

SPECIFIC INTERACTIONS IN SOLUTIONS OF POLYMERS. III.* SORPTION EQUILIBRIA IN THE SYSTEM POLYMER-MIXED SOLVENT**

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The general conditions for the sorption equilibrium in the system polymer-binary solvent were applied to a model system of associates formed by a specific interaction. Equations for the calculation of the preferential and total sorption were derived both for an undiluted and for a very diluted polymeric phase. It was shown on the basis of these equations that in dilute systems the effect of the individual types of specific interactions on the total and preferential sorption may be transformed into an effect of the mean size of the association complexes. It can be demonstrated from the concentration dependence of these sizes that the self-association of one of the low-molecular-weight components can have as its consequence an inversion of the sign in the preferential sorption, if the composition of the mixed solvent varies; the preferential sorption has a convergent character in the neighbourhood of this inversion. At the same time, a maximum appears in the curve representing the dependence of the total sorption on composition. Mutual association of both components of the solvent can cause an inversion of the preferential sorption with a divergent neighbourhood and a minimum in the course of the total sorption. A simultaneous specific interaction of one of the components of the solvent with the polymer may have either a favourable or unfavourable effect on the occurrence of the phenomena described above. With the increasing concentration of the polymer, the effect of the size of unassociated molecules becomes more important. As far as a comparison with the still scarce experimental data is possible, it seems that the suggested theory explains the deviations of the experiment from the predictions based on the Flory-Huggins equation in the right direction, but not to the full extent.

The experimental results obtained by an investigation of the swelling equilibria of a macromolecular coil in contact with a binary solvent¹⁻⁵ indicate that in many cases these equilibria cannot be described in terms of expressions derived⁶ from the Flory-Huggins equation with three parameters of the binary interaction (χ_{AB} , χ_{BC} , χ_{AC}). This concerns mainly systems having polar and specific interactions; the difficulties will appear especially if we do not limit ourselves to a partial characterization of the equilibrium in terms of either the total or the preferential sorption, but offer a complete description, comprising both quantities. It happens in such cases that the behaviour of the ternary system cannot be explained, even if we consider the concentration dependence of the binary χ -parameters¹ or adjust one of the three binary parameters which it was

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not possible to determine from the behaviour of the binary system^{1,5}. The difficulties can be avoided by introducing a ternary interaction parameter χ_{ABC} ^{1,5}. However, a closer insight into the physical meaning hidden behind this formal generalization may only be provided by the application of a more detailed theoretical model than that used as the basis of the Flory-Huggins equation. The laboriousness of the mathematical treatment of the more complex models is considerably reduced by the limit thermodynamic equilibrium conditions, derived for dilute systems².

One of the possible reasons which lead to the above deviations consists in the non-validity of the assumption of random mixing which must be respected particularly in systems with specific interactions. We have therefore used the theory of these systems, based on the model of equilibrium between different types of associates, in a comparatively simple version^{7,8}: we assume that the equilibrium constants of association are independent of concentration, and that the formation of associates does not affect the size of non-specific interactions. This simplification, along with some others, allowed equations to be derived which enable us *a*) to discuss the effect of different types of interactions on the macroscopic values of the preferential and total sorption, *b*) to verify if and to what extent the nature of the ternary interaction parameter in the Flory-Huggins equation may be explained in terms of deviations from the random mixing.

THEORETICAL

General Model of the Sorption Equilibrium

Let us consider the equilibrium between a ternary phase consisting of liquids A and B and polymer C (polymer phase) and a binary mixture of liquids A and B (solvent phase). Such a state of equilibrium may be realized (1) as swelling equilibrium of *a*) a three-dimensional polymeric network in contact with a mixed solvent or *b*) a single macromolecular coil in a dilute solution, (2) as osmotic equilibrium, when the polymer solution is separated from the solvent by a semipermeable membrane, (3) as limit case of phase separation for a polymer having an infinite molecular weight. In contrast with the former two, the latter of the above types of equilibrium is connected with special values of the interaction parameters and may also be regarded as a special case of the osmotic equilibrium at which the osmotic pressure attains zero.

The ternary system has one degree of freedom at the swelling equilibrium at a given temperature and pressure; the choice of the composition of the binary phase determines at the same time the other two data, which are necessary for a full description of the system. This description seems to be best made in terms of the total and preferential sorption.

The total sorption of the solvent in the polymeric phase is characterized by the volume swelling ratio, q , which represents the reciprocal value of the volume fraction of the polymer, v_c . According to the theory of elasticity of rubber at a given network structure, the elastic part of the free enthalpy of the ternary phase G_{e1} is a single-

valued function of v_C . The same holds for its derivative with respect to the volume of the swollen phase.

$$P_{e1} = (\partial G_{e1} / \partial V)_{T,P}, \quad (1)$$

whose equilibrium value can therefore also serve as a characteristic of the total sorption. The preferential sorption of the component A in the polymeric phase is defined as

$$\varepsilon = u_A - v_{A0}, \quad (2)$$

where

$$u_A = v_A / (v_A + v_B); \quad (3)$$

v_A , v_{A0} (and v_B , v_{B0}) are volume fractions of the component A (and B) in the polymeric or the solvent phase, respectively.

At the osmotic equilibrium the osmotic pressure π has a similar function as the elastic pressure P_{e1} at the swelling equilibrium. Since, however, π is an external, adjustable force, no functional relationship exists between π and v_C , so that the system has one degree of freedom more. It is possible, therefore, either to choose π , which makes v_C (or q) the measure of the total sorption, or to choose v_C , in which case the equilibrium value of π gives the potential of the total sorption. The equilibrium conditions can be represented in a general form by means of the equation

$$P = (\mu_{K0} - \mu_K) / \bar{V}_K, \quad K \equiv A, B; \quad (4)$$

here, P is a common symbol for the osmotic pressure and elastic potential, μ_K is the part of the chemical potential of the component K which is due to mixing and does not therefore involve the effect of pressure or deformation, and μ_{K0} is related to the binary solvent phase; \bar{V}_K is the partial molar volume of the component K. The pair of the equilibrium conditions may also be transformed to become⁶

$$(\mu_{A0} - \mu_A) / \bar{V}_A = (\mu_{B0} - \mu_B) / \bar{V}_B, \quad P = \sum_K u_K (\mu_{K0} - \mu_K) / \bar{V}_K, \quad K \equiv A, B. \quad (5), (6)$$

Eq. (5) does not include P and is therefore an appropriate starting point for the calculations of the preferential sorption.

