[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

Formation of Hydrazine from *t*-Butyl Hypochlorite and Ammonia[1]

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t-Butyl hypochlorite has been shown to react with aqueous ammonia to produce hydrazine. The yield of hydrazine is dependent upon three factors: (a) the molar ratio of ammonia to hypochlorite; (b) the presence of a permanent base such as sodium hydroxide; and (c) the use of an inhibitor such as gelatin. The presence of monochloramine as the first product of reaction between equimolar quantities of ammonia and *t*-butyl hypochlorite has been demonstrated spectrophotometrically, and by reaction with *p*-chlorobenzaldehyde to yield *p*-chlorobenzalchlorimine. The mechanism by which hydrazine is formed from monochloramine and excess ammonia in the presence of hydroxyl ions is believed to entail formation of the chloramide ion as the active intermediate.

Introduction

The reaction of hypochlorites of the alkali and alkaline earth metals with ammonia and ammonia derivatives has long been known to lead to compounds with nitrogen-chlorine bonds. Monochloramine, produced by the reaction between hypochlorites and ammonia in equimolar quantities in basic solution, was shown by Raschig[2] to be capable of reacting with further quantities of ammonia to produce hydrazine. This latter reaction, the so-called Raschig synthesis of hydrazine, is the basis of the present commercial method for the production of hydrazine. One of the major difficulties attending a detailed study of the mechanism of the Raschig synthesis is that encountered in evaluating the effects due to sodium chloride and sodium hydroxide inevitably present in solutions of sodium hypochlorite. A search was therefore undertaken for an oxidant that could be prepared easily in a concentrated form, free from the impurities usually found in sodium hypochlorite solutions. *t*-Butyl hypochlorite was selected as fulfilling the requirements for such a compound for several reasons: (a) it can be prepared in a high degree of purity; (b) it is stable at room temperature if stored in subdued light; (c) it provides a source for the introduction of high concentrations of the hypochlorite group, and (d) it was hoped that it would react in a manner similar to sodium hypochlorite.

t-Butyl hypochlorite has been found to serve both as an oxidizing agent and as a chlorinating agent in previous investigations.[3] Its further usefulness as an N-chlorinating agent is described for the first time in the present paper. *t*-Butyl hypochlorite has been found to react with ammonia to yield hydrazine. The yield of hydrazine, as in the Raschig synthesis has been found to depend upon (a) the molar ratio of ammonia to hypochlorite, (b) the presence of a permanent base such as sodium hydroxide, and (c) the use of an inhibitor such as gelatin.

Experimental

Chemicals and Solutions Employed.—All chemicals used were of the C.P. grade. *t*-Butyl alcohol was a Shell product and was distilled before use. The inhibitor was Schaar pure gelatin powder which was weighed directly into the reaction vessels. Aqueous ammonia was prepared by dilution of concentrated ammonia; the ammonia content was determined by comparison with standard hydrochloric acid. Standard potassium iodate was prepared by dilution of the desired amount of the solid. Thiosulfate was standardized against the potassium iodate, starch being used as the indicator. Aqueous sodium hydroxide was compared with standard hydrochloric acid.

Preparation and Use of *t*-Butyl Hypochlorite.—*t*-Butyl hypochlorite was prepared as previously described.[3] The product was analyzed as follows: Small, thin-walled bubbles were blown on the end of small diameter tubing which had been drawn out into a capillary. One drop (*ca.* 8 mg.) of the hypochlorite was drawn into the bubble by cooling the previously warmed sample tube after the tip had been introduced into the hypochlorite. The weighed sample tube was then broken beneath the surface of aqueous, acidified (acetic acid) potassium iodide solution; the iodine liberated by the hypochlorite was determined with thiosulfate. Analysis of typical preparations showed the hypochlorite to be 98% pure, based on the active chlorine content.

The hypochlorite *per se* was not used in the present study since it is insoluble in water and reacts vigorously with aqueous ammonia. A solution of *t*-butyl hypochlorite in *t*-butyl alcohol was employed as the oxidizing agent. The hypochlorite content was *ca.* 0.5 *M* and was determined before use by iodometric analysis.

