

Concentration Dependence of the Flory χ Parameter within Two-State Models

V. A. Baulin and A. Halperin*

UMR 5819 (CEA, CNRS, UJF), DRFMC/SI3M, CEA-Grenoble, 17 rue des Martyrs, 38054 Grenoble Cedex 9, France

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ABSTRACT: The Flory χ parameter is typically assumed to depend only on the temperature, T . Experimental results often require the replacement of this $\chi(T)$ by χ_{eff} , which depends also on the monomer volume fraction, ϕ , $\chi_{\text{eff}}(\phi, T)$. Such $\chi_{\text{eff}}(\phi, T)$ can arise from two-state models, proposed for polyetheleneoxide (PEO) and other neutral water-soluble polymers. The predicted ϕ dependence of $\bar{\chi} = \chi_{\text{eff}} - (1 - \phi)\partial\chi_{\text{eff}}/\partial\phi$, obtainable from colligative properties, differs qualitatively between the various models: (i) The model of Karlstrom (*J. Phys. Chem.* **1985**, 89, 4962) yields $\partial\bar{\chi}/\partial\phi \geq 0$ while the model of Matsuyama and Tanaka (*Phys. Rev. Lett.* **1990**, 65, 341) and of Bekiranov et al. (*Phys. Rev. E* **1997**, 55, 577) allows for $\partial\bar{\chi}/\partial\phi < 0$. (ii) $\bar{\chi}(\phi)$ as calculated from the Karlstrom model, utilizing the parameters used to fit the phase diagram of PEO, agrees semiquantitatively with the experimental values. On the other hand, $\bar{\chi}(\phi)$ similarly calculated from the model of Bekiranov et al. differs qualitatively from the measured results. Altogether, $\bar{\chi}(\phi)$ provides useful measure for the performance of a model.

I. Introduction

The Flory free energy plays a central role in the thermodynamics of polymers. In this free energy, the mixing energy term has the form $\chi\phi(1 - \phi)$ where χ is the Flory interaction parameter and ϕ is the monomer volume fraction. Typically, it is assumed that χ depends only on the temperature, $\chi = \chi(T)$.^{1–4} However, when thermodynamic data are analyzed in terms of the Flory free energy, it is often necessary to replace $\chi\phi(1 - \phi)$ by $\chi_{\text{eff}}\phi(1 - \phi)$ where χ_{eff} is a function of both T and ϕ , i.e., $\chi_{\text{eff}} = \chi_{\text{eff}}(T, \phi)$.^{1,5–8} Considerable effort was devoted to clarifying the statistical mechanical origins of this and other deviations from the Flory–Huggins theory. Various extensions of the Flory–Huggins theory allow for compressibility,⁹ local composition,¹⁰ and the role of intrachain contacts.¹¹ Recently, the lattice cluster theory utilized a more accurate solution of the lattice model while allowing for the structure of the monomers.¹² The Flory–Huggins theory was also extended in order to account for the phase behavior of aqueous solutions of neutral water-soluble polymers and in particular polyetheleneoxide (PEO). In such systems the solubility of the polymers is attributed to the formation of H bonds. These extensions introduce a *two-state model* wherein the monomers of the chain can exist in two distinct and interconverting states^{13–17} (Figure 1). In the following, we demonstrate that “two-state” models yield $\chi_{\text{eff}}(\phi)$ and analyze the ϕ dependence of the resulting χ_{eff} . Our discussion is mostly concerned with two models: The one proposed by Karlstrom (K model)¹⁴ and the model of Matsuyama and Tanaka¹⁵ as formulated by Bekiranov, Bruinsma, and Pincus (MB model).¹⁷ The two models differ, as we shall discuss, in the precise identification of the monomeric states. However, in both cases it is assumed that one monomeric state, A, is “hydrophilic” while the other, B, is “hydrophobic”. As a result, a binary solution of a polymer in water behaves in fact as a *reactive ternary system*. In particular, the

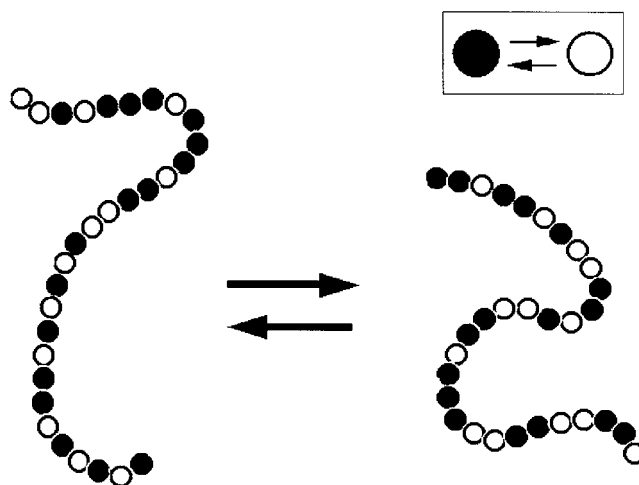


Figure 1. Schematic representation of the dynamic equilibrium in two-state polymers where the monomers exist in two interconverting states (inset): A (empty circle) and B (full circle).

fraction of A monomers, P , depends on both T and ϕ . Consequently the different versions of this model yield, as we shall see, χ_{eff} that depends on both T and ϕ . The original papers proposing these models^{14,15,17} focused on the phase behavior while overlooking the emergence of $\chi_{\text{eff}}(\phi)$.¹⁸ The goal of our work is to obtain explicit expressions for $\chi_{\text{eff}}(\phi)$ for the K and MB models, analyze the ϕ dependence, and compare the results to experimental data. It is noteworthy that by allowing for the internal degrees of freedom of the monomers, the two-state models can rationalize the observed $\chi_{\text{eff}}(\phi)$ while retaining the main approximations of the Flory–Huggins theory, i.e., incompressibility, monomers and solvent molecules of identical size and shape, and local concentration that equals the global one. Aside from the fundamental interest in the origin of the ϕ dependence of χ_{eff} , this analysis underlines the utility of $\chi_{\text{eff}}(\phi)$ as a criterion for the performance of the models. While both the K model and the MB model recover the observed phase diagram of PEO, only the K model yields a

* To whom correspondence should be addressed. E-mail: halperin@drfmc.ceg.fr.

