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between theory and experiment is very satisfactory. It is to be noted that the Yamakawa–Fujii–Yoshizaki theory predicts correctly the S-shaped experimental log $[\eta]$ vs. log M_w relation. The data point for the highest molecular weight fraction may be expected to depart from the theoretical curve because of an excluded-volume effect. In fact, the n_K value of 136 for this sample exceeds the critical n_K ($\sim$50) previously estimated[16] for the onset of volume effect on the average dimensions of a linear polymer chain.

The dashed line in Figure 6 represents the theoretical values calculated from the Yoshizaki–Yamakawa equation[12] for rigid cylinders capped with hemispheres, with $M_L = 760\ \mathrm{nm}^{-1}$ and $d = 1.5$ nm. It substantiates that the PHIC chain in butyl chloride is almost completely rigid for M_w below 10^4. The cross mark in Figure 6 indicates the limit where the axial ratio becomes unity, i.e., a rigid sphere of 1.5 nm in diameter. The theoretical value of $[\eta]$ (2.33 $\mathrm{cm}^3\ \mathrm{g}^{-1}$) for this sphere happens to be very close to 2.38 $\mathrm{cm}^3\ \mathrm{g}^{-1}$ calculated from the Einstein equation for a compact sphere whose density is equal to the inverse of the partial specific volume (0.952 $\mathrm{cm}^3\ \mathrm{g}^{-1}$) of PHIC in butyl chloride.

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Molecular Weight Dependence of Preferential Adsorption

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ABSTRACT: The dependence of preferential adsorption coefficient (λ) on molecular weight (M), or on segment density, is usually expressed empirically by the equations $\lambda = \lambda_\infty + AM^{-1/2}$ or $\lambda = \lambda_\infty + K[\eta]^{-1}$ ($[\eta]$, intrinsic viscosity; A and K, constants). No attempt has been made until now to predict theoretically the magnitude of such dependence (to calculate K or A). Using just general thermodynamic relationships, we derive an equation which allows the calculation of these constants from other experimental properties of the system such as the second virial coefficient or the intrinsic viscosity. This equation predicts that the M dependence of λ should be large in solvent + precipitant mixtures and should vanish when the total sorption potential of the coil is at a maximum. These predictions are in agreement with experimental data from the literature. In order to provide experimental data of K on systems representing different combinations of solvent power, we have determined λ and $[\eta]$, as functions of M, for PMMA samples in three solvent mixtures: good solvent + precipitant (benzene + 1-butanol), a cosolvent pair (CCl_4 + butyl chloride), and two good solvents (1,2-dichloroethane + ethyl acetate). The experimental results for these systems are qualitatively well described by our theoretical equation. Quantitative agreement is also possible if the single-liquid approximation is used for the total sorption.

Introduction

Experimental results of preferential sorption by polymers in mixed solvents have shown that the coefficient of preferential adsorption, λ, for a given polymer in a solvent mixture of fixed composition, depends on the molecular weight of the polymer sample, M.[1-11] However, this dependence of λ on M has not always been detected. According to Dondos and Benoit,[2] it is detectable only for molecular weights lower than a certain value.

The empirical dependence of λ with M was originally described by means of the law[1]

$$\lambda = \lambda_\infty + AM^{-1/2} \tag{1}$$

where λ_∞ is the value of λ extrapolated to $M \rightarrow \infty$, and A is a constant for each solvent composition. The variation of λ with M has been attributed to the influence of the coil segment density on preferential adsorption.[1]

Theoretical expressions from which the molecular weight dependence of λ could be deduced have been derived by Shultz and Flory,[12] by Read,[13] and by Pouchlý, Živný, and Šolc.[14,15] Dondos and Benoit[1] have calculated explicitly the theoretical dependence of λ on M with the result

$$\lambda = \lambda_\infty + A'M^{-1/2}\alpha^{-3} \tag{2}$$

where α is the coil expansion factor and A' a constant. As a measure of coil expansion, Dondos[16] and also Katime[17] have taken the intrinsic viscosity, $[\eta]$. By writing

$$\alpha^3 = [\eta]/K_\Theta M^{1/2} \tag{3}$$

where K_Θ means unperturbed dimensions, they arrive at equations of the form

$$\lambda = \lambda_\infty + K[\eta]^{-1} \tag{4}$$

with K again a constant for each mixed-solvent compo-

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sition. The representation of λ vs. $[\eta]^{-1}$ according to eq 4 has been shown[16-18] to give a better description of the experimental data than the representation of λ vs. $M^{-1/2}$ of eq 1 originally proposed.

