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INTERFACIAL TENSION AND THE OSMOTIC PRESSURE OF SOLUTIONS OF POLAR POLYMERS

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ABSTRACT

It is shown that the Flory-Huggins χ_{12} parameter for a polymer, 1, with a solvent, 2, is proportional to the interfacial tension, γ_{12}, between the polymer and the solvent. In the case of polyethylene glycol (PEG) dissolved in water, the value of γ_{12} is strongly negative. It is shown that this condition gives rise

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to a sizable negative value of χ_{12}, which in turn engenders a strongly positive second virial coefficient of the osmotic pressure (Π) function. χ_{12} values calculated for the PEG–water system from surface tension data of PEG and of water allow the calculation of Π for aqueous solutions of PEG of up to 60% (w/v) for PEG of molecular weights of 150, 400, 6000, and 20 000. The results show an excellent correlation with the Π values earlier measured for these polymers by Arnold et al. and furnish an explanation for the unusual lack of dependence of Π on the polymer molecular weight and for the very high osmotic pressures observed with aqueous PEG and dextran solutions.

INTRODUCTION

It is well known that, while the solubility of apolar polymers in apolar solvents follows rules based on the Scatchard-Hildebrand [2] and Flory-Huggins [3, 4] solubility relations rather closely, the solubility of polar polymers in polar solvents is not as readily predictable. This is mainly because, as we have shown earlier [5], the form of the rules governing the energy of polar interactions is different from that pertaining to apolar interactions. We will, in this paper, investigate the energy rules that actually are applicable to polar systems, and demonstrate how they lead to valid predictions.

It has recently been observed that uncharged polar polymers, dissolved in water, manifest unusually high osmotic pressures, which are remarkably independent of molecular weight [1, 6]. While both the Flory χ and Hildebrand δ parameter are connected with solubility, χ also plays a role in the second virial coefficient of the expression for osmotic pressure [3, 4, 7–10]. χ is a dimensionless expression of the interaction energy between polymer and solvent molecules [3, 7, 10]. It will be shown here that χ can be estimated from the free energy of adhesion between polar polymer and solvent molecules, multiplied by the minimum contactable surface area between two polymer molecules. When this is done, a close correlation is obtained between the calculated and the observed osmotic pressures of polyethylene oxide molecules of different molecular weights, dissolved in water, over a wide range of concentrations [1].

THEORY

The theory of polar and apolar interfacial interaction energies, and their determination, has been given *in extenso* in earlier publications [5, 11, 12], and is only briefly reiterated here.

For the free energies of cohesion and of adhesion, we shall use the superscript LW to designate the Lifshitz-van der Waals (or apolar) component of free energy, and AB to designate the Lewis acid-base (or polar) component [11, 12]:

$$\Delta G = \Delta G^{\mathrm{LW}} + \Delta G^{\mathrm{AB}} \tag{1}$$

The free energies of cohesion ΔG_{11} and of adhesion ΔG_{12} are given by

$$\Delta G_{11} = -2\gamma_i \tag{2}$$

$$\Delta G_{12} = \gamma_{12} - \gamma_1 - \gamma_2 \tag{3}$$

where γ is the interfacial free energy or interfacial tension.

It may be noted that the customary thermodynamic way of treating adhesion, Eq. (3), is as the process of forming a (1,2) interface from a (1, vacuum) surface and a (2, vacuum) surface. Consequently, the sign of ΔG_{12} is the opposite of the sign in the conventionally defined [2, 3] energy of mixing, by means of which the χ parameter was defined [3].

It should also be noted that γ is expressed in units of *free energy* per unit area. Flory [3] pointed out that, in his earliest formulation, χ was defined in terms of total energy (or enthalpy) of mixing. But Flory [Ref. 3, p. 510] and others then reinterpreted it as also containing an entropic component, so that χ has the character of a free energy parameter. Hence, our identification of χ with free energy of adhesion and of interfacial free energy is consistent with the more advanced Flory view of the nature of χ.

From Eqs. (1) and (2), we obtain

$$\gamma_1 = \gamma_1^{\mathrm{LW}} + \gamma_1^{\mathrm{AB}} \tag{4}$$

In accordance with earlier work on electron donor-electron acceptor interactions [13], we have made the postulate, which has proved very fruitful, that for the interaction between two compounds, 1 and 2, which have the capacity for acid-base interaction with each other [11, 12],

$$\Delta G_{12}^{\mathrm{AB}} = -2\sqrt{\gamma_1^+\gamma_2^-}\quad 2\sqrt{\gamma_1^-\gamma_2^+} \tag{5}$$

$$\Delta G_{11}^{\mathrm{AB}} = -4\sqrt{\gamma_1^+\gamma_1^-} \tag{6}$$

from which we obtain the expression

$$\gamma_1^{\mathrm{AB}} = 2\sqrt{\gamma_1^+\gamma_1^-} \tag{7}$$

Here γ_i^+ is the electron-acceptor and γ_i^- is the electron-donor parameter of the polar, Lewis acid-base (or hydrogen bonding) surface tension component of substance *i*.