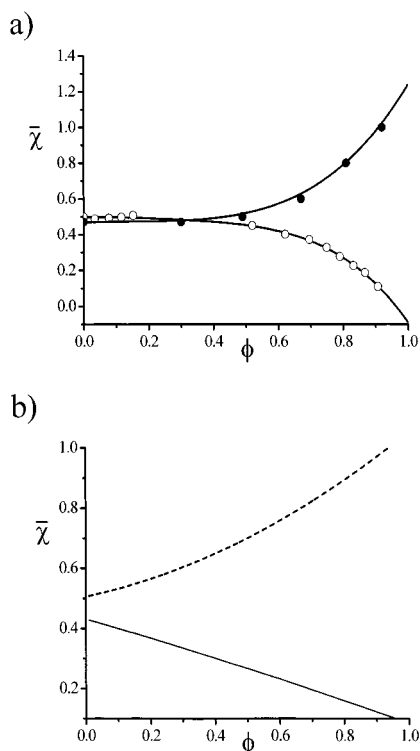


Figure 2. Plots of measured $\bar{\chi} = \chi_{\text{eff}} - (1 - \phi)\partial\chi_{\text{eff}}/\partial\phi$ vs ϕ for (a) aqueous solutions of the neutral water-soluble polymers PEO at $N = 3000$ and $T = 338$ K (full circle, after refs 6 and 7) and PVP at $T = 295$ K (empty circle, modified from ref 19) and for (b) nonaqueous solutions of polyisobutylene in benzene (dashes) and of polystyrene in toluene (continuous line).⁵

qualitatively correct $\chi_{\text{eff}}(\phi)$. On the other hand, an opposite trend is found for $\chi_{\text{eff}}(\phi)$ of poly(vinylpyrrolidone) (PVP) which exhibits a ϕ dependence that differs qualitatively from that of PEO¹⁹ (Figure 2). In this case the K model is inherently incapable of reproducing the experimental results while the MB model does allow for a similar behavior.

Our analysis is mostly concerned with the concentration dependence of

$$\bar{\chi} = \chi_{\text{eff}} - (1 - \phi) \frac{\partial \chi_{\text{eff}}}{\partial \phi} \quad (1)$$

We choose to focus on $\bar{\chi}$ because measurements of colligative properties, such as vapor pressure and osmotic pressure, yield $\bar{\chi}$ rather than χ_{eff} .⁵ As a result, it is the $\bar{\chi}$ values that are usually reported in the literature. Furthermore, it turns out that the ϕ dependence of $\bar{\chi}(\phi)$ is simpler to analyze. Since the different versions of the two-state model aimed to rationalize the phase behavior of aqueous solutions of PEO, the parameters involved were chosen with view of recovering the known phase diagram. However, these models are in fact suitable candidates for the description of aqueous solutions of neutral water-soluble polymers in general. With this in mind we consider the two-state model as a generic model for such systems rather than as a specific model for PEO. Accordingly, we make no specific assumptions regarding the choice of the various parameters involved.

The paper is organized as follows. A unified description of the K and MB models, stressing the similarities and the differences, is presented in section II. Section III contains a brief summary of the thermodynamics of

polymer solutions with $\chi_{\text{eff}}(\phi)$. This discussion introduces the approach utilized later for the study of $\bar{\chi}(\phi)$. $\chi_{\text{eff}}(\phi)$, $\bar{\chi}(\phi)$, and $\partial\bar{\chi}(\phi)/\partial\phi$ for the K and MB models are discussed in sections IV and V, respectively. In the Discussion we compare the K and MB models with two other physically transparent models yielding a ϕ -dependent χ_{eff} .

II. Two "Two-State" Models

In the "two-state" models for water-soluble homopolymers the monomers of the chain may assume two interconverting forms characterized by different interaction energies. In particular, one monomeric state, A, is assumed to be "hydrophilic" while the other, B, is assumed to be "hydrophobic". The K and MB models differ somewhat with respect to the underlying physics. The K model¹⁴ focuses on molecular rotations giving rise to monomeric states of different polarities. The state endowed with a strong dipole moment is identified as the hydrophilic species, A, while the less polar state is identified as the hydrophobic state, B. Within this model the interconversion is a unimolecular reaction, $A \rightleftharpoons B$, and the mass action law is

$$\frac{P}{1 - P} = K_K \quad (2)$$

Here P is the fraction of monomers in a hydrophilic A state and K_K is the corresponding equilibrium constant. The explicit form of K_K , to be given in section IV, is irrelevant at this point. The MB model¹⁷ focuses on the role of H bonds. In particular, a monomer that forms an H bond with water is considered, in effect, as hydrophilic while a monomer that does not form such a bond is hydrophobic. Within this model, one distinguishes between free water molecules (S) and water molecules that are bound to the polymer chain. This distinction has no counterpart in the K model. Accordingly the interconversion reaction is a bimolecular reaction, $B + S \rightleftharpoons A$, and the chemical equilibrium is specified by

$$\frac{P}{(1 - P)\phi_0} = K_{\text{MB}} \quad (3)$$

where ϕ_0 is the volume fraction of water. The explicit expression for K_{MB} , to be given in section V, is not required for the present discussion. Thus, in the K model

$$\phi_0 = 1 - \phi \quad (4)$$

while in the MB model

$$\phi_0 = 1 - \phi - P\phi \quad (5)$$

where P is the fraction of monomers that form H bonds and $P\phi$ is the volume fraction of bound water. As a result, the two models involve different reference states. In particular, the melt state, $\phi = 1$, in the K model is characterized by

