pound obtained was practically the same when either γ-phenylbutyric acid or its methyl ester was cyclized, the yields being 70 and 72%, respectively. Methyl δ-phenylvalerate has been used to give benzosuberone in 90% yield as compared to that of 85% from the corresponding acid.[2]

Experimental[4]

Esterifications.—In all cases the esters were produced by refluxing the acid in 4% methanolic hydrochloric acid and isolating the neutral fraction in the usual manner. Although only methyl esters have been used in the present reported investigation, ethyl esters have been employed with equal success.

Ring Closures.—The preparation of the phosphorus pentoxide–85% orthophosphoric acid slurry and the isolation of the neutral ketonic material were carried out in a manner already described in detail.[2] To ensure homogeneity of the neutral compound from each cyclization, the compound was refluxed for 1 hour in 50 ml. of aqueous ethanol containing 2 g. of sodium hydroxide. The neutral material isolated from this procedure was used for determining the yield of compound and for preparing the reported derivatives. Fifty-four grams of slurry per gram of ester or acid was employed in all instances. The mixture of compound and slurry was heated in a flask protected from moisture by a calcium chloride tube for two hours on a steam-cone, although a shortened working time resulted in no decrease in yield of ketone in one instance.[5]

Derivatives.—The oxime and semicarbazone were prepared by refluxing the neutral compound from each cyclization in absolute ethanol and anhydrous pyridine containing either hydroxylamine hydrochloride or semicarbazide hydrochloride. Mixed melting points of these derivatives were not depressed when prepared from material obtained by cyclizing either the ester or its corresponding acid.

α-Hydrindone.—To 2 g. of methyl β-phenylpropionate was added the commensurate quantity of polyphosphoric acid slurry and the mixture heated. There was obtained 1.5 g. (93%) of neutral compound; oxime, m.p. 143–144°, reported,[6] 143–144°; semicarbazone, m.p. 237° (dec.), reported,[7] 239° (dec.).

α-Tetralone.—One gram of methyl γ-phenylbutyrate and 54 g. of slurry yielded, after the usual procedure, 0.59 g. (72%) of neutral compound; oxime, m.p. 101–102°, reported,[8] 102.5–103.5°; semicarbazone, m.p. 213–215°, reported,[8] 217°.

Benzosuberone.—A sufficient amount of polyphosphoric acid slurry was poured into a flask containing 1.8 g. of methyl δ-phenylvalerate and the usual procedure carried out to give 1.3 g. (90%) of neutral product; oxime, m.p. 107–108°, reported,[9] 108–109°; semicarbazone, m.p. 206–207°, reported,[9] 206–207°.

(4) Melting points are uncorrected.

(5) Methyl γ-phenylbutyrate was cyclized to α-tetralone by heating for only 15 minutes.

(6) F. S. Kipping, J. Chem. Soc., 65, 490 (1894).

(7) C. Revis and F. S. Kipping, ibid., 71, 241 (1897).

(8) F. S. Kipping and A. Hill, ibid., 75, 151 (1899).

(9) F. S. Kipping and A. E. Hunter. ibid., 79, 607 (1901).

DEPARTMENT OF BIOCHEMISTRY
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Occurrence of d-Pinitol in Red Spruce (Picea rubra)

BY SIDNEY GOTTLIEB AND F. E. BRAUNS

d-Pinitol, the monomethyl ether of d-inositol, occurs in many species of plants, having been reported in Pinus lambertiana,[1] senna leaves,[2] Mateza roritina,[3] Sequoia sempervirens,[4] Pinus

(1) Berthelot. Ann. chim. phys., 46, 76 (1856).

(2) Dragendorff and Kubly, Z. Chem., 411 (1866).

(3) Girard. Compt. rend., 77, 995 (1873); ibid., 110, 84 (1890).

(4) Sherrard and Kurth. Ind. Eng. Chem., 20, 722 (1928).

strobus,[5] Astragulus wootoni,[6] Astragulus earliei,[7] Oxytropis lambertii,[7] Lotononis laxi[8] and Lupinus caudatus.[9]

In the course of the preparation of "native lignin" from red spruce (Picea rubra), a crystalline compound was isolated in small yield from the dioxane–ether filtrate obtained in the precipitation of dioxane solutions of crude native lignin into ether. This compound was identified as d-pinitol. The yield was 2.5 g. of d-pinitol from 100 pounds of sawdust.