Proof of Hydrazine Formation and Method of Analysis for Hydrazine.—The formation of hydrazine from aqueous ammonia and *t*-butyl hypochlorite was demonstrated by the isolation and identification of both salicylalazine and benzalazine, the former melting at 215° uncor. (lit. 214°) and the latter at 92° uncor. (lit. 93°). Hydrazine was determined quantitatively by the indirect iodate method.[4] It was found that the direct titration with iodate in strongly acidic media did not give reliable results in the presence of *t*-butyl alcohol.

Monochloramine from *t*-Butyl Hypochlorite and Ammonia. (a).—Fifty ml. of 0.455 *M* *t*-butyl hypochlorite (22.8 mmoles) in *t*-butyl alcohol was placed in a separatory funnel with cracked ice. Twelve ml. of 2.15 *M* ammonia (25.8 mmoles) was added. Dense white fumes appeared as the yellow color of the hypochlorite disappeared. The cold mixture was quickly poured into 50 ml. of a cold ether solution of *p*-chlorobenzaldehyde. The mixture was shaken vigorously in an ice-bath and the aqueous layer separated and placed in the ice chest. The white precipitate which formed in about three hours was identified as *p*-chlorobenzalchlorimine and was recrystallized as previously described,[5] melting at 79–80° uncor. (lit. 79–80°). *Anal.* Calcd. for ClC_6H_4CHNCl: Cl, 20.39. Found: Cl, 20.3.

(b).—Equimolar quantities of *t*-butyl hypochlorite and aqueous ammonia were mixed in *t*-butyl alcohol. The absorption spectrum of the resulting solution was determined with the Cary Recording Spectrophotometer, using the alcohol as the blank. A maximum was observed at 2470 Å. The absorption of a solution of monochloramine, prepared from equimolar amounts of aqueous ammonia and sodium hypochlorite, in a borate buffer of *p*H 8.9, showed a maximum at 2430 Å. These maxima are in good agreement with the observations of Metcalf[6] who reports that monochloramine in the *p*H range 7.5–14 absorbs at 2450 Å.

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[1] Presented at the 124th meeting of the American Chemical Society, Chicago, Illinois, September 6–11, 1953.

[2] F. Raschig, "Schwefel- und Stickstoffstudien," Verlag Chemie, G.m.b.H., Leipzig, Berlin, 1924.

[3] See, *e.g.*, (a) H. M. Teeter, R. C. Bachmann, E. W. Bell and J. C. Cowan, *Ind. Eng. Chem.*, **41**, 849 (1949); (b) D. Ginsberg, *Experientia*, **7**, 95 (1951).

[4] W. C. Bray and E. J. Coy, THIS JOURNAL, **46**, 858 (1924).

[5] C. R. Hauser, M. L. Hauser and A. Gillaspie, *ibid.*, **52**, 4158 (1930).

[6] W. S. Metcalf, *J. Chem. Soc.*, 148 (1942).

Experimental Procedure.—The same procedure was used in all studies designed to determine the effect of such variables as the NH_3/t-BuOCl ratio, the NaOH/*t*-BuOCl ratio and the influence of gelatin on the yield of hydrazine. In evaluating the effect of the NH_3/t-BuOCl ratio the following solutions were prepared: soln. 1, 120 ml. of a 1% by wt. gelatin-water mixture; soln. 2, predetermined quantities of standard ammonia (0.598 *M*) and distilled water to make a total volume of 40 ml.; soln. 3, 50 ml. of the hypochlorite solution, prepared by adding *t*-butyl hypochlorite (98%) in the desired amount to *t*-butyl alcohol. Solutions 1 and 2 were placed in a 500-ml. 3-necked flask equipped with a condenser and a stirrer, the entire apparatus being mounted on a steam-bath. The stirrer was set in motion, and solution 3 was added. The reaction mixture was then heated (temperature of the mixture reached about 95°) under reflux and stirring for 20 minutes, cooled, made up to 250 ml., and a 50-ml. aliquot withdrawn and analyzed quantitatively for hydrazine by the indirect iodate method. The yield of hydrazine is based upon the amount of hypochlorite taken. Individual runs could be reproduced to within 2% of the reported yields. Experimental data are depicted graphically in Fig. 1.

