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Sorption equilibria in ternary systems: polymer/ mixed solvent

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Abstract - A brief review is given of the existing theories of preferential and total sorption of a mixed solvent in a macromolecular coil at high polymer dilution. An application, unpublished as yet, of the Guggenheim-Barker quasichemical theory leads to the following predictions: The preferential sorption is materialized not only in the solvent shell adjacent to the polymer chain, but - depending on the sign and magnitude of mutual interaction of the two components of the solvent - also in the next layers. The preferential sorption affects the total sorption not only by means of the concentration disproportionation effect, included in the general equilibrium condition, but also through the contact balance effect, predictable only by theories considering nonrandom mixing. The contact effect compensates the disproportionation effect partly in some cases and fully in other ones. The shape of the preferential and total sorption dependences on the mixed solvent composition is affected, among other things, by nonrandom mixing. The effect is considerably stronger with molecules containing strongly interacting polar groups bound to an inert residue rather than for molecules with a homogeneous surface.

INTRODUCTION

The sorption equilibrium between macromolecular coil and mixed solvent has a considerable effect on the thermodynamic, transport and optical properties of dilute polymer solutions and may also influence the kinetics of solution polymerization.

If we have a polymer solution in a binary solvent, two data are needed for the description of sorption equilibrium; data on the total and preferential sorption are those which can best be determined experimentally. The total sorption characterizes the degree of expansion of the coil, while the preferential sorption gives the difference in composition of the mixed solvent inside and outside the coil.

The following problems are dealt with in this study: form of the dependence of total and preferential sorption on the composition of mixed solvent; thickness of the layer adjacent to the polymer chain and representing the concentration difference called preferential sorption; and, finally, the effect of preferential sorption on the magnitude of total sorption. The tool used in the study are theories of mixtures in which nonrandom mixing is considered, in particular the theory of quasichemical equilibria, the application of which to sorption in ternary polymer systems has not yet been reported. This is preceded by a concise survey of results based on the random-mixing approximation.

BASIC DEFINITIONS

The following indexes are assigned to components of the ternary mixture: 1 better solvent, 2 poorer solvent, 3 polymer.

The distribution of polymer segments in the domain of the coil is not uniform, and it should therefore be borne in mind that the magnitude of preferential sorption in the coil varies from one volume element to another. Hence, the total difference in the content of component 1 between the domain of the coil and the same volume of the bulk solvent is given by an integral over the volume of the domain:

$$\lambda = (N_A/M) \int (1-\phi_3)\varepsilon(\phi_3)dV \qquad (1)$$

where λ is the preferential sorption related to the mass unit of the polymer, N_A is the Avogadro constant, M is the molar mass of the polymer and ϕ_i is the volume fraction of component i in an element of the domain of the coil. Local preferential sorption ε is defined

by relations

$$\varepsilon = u_i - \phi_{10} \tag{2}$$

$$u_i = \phi_i/(1-\phi_3) \tag{3}$$

where u_i is the local volume fraction of component i in the coil domain related to the volume of the mixture of liquids 1 and 2, and ϕ_{10} is the volume fraction of component i in the domain outside the coil. In this study we concentrate on the case of a very strongly swollen coil (very small ϕ_3); in this limit the local preferential sorption is proportional to the volume fraction of the polymer, and the proportionality constant A is the coefficient of preferential sorption:

$$A = \lim_{\phi_3 \to 0} \varepsilon/\phi_3 = \lim \lambda/\bar{v}_3 \tag{4}$$

where $\bar{v}_3$ is the partial specific volume of the polymer. For the given system, A depends only on the composition of the bulk solvent and on temperature. The coefficient of preferential sorption can be determined by e.g. the method of dialysis equilibrium or by the light scattering measurement.

Measure of the total sorption of the solvent in the coil is represented by the linear expansion coefficient

$$\alpha = (\langle s^2\rangle/\langle s^2\rangle_\theta)^{1/2} \tag{5}$$

in which $\langle s^2\rangle$ is the mean square radius of gyration of the coil, and index θ denotes the Gaussian conditions. The expansion coefficient can be determined directly from the ratio of the radii of gyration determined by light scattering, or indirectly from viscosity values (ref.1). The statistical thermodynamical theory of equilibrium expansion of the coil has led to several different equations (refs 2,3), in which the Shultz-Flory sorption potential (ref. 4) defined by the equation

$$Y = \lim_{\phi_3 \to 0} \pi V_1/(RT\phi_3^2) \tag{6}$$

is calculated from the expansion coefficient; here, π is the osmotic pressure related to the solution of volume fraction ϕ_3 of a polymer with infinite molar mass, and V_i is the molar volume of component i.

GENERAL CONDITIONS OF EQUILIBRIUM

The treatment based on the mean field theory is based on general conditions of osmotic equilibrium between the volume element of the domain of the coil and external solvent (refs 4,5, 6). In the limit for infinite dilution of the polymer ($\phi_3 \to 0$), these conditions become (ref.7)

$$A = - M_{13}/M_{11} \tag{7}$$

$$Y = (V_1/2RT)\ (M_{33} - M_{13}^2/M_{11}) \tag{8}$$

Here, the symbols M_{ij} denote the limiting values of partial derivatives

$$M_{ij} = \lim_{u_3 \to 0} (\partial^2 G_u/\partial u_i \partial u_j) \qquad i;j = 1;3 \tag{9}$$

where G_u is the Gibbs energy of mixing the polymer ($M \to \infty$) with a unit volume of the mixed solvent.

