This proved quite insoluble in ethanol and was treated as above. The recrystallized portion melted at 277–282°, and the alcohol-insoluble portion had an indistinct m. p. above 280°.

In an attempt to encourage coupling without cleavage by buffering, 1-methoxynaphthalene (2 ml.) was treated with a mixture of 15 ml. of the non-aqueous diazo solution, 15 ml. of acetic acid, and 12.3 g. of anhydrous sodium acetate. After addition of more acetic acid (15 ml.), the red-black mixture was shaken thoroughly and poured into water. The red solid was filtered, rinsed, and washed by suspension in methanol and refiltration. The insoluble portion, when dry, melted at 275–280°.

1,3-bis-*p*-Nitrophenyltriazene.—The procedure used in this preparation was a modification of that of Meldola and Streatfield.[5] *p*-Nitroaniline (2.76 g., 0.02 mole) was dissolved with heating in concd. hydrochloric acid (50 ml.). The solution was cooled and a solution of sodium nitrite (0.69 g., 0.01 mole) in water (5 ml.) was slowly added dropwise with stirring. Water (20 ml.) was added to the mixture, which then stood for nineteen hours. The clear yellow solution was thrown into excess water, and on standing fine yellow needles formed. These were filtered and dried *in vacuo;* yield, 0.70 g., m. p. 224–228° (dec.). The mother liquors deposited a second crop, weight 0.05 g., m. p. 228–230° (dec.).

In order to establish without doubt the identity of this material and the product from the previous buffered coupling reaction involving the 1-naphthyl tetraacetyl-β-D-glucoside, absorption spectra of both samples were measured and found identical (Fig. 1). Solutions 10^{-3} molar in each sample were made for the measurements. In taking the readings, it soon became apparent that Beer's law was failing to apply. Thus at 440 mμ the 10^{-3} molar solution of each sample had a density reading on the Beckman Model DU Spectrophotometer of 1.84. A 10^{-4} molar solution at the same wave length had a density of 0.860 instead of 0.184. Similarly, at 410 mμ the density of the 10^{-4} molar solution was 1.800, while that of a 10^{-5} molar solution was 0.360. As the wave length region between 445 and 400 mμ was crossed, the density readings for 10^{-3} molar and 10^{-4} molar solutions approached constant values within the range of the spectrophotometer scale, and it was necessary to use 10^{-5} molar solutions in order to cover the lower visible and ultraviolet spectrum. These effects were observed on two different spectrophotometers. They are probably attributable to the ionization of dinitrodiazoaminobenzene in alcoholic solution, and are currently under more extensive study.

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[5] Meldola and Streatfield, *J. Chem. Soc.*, **49**, 627 (1886).

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The Dissociation of Lead Chloride in Ethylene Glycol–Water Mixtures

BY J. C. JAMES

Norman and Garrett[1] have recently reported measurements of the conductance of lead chloride solutions at 25° in ethylene glycol–water mixtures, and conclude that activity and conductance data for such solutions show deviations from the Debye–Hückel and Onsager theories which cannot be accounted for by the assumption of incomplete dissociation. Discrepancies between theoretical and experimental values were attributed to differences between the macro and micro dielectric constants of the solutions, and "effective microdielectric constants" were calculated by comparison of experimental slopes with those predicted by the Debye–Hückel and Onsager theories.

These conclusions are surprising, as in aqueous solution previous workers[2–4] have assumed that the intermediate ion $PbCl^+$ was present, and have derived dissociation constants of the order of 0.02–0.03 from activity and conductance data; also, Fromherz and Kun-Hou Lih[5] have shown that the ultraviolet absorption spectra indicated presence of this ion. Similarly, conductance data for the salts zinc malonate, zinc sulfate and lanthanum ferricyanide in glycol–water mixtures have been accounted for satisfactorily by assuming dissociation to be incomplete.[6]

Norman and Garrett[1] have rejected this treatment on the grounds that as curves for the plots of both Λ *vs.* $\sqrt{m}$ and γ *vs.* $\sqrt{m}$ were straight in the lower concentration regions, a constant degree of dissociation would result in any solvent. Such behavior, however, does not necessarily imply complete dissociation, as the effect of actual variation in α may be cancelled out almost completely by the effect of higher terms neglected in the limiting Debye–Hückel and Onsager equations. Thus it has been shown by Davies[7] that dissociation is not complete in calcium mandelate solutions, although the Λ *vs.* $\sqrt{m}$ plot is linear up to $m = 0.02$, far beyond the limits of Onsager's equation. It is shown in this Note that the data of Norman and Garrett can be given an alternative explanation on the assumption that the intermediate ion $PbCl^+$ is formed in solution by the process $Pb^{++} + Cl^- \rightleftarrows PbCl^+$, further association to give the neutral salt being negligible.

