conversion to the vitreous form could be realized by more rapid quenching.

Table II shows the data obtained from a similar study of the devitrified glasses.

TABLE II

EFFECT OF DEVITRIFIED POLYPHOSPHATES ON BARIUM CHLORIDE SOLUTIONS

Amount of Phosphate Added = 2.00 milliequivs. per liter
Concentrations of $Ba^{++}$ in milliequivs. per liter.

| $Na_2O/P_2O_5$ | Initial concn. $BaCl_2$ | Final concn. $Ba^{++}$ | Milliequivs. $Ba^{++}$ removed | Average moles $Ba^{++}$ per mole phos. |
|---|---|---|---|---|
| 1.25 | 5.00 | 3.96 | 1.04 | 2.7 |
| | 3.00 | 1.84 | 1.16 | |
| 1.50 | 5.00 | 3.34 | 1.66 | 2.4 |
| | 3.00 | 1.42 | 1.58 | |
| 1.67 | 5.00 | 2.96 | 2.04 | 2.5 |
| | 3.00 | 1.06 | 1.94 | |
| 1.75 | 5.00 | 3.22 | 1.78 | 6.2 |
| | 3.00 | 1.22 | 1.78 | |

According to the thermal studies of Partridge, Hicks and Smith,[3] the crystalline products are mixtures of sodium triphosphate and crystalline metaphosphate or pyrophosphate, depending on whether the $Na_2O/P_2O_5$ ratio is less than or greater than 5/3. Table III gives a comparison between the results expected from this theory and those actually found.

TABLE III

COMPARISON OF THEORETICAL AND OBSERVED VALUES OF MOLES $Ba^{++}$ PER MOLE PHOSPHATE FOR DEVITRIFIED POLYPHOSPHATE GLASSES

| | Composition of 1 mole of phosphate | | | Moles $Ba^{++}$ per mole phos. | |
|---|---|---|---|---|---|
| $Na_2O/P_2O_5$ | Moles $NaPO_3$ (cryst.) | Moles $Na_5P_3O_{10}$ | Moles $Na_4P_2O_7$ | Calcd. | Obs. |
| 1.25 | 5 | 1 | .. | 2.5 | 2.7 |
| 1.50 | 1 | 1 | .. | 2.5 | 2.4 |
| 1.67 | .. | 1 | .. | 2.5 | 2.5 |
| 1.75 | .. | 2 | 1 | 7.0 | 6.2 |

The agreement is such as to inspire additional confidence in the Partridge, Hicks and Smith formulation of the system $NaPO_3$–$Na_4P_2O_7$.

**Acknowledgment.**—The writer wishes to thank his wife, Eunice S. Campbell, for help with much of the experimental work here described.

## Summary

From a polarographic comparison of barium removal by both glasses and the devitrified products of the system $NaPO_3$–$Na_4P_2O_6$, it is concluded that:

1. Sodium phosphate glasses of $Na_2O/P_2O_5$ ratios between 1 and 2 would, if pure, have all sodiums replacable by barium, and thus behave as though they form a continuous series.

2. Additional support has been given to the phase studies of Partridge, Hicks and Smith on the $NaPO_3$–$Na_4P_2O_7$ system.

MOSCOW, IDAHO RECEIVED MARCH 4, 1946

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE OHIO STATE UNIVERSITY]

# The Conductances of Lead Chloride in Ethylene Glycol–Water Mixtures

BY JOHN W. NORMAN AND A. B. GARRETT

The purpose of this investigation is to present data for the conductances of lead chloride at various low concentrations in pure water, pure ethylene glycol and in four mixtures of ethylene glycol and water consisting of 20, 40, 60, 80% of glycol, and to compare these values with the Onsager equation. Previously measured activity coefficients of lead chloride in these six solvents will be compared with the Debye–Hückel limiting law. We shall be able to show qualitatively some of the reasons for the failure of these theories. The general conclusions which will be reached are that the principal cause of discrepancy between theory and experiment is that the effective dielectric constant in the Debye–Hückel equation is less than the measured macroscopic dielectric constant, and that the effective dielectric constant in the Onsager equation, which applies when an external field is present, is considerably less than the effective dielectric constant in the Debye–Hückel equation.

