

Some important aspects of solubility of simple micromolecules in polymeric media

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The solubility of micromolecular solutes in rubbery polymeric media can be treated with reasonable simplicity and generality, when only non-polar or very weakly polar interactions are involved. A regular solution approach yields a useful description of the relative solubility of different gaseous solutes, but more sophisticated treatments are necessary for the evaluation of absolute solubilities. The treatment of excess solubility in glassy polymers seems to be the topic which currently attracts most interest. The dual mode sorption model, which has long been used for this purpose, as well as alternative approaches recently proposed, are discussed critically.

INTRODUCTION

The need for adequate modelling of the solubility of simple micromolecular solutes in polymeric media has been considerably enhanced in recent years, due to the rapid development of gas (and, in suitable cases, vapor) separation applications based on permselective polymer (notably glassy polymer) membranes. The commercial success of such processes depends on the achievement of sufficiently high membrane permeability for the targeted gaseous component (denoted by A) both in absolute terms and relative to that for the other gaseous component(s) from which A is to be separated (permselectivity). The permeability coefficient of A in the polymeric material constituting the membrane can, in turn, be analysed into a kinetic factor (diffusion coefficient) and a thermodynamic factor (solubility coefficient), of which the latter is of interest here. Its usual definition is

$$S_{PA} = C_A / p_A \quad (1)$$

where C_A is the molar concentration of A in the polymeric medium (assumed amorphous and denoted by B) at equilibrium with a given gas-phase pressure of A denoted by p_A . In accordance with what has been said above, one is interested both in the absolute value of S_{PA} and in its magnitude relative to that of other solutes. Both these aspects of the problem can be treated most simply and generally for systems involving only non-polar or very weakly polar interactions, which will be considered here.

RELATIVE SOLUBILITIES IN RUBBERY POLYMERS

Relative solubilities in rubbery polymers can be dealt with, to a useful degree of approximation, by means of the simple Flory-Huggins regu-

lar solution approach, wherein mixing of A (in liquid form) with B is described by

$$(\mu_A - \mu_A^\circ)/RT = \ln a_A = \ln v_A + v_B(1 - \bar{v}_A/\bar{v}_B) + \chi_A v_B^2 \quad (2)$$

In equation (2), μ_A , μ_A° represent the chemical potential of A in the solution and in the pure liquid state respectively; a_A is the corresponding activity, which reduces to the relative vapor pressure p_A/p_{A0} , if deviations from ideal behavior in the gas phase are neglected; v_A , $v_B = 1 - v_A$ and \bar{v}_A , \bar{v}_B denote fractional volume and partial molar volume respectively, the latter taken as constant and equal to the molar volume (\bar{v}_A° , \bar{v}_B°) of the respective pure components (strict volume additivity is assumed); and χ_A is the "interaction parameter". In the simplest case (Flory treatment, cf. ref.1) χ_A is purely enthalpic and expressible in terms of the solubility parameters δ_A , δ_B , namely

$$\chi_A = \chi_A^\circ = \bar{v}_A(\delta_A - \delta_B)^2/RT \quad (3)$$

The remaining terms on the right-hand side of equation (2) are entropic (assuming ideal purely combinatorial entropy of mixing). The only distinction made between micro- and macromolecular solvents is embodied in the value of \bar{v}_A/\bar{v}_B , which is negligible in the latter case.

To obtain the solubility coefficient defined in equation (1), an approximate estimate of p_{A0} (which is often a virtual quantity for gaseous solutes at the temperatures of interest) is obtained via the integral Clausius-Clapeyron equation (refs 2,3). In view of $v_A = \bar{v}_A C_A$ and neglecting terms in \bar{v}_A/\bar{v}_B and v_A^2 (since $v_A \ll 1$ for the systems under consideration), the result is

$$\ln S_{PA} = -\ln \bar{v}_A - (1 + \chi_A) + (1 + 2\chi_A)\bar{v}_A C_A - (L_{bA}/RT_{bA})(1 - T_{bA}/T) = \ln K_A + b_A C_A \quad (4)$$