Activity Data.—Dissociation constants for lead chloride in water at 25° have been calculated from the activity data of Carmody[8] using the method described by Davies,[9] and are given in Table I, γ being the stoichiometric activity coefficient, and f the true mean ionic activity coefficient. Dissociation constants in glycol–water mixtures have been calculated by the same method from the activity data of Garrett, Bryant and Kiefer,[10] up to concentrations of 0.006 N and are summarized in Table III. Mean ionic activity coefficients have been obtained from the empirical equation

$$-\log f = S\left[\frac{\sqrt{\mu}}{1+\sqrt{\mu}} - 0.20\,\mu\right]$$

where S is the limiting Debye–Hückel slope;

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[1] J. W. Norman and A. B. Garrett, THIS JOURNAL, **69**, 110 (1947).

[2] E. C. Righellato and C. W. Davies, *Trans. Faraday Soc.*, **26**, 592 (1930).

[3] G. Scatchard and R. F. Teft, THIS JOURNAL, **52**, 2272 (1930).

[4] H. S. Harned and M. E. Fitzgerald, *ibid.*, **58**, 2624 (1936).

[5] H. Fromherz and Kun-Hou Lih, *Z. physik. Chem.*, **A153**, 321 (1931).

[6] J. C. James, unpublished work.

[7] C. W. Davies, *J. Chem. Soc.*, 271 (1938).

[8] W. R. Carmody, THIS JOURNAL, **51**, 2905 (1929).

[9] C. W. Davies, *J. Chem. Soc.*, 349 (1939).

[10] A. B. Garrett, R. Bryant and G. F. Kiefer, THIS JOURNAL, **65**, 1905 (1943).

this equation fits the data of Knight, Masi and Roesel[11] for the activity of hydrogen chloride in glycol–water mixtures to $\mu = 0.02$ with a maximum deviation of 2%, and is sufficiently accurate for the purpose. Molal quantities have been converted to molar quantities, assuming the densities of the solutions to be equal to those of the pure solvent mixtures.

TABLE I

$m \times 10^4$ (molality)	γ	f	K
3.3333	0.912	0.966	(0.016)
10.000	.847	.926	.019
20.000	.791	.888	.022
26.666	.764	.869	.023
33.333	.740	.850	.024
100.00	.604	.729	.025
200.00	.505	.619	.025
266.66	.464	.568	.024
308.67	.443	.542	.023

Conductance Data.—Dissociation constants have been calculated in water from the data of Norman and Garrett,[1] by the method of Righellato and Davies,[2] evaluating mobility terms from the empirical equations

$$[\Lambda\ (\mathrm{Pb}^{++}) + \Lambda\ (\mathrm{Cl}')] = \Lambda_0 - bf_{2-1}\ (\mu)$$

and

$$[\Lambda\ (\mathrm{PbCl}^{+}) + \Lambda\ (\mathrm{Cl}')] = \Lambda' - b'f_{1-1}\ (\mu)$$

where b, b' are the respective Onsager slopes. For $f_{1-1}(\mu)$ values have been given by Robinson and Davies,[12] and for $f_{2-1}(\mu)$ values were calculated from the data of Shedlovsky and Brown[13] for calcium and magnesium chlorides, which have been assumed to be completely ionized. The mobility of the intermediate ion PbCl^+ at zero concentration has been estimated as 45 at 25°, from the value used by Righellato and Davies[2] at 18°. Values for the ionization constant K were derived from the equation

$$\log K = \log \frac{\alpha(1 + \alpha)}{(1 - \alpha)}\, m - 2 \left[\frac{\sqrt{\mu}}{1 + \sqrt{\mu}} - 0.20\, \mu\right]$$

and are given in Table II.

