

sulted in compounds having greatly reduced curare activity. Thus, tetrahydroerysopine and tetrahydroerysodine hydrobromides showed curare activity under comparable conditions at 40 and >300 mg./kg., respectively.¹

Erysovine differs from erysodine only in the position of one O-methyl group, and from erysopine in the number of O-methyl groups.² Hydrogenation of erysovine likewise resulted in the absorption of two molar equivalents of hydrogen, but the product as the free base, as well as the hydrobromide, failed to crystallize readily. Finally, tetrahydroerysovine base was obtained crystalline and pure. Under conditions where erysovine hydrochloride caused complete paralysis in all of ten frogs for one and one-half to three and one-half hours at a dose level of 2 mg./kg., it was found that tetrahydroerysovine hydrochloride at a dose level of 1 mg./kg. caused complete paralysis of all of ten frogs for three to three and one-half hours. One-half the dose level for each alkaloid caused complete paralysis of just three of ten frogs.

Thus, conversion of erysovine into its tetrahydro derivative increases its curare activity as is the case for the hydrogenation of β -erythroidine, but contrary for erysopine and erysodine. Furthermore, tetrahydroerysovine ranks in potency with the most curare-active *Erythrina* alkaloids, namely, dihydro- β -erythroidine and β -tetrahydro- β -erythroidine.⁴

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Experimental

Tetrahydroerysovine.—Four and one-half grams of erysovine was dissolved in 200 ml. of 1% hydrochloric acid and, after the addition of 100 mg. of Adams platinum catalyst, hydrogenation was carried out at about 40 lb. pressure. Two molar-equivalents of hydrogen was absorbed. The filtrate from the catalyst was neutralized with sodium bicarbonate and extracted with eight 10-ml. portions of chloroform. Removal of the chloroform gave a colorless gummy residue weighing 4.4 g., which was dissolved in 25 ml. of anhydrous ethyl ether. After adding 5 ml. of petroleum ether, the solvent mixture was refrigerated overnight; crystallization took place. The yield of crystals was 3.2 g.: m. p. 149–150. After two recrystallizations from ethyl ether–petroleum ether, the melting point of the tetrahydroerysovine was constant at 153–159°.

Anal. Calcd. for $C_{13}H_{23}NO_3$: C, 71.27; H, 8.30; N, 4.61. Found: C, 71.57; H, 8.17; N, 4.78.

(4) Unna, Kniazuk and Greslin, *J. Pharmacol.*, **80**, 42 (1949).

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The Relationship between Molecular Weight and Polymer Viscosity for Polyisobutylene

By F. P. BALDWIN

In 1940 Flory¹ proposed and illustrated a relationship between the weight average molecular

(1) Flory, *THIS JOURNAL*, **62**, 1057 (1940).

weight, \overline{M}_w , of linear polyesters and their melt viscosity, η . His observations supported the relationship

$$\log \eta = A + C \overline{M}_w^{1/2} \quad (1)$$

Eyring² attempted to theoretically deduce and interpret this relationship and thereafter a number of experimenters^{3,4,5,6} confirmed Flory's observations for polyesters and extended his relationship to include polyethylene, dimethylsiloxane polymers and Butyl (isoprene–isobutylene copolymers).

More recently Fox and Flory⁷ and Spencer and Dillon⁸ have shown that this relationship breaks down for polystyrene and polyisobutylene, and the experimental data for these polymers are best represented by the relationship

$$\log \eta = A + B \log \overline{M}_w \quad (2)$$

Recent data obtained in this Laboratory for unfractionated polyisobutylenes (and two 2.5% isoprene–97.5% isobutylene copolymers) covering the molecular weight range 300,000 to 4,000,000 are in agreement with this latter relationship. The polymer viscosity data were obtained by the method of Dienes and Klemm⁴ at 170°, and the intrinsic viscosities and molecular weights by the method of Flory.⁹ The results are plotted in Fig. 1. Each value of intrinsic viscosity repre-

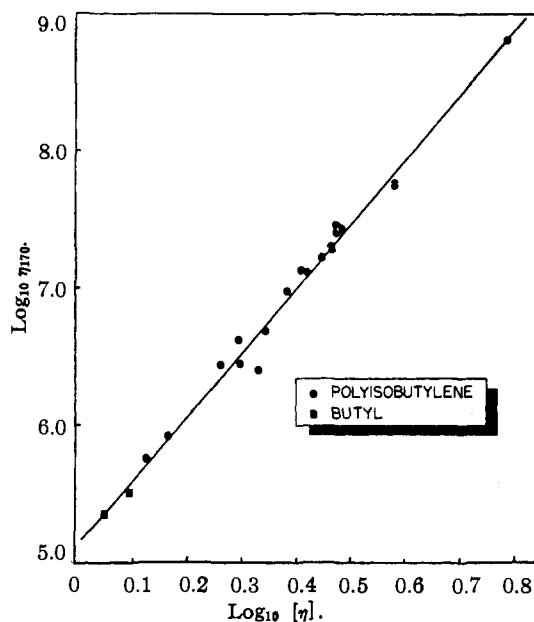


Fig. 1.

