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SURFACE TENSION AND THE SOLUBILITY OF POLYMERS AND BIOPOLYMERS: THE ROLE OF POLAR AND APOLAR INTERFACIAL FREE ENERGIES

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ABSTRACT

Surface tension data can be used for estimating the solubility of polymers in liquids. By determining the apolar and the polar components of the surface tension of polymers and of solvents, the attractive free energy, ΔG_{121}, of a polymer (1) in a given solvent (2) can be established. By also taking into account the contactable surface area of two polymer molecules, immersed in a liquid, ΔG_{121} can be expressed in units of kT. Solubility then is favored when $-1.5\text{ kT} < \Delta G_{121} < 0$ for apolar systems, and when $-1.5\text{ kT} < \Delta G_{121}$ for polar systems. In polar solvents, hydrogen bonding can often increase ΔG_{121} from <-1.5 kT to $>+1.5$ kT. Positive values are frequently attained and this strongly shifts the behavior from insolubility to solubility. A number of proteins exemplify this behavior.

INTRODUCTION

In polymer solubility studies, polar molecular interactions have been treated for a number of years as being comprehensible in the same terms, and with the same formalism, as apolar interactions. This is tacitly assumed in the Scatchard-Hildebrand theory [1], and, for polymers, by Flory [2] and Huggins [3]. (See also Prausnitz [4], Patterson [5], Hansen [6], and Barton [7]). It is also widely recognized that, for polar polymers that form hydrogen bonds, accurate and quantitative predictions of solubility from the molecular properties of the components are hard to come by.

It has been known for several decades that there is a close connection between solubility and surface tension. The earliest treatment of this connection that we have found was given in 1898 by Rhumbler [8] who credited Des Coudres with a discussion in terms of the energies of cohesion of separate components, together with the excess energy of adhesion of the two components. Hildebrand and Scott [1] reported an empirical correlation between the solubility parameter, δ, and surface tension, γ:

$$\delta \propto V^{-2/3}\gamma^{0.44} \cong V^{-2/3}\sqrt{\gamma}. \tag{1}$$

Good and Girifalco [9, 10] showed that the equation for the interfacial tension, γ_{12}, between *apolar* phases, 1 and 2,

$$\gamma_{12} = \gamma_1 + \gamma_2 - 2\sqrt{\gamma_1\gamma_2}, \tag{2}$$

can be put in the form

$$\gamma_{12} = (\sqrt{\gamma_1} - \sqrt{\gamma_2})^2. \tag{3}$$

Here, γ_1 and γ_2 are the surface tensions of pure phases 1 and 2. They pointed out [10] that the right side of Eq. (3) is closely analogous to the Hildebrand-Scatchard expression for the partial molar internal energy of mixing in regular solutions,

$$\overline{\Delta U}_i^m = \phi_j^2 V_i(\delta_i - \delta_j)^2, \tag{4}$$

where ϕ_j is the volume fraction of j, and V_i is the molar volume of component i.

Hildebrand and Scott apparently took it that molecules with appreciable dipole moments could be treated as forming regular solutions. They recognized, however, that when there were "specific interactions" between the components, the heat of mixing was not given by the regular solution approximation. (In this, they were, in effect, following the ideas of Des Coudres and Rhumbler.) They cited, in some detail, treatments of departures from Raoult's law that are due to compound formation.

Good and Girifalco [9] applied the regular-solution model [1] to interfaces. They used the premise that, ideally, the free energy of adhesion between phases 1 and 2 was the geometric mean of the free energies of cohesion of the separate phases. (This leads directly to Eqs. 2 and 3). They lumped departures from regularity into a correction factor, Φ, and wrote

$$\gamma_{12} = \gamma_1 + \gamma_2 - 2\Phi\sqrt{\gamma_1\gamma_2}. \tag{5}$$

The factor Φ took into account the fact that the two phases might be of different physical nature—for example, that one phase was apolar and the other polar.

It has recently been shown [11-13] that these tactics lead to predictions that are in serious disagreement with experiment when applied to interfacial tension problems in certain systems in which hydrogen bonds form. A new theoretical formalism has been proposed [11-14] which departs in an important way from the model that was used heretofore. The new theory both explains and predicts a number of surface phenomena. A start has already been made in the application of the new theory to certain questions of polymer solubility [15]. We will now review this approach and develop it in the direction of solubility questions.