$$P(\phi = 1) = P_* \geq 0 \quad (6)$$

while in the MB model

$$P(\phi = 1) = 0 \quad (7)$$

Both models utilize a Flory type approach to obtain the

thermodynamics of the solution. In particular, random mixing is assumed and the energy per site of a polymer–water solution inscribed on a lattice is written as

$$\frac{E}{kT} = \phi \left[P \frac{z\epsilon_{AA}}{2kT} + (1-P) \frac{z\epsilon_{BB}}{2kT} \right] + (1-\phi) \frac{z\epsilon_{SS}}{2kT} + \phi(1-\phi) [P\chi_{AS} + (1-P)\chi_{BS}] + \phi^2 \chi_{AB} P(1-P) \quad (8)$$

where z is the coordination number of the lattice and k is the Boltzmann constant. ϵ_{AA} , ϵ_{BB} , and ϵ_{SS} denote respectively the energies of A, B, and solvent molecules in a pure bulk phase. χ_{AB} , χ_{AS} , and χ_{BS} denote the Flory interaction parameters corresponding respectively to AB, AS, and BS interactions (where $\chi_{AS} = \epsilon_{AS} - (\epsilon_{AA} + \epsilon_{SS})/2$ etc). The first term allows for the energy of the A and B in a hypothetical pure bulk phase while the second reflects the energy of the solvent molecules in a pure bulk state. The interactions between the two monomeric states and the solvent gives rise to the third term while the last term allows for the AB interactions. For future reference, it is convenient to define a dimensionless parameter

$$\Delta\epsilon = z \frac{\epsilon_{AA} - \epsilon_{BB}}{2kT} \quad (9)$$

characterizing the difference between the energies of the two monomeric states. This expression reduces to the familiar Flory form when $P = 1$ or $P = 0$ that is, when the monomers have only one state. The energy E is supplemented by two entropy contributions per lattice site. One term allows for the different possible sequences of A and B states along the chain

$$\frac{S_{AB}}{k} = -\phi [P \ln P + (1-P) \ln(1-P)] \quad (10)$$

while the second reflects the translational entropy of the chains

$$\frac{S_{trans}}{k} = -\frac{\phi}{N} \ln \frac{\phi}{N} - \phi_0 \ln \phi_0 \quad (11)$$

The S_{AB} term is distinctive to the two-state models. It vanishes when the monomers exist in a single state, i.e., $P = 1$ or $P = 0$. As expected, S_{trans} is identical in form to the entropy term in the Flory free energy. Altogether, the free energy of the solution is $F = E - T(S_{AB} + S_{trans})$ and the mixing free energy is

$$F_{mix} = F(\phi, P) - \phi F(\phi = 1) - (1-\phi) F(\phi = 0) \quad (12)$$

Both models neglect the fluctuations in the number of A monomers per chain, m . Strictly speaking, chains with different m are distinguishable and should be treated as different chemical species.¹⁵ Rather than allow for this multiplies equilibrium the K and MB models consider a single polymer species characterized by an average $\bar{m} = PN$ where N is the polymerization degree. This approximation is justified because the m values are described by a sharply peaked Gaussian distribution.¹⁷ While the two models lead to similar free energies, the free energies invoked in the K and in the MB models differ in two respects. In the MB model, (i) the translational entropy is P dependent because of the $\phi_0 \ln \phi_0$ term, and (ii) since $P(\phi = 1) = 0$, F_{mix} does not

reflect contributions due to $P(\phi = 1) = P^* \geq 0$ that appear in the K model.

Finally, it is helpful to note certain additional differences between the models as described in the original papers.^{14,17} While the physical content of these is minor in comparison to the differences discussed above, they are of interest for comparison purposes. Thus, the analysis of Bekiranov et al. focused on the particular case of $\chi_{AB} = 0$, $\chi_{AS} = \chi_{BS} = \chi = 2.885 - 0.0036T$ and $\Delta\epsilon = 6.38 - 2408/T$ while in the K model $\chi_{AS} = 80.0/T$, $\chi_{BS} = 684.5/T$, $\chi_{AB} = 155.6/T$, and $\Delta\epsilon = -625.2/T + \ln 8$. The temperature dependence of the χ parameters in the two papers is somewhat different. Bekiranov et al. assume $\chi \sim a + bT$ while in the K model $\chi \sim b/T$. In both models, $\Delta\epsilon \sim a + b/T$. In the model of Bekiranov et al. this follows from the identification of $\Delta\epsilon$ with $\Delta F_0/kT$ where $\Delta F_0 = \Delta E_0 - T\Delta S_0$ is the free energy change associated with the formation of the H bond. The $a + b/T$ dependence in the K model is a consequence of the degeneracy of the monomeric states. It assumed that each of the two monomeric forms can exist in a number of equivalent states and the resulting entropy gives rise to a . The analysis of Bekiranov et al. allows for the effect of pressure. This is attributed to the existence of a preferred volume for a H bond.²⁰ The application of pressure is assumed to introduces a geometric constraint resulting in a lower number of bound water molecules. This argument yields a semiquantitative agreement with experimental results on the phase diagram of PEO. Note that this coupling mechanism can only operate within the MB model and cannot be used in the K model. Furthermore, it is not fully consistent with the incompressibility assumption invoked by Bekiranov et al.