Eq.(7) can be rewritten to

$$M_{13}\phi_3 + M_{11}\varepsilon = 0 \qquad (\phi_3 \to 0) \tag{10}$$

The first term in the sum on the left-hand side is a measure of the change in the Gibbs energy after a small volume of component 1 has been transferred from the bulk phase into the coil domain having the same solvent composition, while the same volume of component 2 has been transferred in an opposite direction. The other term gives the change in the Gibbs energy connected with the concentration disproportionation of the solvent; the derivative M_{11} is always positive in stable systems. Hence, the fraction on the right-hand side of Eq.(7) can be interpreted as the ratio of the thermodynamic "driving force" of preferential sorption to the thermodynamic "resistance" against the concentration nonhomogeneity.

In Eq.(8) multiplication carried out on the right-hand side yields two terms which describe two contributions to the osmotic pressure. The first term in the limit for pure solvent ($\phi_1 \to 0$ or $\phi_2 \to 0$) becomes the known expression $(1/2-\chi)/V_1$. The second term can be rewritten to $-\varepsilon^2 M_{11}$ and represents a consequence of the concentration disproportionation caused by the preferential sorption. In stable systems (at the infinite molar mass of the polymer) the first term is always positive, while the other term is always negative.

In the light scattering theory (refs 7,8), similar equations expressing preferential sorption and the second virial coefficient of osmotic pressure have been derived by means of partial derivatives of chemical potentials with respect to molalities. Such choice of the variables is preferred when one of the low-molar mass components (e.g., water) is present in excess, compared with the other component (e.g., salt).

THE FLORY–HUGGINS EQUATION

Shultz and Flory (ref.4) have derived equations for the dependence of preferential and total sorption on composition, using the Flory-Huggins equation for the ternary system. The equations show that the preferential and total sorption are affected not only by values of the interaction parameters, but also by the ratio of molar volumes of both low-molar mass components. Characteristic features of the dependence of sorption on the composition of the mixed solvent, i.e. asymmetry of the A vs. ϕ_{10} dependence and nonlinearity of the Y vs. ϕ_{10} dependence (Fig.1), can very well be explained qualitatively by the effect of interaction between two components of the solvent as characterized by the Flory-Huggins parameter g_{12}. Since in systems with complete miscibility this parameter usually assumes much broader absolute values than the difference between parameters g_{13} and g_{23} which characterize the solvent-polymer interaction, one could expect that the dependences mentioned above would be quite dramatic. In fact, however, the effect of interaction 1-2, though almost always a distinct one, is nevertheless weaker than predicted by the Flory-Huggins theory (refs 10, 11). Read (ref.12), who was aware of this fact, was the first to introduce parameters of ternary interaction into the Flory-Huggins equation when interpreting data on preferential sorption.

The extension of the Flory-Huggins equation by introducing the ternary parameter $g_T \equiv g_{123}$ made possible a much more adequate description of experimental data, if the concentration dependence of interaction parameters was admitted. In our studies (refs 7,13,14) we used the generalized Flory-Huggins equation in the form

$$\Delta G_M/RT = \sum_{i=1}^{3} n_i \ln \phi_i + \sum_{i=1}^{3} \sum_{j>i}^{3} g_{ij}\, n_i \phi_j + g_T n_1 \phi_2 \phi_3 \tag{11}$$

where n_i is the amount of substance of the i-th component, and the functional dependences

$$g_{12} = g_{12}(u_1), \quad g_{13} = g_{13}(\phi_3), \quad g_{23} = g_{23}(\phi_3), \quad g_T = g_T(u_1,\phi_3) \tag{12}$$

are valid. By substitution into Eqs (9), expressions were obtained for the limiting derivatives M_{ij}, in which the parameter g_T could be transferred into the common term with the parameter g_{12}; this also concerns derivatives of both parameters. For this reason, an assumption has been made and verified by many reported experimental data (refs 15,16) that with the exception of the proportionality constant the dependence of g_T and its derivative with respect to ϕ_3 on the composition of the mixed solvent u_1 are the same as the dependence of parameter g_{12}:

$$g_T(u_1) = a_g g_{12}(u_1), \quad \partial g_T(u_1,\phi_3)/\partial\phi_3 = a' g_{12}(u_1) \qquad (\phi_3 \to 0) \tag{13}$$

in which a_g, a' are the proportionality constants. Expressions for the derivatives then assume the form which in the limit holds for $\phi_3 \to 0$:

$$V_1 M_{11}/RT = 1/\phi_1 + 1/\phi_2 - 2g_{12} + 2(\partial g_{12}/\partial\phi_1)(\phi_2-\phi_1) + (\partial^2 g_{12}/\partial\phi_1^2)\phi_1\phi_2 \tag{14}$$

$$V_1 M_{13}/RT = 1 - 1 + g_{13} - lg_{23} + (1-a_g)[g_{12}(\phi_1-\phi_2) - (\partial g_{12}/\partial\phi_1)\phi_1\phi_2] \tag{15}$$

$$V_1 M_{33}/RT = \phi_1 + l\phi_2 - 2(\chi_{13}\phi_1 + l\chi_{23}\phi_2) + 2(1-2a_\chi) g_{12}\phi_1\phi_2 \tag{16}$$

where $l = V_1/V_2$ and in the limit for $\phi_3 \to 0$ we have

$$\chi_{i3} = g_{i3} - (\partial g_{i3}/\partial\phi_3) \qquad i = 1;2 \tag{17}$$

$$\chi_T = g_T - (1/2)(\partial g_T/\partial\phi_3) \tag{18}$$

$$a_\chi = a_g - a'/2 \tag{19}$$

By substituting from (14), (15) and (16) into Eqs (7) or (8), we obtain expressions for preferential sorption and for the potential of total sorption. Of the quantities contained in Eqs (13), (14), (15), $g_{12}(\phi_{10})$ can be determined independently from activity measurements in binary mixtures of liquid components; χ_{13} and χ_{23} can be evaluated from the expansion coefficient of the coil in pure solvent. The parameters g_{13}, g_{23} cannot be identified with χ_{13} and χ_{23}; if the dependence of parameter χ_{13} on ϕ_3 is known, the parameter g_{13} can be determined by an integration procedure (ref.17). Such data on binary systems are not always available, however; in such cases, the difference $g_{13} - lg_{23}$ must be adjusted so as to adequately