## Experimental

**Lead Chloride.**—Triple distilled water at 100° was saturated with Mallinckrodt Analytical Reagent lead chloride. After filtration precipitation was brought about by cooling and by the addition of a small percentage of reagent quality concentrated hydrochloric acid. The product was dried at 110° for twenty-four hours and was stored in a desiccator until used.

**Ethylene Glycol.**—Eastman Kodak best grade ethylene glycol (E. K. Co. 133) was dried over anhydrous sodium sulfate and decanted. The dried glycol was distilled twice at reduced pressure. The middle third was kept each time.

**Solutions.**—The solvents and solutions were prepared gravimetrically and the weights were converted to vacuum weights. All the solvents and solutions were in equilibrium with air. The accuracy desired was 0.1%, and all the weight concentrations were determined to well within this accuracy.

**Apparatus.**—The apparatus has been described by Garrett and Vellenga.[1] The frequency of the oscillator was 2000 cycles/second. The detector was an oscilloscope arranged as suggested by Lamson.[2] The cell was cleaned by the method of Morgan and Lammert,[3] and was kept filled with hot triple distilled water for several days to remove adsorbed ions from the cell and electrode surfaces.

## Data

The data are given in Table I and are shown

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(1) Garrett and Vellenga, THIS JOURNAL, **67**, 225 (1945).

(2) Lamson, *Rev. Sci. Instruments*, **9**, 273 (1938).

(3) Morgan and Lammert, THIS JOURNAL, **45**, 1692 (1923).

TABLE I

MOLAR CONDUCTANCES OF LEAD CHLORIDE IN ETHYLENE GLYCOL–WATER MIXTURES

| % Glycol | $\sqrt{\text{Molarity}}$ | $1/R$(corrected) | $\Lambda_m$ |
|---|---|---|---|
| 0 | 0.07316 | 0.04363 | 232.6 |
| | .05258 | .02417 | 249.5 |
| | .01178 | .001378 | 283.6 |
| | .02194 | .004636 | 274.9 |
| | .07049 | .04076 | 234.1 |
| | .02630 | .006577 | 271.5 |
| | .009935 | .009895 | 285.4 |
| | .02128 | .004373 | 275.3 |
| | .015246 | .0022795 | 279.9 |
| | .024453 | .0057115 | 272.6 |
| | .034542 | .011034 | 264.0 |
| | .049009 | .021192 | 250.6 |
| 20 | .02318 | .0031989 | 169.9 |
| | .01390 | .0011859 | 175.1 |
| | .02495 | .0036817 | 168.8 |
| | .02968 | .0051400 | 166.5 |
| | .03783 | .0080860 | 161.3 |
| | .05453 | .015759 | 151.3 |
| | .08553 | .034821 | 134.8 |
| 40 | .01244 | .00056073 | 103.5 |
| | .02203 | .0017069 | 100.4 |
| | .02731 | .0025670 | 98.39 |
| | .03876 | .0049623 | 94.29 |
| | .05504 | .0093506 | 88.09 |
| | .08553 | .016630 | 81.05 |
| 60 | .01285 | .00034776 | 60.12 |
| | .02136 | .00092576 | 57.92 |
| | .02852 | .0015992 | 56.11 |
| | .04079 | .0030917 | 53.02 |
| | .06015 | .0061638 | 48.63 |
| | .09185 | .012647 | 42.78 |
| 80 | .01684 | .00030181 | 30.38 |
| | .02374 | .00057779 | 29.27 |
| | .02916 | .00084352 | 28.32 |
| | .03770 | .0013415 | 26.95 |
| | .05197 | .0023507 | 24.84 |
| | .08322 | .0051798 | 21.34 |
| 100 | .01406 | .000095426 | 13.78 |
| | .01952 | .00017512 | 13.12 |
| | .02418 | .00025607 | 12.50 |
| | .03215 | .00041740 | 11.53 |
| | .04563 | .00075493 | 10.35 |
| | .06147 | .0012309 | 9.296 |