Fowkes [16, 17] suggested the resolution of surface tension into components in a series of terms that corresponded to the various components of intermolecular force. Fowkes' leading term corresponded to the London "dispersion" force; he called it γ^d. He wrote,

$$\gamma = \gamma^d + \gamma^i + \gamma^p + \gamma^h + \cdots, \tag{6}$$

where i refers to the induction (Debye) force, p to the dipole-dipole (Keesom) force, and h to hydrogen bonding. It was recognized from very early on that γ^i could generally be neglected. Fowkes has, more recently [18], concluded that the dipole-dipole component, as calculated by the Keesom theory, had been an overestimate for interfaces between condensed phases, and thus γ^p is generally negligible. Chaudhury and the present authors [12-15, 19, 20] have shown that the first three terms on the right in Eq. (6) should be incorporated into a single term, γ^{LW}:

$$\gamma^{LW} = \gamma^d + \gamma^i + \gamma^p, \tag{7}$$

where LW refers to "Lifshitz-van der Waals." It was also shown [19, 20] that γ^p is small because of the tendency toward mutual cancellation of fields due to dipoles *in a condensed phase.* This mutual cancellation of dipole fields also takes place in solutions that are not too dilute. Fowkes [18] pointed out that the γ^h term could be treated as an acid-base interaction, so that (in our notation)

$$\gamma = \gamma^{LW} + \gamma^{AB}, \tag{8}$$

where the superscript AB refers to "acid-base."

The present authors [11, 13, 14, 19] have taken into account the intrinsic asymmetry (or complementarity) of the contributions of the two molecules that enter into an acid-base or hydrogen-bond interaction. They showed that, while expressions for γ^{LW} that are formally identical to Eqs. (2) and (3) can be written,

$$\gamma_{12}{}^{LW} = \gamma_1{}^{LW} + \gamma_2{}^{LW} - 2\sqrt{\gamma^{LW}\gamma_2{}^{LW}} = (\sqrt{\gamma_1{}^{LW}} - \sqrt{\gamma_2{}^{LW}})^2, \tag{9}$$

the same is not true of $\gamma_{12}{}^{AB}$. We will furnish, below, a different form that is appropriate for systems that undergo acid-base or hydrogen-bonding interactions in solution [11, 13]. It contains parameters that will separate and quantify the properties that correspond to generalized acid and generalized base behavior.

An important thermodynamic property in a binary system is ΔG_{121}. This is the free energy change per unit area for the process in which, say, molecules of 1 (the polymer) are initially present in phase 2, with an effectively infinite layer of phase 2 separating two surfaces of phase 1. In the process, two surfaces of 1 are brought together seamlessly.

$$\Delta G_{121} = -2\gamma_{12}. \tag{10}$$

If ΔG_{121} is positive, then molecules of 1 will repel each other in liquid 2, and substance 1 will spontaneously disperse or dissolve in 2. If ΔG_{121} is negative, then, at equilibrium, molecules of polymer 1 in solution will attract each other, and so will tend to precipitate from solvent 2. And if ΔG_{121} lies between zero and -1.5 kT, the mean thermal energy per kinetic unit in the system will cause segments of the polymer molecule that meet in a dilute solution to separate again. Hence, $\Delta G_{121} > -1.5$ kT is a general condition for solubility or dispersibility of the polymer. This qualitative criterior is closely analogous to the Hildebrand and Scott criterion [1] for miscibility vs immiscibility of low molecular weight liquids.

The empirically based Flory-Huggins approach [2] to the estimation of the thermodynamic properties of polymer solutions has had some success in correlating the solubility of polymers in various solvents. However, the crucial empirical interaction parameter, χ, employed in that approach, must be determined from the solute activity in dilute solution in the solvent. The parameter χ is not known in advance, before any solution of the polymer in the solvent has been prepared. Thus, there is a need for a theory by which the interaction of a polymeric solute and a solvent can be estimated from experimental data other than the properties of the solutions themselves.

Since Eq. (10) provides an approach to the prediction of solubilities, it remains only to obtain values of γ_{12}. But accurate values of this property cannot be general be measured *directly* for systems in which mutual solubilities are appreciable.

Recently, however, a rigorous characterization of the relation between polar, electron-acceptor and electron-donor, surface tension parameters, and the polar interfacial tension component was proposed by van Oss et al. [11-14]. This concept had been presaged by Small [21]. This opened the way to the determination of the total interfacial tension, and thus of the total interfacial free energy, of polar as well as apolar systems. The new approach makes it possible to treat hydrogen bonding in solution and to predict solubilities of both apolar and polar amorphous polymers in polar as well as apolar solvents from the surface tension properties and the molecular dimensions of the pure polymer and the pure solvent.