Freshly cut logs of 12 year-old red spruce were stripped of bark and reduced to sawdust. The sawdust was thrice extracted in copper percolators with 95% alcohol and worked up according to the method of Brauns.[10] Instead of separating the water-soluble fraction of the initial alcohol extract by decantation from the insoluble solids, dioxane was added and the water and alcohol were removed by azeotropic distillation resulting in a dioxane solution containing the total alcohol extract (except volatile materials). The precipitation of this dioxane solution (adjusted to a concentration of 10% solids) into 20 volumes of diethyl ether and subsequent centrifugation resulted in a clear yellow solution which, when concentrated to a small volume of dioxane, deposited small white prismatic crystals of d-pinitol which, after several recrystallizations from hot butanol, melted at 185–186° (cor.). [α]²⁰D −65.8° (previous values reported −67.7,[5] −62.5,[6] −65.3,[11] −65[7]).

Anal. Calcd. for $C_7H_{14}O_6$: C, 43.27; H, 7.27; OCH₃, 15.9; mol. wt., 194. Found: C, 43.55; H, 7.50; OCH₃, 16.0; mol. wt. (Rast), 189 and 197.

A mixture of the compound with an authentic sample of d-pinitol melted at 185–185.5°.

The pentacetyl and pentabenzoyl derivatives were prepared according to the procedure of Griffin and Nelson[11]; the crystalline pentacetate, m.p. 97.5–98°, [α]²⁰D −9.3°; the amorphous pentabenzoate, m.p. 96–97° [α]²⁰D −31.5°, in good agreement with the values reported in the literature.

A small amount of d-pinitol (0.5 g. per 100 g. sawdust) could be isolated by the direct extraction of ground red sprucewood (60 mesh) with cold water.

(5) Erdtman. Svensk Kem. Tid., 56, 2 (1944).

(6) Knowles and Elderfield. J. Org. Chem., 7, 389 (1942).

(7) Pease. Reider and Elderfield, ibid., 5, 1989 (1940).

(8) de Waal. Onderstepoort J. Vet. Sci. Animal Ind., 13, 22 (1939).

(9) Soine and Jenkins. Pharm. Arch., 12, 65 (1941).

(10) Brauns, THIS JOURNAL, 61, 2120 (1939).

(11) Griffin and Nelson, ibid., 37, 1568 (1915).

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF MARYLAND
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INSTITUTE OF PAPER CHEMISTRY
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The Diffusion Coefficient of Magnesium Sulfate in Dilute Aqueous Solution at 25°

BY HERBERT S. HARNED AND ROBERT M. HUDSON

Recently, the diffusion coefficient of zinc sulfate[1] at high dilutions in water was determined by the conductance method. The present measurements of the diffusion coefficient of magnesium sulfate, extended to somewhat lower concentrations, were carried out to supplement our knowledge of the diffusion behaviors of 2-2 electrolytes.

(1) H. S. Harned and R. M. Hudson. THIS JOURNAL. 73. 3781 (1951).

Experimental Results and Theoretical Calculations

The apparatus, technique and methods of calculation were the same as those described in detail in the previous communications from this Laboratory.[2] The final values for the observed diffusion coefficients at the molar concentrations given in the first column are recorded in the second column of Table I.

TABLE I

OBSERVED AND CALCULATED DIFFUSION COEFFICIENTS OF MAGNESIUM SULFATE AT 25°

c	$\mathfrak{D} \times 10^{5}$		α [3]	λ_{m}^{0}
	Obsd.	Calcd.		
0.0	...	0.849	1.00	..
.00048	0.788	.755	0.93	52
.00080	.779	.735	.87	46
.00167	.739	.699	.85	44
.00170	.746	.698	.85	46
.00208	.740	.686	.83	47
.00272	.730	.669	.81	49
.00457	.716	.646	.76	46
.00481	.709	.643	.73	45
.00610	.703	.642	.72	45
.00636	.702	.630	.725	45

