

DETERMINATION OF THE COEFFICIENT OF PREFERENTIAL SORPTION FROM FREE DIFFUSION MEASUREMENTS WITH POLARIZATION INTERFEROMETER

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An exact procedure of the determination of the coefficient of preferential sorption from two measurements of free diffusion (without and with polymer) in dilute solutions with a polarization interferometer has been suggested. To verify the procedure, the dependence of the coefficient of preferential sorption of benzene on the composition of the system benzene-cyclohexane-poly-styrene was measured, the reproducibility and possible errors were checked. The suggested method also provides the dependence of the binary diffusion coefficient and of the refractive index increment of the diffusing low-molecular weight component of the mixed solvent on its composition.

In solutions of polymers in mixed solvents one low-molecular weight component is sorbed into the domain of the polymer coil. The phenomenon, which is of considerable theoretical and practical importance, is usually investigated by the light scattering method¹, or by analyzing the composition of the ternary system before and after the establishment of dialyzation equilibrium^{2,3}. An original method based on the investigation of the free diffusion of one low-molecular weight component between the solution of polymer in a binary solvent and a binary solvent of somewhat different composition has been suggested by Yoshino and Tanzawa⁴. They used the considerable difference between the diffusion coefficients of the polymer and the low-molecular weight component and showed that the diffusion of the polymer can be neglected within a suitably chosen time of measurement. In this method one tries to find such a composition of the binary solvent at which zero diffusion flux of the low-molecular weight component between the two solutions is observed. The difference in concentrations of the sorbed component in the solution with polymer and in the binary solvent is the measure of preferential sorption of this component in the coil. Recently⁵, a paper has been published describing the procedure of measurement of preferential sorption based on the sedimentation equilibrium of the low-molecular sorbed component, which also makes use of the considerable difference between the diffusion coefficients of the polymer and of the sorbed component of the solvent, respectively.

Strictly speaking, the diffusion in a three-component system should be described in terms of the thermodynamics of irreversible processes by means of four phenomenological coefficients in which all interactions taking place in the system⁶ (flow interactions, preferential sorption *etc.*) are reflected. This procedure results in a purely phenomenological description of the system; the procedure⁴, approximative to some extent, has the advantage of being directly connected with the molecular character of preferential sorption. In any case, non-equilibrium thermodynamics^{6,7} has as its consequence the requirement of working under conditions of small driving forces and at a low polymer concentration so as to make the flow interaction negligible. The measurement

should also be arranged so as to justify the assumption of the negligible polymer diffusion during the time needed for measuring the diffusion of the low-molecular component of the solvent, in order to use the binary diffusion approximation.

In this paper we suggest a suitable and exact procedure of determination of the coefficient of preferential sorption from two measurements of free diffusion (without and with polymer) in dilute solutions by means of polarization interferometer. If solutions used for both measurements are prepared adequately, the procedure inherently involves the possibility of discerning the region of pseudobinary diffusion not influenced by the presence of the polymer. To verify the precision and accuracy of the method we measured the dependence of the coefficient of preferential sorption on composition in the system benzene-cyclohexane-polystyrene, for which data by other authors are also available in the literature. In addition, the method gives the dependence of the binary diffusion coefficient and of the refractive index increment of the diffusing low-molecular component of the mixed solvent on its composition.

THEORETICAL

Let us choose a three-component system solvent (1)-solvent (2)-polymer (3) and assume that component (1) is a thermodynamically better solvent for the given polymer than component (2) which can also act as a precipitant. If the polymer is dissolved in a mixture of two solvents, component (1) is usually sorbed selectively into the domain of the coil. Let us now consider two independent diffusion measurements, A and B: In the case A (without polymer) the diffusion proceeds between two solutions of both low-molecular weight components that differ slightly in their respective concentrations. The case B differs only in that the solution with a higher concentration of component (1) contains also the dissolved polymer. If the solution of the polymer in the case B is sufficiently dilute, the difference in the concentration of component (1) in the two solutions is sufficiently small, and the diffusion coefficients of the polymer and component (1) are sufficiently different, one may assume that the diffusion of the polymer can be neglected, the diffusion of the low-molecular weight component (1) will be independent, and the driving force will be the difference in the concentrations of this component in solutions with and without polymer. This means that the fraction of component (1) preferentially sorbed in the domain of the coil will be apparently inoperative, which will result in an apparent decrease in the driving force of diffusion (*i.e.* concentration difference of component (1)). In other words, in this case the "immobile" polymer behaves as a sorbent which takes component (1) from solution. For the diffusion measurement B thus arranged, the difference in the concentrations of component (1) between the two solutions, $(\Delta c^0)_B$, will represent the driving force, so that we can write