where $b_A = (1 + 2\chi_A)\bar{v}_A$; L_{bA} , T_{bA} denote molar latent heat of evaporation and boiling point respectively. Equation (4) reduces to Henry's law ($S_{PA} = K_A$) at lower C_A and deviates positively from it ($b_A > 0$ since $\chi_A > 0$) at higher C_A . For a series of gaseous solutes $L_{bA}/RT_{bA} = \text{const}$ and the variability of χ_A is limited by the opposing tendencies of its constituent factors shown in equation (3). Thus, an approximate linear correlation is predicted between $\ln K_A$ and T_{bA} . Similar correlations can, therefore, be expected with the critical temperature T_{CA} or the Lennard-Jones "force constant" of the gaseous solute ϵ_A/k (ref.3). It is further predicted that the relative solubilities of different solutes, which are determined by the slope of these correlations, should be largely independent of the nature of the solvent. The properties of the latter enter through χ_A and should, therefore, affect primarily the intercept of the relevant correlations. Considering the oversimplified nature of this treatment, the aforementioned expectations are fulfilled in practice remarkably well (e.g. refs 3,4). Examples of the slope and intercept of the correlation

$$\ln K_A = \ln K_0 + K_E \epsilon_A/k \quad (5)$$

for some liquid and rubbery-polymer solvents are shown in Table 1 (for a more extensive data compilation, see, e.g., ref.6). It is noteworthy that the results of a recent evaluation of gas solubilities in amorphous polypropylene by molecular computer simulation (ref.5) obey a correlation closely analogous to equation (5).

ABSOLUTE SOLUBILITIES IN RUBBERY POLYMERS

Although a dependence of S_{PA} on δ_B generally in line with that suggested by equations (3) and (4) may be noted, this simple approach is considerably less successful as far as the evaluation of absolute solubilities [or K_0 values in equation (5)] is concerned (ref.7). The behavior of real binary solutions incorporating a polymeric component

TABLE 1. Application of equation (5) to gases in various solvent media (K_O in $\text{cm}^3 \text{NTP cm}^{-3} \text{atm}^{-1}$; K_E in K^{-1} ; K_A replaced by K_{A1} for glasses).⁴

		$K_E \times 10^2$	$K_O \times 10^{-2}$
Liquids (25°C):	Benzene	0.95	2.98
	n-heptane	0.94	1.69
Rubbers (25°C):	Natural rubber	0.94	1.11
	Silicone rubber	0.94	1.88
	Butyl rubber	1.00	0.90
	Amorphous polyethylene	0.94	0.72
	Polychloroprene	0.97	1.10
Glasses (35°C):	Polycarbonate	0.92	1.15
	Polysulfone	0.96	0.93
	Copolyester	0.96	1.03
	Poly(phenylene oxide)	0.93	1.65

cannot properly be represented by equation (2), unless χ_A is treated as a composition-dependent "residual chemical potential" parameter, which may include both entropic and additional enthalpic (beyond χ_A^0) contributions (e.g. ref.1). Rigorous solution of the Flory-Huggins lattice model does indeed give rise to correction terms of this kind (e.g. ref. 8), but this is quite insufficient to account for the observed thermodynamic behavior. Furthermore, the aforesaid model cannot represent the associated volume changes upon mixing. More advanced treatments take into account the difference in thermodynamic properties of the macro- and micromolecular components, which are conveniently represented by different values of characteristic variables. The latter are determined by fitting an equation of state to suitable p, V, T data for each pure component. Refs 9 and 10 are examples of such (lattice-based and non-lattice respectively) treatments applicable to gaseous solutes. The former theory, developed by Sanchez and Lacombe (SL), represents a reasonable balance of simplicity and successful application (e.g. refs 11,12). Each pure component is assumed to consist of molecules composed of r segments (where $r_B \rightarrow \infty$) and is characterized by the values of V^* , $T^* = \epsilon^*/k$ and $p^* = Nr\epsilon^*/V^*$ (or $\delta^* = \sqrt{p^*}$); where V^* is the volume occupied in the (disordered) close-packed state; ϵ^* , p^* (or δ^*) are the corresponding interaction energy per segment and cohesive energy density (or solubility parameter) respectively; and N is the number of molecules. The equation of state is

$$(V^*/V)^2 + p/p^* + (T/T^*) [\ln(1 - V^*/V) + (1 - 1/r)V^*/V] = 0$$

which is also applicable to the solution with r , V^* , T^* , and p^* given by prescribed "mixing rules". An explicit expression can be derived for K_A , namely (refs 12,13)

