

**LIGHT SCATTERING IN THE SYSTEM  $\alpha$ -BROMONAPHTHALENE-BUTANONE-POLYSTYRENE**

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The optical behaviour of the systems  $\alpha$ -bromonaphthalene-butanone and  $\alpha$ -bromonaphthalene-butanone-polystyrene was investigated in dependence on their composition. For the individual solvent and solution systems, the polarization ratios together with the scattering ratios and their isotropic and anisotropic components were determined. At the same time, the checking procedure used in the determination of the individual scattering quantities was also described. The results show that under the given conditions the anisotropic part of the scattered light remains virtually unaffected by the assumed interaction  $\alpha$ -bromonaphthalene-polystyrene; if there is any interaction, the corresponding scattering effects lie within the limits of experimental error.

Some time ago, Bushuk and Benoit<sup>1</sup> described a light scattering method allowing the determination of the actual molecular weights of copolymers along with the parameters characterizing the heterogeneity of their chemical composition. The prerequisite consists in the possibility of measuring the copolymer under investigation in three solvents with suitable scattering and refractive properties, which however are not always available. To obtain such properties, the use of mixed solvents has proved both feasible and advantageous<sup>2</sup>. One of the systems used to justify this procedure was a solution of poly(styrene-co-methyl methacrylate) in the mixture  $\alpha$ -bromonaphthalene-butanone<sup>3</sup>. Application of this system brought about a number of experimental difficulties, and it was  $\alpha$ -bromonaphthalene that was made responsible for them and also for some other irregularities observed. We therefore decided to reinvestigate the optical behaviour of both the solvent system itself and the corresponding polystyrene solutions.

The light scattering from liquids has already been studied for a very long time<sup>4-6</sup>; however, so far no satisfactory theory has been suggested which would explain all essential aspects of the interactions of molecules in pure liquids, and particularly in their mixtures<sup>7-9</sup>. It was neither our intention nor was it possible to extend our knowledge in this respect (with the exception of determination of the values of some light scattering quantities): the objective of the present paper is rather to analyse the optical behaviour of one such solvent system and to point out some pitfalls likely to occur in its application in the determination of the molecular weights of polymers.

## EXPERIMENTAL

*Solvents and solutions:*  $\alpha$ -Bromonaphthalene and 2-butanone were carefully purified by distillation on a highly efficient column. The dust particles were removed from solvents and their mixtures by means of a slow pressure filtration through a sintered glass disc G5 (Schott, Jena) in a semi-closed apparatus with saturated vapours of the respective solvent system. Despite careful purification,  $\alpha$ -bromonaphthalene may sometimes contain a small amount of admixtures; their own scattering and refractive contributions are negligible, but they can completely distort the scattering measurements by their ability to absorb visible light. It was therefore necessary to store the samples in darkness and to perform the measurements as soon as possible after purification has been completed (while checking spectrophotometrically the possible absorption at the wavelength used,  $\lambda_0$  436 nm). The polystyrene solutions were prepared by dissolving in a mixed solvent and filtration under conditions similar to those used for pure solvent mixtures.

*Measurements:* The refractive indices of the individual solvents, their mixtures and solutions were determined refractometrically. The values thus obtained were used to check the composition of the mixture, and also to correct the measured data for the divergency of the scattered light on the boundary between the media of higher and lower refractivity (correction is equal to  $n^2$ ). The values of the individual scattering quantities were measured with a simple one-purpose apparatus of our own design, at an angle of  $90^\circ$  and a wavelength of 436 nm. The following intensities of the scattered light were measured:  $R_u$ ,  $R_v$ ,  $R_h$ ,  $V_u$ ,  $H_u$ ,  $V_v$ ,  $V_h$ ,  $H_v$ ,  $H_h$ , and the values obtained were used for the determination of the polarization ratios  $\rho_u = H_u/V_u = (H_v + H_h)/(V_v + V_h)$  and  $\rho = R_h/R_v = (V_h + H_h)/(V_v + H_v)$ ; here,  $R$ ,  $V$ ,  $H$  are the Rayleigh ratios (also called scattering ratios, factors or coefficients) for the total scattered light and for its vertically or horizontally polarized components, and the indexes  $u$ ,  $v$ ,  $h$  are related to the unpolarized, vertically or horizontally polarized primary beam, respectively. The individual measurements were repeated many times. All values of the scattering ratios were referred to a standard (benzene:  $R_u = 46.5 \cdot 10^{-6}$ ). On the contrary, the polarization ratios have an absolute character, *i.e.* they do not, in principle, require calibration; however, to check the functioning of the apparatus the polarization ratio of benzene was also determined; the value thus obtained (0.425 at 436 nm) agreed with that considered the most probable at the present time<sup>8</sup> (0.43).