$$(\Delta c^0)_B = (\Delta c^0)_A - (\Delta c^0)_S, \quad (1)$$

where $(\Delta c^0)_A$ is the concentration difference in the diffusion measurement A between both mixed solvents (where the solvent having a higher concentration of (1) does not contain polymer), $(\Delta c^0)_S$ is the apparent decrease in the force due to the preferential sorption of (1) into the domain of the coil. For both diffusion experiments with polymer, (B), and without it, (A), a quantity X can be defined by

$$X = \frac{(\Delta c^0)_A}{(\Delta c^0)_B} = \frac{(\Delta c^0)_A}{(\Delta c^0)_A - (\Delta c^0)_S}; \quad (2)$$

for $(\Delta c^0)_S$ we obtain

$$(\Delta c^0)_S = (\Delta c^0)_A (X - 1)/X. \quad (3)$$

The above reasoning concerns component (1), so that Eqs (1)–(3) hold also in terms of the difference between the refractive indices, and for X one can write

$$X = (\Delta c^0)_A/(\Delta c^0)_B = (\Delta n^0)_A/(\Delta n^0)_B. \quad (4)$$

The concentration difference $(\Delta c^0)_A$ is determined by preparation of solutions. If the diffusimeter (in our case, polarization interferometer) yields $(\Delta n^0)_A$ and $(\Delta n^0)_B$ with sufficient accuracy, $(\Delta c^0)_S$ can be calculated from Eq. (3). Then it is easy to derive a relationship between the commonly used coefficient of preferential sorption λ^* (expressed in ml of (1) per 1 g of polymer) and the experimentally available $(\Delta c^0)_S$:

$$\lambda^* = (\Delta c^0)_S (a - w_p)/100w_p d_1; \quad (5)$$

concentrations are always expressed in g/100 g of mixed solvent, w_p is the amount of polymer (g) in a grams of solution, and d_1 is the density of pure component (1) (here at 25°C).

To determine $(\Delta n^0)_A$ and $(\Delta n^0)_B$ needed for the calculation of the key quantity X from the data obtained with the polarization interferometer^{8–11}, let us start with the basic condition of interference valid for this apparatus^{8,10}:

$$\left(\frac{\Delta n}{\Delta x}\right)_{\Delta x=b} = j \frac{\lambda}{2bl} = a_j \approx \frac{dn}{dx}, \quad (6)$$

where λ is the wavelength of the light used, l is the cell thickness, b is the birefringence of Savart polariscope, and j is a natural number. After a short time since the beginning of the experiment one can pass from the difference term $(\Delta n/\Delta x)_{\Delta x=b}$ to the refractive index gradient, dn/dx , as after that time the deviations between the two terms becomes negligible^{8,11}. The free diffusion in a two-component system is controlled by the known equation

$$dn/dx = [\Delta n^0/2(\pi Dt)^{1/2}] \exp(-x^2/4Dt), \quad (7)$$

where Δn^0 is the difference between the refractive indices of solutions at a time $t = 0$, D is the diffusion coefficient, and x is the coordinate in the cell. With respect to the bell-shaped function (7) one can see from (6) that one pair of interference fringes corresponding to the respective contour line of the gradient curve is formed for each j . The fringes of each pair first move apart, then approach each other and eventually gradually disappear. Distances $(2x_j)$ between the individual fringes of each pair are experimentally available: these are obtained from the photographs of the interference system at appropriate times t . From Eq. (7) one easily obtains a relationship for $(2x_j)$:

$$(2x_j)^2 = 16Dt \ln [\Delta n^0/2a_j(\pi Dt)^{1/2}]. \quad (8)$$

$(2x_j)^2$ assumes its maximum value at a time $t = t_j$ when the respective interference fringe passes through the inflexion point of the gradient curve; for such maximum one may derive¹¹

$$(2x_j)_{\max} = \frac{\Delta n^0}{a_j} \sqrt{\frac{2}{\pi e}}, \quad (9)$$

where e is the base of natural logarithms.