(2) Glasstone, Laidler and Eyring, "The Theory of Rate Processes," McGraw-Hill Book Co., Inc., New York, N. Y., 1941, pp. 500–503.

(3) Baker, Fuller and Heiss, *THIS JOURNAL*, **63**, 2142 (1941).

(4) Dienes and Klemm, *J. Applied Phys.*, **17**, 458 (1946).

(5) Barry, *ibid.*, **17**, 1020 (1946).

(6) Zapp and Baldwin, *Ind. Eng. Chem.*, **38**, 948 (1946).

(7) Fox and Flory, *THIS JOURNAL*, **70**, 2384 (1948).

(8) Spencer and Dillon, *J. Colloid Sci.*, **4**, 241 (1949).

(9) Flory, *THIS JOURNAL*, **68**, 372 (1943).

sents the average of at least three determinations, and each value of the polymer viscosity is the average of two determinations. The data conform to the equation

$$\log_{10} \eta_{170} = 5.120 + 4.725 \log_{10} [\eta] \quad (3)$$

The relationship yielded by the data of Fox and Flory¹⁰ is

$$\log_{10} \eta_{217} = 4.69 + 5.31 \log_{10} [\eta] \quad (4)$$

Considering the differences in temperature and method of measurement together with the fact that the polymers used in the present experiments were of variable heterogeneity in molecular weight, the agreement is good.

Although only two points are shown, it is likely that copolymers of isobutylene and diolefins, the latter being present in relatively small proportions, will follow the same or similar relationship. Hence the apparent discrepancy between these data and previous data of Zapp and Baldwin⁶ lies in the fact that the molecular weight range previously covered was narrow (140,000 to 550,000). The present data can also be approximated by equation (1) over limited molecular weight ranges.

(10) Private communication.

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Conductance of Long Chain Quaternary Salts in Bromophenolate Blue Solutions

BY EUGENE L. COLICHMAN¹

The affinity of bromophenolate blue anions for long chain quaternary cations is the basis for several analytical methods^{2,3,4} of determining both cationic and anionic active compounds. Such an electrostatic interaction in dilute aqueous solutions results in a color change from purple to blue without precipitation. The optical clarity

TABLE I

CONDUCTIVITY FUNCTIONS OF QUATERNARY SALTS IN $1.5 \times 10^{-5} M$ AQUEOUS BROMOPHENOLATE BLUE SOLUTIONS AT 25°

$C \times 10^5$	$\bar{L}_s \times 10^5$	$(\bar{L}_{RD})_{exp.} \times 10^5$	$\Delta \bar{L}_s / \Delta C \times 10$
<i>n</i> -Myristyltrimethylammonium Bromide			
3.0	3.9	0.0	1.00
4.5	5.4	.1	1.00
6.0	6.9	.0	1.00
8.9	9.8	.0	1.00
11.9	12.8	.0	0.90
17.9	18.2		.983
23.8	24.0		.950
29.8	29.7		

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(2) (a) Auerbach, *Anal. Chem.*, **15**, 492 (1943); (b) **16**, 739 (1944).

(3) Colichman, *ibid.*, **19**, 430 (1947).

(4) (a) Hartley and Runnicles, *Proc. Roy. Soc. (London)*, **168A**, No. 934, 424 (1938); (b) Hartley, *Trans. Faraday Soc.*, **30**, 444 (1934).

n-Cetyltrimethylammonium Bromide

3.0	3.9	0.0	1.00
3.9	4.8	.1	0.943
5.6	6.4	.0	1.00
8.4	9.2	.2	1.07
11.2	12.2		1.07
14.0	15.2		1.07
16.8	18.2		1.11
28.0	29.5		

n-Cetyltrimethylammonium Chloride

3.0	3.8	0.1	1.00
3.5	4.3	.1	0.90
4.5	5.2	.0	.948
6.4	7.0	.0	.942
7.1	7.6	.0	1.00
8.4	8.9	.0	0.50
9.6	9.5		.907
12.8	12.4		.842
19.1	17.7		.852
31.9	28.6		.844
63.8	55.5		

n-Cetyltrimethylammonium Nitrate

3.0	3.7	0.0	0.908
4.1	4.7	.0	.890
5.9	6.3	.0	.920
8.4	8.6	.0	.765
11.8	11.2		.863
14.7	13.7		.867
17.7	16.3		.864
23.6	21.4		

n-Octadecyltrimethylammonium Bromide

3.0	3.9	0.2	1.00
4.1	5.0	.2	1.50
5.1	6.5	.0	1.40
6.1	7.9	.0	1.40
7.1	9.3		1.45
8.2	10.9		1.30
10.2	13.5		1.20
15.3	19.6		

n-Laurylpyridinium Chloride

18.6	22.0		1.17
23.2	27.4		1.20
27.8	32.9		1.12
37.1	43.3		1.08
46.4	53.3		1.12
55.7	63.7		1.11
65.0	74.0		1.09
92.8	104.3		

Hyamine 1622

9.4	10.8		0.892
14.0	13.9		.894
18.7	18.1		.915
25.7	24.5		.943
32.7	30.8		.950
46.8	44.5		.877
93.6	85.5		.847
140.4	125		.832
187.2	164		