$$\ln K_A = \ln(273/T) - r_A [1 + v_{fB} \ln v_{fB} / (1 - v_{fB})] - (1 - v_{fB}) \chi_A^* + (1 - v_{fB}) r_A \epsilon_A^* / kT \quad (6)$$

where $v_{fB} = 1 - V_B^*/V_B$; $\chi_A^* = \bar{V}_A^* (\delta_A^* - \delta_B^*)^2 / RT$; and K_A is given in $\text{cm}^3 \text{NTP cm}^{-3} \text{atm}^{-1}$. Equation (6) is equivalent to equation (5) as far as relative solubility is concerned. An example of its performance in estimating absolute solubilities is given in Table 2a (see also ref.11).

TABLE 2. Comparison of (a) K_A at 308K for silicone rubber (ref.12) and (b) K_{A1} for polycarbonate at 308K deduced by curve-fitting the simple dual mode sorption model to the relevant data (ref.14), with the corresponding results of SL model calculations (in $\text{cm}^3 \text{NTP cm}^{-3} \text{atm}^{-1}$).

	(a)	C_2H_4	CO_2	CH_4	N_2		(b)	C_2H_4	CO_2	N_2
K_A (exp)		1.66	1.28	0.43	0.12	K_{A1} (DMS)		0.37	0.89	0.10
K_A (SL)		1.26	0.98	0.33	0.088	K_{A1} (SL)		0.62	0.80	0.14

EXCESS SOLUBILITY IN GLASSY POLYMERS

Glassy polymers are characterized by "excess" ("out of equilibrium") thermodynamic properties, which appear to enhance solubility therein. This is pictured most simply in terms of gradual "filling" of the excess free volume of the polymer, thus also explaining why S_{PA} typically tends to decrease (i.e. deviate negatively from Henry's law) with increasing C_A (or p_A).

Dual mode sorption model

In the earliest and still most common treatment of the aforementioned phenomenon, the excess free volume of the glassy polymer is considered to consist of frozen microcavities (molecular packing defects) dispersed in the dense polymer matrix. The latter are idealized as Langmuir adsorption sites (molar concentration s_A) which can accommodate individual solute molecules, without significantly disturbing the normal dissolution process in the polymer matrix. According to this "dual mode sorption" model, the overall solubility coefficient of a gaseous solute is given by (e.g. refs 4,15,16)

$$S_{PA} = S_{PA1} + S_{PA2}; \quad S_{PA2} = s_A K_{A2} / (1 + K_{A2} p_A) \quad (7a,b)$$

where S_{PA1} represents the normal dissolution mode (exactly analogous to that observed above the glass transition temperature T_g) and S_{PA2} arises from the aforesaid Langmuir adsorption mode, which is characterized by an affinity constant K_{A2} . In the simplest form of this model, which has been applied extensively to simple gases, $S_{PA1} = K_{A1} p_A$ (Henry's law) and s_A , K_{A2} are also treated as constants at given T . K_{A1} may be determined by extrapolation of data obtained at $T > T_g$ and this is sometimes done (e.g. ref.17). It is common practice, however, to determine all three constants by curve-fitting the solubility (C_A vs p_A) data. This means that the model is used in a "correlative" rather than a "predictive" sense. One should also bear in mind that the physical validity of this approach is restricted by the Langmuir postulates requiring the adsorption sites to be permanent, independent and isoenergetic. The last condition is not normally realistic. This is amply demonstrated for systems of interest here by recent molecular computer simulation results (ref.18). Even so, the simple Langmuir formalism is often found to be applicable in practice, provided one bears in mind that K_{A2} is only an apparent affinity constant (ref.16). The remaining postulates, which imply that polymer properties and structure are unaffected by the presence of the solute, obviously become increasingly unrealistic with rising C_A .