THEORY

It can be demonstrated via the Lifshitz approach [22-24] that all three electrodynamic van der Waals interactions (London, as well as Debye and Keesom) should be treated in the same manner. Indeed, all three follow, on a macroscopic scale, the form of the Hamaker equation [25] for the free energy of attraction between two semi-infinite slabe of substance *i in vacuo* at separation l:

$$\Delta G_{ii} = -A_{ii}/12\pi l^2. \tag{11a}$$

The free energy of attraction of two bodies of 1, in liquid 2, is [26]

$$\Delta G_{121} = -A_{121}/12\pi l^2. \tag{11b}$$

The free energy of cohesion is related to surface tension by

$$\Delta G_{ii} = -2\gamma_i. \tag{12}$$

The parameter A_{ii} is referred to as the Hamaker constant of material *i*. The free energy of cohesion of a material is the sum of an LW component and an AB component:

$$\Delta G^{\mathrm{TOT}} = \Delta G^{\mathrm{LW}} + \Delta G^{\mathrm{AB}}. \tag{13}$$

Hence, from Eqs. (8), (12), and (13):

$$\gamma_i = \gamma_i^{\mathrm{LW}} + \gamma_i^{\mathrm{AB}}, \tag{8a}$$

$$\Delta G_{121}{}^{\mathrm{LW}} = -2\gamma_{12}{}^{\mathrm{LW}}, \tag{10a}$$

$$\Delta G_{121}{}^{\mathrm{AB}} = -2\gamma_{12}{}^{\mathrm{AB}}. \tag{10b}$$

We neglect here, for the present purposes, the electrostatic interaction, ΔG^{EL}. Van Oss et al. [27] have shown that the electrostatic potential of many biopolymers rarely plays a preponderant role in their solubility in water.

Apolar Systems

The interaction between two molecules of polymer 1, immersed in liquid 2, is described by Eq. (10); and, for apolar systems, $\gamma_{12}{}^{\mathrm{LW}}$ is expressed by Eq. (9). The sign and value of $\Delta G_{121}{}^{\mathrm{LW}}$ for any system can thus be determined in all cases where $\gamma_1{}^{\mathrm{LW}}$ and $\gamma_2{}^{\mathrm{LW}}$ are known. For solids, $\gamma_{\mathrm{S}}{}^{\mathrm{LW}}$ can be determined by contact-angle (θ) measurement with an apolar liquid of known surface tension, $\gamma_{\mathrm{L}}{}^{\mathrm{LW}}$, using the Young-Good-Girifalco-Fowkes equation:

$$\gamma_{\mathrm{S}}{}^{\mathrm{LW}} = \frac{\gamma_{\mathrm{L}}{}^{\mathrm{LW}}(1 + \cos\theta)^2}{4} \tag{14}$$

(We neglect the equilibrium spreading pressure, π_e [28]. However, a more general form, including π_e explicitly, is available [9].) For polar liquids, $\gamma_{\mathrm{L}}{}^{\mathrm{LW}}$ can be evaluated by means of contact-angle determination on a known apolar solid (e.g., Teflon, with $\gamma_{\mathrm{S}} = \gamma_{\mathrm{S}}{}^{\mathrm{LW}} \cong 18\ \mathrm{mJ/m^2}$) according to

$$\gamma_{\mathrm{L}}{}^{\mathrm{LW}} = \frac{4\gamma_{\mathrm{S}}{}^{\mathrm{LW}}}{(1 + \cos\theta)^2} \tag{15}$$

If the liquid is apolar, or, more precisely, when there is no polar contribution to the liquid's energy of cohesion, then $\gamma_L^{LW} = \gamma_L$, the total surface tension. Of course, for a contact-angle measurement to be carried out, γ_L must be larger than γ_S^{LW}, so that the liquid will not spread with zero contact angle [29].

Polar Systems

Equation (10) also describes the total interaction between polar polymer molecules, 1, immersed in a polar liquid, 2; but the polar component of the interfacial tensions cannot be described by any equation of the form of Eq. (9). It must be stressed, of course, that no substance is *completely* polar; all compounds are subject to apolar interactions, such as the London force, but polar compounds, in addition, may take part in hydrogen bonding, which may also be described as electron donor-electron acceptor (or proton acceptor-proton donor) interactions.

The electron acceptor parameter of the surface tension of a substance *i* is designated as γ_i^+, and the electron-donor parameter of its surface tension as γ_i^-. (Refs. 11-14 give a detailed explanation of these parameters.) The polar (Lewis acid-base, or AB) component of the surface tension of polar substance *i*, then, is

$$\gamma_i^{AB} = 2\sqrt{\gamma_i^+\gamma_i^-}. \tag{16}$$

If one of these parameters is negligibly small, and the other parameter rather large, the substances may be called "monopolar" [11]. With a monopolar substance *i*, either γ_i^+ or γ_i^- is small enough so that

$$\sqrt{\gamma_i^+\gamma_i^-} << \gamma_i^{LW}. \tag{17}$$

The polar component of the interfacial free energy between substances 1 and 2 is [11-14]

$$\Delta_{12}^{AB} = -2(\sqrt{\gamma_1^+\gamma_2^-} + \sqrt{\gamma_1^-\gamma_2^+}). \tag{18}$$