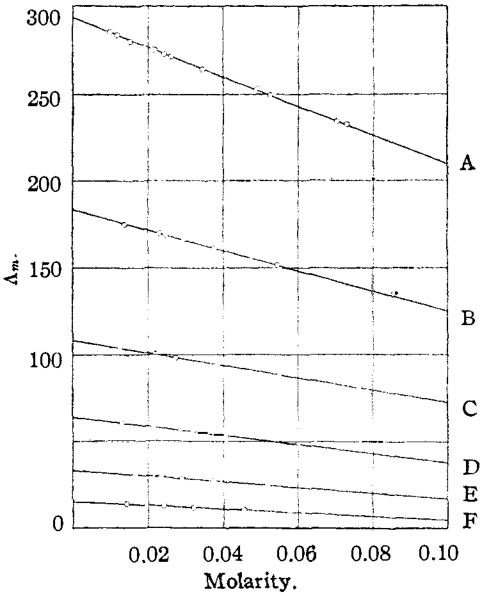

Fig. 1.—Molar conductances of solutions of lead chloride as a function of $\sqrt{\text{molarity}}$ in A, water; B, 20% glycol-80% water; C, 40% glycol-60% water; D, 60% glycol-40% water; E, 80% glycol-20% water; F, 100% glycol.

graphically in Fig. 1 as $\Lambda_m$, the molar conductance, *vs.* $\sqrt{m}$, where $m$ is the molarity of the lead chloride. The densities which are used to convert from weight concentrations to volume concentrations are the densities of the pure solvents.[4] The value of the corrected specific conductance is $L$ (corrected) = $1/R$ (corrected) = $1/R$ (measured) − $1/R$ (solvent). The constant of the conductivity cell used is 0.02854. The slopes and intercepts of these curves, in units consistent with Onsager's equation written in terms of equivalent conductivity and equivalents/liter concentration, are given in Table II. The terms which we shall use are defined by MacInnes.[5] The theoretical slopes, assuming as a first approximation that the transport numbers of the ions do not change with a change in solvent, are also given in Table II. The viscosities of these solvents were taken from Dunstan[6] and the dielectric constants from Akerlof.[7] The value of $w$ in water is obtained as follows: $l_{0^1/_2\text{Pb}^{++}} = \Lambda_0 - l_{0\text{Cl}^-} = 147.0 - 76.34^8 = 70.7$, $n_{^1/_2\text{Pb}^{++}} = 70.7/147.0 = 0.481$, $q = 2(147.0)/3[70.7 + 2(76.34)] = 0.439$, $w = 4(0.439)/(1 + 0.439) = 1.06$. In Table II are also listed the theoretical Debye–Hückel slopes and the actual slopes of the log $\gamma$ *vs.* $\sqrt{\mu}$ curves. The activity coefficients were obtained from the data of Carmody[9] (slightly

TABLE II

EXPERIMENTAL SLOPES AND THEORETICAL SLOPES OF THE DEBYE–HÜCKEL AND ONSAGER CURVES, AND LIMITING EQUIVALENT CONDUCTANCES FOR LEAD CHLORIDE IN ETHYLENE GLYCOL–WATER MIXTURES

| | Experimental slopes | | Theoretical slopes | | |
|---|---|---|---|---|---|
| % Glycol | Debye–Hückel | Onsager | Debye–Hückel | Onsager | $\Lambda_0$ |
| 0 | 1.230 | 310 | 1.012 | 184 | 147.0 |
| 20 | 1.339 | 210 | 1.134 | 120 | 91.8 |
| 40 | 1.536 | 129 | 1.294 | 78.0 | 54.2 |
| 60 | 1.970 | 88.2 | 1.543 | 50.0 | 31.6 |
| 80 | 2.523 | 60.5 | 2.026 | 30.8 | 16.6 |
| 100 | 3.22 | 43.3 | 3.044 | 19.8 | 7.73 |

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(4) Black, Ph. D. Thesis, The Ohio State University, 1942.