Let us now apply the conditions of the sorption equilibrium to a theoretical model⁷ of two liquids A and B and the polymer C, in which associates of a general formula $A_i B_j C_k$ are formed by specific interactions. The associates are in mutual thermodynamic equilibrium, and their free enthalpy of mixing is governed by the Flory-Huggins equation. Although the formation of associates is connected with volume changes, the effect of these changes on the sorption equilibrium may be considered negligible in comparison with the possible consequences of other approximations mentioned in the introduction. We shall therefore replace, in the general equilibrium

equations, the partial molar volumes by molar volumes of pure components, using the latter similarly as before^{7,8} as a basis for the definition of segments. It then holds, for the number of segments in a molecule of the component K, that $r_K = V_K/V_U$, where V_U is the chosen volume of the segment, the same for segments of all components. The change in free enthalpy, which accompanies the formation of a mixture from pure components, is then represented by the relationship (cf.⁷, Eqs (13) and (33))

$$\Delta G_N/RT = \sum_K v_K \ln(p_K/p_K^0) + \sum_K v_K (\sum_S v_S)_K^0 - \sum_S v_S + \sum_{K \neq K'} \sum_{K < K'} \chi_{KK'} v_K v_{K'} \quad K \equiv A, B, C. \quad (7)$$

In this equation, ΔG_N is related to one mol of segments: $\Delta G_N = \Delta G_M/n$, where n is the total number of moles of segments in the system; v_K is the number of moles of the analytical component K per the total number of moles of segments,

$$v_K = n_K/n = v_K/r_K; \quad (8)$$

v_S is an analogously defined concentration of the associate $S \equiv A_i B_j C_k$, and p_K represents v_S for those molecules of the component K which have not entered into any associate. The superscript ⁰ along with the subscript K denotes the pure component K prior to mixing, the summing indexes K, K' designate sums over the analytical components A, B, C, and S denotes the sum over all existing types of associates, inclusive unassociated molecules. The parameters $\chi_{KK'}$ characterize nonspecific interactions. For v_S , the equation of the association equilibrium is valid:

$$v_S = K_S p_A^i p_B^j p_C^k, \quad (9)$$

where i, j, k indicate the composition of the associate $A_i B_j C_k$. The dependence of p_A, p_B, p_C on the analytical composition of the ternary phase is determined by a system of three equations (cf.⁷, Eq. (11)):

$$v_A = \sum_S i K_S p_A^i p_B^j p_C^k, \quad v_B = \sum_S j K_S p_A^i p_B^j p_C^k, \quad v_C = \sum_S k K_S p_A^i p_B^j p_C^k. \quad (10a, b, c)$$

The right-hand sides of these equations can be expressed with advantage using the method of generating functions^{7,8}, the use of which will be described later. The parameters of nonspecific interactions, $\chi_{KK'}$, do not cause any essential trouble in the calculations of the sorption equilibrium owing to the assumption of their independence of the degree of association; however, they complicate the final expressions to a fairly great extent. Therefore, only equations into which a simplifying assumption

$$\chi_{AC}/r_A = \chi_{BC}/r_B = \chi_U, \chi_{AB} = 0 \quad (11)$$

has been introduced will be given in the present communication, so that the last sum in Eq. (7) is reduced to $\chi_U v_C (1 - v_C)$. The equation for the chemical potentials of the components A and B in the polymeric phase (*cf.*⁷, Eq. (37)) then is

$$(\mu_K - \mu_K^0)/RT = \ln(p_K/p_K^0) - r_K[\sum_S v_S - (\sum_S v_S)_K^0] + r_K \chi_U v_C^2, \quad K \equiv A, B; \quad (12a)$$

for the chemical potential in the solvent phase it holds

$$(\mu_{K0} - \mu_K^0)/RT = \ln(p_{K0}/p_K^0) - r_K[(\sum_S v_S)_0 - (\sum_S v_S)_K^0], \quad K \equiv A, B; \quad (12b)$$

here, quantities related to this phase are again designated by the subscript $_0$. By substituting for μ_K and μ_{K0} into Eq. (5) we shall obtain a relationship for the equilibrium in the preferential sorption

$$\ln(p_{A0}/p_A) = s \ln(p_{B0}/p_B); \quad (13)$$

from the equilibrium conditions (4) and (6) we have various alternatives of equation for the osmotic or elastic pressure,

$$P = (RT/V_U) [(1/r_K) \ln(p_{K0}/p_K) + \sum_S v_S - (\sum_S v_S)_0 - \chi_U v_C^2], \quad K \equiv A, B; \quad (14a)$$

$$P = (RT/V_U) [(u_A/r_A) \ln(p_{A0}/p_A) + (u_B/r_B) \ln(p_{B0}/p_B) + \sum_S v_S - (\sum_S v_S)_0 - \chi_U v_C^2]. \quad (14b)$$

To calculate the sorption equilibria, these equations may only be used in connection with Eqs (9) and (10) and with their analogues for the solvent phase. In our computing program, first p_{A0} and p_{B0} were computed from a given v_{A0} from Eqs (10a,b), written for a binary solvent. For a given v_C , v_A was computed by an iterative procedure, consisting in a repeated trial choice of v_A , followed by calculating p_A and p_B from modified Eqs (10) and verifying whether the computed values satisfy the equilibrium condition (13). On finding a satisfying value of v_A , the equations (14a) or (14b) were used for calculating the osmotic pressure.