The variation of λ with M depends on the polymer/mixed-solvent system and, for a given system, it depends on the composition of the liquid mixture. As first realized by Dondos and Benoit,[1] the variation of λ with M is more pronounced (A in eq 1 is larger) in mixtures which are poor solvents close to Θ conditions than in mixtures with excluded volume.

In the present work, we study the variation of λ with molecular weight in several polymer/mixed-solvent systems, which are representative of three possible combinations of solvent quality or excluded volume behavior, namely, solvent + solvent, solvent + precipitant, and cosolvent pair. The polymer studied is poly(methyl methacrylate) (PMMA) and the magnitudes determined are λ and $[\eta]$, from which we obtain λ_∞ and K of eq 4. Both atactic and isotactic samples of the polymer have been studied.

The purpose of the present work is twofold, not only to provide the above experimental results on the molecular weight dependence of λ but also to explore the possibility of predicting such dependence theoretically. Until now, no attempt has been made to predict (either theoretically or from other experimental quantities) the magnitude of constants A, A', or K, in eq 1, 2, and 4. Here, we derive a thermodynamic relationship which allows the prediction of constant K (we focus on K as the quantity to be predicted, since, as mentioned above, eq 4 provides a better description of data than eq 1).

To obtain K theoretically, we use only general thermodynamic relations. No model for the polymer solution is assumed in our derivation, so that the result for K should be of general applicability.

Experimental Section

Polymers. An isotactic PMMA sample was prepared by polymerization of MMA (Fluka) in toluene at low temperature with phenylmagnesium bromide as initiator. The polymer was fractionated by addition of n-hexane to its dilute solution in benzene at 30 °C. Four of the obtained fractions were selected for this work.

An atactic PMMA sample was prepared by free radical polymerization in benzene solution, initiated with azobis(isobutyronitrile). It was divided into 14 fractions by fractional precipitation from benzene solution with methanol.

Molecular weight determinations by both light scattering and membrane osmometry on several fractions showed that $M_w/M_n \leq 1.2$. The range of molecular weights covered is 22 000–880 000.

Mixtures. Binary liquid mixtures were prepared by volume.

Light Scattering. Two types of light scattering measurements have been carried out: one, at wavelength λ' 546 nm, by using a Fica 50 apparatus with a low-pressure mercury lamp and another, at λ' 632 nm, by using a modified Fica 42000 equipped with a He–Ne laser. For the laser light scattering measurements, the commercial Fica 42000 photometer had both its light source and its optical block of the incident beam substituted by a He–Ne laser (Spectra Physics, Model 157), which emits at 632 nm, with a power of 3 mW. The scattered intensity was measured at an angle of 90° with unpolarized as well as with vertical and horizontal polarized incident light. All measurements were carried out at 25.0 ± 0.05 °C.

Light scattering cells were washed before being filled with liquid detergent and then rinsed with distilled water and acetone. Solutions and liquid mixtures were optically clarified by centrifugation for 2 h at 14 000 rpm and then directly pipetted into the cell.

Benzene was used as the standard liquid for the light scattering measurements. Rayleigh ratios, R, were obtained by means of the relation

$$R = R_{\mathrm{B}} \frac{I}{I_{\mathrm{B}}} \left(\frac{n}{n_{\mathrm{B}}} \right)^2 \tag{5}$$

where I is the scattered light intensity for unpolarized incident light, n is refractive index, and subscript B refers to benzene. For R_{B} we use the values 16.3×10^{-6} cm^{-1}, at 546 nm, and 8.96×10^{-6} cm^{-1}, at 632 nm.

The preferential adsorption coefficient has been calculated by light scattering using the equation

$$\lambda = \left[\left(\frac{M_w^*}{M_w} \right)^{1/2} - 1 \right] \frac{\mathrm{d}n/\mathrm{d}c}{\mathrm{d}n/\mathrm{d}\phi} \tag{6}$$

where M_w and M_w^* are the weight-average molecular weights of the polymer in pure and mixed solvents, respectively, c is the polymer concentration, in g·cm^{-3}, and ϕ is the composition of the binary solvent mixture, expressed as volume fraction before mixing.

Refractometry. Refractive indices for binary mixtures were measured, at 25.0 °C, and 546 and 632 nm, with an Abbê refractometer, previously calibrated with several organic solvents for which the refractive indices at those wavelengths are known.