We now come to the thermodynamic function that is relevant to osmotic pressure in nonideal solutions. The free energy of interaction of two similar bodies of material 1 through liquid 2 is given by [5, 12, 14]

$$\Delta G_{121} = -2\gamma_{12} \qquad (8)$$

This is the free energy change for the process in which two bodies of material 1, immersed in liquid 2, are brought together in such a way that the liquid is excluded; see van Oss and Good [14] for a detailed discussion. This process is analogous to the (ideal) precipitation of a linear polymer from solution. The analogy is particularly close with regard to the attraction between polymer molecules due to hydrogen bonding or acid/base interaction. In such interactions, the functionality of an acidic or basic group is much smaller (e.g., 1 or 2) than in London dispersion force interactions, for which the coordination number, *z*, is in the range of 9 to 12. For a monopolar acid such as chloroform or a CHCl group in polyvinyl chloride, the functionality is 1. Far more common are cases where the functionality is 2, as with a hydroxyl group, which can act both as a proton donor and a proton acceptor [11].

If the functional groups on the polymer chain (1) are bipolar, and if the solvent (2) is bipolar, the equation for the free energy of interaction, corresponding to Eq. (8), is

$$\Delta G_{121} = -2\left(\sqrt{\gamma_1^{LW}} - \sqrt{\gamma_2^{LW}}\right)^2 - 4\left(\sqrt{\gamma_1^+\gamma_1^-} + \sqrt{\gamma_2^+\gamma_2^-} - \sqrt{\gamma_1^+\gamma_2^-} - \sqrt{\gamma_1^-\gamma_2^+}\right) \qquad (9)$$

It is interesting to note that the Lewis acid-base interaction shown in the four right-hand terms has been described earlier, in the same manner, by Small [15].

Values of the γ^+ and γ^- parameters have been reported for various substances [11]. These values are based on the reference parameters for water: *

$$\gamma_W^+ = \gamma_W^- = 25.5 \text{ mJ/m}^2 \qquad (10)$$

Finally, the interaction of two *different* bodies, or materials 1 and 2, through liquid 3, is represented by

$$\Delta G_{132} = -(\sqrt{\gamma_1^{LW}} - \sqrt{\gamma_2^{LW}})^2 - (\sqrt{\gamma_1^{LW}} - \sqrt{\gamma_3^{LW}})^2 - (\sqrt{\gamma_2^{LW}} - \sqrt{\gamma_3^{LW}})^2$$
$$+ 2\,[\sqrt{\gamma_3^+}(\sqrt{\gamma_1^-} + \sqrt{\gamma_2^-} - \sqrt{\gamma_3^-}) + \sqrt{\gamma_3^-}(\sqrt{\gamma_1^+} + \sqrt{\gamma_2^+} - \sqrt{\gamma_3^+}) - \sqrt{\gamma_1^+\gamma_2^-} + \sqrt{\gamma_1^-\gamma_2^+}] \quad (11)$$

Equations (9) and (11) describe interfacial ("hydrophobic") attractions when ΔG_{121} or $\Delta G_{132} < 0$, and interfacial ("hydration pressure") repulsions when ΔG_{121} or $\Delta G_{132} > 0$ [11, 12].

Table 1 gives some values of the components of γ for two polymers which will be treated later in this paper.

Now, the crucial step in establishing a chain-chain interaction which would be manifested as a departure from ideality of a polymer solution is the formation of molecular contact between a molecular segment in one chain and a segment in another chain. The chains need not lie parallel; and, indeed, they are likely to come together at an angle, especially when there is a net repulsion between them. Equations (8) and (9) give the thermodynamic description of this process. These equations are written in terms of energy per unit area, so we must multiply ΔG_{121} by an appropriate area to obtain the energy per contact. If the chain diameter is d_c, we can estimate the minimum area of effective contact as the projection of the overlap region when two chains cross at right angles, i.e., as d_c^2. This estimate is likely to be too large because polymer chains are better approximated as cylinders than as having rectangular cross sections. We may also make allowance for the frequency of nonright-angle intersections, and for such interactions the estimate, d_c^2, would be too small. We can thus make an estimate of what we will call the effective "minimum contactable surface area," S_c, as being about d_c^2. Then, for the purpose of estimating osmotic pressure, we equate the energy change in formation of area, S_c, of contact, divided by kT, to $-\chi$, to express the second virial coefficient of osmotic pressure:

$$\chi_{12} = -S_c\Delta G_{121}/kT \quad (12a)$$

or, see Eq. (8):