TABLE II

$m \times 10^4$ (molarity)	α	K
4.5284	0.971	0.025
4.8136	.970	.026
5.9780	.964	.026
6.9169	.963	.028
11.930	.935	.026
24.020	.884	.025
27.646	.886	.028
49.688	.819	.026
53.523	.815	.028

In glycol–water mixtures, the values summarized in Table III have been calculated up to concentrations of 0.002 N, using the limiting forms of the Onsager and Debye–Hückel equations, and assuming that the transport numbers of the ions do not change with the change in solvent. Limiting conductance values have been re-extrapolated by the method of Onsager,[14] as the values given by Norman and Garrett were obtained by Kohlrausch's square-root method, which is known to give Λ_0 values that are too high for incompletely dissociated electrolytes.[15]

TABLE III

% Glycol (ω/ω)	Mean K (conductance data)	Mean K (activity data)
0	0.026	0.023
20	.023	.030
40	.025	.025
60	.012	.015
80	.0083	.0095
100	.0026	∞

Dissociation constants calculated for lead chloride in glycol–water mixtures from conductance and activity data are in good agreement except in 100% glycol, for which the anomalously high activity coefficients appear to indicate complete dissociation. (Similar discrepancies have been noted by Garrett and Vellenga[16] with thallium chloride at high glycol concentrations.)

The results are of interest as lead chloride is one of the few inorganic salts which have been studied in a binary solvent mixture over the entire range of composition. Moelwyn-Hughes[17] has applied the Wynne-Jones equation[18]

$$\left[\frac{\mathrm{d}\ln K}{\mathrm{d}\ (1/D)}\right]_{\mathrm{T,P.}} = \frac{z_A z_B \epsilon^2}{rkT}$$

to dissociation constants calculated from conductance data for silver nitrate in various solvents, plotting ΔG as a function of $1/D$ and obtaining a straight line, from the slope of which a value for r the sum of the ionic radii, was found. Application of this procedure to the data for lead chloride gave a linear plot leading to the value $r = 5.6$ Å. For $K = 0.025$ in water, the Bjerrum equation,[19] however, gives a value of 1.85 Å. for r. The observed decrease in K with decrease in D is considerably less than is to be anticipated from this treatment, which predicts $K = 2.5 \times 10^{-5}$ in 100% glycol, assuming r to remain unchanged. From the abnormally low dissociation constant in water and from the ultraviolet absorption spectra of lead chloride solutions, it appears possible that the ionic interaction goes further than can be explained by Coulomb's law, and that in consequence the

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[11] S. B. Knight, J. F. Masi and D. Roesel, This Journal, **661**, 68 (1946).

[12] R. A. Robinson and C. W. Davies, *J. Chem. Soc.*, 574 (1937).

[13] T. Shedlovsky and A. S. Brown, This Journal, **56**, 1069 (1943).

[14] L. Onsager, *Physik. Z.*, **28**, 277 (1927).

[15] C. W. Davies, *J. Chem. Soc.*, 645 (1933).

[16] A. B. Garrett and S. J. Vellenga, This Journal, **225**, 67 (1945).

[17] E. A. Moelwyn-Hughes, "Kinetics of Reactions in Solution," 2nd Edition, Oxford University Press, 1947, p. 198.

[18] W. K. F. Wynne-Jones, *Proc. Roy. Soc.* (*London*), **A140**, 440 (1933).

[19] N. Bjerrum, *K. danske vidensk. Selskab, Math.-fys. Medd.*, **7**, 9 (1926).

equations of Wynne-Jones and Bjerrum are not applicable to this case.

Since this paper was submitted, R. M. Garrels and F. T. Gucker have published a valuable study of aqueous lead chloride solutions [*Chem. Rev.*, **44**, 117 (1949)]. These authors give considerable additional evidence for incomplete dissociation in such solutions, and derive values for *K* of about 0.03 from e.m.f. and conductance data.

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The Liberation of Diazotizable Amine from Pteroylglutamic Acid[1]

BY B. KOFT AND M. G. SEVAG

During a study of the possible role of pteroylglutamic acid (PGA)[2] and *p*-aminobenzoic acid (*p*-ABA) on the inhibition by sulfonamides of the growth of *Lactobacillus arabinosus* strain 17-5 and other bacteria, certain inconsistancies have been observed by us. These inconsistencies suggested the possibility that pteroylglutamic acid was undergoing decomposition in the sterile medium. Certainly, if this were so, it would have considerable bearing on the interpretations of the results of physiological experiments with pteroylglutamic acid.