Refractive index increments of polymer solutions were determined, at 25.0 °C, by means of a Brice-Phoenix 2000V differential refractometer calibrated with aqueous solutions of highly purified KCl and employing a sealed-type differential cell with ground-glass stoppers to prevent loss of the solvent. The Brice-Phoenix differential refractometer is also equipped with a He–Ne laser of 0.5 mW.

Viscometry. Intrinsic viscosity measurements were performed, at 25 °C, with a modified Ubbelohde viscometer; solutions could be progressively diluted starting from a concentration of 0.8×10^{-2} g·cm^{-3}. The intrinsic viscosities were determined from the Huggins equations by plotting η_{sp}/c vs. c and extrapolating to zero concentration by least squares. Kinetic energy and density corrections were applied.

Theoretical Calculation of K Based on the Total Sorption Function

According to thermodynamic theory,[12-15] λ can be written as (Hert, Strazielle, and Benoit[19])

$$\lambda = A_1'\bar{v}_3 + 2C_M V_1 A_2' M^{-1/2} \alpha^{-3} \tag{7}$$

Here, $\bar{v}_i$ is partial specific volume, V_i molar volume (1 and 2 = solvents, 3 = polymer), and C_M has the usual meaning

$$C_M = \frac{27\bar{v}_3^{\,2}}{2^{5/2}\pi^{3/2}N_{\mathrm{A}}V_1} \left(\frac{M}{\langle R^2 \rangle_0} \right)^{3/2} \tag{8}$$

with $\langle R^2 \rangle_0$ the mean squared unperturbed end–end distance, and N_{A} Avogadro's constant. In eq 7, A_1' and A_2' are given in terms of derivatives of the Gibbs function, ΔG, for the polymer/mixed-solvent system. They are[14,15,19]

$$A_1' = -M_{13}/M_{11} \tag{9}$$

$$A_2' = -(A_1'^{\,2}M_{111} + 2A_1'M_{113} + M_{133})/2M_{11} \tag{10}$$

where the $M_{ij...}$'s are defined by[15]

$$M_{ij...} = \lim_{u_3 \to 0} \left(\frac{\partial}{\partial u_i} \frac{\partial}{\partial u_j} ... \right) G_u^* \tag{11}$$

and

$$G_u^* = (1 + u_3)\frac{\Delta G}{V} - \frac{\mathbf{R}T}{V_3} u_3 \ln \frac{u_3}{1 + u_3} \tag{12}$$

V is the total volume, and $\mathbf{R}T$ is the thermal energy. As composition variables we use volume fractions referred to a unit volume comprising just the mixed solvent. Such volume fractions in the ternary system are denoted by u_i and in the binary solvent mixture without polymer by ϕ_i.

(Thus, we have u_1, u_2, u_3, and ϕ_1, ϕ_2; and in both cases: $u_1 + u_2 = 1$; $\phi_1 + \phi_2 = 1$.)

Comparing eq 4 and 7 and using the Flory–Fox relation

$$[\eta] = \Phi\alpha^3\langle R^2\rangle_0^{3/2}M^{-1} \tag{13}$$

where Φ is Flory's viscosity constant, we finally find

$$K = \left(\frac{9}{2\pi}\right)^{3/2}\frac{\Phi}{N_A}\bar{v}_3^2 A_2' \tag{14}$$

(This result was also given implicitly by Hert, Strazielle, and Benoit,[19] but referring it to the theory of Read.[13])

Equation 14 is a thermodynamic relationship from which one can calculate K if the ΔG of the system is known. A thermodynamic model may be used to write ΔG. Instead, we follow here an alternative procedure, which consists of relating A_2', and hence K, with other experimentally accessible properties of the system.

The total sorption function of the coil, Y, is given by[15]

$$Y = (V_1/2\mathbf{R}T)[M_{33} - M_{11}A_1'^2] \tag{15}$$

Deriving Y with respect to ϕ_1, we get

$$\frac{\partial Y}{\partial \phi_1} = \frac{V_1}{2\mathbf{R}T}\left[\frac{\partial M_{33}}{\partial \phi_1} + A_1'^2\frac{\partial M_{11}}{\partial \phi_1} + 2A_1'\frac{\partial M_{13}}{\partial \phi_1}\right] \tag{16}$$

Now, the derivatives with respect to solvent volume fraction and the limit $u_3 \rightarrow 0$, defining the $M_{ij...}$'s, commute in the following way:

$$(\partial/\partial\phi_1)\lim_{u_3\to 0} = \lim_{u_3\to 0}(\partial/\partial u_1) \tag{17}$$

so that eq 16 can be written as

$$\frac{\partial Y}{\partial \phi_1} = \frac{V_1}{2\mathbf{R}T}(M_{133} + A_1'^2 M_{111} + 2A_1'M_{113}) \tag{18}$$