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*The absolute values of γ^+ and γ^- are not, at present, accessible to experiment. The situation, in this regard, is similar to that for potential energy: only *relative* values are operationally meaningful [11, 16, 17]. In electrochemistry, single-ion activity coefficients are recognized as being inaccessible; and the mean activity coefficient for the two ions in a salt, $\gamma_\pm = (\gamma_+\gamma_-)^{1/2}$, is universally used. Only values of γ^+ and γ^- that are relative to reference parameters, e.g., as defined by Eq. (10), can have any significance. The arbitrariness of the reference parameter assumption does *not* affect *operational* properties such as γ_1, γ_{12}, or free energy of cohesion or adhesion, ΔG [11, 16, 17].

TABLE 1. Surface Tension Parameters and Interfacial Interaction Energies of Polyethylene Glycol (PEG), Dextran T150, and Water, in mJ/m^2

	γ^{LW}	γ^+	γ^-
PEG	43[a]	0	64[a]
Dextran	42[a]	0	55.0[a]
Water	21.8[b]	25.5[c]	25.5[c]

Free energy of interaction between two PEG molecules immersed in water

ΔG_{121} = +51.2 mJ/m^2 (Eq. 9)

Free energy of interaction between a PEG and a dextran molecule immersed in water

ΔG_{132} = +45.9 mJ/m^2 (Eq. 11)

[a] From van Oss et al. [11].

[b] See F. M. Fowkes, *J. Phys. Chem.*, *67*, 2538 (1963).

[c] Standard value assumed for water; the assumption of this standard value permits the expression of γ^+ and γ^- of other compounds, but does not influence the values of γ_{12}, ΔG_{121}, or ΔG_{132} [11, 12].

$$\chi_{12} = 2S_c\gamma_{12}/kT \tag{12b}$$

The osmotic pressure of polymer (1) dissolved in water (2) can be expressed as [7, 8]

$$\Pi = RTc_1\left[\frac{1}{M_1} + B\frac{c_1}{d_1^2}(0.5 - \chi_{12}) + B\frac{c_1^2}{3d_1^3} + \ldots\right] \tag{13}$$

where [7]

$$B = v_2\left(\frac{n_1}{M_1}\right)^2 \tag{14}$$

and where χ_{12} is given in Eq. (12b); c_1 is the fractional (weight/volume) concentration of the polymer; v_2 is the volume of 1 mol of solvent, i.e., water in the solution; M_1 is the molecular weight of the polymer; n_1 is the number of subunits making up each polymer molecule; and d_1 is the relative density of the polymer with respect to water. S_c can be estimated from the molecular structure of the polymer. ΔG_{121} is obtained from Eq. (9), and hence

$$\chi_{12} = \frac{2S_c}{kT}[(\sqrt{\gamma_1^{LW}} - \sqrt{\gamma_2^{LW}})^2 + 2(\sqrt{\gamma_1^+\gamma_1^-} + \sqrt{\gamma_2^+\gamma_2^-} - \sqrt{\gamma_1^+\gamma_2^-} - \sqrt{\gamma_1^-\gamma_2^+})] \quad (15)$$

All the parameters in Eq. (15) can be determined by contact angle (θ) measurements with a number (at least three) of different liquids on the polymer (1), using the Young-Good-Girifalco-Fowkes equation in the form of [11, 12, 16, 17]

$$(1 + \cos\theta)\gamma_2 = 2(\sqrt{\gamma_1^{LW}\gamma_2^{LW}} + \sqrt{\gamma_1^+\gamma_2^-} + \sqrt{\gamma_1^-\gamma_2^+}) \quad (16)$$

It should be stressed that the polar part of the right side of Eq. (15) can assume a negative value [11, 12, 16, 17], which can then cause χ_{12} to be negative, because for such systems the acid-base interaction energies tend to be larger than apolar energies. In such cases the dissolved polymer molecules repel each other. The commonest systems where this effect is important are aqueous solutions. So we shall present the discussion that follows in terms of water as solvent; i.e., we shall take water as being representative of bipolar hydrogen bonding solvents.