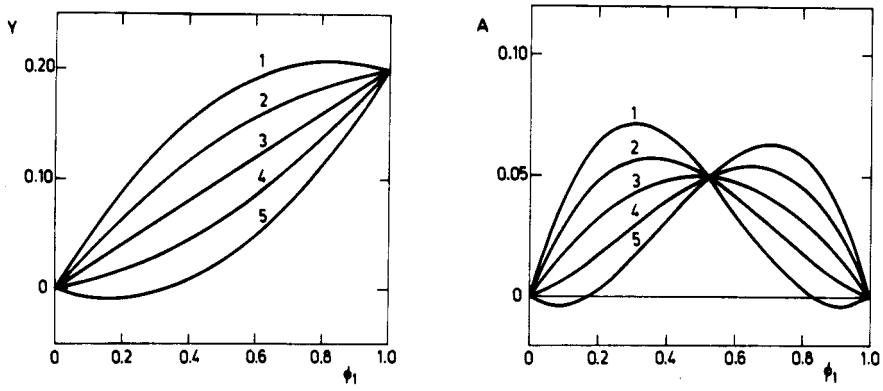

Fig. 1. The dependence of preferential sorption (A) and of the potential of total sorption (Y) on the composition of the mixed solvent ϕ_{10}. According to the Flory-Huggins equation with concentration-independent parameters; Y calculated from single-liquid approximation. $g_{23} - g_{13} = 0.2$ $l = 1$ Values of $(1 - a_g)g_{12}$ in the plot $A = A(\phi_{10})$, or of $(1 - 2a_\chi)g_{12}$ in the plot $Y = Y(\phi_{10})$: *1* 0.3 *2* 0.15 *3* 0 *4* -0.15 *5* -0.3.

describe the dependence of preferential sorption on composition. Linearization procedures have been suggested, which allow the constants a_g and $g_{13} - lg_{23}$ to be determined from data on preferential sorption (ref. 15), and a_χ to be determined from the potential of total sorption (ref. 16). Chu and Munk (ref. 18) suggested an integration procedure of the calculation of the g_T vs. u_1 dependence using data on preferential sorption independently of the assumption expressed by Eq.(13). Figueruelo et coll. (ref. 19) confirmed the validity of this assumption by calculating $g_T(u_1)$ according to ref. 18 and comparing with the $g_{12}(\phi_{10})$ dependence; they also suggested an equation for the prediction of the ternary parameter using binary parameters. As expected, the absolute majority of systems evaluated in refs 15, 16, 19 yielded the a_g and $2a_\chi$ values in the range between 0 and unity. Hence, the parameters g_T and χ_T have the same sign as g_{12}, but in accordance with Eqs (15), (16) they reduce the effect of g_{12} on the form of the sorption dependences. The seemingly paradoxical character of this conclusion can be explained by analyzing changes in the number of interaction contacts during dilution of the polymer with a mixed solvent (ref. 20).

Let us now examine characteristic features of the dependence of preferential sorption on the composition of the mixed solvent recorded in our version of the Flory-Huggins equation. The conclusive role of parameter g_{12} is evident from Eq. (15) in connection with Eq. (7). As far as $g_{12} \neq 0$, the A vs. ϕ_{10} dependence is asymmetrical, and at a sufficiently high g_{12} a point of inversion may appear on the curve, where $M_{13}=0$, and thus also $A=0$ (Fig. 1). An analysis reported in refs 5, 15 shows that an approximate criterion of the occurrence of the point of inversion (exact for g_{12} independent of ϕ_{10}) is given by the condition

$$|1 - 1 + g_{13} - lg_{23}| < |(1 - a_g)g_{12}| \tag{20}$$

In the surroundings of the point of inversion the system may behave in two ways: (1) the component lacking in quantity compared with the system in the point of inversion is sorbed preferentially. Such type of the inversion point is called the "inversion point with converging surroundings"; it can be proved that the condition of its occurrence is the positive sign of the parameter g_{12} (the sign at g_{12} usually coincides with that of the function G^E of the mixture of components 1 and 2). (2) The component present in excess compared with the point of inversion is preferentially sorbed into the coil. The point of inversion has "diverging surroundings"; such case may occur at negative g_{12}.