The interference condition (6) holds only if Savart double-plate is adjusted precisely perpendicularly to the direction of the incident beam. However, by employing Eq. (9) one can circumvent this experimental difficulty and calculate the correction γ for the imperfect adjustment directly from experimental data. The corrected interference condition (6) then reads

$$a_j = \frac{j \frac{\lambda}{2} + \gamma}{bl}; \quad (10)$$

from Eqs (9), (10) we easily obtain (similarly to ref.¹²)

$$\gamma = \frac{\lambda}{2} \left[\frac{1}{\frac{(2x_j)_{\max}}{(2x_{j+1})_{\max}} - 1} - j \right]. \quad (11)$$

Eq. (9) gives for the two diffusion measurements directly

$$\frac{(2x_j)_{\max,A} (a_j)_A}{(2x_j)_{\max,B} (a_j)_B} = \frac{(\Delta n^0)_A}{(\Delta n^0)_B} = X; \quad (12)$$

assuming a precise adjustment of the apparatus ($\gamma = 0$), it obviously holds $(a_j)_A = (a_j)_B$, while in the general case we obtain $(\Delta c^0)_S$ by means of Eqs (3) and (10)–(12).

The other alternative of the calculation of X can be arrived at as follows: In a general case one can write, using Eq. (7) for the experiment A (without polymer) and B (with polymer),

$$\frac{(x_j)_A^2}{4D(t + \Delta t_{cA})} = \ln \frac{(\Delta n^0)_A}{2(a_j)_A \sqrt{[\pi D(t + \Delta t_{cA})]}} \quad (13a)$$

and

$$\frac{(x_j)_B^2}{4D(t + \Delta t_{cB})} = \ln \frac{(\Delta n^0)_B}{2(a_j)_B \sqrt{[\pi D(t + \Delta t_{cB})]}} \quad (13b)$$

Here, the zero-time correction Δt_c has been introduced, which is a measure of the hydrodynamic quality of the initial boundary, and in the case of the apparatus used contains also an optical term⁹. Generally it is different for each experiment (in practice it usually holds $\Delta t_{cB} > \Delta t_{cA}$ owing to the presence of polymer). Let us introduce a corrected time $t' = t + \Delta t_{cA}$; the term $(t + \Delta t_{cB})$ in this notation will be equal to $(t' + \Delta\tau)$ where $\Delta\tau = \Delta t_{cB} - \Delta t_{cA}$. After substitution into Eqs (13a,b), subtraction and rearrangement we obtain

$$\frac{(x_j)_A^2}{4Dt'} - \frac{(x_j)_B^2}{4Dt' \left(1 + \frac{\Delta\tau}{t'}\right)} = \ln \frac{(\Delta n^0)_A (a_j)_B \sqrt{\left(1 + \frac{\Delta\tau}{t'}\right)}}{(\Delta n^0)_B (a_j)_A} \quad (14)$$

By using the approximations $1/(1 + \varepsilon) \approx 1 - \varepsilon$ and $\ln(1 + \varepsilon) \approx \varepsilon$ valid for small ε and rearranging we obtain

$$(x_j)_A^2 - (x_j)_B^2 = 4Dt' \ln \frac{(\Delta n^0)_A (a_j)_B}{(\Delta n^0)_B (a_j)_A} + 2D \Delta\tau - \frac{(x_j)_B^2 \Delta\tau}{t'} \quad (15)$$

After another rearrangement and passing to the experimental values of $(2x_j)$ (cf. Eq. (12)) we obtain the result

$$(2x_j)_A^2 - (2x_j)_B^2 = 16Dt' \ln X + 4\Delta\tau \left(2D - \frac{(x_j)_B^2}{t'}\right) \quad (16)$$

The diffusion coefficient and the Δt_c values needed for the calculation of X from the slope of the plot of $(2x_j)_A^2 - (2x_j)_B^2$ against time t' can be determined according to an

equation derived earlier¹³:

$$(2x_j)^2 - (2x_{j+k})^2 = 8D \ln \frac{(2x_j)_{\max}^2}{(2x_{j+k})_{\max}^2} [t + \Delta t_c]. \quad (17)$$

The latter calculation can be carried out by using both the experiment A and the experiment B where the presence of polymer is reflected in the curvature of the plot of $(2x_j)^2 - (2x_{j+k})^2$ against time in the region of higher t ; from the linear part of the plot one can calculate D (cf.¹³).

