi m_1 RT / (N_a h)^2] - \frac{3}{2} c_2 (1 - x_1) \ln[2 \pi m_2 RT / (N_a h)^2]$$

$$+ c[(1 - \eta)^{-1} + 2 y Q^2 (1.011 Q^2 - 1.2045) / \tilde{T}] / ms$$

with $<s> <m> = x_1 s_1 m_1 + (1 - x_1) s_2 m_2$.

We recognize in eq. 9 contributions from the combinatory entropy of mixing holes and occupied sites of the two constituents, equation of state terms, and kinetic energy contributions. Finally, the chemical potential μ_2 of the condensed gas follows from G_m (4); that is

$$\mu 2 = G_m + (1 - x_1) \partial G_m / \partial x_1 \tag{10}$$

The lengthy analytical expressions for μ_2 has been derived (5). It will be preferable in the present context to employ numerical differentiation.

Applications:

Solubility relations of HFC in polystyrene (PS) have been studied experimentally (6). We now wish to examine these data in terms of the theory presented. The eos of the

polymer is available and has been analyzed (7). As for HFC, gas as well liquid PVT data have been obtained (8) and can now be discussed in terms of the theory.

The various procedures of extracting the scaling parameters from a superposition of the scaled theoretical unto the experimental eos surface have been repeatedly discussed in the literature and we refer to Ref. (1). Table 1 lists the numerical values of several quantities

Table 1.　　　　　　Parameters for HFC/PS Pair

	s	c	m (g)	v* (cc/g)	T* (K)	P* (bar)	ε^*/k (K)	δ_e	δ_v
HFC	1	1	102.0	0.5532	3742.3	5514.2	311.86	1.104	1.166
PS	2134.4	772.1	58.47	0.9657	12725.4	6778.1	460.29	1.104	1.166

in addition to the scaling parameters. The molar mass and hence s for the polymer are arbitrarily assumed. However, as has been shown earlier (1), the final results are practically invariant with the molar mass of the polymer. The definition of the chain segment and consequently the scaling values had to be revised from earlier findings. The lattice picture requires at least approximate equality of the molecular sizes of the two constituents. In this case this implies an adjustment of the chain segment to the repulsion volume of the HFC molecule. The δ-values, disposable parameters, since the eos of the mixture is unknown, are also exhibited. Equation 9 can thus be evaluated.

Reference (8) provides a 32 parameter eos for the vapor. We have not attempted to reduce this equation to a simpler form, in order to maintain a maximal numerical accuracy of the predicted solubilities. The eos is

$$P = \sum_{n=1}^{9} a_n / V^n + \exp(-V_c^2 / V^2) \sum_{n=10}^{15} a_n / V^{2n-17} \qquad (11)$$

V_c is the critical volume, and the a_i are temperature dependent coefficients, with $a_1 = RT$. We dispense with exhibiting the actual expressions for the a_i.

The direct evaluation of μ_1 via the free energy integral, eq. (1), encounters convergence problems. So, we proceed by computing the difference $\Delta\mu_1$, where

$$\Delta\mu_1 = \mu_1 - \mu_{1o} = F_1 - F_{1o} + (PV - RT) = \int_V^{\infty}(P - RT / V)dV$$

$$+(PV - RT) \qquad (1')$$

Here the free energy refers to one mole and the subscript o indicates the ideal gas state. For μ_{1o} we have (9):

$$\mu_{1o} = RT\ell n\left\{P / kT [(N_a h)^2 / 2\pi mRT]^{3/2}\right\} \qquad (12)$$

Finally, the solubility S is related to x_1 by the expression

$$S = x_1 \times 1000 \times m_1 / [(1 - x_1) \times M_2] \qquad (13)$$

where S is in mg HFC/g PS, and m_1 and M_2 are the molar masses of the constituents. Finally, x_1 is the numerical solution of the equation
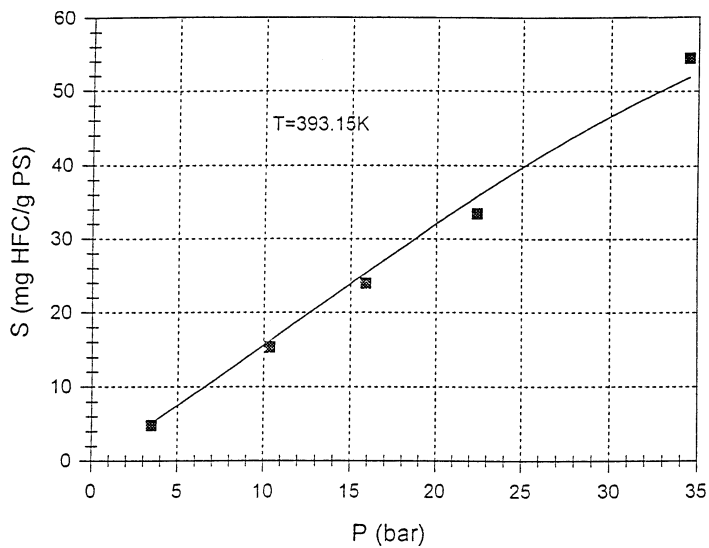
Fig. 1: Solubility isotherm of the PS/HFC pair. Symbols,
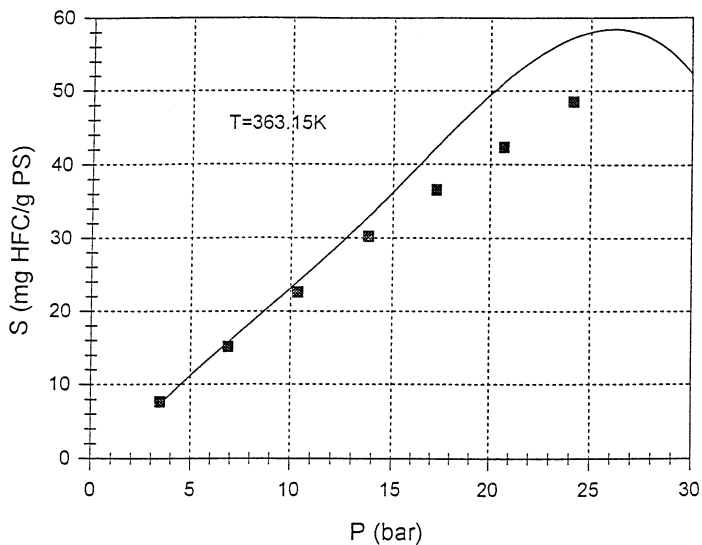   experiment (Ref. 6); line, theory.