In the analysis of total sorption (refs 6, 16) we assume that the effect of preferential sorption, i.e. the effect of the second term in Eq. (8) can be neglected. From Eq. (16) we have, then, that at positive g_{12} a maximum may appear on the $Y(\phi_{10})$ dependence, while at negative g_{12} there will be a minimum. For the occurrence of an extreme we give a condition analogous to Eq. (20):

$$|(1 - 1)/2 + \chi_{13} - l\chi_{23}| < |(1 - 2a_\chi)g_{12}| \tag{21}$$

OTHER RANDOM-MIXING THEORIES

The ternary interaction parameter, the introduction of which into the Flory-Huggins equation considerably improved agreement with the experiment, usually represents a correction for various inaccuracies of the simple theoretical model, rather than a real three-body interaction. To reveal the real physical meaning of parameters g_T and χ_T, we have to resort to more elaborate theories. The ternary system polymer-mixed solvent is a very suitable object in verifying theoretical models, due to the fact that one of the input data is the dependence of G^E of the binary mixture of components 1,2 on composition. Usually, this dependence can be expressed more exactly than that for binary solvent-polymer systems; in the former case, the activity of both components can be measured simultaneously and independently, while in the latter only the activity of the solvent can be measured, mostly in a limited concentration range. Thus, in the evaluation of the ternary system, there is a smaller danger that shortcomings of the theory will be concealed by adjustment of the parameters.

Noel et al. (ref. 10) used the Miller-Orr-Guggenheim theory; later on, various authors turned their attention to the Prigogine-Flory-Patterson equation-of-state theory (refs 21, 22, 23, 24). A common feature of these theories consists in the use of surface fractions instead of volume fractions in expressions derived from the energy balance of intermolecular contacts. The number of contacts 1-2 which disappear after the mixed solvent has been transferred into the bulk of the coil is then determined by the surface and not by the volume of the molecules. Under these assumptions, the relations

$$1 - a_g = s_3/s \quad , \qquad 1 - 2a_\chi = (s_3/s)^2 \tag{22}$$

can be derived, in which s_3 is the molecular surface-to-volume ratio of the polymer, s is the mean value of this ratio for the mixed solvent. A typical value of s_3/s calculated according to Flory (ref. 25) is 0.6.

Another, less pronounced contribution ensues from the difference in the thermal expansion of solvent and polymer, which is considered in the equation-of-state theory: energy of cohesion decreases with increasing thermal expansion, and therefore the interaction energy per one contact of the 1-2 type in the solvent phase is lower than in the polymer phase. The contribution of this real many-body interaction to the ternary parameter is proportional to the difference between the reduced heats of solvent and polymer and to the ratio between their reduced pressures.

SOME PROBLEMS RELATED TO NONRANDOM MIXING

The equation-of-state theory allowed a number of data to be adequately interpreted without taking resource to ternary parameters, and also brought evidence regarding the effect of molecular surface and thermal expansion on the thermodynamic properties of polymer solutions. On the other hand, however, it cannot provide a sufficiently full picture of the behaviour of ternary polymer systems, if those contain polar components whose interactions involve deviations from random mixing. This phenomenon, which consists in the preference for contacts possessing a lower Gibbs energy, cannot be without a pronounced influence on the form of the sorption isotherms. The only theory so far used, in which nonrandom mixing is considered, is the theory of association equilibria (refs 26, 27). A comparison of this theory with experimental data has confirmed, that considerable deviations from the classical Flory-Huggins equation in systems of the hydrocarbon/alcohol/polymer type can be explained by the strongly preferred occurrence of hydrogen bonds between alcohol molecules (ref. 20). Some results of the theory of association equilibria are summarized in the following chapter.

Nonrandom mixing is closely connected with the problem of space distribution of preferentially sorbed molecules around the polymer chain. The assumption of random mixing implies the view of uniform concentration distribution in the polymer phase; hence, the preferential sorption would affect the whole domain of the coil, including molecules of the solvent which are not in direct contact with the polymer chain. Other authors (ref. 28) regard it as useful to assume that the preferential sorption is localized in the monomolecular shell adjacent to the chain. The problem is of importance for the kinetics of solution polymerization: If the preferential sorption of the monomer is to have a considerable influence on the rate of chain propagation, it should be concentrated in the close vicinity of that chain; the concentration difference in the case of uniform distribution would be too small.

The range of preferential sorption is also related to the problem of its effect upon the total sorption. In terms of Eq. (8) and of the analysis attached to it, the preferential sorption can be regarded as the concentration disproportionation of the solvent, leading to a decrease in the potential of total sorption. Quite often, however, a more or less intuitive view is forwarded that due to the preferential sorption the domain of the coil is enriched in the "better" solvent, which brings about a "more favourable" balance of polymer-solvent contacts, and thus also a drop in the Gibbs energy and a rise in the potential Y. Yamamoto and White (ref. 28) argue, that the "disproportionation effect" prevails, if the preferential sorption takes place uniformly throughout the coil. If, however, it is concentrated in the thin layer

adjacent to the chain, the effect of improved polymer solvent contacts ("contact effect") prevails. The equations derived assuming random mixing and for $\phi_3 \to 0$ do not predict such effect. If the application of the theories which consider non-random mixing led to an expression for M_{33}, which would contain a sufficiently great positive term identifiable as "contact term", a single-liquid approach to theories based on non-random mixing would be justified. Such approximation consists in neglecting the second term in Eq. (8) and is consistent with the assumption that both opposite effects considered here just compensate each other. In many cases, when applied to data treatment it gave more plausible results than the use of complete Eq. (8) (refs 16, 21).

THEORY OF ASSOCIATION EQUILIBRIA

The ternary mixture of specifically interacting nominal components can be regarded as a multicomponent mixture of complexes $A_iB_jC_k$ in mutual equilibrium. Assuming that the mixture of complexes obeys the Flory-Huggins equation and that the change in the Gibbs energy due to nonspecific interactions is not affected by the complex formation, the relation for the equilibrium concentration of the complex $S \equiv A_iB_jC_k$ is

$$\nu_S = K_S p_A^i p_B^j p_C^k \tag{23}$$

Here, ν_S is the amount of substance in moles of the complex per one mole of sites in the Flory-Huggins lattice, K_S is the equilibrium constant, and p_A, p_B, p_C are the concentrations of unimers (molecules not included in the complexes). At the given values of nominal concentrations of components ν_A, ν_B, ν_C the concentrations of unimers can be calculated by solving the mass balances for nominal components combined with equilibrium relations (23).