In spite of these limitations and the restricted (and, at present, still ill-defined) permissible C_A range, there is, nevertheless, considerable evidence showing that the simple dual mode sorption model is a useful and physically meaningful theory, as distinct from a mere curve-fitting exercise (refs 4,15-17). Thus, as illustrated by the examples given in Table 1, K_{A1} data for glassy polymers generally fit reasonably well into the correlations with gaseous solute properties established for rubbery polymers. An analogous correlation with ϵ_A/k has been shown for K_{A2} , though in much less detail. Furthermore, the adsorption mode is generally found to be more exothermic than the normal dissolution mode; in keeping with the fact that the energetic penalty involved in pulling polymer segments apart, in order to accommodate solute molecules, is at least partly avoided in the former case. Also, the physically expected close correlation of s_A with the fractional excess free volume of the polymer v_E has been demonstrated in various ways (refs 4,15,16). The latter parameter may be expressed as follows (cf. Fig. 1a)

$$v_E = (V_G - V_L) / V_L = \Delta \alpha (T_g - T) \quad (8)$$

where V_G is the volume of the polymer at $T < T_g$; V_L is the corresponding

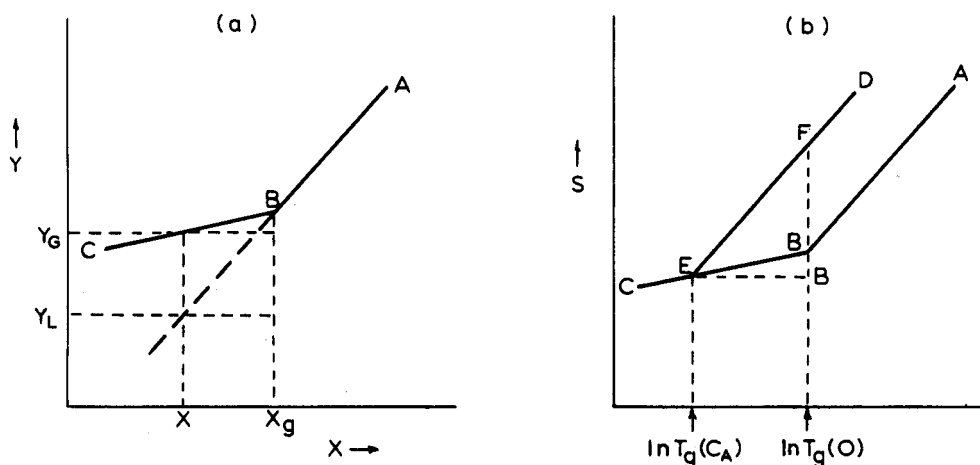


Fig. 1. (a) Schematic plot where Y vs X stands for volume vs T , enthalpy vs T or entropy vs $\ln T$, for a polymeric medium near the glass transition point B . (b) Schematic representation of the presumed effect of solute on the T_g of a polymeric medium (AB , DE correspond to S_B^0 and $S_B^0 + \Delta S_M$ respectively; see text).

presumed equilibrium value deduced by extrapolation of the $V(T > T_g)$ line (AB in Fig. 1a); and $\Delta\alpha$ is the difference in the thermal expansion coefficient of the polymer above and below T_g .

On the other hand, it is not known to what extent the curve-fitting procedure mentioned above can be relied upon to separate excess from normal solubility quantitatively. Curve-fitted K_{A1} values have been compared with those determined by extrapolation from the rubbery state or by calculation on the basis of a reasonably sophisticated model, in very few cases and with results which are not very conclusive (cf. refs 15-17 and Table 2b). Also, the assumed Langmuir adsorption mechanism offers little insight into the reason for the observed marked tendency of s_A for simple gases to increase in line with the adsorbability of the gas (which would be more consistent with a micropore-filling mechanism, cf. ref.19), although the corresponding stronger swelling of the polymer by the dissolved gas may offer a partial explanation (ref.16). A better known effect of polymer-solute interaction is "plasticization" of the polymer, one manifestation of which is depression of T_g . On the basis of equation (8) and the close correlation of v_E to s_A , one, therefore, expects s_A to be a decreasing function of C_A (ref.16), thus impairing a basic assumption of the simple dual mode sorption model. This effect becomes obvious as C_A approaches the value C_{Ag} at which T_g becomes equal to the experimental temperature T and hence $s_A = 0$ (see refs 20-23 for actual examples). Assuming s_A to be proportional to v_E , the following expression is derived in ref.23

$$s_A(C_A) = s_A(0) [T_g(C_A) - T] / [T_g(0) - T]$$

and used in conjunction with the $T_g(C_A)$ relation given in ref.24

$$\ln [T_g(C_A) / T_g(0)] = \beta [\theta \ln \theta + (1 - \theta) \ln (1 - \theta)] \quad (9)$$