## RESULTS AND DISCUSSION

*Light Scattering in Mixtures of Liquids*

The total intensity ( $R_u$ ) of the light scattered from liquid mixtures consists of two components, isotropic  $R_u^i$  and anisotropic  $R_u^a$ , for which the relationships are valid<sup>4-8</sup>:

$$R_u = R_u^i + R_u^a, \quad R_u^i = R_u(6 - 7\rho_u)/(6 + 6\rho_u) = R_u C_u, \quad (1, 2a)$$

$$R_u^a = R_u[13\rho_u/(6 + 6\rho_u)] = R_u(1 - C_u), \quad (2b)$$

where  $C_u$  is the so-called Cabannes factor. For some binary mixtures of liquids having an appropriate composition, both the isotropic and the total light scattering can attain a considerably higher value than each of the two pure components. The cause should be sought in the so-called composition scattering (due to fluctuations in the composition of the mixture), which is added to the density scattering (due

to density fluctuations of the liquid). Thus, for instance, in the mixture methanol-benzene the maximum value of  $R_u$  of the mixture is twice as high as that of benzene alone; the isotropic part  $R_u^i$  of the mixture becomes almost five times higher than that of pure benzene<sup>4</sup>. On the contrary, the anisotropic part of the scattered light varies almost linearly with the composition of the mixture in most cases, especially if the composition is expressed in molar fractions and if the values of the so-called molar anisotropic scattering<sup>5</sup> (a product of the anisotropic scattering factor and molar volume of the mixture or its components) are plotted on the  $y$ -axis. To determine the values of  $R_u^i$  or  $R_u^a$  according to Eqs (2), it is necessary to know the total scattering  $R_u$  and the polarization ratio  $\rho_u$ . An exact determination of the absolute values of scattering ratios remains still an open problem, particularly owing to the necessity of introducing a number of corrections, the most important of which is a correction for the divergency of the scattered light. Although this correction was applied, and care was taken to reduce the occurrence of reflections (among others by introducing an immersion liquid for the cell), a comparatively great experimental error must still be expected, the source of which lies in the geometric-optical factors of the apparatus.

On the other hand, the determination of the polarization ratios is free from most of the errors originating in the geometrical and optical factors of the apparatus: similarly to the other ratio methods, the majority of the correction coefficients is eliminated. An important influence may be exerted by the optical and chemical impurities in the samples under investigation, and also by inaccuracy in the determinations of composition. The determination of  $\rho_u(\rho)$  also lacks in accuracy, if the absolute values of  $V_u$  and  $H_u$  ( $R_v$  and  $R_h$ ) are low, or their difference is small.

The necessity of a simultaneous or alternating use of polaroids on the side of the light source and photomultiplier was turned into a means for testing the consistency of measurements. The introduction of polaroids reduced the light intensity as a consequence of its polarization, but also owing to reflections on their surfaces, or to the real absorption. We first found out that the reduction of light due to both polaroids was equivalent (the difference was virtually indiscernible, less than 1%). If the reduction factor of the polaroid is designated by  $f$  ( $f_s$  for the position closer to the light source,  $f_p$  for the position closer to the photomultiplier) and the photometer reading by  $F$  (the scattering quantity is given in parentheses), we obtain

$$F(R_u)/[F(R_v) + F(R_h)] = f_s, \quad F(R_u)/[F(V_u) + F(H_u)] = f_p, \quad (3a, 3b)$$

$$F(R_u)/[F(V_v) + F(V_h) + F(H_v) + F(H_h)] = f_{sp}, \quad (3c)$$

where  $f_{sp}$  is the reduction factor with both polaroids inserted. If the measurement is consistent, then the values of  $f_s$ ,  $f_p$  or  $f_{sp}$  are identical in all analogous measurements. Since we have here independent measurements, a further consistency criterion lies in a comparison to what extent the product of the individually determined values of  $f_s$  and  $f_p$  approaches the value of  $f_{sp}$  determined according to Eq. (3c).