For the preferential sorption, equations have been derived (ref. 27) from the model of association equilibria

$$A = Z_A/Z_o \tag{24}$$

$$Z_A = (r_B^2\langle jj\rangle + r_A r_B\langle ij\rangle)(\phi_A + r_A i_b) - (r_A r_B\langle ij\rangle + r_A^2\langle ii\rangle)(\phi_B + r_B j_b) \tag{25}$$

$$Z_o = r_A^2\langle ii\rangle + 2r_A r_B\langle ij\rangle + r_B^2\langle jj\rangle \tag{26}$$

The equation derived for the potential of total sorption is

$$Y = (r_A/2)[(1 + r_A i_b + r_B j_b)^2 Z_o^{-1} - k_a] \tag{27}$$

In these equations, r_A and r_B are the numbers of segments in molecules of the nominal components A, B; ϕ_A and ϕ_B are their respective volume fractions. The moment function $\langle ii\rangle$ is given by

$$\langle ii\rangle = \sum_S i_S^2 \nu_S = \sum_S i_S^2 K_S p_A^i p_B^j p_C^k = \partial^2 \sum_S \nu_S / \partial(\ln p_A)^2 \tag{28}$$

Moment functions $\langle ij\rangle$, $\langle jj\rangle$, $\langle ik\rangle$, $\langle jk\rangle$, $\langle kk\rangle$ are given by analogous relations. The expressions i_b, j_b and k_a are defined by

$$i_b = \lim_{\phi_C \to 0}(\langle ik\rangle/\nu_C) \quad , \qquad j_b = \lim_{\phi_C \to 0}(\langle jk\rangle/\nu_C) \tag{29}$$

$$k_a = \lim_{\phi_C \to 0}[(\langle kk\rangle - \nu_C)/v_C^2] \tag{30}$$

The first two quantities give the average number of molecules A or B bound by specific interaction to one polymer segment; the latter quantity characterizes the selfassociation of the polymer. All concentrations and moment functions are related to the infinitely diluted ternary phase. The equations may be supplemented by the Flory-Huggins parameters characterizing nonspecific interactions (refs 20, 27).

Eqs (24)-(26) are general ones; for a system with the given pattern of specific interactions it is sufficient to write (if possibly, in the closed form) the function

$$\sum_S \nu_S = \sum_S K_S p_A^i p_B^j p_C^k \tag{31}$$

and to subject it to partial differentiation so as to obtain the necessary moment functions.

To illustrate the physical meaning, let us rearrange the equations for preferential sorption for two limiting cases. (1) If the polymer is inert, we have $i_b = 0$, $j_b = 0$ and $k_a = 0$ and complexes (A_iB_j) are formed by the solvent components only. Eq. (24) can then be rearranged to the form

$$A = (\bar{r}_{(B)} - \bar{r}_{(A)})\phi_A\phi_B(\bar{r}_{(A)}\phi_A + \bar{r}_{(B)}\phi_B)^{-1} \tag{32}$$

in which

$$\bar{r}_{(A)} = \sum_S r_S i_S \nu_S / \sum_S i_S \nu_S \quad , \qquad \bar{r}_{(B)} = \sum_S r_S j_S \nu_S / \sum_S j_S \nu_S \tag{33}$$

$$r_S = r_A i_S + r_B j_S \tag{34}$$

The expression r_S is the measure of molar volume of the given complex, $\bar{r}_{(A)}$ and $\bar{r}_{(B)}$ represent the average values of r_S, the average in the former case being taken over all molecules A present in the mixture, and in the latter, over all molecules B. Let us compare Eq. (32) and the Flory-Huggins equation for a system of inert components with zero interaction parameters:

$$A = (r_B - r_A)\phi_A\phi_B(r_A\phi_A + r_B\phi_B)^{-1} \tag{35}$$

As can be seen, in the latter system only the ratio of sizes of the molecules, $l = r_A/r_B$, decides about the preferential sorption. In Eq. (32) r_A and r_B have been replaced by the average magnitudes of the association complex, which of course obey the association equilibrium, and thus depend on ϕ_A. Various special features observed in the dependence of preferential sorption on ϕ_A, such as inversion and its type, can then be interpreted as a consequence of the concentration dependence of $\bar{r}_{(A)}$ and $\bar{r}_{(B)}$. (2) In the case that in the system there are no other interactions than the binding of components A, B onto the polymer C, Eq. (24) is simplified to (assuming that $r_A = r_B$)

$$A = i_b\phi_B - j_b\phi_A \tag{36}$$

This equation can also be obtained from a simple mass balance, assuming that i_b moles of component A and j_b moles of component B are bound to one mole of the segments. Hence, in such limiting case the preferential sorption is localized to the closest vicinity of polymer sites of the specific interaction.

THE QUASICHEMICAL THEORY

Molecules with homogeneous surface

In a liquid system approximated by a lattice with the coordination number z a molecule of the i-th component occupying r_i lattice sites may enter into zq_i binary contacts with other molecules. If we denote the number of such contacts between molecules of components i, j by N_{ij}, contacts of component 1 in the ternary system obey the balance equation

$$2N_{11} + N_{12} + N_{13} = zq_1N_1 \tag{37}$$

in which N_1 is the number of molecules of component 1. According to the quasichemical theory, the frequency of various types of contacts is controlled by the equation

$$N_{ij}^2 = 4\eta_{ij}^2 N_{ii} N_{jj} \tag{38}$$

where η_{ij} is a temperature-dependent constant. Eq. (38) has been derived assuming mutual independence of the contacts. At random mixing, for each pair of components i, j we have $\eta_{ij} = 1$.