Limit for a Dilute Ternary Phase

To calculate the sorption equilibria in a macromolecular coil having a low density of segments, it is suitable to transform the general thermodynamic conditions into the form of limit equations valid for very dilute systems. Let us introduce a limit parameter of the preferential sorption A_1

$$A_1 = \lim_{v_C \rightarrow 0} (e/v_C) \quad (15)$$

and the Shultz-Flory potential of the total sorption in a dilute system⁶

$$Y = (\alpha^5 - \alpha^3)/2C_M M^{1/2}, \quad (16a)$$

where α is the linear expansion factor of the coil, M is molecular weight, and C_M is given by

$$C_M = \text{const.} (\bar{v}_C^2/\bar{V}_A) (M/\bar{r}_0^2)^{3/2}. \quad (16b)$$

The equilibrium conditions then are^{1,2}

$$A_1 = (v_{A0}N_{AA} - N_{AC})/N_{AA}, \quad (17a)$$

$$Y = (\bar{V}_A/2RT) [N_{CC} - 2v_{A0}N_{AC} + (v_{A0}^2 - A_1^2)N_{AA}], \quad (17b)$$

the expressions $N_{KK'}$ being defined by

$$N_{KK'} = \lim_{v_C \rightarrow 0} (\partial^2 G_v^* / \partial v_K \partial v_{K'})_{T,P}, \quad K, K' \equiv A, C, \quad (18a)$$

where

$$G_v^* = (\Delta G_M/V) - (RT/\bar{V}_C) v_C \ln v_C. \quad (18b)$$

The second derivatives of the free enthalpy of mixing may be expressed as ratios of determinants (cf.⁷, Eqs (38a) and (39) and Table III)

$$N_{KK'} = -(RT/V_U) \lim_{v_C \rightarrow 0} (D_{KK'}^*/D), \quad K, K' \equiv A, C. \quad (19)$$

The fourth degree determinants $D_{KK'}^*$ may be written with advantage as determinants of matrices divided into blocks

$$D_{KK'}^* = \begin{vmatrix} a_{KK'} & \mathbf{w}_K \\ \mathbf{w}_K^t & \mathbf{D} \end{vmatrix}, \quad K, K' \equiv A, C, \quad (20)$$

where \mathbf{D} is the matrix of the second moments

$$\mathbf{D} \equiv \begin{bmatrix} \langle ii \rangle & \langle ij \rangle & \langle ik \rangle \\ \langle ij \rangle & \langle jj \rangle & \langle jk \rangle \\ \langle ik \rangle & \langle jk \rangle & \langle kk \rangle \end{bmatrix}, \quad (21)$$

the second moments $\langle xx' \rangle$ being defined by

$$\langle xx' \rangle = \sum_S x_S x'_S v_S, \quad x, x' \equiv i, j, k, \quad (22)$$

and it holds $D = \det(\mathbf{D})$. The vectors \mathbf{w}_K and $\mathbf{w}_{K'}$ are row vectors, for which one of the vectors $\mathbf{w}_A, \mathbf{w}_C$ is substituted, depending on whether they are related to a differentiation with respect to v_A or v_C :

$$\mathbf{w}_A = [-r_A^{-1}, r_B^{-1}, 0], \quad \mathbf{w}_C = [0, r_B^{-1}, -r_C^{-1}]; \quad (23)$$

the symbol \dagger denotes transposition into a column vector. For the left upper element $a_{KK'}$ it holds

$$a_{AA} = a_{AC} = 0, \quad a_{CC} = (r_C v_C)^{-1} - 2\chi_U. \quad (24)$$

The determinants must be transformed so as to make possible limitation for $v_C \rightarrow 0$ after their algebraic expansion. The determinants are then substituted into the thermodynamic equilibrium conditions. After rearrangement, we obtained a relationship for the limit parameter of the preferential sorption

$$A_1 = \frac{(r_B^2 \langle jj \rangle_0 + r_A r_B \langle ij \rangle_0) [v_{A0} + r_A (i)_\sigma] - (r_A r_B \langle ij \rangle_0 + r_A^2 \langle ii \rangle_0) [v_{B0} + r_B (j)_\sigma]}{r_A^2 \langle ii \rangle_0 + 2r_A r_B \langle ij \rangle_0 + r_B^2 \langle jj \rangle_0} \quad (25a)$$

and for the potential of the total sorption

$$Y = \frac{r_A}{2} \left\{ \frac{[1 + r_A (i)_\sigma + r_B (j)_\sigma]^2}{r_A^2 \langle ii \rangle_0 + 2r_A r_B \langle ij \rangle_0 + r_B^2 \langle jj \rangle_0} - (k)_a - 2\chi_U \right\}. \quad (25b)$$

The second moments $\langle ii \rangle_0, \langle jj \rangle_0, \langle ij \rangle_0$ are related to the binary solvent phase and characterize the self-association of the components A and B and the mutual association between the components A and B, resp. It holds, namely, $\langle ii \rangle_0 / v_{A0} = (\bar{i}_w)_0$, $\langle jj \rangle_0 / v_{B0} = (\bar{j}_w)_0$, where for instance $(\bar{i}_w)_0$ is the weight average of the "degree of polymerization" of the component A in all associates (including nonassociated molecules) in which molecules of the component A occur. The ratio $\langle ij \rangle_0 / v_A$ then describes the average number of molecules B per one molecule A in associates containing the component A. The expressions $(i)_\sigma, (j)_\sigma$ and $(k)_a$ are defined by

$$(i)_\sigma = \lim_{v_C \rightarrow 0} (\langle ik \rangle / v_C), \quad (j)_\sigma = \lim_{v_C \rightarrow 0} (\langle jk \rangle / v_C), \quad (26a)$$

$$(k)_a = \lim_{v_C \rightarrow 0} [(\langle kk \rangle - v_C) / v_C^2]. \quad (26b)$$

The first two quantities give the number average of the number of molecules of the component A or B, specifically bonded to one polymeric segment in an infinitely diluted ternary phase; the last quantity is in a close relationship with the self-association constant of the polymer (cf.⁸, Eq. (20)).

