(10) H. Benoit and C. Wippler, *J. Chim. Phys. Phys.-Chim. Biol.*, **57**, 524 (1960).
(11) A. Guinier, "Théorie et technique de la Radiocristallographie", Dunod, 1964.
(12) A. Guinier and G. Fourmet, "Small angle scattering of X rays", Wiley, New York, 1955.
(13) J. Des Cloiseaux, *J. Phys. (Paris)*, **31**, 716 (1970).
(14) S. F. Edwards, *Proc. Phys. Soc.*, **85**, 613 (1965).
(15) A. Peterlin, *J. Polym. Sci.*, **47**, 403 (1960).
(16) O. Kratky and G. Porod, *Recl. Trav. Chim. Pays-Bas*, **68**, 1106 (1949).
(17) G. Jannink and P. G. de Gennes, *J. Chem. Phys.*, **48**, 2260 (1968).
(18) S. F. Edwards, *Proc. Phys. Soc.*, **88**, 265 (1966).
(19) J. P. Cotton and H. Benoit, *J. Phys. (Paris)*, **36**, 905 (1975).
(20) G. E. Bacon, "Neutron Diffraction", Oxford, 1962; V. P. Turchin, "Slow Neutrons", Israel Prog. Science (translation) Ltd., 1965; M.I.T. Tables, Feb–Apr 1971.
(21) M. Hert and C. Strazielle, *Eur. Polym. J.*, **9**, 543 (1973).
(22) P. Grosius, Thesis, Strasbourg, 1970.
(23) J. P. Lingelser, P. Marie, Y. Gallot, *C. R. Hebd. Seances Acad. Sci., Ser. C*, **282**, 579 (1976).
(24) J. P. Cotton, D. Decker, H. Benoit, B. Farnoux, J. Hiffins, G. Jannink, R. Ober, C. Picot, and J. Des Cloiseaux, *Macromolecules*, **7**, 863 (1974).
(25) K. Ibel, *J. Appl. Crystallogr.*, **9**, 296 (1976).
(26) J. Boutillier and F. Candau, *C. R. Hebd. Seances Acad. Sci., Ser. C*, **286**, 209 (1978).
(27) F. Candau, J. M. Guenet, J. Boutillier, and C. Picot, *Polymer*, **20**, 1227 (1979).
(28) This ν exponent must not be confused with the average contrast factor introduced above.

Excess Polarizability and Volume of Mixing and Their Effect on the Partial Specific Volume and the Refractive Increment of Polymers in Mixed Solvents

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ABSTRACT: The phenomenon of excess polarizability of mixing was confirmed experimentally and justified theoretically. A unified phenomenological method of treatment of changes of thermodynamic properties resulting from mixing was developed and applied to the changes of volume and polarizability. Formulas were developed which related partial specific volume and refractive increment of polymers in mixed solvents with the experimentally observable phenomenological parameters of mixing. The introduction of the parameters related to the excess polarizability of mixing proved crucial for the proper interpretation of refractive increments. The minimum observed on the dependence of specific volume of polymer on the composition of a mixed solvent is a result of the volume changes related to mixing the solvents themselves.

During our studies of the preferential adsorption onto polystyrene in mixed solvents,[1,2] we needed the values of the refractive increment and of the partial specific volume as a function of the composition of the solvent. At first, we tried to predict these values from the values measured using pure solvents. We made several predictions based on various mixing rules used in literature: they differed substantially among themselves. Also, the preferential adsorption quantities resulting from these calculations were internally inconsistent. Finally, we decided to obtain the necessary data experimentally; our calculation of the preferential adsorption was based fully on experimental values.[1,2]

During the above studies, we obtained the partial specific volume and the refractive increment of polystyrene in two mixed solvent systems as a function of the solvent composition. We tried to analyze the experimental dependences by traditional means:[3,4] they defied interpretation. Realizing that both the specific volume and the refractive increment are strongly influenced by the changes of volume in mixing the *solvent* components, we decided to expand the study to include mixtures of low molecular weight compounds in the absence of polymer. The changes of volume were not sufficient to explain the dependence of refractive index on composition. It became obvious that the mixing rules for refractive index need to be reformulated. However, there already exists a large amount of literature (cf. ref 5 and 6) about the mixing rules and their merits. When more rigorous standards are applied, none of the formulas reproduce the experimental data satisfactorily. The idea of developing still another mixing rule did not seem inviting. On the other hand, we realized that the older theories had one concept in common. They struggled for the best relation between the external field acting on the macroscopic sample and the internal field acting on an individual molecule. All theories implicitly or explicitly assumed that the polarizability of a molecule is its invariant characteristic. Only Letcher and Bayles[7] recognized that this is not satisfactory, and they introduced a concept of "excess molar refraction".

This study will show that a theory using the concept of excess polarizability of mixing leads to a very satisfactory description of the refractive indices and refractive increments. However, we are still not able to solve the old problem of the internal field. Because the Lorenz–Lorentz formula is known to perform best from the existing theories, we have used it as our starting point and combined it with the concept of excess polarizability of mixing. Of course, the Lorenz–Lorentz internal field is still controversial: our relations must therefore be considered as phenomenological.

While the changes of volume in mixing are well-known and their effect on specific volumes and refractive increments is occasionally considered, there does not seem to exist any comprehensive approach. We are therefore presenting in this paper a useful frame of phenomenological relations, which can be used for unified presentation of all the changes accompanying mixing. The somewhat unexpected form of the dependence of specific volume of polymer on the composition of the mixed solvent becomes

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very natural within this framework.

Theoretical

Excess Polarizability of Mixing. When an isolated molecule is placed into an electric (optical) field **E**, a dipole moment $\mathbf{m}_{\text{mol}}$ is induced. Its magnitude is given by

$$\mathbf{m}_{\text{mol}} = \alpha \mathbf{E} \tag{1}$$

where the molecular polarizability α depends on the detailed electronic structure of the molecule. The polarizability varies also with the frequency (wavelength) of the field.

When a dielectric body with volume V is placed into an external electric field $\mathbf{E}_{\text{ext}}$, it is polarized, i.e., it acquires a dipole moment **m**, the magnitude of which is given by

$$\mathbf{m} = \mathbf{P}\mathrm{V} = (\epsilon - 1)\mathbf{E}_{\text{ext}} V / 4\pi \tag{2}$$

Here, **P** is polarization of the medium and ϵ is the dielectric constant. In the range of optical frequencies, ϵ is for most dielectrics related to the refractive index n as

$$\epsilon = n^2 \tag{3}$$

The quantities $\mathbf{E}$, $\mathbf{E}_{\text{ext}}$, $\mathbf{m}$, $\mathbf{m}_{\text{mol}}$, and $\mathbf{P}$ are vectors; α, ϵ, and n can be treated as scalars for isotropic media.

The induced dipole moment of a body is a vector sum of the induced dipole moments of its constituent molecules. Thus, eq 1–3 represent the theory of refractive index of dielectrics. However, the calculation of the refractive index from molecular polarizabilities is not straightforward for two reasons. First, the induced molecular dipoles create an additional electric field, which also acts on the molecules. In other words, the actual electrical field **E** acting on the molecules (internal field) differs from the external field of eq 2.

The common approach for overcoming this problem is based on the cavity model of Clausius–Mosotti and Lorenz–Lorentz. The dielectric is treated as a continuum except for the molecule under consideration. A spherical cavity is imagined around that molecule, and the field inside the cavity, which represents the internal field, is calculated. This model leads to a definition of molar refractivity R_i which for a pure substance i is written as

$$R_i \equiv \frac{n_i^2 - 1}{n_i^2 + 2}\,\frac{M_i}{\rho_i} \tag{4}$$

The molar refractivity is treated as a characteristic of the component, which is independent of the pressure, temperature, and (in mixtures) composition. Of course, the Lorenz–Lorentz expression, eq 4, is just one of a large number of formulas (cf. ref 5 and 6); all of them are equally controversial and do not reproduce the experimental data satisfactorily.