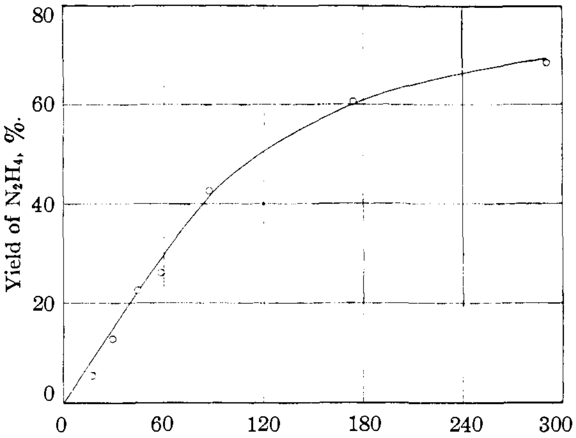

Fig. 1.—Effect of mole ratio of NH_3 to *t*-BuOCl on yield of $N_2H\cdot$; NH_3 concn. constant.

For studies designed to determine the effect of added base, the procedure was the same. Sodium hydroxide was introduced in the desired amount in the form of an aqueous solution, either 0.1 or 0.5 *M*. To determine the effect of gelatin, the reaction vessel was charged with the predetermined quantities of ammonia, water, and sodium hydroxide. A weighed amount of gelatin was then added and the mixture allowed to stand overnight to form a homogeneous solution.

In all of the studies, the total volume, the heating period, the method of analysis and the concentration of the reactants were held constant. Only the specific variable being investigated, *e.g.*, the effect of added base, the effect of gelatin, or the molar ratio of ammonia to hypochlorite, was changed from run to run.

Discussion of Results

That the yield of hydrazine is dependent upon the molar ratio of ammonia to *t*-butyl hypochlorite is immediately evident from Fig. 1. Yields of hydrazine approaching 70% could be realized when the ammonia to hypochlorite ratio approached 300. This observation is strictly analogous to the case for ammonia and sodium hypochlorite[7] and indicates that *t*-butyl hypochlorite does indeed function as does sodium hypochlorite in a Raschig-type synthesis. The formation of monochloramine when equimolar quantities of *t*-butyl hypochlorite and ammonia are allowed to react demonstrates that the alkyl group of *t*-butyl hypochlorite does not alter the behavior of the hypochlorite group in the molecule insofar as its oxidizing action toward ammonia is concerned.

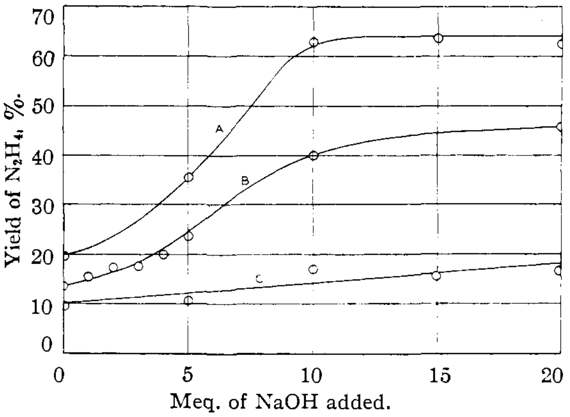

Fig. 2.—Effect of OH^- concn. on yield of N_2H_4 at constant mole ratio of NH_3 to *t*-BuOCl: A, 33:1, B, 13.9:1; C, 3.60:1.

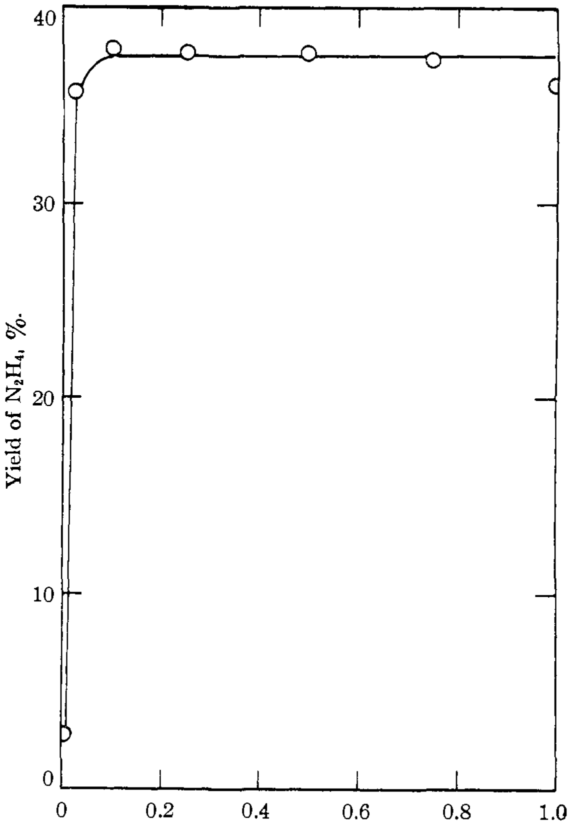

Fig. 3.—Effect of gelatin on yield of N_2H_4. Mole ratio of NH_3 to *t*-BuOCl constant at 15.3:1.