Using specialized model systems as examples we shall show below how the method of generating functions can be used to find relationships describing the dependence of the quantities defined above on concentrations of nonassociated molecules, p_K .

Solvation of the Polymer with the Solvent A, Accompanied by Competitive Inter-association of the Solvents A and B

Let us assume that the component A is able to be specifically bonded to b sites of the other solvent B (the bonding constant to one site is ϱ) and to c sites of the polymer C (the bonding constant η). The molecule A has one bonding site, so that the sorption of A by B and of A by C compete with each other. We also assume that the sorption at any site of the molecule B or C is not affected by the sorption at another site of the same molecule. Such pattern of interactions may be considered, *e.g.*, in the system chloroform (A)–acetone (B)–poly(methyl methacrylate) (C). Analogously to the model of solvation of a single solvent to the polymer (*cf.*⁸, Eq. (23)), the generating function of the association equilibrium in the ternary phase of our model may be represented by

$$\sum_S v_S = p_A + p_B(1 + \varrho p_A)^b + p_C(1 + \eta p_A)^c. \quad (27)$$

Differentiation of this equation with respect to $\ln p_A$, $\ln p_B$, or $\ln p_C$ yields (*cf.*⁷, Eq. (20a)) relationships for the first moments of the stoichiometric coefficients i, j, k , which at the same time (*cf.*⁷, Eq. (21)) are equal to concentrations of the analytical components. We thus obtain a specialized form of equations (10a, b, c):

$$v_A = \langle i \rangle = p_A [1 + b\varrho v_B(1 + \varrho p_A)^{-1} + \eta v_C(1 + \eta p_A)^{-1}], \quad (28a)$$

$$v_B = \langle j \rangle = p_B(1 + \varrho p_A)^b, \quad v_C = \langle k \rangle = p_C(1 + \eta p_A)^c. \quad (28b, c)$$

By means of these equations, it is possible to calculate, on the basis of given analytical concentrations, v_K , concentrations of the individual molecules, p_K , by calculating p_A from Eq. (28a) and then substituting p_A into the other equations. The generating function for the binary solvent phase has the form

$$(\sum v_S)_0 = p_{A0} + p_{B0}(1 + \varrho p_{A0})^b, \quad (29)$$

wherefrom

$$v_{A0} = \langle i \rangle_0 = p_{A0} [1 + b\varrho v_{B0}(1 + \varrho p_{A0})^{-1}], \quad (30a)$$

$$v_{B0} = \langle j \rangle_0 = p_{B0}(1 + \varrho p_{A0})^b. \quad (30b)$$

A twofold differentiation of $\sum v_S$ yields the second statistical moments $\langle xx' \rangle$, from which the solvation and association characteristics of the dilute solution are

obtained; these will then be substituted into Eqs (25a,b):

$$\langle ii \rangle_0 = p_{A0} + \langle ij \rangle_0 (1 + b\varrho p_{A0}) (1 + \varrho p_{A0})^{-1}, \quad (31a)$$

$$\langle ij \rangle_0 = b\varrho v_{B0} p_{A0} (1 + \varrho p_{A0})^{-1}, \quad \langle jj \rangle_0 = v_{B0}, \quad (31b, c)$$

$$(i)_\sigma = (c/r_C) \eta p_{A0} (1 + \eta p_{A0})^{-1}, \quad (j)_\sigma = 0, \quad (k)_a = 0. \quad (31d, e)$$

Solvation with a Self-Associating Solvent A in the Presence of an Inert Diluent B

Let us now assume that the independent solvation sites of a macromolecule are bonded with linear associates of the component A, the equilibrium constant of formation of an i -membered self-associate in the bulk phase being described by $\kappa\sigma^{i-1}$, and the bond of m molecules of A in the form of a linear chain to one site of macromolecule having an equilibrium constant $\eta\sigma_s^{m-1}$. The molecule B does not enter into any specific interactions. Thus, the system differs from the model system described in the preceding paper⁸ only by the presence of an inert diluent B. We may therefore write for the total concentration of associates

$$\sum_S v_S = (1 - \kappa) p_A + \kappa p_A (1 - \sigma p_A)^{-1} + p_B + p_C [1 + (\eta - \sigma_s) p_A]^c (1 - \sigma_s p_A)^{-c}, \quad (32)$$

wherefrom we obtain, by differentiating and rearranging

$$v_A = (1 - \kappa) p_A + \kappa p_A (1 - \sigma p_A)^{-2} + c v_C \eta p_A [1 + (\eta - \sigma_s) p_A]^{-1} (1 - \sigma_s p_A)^{-1}, \quad (33a)$$

$$v_B = p_B, \quad v_C = p_C [1 + (\eta - \sigma_s) p_A]^c (1 - \sigma_s p_A)^{-c}; \quad (33b, c)$$

and for the phase without the polymer

$$(\sum v_S)_0 = (1 - \kappa) p_{A0} + \kappa p_{A0} (1 - \sigma p_{A0})^{-1} + p_{B0}, \quad (34a)$$

$$v_{A0} = (1 - \kappa) p_{A0} + \kappa p_{A0} (1 - \sigma p_{A0})^{-2}, \quad v_{B0} = p_{B0}. \quad (34b, c)$$