In our opinion, this failure is due to the fact that a second complicating effect has been neglected by all previous theories: the effect of excess polarizability of mixing.

When a molecule is transferred from vacuum into a dense medium, the neighboring molecules affect it in a dual way. 1. They magnify whatever external electrical field is present: this leads to the above Lorenz–Lorentz effect. 2. On top of that, the neighbors may also perturb the shape and energy levels of electronic orbitals of the molecule under consideration. This perturbation would lead to a change of the molecular polarizability α itself. Obviously, the effect is mutual: the polarizabilities of both molecules forming the contact are perturbed. The same perturbation of the electronic structure is known to lead to the phenomena of hypochromicity and solvent shift in the absorption spectra.[8,9]

The character of the perturbation depends primarily on the chemical nature of those parts of both molecules which are in direct contact. Thus, the perturbation may be treated in the first approximation as a contact phenomenon. Consequently, formation of each intermolecular contact is accompanied by a change of the overall polarizability of the system. We will call this change the excess polarizability of a contact. The amount of this change obviously depends on the chemical nature of atoms or groups forming the contact. In the process of mixing, some types of contacts are dissolved and other types are created. The net change of polarizability is the excess polarizability of mixing.

Because the relation between the external and internal field in dielectrics is still not properly known, the relation between the scalar polarizability P and the refractive index n is also ambiguous. For this study we have arbitrarily chosen the Lorenz–Lorentz relation

$$P \equiv (n^2 - 1)/(n^2 + 2) \tag{5}$$

Such a choice necessarily implies that all of the following treatment should be considered phenomenological. The refractivity R is defined as a product of the volume of the system V with the polarizability P. For pure components, eq 6 leads directly to eq 4 for molar refractivity.

$$R \equiv PV \tag{6}$$

Phenomenological Treatment of Changes of Thermodynamic Properties Resulting from Mixing. It is possible to express any extensive property X of a mixture by means of its change in mixing ΔX_{mix} defined as

$$X \equiv \sum_i N_i X_i + \Delta X_{\text{mix}} \equiv \sum w_i x_i + \Delta X_{\text{mix}} \tag{7}$$

Here, X may represent the enthalpy H, Gibbs free enthalpy G, volume of the system V, the refractivity R, etc. In our notation, the capital letter without subscript represents the extensive property; the same capital letter with the subscript i is the partial molar property of component i; the corresponding lower-case letter with the subscript is the partial specific property. The bar above the symbol means partial property in a mixture; symbols without a bar correspond to partial properties in a pure component. Obviously, $X_i = M_i x_i$ and $\bar{X}_i = M_i \bar{x}_i$, where M_i is the molecular weight of the ith component.

In the study of mixtures, several different concentration units are used. While most studies on mixtures of low molecular weight components prefer the molar fraction as a unit of concentration, we will use the volume fraction, following the practice common in the theory of polymer solutions since the introduction of Flory–Huggins relations. To avoid ambiguity, we define the volume fraction as a volume fraction before mixing. In our notation, N_i, w_i, c_i, and ϕ_i are respectively the number of moles, mass, concentration (g/mL), and volume fraction of the ith component. ρ is the density; ρ_i is the density of a pure component. These quantities are related by the following relations

$$w_i = M_i N_i \tag{8}$$

$$c_i = w_i/V = M_i N_i/V \tag{9}$$

$$\phi_i = N_i V_i \Big/ \sum_j N_j V_j = w_i v_i \Big/ \sum_j w_j v_j = c_i v_i \Big/ \sum_j c_j v_j \tag{10}$$

$$\rho = \sum_i w_i / V = \sum_i c_i \tag{11}$$

We are primarily interested in the partial specific volume and refractive increment of polymers in mixed solvents. Our experimental data are independent of the molecular weight of the polymer; that implies that they are also independent of the polymer heterogeneity. Under such circumstances, it is legitimate to treat the solutions as three-component systems. Indices 1 and 2 will be used for the components of the mixed solvent, index 3 for the polymer. The superscript zero will refer to a quantity in the limit of zero concentration of the polymer.

According to the Flory–Huggins theory, ΔG_{mix} is expressed as a sum of a combinatory term and a contact term. For enthalpy, volume, and refractivity only the contact term seems to be relevant. In our phenomenological approach, we will formulate ΔX_{mix} for these quantities in an analogous way to the formulation of the contact term in Flory–Huggins theory.

The Flory–Huggins relation for a two-component system is usually written as

$$\Delta G_{\text{mix}} = R_G T[\sum_{i=1}^{2} N_i \ln \phi_i + N_1\phi_2 g_{12}] \qquad (12)$$

where the logarithmic term represents the combinatory term; the second term is the contact term. Here, T is the absolute temperature, R_G is the gas constant, and g_{12} is a phenomenological function of the composition (e.g., of ϕ_2). In the original form of the Flory–Huggins theory, g_{12} was a constant given by

$$g_{12} = (2\epsilon_{12} - \epsilon_{11} - \epsilon_{22})/2kT \qquad (13)$$

where k is the Boltzmann constant and ϵ_{ij} is the contact (free) enthalpy of molecules i and j. The dependence of g_{12} on composition reflects the crudeness of assumptions which led to eq 12.

Equation 12 is not symmetrical with respect to the two components. We have found it convenient to rewrite eq 12 as eq 14, which shows that the quantity (g_{12}/V_1) may have more general meaning than g_{12}

$$\Delta G_{\text{mix}} = R_G T[\sum_{i=1}^{2} N_i \ln \phi_i + (\sum_{i=1}^{2} N_i V_i)\phi_1\phi_2(g_{12}/V_1)] \qquad (14)$$

In our previous studies,[1,2] we have generalized the Flory–Huggins relation for a three-component system. The generalized relation can be written in terms analogous to eq 14 as

$$\Delta G_{\text{mix}} = R_G T\{\sum_{i=1}^{3} N_i \ln \phi_i + (\sum_{i=1}^{3} N_i V_i)[\phi_1\phi_2(g_{12}/V_1) + \phi_1\phi_3(g_{13}/V_1) + \phi_2\phi_3(g_{23}/V_2) + \phi_1\phi_2\phi_3(g_T/V_1)]\} \qquad (15)$$

It is convenient to introduce a measure of the composition of the mixed solvent u_i as

$$u_i \equiv \phi_i/(\phi_1 + \phi_2); \qquad i = 1, 2 \qquad (16)$$

Obviously

$$u_i^0 = \phi_i^0; \qquad i = 1, 2 \qquad (17)$$

When postulating eq 15, we require that g_{12} in eq 15 is independent of the concentration of polymer ϕ_3; it is a function of u_2 identical with the function g_{12} in eq 14. The contact functions g_{13} and g_{23} are functions of ϕ_3 only; g_T is a phenomenological function of u_2 and ϕ_3, which compensates for all the deviations of the real system from the oversimplified model of binary contact interactions.

Our previous studies[1,2] were devoted to the experimental determination of functions g_{12}, g_{13}, g_{23}, and g_T for solutions of polystyrene in two mixed-solvent systems: benzene–cyclohexane and ethyl acetate–cyclohexane. The same systems are studied in the present paper. In one of these papers,[2] we have found it convenient to express ΔH_{mix} for a mixture of two solvents by a relation which in terms similar to eq 14 would read

$$\Delta H_{\text{mix}} = R_G(\sum_{i=1}^{2} N_i V_i)\phi_1\phi_2(h_{12}/V_1) \qquad (18)$$

Again, the ratio (h_{12}/V_1) seems to have more basic significance than the quantity h_{12}.