III. Thermodynamics of Polymer Solutions with $\chi_{eff}(\phi)$

Before we proceed to analyze the ϕ dependence of $\bar{\chi}$ within the two “two-state” models, it is helpful to summarize the thermodynamic relationships that apply when $\chi = \chi(T)$ is replaced by $\chi_{eff} = \chi_{eff}(T, \phi)$.⁵ The Flory like mixing free energy per site, F_{mix} , consists then of two terms. One is an interaction free energy that is the counterpart of the mixing energy $\chi\phi(1-\phi)$

$$\frac{F_{int}}{kT} = \chi_{eff}(\phi)\phi(1-\phi) \quad (13)$$

The second is the translational free energy

$$\frac{F_{trans}}{kT} = \frac{1}{N}\phi \ln \phi + (1-\phi) \ln(1-\phi) \quad (14)$$

The chemical potential of the solvent is $\mu_s = \mu_s^0(P, T) - \pi a^3$ while the osmotic pressure $\pi a^3 = \phi^2 \partial/\partial\phi (F_{mix}/\phi)$ is

$$\frac{\pi a^3}{kT} = \frac{\phi}{N} - \phi - \ln(1-\phi) - \bar{\chi}\phi^2 \quad (15)$$

where $\bar{\chi} = \chi_{eff} - (1-\phi) \partial\chi_{eff}/\partial\phi$ replaces χ . Since μ_s determines the colligative properties of the solution, measurements of such properties yield $\bar{\chi}$ rather than χ_{eff} . In turn, $\bar{\chi}$ is obtainable from F_{int} via

$$\bar{\chi} = -\frac{\partial F_{int}}{\partial\phi kT\phi} = -\frac{1}{kT} \frac{\partial F_{int}}{\partial\phi} \frac{1}{\phi} \quad (16)$$

In the next two sections we will utilize eq 16 to obtain $\bar{\chi}$ from $F_{\text{int}} = F_{\text{mix}} - F_{\text{trans}}$. This equation also shows that terms of the form $\text{const}' \times \phi$ in F_{int} do not contribute to $\bar{\chi}$. This will allow us to ignore such linear terms that arise because of the choice of the reference state.

IV. $\bar{\chi}$ within the K Model

Within the K model the mixing energy per lattice site, E_{mix} , is

$$\frac{E_{\text{mix}}}{kT} = \phi P \Delta\epsilon + \phi(1 - \phi)[P\chi_{\text{AS}} + (1 - P)\chi_{\text{BS}}] + \phi^2\chi_{\text{AB}}P(1 - P) + \text{terms linear in } \phi \quad (17)$$

The first term measures the difference in the energy of isolated A and B monomers. The second term accounts for the interactions between the monomers and the solvent. It is a generalization of the $\chi\phi(1 - \phi)$ term in the Flory free energy for a binary solutions. The third term allows for the interaction between A and B monomers. The mixing entropy is

$$\frac{S_{\text{mix}}}{k} = -\phi[P \ln P + (1 - P) \ln(1 - P)] - \left[\frac{\phi}{N} \ln \phi + (1 - \phi) \ln(1 - \phi) \right] + \text{terms linear in } \phi \quad (18)$$

The first term allows for the AB mixing within the chains and the second for the translational entropy of the chains. In both expressions, the terms linear in ϕ arises because the free energy of the melt state depends on P^* and $F_{\text{mix}} = F - (1 - \phi)F(\phi = 0) - \phi F(\phi = 1, P^*)$. When terms linear in ϕ are discarded, $F_{\text{int}} = F_{\text{mix}} - F_{\text{trans}}$ is

$$\frac{F_{\text{int}}}{kT} = \phi P \Delta\epsilon + \phi(1 - \phi)[P\chi_{\text{AS}} + (1 - P)\chi_{\text{BS}}] + \phi^2\chi_{\text{AB}}P(1 - P) + \phi[P \ln P + (1 - P) \ln(1 - P)] \quad (19)$$

The equilibrium value of P for a given ϕ and T , $P_e = P_e(\phi)$, is specified by the condition $\partial F_{\text{int}}/\partial P = 0$ leading to

$$\frac{P_e}{1 - P_e} = K_K(\phi, P_e, T) = \exp[-\Delta\epsilon - (1 - \phi)(\chi_{\text{AS}} - \chi_{\text{BS}}) - \phi\chi_{\text{AB}}(1 - 2P_e)] \quad (20)$$

where K_K is the equilibrium constant for the unimolecular intrachain $A \rightleftharpoons B$ reaction. When $\chi_{\text{AS}} = \chi_{\text{BS}} = \chi$ and $\chi_{\text{AB}} = 0$, the parameters chosen by Bekiranov et al. K_K is independent of ϕ . Consequently, for this case, P_e is independent of ϕ , $\partial P_e/\partial \phi = 0$, thus leading, as we shall see, to $\partial \bar{\chi}_K/\partial \phi = 0$. To ensure the stability of the $A \rightleftharpoons B$ equilibrium, we further invoke the condition $\partial^2 F_{\text{int}}/\partial P^2 > 0$

$$\frac{\partial^2 F_{\text{int}}}{\partial P^2} = \phi \left[\frac{1}{P(1 - P)} - 2\phi\chi_{\text{AB}} \right] > 0 \quad (21)$$

This ensures that the free energy curve is concave and that fluctuation relax back to the equilibrium state according to the LeChatelier principle. Using $\bar{\chi} = -\partial/\partial \phi F_{\text{int}}/kT\phi$ and the equilibrium condition, we find

$$\bar{\chi}_K = P_e\chi_{\text{AS}} + (1 - P_e)\chi_{\text{BS}} - \chi_{\text{AB}}P_e(1 - P_e) \quad (22)$$