For the dilute ternary phase it holds

$$\langle ii \rangle_0 = (1 - \kappa) p_{A0} + \kappa p_{A0} (1 + \sigma p_{A0}) (1 - \sigma p_{A0})^{-3}, \quad \langle ij \rangle_0 = 0 \quad (35a, b)$$

$$\langle jj \rangle_0 = v_{B0}, \quad (i)_\sigma = (c/r_C) \eta p_{A0} [1 + (\eta - \sigma_s) p_{A0}]^{-1} (1 - \sigma_s p_{A0})^{-1} \quad (35c, d)$$

$$(j)_\sigma = 0, \quad (k)_a = 0. \quad (35e)$$

DISCUSSION

To analyze the effect of individual types of specific interactions on the preferential and total sorption, we shall first use a very dilute polymeric phase, since the limit equations (25a,b) derived for low concentrations of the polymer contain direct quantitative characteristics of the individual interaction types. Eqs (25a,b) confirm what has been expected in that the specific solvation of the polymer by one of the solvent components raises the preferential sorption of this component as well as the total sorption of the binary mixture. The self-association of the macromolecule does not affect the limit parameter of the preferential sorption, but depresses the potential of the total sorption. To elucidate the effect of specific interactions in the binary solvent, we shall transcribe Eqs (25a,b) into the form

$$A_1 = \frac{\bar{r}_{(B)}[1 + r_A(i)_\sigma/v_{A0}] - \bar{r}_{(A)}[1 + r_B(j)_\sigma/v_{B0}]}{\bar{r}_{(A)}v_{A0} + \bar{r}_{(B)}v_{B0}} v_{A0}v_{B0}, \quad (36a)$$

$$Y = \frac{r_A}{2} \left\{ \frac{[1 + r_A(i)_\sigma + r_B(j)_\sigma]^2}{\bar{r}_{(A)}v_{A0} + \bar{r}_{(B)}v_{B0}} - (k)_a - 2\chi_U \right\}, \quad (36b)$$

where $\bar{r}_{(A)}$ and $\bar{r}_{(B)}$ are defined by

$$\bar{r}_{(A)} = \sum r_{ij0} i v_{ij0} / \sum i v_{ij0}, \quad (37a)$$

$$\bar{r}_{(B)} = \sum r_{ij0} j v_{ij0} / \sum j v_{ij0}, \quad r_{ij0} = r_A i + r_B j; \quad (37b, c)$$

the index $ij0$ denotes the associate $A_i B_j$, and the summations have been made over all associates (and uninvolved molecules) capable of existing in a mixture of the components A and B. r_{ij0} stands for the volume of the given associate, represented by the number of segments; $\bar{r}_{(A)}$ and $\bar{r}_{(B)}$ are average values of r_{ij0} , where the average was calculated, in the first case, over all molecules A present in the system, and in the second, over all molecules B. It seems of interest to compare Eqs (36a,b) with equations for a system without specific interactions, but having the same nonspecific interactions (Eq. (11)):

$$A_1 = \frac{r_B - r_A}{r_A v_{A0} + r_B v_{B0}} v_{A0} v_{B0}, \quad Y = \frac{r_A}{2} \left(\frac{1}{r_A v_{A0} + r_B v_{B0}} - 2\chi_U \right). \quad (38a, b)$$

If we omit, in Eqs (36a,b), terms containing $(i)_\sigma$, $(j)_\sigma$ and $(k)_a$ and leave only characteristics of interactions in the binary solvent, we can see that equations thus simplified differ from relationships (38a,b) only in that the data on the size of the individual molecules r_A , r_B have been substituted by mean sizes of the associates, $\bar{r}_{(A)}$, $\bar{r}_{(B)}$.

Therefore the rule that both the preferential sorption of the given component and the total sorption of the mixture decrease with the increasing size of molecules can be generalized to comprise the effect of the average size of the associate. The latter, however, is controlled by the association equilibrium, and its values therefore depend on the composition of the mixture A + B. Various specific features observed in the course of the dependences $A_1(v_{A0})$ and $Y(v_{A0})$ may then be interpreted in terms of the composition dependence of $\bar{r}_{(A)}$ and $\bar{r}_{(B)}$.

In a special case, when the component A self-associates, whereas the component B does not enter into specific interactions, it holds

$$\bar{r}_{(A)} = r_A \sum i^2 v_{i00} / \sum i v_{i00} = r_A (\bar{i}_w)_0, \quad \bar{r}_{(B)} = r_B; \quad (39a, b)$$

here, $\bar{r}_{(A)}$ represents the weight average of the size of self-associates. It should be noted that if the component A was not represented by a self-associating compound but by a polydisperse mixture of oligomers of the same type, then r_A in Eqs (38a,b) ought also to be replaced by the weight average; this value, however, would not vary with v_{A0} in contrast with the case of the self-associating compound. In our case, the numerator in Eq. (36a) may be written as $r_B - r_A (\bar{i}_w)_0$. If v_{A0} increases from zero to unity, $(\bar{i}_w)_0$ increases from unity to higher values. If, therefore, $r_B \leq r_A$, the inert component B is sorbed preferentially over the whole concentration range; if, however, $r_A < r_B$, A_1 must be equal to zero at certain concentration, and the sign of the preferential sorption changes. At this point of inversion the average size of the associate of the component A is comparable with the size of the molecule B. On each side of the point of inversion a different one of the two components is sorbed, namely, the one whose concentration is lower than at the point of inversion. Consequently the composition of the mixed solvent approaches that of the point of inversion more in the polymeric phase than in the equilibrium phase without the polymer; we shall therefore refer to this case as to an inversion with convergent neighbourhood.

The fraction in the expression for Y (Eq. (36b)) may in the above case be written as $1 / \{ r_B + [r_A (\bar{i}_w)_0 - r_B] v_{A0} \}$. It can be shown therefrom that at higher values of the ratio $s = r_A / r_B$ the dependence $Y(v_{A0})$ monotonously decreases; at lower values, it has a maximum. In contrast with the condition of the occurrence of inversion in the preferential sorption, where the critical value of s was equal to unity, the critical value for the occurrence of the maximum is somewhat lower than unity.