The present study is concerned with the changes of volume in mixing, ΔV_{mix}, and the changes of refractivity of mixing, ΔR_{mix}. We propose to write for these quantities relations analogous to eq 14 and 18. For a two-component system the relations are

$$\Delta V_{\text{mix}} = (\sum_{i=1}^{2} N_i V_i) A_{12}\phi_1\phi_2 \qquad (19)$$

$$\Delta R_{\text{mix}} = (\sum_{i=1}^{2} N_i V_i) B_{12}\phi_1\phi_2 \qquad (20)$$

The relations for a three-component system read

$$\Delta V_{\text{mix}} = (\sum_{i=1}^{3} N_i V_i)[A_{12}\phi_1\phi_2 + A_{13}\phi_1\phi_3 + A_{23}\phi_2\phi_3 + A_T\phi_1\phi_2\phi_3] \qquad (21)$$

$$\Delta R_{\text{mix}} = (\sum_{i=1}^{3} N_i V_i)[B_{12}\phi_1\phi_2 + B_{13}\phi_1\phi_3 + B_{23}\phi_2\phi_3 + B_T\phi_1\phi_2\phi_3] \qquad (22)$$

Here, A_{12} and B_{12} are functions of u_2 only; A_{13}, A_{23}, B_{13}, and B_{23} are functions of ϕ_3 only; A_T and B_T are functions of both u_2 and ϕ_3.

Partial Specific Volume. Partial specific volume $\bar{v}_3^0$ of a polymer is defined as

$$\bar{v}_3^0 \equiv \lim_{\phi_3\to 0} \left(\frac{\partial V}{\partial w_3}\right)_{w_1,w_2} \equiv \lim_{\phi_3\to 0} \left(\frac{\partial V}{\partial w_3}\right)_{u_2} \qquad (23)$$

Here, in the second identity we realize that constancy of w_1 and w_2 implies constancy of u_2. To obtain a form suitable for calculation of the derivative which is required in eq 23, we combine eq 7 ($X \rightarrow V$), 8, 16, and 21, getting

$$V = (\sum_{i=1}^{3} w_i v_i)[1 + A_{12}u_1u_2(1-\phi_3)^2 + A_{13}u_1\phi_3(1-\phi_3) + A_{23}u_2\phi_3(1-\phi_3) + A_T u_1u_2\phi_3(1-\phi_3)^2] \qquad (24)$$

Hence, a routine calculation and use of eq 10 and 17 yield

$$\bar{v}_3^0 = v_3[1 + A_{13}^0\phi_1^0 + A_{23}^0\phi_2^0 - \phi_1^0\phi_2^0(A_{12} - A_T)] \qquad (25)$$

For a single component solvent i, eq 25 reduces to

$$\bar{v}_{3,i}^0 = v_3(1 + A_{i3}^0) \qquad (26)$$

where the second subscript in $\bar{v}_{3,i}^0$ refers to the single solvent. The value of A_{i3}^0 may vary from solvent to solvent. Thus, our eq 21 may account for the difference of the values $\bar{v}_{3,i}^0$ measured in different simple solvents.

It should be noted that, as long as the density measurements are not extended toward the pure polymer (which is usually impractical), the individual values of v_3, A_{13}, and A_{23} are not accessible, only the difference $v_3(A_{13} - A_{23})$. We have encountered a similar situation[1,2] when analyzing the preferential adsorption onto polymers in terms of the free enthalpy functions g_{13} and g_{23}.

Returning to the analysis of $\bar{v}_3^0$ in mixed solvents, we substitute A_{i3}^0 from eq 26 back to eq 25 and obtain

$$\bar{v}_3^0 = \bar{v}_{3,1}^0\phi_1^0 + \bar{v}_{3,2}^0\phi_2^0 - v_3\phi_1^0\phi_2^0(A_{12} - A_T) \qquad (27)$$

Thus, $\bar{v}_3^0$ in mixed solvents is not a linear combination of the appropriate $\bar{v}_{3,i}^0$ values. Both the solvent–solvent interaction function A_{12} and the ternary function A_T influence the value of $\bar{v}_3{}^0$. The function A_{12} is easily calculated from density measurements on solvent mixtures in the absence of polymer. Equations 7 ($X \rightarrow V$), 10, 11, and 19 combine to yield

$$A_{12} = (\phi_1{}^0\rho_1 + \phi_2{}^0\rho_2 - \rho^0)/\phi_1{}^0\phi_2{}^0\rho^0 \qquad (28)$$

Here, $\rho_i \equiv 1/v_i$ is the density of pure component i. The value of $\bar{v}_3{}^0$ is related to the experimentally accessible quantity $(\partial\rho/\partial c_3)_{u_1}{}^0$. Combination of eq 9, 11, and 23 gives the necessary relation as

$$\bar{v}_3{}^0 = [1 - (\partial\rho/\partial c_3)_{u_1}{}^0]/\rho^0 \qquad (29)$$

Finally, combining eq 27–29 and using a reasonable value for v_3 we can calculate A_{T} from appropriate experimental data.

Refractive Increment. For the analysis of the refractive increment $(\partial n/\partial c_3)_{u_2}{}^0$ it is convenient to start with the polarizability increment $(\partial P/\partial c_3)_{u_2}{}^0$. These two quantities are related as

$$(\partial P/\partial c_3)_{u_2}{}^0 = (\mathrm{d}P/\mathrm{d}n)^0\,(\partial n/\partial c_3)_{u_2}{}^0 \qquad (30)$$

where from eq 5

$$(\mathrm{d}P/\mathrm{d}n)^0 = 6n^0/[(n^0)^2 + 2]^2 \qquad (31)$$

From eq 6 we get

$$(\partial P/\partial c_3)_{u_2}{}^0 = [(\partial R/\partial c_3)_{u_2}{}^0 - P^0\,(\partial V/\partial c_3)_{u_2}{}^0]/V^0 \qquad (32)$$

Recognizing that eq 9 leads to

$$(\partial w_3/\partial c_3)_{u_2}{}^0 = V^0 \qquad (33)$$

we obtain the following identities

$$(\partial R/\partial c_3)_{u_2}{}^0 = (\partial R/\partial w_3)_{u_2}{}^0\,(\partial w_3/\partial c_3)_{u_2}{}^0 = V^0\,(\partial R/\partial w_3)_{u_2}{}^0 \qquad (34)$$

$$(\partial V/\partial c_3)_{u_2}{}^0 = (\partial V/\partial w_3)_{u_2}{}^0\,(\partial w_3/\partial c_3)_{u_2}{}^0 = \bar{v}_3{}^0V^0 \qquad (35)$$

Substitution into eq 32 yields

$$(\partial P/\partial c_3)_{u_2}{}^0 = (\partial R/\partial w_3)_{u_2}{}^0 - P^0\bar{v}_3{}^0 \qquad (36)$$

In a procedure analogous to our derivation of eq 24, we combine eq 7 ($X \rightarrow R$), 8, 16, and 22 to obtain

$$R = \sum_{i=1}^{3} w_ir_i + (\sum_{i=1}^{3} w_iv_i)[B_{12}u_1u_2(1 - \phi_3)^2 + B_{13}u_1\phi_3(1 - \phi_3) + B_{23}u_2\phi_3(1 - \phi_3) + B_{\mathrm{T}}u_1u_2\phi_3(1 - \phi_3)^2] \qquad (37)$$

Hence, the needed derivative is obtained with the help of eq 10 and 17 as

$$(\partial R/\partial w_3)_{u_2}{}^0 = r_3 + v_3[B_{13}{}^0\phi_1{}^0 + B_{23}{}^0\phi_2{}^0 - (B_{12} - B_{\mathrm{T}})\phi_1{}^0\phi_2{}^0] \qquad (38)$$