Therefore

$$A_2' = -\frac{\mathbf{R}T}{V_1 M_{11}}\frac{\partial Y}{\partial \phi_1} \tag{19}$$

and

$$K = -\left(\frac{9}{2\pi}\right)^{3/2}\frac{\mathbf{R}T\bar{v}_3^2}{M_{11}V_1}\frac{\Phi}{N_A}\frac{\partial Y}{\partial \phi_1} \tag{20}$$

In the limit $u_3 \rightarrow 0$, ΔG is just the Gibbs function for the binary liquid mixture, which we write as

$$\lim_{u_3\to 0}\Delta G = -T\Delta S^{\mathrm{id}} + G^{\mathrm{E}} \tag{21}$$

ΔS^{id} is the entropy of mixing for an ideal mixture ($\Delta S^{\mathrm{id}} = -n\mathbf{R}(x_1 \ln x_1 + x_2 \ln x_2)$, where x_i is the mole fraction and n is the total amount of substance) and G^{E} the excess Gibbs function for the actual liquid mixture. Then, M_{11} is simply (applying eq 11, 12, and 17)

$$M_{11} = \frac{\partial^2}{\partial \phi_1^2}\left(-T\frac{\Delta S^{\mathrm{id}}}{V} + \frac{G^{\mathrm{E}}}{V}\right) \tag{22}$$

Since the variables for G^{E} are usually mole fractions, we change the derivative in eq 22 from ϕ_1 to x_1. Assuming additivity of volumes ($V/n = x_1V_1 + x_2V_2$), the result is

$$M_{11} = \mathbf{R}T\frac{l}{V_1}[\phi_1\phi_2(\phi_1 + l\phi_2)]^{-1} \times \left[1 + \frac{l\phi_1\phi_2}{(\phi_1 + l\phi_2)^2}\frac{\partial^2}{\partial x_1^2}\left(\frac{G^{\mathrm{E}}}{n\mathbf{R}T}\right)\right] \tag{23}$$

where $l = V_1/V_2$.

Substituting into eq 20, we get

$$K = -\left(\frac{9}{2\pi}\right)^{3/2}\frac{\Phi}{N_A}\bar{v}_3^2\frac{\phi_1\phi_2(\phi_1 + l\phi_2)}{l\left[1 + \frac{l\phi_1\phi_2}{(\phi_1 + l\phi_2)^2}\frac{\partial^2}{\partial x_1^2}\left(\frac{G^{\mathrm{E}}}{n\mathbf{R}T}\right)\right]} \times \left(\frac{\partial Y}{\partial \phi_1}\right) \tag{24}$$

This result allows the calculation of K from experimental properties (other than λ itself), without recourse to any model for the solution, by measuring the function of total sorption of the polymer/mixed-solvent system (Y) and the excess Gibbs function (G^{E}) of the liquid mixture. Several techniques are useful for determining Y, for example, light scattering or intrinsic viscosity. From the second virial coefficient, A_2, it is

$$Y = \frac{V_1}{\bar{v}_3^2}\frac{A_2}{h(\bar{z})} \tag{25}$$

with $h(\bar{z})$ a function of excluded volume whose value tends to unity as the system approaches the Θ state. From the molecular weight dependence of intrinsic viscosity, one obtains the interaction parameter B of the Stockmayer–Fixman plot:

$$[\eta]M^{-1/2} = K_\Theta + C\Phi BM^{1/2} \tag{26}$$

where C is a numerical constant, and from B

$$Y = \frac{V_1}{\bar{v}_3^2}\frac{N_A}{2}B \tag{27}$$

Also, from the $[\eta]/K_\Theta M^{1/2}$ ratio the expansion factor α can be calculated, and from α the function Y obtained by means of

$$Y = \frac{\alpha^5 - \alpha^3}{2C_M M^{1/2}} \tag{28}$$

Therefore, measurements of λ and A_2, or of λ and $[\eta]$, allow the calculation of K. An application of this result may be to determine λ_∞ from measurements on a single molecular weight sample. Measuring A_2 in addition to λ for such a molecular weight or knowing B or α from independent measurements will allow the calculation of λ_∞ from a single experimental λ.