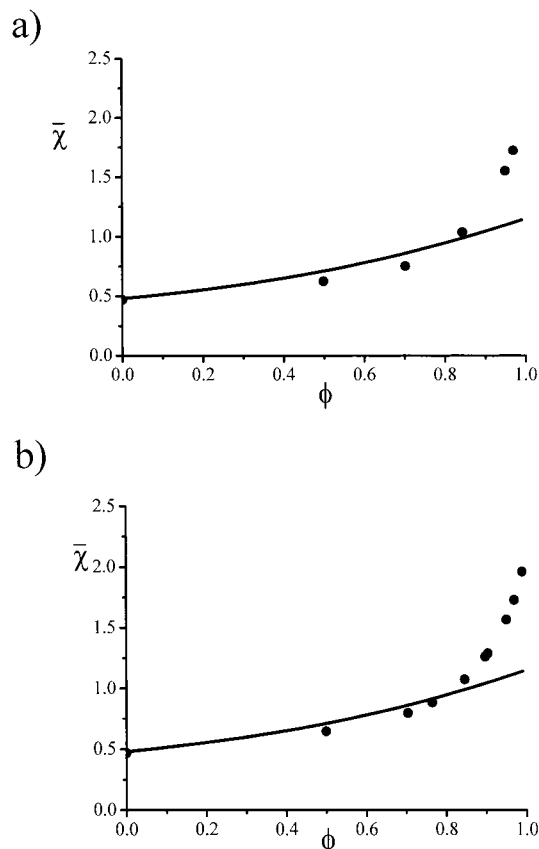


Figure 3. $\bar{\chi}_K$ vs ϕ (continuous line) calculated using $\chi_{\text{AS}} = 80.0/T$, $\chi_{\text{BS}} = 684.5/T$, $\chi_{\text{AB}} = 155.6/T$, and $\Delta\epsilon = -625.2/T + \ln 8$. These parameters, used to fit the phase diagram of PEO, agree semiquantitatively with the experimental values of $\bar{\chi}$ (full circles) as measured with $N = 3000$ at (a) $T = 328$ K and (b) $T = 338$ K. While the numerical values and the curvature of $\bar{\chi}_K$ change with the choice of χ_{AS} , χ_{BS} , χ_{AB} , and $\Delta\epsilon$, it is normally a monotonically increasing function of ϕ .

Thus, within the K model, the ϕ dependence of $\bar{\chi}_K$ is due to $P_e(\phi)$. To specify $\partial \bar{\chi}_K/\partial \phi$, it is first necessary to obtain $\partial P_e(\phi)/\partial \phi$ by differentiating the equilibrium condition (20) with respect to ϕ , leading to

$$\frac{\partial P_e(\phi)}{\partial \phi} = \frac{\partial \bar{\chi}_K}{\partial P_e} \frac{\phi}{\partial^2 F_{\text{int}}/\partial P^2} \quad (23)$$

Here, and later in (24), $\partial^2 F_{\text{int}}/\partial P^2$ signifies the value of (21) in equilibrium i.e., $P = P_e(\phi)$. Equation 23 indicates that the sign of $\partial P_e(\phi)/\partial \phi$ is determined by $\partial \bar{\chi}_K/\partial P_e$. This reflects the concentration dependence of $K_K = \text{const}' \exp(\phi \partial \bar{\chi}_K/\partial P_e)$. Altogether

$$\frac{\partial \bar{\chi}_K}{\partial \phi} = \frac{\partial \bar{\chi}_K}{\partial P_e} \frac{\partial P_e}{\partial \phi} = \left(\frac{\partial \bar{\chi}_K}{\partial P_e} \right)^2 \frac{\phi}{\partial^2 F_{\text{int}}/\partial P^2} \geq 0 \quad (24)$$

and $\bar{\chi}_K$ is an increasing function ϕ for any choice of the parameters χ_{AS} , χ_{BS} , χ_{AB} , and $\Delta\epsilon$ except for the case $\chi_{\text{AS}} = \chi_{\text{BS}}$ and $\chi_{\text{AB}} = 0$ when $\partial \bar{\chi}_K/\partial \phi = 0$. The calculated $\bar{\chi}_K(\phi)$, utilizing the parameters used to fit the phase diagram of PEO, is in semiquantitative agreement with the experimental results for $\bar{\chi}(\phi)$ (Figure 3). The resulting curve is representative of the behavior of $\bar{\chi}_K(\phi)$ in general.

V. $\bar{\chi}$ within the MB Model

The mixing energy per site in the MB model is essentially identical with that of the K model

$$\frac{E_{\text{mix}}}{kT} = \phi P \Delta\epsilon + (1 - \phi)\phi[P\chi_{\text{AS}} + (1 - P)\chi_{\text{BS}}] + \phi^2\chi_{\text{AB}}P(1 - P) \quad (25)$$

while the mixing entropy per site is

$$\frac{S_{\text{mix}}}{k} = -\phi[P\ln P + (1 - P)\ln(1 - P)] - \left[\frac{\phi}{N}\ln\phi + (1 - \phi - P\phi)\ln(1 - \phi - P\phi)\right] \quad (26)$$

These differ from the corresponding expressions within the K model in two respects: (i) Terms linear in ϕ are no longer present because the dependence on P_* disappears since $P(\phi = 1) = 0$. (ii) The translational entropy contribution to S_{mix} now depends on P because $\phi_0 = 1 - \phi - P\phi$. $F_{\text{int}} = F_{\text{mix}} - F_{\text{trans}}$ is

$$\frac{F_{\text{int}}}{kT} = \phi P \Delta\epsilon + \phi(1 - \phi)[P\chi_{\text{AS}} + (1 - P)\chi_{\text{BS}}] + \phi^2\chi_{\text{AB}}P(1 - P) + \phi[P\ln P + (1 - P)\ln(1 - P)] - P\phi\ln(1 - \phi) + (1 - P\phi - \phi)\ln\left(1 - \frac{P\phi}{1 - \phi}\right) \quad (27)$$