Combination of eq 36 and 38 yields the sought relation

$$(\partial P/\partial c_3)_{u_2}{}^0 = r_3 - P^0\bar{v}_3{}^0 + v_3[B_{13}{}^0\phi_1{}^0 + B_{23}{}^0\phi_2{}^0 - (B_{12} - B_{\mathrm{T}})\phi_1{}^0\phi_2{}^0] \qquad (39)$$

In the above relations, $(\partial R/\partial w_3)\mu_2{}^0$ is actually the specific refractivity of polymer $\bar{r}_3{}^0$. Thus, eq 36 reads after rearrangement

$$\bar{r}_3{}^0 \equiv (\partial P/\partial c_3)_{u_2}{}^0 + P^0\bar{v}_3{}^0 \qquad (40)$$

Equations 39 and 40 yield

$$\bar{r}_3{}^0 = r_3 + v_3[B_{13}{}^0\phi_1{}^0 + B_{23}{}^0\phi_2{}^0 - (B_{12} - B_{\mathrm{T}})\phi_1{}^0\phi_2{}^0] \qquad (41)$$

For a single component solvent i, eq 41 reduces to

$$\bar{r}_{3,i}{}^0 = r_3 + v_3B_{i3}{}^0 \qquad (42)$$

where the second subscript i in $\bar{r}_{3,i}{}^0$ refers to pure solvent i. If the effect of excess polarizability of mixing were absent, the specific refractivity of the polymer $\bar{r}_3{}^0$ would be the same for all solvents. However, the value of $B_{i3}{}^0$ may differ for different solvents and $\bar{r}_3{}^0$ may vary from solvent to solvent.

Substituting $B_{i3}{}^0$ from eq 42 back to eq 41 we obtain

$$\bar{r}_3{}^0 = \bar{r}_{3,1}{}^0\phi_1{}^0 + \bar{r}_{3,2}{}^0\phi_2{}^0 - v_3(B_{12} - B_{\mathrm{T}}{}^0)\phi_1{}^0\phi_2{}^0 \qquad (43)$$

Thus, in complete analogy to the specific volume $\bar{v}_3{}^0$, the specific refractivity of polymer $\bar{r}_3{}^0$ is not only different for different single solvents: for mixed solvents it may not be a linear combination of specific refractivities in appropriate single solvents, being influenced both by B_{12} and $B_{\mathrm{T}}{}^0$. The function B_{12} is calculated from measurements of density and refractive index of the solvent mixtures. Equations 7 ($X \rightarrow R$), 10, 11, and 20 combine to yield

$$B_{12} = [P^0(\phi_1{}^0\rho_1 + \phi_2{}^0\rho_2)/\rho^0 - P_1\phi_1{}^0 - P_2\phi_2{}^0]/\phi_1{}^0\phi_2{}^0 \qquad (44)$$

The experimental value of $B_{\mathrm{T}}{}^0$ may be obtained from combining eq 43 and 44.

Finally, when eq 43 is combined with eq 40 and the polarizabilities are replaced by refractive indices as in eq 5, 30, and 31, the refractive increment of a polymer in mixed solvent is expressed as

$$\left(\frac{\partial n}{\partial c_3}\right)_{u_1}^0 = \frac{[(n^0)^2 + 2]^2}{6n^0}\left[\phi_1{}^0\left(\frac{\partial n}{\partial c_3}\right)_1^0\frac{6n_1}{(n_1{}^2 + 2)^2} + \phi_2{}^0\left(\frac{\partial n}{\partial c_3}\right)_2^0\frac{6n_2}{(n_2{}^2 + 2)^2} - \left(\bar{v}_3{}^0\,\frac{(n^0)^2 - 1}{(n^0)^2 + 2} - \phi_1{}^0\bar{v}_{3,1}{}^0\,\frac{n_1{}^2 - 1}{n_1{}^2 + 2} - \phi_2{}^0\bar{v}_{3,2}{}^0\,\frac{n_2{}^2 - 1}{n_2{}^2 + 2}\right) - v_3\phi_1{}^0\phi_2{}^0(B_{12} - B_{\mathrm{T}}{}^0)\right] \qquad (45)$$

It is obvious that for the prediction of the values of $(\partial n/\partial c_3)_{u_1}{}^0$ we need to know not only the refractive increments and specific volumes in the two pure solvents, but also the values of B_{12} and $B_{\mathrm{T}}{}^0$ as well as the value of $\bar{v}_3{}^0$ in the mixed solvent. The latter value could be obtained either experimentally or from eq 27, provided that the values of A_{12} and A_{T} are known.

Experimental Section

All solvents were reagent grade and were used without further purification. Gas chromatography of these solvents did not detect any impurity except in the case of cyclohexane. Different batches of cyclohexane contained from 0.2 to 1.0% of an impurity, and their physical properties varied accordingly. However, each series of experiments, as described below, was performed with a single batch of cyclohexane, and values of density and refractive index applicable to each batch were used for its evaluation. Whenever a set of measurements was duplicated, using another batch of cyclohexane, the values of all quantities of interest ($\bar{v}_3{}^0$, $(\partial n/\partial c_3)_{u_1}{}^0$, A_{12}, B_{12}) were identical within experimental error.

The solvent mixtures were prepared by weighing appropriate volumes of pure solvents; the volume fractions were calculated from the weights and from densities of pure components. Polystyrene samples were purchased from Pressure Chemical Co., Pittsburgh, Pa.

Refractive indices of pure solvents and solvent mixtures were measured, using a Bausch and Lomb Precision Refractometer equipped with mercury and sodium light sources. The precision of the instrument as quoted by the manufacturer is ±0.00003 units. The initial calibration of the instrument was made at 20 °C, using the standard glass test piece provided by the manufacturer. Calibration checks were run routinely with distilled water, and occasional rechecks were made with the glass test piece. Samples

Table I
Densities and Refractive Indices of Pure Solvents at 20 °C

solvent	density, g/mL	refractive index 589 nm	546 nm	436 nm
benzene (B)	0.87916	1.50111	1.50521	1.52303
cyclohexane[a] (CH)	0.7765- 0.7788	1.4262	1.4273- 1.4281	1.4357- 1.4371
ethyl acetate (EA)	0.90068	1.37226	1.37382	1.38027
carbon tetrachloride (CCl)	1.59427	1.46003	1.46239	1.47214

[a] Different batches.

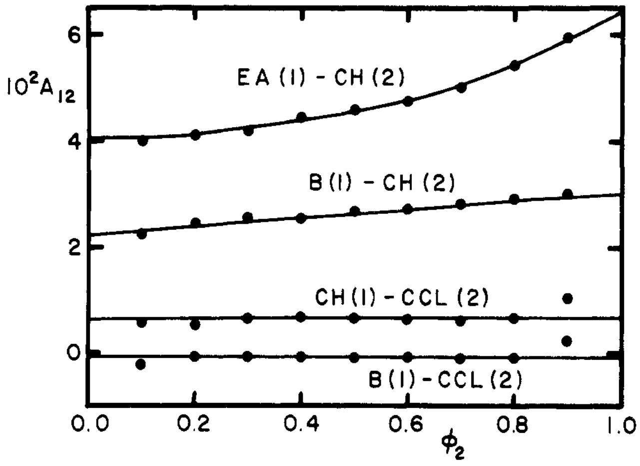

Figure 1. Dependence of A_{12} on composition for four two-component systems indicated. The lines represent the data from Table II.

were applied to the prism of the refractometer as quickly as possible to minimize possible evaporation and changes in composition. All measurements were made at 20 °C, using the sodium (589 nm) line and mercury green (546 nm) and blue (436 nm) lines.