In another case, when none of the components undergoes self-association, but a complex A_1B_1 is formed, the average sizes of the associates may be represented by

$$\bar{r}_{(A)} = r_A + r_B (v_{110} / v_{A0}), \quad \bar{r}_{(B)} = r_B + r_A (v_{110} / v_{B0}); \quad (40a, b)$$

here, v_{110} is the concentration of the complex A_1B_1 ; v_{A0} and v_{B0} are again the total concentrations of the analytical components. It follows therefrom that an increase

in the effective size of the molecule ($r_K \rightarrow \bar{r}_{(K)}$) due to interassociation will manifest itself more in the case of the component which is present in a low concentration. The difference $\bar{r}_{(B)} - \bar{r}_{(A)}$, which decides about the sign of the preferential sorption A_1 , can therefore pass from negative to positive values, if v_{A0} varies from zero to unity. Consequently the inversion point of this type has "divergent" neighbourhood in which the polymer is enriched by the component present in excess; the mixture of solvents in the polymeric phase has thus a composition more remote from the inversion composition than the solvent outside the polymer (Fig. 1a, curves 1, 2).

The denominator in Eq. (36b) is then equal to $r_A v_{A0} + r_B v_{B0} + 2r_A r_B v_{110}$; the concentration v_{110} is proportional to the product $p_A p_B$ and its dependence on v_{A0} exhibits a maximum. Consequently curve $Y(v_{A0})$ has a minimum (Fig. 1b, curves 1, 2). In the neighbourhood of the minimum the potential Y can even attain negative values, so that in a dilute solution of a linear polymer having a sufficiently high molecular weight, separation into two phases should occur in a mixture of two good solvents, specifically interacting with each other. An experimental indication of this assumption was obtained by Dondos⁹ for the system chloroform-dioxane-poly(*p*-bromostyrene). If, therefore, an inversion in the preferential sorption or/and an extremum

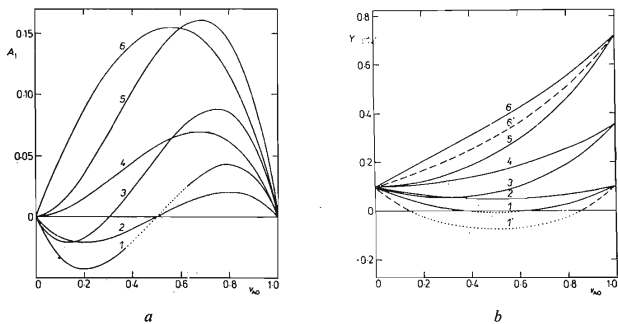


FIG. 1

System with a Mutual Association of the Solvent Components A + B and a Possible Solvation of the Polymer with the Component A (Limit for an Infinite Dilution of the Polymer): a) Dependence of the Preferential Sorption A_1 , b) of the Potential of the Total Sorption Y on the Composition of the Mixed Solvent v_{A0}

$r_A = r_B = 1$, $b = 1$, $c = r_C$, $\chi_{AB} = 0$, $\chi_{AC} = \chi_{BC} = 0.4$. Full curves: 1, 3, 5 $q = 1$, 2, 4, 6 $q = 0.3$, 1, 2 $\eta = 0$, 3, 4 $\eta = 0.3$, 5, 6 $\eta = 1$. Broken curves: calculated from the binary parameters of the Flory-Huggins equation (1', 6' cf. with 1, 6). Spotted parts of the curves: region of phase separation for $r \rightarrow \infty$.

of the potential of the total sorption appears in the case under consideration, their character is opposite to that of the preceding case, which is characterized by self-association of one of the components.

Both specialized models which have been dealt with in the theoretical part may serve as an example of systems in which the solvation of one of the components on the polymer plays role along with the specific interaction in the mixed solvent. If the mutual solvation of the components A and B is accompanied by the competitive solvation of A on the polymer, the values of both A_1 and Y become increased (Fig. 1a,b). Inversion in the preferential sorption is shifted towards $v_{A0} = 0$, until it disappears at a sufficiently strong solvation on the polymer. Only the asymmetry of the curve $A_1(v_{A0})$ remains; the curve has its maximum shifted toward higher values of v_{A0} and in the region of low v_{A0} it may be S-shaped. Such asymmetry is found with the curve obtained by Jacob and Daune¹⁰ by means of the method of sedimentation for the preferential sorption in the system chloroform (A)–butanone (B)–poly(methyl methacrylate) (C). Also the position of the minimum in the dependence $Y(v_{A0})$ is shifted toward low values of v_{A0} with the increasing constant of solvation to the polymer η ; on curves for a large η the minimum disappears, but the sign of curvature remains unchanged. The minimum can for instance be observed on the curve of the intrinsic viscosity of a polystyrene solution in the chloroform–dioxane mixtures, but not in the case of poly(methyl methacrylate)–solutions in the same solvents^{3,4} (chloroform is more bonded to the latter polymer).

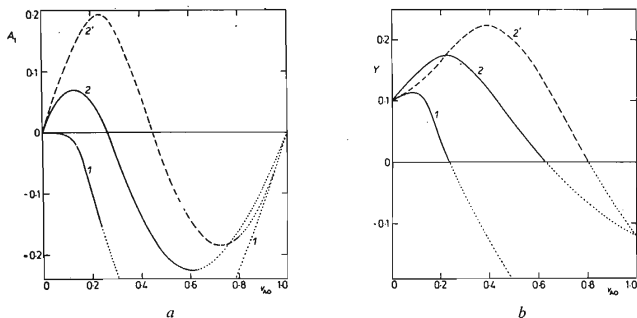


FIG. 2

System with Self-Association of the Component A and its Possible Specific Bond to the Polymer (Limit for an Infinite Dilution of the Polymer) a) Dependence of the Preferential Sorption, b) of the Potential of the Total Sorption on the Composition of the Mixed Solvent v_{A0}

$r_A = 1, r_B = 2, c = r_C/2, \chi_{AB} = 0, \chi_{AC} = 0.4, \chi_{BC} = 0.3, \kappa = 0.2, \sigma = 4.46$. Curves: 1 $\eta = 0, \sigma_s = 0, 2 \eta = 0.89, \sigma_s = \sigma$. Broken and spotted curves cf. text of Fig. 1. (2' cf. with 2).