The effect of an inhibitor such as gelatin in the synthesis of hydrazine by a Raschig-type process is also very striking (see Fig. 3). These results are not entirely unexpected, for previous investigations[8,9] have also shown the dependence of the

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[7] L. F. Audrieth and B. A. Ogg, "The Chemistry of Hydrazine," John Wiley and Sons, Inc., New York, N. Y., 1951, p. 31.

[8] R. A. Joyner, *J. Chem. Soc.*, **123**, 1114 (1923).

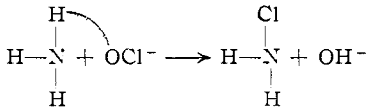
[9] M. Møeller, *D. Kgl. Danske. Vidensk. Selsk, Math-fys. Medd.* **XII**, 16 (1934).

yield of hydrazine on the presence of an inhibitor. It is now well established that the inhibitor functions to remove traces of heavy metal cations, especially copper, which appear to catalyze either a secondary reaction between the chloramine and hydrazine or the decomposition of chloramine by some yet unknown route.[10]

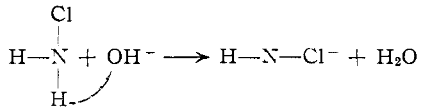
What is most significant and what has been more or less taken for granted up to the present time is the necessity for the presence of a permanent base, such as sodium hydroxide, in order to realize substantial yields of hydrazine from ammonia and hypochlorite[11] (see Fig. 2). The data presented by the authors, together with accumulated information in the literature dealing with the ammonia–hypochlorite reaction demonstrate that only in alkaline solution does chloramine react with ammonia to yield hydrazine.

Chloramine may be regarded as an ammono-hypochlorous acid, the nitrogen analog of hypochlorous acid. Replacement of the OH group in HOCl by its nitrogen equivalent, the amide group, results in a corresponding decrease (with respect to water as the solvent) in the acid strength of the nitrogen analog. The *pK* value for chloramine as an acid has been estimated to be 15 ± 2.[12] It is only in strongly alkaline solutions, therefore, that actual or transient formation of a chloramide ion, $NHCl^-$, may be expected.

It is therefore proposed that the active intermediate in the hydrazine synthesis is the chloramide ion, $NHCl^-$, which may result in a manner analogous to that proposed by Mauger and Soper[13] in their studies on the mechanism of N-chlorinations,



$$\mathrm{H{-}\overset{\displaystyle H}{\underset{\displaystyle H}{N}} + OCl^- \longrightarrow H{-}\overset{\displaystyle Cl}{\underset{\displaystyle H}{N}} + OH^-} \qquad (A)$$



$$\mathrm{H{-}\overset{\displaystyle Cl}{\underset{\displaystyle H}{N}} + OH^- \longrightarrow H{-}N{-}Cl^- + H_2O} \qquad (B)$$

Chloramine is believed to form as the result of an ionic reaction involving the hypochlorite ion in accordance with equation A. An inductive effect of the negative chlorine atom attached to the nitrogen atom labilizes an N–H bond which can then dissociate the proton in strongly alkaline solution to yield the chloramide ion. The same ultimate result would occur if the equation were written as

$$NH_2Cl + OH^- \longrightarrow NHCl^- + H_2O \qquad (C)$$

The chloramide ion then undergoes the slower reaction with typical molecular bases such as ammonia, amines, water (and the alcohols?) in accordance with the type equation

$$H{-}N{-}Cl^- + B \longrightarrow HN \longleftarrow B + Cl^- \ (D)$$

where B = NH_3, RNH_2, R_2NH, H_2O and ROH (?).