The value of χ is known to vary with concentration for apolar polymer–solvent systems [3]. The same should be true for hydrogen bonding systems such as PEG/water, even though here the interaction between polymer molecules is one of repulsion, not attraction, when γ_{12} and χ_{12} are negative. We can estimate this concentration dependence by treating each polymer molecule as being surrounded by a hydration sheath whose radius is of the order of half the mean distance between polymer molecules in the solution. In that hydration layer, as observed by contact angle measurements, the water molecules would appear to be oriented; they are probably virtually completely oriented [18] in the first layer if the basic groups in the polymer are strong electron donors, as with ether oxygens. (The same would hold with respect to strong acidic groups in a polymer, of course.) However, as measured by NMR, the apparent orientation of water molecules in the first hydration layer tends to be lower. Water interacting with PEG shows an isotropic NMR signal [19], i.e., within the NMR time scale (of ~10^{-5} s), any observable orientation of water as well as of PEG molecules is already averaged out, relative to the laboratory coordinate system. However, there is likely to be a direct correlation of the orientation of the water molecules with respect to the PEG segments in the first hydration layer, and this orientation normally would not be readily measured by NMR.

The orientation decays with distance from the polymer molecule [18]. It is known that the polar repulsion energy (hydration pressure) decays exponentially with distance [12, 20], so the following form will hold:

$$\Delta G_{121}{}^{AB}(\ell) = \Delta G_{121}{}^{AB}(\ell = \ell_0) \exp\left(\frac{\ell_0 - \ell}{\lambda}\right) \qquad (17)$$

where λ is the decay length for the particular liquid. A plot of log ΔG_{121} vs ℓ or versus an appropriate function of concentration (see the Appendix) should be a straight line. The application of this relation will be demonstrated below.

OSMOTIC PRESSURES OF POLYETHYLENE GLYCOL-WATER SOLUTIONS

Osmotic pressures of PEG-water solutions have been reported by several authors. Malcolm and Rowlinson [21] measured water activities of PEG-water solutions via the water vapor pressure for polyethylene glycols (PEG) of molecular weights 300, 3000, and 5000. The measurements were done in the region of higher PEG concentrations (above 50 wt%) and mainly at higher temperatures (typically at 50 to 65°C; i.e., at or above the θ point). Rogers and Tam [22] measured water activities for PEG 600, 1001, 1513, 3035, and 7980 solutions in the region of moderately dilute solutions (<20 wt% PEG) at 35, 45, and 69.5°C. Chirife and Fontan [23] measured water activities for PEG 200, 400, and 600 for PEG concentrations between 0 and 65 wt% at 25°C. In several other papers (see, e.g., Refs. 24–27) osmotic pressure data or water activities for special PEG concentration regions, temperatures, and molecular weights are given. Some of the results obtained under comparable experimental conditions deviate significantly from one paper to another.

For the data analysis in the present paper, the osmotic pressures of aqueous solutions of polyethylene glycols with molecular weights from 150 to 20 000 and concentrations from 0 to 60 wt% were measured at 25°C. The data were calculated from the water vapor pressure over the solution, relative to the vapor pressure over pure water at the same temperature [1, 19]. The equipment developed for these measurements is described in Ref. 6. The experimental data of the osmotic pressures were fitted to an analytical expression proposed by Norrish [28]; these are shown in Fig. 1. The deviations of the single experimental points from these curves are smaller than ±0.5 MPa. Our osmotic pressure data for PEG 6000 are in good agreement with the data of Michel and Kaufman [24] (0–30 wt% PEG). The PEG 20 000 data agree reasonably with data published by Parsegian et al. [29]. The PEG 400 data are nearly identical with values published by Chirife and Fontan [23].

With polymers that act as strong electron donors when they take part in hydrogen bonding, γ_{12} has been determined [18] on the dry solid and on the solid swelled by amounts of water equivalent to a single layer of hydration per chain segment,