Mean 46.5

Since no accurately determined activity coefficients in dilute solutions of magnesium sulfate at 25° are available, we have used for the following theoretical computations values of the activity coefficient of zinc sulfate derived from electromotive force measurements.[4] This procedure should be a close approximation because the activity coefficients of magnesium sulfate and zinc sulfates are approximately the same at higher concentrations. Upon substituting the values $\lambda_1^0 = 53.06$,[5] $\lambda_2^0 = 79.8$,[6] $a = 3.64$ Å.,[4] $D = 78.54$,[7] $\eta_0 = 8.949 \times 10^{-3}$,[7] $|z| = 2$, and $T = 273.16$ in the equations of the theory of Onsager and Fuoss[8] we obtain

$$\mathfrak{D} = 4.958 \times 10^{13} \left(\frac{\overline{\mathfrak{M}}}{c}\right)\left(1 + c\frac{\partial \ln y_{\pm}}{\partial c}\right) \quad (1)$$

where the mobility term is

$$(\overline{\mathfrak{M}}/c) \times 10^{20} = 17.115 - \frac{1.3173\sqrt{c}}{1 + 2.3922\sqrt{c}} + 303.35c\,\phi\,(2.3922\sqrt{c}) \quad (2)$$

and the thermodynamic term is

$$\left(1 + c\frac{\partial \ln y_{\pm}}{\partial c}\right) = 1 + 28.48c - 6.187c^{3/2} \quad (3)$$

$\mathfrak{D}$ is the diffusion coefficient in cm.² sec.⁻¹ and $\phi(2.3922\sqrt{c})$ is the exponential integral term of the theory.

The third column in Table I contains values of $\mathfrak{D}$ computed by these equations. These values are

(2) H. S. Harned and R. L. Nuttall, THIS JOURNAL, **69**, 737 (1947).

(3) R. W. Gurry, Dissertation, Department of Chemistry, Yale University, June, 1937.

(4) I. A. Cowperthwaite and V. K. LaMer, THIS JOURNAL, **53**, 4333 (1931).

(5) B. B. Owen and R. W. Gurry, *ibid.*, **60**, 3078 (1938).

(6) D. A. MacInnes, "Principles of Electrochemistry," Reinhold Publishing Corp., New York, N. Y., 1938, p. 342.

(7) H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," 2nd Ed., Reinhold Publishing Corp., New York, N. Y., 1950, pp. 118 and 128.

(8) L. Onsager and R. M. Fuoss, *J. Phys. Chem.*, **36**, 2689 (1932); see Ref. (1).

considerably less than the observed results recorded in the second column of the table. In Fig. 1, the diffusion coefficients of both zinc and magnesium sulfates are plotted against the molar concentration. The lowest curve represents the values calculated by equations (1) to (3) which were derived upon the assumption of complete ionization. It is apparent that the magnesium sulfate results approach the theoretical values satisfactorily as the concentration of this salt decreases.
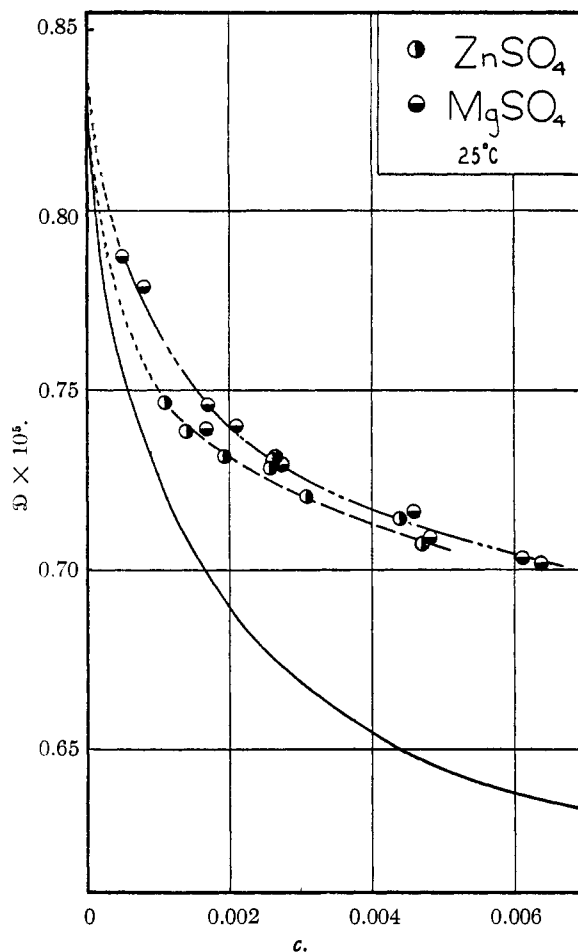

Fig. 1.—The diffusion coefficients of zinc and magnesium sulfates in aqueous solution: lower curve represents calculation according to equations (1), (2) and (3).