Let us discuss now the general behavior expected for K depending on the characteristics of the system. If the liquid mixture is composed of a good solvent and a nonsolvent, then Y should be a monotonously decreasing function of the volume fraction of the nonsolvent in the mixture, and $\partial Y/\partial\phi_1$ should then be a smooth function of ϕ_1. On the other hand, if Y presents a maximum, as is the case of cosolvent systems and in many mixtures of two poor solvents, then $\partial Y/\partial\phi_1$ vanishes at the composition of the maximum, and K should be zero at this same composition, according to eq 24. Points at which λ is constant and shows no M dependence have been termed "isosbestic points" by Dondos.[20] Equation 24 predicts that such "isosbestic points" should occur when Y is maximum.

A maximum in Y is also very often accompanied by inversion in λ, the inversion point being located at compositions close to that of maximum Y (except if the two liquid components have very large differences in molecular size or in solvent quality toward the polymer).[21-24] Therefore, isosbestic points are expected to occur close to inversion points, according to the predictions of eq 24. Experimental evidence showing the simultaneous occurrence of inversion and isosbestic points in close proximity has been actually given by Dondos for a cosolvent of

Table I
Excess Gibbs Function Determined for the Binary Liquid Mixtures Used as Mixed Solvents

	$G^E/J{\cdot}mol^{-1}$		
x_1	C_6H_6 (1) + BuOH (2)	CCl_4 (1) + BuCl (2)	DCE (1) + EtAc (2)
0.10	251	265	55
0.20	477	413	115
0.30	669	512	135
0.40	816	576	160
0.50	900	605	180
0.60	916	590	217
0.70	845	531	240
0.80	682	418	250
0.85	561		
0.90	410		220

polystyrene[20] and can also be found in the results of Katime et al. for a cosolvent of poly(methyl methacrylate).[8]

In the cases where the system is of the good solvent + nonsolvent type, the slope of Y with ϕ_1 becomes steeper as the mixture gets poorer. Therefore, $|\partial Y/\partial\phi_1|$ should be larger and contribute to determine a higher value of $|K|$ the closer the mixture composition is to Θ or critical conditions. This prediction is in agreement with literature results of this type of system, where it has been found that K increases as the solvent quality of the mixture decreases.[1,7,16,17] Initially, the constant being determined from experiment was A, and its increase on approaching poor solvent conditions could be attributed to the influence of α^3 (compare eq 1 and 2).[1,7] However, the same data, when fitted to eq 4, which incorporates the influence of α^3 on $[\eta]$, still give a K increasing as the solvent quality decreases.[16,17]

Results and Discussion

The systems measured by us are atactic and isotactic PMMA in carbon tetrachloride + butyl chloride (CCl_4 + BuCl), atactic PMMA in benzene + 1-butanol (C_6H_6 + BuOH), and atactic PMMA in 1,2-dichloroethane + ethyl acetate (DCE + EtAc). In these systems we have determined λ (by light scattering) and $[\eta]$, for fractions of different molecular weights, at several compositions of the mixed solvents. From these $\lambda - [\eta]$ results, we have obtained the experimental values of λ_∞ and K, corresponding to eq 4.

To calculate K theoretically via eq 24, we use B as a measure of Y (eq 27). If instead of B we use α (eq 28), the results for $\partial Y/\partial\phi_1$ are very similar. The data necessary to calculate K according to eq 24 and 27 are G^E of the binary liquid mixture and the polymer/solvent interaction parameter B, both as functions of liquid mixture composition. We have obtained B from the $[\eta]$–M_w results on the fractions (using $C = 0.51$ and $\Phi = 2.5 \times 10^{23}$ in eq 26), and we have determined G^E by light scattering (following the method described elsewhere[25]). The experimental results of G^E for the three mixtures are given in Table I.

The experimental results of λ_∞, K, and B, for the polymer/mixed-solvent systems, are given in Table II. The solvent quality toward PMMA differs widely from one liquid to another. C_6H_6, DCE, and EtAc are good solvents of the polymer, CCl_4 and BuCl are poor solvents, and BuOH is a nonsolvent or precipitant. Thus, the mixture C_6H_6 + BuOH is of the good solvent + precipitant type, the mixture DCE + EtAc is of the good solvent + good solvent type, and the mixture CCl_4 + BuCl is a cosolvent of PMMA.

Inversion in λ is observed only in the mixture having the largest G^E: C_6H_6 + BuOH. In this same mixture is also the only case in which the molecular weight dependence of λ is important. According to the predictions of eq 24, a large G^E favors large absolute values of K because the negative curvature of the bell-shaped G^E vs. x_1 curve (the derivative $\partial^2G^E/\partial x_1^2$) is more pronounced the higher is the maximum of G^E. However, the main reason for the large values of $|K|$ found in this system has to be sought in $\partial Y/\partial\phi_1$. B, and hence Y, drops from a large value, corresponding to the good solvent benzene, down to negative in a short range of x_1. The derivative $\partial Y/\partial\phi_1$ reaches the largest values in the C_6H_6 + BuOH system and this explains, according to eq 24, why $|K|$ is much larger in this system than in the others.