All densities were measured by a Precision Density Meter, Model DMA 02C, manufactured by Anton Paar K. G., Austria. The refractive increments were measured at 20 °C by a Brice-Phoenix differential refractometer Model BP-2000-V equipped with a special glass cell R-101-4, using the blue and green mercury lines. The details of the measurements of partial specific volumes and refractive increments are given in our previous paper.[2]

Results and Discussion

Solvent Mixtures. The first part of this study is concerned with the test of our relations for excess polarizability and volume of mixing, using binary solvent mixtures in the absence of polymer. We have studied all six binary solvent systems composed from the following four solvents: benzene (B), cyclohexane (CH), ethyl acetate (EA), and carbon tetrachloride (CCl). While these solvents represent rather different chemical classes, they all have approximately the same boiling point: this feature partially alleviates the problem of the change of the composition of the mixture due to the evaporation during the handling of the samples. The densities and refractive indices of the four pure solvents are given in Table I.

For each binary system, a set of 11 mixtures was prepared with ϕ_2 changing from 0.0 to 1.0 in steps of 0.1. Density and refractive index were measured for each mixture. The values of A_{12} were calculated, using eq 28; the results are plotted in Figure 1. (To avoid overcrowding of the plot only four binary systems are shown.) The largest values of A_{12} were exhibited by the system ethyl acetate–cyclohexane; the values in benzene–cyclohexane mixtures were about half as large. The volume change in the remaining four systems was much smaller but still significant. The data were fitted to the following relation by using the method of least squares.

Table II
The Coefficients Needed for Evaluation of A_{12} by Equation 46 for Six Binary Systems

solvent mixture	10^3a_0	10^3a_1	10^3a_2
EA (1)-CH (2)	45.8	11.0	6.0
B (1)-CH (2)	26.6	3.9	0.0
B (1)-EA (2)	6.2	0.0	0.0
CH (1)-CCl (2)	6.8	0.0	0.0
B (1)-CCl (2)	−0.5	0.0	0.0
EA (1)-CCl (2)	1.9	0.0	0.0

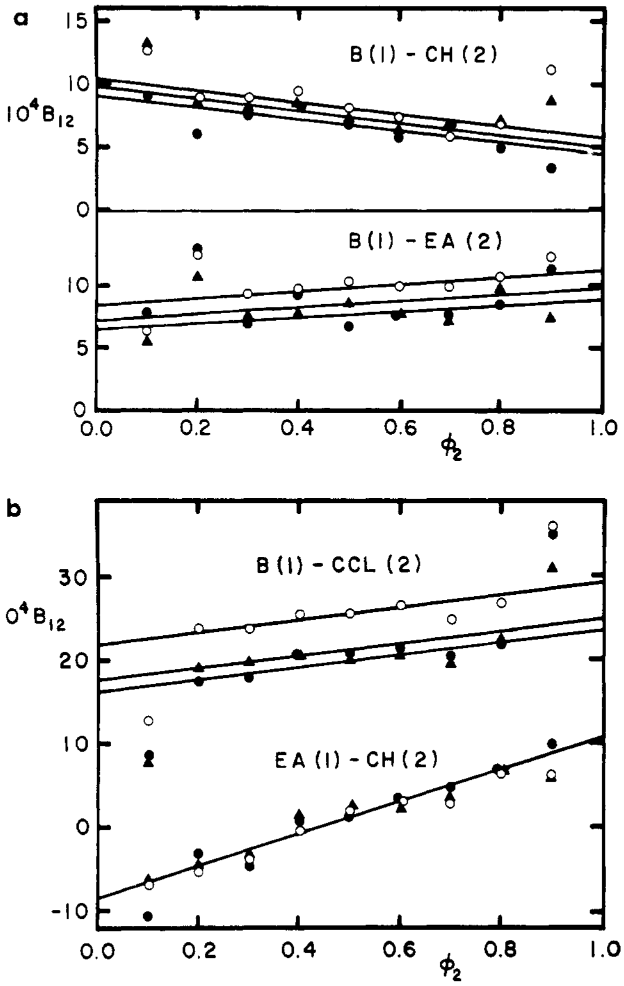

Figure 2. Dependence of B_{12} on composition for two-component systems indicated: wavelengths (●) 589 nm, (▲) 546 nm, and (○) 436 nm. The lines represent the data from Table III.

$$A_{12} = a_0 + a_1(\phi_2 - \phi_1) + a_2(\phi_2 - \phi_1)^2 \qquad (46)$$

The three terms were needed only for the ethyl acetate–cyclohexane system; for benzene–cyclohexane, a linear relation was satisfactory, while the remaining four systems were sufficiently described by the constant term. The values of a_0, a_1, and a_2 are collected in Table II. When the values from Table II are employed, the experimental values of density are reproduced within a few units of the fifth decimal place.

The experimental values of B_{12} were calculated according to eq 44 and 5; some results are plotted in Figure 2. The data were fitted to the relation

$$B_{12} = b_0 + b_1(\phi_2 - \phi_1) \qquad (47)$$

The values b_0 and b_1 are collected in Table III. When the refractive indices are calculated back, using these values of b_0 and b_1 together with the data for pure solvent com-

Table III
The Coefficients Needed for Evaluation of B_{12} by Equation 47 for Six Binary Systems

solvent mixture	wave-length, nm	$10^4 b_0$	$10^4 b_1$
EA (1)-CH (2)	*a*	1.3	9.7
B (1)-CH (2)	589	6.8	−2.3
	546	7.5	−2.3
	436	8.1	−2.3
B (1)-EA (2)	589	7.7	1.2
	546	8.6	1.3
	436	9.9	1.4
CH (1)-CCl (2)	*a*	7.6	4.3
B (1)-CCl (2)	589	20.1	3.7
	546	21.5	3.7
	436	25.7	3.7
EA (1)-CCl (2)	589	8.6	1.2
	546	7.2	1.1
	436	6.2	1.0

[a] The same dependence is valid for all three wavelengths.

ponents and the appropriate density values, the experimental values are reproduced within a few units in the fifth decimal place, i.e., within experimental error. On the other hand, if the values of B_{12} were neglected, the calculated values of refractive index would differ by up to five units in the fourth decimal place, i.e., well above the experimental error. Thus, the necessity of introduction of the excess polarizability of mixing seems to be well established.

For most of the systems, the amount of the excess polarizability of mixing is dependent on the wavelength. Such a dependence is not surprising if the excess polarizability is due to the perturbation of molecular orbitals as we have assumed in the theoretical part.

While our data are not extensive enough for relating the excess polarizability with the chemical structure, some tendencies may be observed. The largest excess polarizability is observed for the system benzene–carbon tetrachloride. The intermediate values are found for mixtures containing one of these solvents, while the mixture containing none (EA–CH) has the lowest value and change of sign. According to our tentative interpretation, the molecules with many π electrons (benzene) or many unbonded electron pairs (CCl_4) are more easily perturbed than the more saturated species.[10] Relations between B_{12} and chemical structure are also observed in the data of Letcher and Bayles.[7]

Of course, it should not be forgotten that the perturbation due to the dense medium manifests itself primarily in the contact polarizabilities. The excess polarizabilities are linear combinations of the appropriate contact polarizabilities and may happen to be small even if the relevant contact polarizabilities are high.

Still another question merits consideration. Is it possible that the effect of the excess polarizability is only apparent and that it is due to the improper use of the Lorenz–Lorentz relation (eq 5) for the calculation of the polarizability? Could some other relation yield B_{12} identically equal to zero for all mixtures? We have repeated our calculations, using other expressions for P. For example, the Gladstone–Dale expression

$$P = n - 1 \tag{48}$$

yielded values of B_{12} which had much higher numerical values than the values from the Lorenz–Lorentz calculation but were fully acceptable on the phenomenological level. In this context, we consider it very significant that B_{12} for some systems is positive (most of our mixtures) and for other systems negative (mixtures of different amines in the Letcher and Bayles[7] data) and that B_{12} changes sign with the composition (EA–CH). The numerical values also vary quite appreciably. These effects do not seem to be in any relation to the difference in refractive indices of the two components of the mixture. We believe that such behavior proves the existence of the excess polarizability and the necessity of its introduction into the mixing formula for refractive indices, regardless of what expression is used for the internal field. Of course, since the Lorenz–Lorentz formula is still somewhat doubtful, it would be dangerous to use the experimental values of B_{12} for any far-reaching conclusions about the extent of intermolecular interactions in the mixtures.