Let us define, now,

$$y_{ij} = (1 + \delta_{ij})N_{ij}/(z\sum_k q_k N_k) \tag{39}$$

where δ_{ij} is the Kronecker delta, and

$$y_i = y_{ii}^{1/2} \tag{40}$$

Eq. (38) then becomes

$$y_{ij} = \eta_{ij} y_i y_j \tag{41}$$

and the balance equation of component 1 is

$$y_1^2 + \eta_{12}y_1y_2 + \eta_{13}y_1y_3 = \theta_1 \tag{42}$$

where θ_1 is the contact site fraction (surface fraction). Similar equations can be written for components 2,3. For the Gibbs energy of mixing, the relation

$$\Delta G_M/RT = \sum_i n_i \ln \phi_i + (z/2)\sum_i n_i q_i \ln(\theta_i/\phi_i) + z\sum_i n_i q_i \ln(y_i/\theta_i) \tag{43}$$

is valid. In this study we examine only the case where both liquid components have the same molar volume and surface:

$$r_1 = r_2 = 1 \qquad q_1 = q_2 = 1 \tag{44}$$

If the expression in Eq. (43) is subjected to operations prescribed by Eq. (9), after major rearrangements we obtain

$$V_1M_{11}/RT = (x_1x_2)^{-1} + s[y_{12}/(x_1x_2) - 1](2x_1x_2 - y_{12})^{-1} \tag{45}$$

$$V_1M_{13}/RT = -s_3(\xi_{13} - x_1)(2x_1x_2 - y_{12})^{-1} \tag{46}$$

$$V_1M_{33}/RT = 1 - (s-s_3)^2/(2s) + (s_3^2/s)[1 - L + (\xi_{13}-x_1)^2(2x_1x_2-y_{12})^{-1}] \tag{47}$$

Here, $s_3 = zq_3/r_3$ is the measure of the molecular surface-to-volume ratio (according to Eq. (44), for components 1, 2 we have $s = z$); x_1, x_2 and y_{12} are related to the volume phase outside the coil. The expression ξ_{13} is defined as

$$\xi_{13} = \lim_{\theta_3\to 0}(y_{13}/\theta_3) \tag{48}$$

and gives the fraction of polymer contact sites interacting with molecule 1:

$$\xi_{13} = \lim_{\theta_3\to 0}[y_{13}/(y_{13} + y_{23})] = \eta_{13}y_1(\eta_{13}y_1 + \eta_{23}y_2)^{-1} \tag{49}$$

The expression L is defined by

$$L = \lim_{\theta_3\to 0}(y_{33}/\theta_3^2) \tag{50}$$

and gives us the ratio of the number of polymer-polymer contacts to that of these contacts at random mixing. The relation

$$L = (\eta_{13}y_1 + \eta_{23}y_2)^{-2} \tag{51}$$

is valid. The y_1, y_2, y_{12} values can be calculated from

$$y_1 = (x_1-y_{12})^{1/2}\ , \qquad y_2 = (x_2-y_{12})^{1/2} \tag{52}$$

$$y_{12} = \{1 - [1 - 4(1-\eta_{12}^{-2})x_1x_2]^{1/2}\}[2(1-\eta_{12}^{-2})]^{-1} \tag{53}$$

According to Eq. (7), for the coefficient of preferential sorption we have, then,

$$A = E\{1 - (s-1)[1 - y_{12}/(x_1x_2)]\}^{-1} \tag{54}$$

$$E = s_3(\xi_{13}-x_1) \tag{55}$$

In an approximation given by the assumption of mutual independence of contacts, ξ_{13} can be regarded as the composition of that part of the solvent which is in direct contact with the chain. Hence, E in the same approximation is the contribution to preferential sorption originating in molecules which are in contact with one segment of the polymer. At random mixing of components of the solvent ($\eta_{12} = 1$; $y_{12} = x_1x_2$) we simply have $A = E$; preferential sorption is then localized in the monomolecular layer near the chain surface. According to Eq. (54), in a general case the relation between A and E depends on the constant η_{12}. If $\eta_{12} < 1$, the tendency of clustering of molecules of the same type becomes operative, so that preferential sorption established in the layer adjacent to the polymer is partly reproduced in layers close to it. In this way, a polymolecular envelope layer is formed, which diffusely passes into the bulk phase, and $A/E > 1$. If $\eta_{12} > 1$, the component which in the layer (n-1) has negative adsorption accumulates in the n-th layer; consequently, the sign of sorption should oscillate from one layer to another. Due to the damped oscillation of partial contributions, the sum of preferential sorption is smaller than adsorption in the first layer.