Table II
Parameters of Preferential Adsorption, λ_∞ and K, of Eq 4, and Interaction Parameter, B, of Eq 26, Determined Experimentally

x_1	λ_∞, $cm^3{\cdot}g^{-1}$	K, $(cm^3{\cdot}g^{-1})^2$	$10^{28}B$, $cm^3{\cdot}mol^2{\cdot}g^{-2}$
	a-PMMA/C_6H_6 (1) + BuOH (2)		
0.40	0.604	−10	1.3
0.50	0.451	−12	5.2
0.60	0.242	−10	8.5
0.70	0	−7.5	9.8
0.80	−0.249	−3	10.2
0.85	−0.301	0	10.3
0.90	−0.178	0	10.2
1.00			9.7
	a-PMMA/CCl_4 (1) + BuCl (2)		
0.20	0.05	0	1.55
0.30	0.06	0	2.50
0.40	0.06	0	3.25
0.50			3.70
0.60	0.02	0	4.00
0.70	0.02	0	4.10
0.80	0.01	0.8	
	i-PMMA/CCl_4 (1) + BuCl (2)		
0.20	0.14	0	1.05
0.30	0.16	0	1.70
0.40	0.15	0	2.40
0.50	0.12	0	3.00
0.60	0.09	0	3.30
0.70	0.06	0	3.20
0.80	0.04	0	2.70
	a-PMMA/DCE (1) + EtAc (2)		
0.00			3.01
0.10	−0.05	−0.2	3.93
0.30	−0.08	−0.2	5.49
0.50	−0.11	−0.2	7.09
0.70	−0.15	0	8.20
0.80	−0.13	0	8.35
0.90	−0.06		8.74
1.00			8.75

Even the variation of K with solvent composition appears to be well correlated with the corresponding variation of $\partial Y/\partial\phi_1$ in the C_6H_6 + BuOH system. As we can see (Table II), in this system B remains almost stationary in the range $0.9 \leq x_1 \leq 0.8$, so that $\partial Y/\partial\phi_1 \simeq 0$ in this range. In consequence, $K \simeq 0$ is found here. On the other hand, B varies rapidly with x_1 in the range $0.7 \leq x_1 \leq 0.4$ and, as expected, the $|K|$'s found in such a range are large.

In the DCE + EtAc system, the G^E values are comparatively low and the variation of B with x_1 is rather smooth, which explains, according to eq 24, the low $|K|$'s found in this system. The variation of B with x_1 is steeper in the range $0 \leq x_1 < 0.7$ than in the range $0.7 \leq x_1 \leq 1.0$ and, in consequence, the only appreciable values of K are found for $0 < x_1 < 0.7$.

In the cosolvent system CCl_4 + BuCl, the variation of B for isotactic PMMA is very flat and, consequently, $K \simeq 0$. For atactic PMMA, a similar situation holds, with the possible exception of the range $0.7 \leq x_1 \leq 1.0$, where B should drop from the relatively high 4.10×10^{-28} cm^3

Table III
Comparison between Experimental and Theoretical Values of Parameter *K*

	a-PMMA/C_6H_6 + BuOH		a-PMMA/CCl_4 + BuCl		i-PMMA/CCl_4 + BuCl		a-PMMA/DCE + EtAc	
x_1	exptl	theor	exptl	theor	exptl	theor	exptl	theor
0.10							−0.2	−0.14
0.20			0	−0.57	0	−0.1		
0.30			0	−0.67	0	−0.42	−0.2	−0.19
0.40	−10	−8.5	0	−0.60	0	−0.56		
0.50	−12	−7.1	0	−0.37	0	−0.54	−0.2	−0.15
0.60	−10	−8.0	0	−0.09	0	−0.06		
0.70	−7.5	−6.9	0	0.20	0	0.09	0	−0.06
0.80	−3	−2.2	0.8	0.20	0	0.35	0	−0.03
0.85	0	−0.3						
0.90	0	0.7						

mol^2 g^{-2} value at $x_1 = 0.7$ down to $B < 0$ at $x_1 = 1.0$. This amounts to an appreciable negative value of $\partial Y/\partial\phi_1$ and hence, according to eq 24, to a positive K. This is actually found for $x_1 = 0.8$.