Fig. 2: Solubility isotherm of the PS/HFC pair. Symbols,
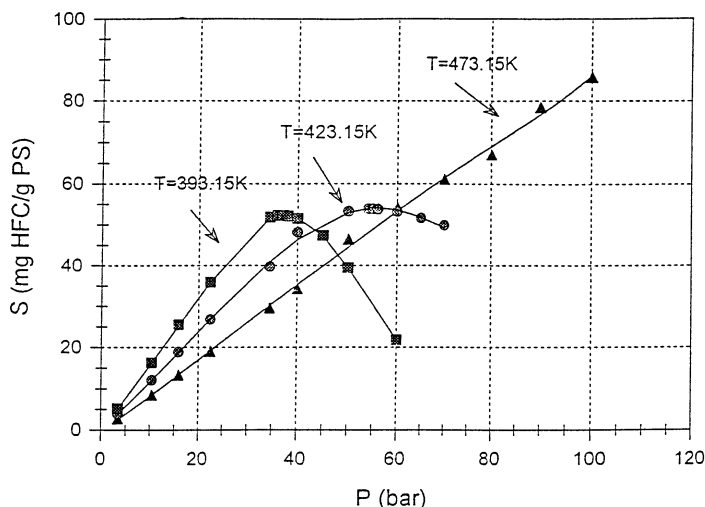   experiment (Ref. 6); line, theory.

Fig. 3: Predicted solubility isotherms of the PS/HFC pair.
Symbols, theory; lines, computer fits.

$$\mu_1(T,P) = \Delta\mu_1 + \mu_{10} = \mu_2(x_1,T,P) \tag{14}$$

Figure 1 displays the experimental solubility isotherm at 120°C and the solution of eq. 14. A gratifying agreement between theory and experiment is noted, with deviations below 10%.

Figure 2 exhibits the results at 90°C. Systematic deviations appear above 10-15 bar. It will be noted that we are in the glass transition region and the present theory applies only to the equilibrium melt. On the other hand, as pointed out to us by Dr. P. Handa, the problem may rest on the eos of the vapor at pressures approaching the saturation pressure. In Fig. 2 as well as in Fig. 3 which shows computed points together with computer fitted lines, maxima are predicted, shifting to higher pressures with increasing temperature. It should be noted however, that the eos of the gas has been proven accurate only below 175°C and 65 bar. Moreover the computed chemical potential of the gas decreases with increasing pressure at high pressures. Thus the predicted solubility at P > 65 bar is not reliable.

Outlook. The way to a consideration of further systems, such as polystyrene paired with CO_2 or 1,1-dichloro-222-trifluoroethane, is open. Experimental tests of predictions over wider ranges of variables are desirable, and hence also corresponding eos data. Next there is the extension to gaseous mixtures. Finally, a consideration of solubility in the non-equilibrium polymer glass comes to mind. Important results in the frame of the SS theory have been obtained for the glassy state. Here the additional features of glass formation history and relaxation toward equilibrium (physical aging) come into play.

References

(1)   Xie, H., Simha, R. (1997) Polym. Int. 44: 348
(2)   Simha, R., Somcynsky, T. (1969) Macromolecules 2: 342
(3)   Jain, R. K., Simha, R. (1980) Macromolecules 13: 1501; (1984) ibid. 17: 2663
(4)   Guggenheim, E. A. (1959) Thermodynamics. North Holland, Amsterdam
(5)   Nies, E., Stroeks, A., Simha, R., Jain, R. K. (1990) Colloid Polym. Sci. 268: 731
(6)   Handa, P., Wong, B., submitted J. Polym. Sci. B: Polym. Phys.
(7)   Quach, R., Simha, R. (1971) J. Appl. Phys. 42: 4302
(8)   McLinden, M. O., et al. (1989) ASHRAE Transacts. 95: 263
(9)   Aston, J. G., Fritz, J. J. (1959) Thermodynamics and Statistical Thermodynamics, Wiley, New York