Let us now concentrate on the potential of total sorption Y. The nonathermal part of the expression on the right-hand side of Eq. (47) contains two terms. The first term, proportional to $1 - L$, gives the contribution of polymer-polymer contacts. According to Eq. (50), the tendency of the polymer to self-association ($L > 1$) leads to a decrease in Y, while solvation of the polymer ($L < 1$) has the opposite effect. The second term proportional to E^2 is always positive, and it may be supposed to express the influence of preferential sorption in the first layer on the rise in total sorption. What we have here is obviously the longed-for "contact" term, which does not occur in equations derived assuming random mixing for an infinitely diluted polymer component. In Eq. (8), along with the expression M_{33}, there is of course a negative term $-A^2M_{11}$, which we call the disproportionation term and which reduces the total sorption. By substitution for A from Eq. (54) and dividing, we obtain

$$\text{contact term : disproportionation term} = -\ s^{-1}\{1+(s-1)[y_{12}/(x_1x_2)-1]\} \tag{56}$$

Thus, in the case of an ideal behaviour of the binary mixture ($\eta_{12} = 1$), the contact term is a mere s-th part of the disproportionation term; in a general case, however, the ratio also depends on the value of η_{12}. In this paragraph we assume a homogeneous molecular surface and $s = z$. Hence, compensation of one term with the other is only partial.

Let us now compare the concentration dependences of preferential sorption according to the quasichemical theory with those derived from the extended Flory-Huggins equation, using a series expansion for small values $a_{ij} = -\ln \eta_{ij}$. For binary interaction parameters we obtain

$$g_{12} = sa_{12}(1 - a_{12}x_1x_2 + \ldots) \tag{57}$$

$$g_{i3}(\theta_3=0) = s_3a_{i3} \qquad i = 1;2 \tag{58}$$

By comparing equations for preferential sorption, integration and rearrangement we obtain an expression of the asymmetry index of preferential sorption $1-a_g$, cf. Eq.(13), in terms of the parameters of the quasichemical theory

$$1 - a_g = (s_3/s) + (1/s)[(s_3g_{12}/2s)(1-4x_1x_2) - (g_{13}-g_{23})(x_2-x_1) + (s/2s_3)(g_{13}-g_{23})^2/g_{12}] \tag{59}$$

On the right-hand side the first term predominates, known already from the treatment of the problem by means of the equation-of-state theory. This is obviously characteristic of each theoretical model, in which an energetically homogeneous surface of the molecule is considered to be the site of interaction. Due to the factor (1/s), terms originating from nonrandom mixing are minor ones; for the same reason, the $1-a_g$ vs. x_1 dependence introduced by these expressions is not pronounced. It should be borne in mind that the symbols g_{ij} in Eqs (57)-(59) denote contributions of contact interactions to the respective parameters and not the full values of these parameters.

Qualitatively similar conclusions can also be derived from the equation for the nonlinearity index of total sorption, where the term $(s_3/s)^2$ predominates, while terms of nonrandom mixing are of minor importance.

In this paragraph we examined systems with a homogeneous molecular surface. A more detailed analysis of the derived equations leads to a conclusion that in these systems we usually have small deviations from random mixing. Also, preferential sorption in the first layer is not great; if, of course, η_{12} approaches the critical value, preferential sorption may increase significantly, due to its reproduction in the second layer and the following ones.

The cause underlying small deviations from random mixing is the fact that the interaction energy of the molecule is uniformly divided between qz contact sites. In the subsequent part we investigate molecules with heterogeneous surface containing a strongly interacting group which may become the source of strongly preferred contacts.

Molecules with heterogeneous surface

Barker has extended the Guggenheim quasichemical theory by including systems of molecules, the surface of which contains several types of contact sites. Theory in this form is applied to a ternary system in which the molecular surface of each component contains polar (strongly interacting) groups and a nonpolar (inert) residue. Polar groups of components 1, 2, 3 differ from each other and are denoted respectively A, B, C; the nonpolar part is the same in all components, and the sum of nonpolar residues of all components is denoted with R. Indexes 1, 2, 3 are related to the components, indexes A, B, C, R are related to surface groups. The symbol α_A is used to denote the fraction which in the surface of the molecule of component A is occupied by groups A; $\alpha_A s_1 r_1$ give the number of contacts entered by groups A present in molecule 1. In a similar way, α_B and α_C can be defined. The contact balance equations must be written for groups A, B, C and R; in the equation for the Gibbs energy of mixing the individual terms of the last sum are also related to groups A, B, C, and R and not to the components; unlike Eq. (43), the expressions characterizing the initial state must also be explicitly included. Let us also introduce the assumption that, along with equations (44), the relation

$$\alpha_A = \alpha_B = \alpha \tag{60}$$

is valid.

The derived relations have become much more complicated. If, for instance, we are interested in the fraction of preferential sorption due to the direct polymer-solvent contacts, there are two contributions to be considered, viz., contribution E_C ensuing from the interaction of polar groups C in the polymer, and contribution E_R due to nonpolar residues of the type R which belong to the macromolecule. The total preferential sorption in the layer adjacent to the polymer, E, is the sum of these two contributions. For the former of these, a relation

$$E_C = s_3(\xi_{AC}x_2 - \xi_{BC}x_1) \tag{61}$$

can be derived from the mass balance; here, ξ_{AC} and ξ_{BC} are given by the equation

$$\xi_{KC} = \lim_{\theta_3 \to 0} (y_{KC}/\theta_3) = \alpha_C \eta_{KC} y_K / \sum_L \eta_{LC} y_L \tag{62}$$

where K;L = A;B;R. For the contribution of nonpolar groups of the polymer, the relation

$$E_R = s_3 (1-\alpha_C)(1-\alpha)^{-1} (y_{AR} x_2 - y_{BR} x_1) \tag{63}$$

has been derived. It is not the sum $E_C + E_R$, that enters the equation for the preferential sorption A, but a linear combination of these partial contributions, which moreover have concentration-dependent coefficients. As a consequence, in the equation for the potential of total sorption identification of the contact term is not unambiguous. For these reasons, we investigate below only two special cases for which the simplifying condition $E_R = 0$, and thus $E = E_C$, is valid. A more general analysis will be published elsewhere (ref. 29). (1) The case of strong interactions A-C and B-C (when $\eta_{AC} > 1$; $\eta_{BC} > 1$); for the other interactions, random mixing is valid ($\eta_{AB} = \eta_{AR} = \eta_{BR} = \eta_{CR} = 1$). In this case we have