TABLE I

RATE OF THE DECOMPOSITION OF PTEROYLGLUTAMIC ACID (PGA)

Pteroylglutamic acid solutions[a]	μg *p*-ABA/1000 μg of PGA[c] 0 hr.	20 hr.	40 hr.	64 hr.	120 hr.	168 hr.
1 Distilled water brought to *p*H 7.0	1.62	3.00	3.91	6.36	9.09	11.82
2 *M*/30 phosphate buffer *p*H 7.3	1.72	2.73	4.27	6.36	9.54	12.36
3 *M*/30 Na_2HPO_4, *p*H 9.18	1.36	2.55	4.27	11.36	13.63	81.82
4 *M*/30 KH_2PO_4 *p*H 4.5[b]	1.36	2.18	2.72	3.36	4.32	5.45
5 Growth medium (*p*H 7.0) (used for *L. arabinosus*[3])	2.50	3.82	6.18	14.54	18.86	45.44
6 Medium as in (5) without PGA	0	0	0	0	0	0
7 1 μg *p*-ABA/ml. of *M*/30 phosphate buffer of *p*H 7.3	1	1	1	1	1	1

[a] All solutions were autoclaved for ten minutes at 10 lb. pressure. Systems 1 to 5 contained 500 μg of PGA/ml. The solutions were then kept in a constant temperature incubator at 30°. [b] Pteroylglutamic acid dissolves on autoclaving and a precipitate forms on cooling; determinations for *p*-ABA were made on uniform suspensions. [c] *p*-ABA content of the various systems were determined according to Bratton and Marshall[4] using Klett–Summerson photoelectric colorimeter with filter No. 54, 1 μg of *p*-ABA/10 ml. reaction system gives a colorimetric reading of 22.

The data presented in Table I pertain to this observation.

It can be seen from the table that PGA decomposes at a regular rate on incubation at 30°. A very great rate of decomposition occurs in the sterile medium which has been generally used for the growth of *Lactobacillus arabinosus* 17-5. In this medium, 6.18 to 14.54 μg. of diazotizable amine calculated as *p*-ABA per 1000 μg. of PGA are liberated during an incubation period of from forty to sixty-four hours. The diazotizable component liberated in this medium is significantly greater than the amounts liberated in either aqueous or neutral phosphate buffer solutions of PGA. These results indicate that certain substances in the sterile medium accelerate the decomposition of PGA. The nature of these substances is under investigation.

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[2] The authors are indebted to Dr. C. W. Waller, Lederle Laboratories, Pearl River, New York, for a freshly recrystallized sample of PGA. It contained 1 μg of *p*-ABA/1000 μg of PGA.

[3] T. D. Luckey, G. M. Briggs, Jr., and C. A. Elvehjem, *J. Biol. Chem.*, **152**, 157 (1944).

[4] A. C. Bratton and E. K, Marshall, Jr., *ibid.*, **128**, 537 (1939).

Lithium Borohydride as a Reducing Agent

BY ROBERT F. NYSTROM, SAUL W. CHAIKIN AND WELDON G. BROWN

Lithium borohydride shares with lithium aluminum hydride the property of solubility in ether and other organic solvents. In ether solution it is a more powerful reducing agent than sodium borohydride (in water or alcohol solution) but is milder than lithium aluminum hydride. This combination of properties, together with the prospect of early commercial availability, suggests useful applications for lithium borohydride particularly in the execution of selective reductions.

Solid lithium borohydride has been known to flash on exposure to humid air, some samples being more prone than others, and for this reason transfers of the solid should be conducted in a dry atmosphere. However, solutions of lithium borohydride are relatively insensitive to moisture and in the experiments to be described no special precautions were taken to exclude moisture. Otherwise the procedures followed in lithium borohydride reductions were generally similar to those employed in reductions by lithium aluminum hydride. Tetrahydrofuran proved advantageous as a solvent, since more concentrated solutions of the hydride could be used, *viz.*, 3.5 *M* as compared with 0.5 *M* in diethyl ether.

The aldehydes and ketones (*cf.* Table I) were reduced rapidly at room temperature in exothermic reactions whereas the esters reacted slowly and the mixtures were heated to reflux for periods up to six hours. In the selective reduction of the ketone groups of the keto-esters, and of *m*-nitroacetophenone, ice-bath cooling was employed to enhance selectivity. The attempted selective reduction of ethyl acetoacetate gave rise to a borate complex from which the reduction product could not be