TABLE I

Scattering Ratios  $R = R_p, V_p$  and  $H_p$  ( $p = u, v, h$ ) of the System  $\alpha$ -Bromonaphthalene-Butanone  
 $\varphi$  is the volume fraction of  $\alpha$ -bromonaphthalene in the mixture,  $R_u^i$  or  $R_u^a$  is the isotropic or anisotropic scattering factor. For the rather unusual definition of  $R_p, V_p$  and  $H_p$  see the text.

$R \cdot 10^6 / \varphi$	0.2	0.4	0.6	0.8	1.0
$R_u$	84.0	128	153	161	177
$R_v$	68.3	101	112	107	103
$R_h$	15.7	27.1	41.3	54.6	74.0
$V_u$	67.8	100	110	105	102
$H_u$	16.2	28.0	43.0	56.4	75.6
$V_v$	61.6	88.8	92.7	81.4	69.6
$V_h$	7.1	12.8	19.7	25.8	34.4
$H_v$	7.1	12.9	20.0	26.2	35.2
$H_h$	8.2	13.8	21.3	27.6	37.6
$R_u^i$	50.7	68.0	61.0	37.0	11.8
$R_u^a$	33.3	60.3	92.0	124	165

TABLE II

Polarization Ratios and the Cabannes Factors of the System  $\alpha$ -Bromonaphthalene-Butanone

$\varphi$  is the volume fraction of  $\alpha$ -bromonaphthalene in the mixture,  $\bar{\varrho}$  or  $\bar{\varrho}_u$  are mean values of  $\varrho = R_h/R_v$  or  $\varrho_u = H_u/V_u, \langle \varrho \rangle$  or  $\langle \varrho_u \rangle$  is the difference between the highest and the lowest values determined for the respective quantity,  $n$  is the number of determinations,  $C_u$  is Cabannes factor.

$\varphi$	Polarization ratio $\varrho$			Polarization ratio $\varrho_u$			$C_u$
	$\bar{\varrho}$	$\langle \varrho \rangle$	$n$	$\bar{\varrho}_u$	$\langle \varrho_u \rangle$	$n$	
0.0	0.193	—	1	0.193	—	1	0.649
0.2	0.220	0.016	3	0.224	0.022	3	0.603
0.4	0.267	0.002	2	0.278	0.004	2	0.529
0.6	0.368	0.009	3	0.382	0.013	3	0.401
0.8	0.529	0.025	4	0.550	0.027	4	0.231
1.0	0.737	0.033	4	0.756	0.035	4	0.067

### The System $\alpha$ -Bromonaphthalene-Butanone

To obtain an optical characterization of the system  $\alpha$ -bromonaphthalene-butane, we determined scattering ratios  $R_p, V_p$  and  $H_p$  ( $p = u, v, h$ ) and their isotropic or anisotropic parts (Table I), as well as the values of polarization ratios and Cabannes' factors (Table II). It should be noted that for reasons of comparison, some values of  $R_p, V_p$  and  $H_p$  given in the present paper (and particularly in Tables I and III),

TABLE III

Scattering Ratios  $R = R_p, V_p$  and  $H_p$  ( $p = u, v, h$ ) of the System  $\alpha$ -Bromonaphthalene-Butanone-Polystyrene

$\varphi$  Volume fraction of  $\alpha$ -bromonaphthalene in the solvent system; polymer concentration in the system:  $c_0 = 0$ ,  $c_1 = 1.5$ ,  $c_2 = 3.0$ ,  $c_3 = 4.5$  mg/ml. For the rather unusual definition of  $R_p, V_p$  and  $H_p$  see the text.