Let us now compare the case of solvation of the self-associating solvent A to the polymer C (in the presence of the inert component B) with the case when the system contains the same low-molecular-weight components, but the polymer is inert and incapable of a specific interaction (Figs 2*a,b*). We can see that a specific solvation of the polymer may bring about the occurrence of inversion in the preferential sorption and of a maximum on the concentration dependence of the total sorption even there where they would not occur in the case of an inert polymer. The effect is thus quite opposite to that illustrated in Fig. 1. It is also worth noticing that no inversion can be observed on curves marked with 1 (Fig. 2), although $s = 1/2$, and the above condition for its occurrence would thus be fulfilled. This is because in this case, $\chi_{BC} > \chi_{AC}/s$ has been chosen, and the simplifying condition given by Eq. (11) is therefore not fulfilled. To calculate the curves, more complicated equations than (25*a,b*) had to be used.

Equations for an undiluted ternary phase do not admit of a similar deductive discussion as equations for diluted systems. It seems that the easiest way how to obtain an idea of the effect of the individual types of interaction is to compare the results of numerical calculations. The results can be suitably represented by a plot of v_C vs. u_A , containing two systems of lines: *a*) Coexistence lines are loci of all ternary systems which at appropriate pressure differences, π , can be in an osmotic equilibrium with the same binary solvent having the composition v_{A0} (and thus also in a mutual osmotic equilibrium). Using Eq. (2), the preferential sorption ε is then read off as a horizontal deviation of the coexistence line from the vertical straight line $v_A = v_{A0}$ at a distance v_C from the x -axis; *b*) the osmotic isobars connect points having the same osmotic pressure π (the position of these points can be calculated by an inversion interpolation of the dependence $\pi(v_C)$ at a constant v_{A0}). For the case of the gel swelling, it would be more suitable to replace the latter system of lines by curves of the total swelling of gels differing by the degree of crosslinking; their course, however, would not differ too much from that of the osmotic isobars. Two such plots can be seen in Figs 3 and 4: the one for a system with the interactions A + B and A + C, the other for the case of self-association of A and solvation of A to C.

It can be deduced from Fig. 3 that if both low-molecular-weight components have the same molar volume ($s = 1$), the character of the dependence of ε and π on the composition of the mixed solvent found for dilute solutions remains without change up to high concentrations of the polymer. Fig. 3 shows that the position of the inversion point ($u_A = v_{A0} = 0.3$) does not virtually vary with increasing v_C , the preferential sorption has a divergent character in all places (the coexistence curves diverge in the upward direction), and ε increases almost linearly with v_C . All osmotic isobars have a maximum, which corresponds to the minimum of the dependence $\pi(v_{A0})$ at a constant v_C ; the position of this maximum is almost identical for all isobars. If, however, both solvents differ in molar volumes, the effect of this difference plays a still more and more important role with increasing v_C . It can be shown, independent-

ly of any model, that in the limit for $v_C \rightarrow 1$ it must hold for $s > 1$

$$u_A \approx K(v_{A0}/v_{B0}^s)(1 - v_C)^{s-1} \rightarrow 0, \quad u_B \rightarrow 1 \quad (41a)$$

and for $s < 1$

$$u_A \rightarrow 1, \quad u_B \approx K'(v_{B0}/v_{A0}^{1/s})(1 - v_C)^{(1/s)-1} \rightarrow 0, \quad (41b)$$

where the constants of proportionality K, K' depend on the thermodynamic parameters of the system. Therefore, as long as $s \neq 1$, there is always such a concentration v_C above which for all values of v_{A0} the component having a smaller molar volume is sorbed preferentially. It is evident that in the region near to $v_C = 1$ all the self- and inter-associates present in the mixture of solvents disintegrate owing to its high dilution, so that the size of the single molecules plays the decisive role. Thus, if at lower v_C there is an inversion in the preferential sorption, it must vanish at $v_C \rightarrow 1$. This phenomenon is shown in Fig. 4, representing a system having the convergent character of the preferential sorption. Owing to the inequality $r_A < r_B$ the coexistence curves meet in the right upper corner of the diagram. The inversion line (*i.e.* the locus of all the inversion points) is considerably curved in the upper part of the graph and ends in the right margin of the diagram. The osmotic isobars have a minimum, which corresponds to the maximum on the curve representing the

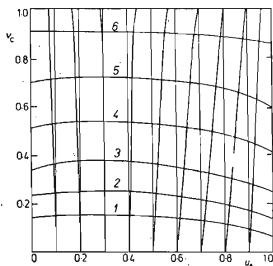


FIG. 3

System with Specific Interactions A + B and A + C: Coexistence Curves and Osmotic Isobars

Parameters of the system are identical with those of the system represented by curves 3 in Figs 1a,b. Values of $\pi V_1/RT$ for isobars: 1 $3 \cdot 10^{-3}$, 2 $1 \cdot 10^{-2}$, 3 $3 \cdot 10^{-2}$, 4 0.1, 5 0.3, 6 1.0.

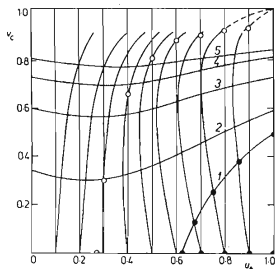


FIG. 4

System with Self-Association of A and its Specific Bond to Polymer: Coexistence Curves and Osmotic Isobars

Parameters of the system are identical with those of the system represented by curves 2 in Figs 2a,b. Values $\pi V_1/RT$ for isobars: 1 0, 2 0.02, 3 0.1, 4 0.2, 5 0.3, zero preferential sorption \circ , phases coexisting at demixing \bullet .

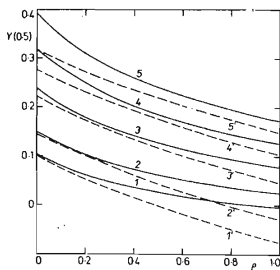
dependence of the potential of the total sorption on the composition of the mixed solvent. The diagram also contains the isobar $\pi = 0$, which limits the region of restricted miscibility.