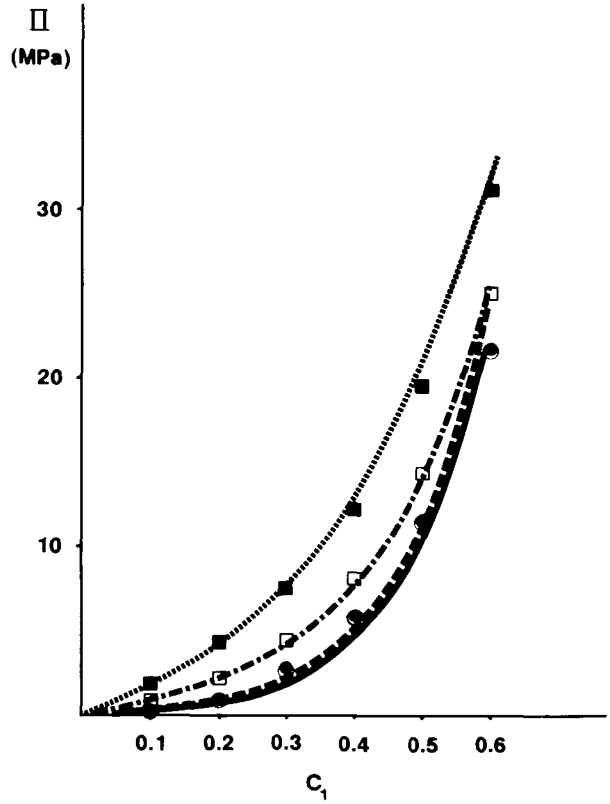

FIG. 1. Plot of the osmotic pressure, Π, vs the PEG concentration, c_1, for four different molecular weights of PEG. The *curves* are based upon the experimental results obtained by Arnold et al.: (...) M = 150; (- · -) M = 400; (- - -) M = 6000; (—) M = 20 000. The *points* are calculated via Eq. (13): (■) M = 150; (□) M = 400; (●) M = 6000; (○) M = 20 000 by using the χ_{12} values from Table 3.

as well as on the solid with various higher degrees of hydration. It was found that the exponential decay of the apparent value of γ_{12} sets in only with the second layer of hydration. For 60% PEG/40% water, the first layer of hydration is barely completed, and that completeness is only on a statistical average basis. Energetically and geometrically, the formation of clusters of water molecules should compete with the formation of ether oxygen-hydroxyl structures, and entropic considerations lead to the expectation of the widest possible variety of microscopic structures.

So we may assume that the value of γ_{12} found with water on dry PEG will give a good approximation to the value for PEG in 60% solution. This value was found [11, 16] to be -26.25 mJ/m^2.

If a plot of log ΔG^{AB} vs χ_{12} may be assumed to be a straight line, and assuming that hydration may be ignored at 60% PEG, this allows us to establish one point on that straight line, i.e., $\Delta G^{AB} = 2 \times 26.5$ or 52.5 mJ/m^2 at 60% PEG. The thickness of the PEG strands should be about 4.6 Å, which is the same as that of linear polyethylene [30], so an estimate of the contactable surface area is $S_c = 4.6^2 = 21.2$ Å^2 $= 21.2 \times 10^{-20}$ m^2. Thus $\chi_{12} = 2S_c\gamma_{12} = -1085 \times 10^{-23}$ J. At room temperature, $kT \approx 4 \times 10^{-21}$ J, so $\chi_{12} = -2.78$.

The slope of ΔG^{AB} vs χ_{12} is not known directly, but we can estimate another point on the line, because we do know [31] that incipient phase separation takes place with 4% PEG 6000 and 4% dextran ($M \approx 180\,000$), in water. At this point we might take $\Delta G_{121}^{AB} = +1.5kT$ [24], *or* $+\ 0.5kT$. The term $1.5kT$ (which comes from the kinetic theory of gases) would pertain to the interaction between spherical (or point) particles with three translational degrees of freedom. For polymer chains, the motion in which contact is established or broken is predominantly along the line perpendicular to the axes of the two chains, i.e., it is one-dimensional. Hence, only one degree of freedom is involved, and $0.5kT$ is thus the more appropriate value of ΔG_{121}^{AB}. The strand width of dextran is about 7.5 Å [25], so that $S_c = 4.6 \times 7.5 \approx 34$ Å^2; see Table 2. Substituting another 4% PEG 6000 for the 4% dextran (see Table 1), we find for just 8% PEG 6000 in water:

$$\chi_{12}^{(8\%)} = -\frac{52.5}{46.8} \cdot \frac{(4.6)^2}{4.6 \times 7.5} \times 0.5 = -0.34$$

The quotient, 52.5/46.8, is the correction needed to convert from the interaction energy between PEG and dextran in water ($\Delta G_{132} = +46.8$ mJ/m^2, using Eq. 11 and the data given in Table 1) to the interaction energy between two PEG molecules in water ($\Delta G_{121} = +52.5$ mJ/m^2, using Eq. 9 and the data from Table 1). Data derived from $\Delta G = 0.5kT$ (for incipient phase separation of 4% PEG and 4% dextran) are used here for the calculation of χ_{12} values

TABLE 2. Properties of Dextran (M = 180 000) and Polyethylene Glycol (PEG) Used in Calculations of χ_{12} and Osmotic Pressure

	Concentration c_1 in aqueous solution, w/v	Density d_1 (with respect to water)	Thickness, Å
Dextran (*180 000*)			7.5[c]
PEG (unhydrated)	0.6	1.15[a]	4.6[d]
PEG (hydrated)	0.5	1.124[b]	
PEG (hydrated)	0.4	1.1098[b]	
PEG (hydrated)	0.3	1.073[b]	
PEG (hydrated)	0.2	1.048[b]	
PEG (hydrated)	0.1	1.023[b]	

[a] *Merck Index.*

[b] Interpolated on a straight line in a semilogarithmic plot between d_1 = 1.15 at c_1= 0.6 and d_1 = 1.00 at c_1 = 0.