EXPERIMENTAL

Polystyrene was prepared by block polymerization initiated with di(tert-butyl)hyponitrite and fractionated by gradual precipitation from benzene with methanol; the fractions were reprecipitated and dried over P_2O_5 at 60°C. The second fraction used in the experiments had the viscometric average molecular weight (M_η) $2.6 \cdot 10^6$. Benzene and cyclohexane (both reagent grade, Lachema Brno) were distilled on a column (150 cm, Berl's saddles). The apparatus, thermostat, recording device and measurement of distances between the interference fringes have been described elsewhere^{11,12}.

Preparation of solutions and measurements. The basic mixed solvent of a chosen composition was prepared first. A small amount of benzene was added to one part of the mixture to attain the required $(\Delta c^0)_A$ ("enriched mixed solvent"). Polymer was then dissolved in one part of this solvent to make the polymer concentration c 0.5 g/dl. Diffusion was measured between the above "enriched" solvent and the basic mixed solvent (exp. A), and between the solution of polystyrene in the "enriched" solvent and the basic solvent (exp. B), always at 25°C.

A stainless steel diffusion cell¹⁴ was filled (by means of injection syringes) with the denser solution up to the orifice of both solution reservoirs; the reservoir for the solution of lower density was then rinsed three times with this solution in order to remove the insignificant amount of the denser solution. Two diffusion experiments could be performed with one filling of the diffusion cell; thus, four experiments, A, A', and B, B' were carried out for each composition of the mixed solvent.

RESULTS AND DISCUSSION

In order to calculate X according to Eq. (12) it is necessary to determine maxima of the time dependences of $(2x_j)$. In this paper we always used fringe pairs with $j = 2, 3, 4$. The maxima were read off from the plot; an example illustrating the precision of the graphic determination can be seen in Fig. 1 (volume fraction of benzene in a mixed solvent v_1 0.60, experiments 5A, 5B). It can be seen that the last points of the curve B($j = 2$) are affected by the diffusion of the polymer. For clarity's sake only a part of the curve B($j = 3$) is shown and the curves for $j = 4$ have been omitted. The repeated experiments A, A' and B, B' thus yield 12 values of X on the whole.

An example of the use of Eq. (16) for the calculation of X (the same experiments and the same v_1) is shown in Fig. 2; for clarity, some points of the straight line for $j = 2$

were omitted. The curvature of the plot indicates when the starting assumption of binary diffusion ceases to be valid, *i.e.* when the diffusion of the polymer becomes operative. It follows from Eq. (16) that if $(a_j)_A \neq (a_j)_B$, the slopes of the straight lines for different j should be somewhat different; this difference can be seen in Fig. 2. According to Eq. (11) we obtain for the experiment 5A $\gamma = -0.025\lambda$, whereas for 5B it holds $\gamma = 0$. Let us also note that this error of adjustment was the highest we found and that with the exception of experiments 1, 4, and 5 it has always held with sufficient accuracy that $(a_j)_A = (a_j)_B$. The presence of the second term on the right-hand side of Eq. (16) leads to the result that in a general case, when $\Delta\tau \neq 0$, the dependence in Fig. 2 ceases to be linear for small t' . However, in the experiments shown in Fig. 2 it was found that Δt_{cA} was 56 s, and Δt_{cB} was 52 s, so that the above effect was not significant. The procedure employed for the calculation of the diffusion coefficient according to Eq. (17) has been described in our earlier paper¹³. For four measurements A, A', B, B' and three pairs of fringes the least squares method yields again 12 values of X from which the mean value is calculated. An advantage of Eq. (16) consists in that it is not necessary to meet the requirement that in the experiment B the maximum of the dependence $(2x_j) = f(t)$ should remain unaffected by the diffusion of the polymer; it is sufficient to obtain an adequately long linear part of Eq. (16). The required D is obtained with sufficient accuracy

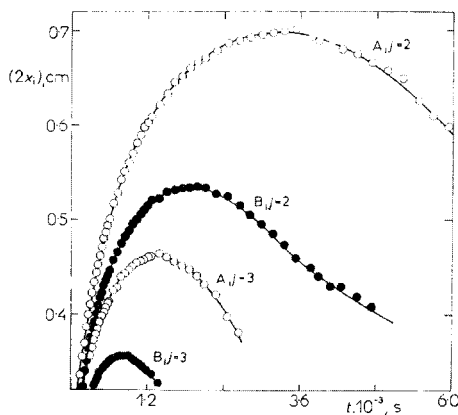


FIG. 1

Time Dependence of Distances Between Interference Fringes $(2x_j)$ for Experiments 5 A, B

Numbers are serial numbers of fringes j ; A diffusion measurement without polymer, B diffusion measurement with polymer. Volume fraction of benzene $v_1 = 0.60$.