$R \cdot 10^6$	$\varphi = 0.2$					$\varphi = 0.8$					$\varphi = 1.0$					
	$c_0^a$	$c_1$	$c_2$	$c_3$	$c_0^a$	$c_1$	$c_2$	$c_3$	$c_0^a$	$c_1$	$c_2$	$c_3$	$c_0^a$	$c_1$	$c_2$	$c_3$
$R_u$	80.0	142	192	240	158	155	156	157	189	194	196	199	189	194	196	199
$R_v$	66.0	128	177	224	104	101	102	102	109	114	117	121	109	114	117	121
$R_h$	14.5	14.1	14.8	15.4	54.6	53.4	53.7	54.3	80.5	79.3	78.5	77.4	80.5	79.3	78.5	77.4
$V_u$	65.0	128	177	224	102	100	101	102	107	112	116	120	107	112	116	120
$H_u$	14.4	14.2	15.0	15.7	55.9	54.5	54.9	55.2	82.0	81.4	80.3	78.4	82.0	81.4	80.3	78.4
$V_v$	59.5	122	169	216	78.4	78.0	78.4	78.9	72.5	78.5	82.8	85.6	72.5	78.5	82.8	85.6
$V_h$	6.7	6.0	7.6	8.0	25.9	24.8	24.7	25.1	37.5	37.2	36.6	36.4	37.5	37.2	36.6	36.4
$H_v$	6.7	6.7	7.6	8.0	25.9	24.8	25.4	25.1	38.4	37.8	37.4	37.2	38.4	37.8	37.4	37.2
$H_h$	6.7	6.9	7.6	7.7	27.7	27.0	27.5	27.7	41.1	40.2	39.3	39.4	41.1	40.2	39.3	39.4
$R_u^a$	48	107	159	206	37	37	37	37	12	17	22	29	12	17	22	29
$R_v^a$	32	35	33	34	121	118	119	120	177	177	174	170	177	177	174	170
$C_u$	0.614	0.749	0.830	0.858	0.234	0.237	0.237	0.237	0.063	0.089	0.112	0.146	0.063	0.089	0.112	0.146

<sup>a</sup> The  $R$  values for  $c_0$  at  $\varphi = 0.2, 0.8$  and  $1.0$  show larger deviations (sometimes exceeding even 5%) from data in Table I: two different preparations of  $\alpha$ -bromonaphthalene have been used. With data summarized in this Table, emphasis has been laid on the internal consistency of values in the individual groups (concentration dependences).

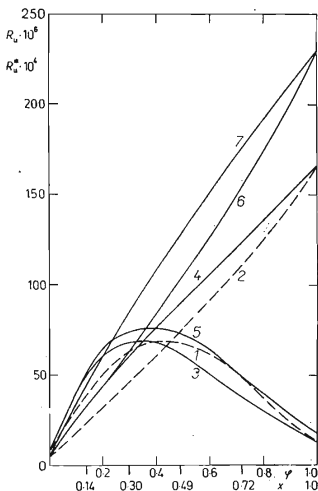
are defined in a rather unusual manner (the usage has not been settled yet). Thus instead of  $R_u = \frac{1}{2}(R_v + R_h) = \frac{1}{2}(V_v + H_v + V_h + H_h)$  we write  $R_u = R_v + R_h = V_v + H_v + V_h + H_h$  (so that  $R_v = V_u$  and  $R_h = H_u$ , which is not always respected). To obtain the usual values for  $R_v$ ,  $R_h$ ,  $V_v$ ,  $V_h$ ,  $H_v$  and  $H_h$  the respective data in Tables I and III must be multiplied by two.

Let us now compare (Fig. 1) the plots of the usual scattering ratios  $R_u^i$  and  $R_u^a$  (related to a volume unit) and molar scattering ratios  $R_u^{i*}$  and  $R_u^{a*}$  against the volume ( $\varphi$ ) and molar ( $x$ ) fraction of  $\alpha$ -bromonaphthalene in 2-butanone. The curves  $R_u^i(\varphi)$  or  $R_u^i(x)$  have a typical character with a maximum near  $\varphi = 0.4$  to  $0.5$  or  $x = 0.3$  to  $0.4$ ;  $R_u^i$  or  $R_u^{i*}$  reaches a value as high as five times that of pure  $\alpha$ -bromonaphthalene. The functions  $R_u^a(\varphi)$  and  $R_u^a(x)$  or  $R_u^{a*}(\varphi)$  and  $R_u^{a*}(x)$  exhibit small but distinct deviations from linearity: those of the function  $R_u^a(\varphi)$  and  $R_u^{a*}(\varphi)$  are negative (the values are higher than corresponds to a linear course), while those of the function  $R_u^a(x)$  and  $R_u^{a*}(x)$  are positive. The positive deviations from linearity in the case of the function  $R_u^a(\varphi)$  or  $R_u^a(x)$  are more pronounced than the deviations exhibited by the functions  $R_u^{a*}$ , owing to the large curvature of the function  $R_u^i(\varphi)$  or  $R_u^i(x)$ ; however, they do not reach the deviations observed with *e.g.* the system tetrachloromethane-nitrobenzene<sup>5</sup>. On the whole, the system  $\alpha$ -bromonaphthalene-butanone pertains by its behaviour to the type represented by the system 1,5-hexadiyne-cyclohexane and tetrachloromethane-carbon disulphide, or with nitrobenzene<sup>5</sup>.