After the above qualitative considerations, we apply now eq 24 in a quantitative way, to check more precisely its predictive capacity. To this end, we calculate the numerical value of K by using the following data: G^E, contained in Table I, and B, contained in Table II. We obtain Y via eq 27 and assume $\bar{v}_3$ constant ($\bar{v}_3 = 0.804$ cm^3·g^{-1}). The results thus calculated for K turn out to be much smaller than the experimental ones (1 order of magnitude or more, smaller). The qualitative behavior is well predicted by eq 24 and 27 in that the sign of K and the relative values between systems or between the different ranges of x_1 within a given system are correct, as discussed above, but the absolute values are much too low.

An improvement of these theoretical values may be sought by using the single-liquid approximation for the total sorption function. This approximation is routinely made when comparing theoretical Y's with experiment. Recently, Pouchlý and Živný[26] have analyzed the intrinsic viscosity of a large number of polymer/mixed-solvent systems, finding that the best description of the experimental data is provided by the single-liquid approximation for Y (in their modified Flory–Huggins theory). In such approximation, Y is given by

$$Y_{\mathrm{sl}} = \frac{V_1}{2\mathbf{R}T} M_{33} \tag{29}$$

(subscript "sl" denotes the single-liquid approximation).

The complete expression of Y, eq 15, can then be written as

$$Y = Y_{\mathrm{sl}} - \frac{V_1}{2\mathbf{R}T} M_{11} \left(\frac{\lambda_\infty}{\bar{v}_3} \right)^2 \tag{30}$$

with M_{11} given by eq 23. Substituting eq 30 into eq 20, we get

$$K = -\left(\frac{9}{2\pi} \right)^{3/2} \frac{\mathbf{R}T}{M_{11}} \frac{\bar{v}_3{}^2}{V_1} \frac{\Phi}{N_A} \frac{\partial}{\partial\phi_1} \left[Y_{\mathrm{sl}} - \frac{V_1}{2\mathbf{R}T} M_{11} \left(\frac{\lambda_\infty}{\bar{v}_3} \right)^2 \right] \tag{31}$$

Accepting now that our experimental B's correspond to theoretical Y's in the single-liquid approximation, we write

$$Y_{\mathrm{sl}} = \frac{V_1 N_A}{2\bar{v}_3{}^2} B \tag{32}$$

in place of eq 27.

We now calculate K according to eq 31 and 32,[27] using the G^E of Table I and the B and λ_∞ data of Table II (assuming, as before, $\bar{v}_3$ constant). The results of such calculation of K are given in Table III in comparison with the experimental values. As we can see, the agreement with experiment is now excellent.

Only one of the systems here studied has large values of $|K|$, so that this agreement may be not very significative and requires further checking with other systems. Besides, the calculated values are highly dependent on the accuracy with which the second derivative of G^E and the derivative of the term within square brackets in eq 31 can be calculated.

Finally, we point out that in the C_6H_6 + BuOH system, K is negative in the range of solvent compositions where λ_∞ is positive. This means that the preferential adsorption of C_6H_6 diminishes as the molecular weight of the sample decreases. This behavior is opposite to that found in the majority of systems reported in the literature,[1–8,10,17,18,20] where the rule is that preferential adsorption becomes more important for the lower molecular weights. However, the opposite behavior here found for PMMA/C_6H_6 + BuOH is correctly predicted by our thermodynamic theory. Another example in which this same type of behavior can be found is the cosolvent system polystyrene/cyclohexane + acetone,[11] where the preferential adsorption of acetone (in a given composition range) also decreases with M.

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(27) Note that eq 24 and 31 are identical. We simply use eq 32 in place of eq 27 when the single-liquid approximation is assumed for *Y*.

Triplet Excimer Emission from Carbazolyl Chromophores in Polystyrene Matrices

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ABSTRACT: The delayed emission from polystyrene containing *N*-ethylcarbazole (NEC) and 1,3-bis(*N*-carbazolyl)propane (BNCP) shows no evidence of excimeric emission at 77 K but a distinct excimeric phosphorescence and fluorescence at 298 K. Although excimer fluorescence of BNCP and delayed excimer fluorescence of NEC have been reported earlier, the present work is the first report of triplet excimer emission from these species. A small activation energy of 1.7 kJ/mol was found to be associated with triplet excimer formation, thus explaining why no emission from these species has been observed at 77 K.