[c] Estimated by using the analogy of the crystal structure of cellulose [25].

[d] Estimated from the crystal structure of linear polyethylene [22].

for PEG at concentrations c_1 from 0.1 to 0.5. The results are shown in Table 3.

Table 4 shows the values of osmotic pressure calculated by using Eq. (13) for the four different molecular weights and six different concentrations. The concentration-dependent values of χ_{12} were employed, and the solute densities were taken from Table 2. The contributions to Π from each of the first three virial coefficients are shown, together with the total osmotic pressure.

Figure 1 shows the osmotic pressures calculated for PEG of MW 150, 400, 6000, and 20 000 via Eq. (13), superimposed on the values found experimentally by Arnold et al. [1] with aqueous solutions of the same polymers. The agreement is quite satisfactory.

DISCUSSION

In previous work it was shown that the interfacial free energy (per contactable surface area) of a polymer, vis-á-vis the solvent in which it is immersed, allows the prediction of its solubility in that solvent [5]. The interfacial free energies in question can readily be determined from the (measured) contact angles and surface tensions of polymer and solvent. This provides a significant advance over previous approaches in which certain solubility characteristics already had to be known before further predictions could be made concerning the solubility of a polymer in a given solvent. In this paper it is shown that (minus) the interfacial free energy

TABLE 3. Values of χ_{12} for the PEG–Water System

c_1 fractional concentration, w/v	χ_{12}
0.08	-0.34^a
0.1	-0.37^b
0.2	-0.55^b
0.3	-0.83^b
0.4	-0.24^b
0.5	-1.86^b
0.6	-2.78^c

[a] Based upon the assumption that incipient phase separation between PEG 6000 and dextran 180 000 occurs at $\Delta G_{121} = 0.5kT$; see text.

[b] Interpolated values on a semilog plot; see Appendix.

[c] From $\Delta G_{121} = +52.5$ mJ/m^2 and $S_c = 21.2$ Å^2; see Eq. (12a).

ΔG_{121} (per contactable surface area, S_c, and expressed in units of kT) of a polymer, dissolved in a given solvent, can be equated with the Flory-Huggins χ-parameter (Eq. 12a). Thus, in cases where a strong polar repulsion exists between polymer moieties dissolved in water (as occurs with polyethylene glycols to a very pronounced degree, [11]), $S_c\Delta G_{121}$ is strongly positive, making χ_{12} strongly negative. A strongly negative χ_{12} in the second virial coefficient (Eq. 13) indicates that the osmotic pressure of such mutually repulsive polymers is extremely high, especially at higher concentrations. In completely apolar (soluble or miscible) sequences, on the other hand, χ_{12} is always positive, and varies from very low values (close to $\chi_{12} = 0$) to $\chi_{12} \approx 0.5$. Beyond $\chi_{12} \approx 0.5$ the θ point is reached and solubility, or miscibility, quickly diminishes.

In the case of polar polymers which mutually repel each other when dissolved in an appropriate polar solvent, (i.e., $\chi_{12} < 0$), the classic lattice model (see, e.g., Nies, Koningsveld, and Kleintjens [34]), is *not* applicable. In these cases our theory diverges significantly from the lattice model, and takes the mutual repulsion between polymers into account. It leads to a quantitative prediction of the dependence of χ on concentration, while the treatment by Nies et al. [34] is "predictive" only in terms of solubility properties that are themselves determined from solubility measurements. Our theory predicts solubility properties from entirely independent measurements, namely surface and interfacial tension data. The decay of the free energies thus obtained, as a function of distance, and thus of dilution, can also be quantitatively determined for apolar as well as for polar systems.