(5) MacInnes, "The Principles of Electrochemistry," Reinhold Publishing Corp., N. Y., 1939, Chap. 18.

(6) Dunstan, *J. Chem. Soc.*, **87**, 11 (1905).

(7) Akerlof, THIS JOURNAL, **54**, 4125 (1939).

(8) MacInnes, ref. 5, p. 342.

(9) Carmody, THIS JOURNAL, **51**, 2905 (1929).

modified by Fromherz[10] by a better extrapolation to infinite dilution) in water, and the data of Garrett, Bryant and Kiefer in the glycol–water mixtures and in pure glycol.[11]

## Discussion

Attempts were made to explain these discrepancies between actual and theoretical slopes by the usual methods. The Ostwald dilution law and the Kraus–Fuoss developments failed to yield an ionization constant. Since it was found that the curves were straight in the low concentration region for plots of both $\Lambda$ *vs.* $\sqrt{m}$ and $\log \gamma$ *vs.* $\sqrt{m}$, it is impossible to explain these discrepancies between theory and experiment as due to incomplete dissociation in the usual sense of the term since a constant $\alpha$ will result in any single solvent. In water, $-\log \gamma = 1.012 \sqrt{\mu}$ (theoretical) $= 1.230 \sqrt{\alpha\mu}$ (experimental), or $\sqrt{\alpha} = 1.012/1.230$, and similarly for the Onsager equation. The ionic strength, $\mu$, is in volume concentration units. In order to obtain a basis for more direct comparison between the Onsager and the Debye–Hückel theories we shall use the dielectric constant as the principal variable.

**The Effective Dielectric Constants for the Debye–Hückel and the Onsager Equations.**—The dielectric constant appears in both the Debye–Hückel and Onsager equations. To make possible a discussion of the data in terms of the structures of these solutions and to permit a qualitative explanation of the results we shall equate the theoretical expression for the slopes of these curves, as a function of the dielectric constant, to the observed slope, and shall solve the equations for the effective dielectric constants. These calculated values are listed in Table III. In order to completely discuss these systems in a quantitative manner more definite information is necessary concerning the effective values of viscosities and the actual values of the transference numbers of the ions in these solvents. Such a discussion is not now possible. In order to justify the relative magnitudes of these calculated dielectric constants some information about the structure of these liquid solvents is necessary.

TABLE III

DIELECTRIC CONSTANTS OF ETHYLENE GLYCOL–WATER MIXTURES, AND CALCULATED DIELECTRIC CONSTANTS WHICH PRODUCE CONFORMITY BETWEEN LEAD CHLORIDE CONDUCTANCE DATA AND THE ONSAGER EQUATION, AND BETWEEN LEAD CHLORIDE ACTIVITY COEFFICIENT DATA AND THE DEBYE–HÜCKEL THEORY IN THESE MIXED SOLVENTS

| Glycol, % | Dielectric constants | | |
|---|---|---|---|
| | Measured[a] | Debye–Hückel | Onsager |
| 0 | 78.5 | 69.0 | 45.7 |
| 20 | 72.8 | 65.2 | 41.7 |
| 40 | 66.7 | 59.5 | 37.4 |
| 60 | 59.3 | 50.4 | 34.6 |
| 80 | 49.4 | 42.7 | 26.9 |
| 100 | 37.7 | 36.3 | 19.2 |

[a] Ref. 7.