The interfacial tension between substances 1 and 2 then may be expressed as

$$\gamma_{12}^{AB} = 2(\sqrt{\gamma_1^+\gamma_1^-} + \sqrt{\gamma_2^+\gamma_2^-}) - (\sqrt{\gamma_1^+\gamma_2^-} - \sqrt{\gamma_1^-\gamma_2^+}), \tag{19}$$

or as

$$\gamma_{12}{}^{AB} = 2(\sqrt{\gamma_1{}^+} - \sqrt{\gamma_2{}^+})(\sqrt{\gamma_1{}^-} - \sqrt{\gamma_2{}^-}). \tag{20}$$

The form of Eq. (20) stands in contrast to that of Eq. (9). It is clear from Eq. (20) that $\gamma_{12}{}^{AB}$ will be negative when

$$\gamma_1{}^+ > \gamma_2{}^+ \quad \text{and} \quad \gamma_1{}^- < \gamma_2{}^-,$$

and also when

$$\gamma_1{}^+ < \gamma_2{}^+ \quad \text{and} \quad \gamma_1{}^- < \gamma_2{}^-.$$

In view of Eqs. (8), (9), and (19), the total interfacial tension between substances 1 and 2 is described and predicted by

$$\gamma_{12} = (\sqrt{\gamma_1{}^{LW}} - \sqrt{\gamma_2{}^{LW}})^2 + 2(\sqrt{\gamma_1{}^+} - \sqrt{\gamma_2{}^+})(\sqrt{\gamma_1{}^-} - \sqrt{\gamma_2{}^-}). \tag{21}$$

By using Eqs. (10) and (19), the total interaction between polar polymer molecules, 1, immersed in polar liquid 2, can be expressed as

$$\Delta_{121}^{TOT} = -2(\sqrt{\gamma_1{}^{LW}} - \sqrt{\gamma_2{}^{LW}})^2 - 4(\sqrt{\gamma_1{}^+\gamma_1{}^-} + \sqrt{\gamma_2{}^+\gamma_2{}^-} - \sqrt{\gamma_1{}^+\gamma_2{}^-} - \sqrt{\gamma_1{}^-\gamma_2{}^+}). \tag{22}$$

The complete contact-angle equation for polar systems then becomes

$$(1 + \cos\theta)\gamma_L = 2(\sqrt{\gamma_S{}^{LW}\gamma_L{}^{LW}} + \sqrt{\gamma_S{}^+\gamma_L{}^-} + \sqrt{\gamma_S{}^-\gamma_L{}^+}). \tag{23}$$

It can be seen from Eq. (23) that, for a particular solid S, the three parameters $\gamma_S{}^{LW}$, $\gamma_S{}^+$, and $\gamma_S{}^-$ can be determined by measurement of the contact angles of three liquids which have been characterized for their $\gamma_L{}^{LW}$, $\gamma_L{}^+$, and $\gamma_L{}^-$ properties.

It may also be noted that, for any given solid/liquid system, Young's equation,

$$\gamma_{SL} = \gamma_S - \gamma_L \cos\theta, \tag{24}$$

is always true. Since the value of γ_L is readily measurable, the ease of obtaining γ_{SL} directly via Eq. (24) hinges on the determination of γ_S. To make this determination, we may use

$$\gamma_S = \gamma_S^{LW} + 2\sqrt{\gamma_S^+\gamma_S^-}, \tag{25}$$

which can be obtained from Eqs.(8) and (16). Thus, to determine γ_S, it remains necessary to make at least three contact-angle determinations (with three different liquids) in order to use Eq. (23). However, once γ_S has been determined via Eq. (25), there is some advantage to obtaining γ_{SL} from Eq. (24) via contact angle determinations with the same liquid L in which the solubility of a given solid S is being studied. This is especially true of very polar systems.

It is clear, on comparing Eq. (21) with Eq. (8), that an important difference between polar and apolar systems is that γ_{12} can be negative in polar systems, while the lowest value that γ_{12} can attain in strictly apolar systems is zero. Thus, ΔG_{121}^{TOT} is always negative, or zero in apolar systems. Hence, the value of ΔG_{121}^{TOT} must be no more negative than -1.5 kT to achieve solubility in apolar systems. (See above.)

On the other hand, the range of conditions which permit solubility in polar systems is much wider: solubility will prevail not only when ΔG_{121}^{TOT} has values between -1.5 kT and zero, but also for all the positive values of ΔG_{121}^{TOT} that can exist, and hydrogen bonding may lead to just such positive values. This is probably the reason why there exists such a vast array of biopolymers that are soluble in water.