FIG. 1

Scattering Ratios of the System  $\alpha$ -Bromonaphthalene-Butanone

1  $R_u^i(\varphi)$ , 2  $R_u^a(\varphi)$ ; 3  $R_u^i(x)$ , 4  $R_u^a(x)$ ; 5  $R_u^{i*}(x)$ , 6  $R_u^{a*}(\varphi)$ , 7  $R_u^{a*}(x)$ .  $R_u^i$  the isotropic,  $R_u^a$  the anisotropic scattering factor (component of the total scattering intensity);  $R_u^{i*}(x) = V R_u^i(x)$  or  $R_u^{a*}(x) = V R_u^a(x)$  are the molar isotropic or anisotropic scattering factors,  $\varphi$  is the volume and  $x$  is the molar fraction of  $\alpha$ -bromonaphthalene in the mixture,  $V$  is the molar volume of the given mixture of pure component; the dependence  $V$ - $x$  was approximated as linear;  $V = 90$  (2-butanone) or  $139.2$  ( $\alpha$ -bromonaphthalene).



When working with binary liquid mixtures of similar properties (which will be used as mixed solvents for polymers) the above facts ought to be borne in mind: the principle of additivity does not virtually hold at all for scattering contributions of the components of the mixture. The above-mentioned almost linear course of the function  $R_u^a(\varphi)$  or  $R_u^a(x)$  (and particularly  $R_u^{a*}$ ) may in some special cases also be used for analytical purposes. Thus, for instance, a single measurement of polarization ratio (needed for determination of  $R_u^i$  and  $R_u^a$ ) allows to determine at the same time the composition of the mixture of liquids directly in the light scattering cell without contaminating its contents (this procedure is of advantage especially for high volatile liquids). Although as a rule another (and simpler) technique was used in the concentration determinations,  $R_u^a$  was commonly employed to check the consistency of the scattering measurements within the individual sets and between them.

Apart from the isotropic and anisotropic scattering another two important structural optical constants of liquids are derived from the scattering rations, namely, polarization ratio  $\rho_u$  and the Cabannes factor  $C_u$  (Table II). Their remarkable advantage consists in a virtually complete independence of the geometric optical factors of the apparatus. Accordingly, the polarization ratios showed only very small deviations (Table II summarizes — in addition to the average values of  $\rho$  and  $\rho_u$  — the difference between the highest and the lowest values measured). It should also be mentioned, however, that the polarization ratio determined for 2-butanone (0.19 at 436 nm) is somewhat higher than may be expected according to the value determined at 546 nm (0.16, ref.<sup>8</sup>). The polarization ratio determined here for  $\alpha$ -bromonaphthalene (0.75 at 436 nm) is a little too low in comparison with the value published for  $\alpha$ -chloronaphthalene (0.78, ref.<sup>8</sup>): this conclusion has been derived by analogy with the polarization ratios published for other pairs of halogen derivatives. Our value was obtained as the mean value from a great number of determinations having a comparatively small scatter (Table II). The only explanation can therefore be looked for either in the still insufficient purity of the sample used, or too high a value given for  $\alpha$ -chloronaphthalene in the literature. Apart from the polarization ratios  $\rho_u = H_u/V_u$  we also give the values  $\rho = R_h/R_v$ ; although systematically somewhat lower, they are nevertheless very close to  $\rho_u$ . The polarization ratios also yield the Cabannes factor,  $C_u = (6 - 7\rho_u)/(6 + 6\rho_u)$  giving the isotropic component in the case of a unit total light scattering; the scatter of the data obtained is analogous to that of the polarization ratios (only average values of  $C_u$  are listed in Table II).