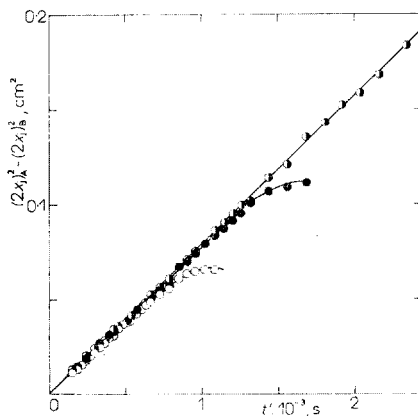


FIG. 2

Example of Use of Eq. (16) for Calculation of $(\Delta n^2)_A/(\Delta n^2)_B$

j : \circ 4; \bullet 3, \ominus 2. Experiments 5 A, B; volume fraction of benzene $v_1 = 0.6$.

from the experiment A (Eq. (17)). Moreover, the plot in Fig. 2 allows us to estimate the possible differences in the adjustment of the apparatus in both measurements and to determine with better accuracy the part of the plot unaffected by the diffusion of the polymer. Both procedures of calculation according to Eq. (12) and (16) respectively are compared in Table I. It can be seen that the limits within which the coefficient λ^* varies are almost identical (2.5% and 3%), although the limits of X (columns 3 and 6, Table I) are somewhat higher for the procedure according to (16); the mean values calculated by either procedure coincide within 0.5%.

It is rather difficult to estimate the effects of other factors on the errors of the above method. The main problem is seen in the danger of a convective flow through the boundary^{5,15,16} because of its gravitational instability. From the standpoint of the possible appearance of convections all three components must be taken into account; criteria of the gravitational stability of the boundary in a three-component system have been derived by Wendt¹⁷, and in a simplified form by Reinfelds and Gosting¹⁸. Since however the cross-term diffusion coefficients remain unknown (in ternary systems containing a polymer they can assume values comparable with the main term diffusion coefficients⁶), the respective conditions cannot be calculated; they can be used only as a suitable guiding factor and the stability of the boundary must be checked experimentally. The procedure of preparation of solvents described above, which guaranteed a positive change in the concentration of benzene, $\Delta c_1 = (c_1)_{II} - (c_1)_I$ (indices II, I respectively denote the concentration below and above the boundary) also in presence of the polymer, yielded a convection-free boundary. On the other hand, we established in an attempt to form a boundary between a polystyrene solution in the basic solvent and the basic solvent itself that in this case the convective flow through the boundary was definitely observed.

TABLE I

Coefficients of Preferential Sorption (λ^*) Calculated from Eqs (12) and (16)

Volume fraction of benzene $v_1 = 0.35$, $(\Delta c^0)_A = 0.3082$ g/100 g, polymer concentration 0.5084 g/100 ml; $X = (\Delta n^0)_A / (\Delta n^0)_B$, ΔX difference between the highest and lowest value in per cent of mean.

Combination of experiments	Eq. (12)			Eq. (16)		
	X	$\Delta X, \%$	λ^*	X	$\Delta X, \%$	λ^*
3A — 3B	1.2572	1.0	0.1153	1.2553	2.4	0.1146
3A — 3B'	1.2655	0.6	0.1175	1.2651	1.7	0.1181
3A' — 3B	1.2638	0.9	0.1176	1.2575	2.9	0.1154
3A' — 3B'	1.2658	0.2	0.1183	1.2651	3.3	0.1181

Another problem consists in the possibility of relative changes in the concentration of both components of the mixed solvent during the preparation and manipulation with the solutions (including the filling of the cell) which can never be fully ruled out. Deviations of the Δc^0 values calculated from the weighed amount of biphenyl on the one hand and from Eq. (9) on the other in test measurements carried out with the system biphenyl–benzene lay within $\pm 1\%$. Let it be pointed out that the above system should be more sensitive towards possible changes due to evaporation than the mixed solvent used. It follows from Eqs (2) and (3) that the errors will be the smaller the higher $(\Delta c^0)_s$. From the other side we are limited by the requirement of applicability of Eqs (12) and (16). In other words, we must choose the weighed amount of polymer and $(\Delta n^0)_\lambda$ so as to make the effect of preferential sorption as high as possible while obtaining with Eq. (16) a sufficiently long linear part of the plot, or with Eq. (12) maxima of the dependence $(2x_j)^2 = f(t)$ unaffected by the diffusion of the polymer.