EXPERIMENTAL

Advancing contact angles were measured at 20°C on various solids by the captive-drop method with Gilmont Teflon syringes and a Gaertner goniometer attached to a Gaertner X-Y traveling microscope fixed to an optical bench. The liquids used for the contact angle measurements on polymer surfaces are characterized in Table 1 as to their γ_L^{LW}, γ_L^+, and γ_L^- values. Table 2 gives the corresponding characteristics for other solvents used in this work. Contact angles found with the liquids listed in Table 1 for the various solids are given in Table 3A. The surface tension parameters derived for the various solids from data in Table 3A are given in Table 3B. These were determined by two methods: a) Contact-angle measurements were made on flat, smooth layers of the polymer in question, obtained by depositing a solution of the polymer or biopolymer in an appropriate solvent on a glass slide and allowing the solvent to evaporate; b) contact-angle measurements were made on hydrated proteins, by preparing thick layers of concentrated protein, dissolved in water and further concentrated upon anisotropic cellulose acetate membranes which are impermeable to the dissolved protein mole-

TABLE 1. Surface-Tension Parameters of Liquids Used in Contact Angle Determinations (in mJ/m^2)

Liquid	γ	γ^{LW}	γ^+	γ^-
Water	72.8[a]	21.8[b]	25.5[c]	25.5[c]
Diiodomethane	50.8[d]	50.8	0[e]	0[e]
α-Bromonaphthalene	44.4[a]	43.6	0[e]	0[e]
Glycerol	64[a]	34[d]	3.92[f]	57.4[f]
Formamide	58[a]	39[d]	2.28[f]	39.6[f]

[a] Reference 38.

[b] Reference 17.

[c] These values are used as reference values, they are not known as absolute quantities. The assumption of specific values may be obviated by using known γ_1^+/γ_2^+ and γ_1^-/γ_2^- ratios; then by the use of these (known) ratios, γ_{12}^{AB} and ΔG^{AB} can be obtained. These operational values are, then, *not* dependent on any assumption, and they are the same as those obtained with the above reference assumption. However, in order to express γ^+ and γ^- values in SI units, the assumption of a γ^+/γ^- ratio for water remains necessary, and all γ^+ and γ^+ values given here and in the following tables are based on the above reference values for water [11-14].

[d] Reference 24.

[e] These values may not be exactly equal to zero (see the interfacial tensions of these liquids with water, given in Ref. 9), but for all practical purposes they may be neglected.

[f] From Ref. 39.

cules [30, 31]. The solubility was determined qualitatively by visual observation; swelling was determined by microscopic inspection.

RESULTS

Apolar Interactions

Polyisobutylene (PIB), a typical apolar polymer, is soluble, inter alia, in decane, hexadecane, carbon tetrachloride, chloroform, tetrahydroguran, toluene, and benzene, Table 4 shows the ΔG_{121} values for PIB immersed in these solvents. As the interaction with these solvents is apolar, the ΔG_{121} values

TABLE 2. Surface-Tension Parameters of Solvents Used (in mJ/m^2)

Liquid	γ^a	γ^{LW}	γ^+	γ^-
Decane	23.8	23.8	0	0
Methyl ethyl ketone	24.6	24.6	0	24[b]
Carbon tetrachloride	26.8	26.8	0	0
Chloroform	27.3	27.3	3.8[b]	0
Tetrahydrofuran	27.4	27.4	0	15[b]
Hexadecane	27.5	27.5	0	0
Toluene	28.3	28.3	0	2.7
Benzene	28.9	28.9	0	2.3
Ethyl glycol	48	29[c]	3.0[d]	30.1[d]

[a] Reference 38.

[b] Reference 15.

[c] Reference 24.

[d] From the values found by contact-angle measurements on ethylene glycol-containing gels [40] adjusted to $\gamma_{EG}{}^{AB}$ = 19 mJ/m^2 [24].

can be obtained directly from Eq. (22) in which the γ^+ and γ^- terms are set equal to zero. The polar solvents in the list given above are monopolar, so their polar moieties neither contribute to their own cohesion, as pure liquids, nor do they interact with the apolar PIB. For PIB with α-bromonaphthalene, $\Delta G_{121} = -5.53$ mJ/m^2, and PIB is insoluble in this liquid.

Now, an estimate can be made of the attraction of two solute polymer chains for each other that is relevant to the question of whether the polymer will start to coil up or to precipitate. This is based on the free energy, ΔG_{121}, times the area of contact of two *crossed* chains.

For two chains at right angles to each other, the minimum effective area (which we may call the "contactable area," A_c) should be about 1 nm^2. Then $A_c \Delta G_{121} \approx -5.5 \times 10^{-21}$ J, which may be compared to -1.5 kT at 20°C, which is about -6×10^{-21} J. If, instead of two chains being crossed at right angles, they run parallel to each other for only about 4 or 5 carbon atoms in the chains, then A_c will be about 2 nm^2, and $A_c \Delta G_{121} \approx -11 \times 10^{-21}$ J. This energy is sufficiently large compared to kT that precipitation may be