Table IV
Partial Specific Volume, Refractive Increment, and Specific Refractivity of Polystyrene in Benzene(1)-Cyclohexane(2) Mixtures at 20 °C

		$(\partial n/\partial c_3)_{u_2}{}^0$		$\bar{r}_3{}^0$	
$\phi_2{}^0$	$\bar{v}_3{}^0$	546 nm	436 nm	546 nm	436 nm
0.0	0.9152	0.1035	0.1068	0.3229	0.3319
0.1	0.9121	0.1126	0.1164	0.3228	0.3316
0.2	0.9121	0.1200	0.1258	0.3229	0.3322
0.3	0.9109	0.1292	0.1353	0.3237	0.3328
0.4	0.9125	0.1350	0.1440	0.3237	0.3338
0.5	0.9126	0.1421	0.1513	0.3241	0.3339
0.6	0.9139	0.1482	0.1580	0.3244	0.3341
0.7	0.9147	0.1543	0.1648	0.3248	0.3345
0.8	0.9167	0.1585	0.1707	0.3246	0.3349
0.9	0.9209	0.1624	0.1750	0.3249	0.3351
1.0	0.9253	0.1662	0.1795	0.3254	0.3355

Table V
Partial Specific Volume, Refractive Increment, and Specific Refractivity of Polystyrene in Ethyl Acetate(1)-Cyclohexane(2) Mixtures at 20 °C

		$(\partial n/\partial c_3)_{u_2}{}^0$		$\bar{r}_3{}^0$	
$\phi_2{}^0$	$\bar{v}_3{}^0$	546 nm	436 nm	546 nm	436 nm
0.0	0.9123	0.2180	0.2310	0.3272	0.3369
0.1	0.9089	0.2163	0.2289	0.3270	0.3365
0.2	0.9082	0.2130	0.2261	0.3267	0.3365
0.3	0.9066	0.2100	0.2229	0.3265	0.3362
0.4	0.9074	0.2062	0.2194	0.3266	0.3364
0.5	0.9068	0.2025	0.2159	0.3265	0.3365
0.6	0.9071	0.1973	0.2109	0.3260	0.3361
0.7	0.9077	0.1912	0.2061	0.3253	0.3361
0.8	0.9151	0.1836	0.1976	0.3257	0.3361
0.9	0.9184	0.1759	0.1888	0.3254	0.3353
1.0	0.9253	0.1662	0.1795	0.3254	0.3355

Partial Specific Volume and Refractive Increment. Our experimental values of partial specific volume $\bar{v}_3{}^0$, refractive increment $(\partial n/\partial c_3)_{u_2}{}^0$, and specific refractivity $\bar{r}_3{}^0$ (evaluated using eq 40) are summarized in Tables IV and V. The partial specific volume is plotted as a function of composition in Figures 3 and 4. The dotted line in Figures 3 and 4 represents the linear combination of the specific volumes in pure solvents. This representation is clearly inadequate. The broken line in these Figures represents eq 27 where the values of A_{12} were calculated, using the data from Table II and neglecting the ternary parameter A_T. This representation is much better but still not fully satisfactory. For an achievement of a better fit, an introduction of the ternary parameter A_T was necessary: the full lines were computed, using $A_T = -0.010$ for the B–CH solvent mixture and $A_T = -0.008$ for the EA–CH solvent mixture.

The specific refractivity $\bar{r}_3{}^0$ is plotted as a function of composition in Figures 5 and 6. It is obvious that the value of $\bar{r}_3{}^0$ for our three single solvents (B, CH, EA) is different. Thus, according to eq 42, the introduction of the excess polarizability of mixing is necessary for proper

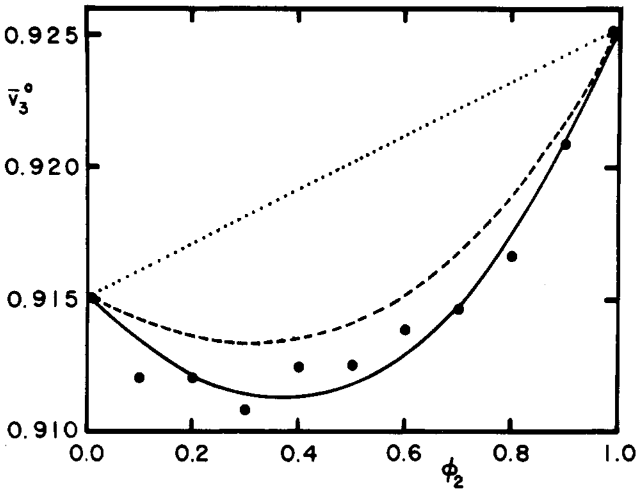

Figure 3. Dependence of partial specific volume $\bar{v}_3^0$ of polystyrene on the composition of the benzene(1)-cyclohexane(2) solvent mixture at 20 °C. Dotted line: linear combination of $\bar{v}_{3,i}^0$ for pure solvent components. Broken line: results from eq 27 neglecting A_T. Full line: results from eq 27 with $A_T = -0.010$.

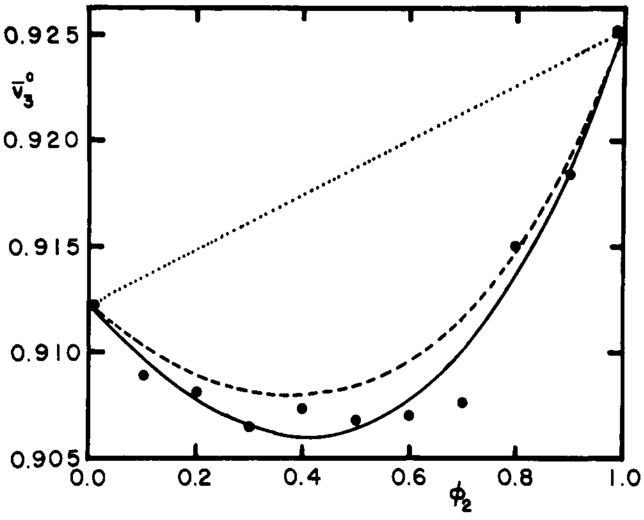

Figure 4. Dependence of partial specific volume $\bar{v}_3^0$ of polystyrene on the composition of the ethyl acetate(1)-cyclohexane(2) solvent mixture at 20 °C. The lines have the same significance as those in Figure 3 ($A_T = -0.008$ for the full line).

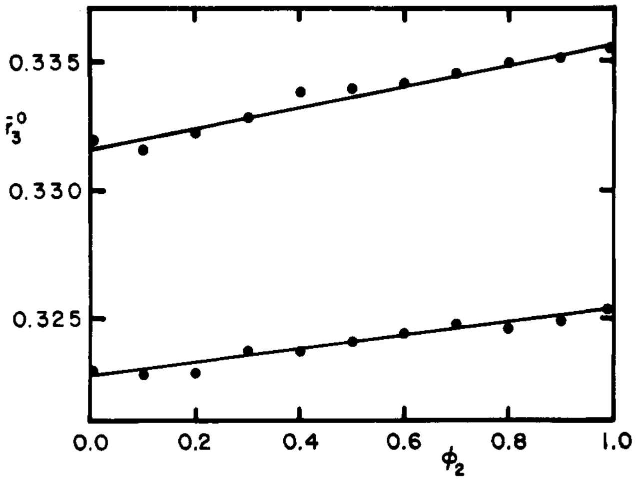

Figure 5. Dependence of specific refractivity $\bar{r}_3^0$ of polystyrene on the composition of the benzene(1)-cyclohexane(2) solvent mixture at 20 °C: upper line, 436 nm; lower line, 546 nm.