$$A = E_C \tag{64}$$

Preferential sorption is localized on binding sites of the polymer, because in the mixture 1-2 mixing is random. The nonathermal part of the potential of total sorption is given by the equation

$$V_1 M_{33}^R / RT = E_C^2 / (\alpha s x_1 x_2) - (s_3^2/s)\{L_C - \alpha_C^2 + \alpha(1-\alpha)^{-1}[(1-\alpha_C)^2 \alpha^2 - (\xi_{AC} + \xi_{BC} + \alpha - 2\alpha\alpha_C)^2]\} \tag{65}$$

where

$$L_C = \lim_{\theta_3 \to 0} (y_{CC}/\theta_3^2) = \alpha_C^2 / \sum_K \eta_{KC} y_K \tag{66}$$

The first term on the right-hand side is obviously a contact one. The ratio of the contact term to the disproportionation term is $-1:(\alpha s)$; hence, full compensation of both terms takes place in the case where molecules 1 and 2 contain one strongly interacting group each, and this group occupies one contact site ($\alpha s = 1$). (2) The case where $\eta_{AR} \to 0$, $\eta_{BR} \to 0$ and $\eta_{CR} \to 0$ (strong aversion from the part of the sites A, B towards contacts with nonpolar residues).

G^E of the mixture of liquids 1, 2 has now the same sign as the expression $1-\eta_{AB}$. For preferential sorption we have

$$A = E_C\{1 + (\alpha s - 1)[y_{AB}/(\alpha x_1 x_2) - 1]\}^{-1} \tag{67}$$

For $\alpha s = 1$, $A = E_C$, in spite of the fact that the mixing of components 1, 2 is nonrandom. It should be pointed out, namely, that only contacts A-B, A-C, B-C and R-R are permitted. In such limiting case "induction" of preferential sorption from the layer adjacent to the chain into neighbouring layers is possible only through contacts between polar groups; since molecule 1 or 2 which contributes to the value of E_C is by one group - A or B - engaged in an interaction with the polymer site C, the molecule must possess at least one additional group A or B ($\alpha s \geqq 2$), in order to be able to interact with the molecule in the second layer.

We have, also

$$V_1 M_{33}^R / RT = E_C^2 s^{-1} (2\alpha x_1 x_2 - y_{AB})^{-1} - (s_3^2/s)\{L_C - \alpha_C^2/\alpha + (\alpha - \alpha_C)^2 [2\alpha(1-\alpha)]^{-1}\} \tag{68}$$

and

$$\text{contact term : disproportionation term} = -(\alpha s)^{-1}\{1 + (\alpha s - 1)[y_{AB}/\alpha x_1 x_2) - 1]\} \tag{69}$$

Again, both terms are fully compensated, if $\alpha s = 1$.

Thus, the single-liquid approximation is fully justified, if molecules of liquid components contain one small site of strong interaction each, and when preferential sorption is brought about exclusively by these sites. A similar conclusion may be reached using the theory of association equilibria in that case which in the paragraph devoted to this theory has been analyzed sub (2). Let it be added that both cases treated in the present chapter are limiting ones. The opposite limit can be seen in the system of molecules with homogeneous surface, when in terms of the quasichemical theory the contact term is z times smaller by its order of magnitude than the disproportionation term.

The effect of nonrandom mixing on the shape of the sorption curves is discussed in case 2), where the parameter g_{12} may assume a nonzero value, and, consequently, a_g and a_χ can be defined, cf. Eqs (13) and (19). Unlike systems with homogeneous molecular surface, when these parameters are a function of s_3:s, in our case the parameters a_g, a_χ at the given values of constants η_{AB}, η_{AC} and η_{BC} depend on $(\alpha_C s_3):(\alpha s)$; hence, the surface of strongly interacting groups, and not the surface of whole molecules plays the decisive role in this case. The

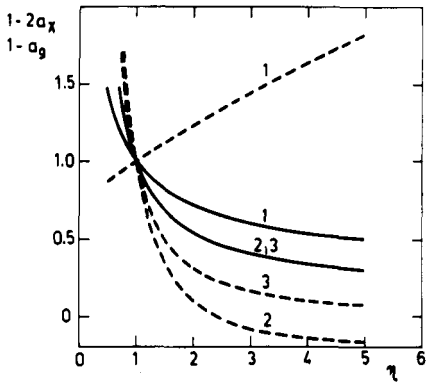

Fig. 2. The dependence of the asymmetry index $1-a_g$ (solid lines) and of the nonlinearity index $1-2a_\chi$ (broken lines) on the constants η.
$s = s_3 = 8$; $\alpha s = \alpha_C s_3 = 1$
1 $\eta_{AB} = \eta$ $\eta_{AC} = 1$ $\eta_{BC} = 1$
2 $\eta_{AB} = \eta$ $\eta_{AC} = 1$ $\eta_{BC} = \eta$
3 $\eta_{AB} = \eta$ $\eta_{AC} = \eta$ $\eta_{BC} = \eta$

dependence on values of the constants η is illustrated for some cases in Fig. 2; the geometrical parameters were chosen so as to eliminate their effect completely. In this case the effect of nonrandom mixing is much stronger than in the case of molecules with homogeneous surface.

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