The above discussion indicates that the theory of association equilibria allows – especially in the limit for dilute systems – to obtain a more profound interpretation of the semiquantitative characteristics of the system polymer–mixed solvent; this interpretation has so far been possible only on the basis of global interaction parameters of the Flory–Huggins equation. Let us now compare, at least by way of illustration, the quantitative predictions of the suggested theory with those of the Flory–Huggins theory. For some of the model systems described above, Figs 1 and 2 also contain curves obtained as follows: For three binary subsystems of our ternary model system, the effective values of binary interaction parameters have been calculated: for the parameters χ_{AC}^* and χ_{BC}^* their limit values for $v_C \rightarrow 0$ (according to⁸, Eq. (13)), for the parameter χ_{AB}^* its dependence on v_{A0} . The data obtained were substituted into equations derived on the basis of the Flory–Huggins equation for the total and preferential sorption², while the value of the ternary interaction parameter remained zero. We can see that in comparison with the results of our theory, the dependence of the total sorption on the composition of the mixed solvent according to the Flory–Huggins equation gives too large deviations from a linear course. Consequently, the new theory is in qualitative agreement with the experimental conclusions of Dondos and Patterson⁴, who have established for four ternary systems that the intrinsic viscosity of a polymer in a mixed solvent exhibits deviations from additivity depending on the composition of the solvent; these deviations have the same sign as predicted by the Flory–Huggins theory, but are lower by an order as to their absolute value. It seems that our theory corrects the Flory–Huggins equation in the right direction, but not to such an extent as required by the results obtained by Dondos and Patterson.

FIG. 5

Potential of the Total Sorption Y at $v_{A0} = 0.5$ in Dependence on the Mutual Association Constant $A + B$ (ρ) and on the Solvation Constant of the Component A to the Polymer.

Values of η : 1 0, 2 0.1, 3 0.3, 4 0.5, 5 0.7; the other parameters of the system as in Fig. 1. Full lines calculated from the theory of the equilibrium associates, broken lines calculated from the binary parameters of the Flory–Huggins equation.



A more systematic view of the consequences of non-random mixing is offered by Fig. 5, which again shows systems with the interactions A + B, A + C. We can see that the difference between the model system and the prediction of the Flory-Huggins equation is the larger, the more the solvation constants ϱ and η differ from each other. The deviations from random mixing apparently attain a minimum when A is bonded to B with the same affinity as to C ($\varrho = \eta$), in which case both procedures give similar results. To attain a quantitative agreement with the experiment it will be necessary to reinvestigate the justifiability of the simplifying assumptions of the theory. Also new experimental data on appropriately chosen systems are desirable. For instance, the existence of inversion in the preferential sorption with divergent neighbourhood has not been confirmed experimentally. Data which exhibit an inversion of the opposite type together with a maximum in the total sorption^{1,4,11,12} were obtained on systems having a complicated combination of the specific interactions so that they cannot be quantitatively evaluated without a knowledge of systems with simpler interactions.

LIST OF SYMBOLS

A_1	limit parameter of the preferential sorption for a diluted system
b	number of interaction sites in a molecule of B
c	number of interaction sites in a molecule of C
D	determinant of the second moments i, j, k
D_{KK}^*	determinant for the calculation of the second derivative G_v^* with respect to v_K and $v_{K'}$
G_{el}	elastic part of the free energy
ΔG_N	mixing free enthalpy (per lattice site)
G_v^*	quantity derived from the mixing free enthalpy of a volume unit
i, j	number of molecules of A or B in the associate S
\bar{i}_w, \bar{j}_w	weight average of the number of molecules A or B in the associate
$(i)_\sigma, (j)_\sigma$	specific sorption of A or B on a polymer segment in an infinitely dilute solution
K_S	equilibrium constant of formation of the associate S
k	number of molecules of C in the associate S
$(k)_a$	self-association parameter of the polymer in a dilute system
$N_{K, K'}$	limit of the second partial derivative of G_v^* with respect to v_K and $v_{K'}$ at $v_C \rightarrow 0$
n	total number of segments in the system
P	common symbol for the osmotic pressure and elastic potential
P_{el}	elastic potential
p_K	concentration (in molecules per lattice site) of unassociated molecules of the component K
q	volume ratio of swelling
R	gas constant
r_K	number of segments in a molecule of K
r_{ij0}	total number of segments in the associate $A_i B_j$
$(\bar{r})_K$	average r_{ij0} calculated over all molecules of the component K
s	ratio of the molar volumes V_A/V_B
T	absolute temperature

μ_K	volume fraction of the component K related to the volume of both low-molecular-weight components present in the ternary phase
V	total phase volume
V_K	molar volume of the component K
\bar{V}_K	partial molar volume of the component K
V_U	molar volume of the segment
v_K	volume fraction of the component K
\bar{v}_C	partial specific volume of the polymer
x	general symbol for i, j, k
$\langle x \rangle$	first statistical moment of x
$\langle xx' \rangle$	mixed second moment of x, x'
Y	potential of the total sorption according to Shultz and Flory
ϵ	preferential sorption of A
η	equilibrium constant of the bonding of A to one site of C
α	parameter of the self-association equilibrium of A
μ_K	chemical potential of the component K
ν_K	concentration of the component K (in molecules per lattice site)
ν_S	concentration of the associate $S \equiv A_i B_j C_k$
ν_{ij0}	concentration of the associate $A_i B_j$
π	osmotic pressure
ρ	equilibrium constant of the bonding of A to one site of B
σ	equilibrium growth constant of a free self-associating chain
σ_s	equilibrium growth constant of a bonded self-associating chain
$\chi_{KK'}$	binary parameters of nonspecific interactions
χ_U	parameter of nonspecific interaction per one segment

Subscripts

Superscript

A, B	low-molecular-weight components	0	standard state
C	polymeric component		
K, K'	general symbol for components		
0	solvent (binary) phase		
S	general symbol for an associate		

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