#### *System $\alpha$ -Bromonaphthalene-Butanone-Polystyrene*

In connection with the application of the system  $\alpha$ -bromonaphthalene-butanone for the determination of molecular parameters of some copolymers<sup>3</sup> we regarded it as appropriate to investigate their optical behaviour also in the presence of polystyrene. Despite all the care devoted to the preparation of samples and to the mea-

surements, the values of scattering ratios (Table III) are undoubtedly subjected to larger errors; however, we still consider the individual concentration dependences to be internally consistent within limits of errors usual in the determinations of the molecular weights of polymers. This assumption is corroborated by satisfactory results of the test (Table IV) defined by Eqs (3a-c).

If the concentration of  $\alpha$ -bromonaphthalene in the mixture is 20% by vol., then the polymer concentrations  $c_1 = 1.5$ ,  $c_2 = 3.0$ , and  $c_3 = 4.5$  mg/ml, the contribution of the polystyrene molecules to the total scattering is the same (at  $c_1$ ) or double (at  $c_3$ ) in comparison with the contribution of the mixed solvent (data for  $c_0$ ); this contribution in the group  $c_1(80) - c_3(80)$  (the values in parentheses give the concentration of  $\alpha$ -bromonaphthalene in % by vol.) is zero and in the group  $c_1(100) - c_3(100)$  it is very low (approximately 2.5 to 10% of the contribution of the solvent). The excess scattering in the first group of measurements ( $\varphi = 0.2$ ) is thus sufficiently high to allow fairly accurate measurements of the molecular weight of polystyrene. However, the values of  $R_0^a$  exhibit such a large relative scatter (even though the dif-

TABLE IV

Internal Consistency Test of the Measured Intensities of Light Scattered from the System  $\alpha$ -Bromonaphthalene-Butanone-Polystyrene

$c$  Concentration of polystyrene in mg/ml,  $\varphi$  volume fraction of  $\alpha$ -bromonaphthalene in the mixture; factors  $f_s, f_p, f_{sp}$  are defined in the text (Eqs (3a-c)).

$c$	$f_s$	$f_p$	$f_{sp}$	$f_s f_p$	$\varphi$
0.0	1.556	1.577	2.402	2.454	0.2
1.5	1.579	1.590	2.502	2.510	
3.0	1.594	1.600	2.520	2.550	
4.5	1.598	1.595	2.552	2.550	
<i>Average</i>	<i>1.582</i>	<i>1.590</i>	<i>2.494</i>	<i>2.516</i>	
0.0	1.596	1.608	2.508	2.567	0.8
1.5	1.571	1.591	2.497	2.500	
3.0	1.580	1.592	2.489	2.515	
4.5	1.575	1.599	2.565	2.519	
<i>Average</i>	<i>1.580</i>	<i>1.597</i>	<i>2.515</i>	<i>2.525</i>	
0.0	1.586	1.583	2.456	2.511	1.0
1.5	1.580	1.573	2.479	2.485	
3.0	1.580	1.608	2.486	2.540	
4.5	1.568	1.578	2.492	2.474	
<i>Average</i>	<i>1.578</i>	<i>1.586</i>	<i>2.478</i>	<i>2.502</i>	
<i>Average</i>	<i>1.580</i>	<i>1.591</i>	<i>2.496</i>	<i>2.514</i>	



ference between the highest and the lowest value represents merely 1–2% of the measured value of  $R_u$ , which is completely within the limits of experimental error) that they do not allow us to decide if any specific interaction of  $\alpha$ -bromonaphthalene with polystyrene takes place. The results of the other group of measurements ( $\varphi = 0.8$ ), where the contribution of polystyrene to the total light scattering is virtually zero, clearly indicate that this interaction – if any – does not affect the experimentally determined values of the anisotropic scattering  $R_u^a$ , which remain constant within the whole concentration range (the difference amounts to 2%). A more significant difference (4%) is observed with the third group ( $\varphi = 1.0$ ), where the values of  $R_u^a$

TABLE V

Polarization Ratios,  $\varrho$  and  $\varrho_u$ , in the System  $\alpha$ -Bromonaphthalene–Butanone–Polystyrene

$\varphi$  Volume fraction of  $\alpha$ -bromonaphthalene in the mixture;  $c$  concentration of polystyrene (mg/ml);  $\varrho = R_h/R_v$  (first row);  $\varrho_u = H_u/V_u$  (second row).