TABLE 3A. Contact Angles Measured on Various Solid Polymer Surfaces

	Liquid					
Polymer	Diiodomethane	α-Bromonaphthalene	Water	Glycerol	Formamide	Hexadecane
Polyisobutylene		60°[a]				
Poly(methyl methacrylate)	40°[b]	13°[b]	72°[b]	65.5°[b]	53°[b]	
Polystyrene			91.4[c]			
Polyvinylpyrrolidone	30°	17°	56.6°	51.8°	49.5°	
Poly(ethylene glycol) 6000	18.3°[b]	11°[b]	21.5°[b]	43.5°[b]	25°[b]	
Dextran T-70	33.5°	23°	23°	33°		
Human serum albumin (with 2 layers of hydration			0°	14.5°[e]		13°[e]
Human serum albumin (dry)	37°[e]	23.2°[e]	65.3°[e]	59.5°[e]		
Gelatin	44°	32.5°	67°	66°	51°	
Zein	36°[f]	24°[f]	64°[f]	65°[f]	40°[f]	

[a] Reference 15.
[b] Reference 39.
[c] Reference 41.
[d] See Table 2.
[e] Reference 33.
[f] Reference 31.

TABLE 3B. Surface-Tension Parameters of Solid Polymers (in mJ/m^2)

Polymer	γ^{LW}[a]	γ^+	γ^-
Polyisobutylene	25[b]	0	0
Poly(methyl methacrylate)	41.9	0.02[c]	11.1[c]
Polystyrene	42[d]	0	1.1[e]
Polyvinylpyrrolidone	43.4	0	29.9[c]
Poly(ethylene glycol) 6000	43.5[b]	0.05[c]	57.6[c]
Dextran T-70	41.8	0.99[c]	47.2[c]
Human serum albumin (with 2 layers of hydration)	26.8[f]	6.0[c]	51.5[c]
Human serum albumin (dry)	41.0	0.13[c]	17.2[c]
Gelatin	37.6	0.013[c]	18.0[c]
Zein	41.1	0	18.3[g]

[a] From the average γ^{LW} values obtained with diiodomethane and α-bromonaphthalene contact angles.
[b] From θ of α-bromonaphthalene.
[c] From θ of H_2O and glycerol.
[d] Reference 42.
[e] Reference 41.
[f] From θ of hexadecane.
[g] From the average γ^- values obtained with water, glycerol, and formamide contact angles.

predicted. Thus, we explain the insolubility of PIB in α-bromonaphthalene. In water, PIB would have an $A_c\Delta G_{121}$ value of approximately -25 kT, corresponding to complete insolubility. In all the other solvents shown, the ΔG_{121} values vary from 0.003 to 0.30 mJ/m^2 and strongly favor solubility.

The cases of poly(methyl methacrylate) (PMMA) and polystyrene (PST) (see Table 4) appear somewhat more complex. Both PMMA and PST are soluble in the apolar solvent carbon tetrachloride. A contactable surface area of not more than about 1.2 nm^2 would, for both polymers, yield a value for $A_c\Delta G_{121}$ in carbon tetrachloride of about -0.9 to -1.0 kT, which may be still compatible with solubility. However, as shown by the insolubility of both

TABLE 4. Values of ΔG_{121}^{TOT} (in mJ/m^2) of Three Polymers for a Number of Solvents (from Eq. 22)

		Polymers					
Solvent	γ_L, mJ/m^2	PIB ($\gamma^{LW} = 25$)	Soluble	PMMA ($\gamma^{LW} = 41.9$)	Soluble	PST ($\gamma^{LW} = 42$)	Soluble
Decane	23.8	-0.03	+	-5.08	-	-5.13	-
Methyl ethyl ketone	24.6	-0.003	+	-4.58	+	-4.63	+
Carbon tetrachloride	26.8	-0.06	+	-3.36	+	-3.40	+
Chloroform	27.3	-0.10	+	+23.5	+	+4.78	+
Tetrahydrofuran	27.4	-0.11	+	-3.06	+	-3.11	+
Hexadecane	27.5	-0.12	+	-3.02	-	-3.06	-
Toluene	28.3	-0.20	+	-2.66	+	-2.70	+
Benzene	28.9	-0.28	+	-2.41	+	-2.44	+
α-Bromonaphthalene	44.4	-5.53	-	-0.07	±[a]	-0.07	+
Water	72.9	-102.22	-	-40.23	-	-87.83	-

[a] ± = slightly soluble.

TABLE 5. ΔG_{121} Values (in mJ/m^2)

	PMMA	Solubility	PST	Solubility
Methyl ethyl ketone	-0.62	+	+0.25	+
Tetrahydrofuran	-1.69	+	+0.46	+

[a] Recalculated for PMMA and PST in methyl ethyl ketone and tetrahydrofuran, taking into account putative values for γ^+ of 0.4 and 0.1 mJ/m^2 for PMMA and PST, respectively. For the γ^{LW} and γ^- values, see Tables 2 and 3B.