The equilibrium value of P , for a given ϕ and T , is specified by the condition $\partial F_{\text{int}}/\partial P = 0$

$$K_{\text{MB}}(\phi, P_e, T) = \frac{P_e}{(1 - P_e)(1 - P_e\phi - \phi)} = \exp[1 - \Delta\epsilon - (1 - \phi)(\chi_{\text{AS}} - \chi_{\text{BS}}) - \phi\chi_{\text{AB}}(1 - 2P_e)] \quad (28)$$

where $K_{\text{MB}} = eK_K$ is the equilibrium constant for the $B + S \rightleftharpoons A$ reaction. As in the K model, K_{MB} is independent of ϕ when $\chi_{\text{AS}} = \chi_{\text{BS}}$ and $\chi_{\text{AB}} = 0$. However, in the MB model, P_e depends on ϕ even when K_{MB} does not because of the loss of translational entropy of the bound water. The stability condition for the $B + S \rightleftharpoons A$ reaction, $\partial^2 F_{\text{int}}/\partial P^2 > 0$, leads to

$$\frac{\partial^2 F_{\text{int}}}{\partial P^2} = \phi \left[\frac{1}{P(1 - P)} - 2\phi\chi_{\text{AB}} + \frac{\phi}{1 - \phi - P\phi} \right] > 0 \quad (29)$$

Using $\bar{\chi} = -\partial/\partial\phi (F_{\text{int}}/kT\phi)$ and the equilibrium condition (28), we find

$$\bar{\chi}_{\text{MB}} = P_e\chi_{\text{AS}} + (1 - P_e)\chi_{\text{BS}} - \chi_{\text{AB}}P_e(1 - P_e) + \frac{P_e}{\phi} + \frac{1}{\phi^2} \ln\left(1 - \frac{P_e\phi}{1 - \phi}\right) \quad (30)$$

While the first three terms are identical in form to $\bar{\chi}_K$ these are now supplemented by two additional terms arising from the translational entropy of the water. When $\chi_{\text{AS}} = \chi_{\text{BS}} = \chi$ and $\chi_{\text{AB}} = 0$, the interaction terms are constant, $\bar{\chi}_K = \chi$, and the ϕ dependence of $\bar{\chi}_{\text{MB}}$ reflects solely the entropic contribution. Again we obtain $\partial P_e(\phi)/\partial\phi$ by differentiating the equilibrium condition, eq 28, with respect to ϕ , finding

$$\frac{\partial P_e(\phi)}{\partial\phi} = \frac{\partial\bar{\chi}_{\text{MB}}}{\partial P_e} \frac{\phi}{\partial^2 F_{\text{int}}/\partial P^2} \quad (31)$$

In eq 31, and later in eq 32, $\partial^2 F_{\text{int}}/\partial P^2$ denotes the value of eq 29 in equilibrium. While eq 31 is similar in form

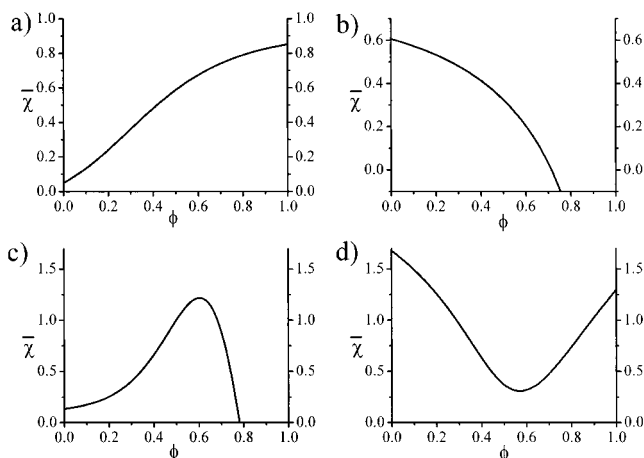


Figure 4. $\bar{\chi}_{\text{MB}}$ vs. ϕ plots exhibit qualitatively different forms, depending on the choice of parameters: (a) monotonically increasing $\chi_{\text{AS}} = 0.7$, $\chi_{\text{BS}} = 0.9$, $\chi_{\text{AB}} = 2$, and $\Delta\epsilon = 4$; (b) monotonically decreasing $\chi_{\text{AS}} = 0.1$, $\chi_{\text{BS}} = 0.4$, $\chi_{\text{AB}} = -3$, and $\Delta\epsilon = 5$; (c) maximum $\chi_{\text{AS}} = 9$, $\chi_{\text{BS}} = 0.1$, $\chi_{\text{AB}} = 0.1$, and $\Delta\epsilon = -5$; (d) minimum $\chi_{\text{AS}} = 3$, $\chi_{\text{BS}} = 3$, $\chi_{\text{AB}} = 0.5$, and $\Delta\epsilon = -2$.

to eq 23, the two are not identical because the two models yield different P_e and because $\partial\bar{\chi}_{\text{MB}}/\partial P_e \neq \partial\bar{\chi}_K/\partial P_e$. As before, the sign of $\partial P_e(\phi)/\partial\phi$ is determined by $\partial\bar{\chi}_{\text{MB}}/\partial P_e$. This reflects the concentration dependence of $K'_{\text{MB}} = (1 - \phi - P\phi)K_{\text{MB}}$ in particular, $\partial\bar{\chi}_{\text{MB}}/\partial P_e = \partial \ln K'_{\text{MB}}/\partial P_e$. Upon substituting $\partial P_e(\phi)/\partial\phi$ into $\partial\bar{\chi}_{\text{MB}}/\partial\phi$ as found from (30), we obtain

$$\frac{\partial\bar{\chi}_{\text{MB}}}{\partial\phi} = \left(\frac{\partial\bar{\chi}_{\text{MB}}}{\partial P_e}\right)^2 \frac{\phi}{\partial^2 F_{\text{int}}/\partial P^2} - \frac{2}{\phi^3} \ln\left(1 - \frac{P_e\phi}{1 - \phi}\right) - \frac{P_e}{\phi^2} \left[1 + \frac{1}{(1 - \phi)(1 - P_e\phi - \phi)}\right] \quad (32)$$

The first two terms are positive. Of these, the first is analogous to the corresponding result within the K model. The third term is negative. As a result, $\partial\bar{\chi}_{\text{MB}}/\partial\phi$ is no longer positive definite. Depending on the choice of χ_{AS} , χ_{BS} , χ_{AB} , and $\Delta\epsilon$ the calculated $\bar{\chi}_{\text{MB}}$ can be monotonically increasing or decreasing as well as exhibiting a minimum or a maximum (Figure 4). In the case of PEO, the calculated $\bar{\chi}_{\text{MB}}(\phi)$, utilizing the parameters used to fit the phase diagram of PEO, differs qualitatively from the experimentally measured $\bar{\chi}(\phi)$ (Figure 5).