$c_0$ 0	$c_1$ 1.5	$c_2$ 3.0	$c_3$ 4.5	$c_0$ 0	$c_1$ 1.5	$c_2$ 3.0	$c_3$ 4.5
$\varphi$ 0.2				$\varphi$ 0.8			
0.213	0.129	0.083	0.068	0.547	0.543	0.543	0.543
0.217	0.131	0.085	0.070				
$\varphi$ 0.8				$\varphi$ 1.0			
				0.739	0.693	0.668	0.639
0.529	0.527	0.525	0.530	0.762	0.726	0.694	0.650

TABLE VI

Polarization Ratios and the Cabannes Factors ( $C_u$ ) of the System  $\alpha$ -Bromonaphthalene–Butanone–Polystyrene ( $c = 1.5$  mg/ml)

$\varphi$  Volume fraction of  $\alpha$ -bromonaphthalene in the mixture;  $\bar{\varrho}$  or  $\bar{\varrho}_u$  are the mean values of  $\varrho = R_h/R_v$  or  $\varrho_u = H_u/V_u$ ;  $\langle \varrho \rangle$  or  $\langle \varrho_u \rangle$  is the difference between the highest and the lowest value determined for the respective quantity,  $n$  is the number of determinations.

$\varphi$	Polarization ratio $\varrho$			Polarization ratio $\varrho_u$			$C_u$
	$\bar{\varrho}$	$\langle \varrho \rangle$	$n$	$\bar{\varrho}_u$	$\langle \varrho_u \rangle$	$n$	
0.2	0.129	0.006	3	0.131	0.010	3	0.749
0.4	0.229	0.002	2	0.235	0.002	2	0.588
0.6	0.353	0.005	3	0.365	0.005	3	0.421
0.8	0.532	0.009	4	0.549	0.012	4	0.232
1.0	0.700	0.033	3	0.727	0.021	3	0.088

decrease with the increasing concentration of polystyrene from  $177 \cdot 10^{-6}$  to  $170 \cdot 10^{-6}$ . The decrease in  $R_u^a$  due only to "dilution" of the system with the polystyrene molecules would not exceed  $1 \cdot 10^{-6}$ . Also the value  $\varrho_u = 0.695$ , obtained from

$$\varrho_u = (6 - 6C_u)/(7 + 6C_u) \quad (4)$$

for  $R_u^a = 177 \cdot 10^{-6}$  instead of  $170 \cdot 10^{-6}$  (Table III, concentration  $c_3$ ,  $\varphi = 1.0$ ), seems unacceptably high if compared with the experimentally determined value  $\varrho_u = 0.650$  (Table V, concentration  $c_3$ ,  $\varphi = 1.0$ ). However, not even in this case is it feasible to infer with certainty a specific interaction of  $\alpha$ -bromonaphthalene with polystyrene, because there still is a possibility of a random cumulation or compensation of errors in the determination of  $R_p$ ,  $V_p$  and  $H_p$  (where  $p = u, v, h$ ) and the values derived therefrom,  $\varrho$ ,  $\varrho_u$ , and also  $C_u$ ,  $R_u^i$  and  $R_u^a$ . To illustrate the scatter of data we collected the experimentally determined  $\varrho$  and  $\varrho_u$  values in dependence on the polystyrene concentration at a given composition of the mixture and on the composition of the mixture at a given concentration of polystyrene (Table VI). Both tables not only corroborate the very good internal consistency of the experimental data, but also justify the necessary caution while formulating unambiguous conclusions. To decide whether the interaction under consideration or an analogous one may affect the final values  $R_u^a$  will probably require a more appropriately chosen system. Besides, this problem goes beyond the objective of the present work, limited by the aspects of application of the system under investigation.

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