

By changing the solvent,  $R$  could be made to vary independently of the molecular weight: on passing from a good solvent to a bad one the size of the molecules decreases considerably, especially near the precipitation threshold.

Mol. wt.	Solvent	$R$ (A.)	$\{\eta\}$ (litre/gm.)
<i>Polystyrene</i>			
$0.83 \times 10^6$	benzene	960	0.125
"	benzene + 50% hexane	750	0.085
"	benzene + 50% hexane	580	0.075
$2.00 \times 10^6$	benzene	1580	0.246
"	chloroform	1580	0.212
"	ethyl acetate	1040	0.115
"	benzene + 50% acetone	1120	0.150
$2.28 \times 10^6$	benzene	1640	0.236
"	benzene + 12.5% ethanol	1510	0.209
"	benzene + 17.6% ethanol	1420	0.194
"	benzene + 22.2% ethanol	1270	0.157
"	benzene + 26.3% ethanol	1060	0.121
"	benzene + 28.5% ethanol	870	0.101
"	benzene + 50% hexane	1280	0.155
"	benzene + 58% hexane	860	0.11
$7.7 \times 10^6$	benzene	2900	0.82
"	benzene + 50% hexane	2000	0.37
"	benzene + 40% acetone	2300	0.45
<i>Polyisobutylene</i>			
$0.17 \times 10^6$	<i>n</i> -heptane	690	0.045
"	<i>n</i> -heptane + 20% propanol	660	0.033
$0.50 \times 10^6$	<i>n</i> -heptane	1010	0.117
"	<i>n</i> -heptane + 10% propanol	960	0.099
"	<i>n</i> -heptane + 20% propanol	870	0.085
$1.2 \times 10^6$	<i>n</i> -heptane	1470	0.311
"	<i>n</i> -heptane + 10% propanol	1320	0.250
"	<i>n</i> -heptane + 20% propanol	1170	0.197
$1.9 \times 10^6$	<i>n</i> -heptane	1860	0.450
"	<i>n</i> -heptane + 10% propanol	1710	0.401
"	<i>n</i> -heptane + 20% propanol	1320	0.230
"	<i>n</i> -heptane + 14% ethanol	1460	0.294

The most remarkable feature of the experimental results (see table) is that  $\{\eta\}$  is essentially a function of  $R$  only, that is, that molecules of different weight but of the same size have nearly the same intrinsic viscosity. This fact cannot be explained by a theory involving particles completely impermeable to the solvent, as in that case  $\{\eta\}$  would be inversely proportional to the molecular weight for constant  $R$ . Complete permeability, on the other hand, is fairly satisfactory in the case of polyisobutylene, as it predicts that  $\{\eta\}$  would be proportional to  $R^2$ , regardless of molecular weight, in reasonable accordance with experiment; but it does not agree with the relations found in the case of polystyrene, where the exponent of  $R$  for a given molecular weight appears to be smaller than 2 and to increase with molecular weight. A theory of the Brinkman-Debye type<sup>4</sup>, supposing partial permeability, was tried; but here, too, the agreement was only qualitative and far from satisfactory.

Thus it appears that none of the existing theories is confirmed by experiment. It is hoped that measurements now in progress on other polymers may shed some light on this problem.

I wish to thank Mrs. G. Gavoret, who collaborated in part of this work, and Dr. M. Magat for his stimulating interest and guidance. Thanks are also due to the management of the Koninklijke/Shell-Laboratorium, Amsterdam, for sponsoring this research and for their permission to publish these results.

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<sup>1</sup> Debye, P., *J. Phys. and Coll. Chem.*, **51**, 18 (1947).

<sup>2</sup> Zimm, B. H., Stein, R. S., and Doty, P. M., *Polymer Bull.*, **1**, 90 (1945).

<sup>3</sup> Zimm, B. H., *J. Chem. Phys.*, **16**, 1093, 1099 (1948).

<sup>4</sup> Brinkman, H. C., *Proc. Kon. Ned. Acad.*, **50**, 618, 821 (1947). Debye, P., and Bueche, A. M., *J. Chem. Phys.*, **16**, 572 (1948).

## A Method of Breaking Emulsions

DURING the last few months, five emulsions formed during extractions, and unbreakable by any of the usual methods, have been broken rapidly and completely by addition of a wetting agent under the conditions described elsewhere for breaking emulsions of sea-water in fuel oil<sup>1</sup>. In three cases, "Teepol" was used, and in two, Turkey Red Oil. The emulsions were formed during ether extractions in all cases; but other solvents were also present.

The emulsifying agent appeared to be finely divided precipitate, coated, in one case, by tarry products and in another by waxy impurity. Finely divided inorganic material can be made into a most efficient emulsifying agent by addition of organic substance which is adsorbed upon it; for example, addition of a small amount of fatty acid to iron rust makes it a most dangerous emulsifier of water in turbine oils. Wetting agents, being more surface-active than such emulsifying agents, which act by differential wetting by the two liquid phases, displace them and the emulsion breaks. The proper dosage of wetting agent is that amount required to form its critical concentration in the aqueous phase. This will vary widely in emulsions formed by chance during organic preparations; but, as a guide, it may be laid down that not more than 1 per cent should ever be used; with excess, there is danger of re-emulsification of the non-aqueous phase in the aqueous one. It is obvious that no general claim can be made. The wetting agent could even make things worse by forming a complex with substances present. The success of the method was, however, so spectacular in the five different cases cited that it is felt that the method should be a boon to organic chemists embarrassed by emulsions. A small test should be tried first. Moderate heating accelerates breaking.

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<sup>1</sup> Lawrence, A. S. C., *Chem. and Indust.*, 615 (1948). Lawrence, A. S. C., and Killner, W., *J. Inst. Petroleum*, **34**, 821 (1948).

## Surface Effect and Structure of Single Crystal Wires

SOME months ago, Mr. R. F. Y. Randall and I<sup>1</sup> reported on the effect of certain electrolytes, applied at the surface, on the flow of cadmium single crystals. We recorded that the immersion in solutions of cadmium sulphate and chloride, and particularly in commercial plating solution, led at once to a permanent increase in the rate of flow of single-crystal cadmium wires which were under stress, while cadmium nitrate solutions caused an immediate increase of rate followed by a decrease and final cessation of flow, a hardening effect which we attributed to the formation of a surface film, probably of oxide.

Since then, as surface effects were clearly involved, we have been working with single crystal wires which have been heated *in vacuo* under conditions that allow free evaporation, with consequent formation of a really clean surface. With such wires cadmium sulphate and chloride solutions have no effect on the