VI. Discussion

As we have seen, two versions of the “hydrophobic–hydrophilic” two-state model for water-soluble polymers in aqueous solutions lead to a ϕ dependent χ_{eff} . The K version, where the two states undergo unimolecular intrachain conversion, results in $\partial\bar{\chi}/\partial\phi > 0$. Using χ_{AS} , χ_{BS} , χ_{AB} , and $\Delta\epsilon$ as obtained by fitting the phase diagram of PEO, this model yields $\bar{\chi}$ that agrees semiquantitatively with the experimentally observed values^{6,7} (Figure 3). Within the MB model the hydrophilic monomeric state binds a water molecule. As a result, the interconversion reaction is bimolecular and the translational entropy of the water plays a role in determining the equilibrium state. In this model $\bar{\chi}$ can display a number of scenarios (Figure 4): $\bar{\chi}(\phi)$ can be monotonically increasing, can be monotonically decreasing, or can exhibit an extremum (maximum or minimum). The $\bar{\chi}$ vs ϕ , as calculated with the parameters used to fit the

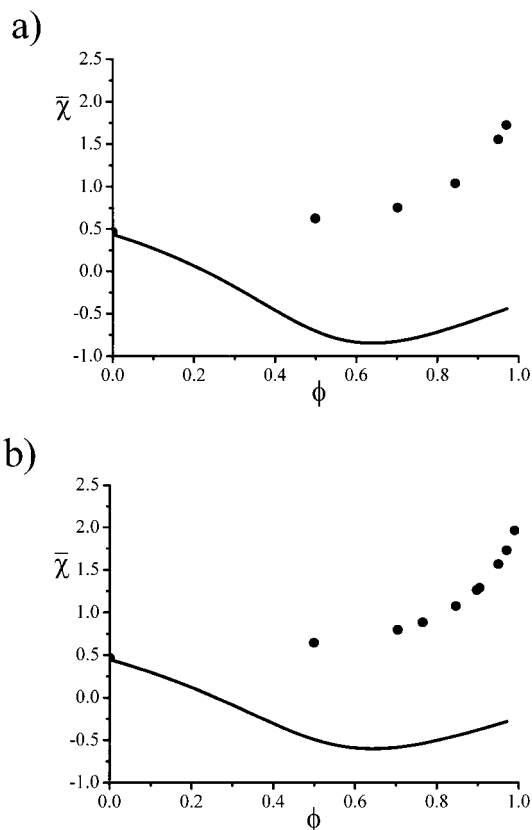


Figure 5. $\bar{\chi}_{MB}$ vs ϕ (continuous line) calculated using $\chi_{AS} = \chi_{BS} = \chi = 2.885 - 0.0036T$, $\chi_{AB} = 0$, and $\Delta\epsilon = 6.38 - 2408/T$. These parameters, used to fit the phase diagram of PEO, qualitatively differ from the experimental values of $\bar{\chi}$ (full circles) as measured with $N = 3000$ at (a) $T = 328$ K and (b) $T = 338$ K.

phase diagram of PEO, differs qualitatively from the experimentally obtained curve (Figure 5). However, the $\partial\bar{\chi}/\partial\phi < 0$ behavior allowed by this model is of interest since it has been observed in aqueous solutions of the neutral water-soluble polymer PVP¹⁹ (Figure 2). These results stress the importance of using the experimental values of $\bar{\chi}$ in fitting χ_{AS} , χ_{BS} , χ_{AB} , and $\Delta\epsilon$ and in evaluating the performance of the model. From the perspective of the general theory of polymers it is of interest that the “two-state” models can account for the dependence of χ_{eff} on ϕ and T and the pressure while retaining the principal approximations of the Flory–Huggins theory, i.e., incompressibility, monomer, and a solvent of identical size and shape and local composition that equals the global one.

At this point it is helpful to consider alternative mechanisms leading to $\chi_{eff}(\phi)$. For brevity we limit this discussion to two physically transparent models. One is the n -cluster model proposed by de Gennes for aqueous solutions of PEO.¹⁶ This model was motivated by two experimental observations concerning the behavior of such solutions: (i) the interpretation of calorimetric measurements in terms of the Flory mixing free energy yields a $\bar{\chi}$ that increases strongly with ϕ ^{6,7} and (ii) reports of formation of aggregates in concentrated solutions of PEO.²¹ Within this model, the concentration dependence of χ_{eff} is attributed to attractive interactions leading to stable clusters of $n > 2$ monomers while binary monomer–monomer interactions remain repulsive. This is another variation of a two-state model involving a dynamic equilibrium between “clustered” and “unclustered” monomers. In mo-

lecular terms, a n -cluster may correspond to a micelle or a mixed helix. The formation of the n -clusters gives rise to an additional term, $-\rho(T)\phi^n$ (with $\rho > 0$), in the interaction free energy. Thus, the mixing free energy per site is

$$\frac{F_{mix}}{kT} = \chi\phi(1 - \phi) + \rho(T)(\phi - \phi^n) + \frac{\phi}{N} \ln \phi + (1 - \phi) \ln(1 - \phi) \quad (33)$$