We showed[1] that the difference between the calculated and observed results for the diffusion coefficient of zinc sulfate is due to ion-pair formation and deduced a correction factor for this effect. If n_i and n_m are the concentrations of the ions and ion-pair, respectively, then the total flow J is

$$J = -n_i\frac{\omega_1\omega_2}{\omega_1 + \omega_2}\nabla\mu - n_{in}\omega_m\nabla\mu \quad (4)$$

where ω_1, ω_2 are the mobilities of the cation and anion, respectively, ω_m the mobility of the ion-pair and μ is the chemical potential. From this relation, the correction factor for ion-pair formation may be deduced and expressed in the form

$$\mathfrak{D}_{obsd}/\mathfrak{D}_{calcd} = 1 + (1 - \alpha)\left[\omega_m\middle/\frac{\omega_1\omega_2}{\omega_1 + \omega_2} - 1\right] \quad (5)$$

We note that the fraction within the brackets is a

measure of the relative flow rates of the ion-pair and the electrolyte. This may be expressed by the equivalent conductances by multiplying both numerator and denominator of this fraction by the faraday. Thus

$$\mathfrak{D}_{obsd}/\mathfrak{D}_{calcd} = 1 + (1 - \alpha)\left[\lambda_m^0 \bigg/ \frac{\lambda_1^0\lambda_2^0}{\lambda_1^0 + \lambda_2^0} - 1\right] \quad (6)$$

where λ_m^0 is 96,500 ω_m. This equation yields

$$\mathfrak{D}_{obsd}/\mathfrak{D}_{calcd} = 1 + (1 - \alpha)[0.0314 \lambda_m - 1] \quad (7)$$

upon substituting the numerical values of λ_1^0 and λ_2^0 for the equivalent conductances of the magnesium and sulfate ions.

By utilizing the values of α for zinc sulfate given in the fourth column of Table I, the values of λ_m^0 recorded in the last column are obtained. It is to be observed that these results do not vary greatly with concentration. The mean value of 46 is slightly greater than that of 44 obtained for λ_m^0 of zinc sulfate. Both of these results are greater than $\lambda_1^0\lambda_2^0/(\lambda_1^0 + \lambda_2^0)$ which computation shows to 31.9. The higher flow rate for the ion-pairs may be explained by the loss of water of hydration as a result of their formation.

DEPT. OF CHEMISTRY
YALE UNIVERSITY
NEW HAVEN, CONNECTICUT   RECEIVED JULY 10, 1951

The Diffusion Coefficient of Cesium Sulfate in Dilute Aqueous Solution at 25°

BY HERBERT S. HARNED AND CHARLES A. BLAKE, JR.

The present series of results supplements our earlier determinations of the diffusion coefficients of lithium and sodium sulfates.[1] When these measurements were made the limiting equivalent conductance of the cesium ion was not known with sufficient accuracy to permit a precise application of theory. This discrepancy in our knowledge has been remedied by recent accurate measurements of the conductance of cesium chloride in water.[2]
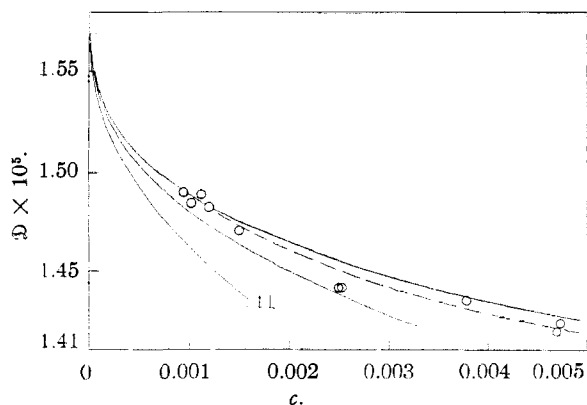

Fig. 1.—The diffusion coefficient of cesium sulfate as function of concentration in dilute aqueous solution: top curve, complete theory; circles, experimental results; dashed curve represents mean of experimental results; center solid curve, equation (6); lower curve, limiting law.

