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1. *Introduction*

In the process of chlorination rubber undergoes certain changes which result in some marked differences in physical and chemical properties between the raw rubber and the chlorinated product [Tinsley (1)]. Both substances form colloidal solutions in organic solvents, and one can expect to find differences in properties such as for example, in the size, shape and molecular weight of the colloidal particles. Comparatively little work has, however, been done on this aspect of the problem. Investigations on the scattering of light by chlorinated rubber in solutions have therefore been made with the object of getting some information concerning the size and shape of chlorinated rubber molecules.

2. *Experimental Details*

Preparation of solutions:

Four samples of chlorinated rubber designated as *A*, *B*, *C*, and *D* were used for the present investigation. The samples *A*, *B* and *C* were prepared by Sivaramakrishnan, Iyer and Rao (2) whilst sample *D* was an I.C.I. Product called Alloprene. Solutions of the respective samples were made up in dust-free carbon tetrachloride and were filtered through ultrafine sintered glass filters to remove traces of dust and other suspended impurities. The actual concentration of each solution was determined by evaporating in vacuo measured quantities of the solution and weighing the residues.

Depolarisation measurements:

Using Krishnan's techniques (3) and with sunlight as the source of incident radiation, the depolarisation factors ϱ_u, ϱ_v, ϱ_h of the light scattered by the sols in a horizontal transverse direction were measured visually by the Cornu method. Necessary precautions were taken to eliminate all stray light coming from the rectangular glass cell containing the scattering medium. Errors due to convergence were avoided by using a nearly parallel beam of light for incidence. Measurements were made in the case of *A* and *B* with a blue filter and for *C* and *D* with a green filter, both filters transmitting a fairly narrow band of wavelengths. Measurements were repeated for different concentrations of the solutions.

Table I

Sample	Colour	% Chlorine	Viscosity of 20% solutions in centipoise	Density
A	White	69	2.3	1.58
B	White	66	6.2	1.485
C	Brown	65	14.3	1.639
D	Brown	63.6	—	—

Table II

Sample	ϱ_u%	ϱ_v%	ϱ_h%	ϱ_u% Corrected for solvent	M. Wt.
A	4.5	2.23	100	.24	20,300
B	3.1	1.5	100	.175	89,000

Table III

Sample	Concentration c in gm/100 ccs.	ϱ_u%	ϱ_v%	ϱ_h%
	1.19	3.4	.52	18
	0.794	3.0	.52	21
	0.397	2.55	.52	26
C	0.15	2.4	.52	31
	0.066	2.1	.52	35
	$c \to 0$	—	—	40
	1.664	3.0	.62	32
	1.11	2.4	.62	40
	0.555	1.9	.62	49
D	0.208	1.6	.62	63
	0.092	1.2	.62	71
	$c \to 0$	—	—	78

Table IV

Sample	Parlon 20 cps	Parlon 72 cps	CC 6 Pechiney	CC 4 Pechiney	CC 2 Pechiney	Laboratory Product
Molecular weight	110,000	125,000	210,000	180,000	93,000	320,000
% Chlorine	62	62	61	60.5	62	60

Intensity measurements and the determination of molecular weight:

Relative intensities of scattering in the transverse horizontal direction by solutions of A and B were measured using the optical arrangements and photomultiplier equipment which have already been described in detail elsewhere [Sivarajan (4)] and employing benzene as the standard scattering substance. The λ 4358 radiation of mercury was used as the incident radiation. Since ϱ_h was 100% for solutions of A and B and there was no dissymetry of scattering, molecular weights were determined by measuring the reduced intensity of scattering in the horizontal transverse direction, i.e. R_{90} as a function of concentration and applying the well-known Debye equation (5)

$$\frac{K c}{R_{90}} = \frac{1}{M} + 2 B c \quad , \qquad [1]$$

where K the refraction constant is given by

$$K = 2 \pi^2 n_o^2 (n - n_o/c)^2 / N \lambda^4 ,$$

c being the concentration in grams per cc, n and n_o the refractive index of solution and solvent respectively, λ the wavelength and N the Avogadro number. M represents the molecular weight of the solute and B is analogous to the Van't Hoff i factor in the corresponding equation for osmotic pressure. The value of $n - n_o/c$ was determined accurately using a Pulfrich refractometer. From the linear plots of Kc/R_{90} as a function of c,[1] the intercept $1/M$ was obtained and hence M was evaluated. The slope of the straight line plot gave the quantity B.

3. *Results and Discussion*

The depolarisation data for sols A and B as given in Table II represent the average values over a range of concentration 1% — .01% since ϱ does not show any change with concentration. Since $\varrho_h = 100\%$ and ϱ_v has a small though finite value in both cases, it can be concluded that the particles are present in the form of slightly anisotropic micelles with their longest dimension not exceeding $\lambda/20$. A value for the depolarisation factor due to the solute molecules can be obtained from intensity data using equations as given by Doty and Kaufman (6); Guinand and Tonnelat (7). This is necessary in cases where the solution scattering is not very large compared to solvent scattering, since then the solvent makes a significant contribution to the depolarisation value for the solution. The ϱ values now obtained can be compared with values for small ellipsoidal particles as derived from Gans' theory (8). [see also Gehman and Field (9)]. For the two extreme cases of a rod and a flat disk the values for ϱ_u are given by the following formulae.