leading to

$$\chi_{eff} = \chi + \rho \frac{1 - \phi^{n-1}}{1 - \phi} \quad (34)$$

The corresponding $\bar{\chi}$ is

$$\bar{\chi} = \chi + \rho(n - 1)\phi^{n-2} \quad (35)$$

and $\partial\bar{\chi}/\partial\phi > 0$. The n -cluster model is indeed capable of rationalizing the two experimental observations noted above. However, of these, the second observation is now a subject of debate.²² Furthermore, the molecular structure of the ethylenoxide monomers does not reveal amphiphilic motifs. It is thus difficult to justify the assumption of cluster formation in solutions of PEO. Accordingly, the validity of this model in the case of aqueous solutions of neutral water-soluble polymers such as PEO is not obvious. On the other hand, the model is indeed applicable to solutions of polysoaps where formation of inter- and intrachain micelles does occur.²³ The second model, advanced by Painter et al., is applicable to all polymer solutions.¹¹ Within this model, the ϕ dependence of χ_{eff} is attributed to the interplay of intrachain and interchain contacts. The authors argue that there is a probability γ for intrachain monomer–monomer contacts. As a rough approximation, γ can be identified with the monomeric volume fraction, ϕ_G , within a Gaussian coil of radius $R_G \approx N^{1/2}a$ where N is the polymerization degree and a is the monomer size, $\phi_G \approx Na^3/R_G^3 \approx N^{-1/2}$. In a lattice comprising of N_T sites of coordination number z there are $N_T\phi$ sites occupied by monomers with a total of $N_Tz\phi$ adjacent sites. Of the $N_Tz\phi$ adjacent sites $N_Tz\phi\gamma$ are occupied by monomers because of intrachain contacts. The total number of free, unblocked adjacent sites is thus $N_Tz(1 - \phi\gamma)$ while the number of free sites adjacent to monomers is $N_Tz\phi(1 - \gamma)$. The probability of a free site adjacent to a monomer is thus $\phi(1 - \gamma)/(1 - \phi\gamma)$. Accordingly, the number of monomer–solvent contacts is $N_T(1 - \phi)\phi(1 - \gamma)/(1 - \phi\gamma)$. This expression allows for the requirement that a solvent molecule occupies an unblocked site adjacent to a monomer. Accordingly, the mixing energy term per site is $E_{mix}/kT = \chi(1 - \phi)\phi(1 - \gamma)/(1 - \phi\gamma)$ yielding an enthalpic contribution to χ_{eff}

$$\chi_{eff} = \chi \frac{1 - \gamma}{1 - \phi\gamma} \quad (36)$$

and to a corresponding enthalpic $\bar{\chi}$

$$\bar{\chi} = \chi \left(\frac{1 - \gamma}{1 - \phi\gamma} \right)^2 \quad (37)$$

where, again, $\partial\bar{\chi}/\partial\phi > 0$. In their original paper, Painter et al. supplemented this enthalpic $\bar{\chi}$ by an entropic one, allowing for the effect of the chain bending back on itself following the analysis of Huggins.²⁴

Aside from physical insight regarding the molecular origins of $\chi_{\text{eff}}(\phi)$, the above discussion identifies certain difficulties. Overall, it seems unlikely that one of the four models described above will emerge fully victorious. By construction, the n -cluster model is applicable only to solutions of associating polymers. The two "two-state" models are suitable candidates for the description of aqueous solutions of neutral water-soluble polymers exhibiting insolubility gap. While the model of Painter et al. applies, in principle, to all polymeric systems it cannot account for systems exhibiting $\partial\bar{\chi}/\partial\phi < 0$. Such behavior was actually observed in both aqueous and nonaqueous solutions, yet of the four models considered above only the MB model yields a scenario involving $\partial\bar{\chi}/\partial\phi < 0$. Altogether one can thus envision situations where *all the different mechanisms described may contribute simultaneously*. Another discouraging observation concerns the number of parameters involved. All four models introduce additional parameters that do not appear in the familiar Flory–Huggins theory: γ in the model of Painter et al., ρ and n in the n -cluster model; $\Delta\epsilon$, χ_{AB} , χ_{AS} , and χ_{BS} for the two "two-state" models. The necessity to unambiguously determine the additional parameters limits the predictive power of the models. Clearly, this problem is even more serious when a number of mechanisms contribute simultaneously to the ϕ dependence of χ_{eff} . Note, however, that this last difficulty can be partially resolved in certain cases. Thus, the contribution of the mechanism of Painter et al. can be separated from the one due to the "two-state" mechanism. This is because the mechanism of Painter et al. is inherently a polymeric effect that disappears in the monomeric limit, $N = 1$. On the other hand, *the two state models also apply to solution of the unpolymerized monomers; i.e., χ_{eff} and $\bar{\chi}$ are independent of N .*

Following our discussion of alternative models for $\chi_{\text{eff}}(\phi)$, it is helpful to summarize the evidence favoring the two-state models. Using these models, it was possible to derive the phase diagram of PEO^{14,17} and its pressure dependence.¹⁷ In addition, the K model was successfully utilized to rationalize a variety of systems involving PEO, Polypropyleneoxide (PPO) and PEO–PPO copolymers.²⁵ These successes lend support to the validity of the two-state model. On the negative side, there is relatively little direct evidence for the existence of the two monomeric states. Computational studies lend the most direct support to the two-state models. The K model is supported by recent molecular dynamics study that monitored the population of hydrophilic and hydrophobic conformations as a function of temperature and concentration and relates their relative stability to polar interactions.²⁶ This study utilized force fields obtained from quantum mechanical calculations of dimethoxyethane.²⁷ Somewhat different conclusions were reached in studies of higher oligo(ethylene oxides).²⁸ In particular, these studies (i) support the MB model, (ii) stress the importance of conformers allowing formation of "water bridges", i.e., where a single water molecule forms two hydrogen bonds with the oxygens in the oligo(ethylene oxides) (one such conformer, though not the most stable, is helical), and (iii) allow to rationalize force measurements of PEO²⁹ and, in par-

ticular, the difference in the extension force laws found in water and in nonaqueous solvent.³⁰ Thus, while a consensus on the computational results is yet to emerge, this approach may eventually allow to identify the relevant monomeric states and to obtain $\Delta\epsilon$, χ_{AB} , χ_{AS} , and χ_{BS} .

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