The first step in the Raschig synthesis, therefore, involves the reaction between equimolar quantities of ammonia and hypochlorite, in alkaline solution, to give chloramine, as shown in equation A above. Chloramine may then be thought of as reacting with hydroxyl ions to form the proposed chloramide ion as shown in either B or C. In this respect, it becomes apparent that the proposed mechanism for the Raschig synthesis is similar to that which has been established for the well-known Hofmann rearrangement in which formation of the $RCONCl^-$ ion as the active intermediate has been demonstrated (a) by the isolation of alkali metal salts and (b) by kinetic studies which show that the rearrangement processes are a function of the OH^- concentration.[14] As in the Hofmann rearrangement, it may then be postulated that the second step involves either a direct reaction of the molecular base with the chloramide ion, as shown in equation D, or the transient formation of a very reactive imide molecule which could then condense as implied by the equations

$$NHCl^- \longrightarrow [NH] + Cl^- \qquad (E)$$

$$[NH] + B \longrightarrow HN \longleftarrow B \qquad (F)$$

Unlike the Hofmann reaction, where rearrangement of the acylated imide molecule, RCON, occurs, no such process can take place when only imide itself is involved.[15]

No definitive choice is possible at this time with respect to either of the processes represented by the type equations D and F. The proposed mechanism suggests that not only ammonia, but also substituted amines and even water (and possibly alcohols) should be capable of reacting with chloramine to form hydrazine, substituted hydrazines, hydroxylamine (and possibly O-substituted hydroxylamines), respectively. One might therefore anticipate that the base strengths of each of these species would also influence the ease with which each of these reactions occurs. McCoy[16] has shown that chloramine in hot strongly alkaline solutions reacts with the solvent water to yield hydroxylamine whose formation was verified by the isolation of cyclohexanone oxime. These theoretical considerations have been given added credence by findings in our laboratory that alkyl hydrazines result when strongly basic amines are added to cold alkaline solutions of chloramine. It has therefore been possible to modify the Raschig synthesis and adapt it to the preparation of N-substituted hydrazines.

Acknowledgment.—The authors are indebted to Dr. M. Tecotzky for carrying out the spectrophoto-

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(10) Unpublished work in this Laboratory demonstrates conclusively that the decomposition of chloramine in aqueous solution is catalyzed markedly by presence of trace amounts of metal ions, notably copper.

(11) Unpublished results from our laboratory have shown that the presence of sodium hydroxide also increases the yield of hydrazine when aqueous ammonia and pure chloramine solutions, in the presence of gelatin, are allowed to react.

(12) Unpublished results by W. L. Jolly. A comparative method was used to arrive at this figure by consideration of the relative strengths in water of pairs of aquo and ammono acids.

(13) R. P. Mauger and F. G. Soper, *J. Chem. Soc.*, 71 (1946).

(14) R. Adams, "Organic Reactions," Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1946, Chapter VII.

(15) The suggestion that imide is the reactive intermediate in the hydrazine synthesis was first advanced by Raschig (ref. 2) who found that hot strongly alkaline solutions of chloramine decompose to give substantial quantities of hydrogen, whose formation could only be explained by dimerization to diimide and attendant decomposition into nitrogen and hydrogen.

(16) R. E. McCoy, paper presented at the 124th A.C.S. Meeting, Chicago, Ill., Sept. 6–11, 1953.

metric studies on chloramine. This investigation was carried out under the sponsorship of the Office of Ordnance Research as one phase of a fundamental study of the synthesis of hydrazine, Contract No. DA-11-022-ORD-828.

URBANA, ILLINOIS

[CONTRIBUTION FROM THE NAVAL ORDNANCE LABORATORY]

The Limiting Current on a Rotating Disc Electrode in Potassium Iodide–Potassium Triiodide Solutions

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The theory of concentration polarization proposed by B. Levich (1942) for a rotating disc electrode was extended to the ternary system KI–KI$_3$ with KI present in large excess. Using platinum electrodes, the predicted linear relationship between the steady state limiting current and the square root of the angular speed of the disc was verified. These measurements were made at angular speeds such that the critical Reynolds number was not exceeded. The diffusion coefficient of the triiodide ion was calculated from these data.

Introduction

In a solution with imposed steady state laminar flow conditions, ions are transferred to an electrode by three principal mechanisms: (a) migration, (b) diffusion and (c) convection due to mechanical stirring. At a polarized electrode in such a solution containing an excess of indifferent electrolyte, the current is fixed by the rate of diffusion of the reacting ion species to the electrode. Over a limited voltage range, the current is dependent only on the steady state hydrodynamic stirring conditions which determine the effective thickness of the diffusion boundary layer at the electrode surface.