Introduction

N-Alkylcarbazoles have frequently served as useful monomeric models in connection with photophysical studies of poly(*N*-vinylcarbazole) (PVCA). For example, fluorescence spectra of *N*-isopropylcarbazole (NIPC), 1,3-bis(*N*-carbazolyl)propane (BNCP), and 1,4-bis(*N*-carbazolyl)butane (BNCB) have been useful in establishing the excimeric nature of the PVCA fluorescence.[1-6] Recent elegant syntheses and spectral analyses of *rac*- and *meso*-2,4-bis(*N*-carbazolyl)pentane[7] have added significant credibility to the earlier proposals that two types of singlet excimers exist and that they correspond to a sandwich-like structure and to a half-eclipsed structure.

In view of the strong propensity for carbazolyl chromophores to engage in intramolecular excimer formation, it is curious that very little evidence has been uncovered in favor of intermolecular excimer formation for any of the *N*-alkylcarbazoles. Since it is now rather commonly accepted that solutions and solid films of PVCA emit fluorescence which is almost exclusively excimeric in character[8] and that the phosphorescence emission from solid films is also exclusively excimeric,[9] it is possible to use these emission spectra as standards against which one may test for the presence of excimeric emission in the *N*-alkylcarbazoles.

In these laboratories, an emphasis has been placed upon the triplet-state properties of various aromatic molecules present as dopants in polystyrene films. It has been noted, for example, that delayed excimer fluorescence is present as a very prominent emission in polystyrene films containing 1,2-benzanthracene.[10] It seemed likely that a dopant such as *N*-ethylcarbazole (NEC) might also display excimeric emission in polystyrene films. The advantage of using polymer films is that reasonably strong triplet emission signals can be obtained over a wide temperature range. In the experimental work which follows, it will be seen that this is, in fact, a critical advantage when one attempts to find and characterize excimeric emission.

Experimental Section

Chemicals. *N*-Ethylcarbazole was obtained from Aldrich Chemical Co. It was purified by two vacuum sublimations followed by zone refining using 100 passes of the molten zone. The middle 75% of the original material was retained. High-purity 1,3-bis(*N*-carbazolyl)propane was supplied to us by Dr. G. E. Johnson of the Webster Research Center, Xerox Corp., Webster, NY. Polystyrene (Scientific Polymer Products) having an average molecular weight of 2.2×10^4 was purified by multiple reprecipitation using toluene as solvent and methanol as nonsolvent. Reagent grade toluene was purified by shaking with concentrated H_2SO_4 until no further discoloration of the acid layer occurred. After washing with water and dilute aqueous NaOH, the toluene was distilled from P_2iO_5, discarding the first and last 10% fractions. Methanol (reagent grade) was purified by first refluxing with and then distilling from $CuSO_4$, Ca shavings, and $AgNO_3$, respectively.

Sample Preparation. The sample films were prepared by first weighing and dissolving the required amounts of polystyrene and either NEC or BNCP in toluene. The solution was deoxygenated by purging with purified nitrogen gas in a glovebox for about 1 h. Then, still under nitrogen atmosphere, the solvent was slowly evaporated under constant stirring on a hot plate set at 180 °C until a molten solution had formed. The molten material was then deposited on an optically flat quartz disk. A similarly shaped disk was placed over the solution and pressure applied to remove all gas bubbles, thus forming a sandwich film. The disks were preheated to 180 °C prior to making the film and, once the film was made, it was allowed to cool to room temperature before being exposed to the atmosphere. In all cases of film preparation, the resulting films appeared visually to be quite uniform in thickness and were optically clear.

Instrumentation. The UV absorption spectra were recorded on a Cary 14 spectrophotometer. Fluorescence and fluorescence excitation spectra were recorded on a Perkin-Elmer (MPF-44A) spectrofluorimeter. Most of the delayed emission spectra and all luminescence lifetimes were obtained on a homemade spectrophosphorimeter described below. All spectra were uncorrected for either source output or detector response.

A schematic of the phosphorimeter used in this study is given in Figure 1. The instrument was constructed in the laboratory and was modified as necessary to suit the source of excitation, S. When the excitation source was a Hg–Xe arc lamp (Oriel Corp. Model 6140) with a maximum output of 1000 W, two choppers were used in order to create the necessary intermittent irradiation. The first chopper (C_1) was positioned in the exciting light beam and the second (C_2) in the emission beam. The choppers were driven by synchronous motors of various speeds, motors with speeds of 6, 30, 120, and 900 rpm being used during the course of this study. The choppers could be put in or out of phase by manually retarding one of them. The synchronous choppers enable the observation of the emission after the exciting light has been cut off and at the same time eliminate short-lived emission

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