**Solvents.**—An analysis of the known structure of the solvents may be useful in attempting to explain the above discrepancies. Pure water consists of a very open, tetrahedral structure.[12] The combination of the individual electric moment vectors of the molecules to form a vector for a given group of molecules at a given time results in a dielectric constant which is much less than would be expected for water if each molecule acts as an independent unit. The average size of these groups and the magnitude of their electric moments determine the magnitude of the effective dielectric constant between the ions. If the groups are large, the dielectric constant which effectively determines the forces between ions will be smaller than the measured dielectric constant because the number of these groups in the region between the ions will be relatively small. However, the spatial extent of this region between the ions in which an electric moment vector must be present to influence the force between the ions also depends on $z/r$, where $r$ is the ionic radius and $z$ is the ionic charge. Significant deviations of the effective dielectric constants from the measured ones will be expected only in cases which involve small, highly charged ions.

In glycol the facts that the electric moment is greater than that of water and that the dielectric constant is less than that for water suggest that the individual molecular electric moments are cancelled more effectively in glycol than in water. This cancellation can occur if more molecules are arranged in small units, such as one consisting of two molecules, so that the moments are practically cancelled. In this case the number of units which have a moment which contributes to the dielectric constant of the medium is much larger than in water. Hence, the effective dielectric constant should not differ significantly from the macroscopic dielectric constant in glycol, and the differences between these quantities should decrease as the glycol percentage increases. Table III shows that these general conclusions are confirmed.

The difference between the dielectric constants in the presence of a field, which were calculated by use of the Onsager equation, and in the absence of a field, which were calculated by use of the Debye–Hückel equation, is large. This should be true because the constants depend on the number of electric moment vectors which are free to orient themselves in the fields of the ions, and if an external field is present, the vectors are already held in a more or less constrained condition so that the effect of the ions on the orientation of the vectors is decreased. Hence, the dielectric constant in the presence of a field is less

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[10] Fromherz, *Z. physik. Chem.*, **A153**, 376 (1931).

[11] Garrett, Bryant and Kiefer, THIS JOURNAL, **65**, 1905 (1943).

[12] Bernal and Fowler, *J. Chem. Phys.*, **1**, 515 (1933).

than in the absence of a field. However, no attempt to estimate the theoretical relative magnitude of these dielectric constants can now be made.

## Summary

1. Conductances of lead chloride have been measured in ethylene glycol–water mixtures which contain 0, 20, 40, 60, 80 and 100% glycol. The precision was 0.1%. The limiting conductances and the slopes were determined to an estimated precision of 0.2%.

2. Activity coefficients of lead chloride in these solvents have been compared with the Debye–Hückel limiting law by comparing the theoretical slopes of the limiting equation to the experimental slopes and the measured conductances have been compared with the Onsager equation by comparing the theoretical slopes with the experimental slopes.

3. The discrepancies between theory and experiment have been attributed to a difference between the macroscopic and microscopic dielectric constants of the solutions, and the effective microscopic dielectric constants have been calculated from the experimental slopes of the curves in the cases of the Debye–Hückel and Onsager equations.

4. The known structural properties of these solvents have been used to show that such differences between macroscopic dielectric constants and microscopic dielectric constants in the presence and the absence of a field are qualitatively consistent with these structural properties.

COLUMBUS, OHIO RECEIVED AUGUST 16, 1946

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY, THE OHIO STATE UNIVERSITY]

# Solvent Effect in the Curtius Rearrangement of Benzazide

BY MELVIN S. NEWMAN, SAMUEL HUNT LEE, JR.,[1] AND A. B. GARRETT

A study of the effect of the solvent on the rate of decomposition of benzazide is presented in this paper. This study was undertaken in an attempt to correlate the solvent effect on the kinetics of the reaction with some property of the solvents involved and also to seek for any further evidence as to the mechanism of the reaction. During this investigation we also observed unexpected reactions with nitromethane, acetic acid, butylamine, morpholine and piperidine.