Equations for the steady state rate of diffusion at a rotating disc electrode have been solved by Levich[1,2] for a binary electrolyte system. In the present study, these equations have been extended to the system KI–KI$_3$, with KI as an indifferent electrolyte. Experimental data have confirmed the relationships derived for this system. The data also have been used to calculate the diffusion coefficient of the triiodide ion.

Experimental

Preparation of Materials.—Boiled, distilled water was used in the preparation of all solutions.

Using reagent grade KI, a 0.1 *N* stock solution was prepared and oxygen removed by bubbling with tank nitrogen which was equilibrated with 0.1 *N* KI prior to introduction into the stock solution. The KI$_3$ complex was obtained by dissolving reagent grade iodine in a concentrated KI solution and diluting so that the resultant solution was 0.1 *N* KI and 0.0601 *N* I$_2$. The water used in preparing the complex was also bubbled with tank nitrogen.

Apparatus.—The platinum rotating disc cathode, approximately 2 cm. in diameter, was mounted on a shaft connected to a variable speed motor. The anode consisted of platinum foil whose area was about 20 times that of the cathode and was placed 5 cm. from it. A platinum wire potential probe was positioned near the disc. The vessel containing the electrodes and probe held 600 ml. of electrolyte and was approximately 9 cm. in diameter. Nitrogen was led into the vessel so that a positive pressure was exerted above the electrolyte at all times.

Kinematic viscosity measurements of the 0.1 *N* KI solution at room temperature was made using an Ostwald–Fenske viscometer.[3]

Procedure.—Current and voltage measuring apparatus was connected to the electrolysis cell as shown in Fig. 1. Known amounts of iodine complex were added to the KI solution by means of calibrated pipets, and the voltage across the diffusion boundary layer of the cathode was maintained at 0.4 volt for all readings by compensating for the ohmic drop in the solution. Limiting current values were then read for each concentration of iodine complex using various cathode speeds. All measurements were made in a temperature-controlled room.

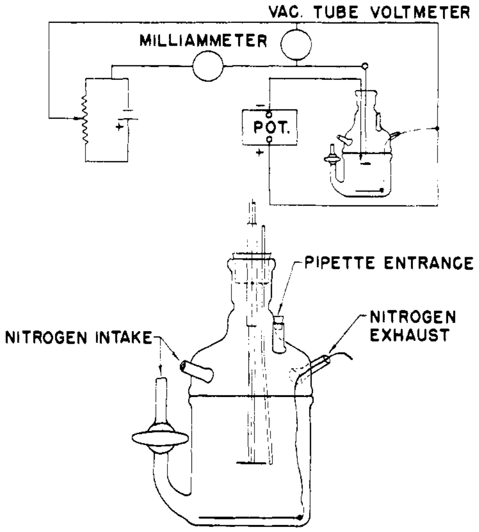

Fig. 1.—Electrolysis cell and circuit connections

Theoretical

The steady state equation of transfer due to convection, diffusion and migration of ions of type *i* is given by[1]

$$\mathrm{v}\cdot\nabla c_{\mathrm{i}} = D_{\mathrm{i}}\nabla^2 c_{\mathrm{i}} + \frac{n_{\mathrm{i}}eD_{\mathrm{i}}}{kT}\nabla\cdot(c_{\mathrm{i}}\nabla\phi) \qquad (1)$$

where $\mathbf{v}$ is the velocity of convection; c_i is the concentration of ions of type i; D_i is the diffusion constant; n_i is the ion valence; e is the unit electronic charge; k is the Boltzmann constant; T is the absolute temperature; ϕ is the potential at any point in the electrolyte.

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(1) B. Levich, *Acta Physicochim. U.R.S.S.*, **17**, 257 (1942). Review of the above article by C. W. Tobias, M. Eisenberg and C. R. Wilke, *J. Electrochem. Soc.*, **99**, 359C (1952).

(2) S. Goldstein, "Modern Developments in Fluid Dynamics," Vol. 1, Oxford Press, New York, N. Y. 1938, pp. 110–113.

(3) M. R. Cannon and M. R. Fenske, *Ind. Eng. Chem., Anal. Ed.*, **10**, 297 (1938).