TABLE 4. Osmotic Pressures, in MPa, of Aqueous Solutions of PEG of Various Molecular Weights Calculated According to Eq. (13), Broken Down into the First Three Virial Coefficient Terms

Concentrations c_1	MW	$(1/2 - \chi)$	$\Pi1 + \Pi2 + \Pi3 = \Pi$ total
0.6	150	3.28	9.76[a] + 20.25[a] + 1.07[a] = 31.09[a]
	400		3.66 + 20.25 + 1.07 = 24.99
	6 000		0.34 + 20.25 + 1.07 = 21.57
	20 000		0.07 + 20.25 + 1.07 = 21.40
0.5	150	2.36	8.13 + 10.59 + 0.66 = 19.37
	400		3.05 + 10.59 + 0.66 = 14.30
	6000		0.20 + 10.59 + 0.66 = 11.44
	20 000		0.06 + 10.59 + 0.66 = 11.31
0.4	150	1.74	6.51 + 5.25 + 0.37 = 12.13
	400		2.44 + 5.25 + 0.37 = 8.05
	6 000		0.17 + 5.25 + 0.37 = 5.78
	20 000		0.05 + 5.25 + 0.37 = 5.66
0.3	150	1.33	4.88 + 2.37 + 0.17 = 7.42
	400		1.83 + 2.37 + 0.17 = 4.37
	6 000		0.12 + 2.37 + 0.17 = 2.66
	20 000		0.04 + 2.37 + 0.17 = 2.57
0.2	150	1.05	3.25 + 0.87 + 0.05 = 4.16
	400		1.22 + 0.87 + 0.05 = 2.14
	6 000		0.08 + 0.87 + 0.05 = 1.00
	20 000		0.02 + 0.87 + 0.05 = 0.94
0.1	150	0.87	1.63 + 0.19 + 0.006 = 1.83
	400		0.60 + 0.19 + 0.006 = 0.80
	6 000		0.04 + 0.19 + 0.006 = 0.24
	20 000		0.01 + 0.19 + 0.006 = 0.21

[a] All figures are rounded off to the nearest 10 kPa.

Inspection of Fig. 1 and Table 4 shows that the second virial coefficient is the major cause for the striking lack of dependence of Π on the molecular weight of the polymer. The major factor in this term in Eq. (13) is the square of the (inverse) molecular weight of the polymers' *subunits*; and this molecular weight ($M/n = 44$ for PEG) is constant for all linear polymers of the same monomer. But this term can only attain significant influence when the value for χ_{12} is negative and of the order of −1 or −2 or so, as is indeed the case with PEG. This is also the case with dextrans, although to a lesser extent. For dextrans, $M/n = 180$, which makes for the much lower value $(1/180)^2$, as compared to $(1/44)^2$ for PEG (i.e., 16.7 × lower). However, the S_c value for dextran is 2.66 times greater than for PEG. Thus, in general the magnitude of the value of Π2 for dextran would be only about 6.3 smaller than that for PEG. Hence, for dextran also, Π still will be strongly dependent on the second virial coefficient, and thus, also largely independent of molecular weight (see, e.g., Ref. 35), especially for M_1 . 1000; see also Ref. 31.

In Fig. 1 it can be seen that by using the χ_{12}* values that we obtained for PEG in calculating the second virial coefficient, Π values are found which correspond closely to the experimental results from PEG 150, 400, 6000 and 20 000 [1]. The third virial coefficient was also taken into account in the computation, as it can represent up to 6.5% of the total value of Π for aqueous PEG solutions. For molecular weights of PEG of 6000 and higher, the first term of Π (RTc_1/M_1) accounts for less than 10% of the total at $c_1 > 0.2$. Thus, Table 4 reveals the fundamental reasons for the molecular weight independence of Π at the higher concentrations in this system.

For linear polymers which have a negative interfacial tension with the solvent, and which have subunits of a small molecular weight (such as PEG), the osmotic pressure, Π, with the higher molecular weights, mainly depends upon the value of the second virial coefficient (see Eq. 13), and this coefficient is governed by the value of χ_{12}. Clearly, strongly negative χ_{12} values will give rise to more highly positive values of the second virial coefficient.

While it has been recognized in the past that negative χ_{12} values can occur, they are not encountered with great frequency in the literature. One case, given by Hermans in 1949 [7], shows a value of $\chi_{12} = -1.8$ for cellulose acetate in tetrachloroethane, which is a weak electron acceptor. That value is now entirely understandable, as cellulose acetate is a strong electron donor [11, 36]. Its ΔG_{121} value (see Eq. 9) in tetrachloroethane should be positive, which would give rise to a negative χ_{12} (Eq. 15) of about the order of magnitude found by Hermans [7]. With most other organic solvents, such situations would, however, be rather unlikely. However, with solvents such as chloroform (which is an electron acceptor [5]), and water, formamide, or glycerol (which are self-hydrogen bonding, and thus bipolar [5]), negative χ_{12} values can occur with polymers that have electron donor properties. It should be noted that the positive χ_{12} values reported for PEG of various MWs in water in Ref. 37 all pertain to conditions above the θ-point (i.e., from 55 to 65°C), at which water becomes a less than ideal solvent for PEG [38].