In this rearrangement[1a] the R group shifts

$$RCON_3 \longrightarrow RNCO + N_2$$

from carbon to nitrogen in an irreversible intramolecular reaction exhibiting first order kinetics. The known experimental facts[2] indicate that the R group never leaves the influence of the molecule. The postulate[3] that on migration the R group carries with it the electrons which bind it to the carbon is in harmony with these facts and with the activated complex theory.[4]

## Experimental

**Materials Benzazide.**—One preparation[5] (70% of theoretical) was made from nitrous acid and benzhydrazide.[6] The white needles of the lachrymatory azide, after two recrystallizations each from acetone and petroleum ether (30–60°), melted at 27.0–27.5°.

Another preparation (50% of theoretical) was made from benzoyl chloride and sodium azide[7b] and recrystallized from acetone and petroleum ether using a Dry Ice-acetone bath and inverted filtration (suction through a sintered glass funnel) as was done before. A cooling curve for this product, also white needles, showed the freezing point to be 27.2° and attested to the purity of the sample. A melting curve on the same sample indicated a melting point of 27.2°. Plates from acetone melting at 32° have been reported,[1,7] but a m. p. of 26.0–28.0° has also been found.[8] In the present work plates were obtained only in the presence of water and melted at 26.5–27.4°, a mixed m. p. with the needles being 27.0–27.5°.

**Anilinium Chloride.**—Concentrated hydrochloric acid was added to purified aniline and the salt, precipitated by the addition of ether and recrystallized twice from hot water, melted at 196.4–197.4°.

**2,4-Dinitrophenylpyridinium Chloride.**—This was prepared from 1-chloro-2,4-dinitrobenzene and pyridine[9] and recrystallized three times from boiling ethanol to give needles with a slight cream color. No m. p. was taken because of the wide melting range and decomposition reported.[10]

**Solvents.**—In general, the solvent, in as pure a grade as could be obtained readily, was thoroughly dried and fractionated in a glass-helices-packed column at reflux ratios of 10:1 to 20:1. The middle, constant-boiling fraction was saturated with nitrogen, purified by passing through Fieser solution,[11] anhydrous calcium chloride, and phosphoric oxide, and the purified solvent was stored under this nitrogen in bottles paraffined to prevent the introduction of moisture. Solvents of a water white color were obtained in all cases.

**Apparatus.**—The reactions were run in a large, Thyraton-controlled[12] oil thermostat which gave temperature

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[1] Du Pont Fellow, 1944. Material herein presented contained in the Ph.D. thesis of Samuel Hunt Lee, Ohio State University, August 1944. Present address: Department of Chemistry, University of Texas, Austin, Texas.

[1a] Curtius, *Ber.*, **27**, 778 (1894); *J. prakt. Chem.*, [2] **52**, 210 (1895).

[2] Wallis in Gilman, "Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1943, Chaper 12.

[3] Whitmore, THIS JOURNAL, **54**, 3274 (1932); Hauser, *ibid.*, **62**, 933 (1940).

[4] Glasstone, Laidler and Eyring, "The Theory of Rate Processes," McGraw-Hill Book Co., Inc., New York, N. Y., 1941, p. 86.

[5] Gattermann and Wieland, "Laboratory Methods of Organic Chemistry," The Macmillan Co., New York, N. Y., 1937, p. 153.

[6] Curtius and Struve, *J. prakt. Chem.*, [2] **50**, 295 (1894).

[7] (a) Curtius and Hofmann, *ibid.*, [2] **53**, 518 (1896); (b) Barrett and Porter, THIS JOURNAL, **63**, 3434 (1941).

[8] Vasilevski, Bloshtein and Kustrya, *J. Gen. Chem.*, U. S. S. R., **5**, 1652 (1935).

[9] Vongerichten, *Ber.*, **32**, 2571 (1899).

[10] Zincke, Heuser and Moeller, *Ann.*, **333**, 296 (1904).

[11] Fieser, THIS JOURNAL, **46**, 2639 (1924).

[12] Garrett, *Ind. Eng. Chem., Anal. Ed.*, **10**, 324 (1938).