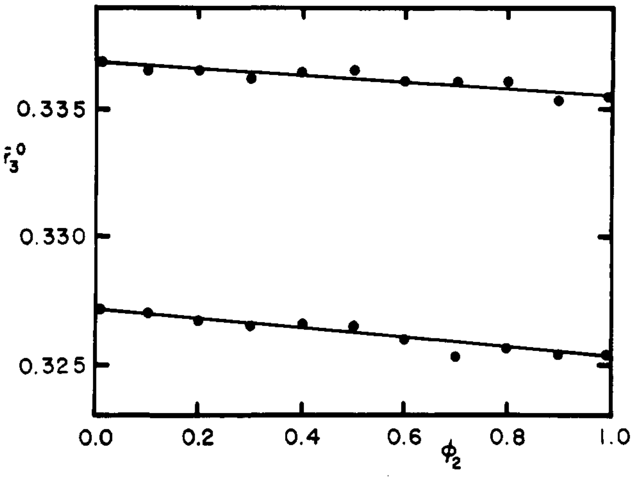

Figure 6. Dependence of specific refractivity $\bar{r}_3^0$ of polystyrene on the composition of the ethyl acetate(1)-cyclohexane(2) solvent mixture at 20 °C: upper line, 436 nm; lower line, 546 nm.

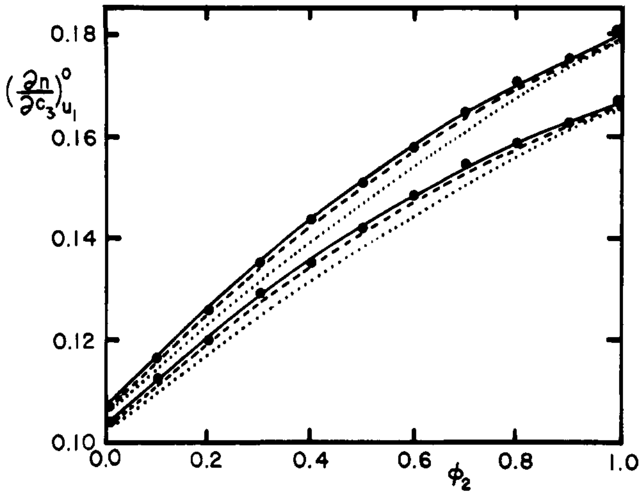

Figure 7. Dependence of the refractive increment $(\partial n/\partial c_3)_{u_1}^0$ of polystyrene on the composition of the benzene(1)-cyclohexane(2) solvent mixture at 20 °C: upper set of lines, 436 nm; lower set of lines, 546 nm. The theoretical lines were calculated from eq 45, neglecting B_{12} and B_T^0. $\bar{v}_3^0$ calculated from eq 27 where: A_{12} and A_T were neglected (dotted lines); A_{12} was from Table II and A_T was neglected (broken lines); A_{12} was from Table II and $A_T = -0.010$ (full lines).

interpretation of refractive increments. The dependences in Figures 5 and 6 are linear within the experimental error. That means that the last term in eq 43 is smaller than the experimental error. In fact, if B_T^0 is neglected and the last term is calculated, using the values from Table III, its value for all of our mixtures is less than two units in the fourth decimal place, i.e., it is completely negligible.

The refractive increment $(\partial n/\partial c_3)_{u_1}^0$ is plotted as a function of composition in Figures 7 and 8; the lines represent the theoretical predictions according to eq 45. In all of these theoretical lines the term $v_3\phi_1^0\phi_2^0(B_{12} - B_T^0)$ was neglected. The inclusion of this term (B_{12} from Table III, B_T^0 neglected) would change the values of $(\partial n/\partial c_3)_{u_1}^0$ by at most 0.0003. When the value of $\bar{v}_3^0$, which is needed in eq 45, is calculated from eq 27, using the appropriate values of A_{12} and A_T, the refractive increments are reproduced within a maximum (random) deviation of 0.0008. However, if the A_{12} and A_T terms were neglected, and $\bar{v}_3^0$ was calculated as a linear combination of $\bar{v}_{3,i}^0$'s for pure solvents, an appreciable error would result: this is apparent from the dotted lines in Figures 7 and 8. For a precision work not only the major term A_{12} but also the minor term A_T should be included; its neglect would produce an additional (nonrandom) error of up to 0.0010 in the values

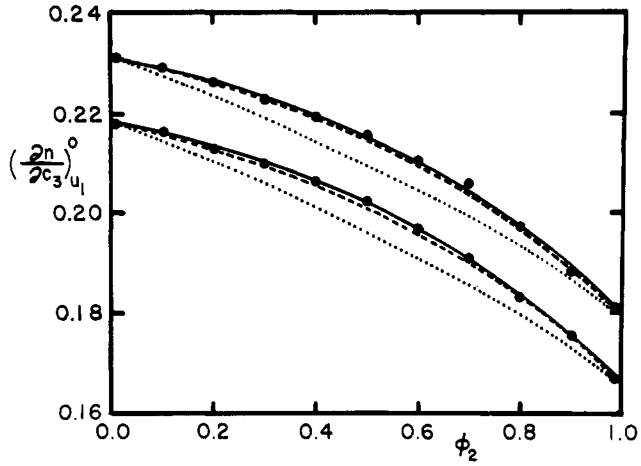

Figure 8. Dependence of refractive increment $(\partial n/\partial c_3)_{u_1}{}^0$ of polystyrene on the composition of the ethyl acetate(1)–cyclohexane(2) solvent mixture at 20 °C. The same designation of lines as in Figure 7. A_T = −0.008 for full lines.

of the refractive increment (broken lines in Figures 7 and 8).

Conclusions

The analysis of the measurements of density and refractive index of solvent mixtures has definitely shown that the phenomenon of excess polarizability of mixing, which was in detail outlined in the theoretical part, is needed for the proper interpretation of experimental data. This conclusion remains valid without respect to the form of the relation between polarizability and refractive index.

The measurement of the refractive increment of polystyrene in several solvents and solvent mixtures has shown clearly that the phenomenon of excess polarizability is also operative in polymer solutions: the specific refractivity of polystyrene varies from solvent to solvent.

For the prediction of the values of partial specific volume and refractive increment of polymers in mixed solvents, a detailed knowledge of the volume changes accompanying the mixing of the solvents themselves is obligatory. For a precision work, even the knowledge of the ternary parameter A_T is needed. It follows that the prediction should be preceded by measurement of the partial specific volumes of polymers in at least some of the solvent mixtures of interest.

The effect of the excess polarizability of mixing of the solvent components themselves on the values of the refractive increment of the polymer was very small for our experimental data. However, it may become significant for solvent mixtures exhibiting a rather large effect (e.g., a benzene–carbon tetrachloride mixture).

Rather precise values of refractive increments and partial specific volumes are needed for the measurement of molecular weight of polymers by the light-scattering and sedimentation techniques and, especially, for the measurement of preferential adsorption of solvent components onto polymer. We have shown that for an acceptable prediction of these values a rather detailed knowledge of the mixtures of interest is needed. Use of unjustified assumptions (linear interpolation) may lead to serious errors. In cases where the behavior of the mixtures is not known in detail, we recommend that the refractive increments and partial specific volumes are measured experimentally and not predicted.