(1) H. S. Harned and C. A. Blake, THIS JOURNAL, **73**, 2448 (1951).
(2) W. E. Voisinet, Jr., Dissertation, Yale University, June, 1951.

Experimental Results and Theoretical Calculations

The apparatus and technique were the same as those described in detail by Harned and Nuttall[3] and require no amplification. Cesium sulfate was prepared from a carefully purified sample of cesium chloride. The chloride was converted to sulfate by addition of the required amount of sulfuric acid and by surface evaporation. The dried salt was dissolved in water and precipitated with a large volume of ethyl alcohol. Further purification was obtained by recrystallization from water. Spectrographic analysis of this material showed no potassium, less than 0.001% of sodium or lithium, and less than 0.01% of rubidium. The pH of a 0.01 solution was found to be 6.

The second column of Table I contains the observed diffusion coefficients at the concentrations designated in the first column. The theoretical equations[4] are written in full in our earlier communication[1] and only the final numerical equations derived from the quantities recorded at the bottom of the table will be given. Thus

$$\mathfrak{D} = 7.437 \times 10^{13}(\overline{\mathfrak{M}}/c)\left(1 + c\frac{\partial \ln y_\pm}{\partial c}\right) \quad (1)$$

$$(\overline{\mathfrak{M}}/c) \times 10^{20} = 21.097 - \frac{2.114 \sqrt{c}}{1 + 2.135 \sqrt{c}} + 116.21c\ \phi\ (2.135\sqrt{c}) \quad (2)$$

$$\left(1 + c\frac{\partial \ln y_\pm}{\partial c}\right) = 1 - \frac{2.0306 \sqrt{c}}{(1 + 2.135 \sqrt{c})^2} - 0.157c - c\ \psi\ (d) \quad (3)$$

$$c\ \psi\ (d) = \frac{-0.0026c - 0.1824c^{3/2}}{0.9970 - 0.0026c - 0.01216c^{3/2}} \quad (4)$$

The theoretical limiting equation is

$$\mathfrak{D} \times 10^5 = 1.569 - 3.343 \sqrt{c} \quad (5)$$

TABLE I

OBSERVED AND CALCULATED DIFFUSION COEFFICIENT OF CESIUM SULFATE

	$\mathfrak{D} \times 10^5$	
c	Obsd.	Calcd.
0.00000	. . .	1.569
.00096	1.490	1.490
.00102	1.484	1.488
.00112	1.489	1.485
.00120	1.482	1.482
.00150	1.470	1.475
.00248	1.442	1.455
.00251	1.441	1.454
.00378	1.435	1.436
.00468	1.419	1.426
.00472	1.424	1.426

$\lambda_1^0 = 77.27^2$; $\lambda_2^0 = 79.8^5$; $A'^{(6)} = 2.135$; a (Å.) = 3.75; $S_{(f)} = 1.7636^7$; $B = -0.068^6$; $d_0 = 0.9970$; $M_2 = 361.88$; $\phi_v^0 = 56.9^7$; $S_v = 12.2^7$ $S_{(\mathfrak{D})} = 3.343 \times 10^{-5}$; $D = 78.54$; $\eta_0 = 8.949 \times 10^{-3}$.

It is apparent from comparison of the values in columns two and three of Table I that the agree-

(3) H. S. Harned and R. L. Nuttall, THIS JOURNAL, **69**, 737 (1947).
(4) L. Onsager and R. M. Fuoss, J. Phys. Chem., **36**, 2689 (1932).
(5) D. A. MacInnes, "The Principles of Electrochemistry," Reinhold Publishing Corp., New York, N. Y., 1939, p. 342.
(6) R. H. Stokes, Trans. Faraday Soc., **44**, 295 (1948).
(7) H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," 2nd Edition, Reinhold Publishing Corp., New York, N. Y., 1943, p. 233 or 587.