where $\beta = z r_M R / \Delta \bar{c}_p$; $\theta = \bar{v}_B v_A / z r_M \bar{v}_A v_B$; $\Delta \bar{c}_p$ is the difference in molar heat capacity of the polymer above and below T_g ; r_M is the mean number of monomer units per polymer chain; while z is referred to as "the lattice coordination parameter" and given a value of 1 or 2 (refs 23-25). Once $T_g(C_A)$ is known, it is possible to determine K_{A1} , K_{A2} and $s_A(0)$ by a suitable curve-fitting procedure. An additional complication can arise, however, due to the fact that S_{A1} tends to deviate (positively) from

Henry's law at higher C_A in the manner indicated by equation (4), thereby introducing one more constant (b_{A1}) to be determined (see, e.g., ref.22). The aforementioned extensions of the simple dual mode sorption model are physically reasonable and necessary but make it quite cumbersome for practical application.

Alternative macroscopic treatments

The simplest alternative approach (ref.26) relies on the more direct link which may be expected to exist between excess solubility and the excess free energy of the polymer $G_{BG}^{\circ}-G_{BL}^{\circ}$ (where the subscripts G and L denote, as before, the actual and corresponding presumed equilibrium state of the glassy polymer respectively). The latter may be analysed into its enthalpic and entropic parts, which can, in turn, be evaluated in terms of T_g , on the basis of Fig. 1a. Assuming constant polymer heat capacity c_p above and below T_g , the result is

$$G_{BG}^{\circ}-G_{BL}^{\circ}=(H_{BG}^{\circ}-H_{BL}^{\circ})-T(S_{BG}^{\circ}-S_{BL}^{\circ})=\Delta c_p[(T-T_g)-T\ln(T/T_g)] \quad (10)$$

In ref.26, G_{BG}° is considered to vary with C_A in accordance with $T_g(C_A)$. This is interpreted physically as a "structural change" of the pure glassy component B, which ends at the point where B assumes the rubbery structure ($G_{BG}^{\circ}=G_{BL}^{\circ}$ for $C_A \geq C_{Ag}$ at the given T) and leads directly to an excess chemical potential for A in the glassy solution, on the basis of equation (10), namely

$$\begin{aligned} \mu_{AG}-\mu_{AL} &= RT\ln(a_{AG}/a_{AL}) = \partial(G_{BG}^{\circ}-G_{BL}^{\circ})/\partial n_A = \Delta c_p(T_g-T)\partial \ln T_g/\partial n_A \\ &= (\Delta c_p/r_M n_B)(T_g-T)(\partial \ln T_g/\partial C_A') \end{aligned} \quad (11)$$

where n denotes number of moles; $C_A' = n_A/n_B r_M$; and $\partial G_{BL}^{\circ}/\partial n_A = 0$. Swelling behavior is described in terms of the analogous expression for $\bar{V}_{AG}-\bar{V}_{AL}$ based on equation (8). Equation (11) provides a correlation between excess solubility ($S_{PA}/S_{PAL} \approx a_{AL}/a_{AG}$, where a_{AL} , S_{PAL} are determined by extrapolation from the rubbery state) and $T_g(C_A)$ data.

A complete theory for a_{AG} (and hence $S_{PA} \approx C_A/a_{AG} P_{AO}$) should, of course, include appropriate treatments for a_{AL} and $T_g(C_A)$. In ref.26, equations (2) and (9) respectively have been used for this purpose and the experimental polycarbonate(PC)-CO₂ (308K) data of ref.27 (up to $a_{AG} \approx 0.3$) were fitted successfully, using $\chi_A = 1.75$ and $z = 2$. However, both this result and the ensuing claim that this approach may be considered a satisfactory quantitative theory for a_{AG} , should be viewed with caution. On one hand, the use of regular solution theory imposes significant limitations in this respect, which have already been discussed, and estimates of χ_A for this particular system vary rather widely (cf. refs 28,29). On the other hand, the physical basis of equation (9) is obscure. As far as one can see, the reasoning given in ref.24 for this purpose effectively reduces to the assumption that the polymeric medium attains the glassy state when the configurational entropy approaches some universal low value ("configurational isentropic state" principle analogous to the well-known "iso-free volume" principle). The effect of an added solute is represented solely as an increase in the configurational entropy which determines T_g equal to the combinatorial entropy of mixing ΔS_M (represented by BF in Fig. 1b). Taking into account also the corresponding thermal entropy increment (BB' in Fig. 1b), there results a shift of the glass transition point from B to E in Fig. 1b. It follows that