List of Symbols

A_{ij}	binary interaction parameter related to ΔV_{mix} (eq 19)
A_T	ternary interaction parameter related to ΔV_{mix} (eq 21)
a_0, a_1, a_2	coefficients in expansion of A_{12} (eq 46)
B	designation of benzene
B_{ij}	binary interaction parameter related to ΔR_{mix} (eq 20)
B_T	ternary interaction parameter related to ΔR_{mix} (eq 22)
b_0, b_1	coefficients in expansion of B_{12} (eq 47)
c_i	concentration of the *i*th component (g/mL)
CH	designation of cyclohexane
CCl	designation of carbon tetrachloride
$\mathbf{E}$	electric field
$\mathbf{E}_{\mathrm{ext}}$	external electric field
EA	designation of ethyl acetate
G	Gibbs free enthalpy
ΔG_{mix}	change of G during the process of mixing
g_{ij}	binary interaction parameter related to ΔG_{mix} (eq 14)
g_T	ternary interaction parameter related to ΔG_{mix} (eq 15)
H	enthalpy
ΔH_{mix}	change of H during the process of mixing
h_{ij}	binary interaction parameter related to ΔH_{mix} (eq 18)
k	Boltzmann constant
M_i	molecular weight of the *i*th component
$\mathbf{m}$	induced dipole moment of a body
$\mathbf{m}_{\mathrm{mol}}$	induced dipole moment of a molecule
N_i	number of moles of the *i*th component
n	refractive index
n_i	refractive index of the pure *i*th component
P	Lorenz–Lorentz polarizability (eq 5)
$\mathbf{P}$	polarization of the medium
R	refractivity (eq 6)
R_G	gas constant
R_i	molar refractivity of the pure *i*th component
ΔR_{mix}	change of R during the process of mixing
r_i	partial specific refractivity of the pure *i*th component
$\bar{r}_3{}^0$	partial specific refractivity of polymer at vanishing concentration (eq 40)
$\bar{r}_{3,i}{}^0$	partial specific refractivity of polymer at vanishing concentration in the pure *i*th solvent
T	absolute temperature
u_i	$\phi_i/(\phi_1 + {}_{\varphi 2})$: volume fraction referred to the solvent mixture only
V	volume
V_i	partial molar volume of the pure *i*th component
ΔV_{mix}	change of volume during the process of mixing
v_i	partial specific volume of the pure *i*th component
$\bar{v}_i$	partial specific volume of the *i*th component
$\bar{v}_{3,i}{}^0$	partial specific volume of polymer in pure solvent i at a vanishing concentration of polymer
w_i	mass of the *i*th component
X	any extensive property
X_i	partial molar X of the pure *i*th component
$\bar{X}_i$	partial molar X of the *i*th component
ΔX_{mix}	change of X during the process of mixing
x_i	partial specific X of the pure *i*th component
$\bar{x}_i$	partial specific X of the *i*th component
α	molecular polarizability
ϵ	dielectric constant

ϵ_{ij}	contact free enthalpy of molecules i and j
ρ	density
ρ_i	density of the pure ith component
ϕ_i	volume fraction before mixing of the ith component (eq 10)
^{0}	superscript denotes the limit at vanishing concentration of polymer

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References and Notes

(1) S. G. Chu and P. Munk, *Macromolecules*, 11, 879 (1978).
(2) T. M. Aminabhavi and P. Munk, *Macromolecules*, 12, 607 (1979).
(3) W. Heller, *J. Polym. Sci., Part A-2*, 4, 209 (1966).
(4) Th. G. Scholte, *J. Polym. Sci., Part A-2*, 10, 519 (1972).
(5) J. R. Partington, "An Advanced Treatise on Physical Chemistry", Vol. 4, Longmans and Green, London, 1953.
(6) C. J. F. Böttcher, "Theory of Electric Polarization", Elsevier, Amsterdam, 1952.
(7) T. M. Letcher and J. W. Bayles, *J. Chem. Eng. Data*, 16, 266 (1971).
(8) A. T. Amos and B. L. Burrows, *Adv. Quantum Chem.*, 7, 289 (1973).
(9) V. M. Story, D. McIntyre, and J. H. O'Mara, *J. Res. Natl. Bur. Stand., Sect. A*, 71, 169 (1967).
(10) **Note Added in Proof.** Our most recent experiments indicate that this effect is very large for the mixture of bromobenzene (1)-carbon tetrachloride (2), for which the parameters of eq 47 assume the values $b_0 = 2.11 \times 10^{-2}$ and $b_1 = 0.00$ (546 nm).

Measurement of Diffusion Coefficients of Polymer Solutions Using the Ultracentrifuge

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ABSTRACT: A diffusion experiment in the synthetic boundary cell of an ultracentrifuge yields reproducible values of the diffusion coefficient. For poor and intermediate solvents, these values (uncorrected for the effect of polymer concentration) lead to reasonable values of the Flory–Mandelkern invariant β. Hence, the method in combination with the measurement of either the intrinsic viscosity or the sedimentation coefficient may yield a good estimate of molecular weight. However, for good solvents (highly nonideal solutions), the effect of the polymer concentration cannot be neglected.

In a previous study,[1] we have used a diffusion experiment in the synthetic boundary cell of an ultracentrifuge to measure the refractive increment of polymer solutions. However, these experiments also yielded with good reproducibility the polymer translational diffusion coefficient. While recent developments of quasielastic laser light scattering[2,3] make it possible to measure polymer diffusion coefficients in solution rather rapidly, with accuracies which are claimed to be better than 1%, some problems still remain (effect of dust particles, etc.). Moreover, light-scattering equipment may not be readily available in some laboratories. Thus, it is interesting to see whether our method yields values comparable to the light-scattering results, as well as whether it may yield the basic information which is usually extracted from diffusion data. The main problem is expected to be related to the concentration dependence of the diffusion coefficient. While the theoretical treatments require the diffusion coefficient to be extrapolated to vanishing concentration of polymer, our method yields an integral diffusion coefficient for a boundary between a pure solvent and a polymer solution with a concentration of about 0.004 g/mL.

Experimental Procedure and Results

Polystyrene samples with a narrow distribution of molecular weight obtained from Pressure Chemical Co., Pittsburgh, Pa., were the same ones as those used in our previous studies.[1,4-6] The molecular weight measured by the sedimentation equilibrium method in benzene solutions was found to be 117 000 for sample 4b, 186 000 for sample 1c, 372 000 for sample 3b, and 596 000 for sample 13a. Viscosity of the solvents was measured at 20 °C by the automatic viscometer Fica Viscomatic. The preparation of the solutions and the synthetic boundary experiment were described in detail in our previous publication.[1] All samples were measured in pure benzene, ethyl acetate, and cyclohexane (only sample 4b) as well as in several benzene–cyclohexane mixtures and ethyl acetate–cyclohexane mixtures.

Table I
Diffusion Coefficient of Four Polystyrene Samples in Benzene (1)-Cyclohexane (2) Solvent Mixtures at 20 °C and the Viscosity of the Solvent Mixtures

	$D \times 10^7$ cm^2/s for sample				
ϕ_2[a]	4b	1c	3b	13a	η, cP
0.0	4.17	3.26	2.29	1.92	0.662
0.1	4.23	3.42	2.30	1.84	0.646
0.2	4.14	3.33	2.27	1.80	0.638
0.3	4.15	3.26	2.24	1.74	0.637
0.4	4.15	3.37	2.26	1.82	0.644
0.5	4.18	3.24	2.15	1.69	0.660
0.6	3.96	3.12	2.25	1.75	0.686
0.7	3.86	2.96	2.00	1.75	0.724
0.8	3.64	2.88	1.99	1.57	0.781
0.9	3.39	2.64	1.88	1.48	0.866
1.0	3.14				0.985

[a] Volume fraction of component 2.

In Tables I and II we have collected our experimental values of solvent viscosity together with the values of our diffusion coefficients. For those measurements, which were made in duplicate, the difference between the two values reaches 5% only for one pair; for the other measurements the reproducibility is much better.

Discussion

The relation between the diffusion coefficient D and the molecular weight of polymer M is usually written as

$$D = K_D M^{-a_D} \qquad (1)$$

where the constants K_D and a_D are characteristic of the polymer–solvent system. The exponent a_D should be re-

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