The contribution of the polymer to $(dn/dx)_j = a_j$ in the maximum of the time dependence of $(2x_j)^2$ can be calculated taking into account the superposition of two independent gradients (of Gaussian shape). For the maximum of this dependence (inflexion point of the gradient curve) it holds⁸ $x_i = \pm \sigma = \pm 2Dt_i$; after substitution into Eq. (7) and rearrangement we obtain the gradient of the low-molecular component of the solvent at the inflexion point in the form

$$(dn/dx)_{i,s} = (\Delta n^0)_B / 2 \sqrt{(\pi D_s t_i e)}. \quad (18)$$

Similarly for the gradient of the polymer at a time t_i we obtain

$$(dn/dx)_p = [(\Delta n^0)_p / 2 \sqrt{(\pi D_p t_i)}] \exp(-D_s / 2D_p) \quad (19)$$

and the ratio of the two gradients will be given by

$$\frac{(dn/dx)_{i,s}}{(dn/dx)_p} = \frac{(\Delta n^0)_p}{(\Delta n^0)_B} \sqrt{\left(\frac{D_p}{D_s}\right)} \exp(D_s / 2D_p). \quad (20)$$

For instance, for a 0.5% error it must hold $0.05(dn/dx)_{i,s} = 0.05a_j = (dn/dx)_p$. If we know the respective diffusion coefficients and the refractive index increment of the polymer, we can calculate $(\Delta n^0)_B$ for the chosen weighed amount of the polymer; by estimating the coefficient λ^* , it is possible to estimate $(\Delta n^0)_\lambda$ by using Eqs (1) and (5). In this case we are virtually restricted by the fact that the duration of the diffusion measurements must never be too short, because the boundaries thus obtained are never ideal, and the validity of approximations introduced in Eq. (6) must be guaranteed. On the other hand, it is possible to estimate from Eq. (2) the ratio D_p/D_s and thus also the lowest possible molecular weight of the polymer (from the

relationship $D_p \sim M$); it can be seen immediately that the validity of $D_p \ll D_s$ is desirable.

The results of measurements of the dependence of the coefficient of preferential sorption of benzene, λ^* , in the system benzene–cyclohexane–polystyrene on the composition of the mixed solvent are summarized in Table II. The fact that the values of λ^* in this system are comparatively small¹⁹ is rather an advantage for the verification of the suggested method; besides, data of three authors are available for the above system^{4,20,21}. The coefficients λ^* (Table II, 4th column) for each combination of experiments are a mean from eight values (Table I); the fifth column contains differences between their maximum and minimum value in per cent of the mean. The sixth column of Table II gives the $\Delta n/\Delta c$ values calculated from the experiments A, A' by using Eq. (9); the respective limits (column 7) indicate the difference between the experiments A and A'. In Fig. 3 there is a plot of the refractive index increment against the composition of the solvent. It can be seen that the individual points exhibit only a small scatter, which can be regarded as an indirect proof of the sufficiently precise preparation of solutions (*cf.* above). The binary diffusion coefficients of benzene needed for the calculation according to Eq. (16) were calculated by using Eq. (17) in all measurements A, A', B, B'; the last but one and the last column of the Table give the mean values of D and the limits of the maximum departures of D in per cent of the mean. The identical D values in the experiments A, B are again a proof of the convection-free course of the experiment with polymer. The values determined by us are by some 1.5% higher than the binary diffusion coefficients determined for the

TABLE II

Dependence of the Coefficient of Preferential Sorption (λ^*), of the Binary Diffusion Coefficient (D) and of the Refractive Index Increment ($\Delta n/\Delta c$) of Benzene in the System Benzene(1)–Cyclohexane(2)–Polystyrene(3) on Composition of Mixed Solvent

v_1 Volume fraction of benzene, $\Delta\lambda^*$, $\Delta(\Delta n/\Delta c)$ and ΔD denote always the difference between the highest and lowest experimental value of the given quantity (expressed in per cent of mean).