$$\ln[T_g(C_A)/T_g(0)] = -\Delta S_M/\Delta c_p \quad (12)$$

Elimination of $T_g(C_A)$ between equations (11) and (12) yields

$$\mu_{AG}-\mu_{AL} = RT\ln(a_{AG}/a_{AL}) = [T-T_g(0)\exp(-\Delta S_M/\Delta c_p)]\Delta \bar{S}_{MA} \quad (13)$$

where ΔS_M and $\Delta \bar{S}_{MA} = \partial(\Delta S_M)/\partial n_A$ should obviously be evaluated in a

manner consistent with that used for a_{AL} . According to the regular solution approach of equations (2) and (3)

$$\Delta S_M = -R(n_A \ln v_A + n_B \ln v_B); \quad \Delta \bar{S}_{MA} = -R(\ln v_A + v_B) \quad (14a, b)$$

In this manner, a physically acceptable treatment of excess solubility, consisting of equations (13) and (14) and requiring knowledge of pure polymer properties only, namely $T_g(0)$ and Δc_p , can be put forward. Its derivation is, however, subject to drastic assumptions and aspirations of quantitative applicability can, therefore, hardly be entertained [as illustrated by a test of equations (12) and (13) against a set of experimental $T_g(C_A)$ data in Fig. 2b]. On the other hand, the derivation of equation (9) in ref.24 is based on what seems to us an inappropriate combinatorial entropy expression; while the appearance and actual meaning of the "lattice coordination number" z therein is unexplained. Note that the normal lattice coordination number (which cannot, of course, properly assume values as low as 1 or 2) appears only in the correction terms which arise in equations (14) in a more rigorous solution of the Flory-Huggins lattice model (ref.8). Thus, failing a proper physical basis, equation (9) must be regarded as purely empirical. In this capacity, it can often provide a useful analytical representation of $T_g(C_A)$ data (after proper adjustment of z), as illustrated in refs 24,25 and in Fig. 2b (but see also ref.30). Its application in ref.26 is, therefore, justified in this sense and only to the extent that it