For strongly polar polymers the most favorable solvent usually is water, which is strongly hydrogen bonding and markedly bipolar. Many such polar polymers are very soluble in water; this is largely due to their negative interfacial tensions with water, which gives rise to positive ΔG_{121} values [5]. Examples besides PEG and dextrans [5, 11] are nucleic acids [11, 36], hydrated serum proteins [18, 39], and polyvinyl alcohol.

*Various approaches to the interpolation of values for χ_{12} are possible for polymer concentration c_1 between 0.08 and 0.60; their merits and drawbacks are discussed in the Appendix.

In Eq. (13) the activity coefficients of PEG are not taken into account. However, it should be understood that Eq. (13) serves to *determine* the activity of PEG at various concentrations and relates it to the osmostic pressure, Π. So to include activity coefficients in Eq. (13) would be redundant. It should also be noted that in the case of aqueous solutions of PEG, Π/c_1 increases with the concentration, c_1; this is a phenomenon which has been recognized as peculiar to polymers dissolved in "good" solvents [9]. Thus, in the case of PEG, its activity increases with concentration. This is largely due to the fact that with increasing concentration, PEG becomes less hydrated (because of the lack of a surplus of water molecules), which leads to an increase in the positive value of ΔG_{121}^{AB}, i.e., to an increase in mutual repulsion between PEG molecules and a tendency to draw more water into the polymer—in other words, high osmotic pressure. While hydration is, of course, the mechanism by which polar repulsion is propagated some appreciable distance beyond the very close range of direct hydrogen bonds (a phenomenon known as hydration pressure [18]), the hydration orientation decreases with distance, and the result is the decay of polar repulsion. Thus, the greater the dilution, the weaker the polar repulsion.

The pronounced positive value of ΔG_{121} for PEG in water, and thus its strongly negative χ_{12} value, therefore not only cause the unusually high (and largely molecular weight-independent) osmotic pressure, but it also is the real origin of the strong stabilizing power of PEG for aqueous suspensions of hydrophobic particles (cf., e.g., Ref. 9), as well as of its flocculating power for various proteins [40] and of its capacity to cause and/or to facilitate cell or liposome fusion [1, 41].

APPENDIX

On the Interpolation of Values of χ_{12} vs Polymer Concentration

The exponential decay relation, Eq. (17), was developed [12, 18, 20] to describe the interaction between two parallel, semi-infinite slabs. For a pair of real, nonparallel polymer chains, the decay cannot be given exactly by Eq. (17). The change in geometry from parallel slabs to crossed cylinders should lead to a change in the decay function. There is, in addition, the important question of how the first hydration layer affects the mechanics of attraction of the crossed cylinders: the effective contactable area will be larger if the hydration layer is so tightly bound that, in the attraction or repulsion, it acts as part of the core of the chain. This increase in S_c will tend to counterbalance the decrease in ΔG that accompanies dilution and the increase in l.

For the purpose of interpolating χ_{12} as a function of concentration between the values at $c_1 = 0.08$ and $c_1 = 0.6$, Eq. (17) points to the plotting of log χ_{12} vs $(c_1)^{-1/3}$ for spherical particles or log χ_{12} vs l for parallel, cylindrical particles. On the other hand, following Napper [9], one may (at least at the lower concentrations) expect a reasonable correlation when plotting ΔG directly vs c_1. However, especially if one wishes to include the higher concentrations, a more reasonable connection between the virial coefficients and the concentration (by analogy with Napper [9]) leads to a correlation between ΔG (and thus χ_{12}) and c_1^2; cf. Eq. (13).

The order of decreasing correlation between the observed values for the osmotic pressure, Π, and the values calculated by means of Eq. (13), obtained with χ_{12} for $c_1 = 0.1$ to 0.5, for the various methods for interpolating χ_{12} vs c_1 between the known values for χ_{12} for $c_1 = 0.08$ and $c_1 = 0.6$, was found to be

$\log \chi_{12}$ vs c_1 (A)

χ_{12} vs c_1^2 (B)

$\log \chi_{12}$ vs $(c_1)^{1/3}$ (C)

χ_{12} vs c_1 (D)

$\log \chi_{12}$ vs $(c_1)^{1/2}$ (E)

Figure 1 was obtained by using approach (A). (B) yields very similar results. The others gave Π values which increasingly diverge from the observed osmotic pressure from (C) to (E).

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