Combination of experiments	v_1	$(\Delta c^\circ)_A$ g/100 g	λ^* ml/g	$\Delta\lambda^*$ %	$(\Delta n/\Delta c) \cdot 10^4$ 100 g/g	$\Delta(\Delta n/\Delta c)$ %	$D \cdot 10^5$ cm ² /s	ΔD %
1	0.10	0.3345	0.0644	10.2	5.852	0.64	1.887	3.5
2	0.20	0.3055	0.1139	6.4	6.608	0.61	1.859	4.5
3	0.35	0.3082	0.1169	3.2	7.400	0.17	1.838	3.6
4	0.50	0.2339	0.1235	4.1	8.010	0.44	1.847	2.4
5	0.60	0.2428	0.0991	2.2	8.382	0.49	1.839	1.4
6	0.80	0.2239	0.0595	7.3	9.290	1.40	1.965	0.8
7	0.90	0.2482	0.0214	10.2	9.471	0.39	2.035	0.7

same system by Rodwin and coworkers²² (the authors however did not state the temperature of measurement). Since our method gives the dependence of D on composition as a side result, and also in view of the data scatter (*cf.* the last columns of Table II), such agreement can be regarded as satisfactory.

The dependence of our values of the coefficient λ^* on the composition of the binary solvent has been compared with the published results in Fig. 4. The Figure shows that our experimental data represent in principle mean values from the results obtained by the other authors. The total error involved in our method in the determination of the coefficient λ^* in the above system can be estimated as $\pm 5\%$. The main source of errors are inaccuracies in the concentrations of the starting solutions due to evaporation during manipulation. These inaccuracies influence $(\Delta c^0)_s$, and thus the resulting coefficient λ^* through the term $(X - 1)/X$ in Eq. (3).

With respect to the error estimated above it follows from Fig. 4 that there is no change in the sign of the coefficient of preferential sorption in the region $v_1 \rightarrow 1$. This change is predicted by a theoretical expression derived by Read²¹ if one neglects the ternary parameters χ . The full line in Fig. 4 has been calculated under such assumption (the values used were²¹ $\chi_{1,2} = 0.476$, $\chi_{1,3} = 0.30$, $\chi_{2,3} = 0.53$); by adjusting the parameters within the limits given by the scatter of their experimental

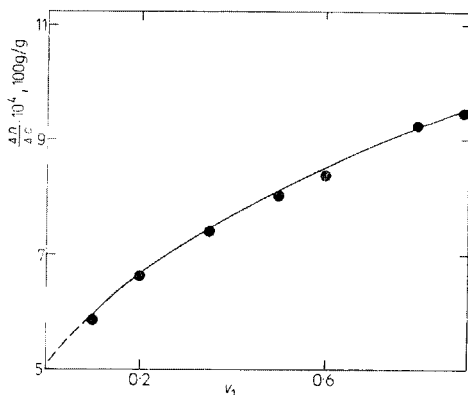


FIG. 3

Dependence of the Refractive Index Increment $\Delta n/\Delta c$ of Benzene on the Composition of Mixture Benzene-Cyclohexane Expressed by the Volume Fraction of Benzene (v_1)

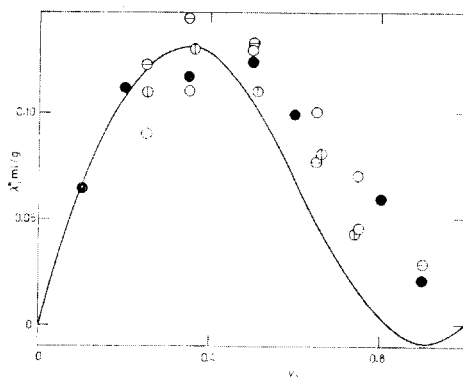


FIG. 4

Dependence of the Coefficient of Preferential Sorption on the Composition of Solvent in the System Benzene-Cyclohexane-Polystyrene

● This paper, ○ Read's data²¹, ⊙ data of Strazielle and Benoit²⁰, ⊕ data of Yoshino and Tanzawa⁴. Full line was calculated by using experimental values of the χ parameters and neglecting ternary interactions according to a relationship derived by Read²¹.

values one can neither describe the experimental data more adequately nor remove the negative part of the curve.

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