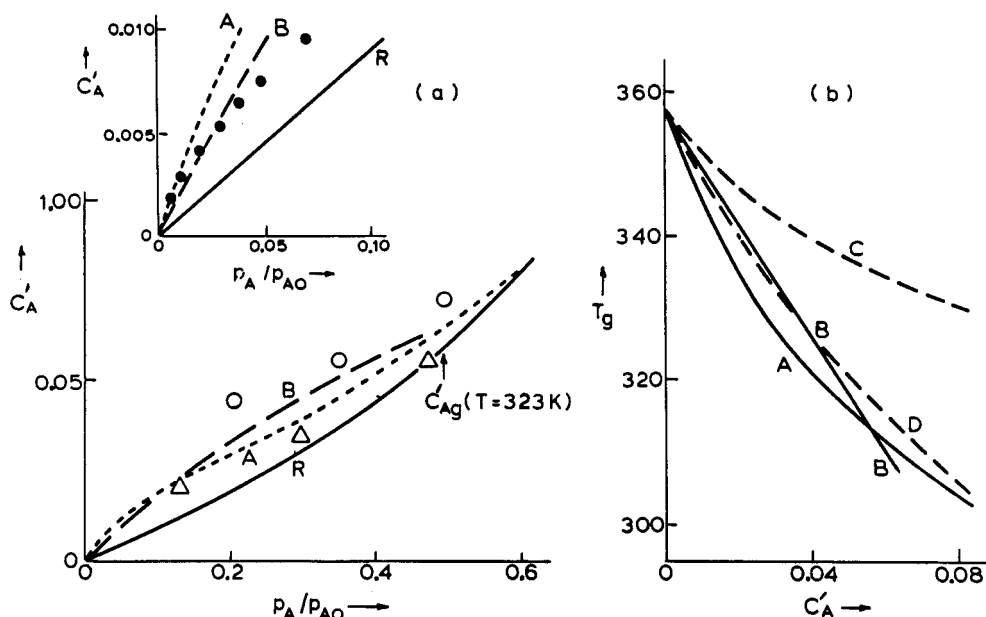


Fig. 2. (a) Apparent solubility of vinyl chloride (VC) in polyvinyl chloride (PVC) powder (C_A' in mol A per mol B monomer units) at 303K (o) or 323K (Δ) for equilibration times of several hours (refs 20,21). Inset: VC in PVC microspheres at 303K (\bullet) for 30s equilibration times (ref.21). Curves calculated for the rubbery state (R) by equation (2) with $\chi_A=0.98$ (as indicated in ref.20) and for the glassy state at 303K (A, B) by equation (11), with $T_g(C_A')$ as given by lines A, B of Fig. 2b respectively. (b) Composition dependence of T_g for PVC-VC: line A corresponds to the C_{Ag} values determined in ref. 21 (one example only is shown in Fig.2a); line B corresponds to that given in ref.21 as representative of all T_g data shown therein; line C calculated by equations (13) and (14); line D calculated by equation (9) with $z=2$.

can actually fit the relevant data (for the PC-CO₂ system under consideration, only one experimental T_g value is available for C_A>0; the value of z=2 does not, incidentally, produce a very close fit, see ref. 25). One should, finally, constantly keep in mind the well-known history dependence and continuing slow relaxation or drift of the thermodynamic properties of glassy materials, which are reflected in solubility properties in the form of conditioning, ageing and hysteretic effects. As pointed out in ref.26, proper application of equation (11) presupposes a particular experimental protocol (namely mixing the solute with polymer in the rubbery state and then cooling to the experimental temperature and measuring a_{AG}), which is not in keeping with normal experimental practice.

The foregoing discussion indicates that (a) it is certainly overoptimistic to expect, at this early stage, a full quantitative theory for a_{AG} on the above lines and (b) considerable further experimental evidence is required for an informed assessment of the performance of equation (11) as it stands. With respect to (b), the extensive data reported in refs 20 and 21 on the polyvinyl chloride (PVC)-vinyl chloride (VC) system (cf. Fig. 2) are of considerable interest. On one hand, this system is very nearly athermal. Thus, by measuring solubilities over a wide temperature and composition range, rubbery state behavior (curve R in Fig. 2a) can be defined reasonably unambiguously (ref.20). On the other hand, T_g(C_A) data are available both from solubility (curve A in Fig. 2b) and from other measurements (the overall representative line given in ref.21 is shown as line B in Fig. 2b). Finally, relaxation (ageing) effects were put in evidence by varying the equilibration time from 30s (using PVC microspheres small enough to ensure attainment of diffusion equilibrium; see points in inset of Fig. 2a) to several hours (points in main Fig. 2a). At the latter stage, significant relaxation may still be occurring but the relevant solubilities (white circles) already lie well beyond the calculated curves A, B [these curves, incidentally illustrate the sensitivity of the calculated excess solubility to the functional form of T_g(C_A)]. The picture of the performance of equation (11) which emerges from Fig. 2a is, thus, distinctly more pessimistic, but probably more realistic (considering the simplicity of the treatment), than that implied in ref.26.

In a more restricted approach proposed in ref.29, excess solubility is essentially described in terms of the associated swelling of the polymer. The difference between rubbery and glassy states is considered to be embodied in (a) a lower value of \bar{V}_A in the latter ($\bar{V}_{AG} < \bar{V}_{AL}$), while the excess free volume is being "filled" and (b) a much higher elastic modulus in the latter. Because of (b), an elastic deformation term (which is deemed negligible in μ_{AL}) appears in μ_{AG} . The essential (somewhat simplified) final result, based on equation (4), is

$$\ln(S_{PA}/S_{PAL}) = \ln(\bar{V}_{AL}/\bar{V}_{AG}) - (1+2\chi_A)(\bar{V}_{AL}-\bar{V}_{AG})C_A - (B_0\bar{V}_{AG}^2/RT)C_A' \quad (15)$$

where B₀ is the bulk modulus of the glassy polymer and small C_A and degrees of swelling are assumed. In ref.25, the equivalent of equations (4) and (15) was used to fit the PC-CO₂ data of ref.27, using χ_A as an adjustable parameter (the resulting value of 0.16 is close to that given in ref.28 but much lower than that used in ref.26, v.s). Different fixed values of \bar{V}_{AG} (consistent, as far as possible, with the corresponding dilatometric data of ref.27) were used to fit the low-and higher-pressure solubility data, with considerable, but still only partial, success. In this application, the decline of S_{PA} with increasing C_A is described exclusively by the last term with constant B₀, whereas in reality both \bar{V}_{AG} and B₀ also vary with C_A.