PMMA and PST in hexadecane, $A_c\Delta G_{121} \approx 0.9$ kT is clearly a borderline condition. A more curious phenomenon is the solubility of PMMA and of PST in methyl ethyl ketone (MEK) vs their insolubility in decane, although in both solvents $\Delta G_{121} \approx -1.3$ to -1.5 kT. The absolute values of ΔG_{121} of both polymers in decane are slightly higher than in MEK, but it seems unlikely, in the light of the insolubility of both polymers in hexadecane, that the cut-off lies precisely between these two solvents. What seems more likely is that the existence of a minute amount of electron-acceptor character in PMMA (which is difficult to determine with any precision with the array of liquids currently available for contact-angle measurements) would give rise to significantly lower ΔG_{121} values in monopolar electron-donor solvents, such as MEK and tetrahydrofuran. On the other hand, some electron-acceptor character might exist in the liquid, e.g., due to an enol form of MEK. Thus, assuming a hitherto neglected value of, e.g., $\gamma^+ \approx 0.1$ mJ/m^2 for PST and $\gamma^+ \approx 0.4$ mJ/m^2 for PMMA, one would obtain ΔG_{121} values for these polymers in MEK and in tetrahydrofuran that are much more compatible with the solubility of PMMA and PST in these two monopolar solvents (see Table 5).

To summarize, apolar polymer-solvent interactions correlate very well with ΔG_{121} found via surface tension data; and when in addition the polar polymer-solvent interactions are taken into account, the observed solubilities also correlate quite generally with ΔG_{121} for polar polymers.

The Miscibility of Polar Liquids

An extensive list of measured interfacial tensions between water and various (water-insoluble) organic liquids was compiled by Girifalco and Good [9]. Interestingly, in the alcohol series the cut-off between slight solubility and almost total insolubility in water appears to lie between *n*-hexanol and *n*-heptanol, for which ΔG_{121} values are -13.6 and -15.4 mJ/m^2, respectively. Taking the

TABLE 6. ΔG_{121} (in mJ/m^2) of a Number of Biopolymers and Strongly Polar Synthetic Polymers with Respect to Water (from Eqs. 10 and 24)

Polymer or biopolymer	ΔG_{121}	Solubility
Poly(ethylene glycol) 6000	+41.5	+
Dextran T-70	+23	+
Polyvinylpyrrolidone	-7.0	+[a]
Human serum albumin (with 2 layers of hydration)	+21.6	+
Human serum albumin (dry)	-23	-[b]
Gelatin	-20.3	-[c]
Zein	-18.4	-

[a] From contact angles of water and formamide and Eq. (22), $\Delta G_{121} = 0.09$.

[b] It is assumed that dry HSA is insoluble in water until it becomes hydrated.

[c] Soluble upon boiling but insoluble at 20°C. Boiled solutions gelled upon cooling.

contactable surface areas of such molecules to be of the order of 0.45 nm^2, one arrives again at $\Delta G_{121} \approx -6 \times 10^{-21}$ J/molecule pair, which is about -1.5 kT at the cut-off of miscibility. With completely miscible liquids, the interfacial tension (and thus ΔG_{121}) is not directly measurable, but it can be estimated from the values of the surface tension components and parameters of the liquids in question (see Tables 1 and 2). For instance, ΔG_{121} of water with respect to several polar solvents is: glycerol, +28.6 mJ/m^2; formamide, +12.7 mJ/m^2; ethylene glycol, +4.8 mJ/m^2. All of these values correlate well with the pronounced miscibility of these three solvents with water. It is clear that negative interfacial tensions (corresponding to positive ΔG_{121} values) are quite common and lead to high solubility or miscibility [15, 32].

Strongly Polar Interactions and the Influence of Polymer Solvation

In Table 6 it can be seen that positive values of ΔG_{121} occur quite commonly among biopolymers and highly polar synthetic polymers with water, and positive values of ΔG_{121} here correlate with pronounced solubility.

Gelatin, on the other hand, is insoluble in water at room temperature, and zein (a corn protein) is insoluble in water at any temperature. Curiously, human serum albumin (HSA), like other serum proteins [26, 31, 33], is initially insoluble in water when dry but becomes very soluble upon hydration. It is, indeed, typical of such proteins, when they are added to water as dry powders, that the dry particles first have to swell quite visibly before they undergo dissolution as a second step. However, their solubility, once hydrated, is very high. It is possible that freeze-dried HSA, which dissolves much more quickly in water than the air-dried material, has different surface properties from air-dried HSA. Since it is, unfortunately, not possible as yet to make a smooth, nonporous flat surface from freeze-dried proteins, no usable contact angles can be measured on freeze-dried materials. It is quite likely that air-drying causes a certain degree of denaturation in HSA, but in view of its unaltered properties on redissolution, that denaturation appears to be entirely reversible. It should be noted that even in aqueous solution, serum albumin denatures reversibly at the liquid-air surface (as well as at liquid-solid interfaces) as judged, for example, by its drastic lowering of the surface tension of water [34]. The inherent water-insolubility of dry proteins is also supported by the propensity of most proteins to undergo salting out [31] and by the possibility of precipitating them with the help of poly(ethylene glycol) [26, 35-37]. In both these cases, depletion of water of hydration plays an important role.