Rods

$$\varrho_u = \frac{(m^2 - 1)^2}{m^4 + 8m^2 + 21} ,$$

Flat disks

$$\varrho_u = \frac{2 (1 - m^2)^2}{7 m^4 + 6 m^2 + 2} ,$$

where

$$m = \frac{\text{refractive index of solute}}{\text{refractive index of solvent}} = \frac{n_p}{n_0} .$$

From the refractive index increments $(n - n_o/c)$ measured for sols A and B, n_p can be calculated from Heller's refractive index equation (10). The values of n_p thus obtained for A and B come out as 1.598 and 1.603 for λ 4358. For the D line values for chlorinated rubber ranging from 1.55 — 1.60 have been reported by other workers [(Baxter and Moore (11); Tinsley (1)]. ϱ_u can now be calculated and the values for Rods are. 108 (A) and .115% (B). For discs the values are .36% (A) and .386% (B). Comparison with the corrected ϱ_u values for A and B (Table II) thus reveals that the particles are present in the form of small ellipsoids of revolution. Since the calculation of the depolarisation factor due to the solute involves differences between two comparable small quantities the values calculated from one measurement give only the orders of magnitude and are not exact. Hence a more specific comparison as to whether the particles are prolate or oblate spheroids is not possible at present. The molecular weights of A and B in solution are seen to be quite different, A having a much smaller molecular weight than B. Calculations of approximate molecular weights M from some reported viscosity data for solutions of chlorinated rubber in carbon tetrachloride and toluene [(Davies and Blake (12); Baxter and Moore (11), Tinsley (1)] give values of about 60,000 for M. From the detailed viscosity and osmotic pressure data of Riou and Pibarot (13) (see Table IV) it can be seen that the molecular weights of their samples of chlorinated rubber range from 93,000 —320,000. The molecular weights of the present samples investigated by the author range from

about 20,000 – 100,000 whereas the molecular weight of the original rubber from which A, B, C and D were obtained ranges from 230,000 – 420,000. Chlorination has thus resulted in a degradation of the molecular chain in rubber.

Coming next to the case of sols C and D, it becomes evident from a perusal of the depolarisation data in Table III that the micelles in these cases are $> 1/20\ \lambda$ in size since ϱ_h has finite values $< 100\%$. These therefore differ from A and B. The changes in ϱ that occur with concentration are probably due to some interference effects arising from the effect of finite size and concentration as such results have often been reported in the case of high polymer compounds in solution [Oster (14)]. It is therefore necessary to extrapolate the results to infinite dilution, $c \to 0$, in such cases. The small finite ϱ_v values for both C and D indicate the presence of anisotropic micelles in solution. An approximate calculation of the dimension of the micelles in sols C and D can be made by assuming the validity of the following equation for rods given by Vrklajan and Katalinic (15).

$$l^2 = \left(\frac{1}{\varrho_h} - 1\right)\frac{84}{k^2},$$

where l is the length of the rod and $k = 2\pi/\lambda'$, λ' being the wavelength of light in the medium. Using the extrapolated values of ϱ_h (Table III) and a mean value of 5400 Å for λ the lengths of the micelles in C and D are found to be 6570 Å and 2850 Å respectively. Assuming further that the dimensions of the single molecule are the same as for normal rubber, the molecular weight comes out roughly as 97,000 for C and 42,000 for D. It might be mentioned that though the assumption of a rod-like shape is apparently inconsistent with the small values for ϱ_u and ϱ_v in the case of C and D, it is not really new. For, it is known that several dielectric particles in solution such as the proteins with elongated rod-shaped molecules exhibit much lower ϱ_u values than the corpuscular proteins [Doty and Edsall (16)].

Finally it can be seen generally, from the data in Tables I – IV that as the percentage of chlorine increases, the molecular weight decreases and that even a 1% difference in the chlorine content causes large changes in the molecular weight. Also from the depolarisation data it is found in general that the anisotropy decreases with increasing molecular weight.

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Summary

Measurements have been made of the depolarisation factors ϱ_u, ϱ_v, ϱ_h, and the intensity of scattering in the horizontal transverse direction, in the case of solutions of four different samples of chlorinated rubber in carbon tetrachloride. The size, shape and molecular weight of the micelles have been deduced by the application of the light scattering theories of Gans, Vrklajan and Katalinic and Debye. The extent to which the degradation of the rubber molecule occurs on chlorination has also been assessed.

Zusammenfassung

Für Lösungen von vier verschiedenen Proben von chloriertem Kautschuk in Tetrochlorkohlenstoff wurden Messungen der Depolarisation und der Lichtstreuung durchgeführt. Größe, Gestalt und Molekulargewicht wurden unter Verwendung der Theorien der Lichtstreuung von Gans, Vrklajan, Katalinic und Debye abgeleitet. Die Stärke des Abbaues, dem die Kautschukmoleküle bei der Chlorierung unterworfen sind, wurde abgeschätzt.

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