The Characterization of Semi-Permeable Membranes for Osmotic Measurements

In a recent paper[1] Meyerhoff has compared the osmotic properties of several semi-permeable membranes by using each membrane to measure the number-average molecular weight, $\bar{M}_n$, of the BASF polystyrene PIII. Fractionation experiments had shown that this polymer has a wide molecular weight distribution and by means of this data Meyerhoff assigned a limit of solute permeability to each membrane (see Table II). Recently in this laboratory it has been found that ultrafein filters allerfeinst (UFF/AF) can be used to measure comparatively low molecular weights[2] and it seemed of interest therefore to characterize a pair of these membranes in the same way. Accordingly a sample of the BASF polystyrene PIII was obtained from Professor Meyerhoff and the $\bar{M}_n$ was determined in benzene solution at 30°C. using membranes UFF/AF 1257/2 assembled in a standard Zimm-Myerson-type osmometer.

An estimate of the solvent permeability of these membranes was obtained by measuring the rate of fall of the meniscus in the osmometer measuring capillary under a head of 10 cm. of benzene.[3] After 30 minutes the meniscus fell only 0.48 cm., and since this is a comparatively low rate of solvent permeation the meniscus was allowed to fall freely to zero in order to prove the membranes were truly semi-permeable. After 48 hours the difference in levels in the measuring and reference capillaries was only 0.07 cm., show-

TABLE I
Measurements at 30°C. with Benzene Solutions of Polystyrene PIII

Concentration, % (w/v)	"Equilibrium" osmotic pressures: Rising h_r, cm.	Rising Time, hr.	Falling h_f, cm.	Falling Time, hr.	h, cm.	h/c	Number-average molecular weight, $\bar{M}_n$
1.00	8.95	70	8.89	29	8.95	8.95	
0.80	6.92	46	6.85	46	6.92	8.65	
0.60	5.10	94.5	4.76	46	5.10	8.50	
0.40	3.14	95	3.17	48	3.14	7.85	
0.20	1.69	119	1.74	50	1.69	8.45	
→ 0						7.66	39,000 ±3,000

TABLE II[1]

Membrane	Measured molecular weight	Limit of permeability
Ultracella fine	225,000	35,000
Cellophane 300 gel	145,000	25,000
Ultracella finest	125,000	20,000
Polyvinyl alcohol I	100,000	15,000
Cellophane 600 gel	90,000	15,000
Ultracella finest contracted	45,000	7,000
Ultrafein filter allerfeinst (UFF/AF 1257/2)	39,000	5,000?
Polyvinyl alcohol II	14,000	2,000
Polyvinyl alcohol III	11,000	1,700
Polyvinyl alcohol IV	8,000	1,200
Polyvinyl alcohol V	7,000	1,000

TABLE III
Measurements at 30°C. in Benzene Using Membranes UFF/AF 1257/2

Concentration, % (w/v)	"Equilibrium" osmotic pressures: Rising h_r, cm.	Rising Time, hr.	Falling h_f, cm.	Falling Time, hr.	Observed, h_o, cm.	Theoretical, h_{th}, cm.	Reflection coefficient, h_o/h_{th}
			Pentaerythritol Tetrastearate, MW 1200				
0.025	6.13	69	6.00	96	6.13	6.15	1.00
0.025	6.02	69	5.84	168	6.02	6.15	0.98
			Tristearin, MW 891				
0.010	2.77	140	2.83	94	2.80	3.32	0.84
0.030	9.19	95	8.75	24	8.97	9.96	0.90
			Sucrose Octaacetate, MW 679				
0.025	5.30	48.5	5.23	30	5.30	10.87	0.49
0.025	5.29	95	5.10	43	5.29	10.87	0.49
0 025	4.47	72	5.22	140	5.22	10.87	0.48
0.050	10.81	43.5	9.91	65	10.81	21.74	0.50

ing that the membranes were permeable to benzene and also that the asymmetry correction was negligible.

The osmotic measurements were made by the static method for attaining equilibrium, and with each solution the rising and falling osmotic heads were measured (see Tables I and III). In each case the original setting of the meniscus was as far from the equilibrium as possible (i.e., since the measuring capillary was 12 cm. long, in one of the measurements the meniscus moved at least 6 cm.) and in practically every case the falling head was equal to or slightly lower than (i.e., some solute diffusion) the rising head. This good agreement between the rising and falling osmotic heads is further confirmation of the semi-permeable nature of these membranes.

With the BASF polystyrene PIII, measurements were carried out at five concentrations from which a value for $\bar{M}_n$ of 39,000 ± 3000 was calculated (see Table I). By comparison with the data in Meyerhoff's table (see Table II), it appeared therefore that the membranes had a limiting solute permeability of approximately 5000. This was a very surprising conclusion since other membranes of this type had been used to successfully measure an $\bar{M}_n$ of 2000.[2] Subsequent measurements of reflection coefficients[3] with benzene solutions of (*1*) pentaerythritol tetrastearate (MW 1200), (*2*) tristearin (MW 891), and (*3*) sucrose octaacetate (MW 679), see Table III, confirmed that the limit of solute permeability for these membranes is in fact much lower and is probably in the region of 1000.

It would appear therefore that, while the measurement of the $\bar{M}_n$ of BASF polystyrene PIII is a useful method for the empirical characterization of semi-permeable membranes (in our own work we use a similar material[3]) in order to estimate the limits of solute permeability it is more satisfactory to measure reflection coefficients of pure chemicals such as pentaerythritol tetrastearate, tristearin, and sucrose octaacetate.

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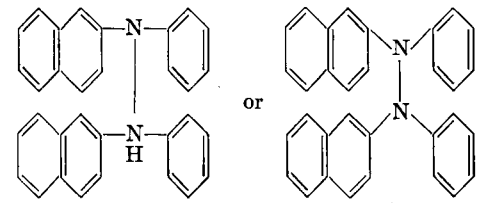
On the Oxidation Mechanism of Rubbers in the Presence of Inhibitors

In a recent paper[1] under the above title, Angert and Kuzminskii have reported infrared absorption curves for *N*-phenyl-2-naphthylamine after oxidation with molecular oxygen, and also for a similarly oxidized extract of rubber containing this inhibitor. On the basis of the spectral results, the authors state that "in both cases one can assume [*sic*] the formation of the products of the type:"



(I) (II)

Angert and Kuzminskii were apparently unaware that experiments carried out in this Laboratory in 1945[2] showed that permanganate oxidation of *N*-phenyl-2-naphthylamine yields a mixture of oxidation products containing *N*-(2-naphthyl)-*N*,*N*′-diphenyl-1,2-naphthylenediamine (Angert and Kuzminskii's assumed product (I)), and also 7-phenyldibenzo(*c*,*g*)carbazole. More recently, Schneider has shown,[3] through a combination of coupling reactions and paper chromatography, that both (I) and the carbazole occur in naturally aged rubber vulcanizates containing *N*-phenyl-2-naphthylamine. The presence of (I) in these oxidation products is therefore an established fact, and need not be assumed.

Angert and Kuzminskii also state that the ultraviolet spectra of their oxidation products "were identical, an indication of the absence of any changes in the aromatic nuclei." Since a carbazole is formed in the oxidation reactions, their indication is incorrect. The error probably arose from the fact that Angert and Kuzminskii carried out their ultraviolet examinations on unresolved mixtures of oxidation products. One would therefore expect the results to appear more or less identical, since the ultraviolet spectra[2] of *N*-phenyl-2-naphthylamine and some of its oxidation products, although they are not identical, nevertheless do not differ strongly.

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