The polysaccharides studied here, on the other hand, do not appear to denature upon air-drying, and they are immediately soluble in water, even though the highest molecular weight material (dextran T-2000, with $\bar{M}_w$ 2 000 000) dissolves more slowly than the lower molecular weight polysaccharides [20].

Zein is a curious protein which is insoluble in water but soluble in formamide, ethylene glycol, and in a 70/30 (v/v) acetone/water mixture. The large negative ΔG_{121} of zein with water (see Table 3A) explains the low solubility in water. From the ΔG_{121} values, the solubility of zein in ethylene glycol would also be unexpected. It seems, however, that like HSA in water, zein becomes solvated in ethylene glycol and probably also in formamide. The solvation of zein in these solvents, unfortunately, is not easily directly measurable for practical reasons. Nevertheless, there is a strong indication for such an effect from the following observations: 10% solutions, which can be prepared in formamide and in ethylene glycol, precipitate upon the addition of water (approximately 45 vol% water added to a zein solution in formamide, and less than 3 vol% water added to a zein solution in ethylene glycol). Thus, the addition of a rather minute amount of water to solutions of zein in ethylene glycol causes insolubilization, which strongly hints at a displacement of a solvation layer of ethylene glycol by water, which then causes precipitation.

It may be mentioned that zein is less readily soluble in ethylene glycol than in formamide (see Table 7). The calculated value of $\Delta G_{Z\text{-}W\text{-}EG}$ (where Z stands for zein, W for water, and EG for ethylene glycol) is found to be +8.1 mJ/m^2, indicating that W tends to replace EG near the Z surface. Similarly, $\Delta G_{Z\text{-}EG\text{-}W}$ = -3.2 mJ/m^2, which also shows that W is more attracted to Z than EG. Thus, even though water hydrates zein to a rather feeble degree [26], this appears sufficient to break the solvation of zein by ethylene glycol and cause precipitation. The same thing happens with formamide (FO): $\Delta G_{Z\text{-}W\text{-}FO}$ = +11.0 mJ/m^2, while $\Delta G_{Z\text{-}FO\text{-}W}$ = -28.7 mJ/m^2. Thus, Z repels FO in the presence of water (like EG) and attracts water in FO (as it does in EG).

It would be expected that polyvinylpyrrolidone (see Table 6) should be fairly close to insoluble in water. However, from Eq. (22), ΔG_{121} for polyvinylpyrrolidone would have a value of +0.9 mJ/m^2. The clear advantage of using the approach of Eq. (22) is that the value of ΔG_{121} is obtained from contact angle measurements with several liquids, which minimizes certain errors through averaging.

DISCUSSION

If one can measure or estimate the approximate dimensions of a polymer molecule dissolved in a given solvent, the average contactable surface area, A_c, can be evaluated. Once the value of the interaction energy between polymer particles *y*, *vis-à-vis* a solvent *z* (ΔG_{yzy}), has been obtained, e.g., via Eq. (22), the total interaction energy, *X*, can be expressed as follows:

$$\chi = A_c \Delta G_{yzy}. \tag{26}$$

When A_c is expressed in cm^2 and ΔG_{yzy} in ergs/cm^2, χ must be divided by 4×10^{-14} to find the interaction energy in units of kT. Solubility is then favored for apolar interactions when

$$-1.5\ \mathrm{kT} < \chi < 0, \tag{27}$$

and for polar interactions when

$$-1.5\ \mathrm{kT} < \chi. \tag{28}$$

It thus becomes clear that the potentiality for solubility or miscibility in polar systems is vastly greater than in apolar systems. The reason for the

TABLE 7. Values of ΔG_{121}^{TOT} (in mJ/m^2) of Zein (from Eqs. 10 and 24)

Solvent	ΔG_{121}	Solubility
Water	-18.4	-
Ethylene glycol	-3.6	+
Formamide	+6.6	+

versatility of water as a strongly polar solvent for biopolymers becomes evident when it is realized that many biopolymers manifest a negative interfacial tension with water, which gives rise to a positive value for ΔG_{yzy} (see Table 6), especially when the biopolymers are hydrated. Solvation in nonaqueous polar solvents (as was found with formamide and ethylene glycol) probably is the mechanism of the solubility of the water-insoluble protein zein in these two solvents.

CONCLUSIONS

A theory of polymer solubility is presented based upon the dimensions of the polymer molecules and upon the interfacial free energies of the polymer vis-*à*-*vis* the solvent, determined from the surface tension data of the polymer and the solvent by taking into account the polar as well as the apolar surface tension components and parameters. The effect of solvation upon the interfacial free energy of a polymer *vis-à-vis* the solvent can be an important factor in the solubilization of certain biopolymers, and especially proteins.

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