A semiempirical approach which leads to a description of the functional form of S_{PA}(C_A)/S_{PA}(0), on the basis of T_g(C_A) and an adjustable constant, has also been proposed (ref. 31).

Molecular (lattice) treatments

Molecular treatments of excess solubility can be developed on the basis of lattice models of the type currently applied to the rubbery state, by devising ways of representing the glassy state in terms of one or more model parameters ("order parameters"). A parameter suitable for this purpose is the fractional free volume v_f . In ref.30, v_f is assumed to remain frozen in the glassy state at the value attained at T_g (denoted by v_{fg}). The basic model used is that of Panayiotou and Vefa (PV, see ref.32); which was chosen in preference to the simpler SL model, because it incorporates one more possible order parameter, namely the number of polymer segment-to-segment contacts per molecule. However, freezing the latter parameter turned out not to yield realistic results. The PV model uses two parameters to characterize the solution (against one, or none if the form of the SL model presented here is adopted), which are determined by fitting the solubility data in the rubbery region. The equilibrium values C_{AL} and v_{fL} corresponding to any p_A at a given T can then be evaluated. The calculation corresponding to $C_A=C_{Ag}$ yields the value of v_{fg} . For values of p_A which result in $C_{AL}<C_{Ag}$ (glassy state), the calculation is repeated using $v_f=v_{fg}$ to obtain the predicted glassy-state solubilities C_{AG} (and hence $S_{PA}=C_{AG}/p_A$). Comparison with experimental results (even with some ad hoc readjustment of the PV solution parameters) shows that the treatment is only partially successful. This is true also as far as prediction of glassy-state volumetric (swelling) behavior is concerned. The fact that the assumption of frozen v_f is a gross one is also indicated by the prediction of $V_G(T)=\text{const}$ for the pure glass (corresponding to a horizontal BC line in Fig. 1a).

In ref.33, v_f in the glassy state is allowed to vary in the manner required to fit the volumetric data. If this modification were introduced in the foregoing treatment, the defect just noted would obviously be largely corrected, at the (equally evident) expense of reducing it to a correlation of solubility and swelling data (as in the treatment of ref.29 discussed above). However, the strategy followed in ref.33 is quite different. Apart from an extrapolation of the $V(T>T_g)$ line of the pure polymer (AB in Fig. 1a) to $T=0$ to determine v_f at $C_A=0$, there is no reliance on rubbery state properties. This has the effect of further limiting the treatment to (a) a description of the functional form of $S_{PA}(C_A)/S_{PA}(0)$ only and (b) use of the polymer segment-to-segment energy interaction parameter as an adjustable constant. The value obtained for this parameter by fitting PC-CO₂ and PC-CH₄ data is admittedly reasonable. On the other hand, the fitted $S_{PA}(0)$ values turn out to be much lower than those commonly accepted.

CONCLUSION

As indicated above, modelling of varying degree of complexity is required to deal with different aspects of solubility properties. In rubbery polymers a reasonable picture of relative solubility can be obtained from regular solution theory. To treat absolute solubility, individual pure solvent and solute properties should be taken into account. The resulting more refined models also permit a reasonably realistic representation of volumetric behavior. The natural extension of this approach to glassy polymeric solvents is to seek a description of excess solubility in terms of the excess thermodynamic properties of the pure polymer. Substantial progress along these lines has been made on the basis of the dual mode sorption model, but the possibility of alternative simpler and/or more fundamental treatments clearly exists. The most significant new lines of approach seem to be those initiated in refs 26 and 30. These treatments have the capability of modelling both solubility and volumetric behavior on the basis of $T_g(C_A)$ data or an adequate theory for $T_g(C_A)$. In fact, the establishment of an adequate single theoretical framework for the treatment of solubility, volumetric and T_g behavior, should be an important objective of further modelling efforts in this field.

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