hydration in the association process while the sulfates listed in Table II do not. The first group should be particularly susceptible to the formation of covalent complexes in solution.

Not all the available data in aqueous solution can be assigned satisfactorily to one or other of these types of behavior. Particularly surprising are the hydroxides of the alkaline earth metals[19] which do not conform to equation 1 in spite of other evidence[20] that they exhibit the same type of "localized hydrolysis" as other salts of weak acids. The assumptions made in the consideration of the hydration cycle are no doubt an over-simplification in such systems.

Acknowledgment.—The author wishes to thank Professor R. M. Fuoss for some very helpful suggestions.

CAMBRIDGE, MASS.

---

[19] F. G. R. Gimblett and C. B. Monk, *Trans. Faraday Soc.*, **50**, 965 (1954).

[20] R. M. Diamond, THIS JOURNAL, **80**, 4808 (1958).

[CONTRIBUTION NO. 891 FROM THE DEPARTMENT OF CHEMISTRY, INDIANA UNIVERSITY]

Conductance Measurements of the Halides, Nitrates and Nitrites of the Alkali Metals in Anhydrous Ethanolamine

BY PHILLIP W. BREWSTER,[1] FREDERIC C. SCHMIDT AND WARD B. SCHAAP

RECEIVED FEBRUARY 16, 1959

Conductances of a number of salts of the alkali metals have been measured in anhydrous ethanolamine at 25°. Linear plots of Λ *vs.* $c^{1/2}$, approach the Onsager tangent from below (catabatic phoreograms in Fuoss Nomenclature[2]) are obtained up to about $c = 0.005\ M$. Owing to the magnitude of the solvent correction, the data do not allow extrapolation by the Fuoss *x–y* plot. The data, however, give good extrapolations by the Fuoss–Shedlovsky procedure and Λ_0 and $1/K_D$ values determined by this method are reported. The results reported here also do not confirm the behavior obtained by Briscoe and Dirske for the salts in this solvent. A reason for this discrepancy is suggested. Also, these results are not in agreement with results recently published by Muniyapan and Anjaneyalu on the conductances of solutions of alkali metal and silver nitrites. The limiting conductance data afford numerous confirmations of the Kohlrausch Law of independent ion migration in anhydrous ethanolamine solutions. The usual trend is observed in the limiting equivalent conductances of the salts of a given anion type, *i.e.*, Li < Na < K. However, for a given cation, the conductance increases in the order I < Br < Cl. This is exactly opposite to the effect observed in anhydrous N-methylformamide and in the substituted acetamides.

Introduction

Briscoe and Dirkse[3] have reported conductances at various concentrations of a number of quaternary picrates and halides. These authors conclude from the slope of the Λ *vs.* $c^{1/2}$ plots (phoreograms), typical of those obtained in solvents of low dielectric constant, that all salts are weakly ionized in ethanolamine, or in terms of Fuoss nomenclature[2] these salts behave as weak ionogens. Extrapolation of the very catabatic phoreograms by the method of Fuoss led in some cases to limiting equivalent conductances in excess of 2000. No explanation was given for this apparently remarkable behavior which would certainly seem to involve an entirely new conductance mechanism, since the viscosity of ethanolamine is about eight times that of water. The weakly ionized character of the salts was attributed to the high viscosity of the solvent. The possibility that the viscosity of the solvent could affect the dissociation of a species in solution seemed unlikely to the present authors. Therefore, it was of interest to re-investigate the properties of ethanolamine as a conducting solvent, using initially the simple alkali metal salts instead of the high molecular weight quaternary ammonium salts.

Experimental

Preparation of the Solvent.—Eastman "White Label" ethanolamine was used throughout this investigation. The slight decomposition of the solvent and the resulting formation of conducting impurities when distilled at atmospheric pressure rendered imperative a purification by vacuum distillation. A suitable desiccant was not found for the solvent, so that a straight vacuum distillation at about 5 mm. pressure was used to purify all solvent used in the measurements. One distillation of the purchased ethanolamine gave a specific conductance of about 10^{-5}. It seemed impossible to obtain a solvent of lower conductance. Thus it was concluded that this relatively high conductance was due to remarkably high self-ionization (autoprotolysis) of the solvent. The distillations were carried out on three-liter batches, the first 200 ml. and the last 300 ml. being rejected as precaution. However, failure to reject forerun portions of this size causes only a slight increase in the solvent correction. It would seem that the main impurities in the crude amine are non-volatile salt-like substances which remain in the stillpot.

The following data for ethanolamine were used in the calculations: density, 1.0117; viscosity, 0.19346 poise; dielectric constant, 37.72.[3] Values of constants used in the evaluation of the Onsager slopes were taken from those of Fuoss and Shedlovsky.

Chemicals.—The salts, Baker's Reagent Grade, were powdered and dried at 150–200° and finally over phosphorus(V) oxide *in vacuo*. The samples of NaCl and KCl were Johnson–Matthey "*Spec pure*" reagents. These were similarly powdered and dried. It was found that recrystallization of the Baker salts produced no detectable change in conductance. The silver nitrite was C.P. material and was twice recrystallized from conductivity water in the dark. This salt was dried in the dark *in vacuo*. The pale yellow-needle-like crystals of silver nitrite dissolved in ethanolamine to give colorless solutions.

Conductance Cells.—The cells used were of two types and were made of Pyrex glass in this Laboratory. Platinum electrodes were sealed into the cell with uranium glass, giving a seal which did not leak.

Cells of the first type were similar in design to those used by Hibbard and Schmidt.[4] These cells had a capacity of about 120 ml. The solute was added portionwise to the cell

---

[1] Address all correspondence to F. C. Schmidt. This investigation was carried out under contract No. AT(11-1)256 and was presented at the 134th meeting of the American Chemical Society in Chicago, September, 1958.

[2] R. M. Fuoss, *J. Chem. Ed.*, **32**, 527 (1955).

[3] W. T. Briscoe and T. P. Dirkse, *J. Phys. Chem.*, **44**, 388 (1940).

[4] B. B. Hibbard and F. C. Schmidt, THIS JOURNAL, **77**, 225 (1955).

in weighed cups. An atmosphere of nitrogen was maintained in the cell. Stirring was accomplished magnetically. This type of cell was used in those cases where the salt was insufficiently soluble to make up a concentrated solution. No Parker effect was noticed using this type of cell.

The second type cell was similar to the bottle type of Dippy[5] and consisted of a cylinder 20 cm. high and 6 cm. in diameter with the platinum electrodes 4 cm. apart in a bulge on the side of the cylinder. These electrodes were 1.5 cm. in diameter and were set 5 cm. from the base of the cell. The cell had a working volume of about 600 ml. and was always filled to within 30 ml. of the total capacity. At this level the cell constant was independent of the depth of filling. Solute in the form of a known concentration solution was added by means of weighed syringes throughout. Both the cell and magnetic mechanism for the stirrer were kept at 25.00° in an 80 gallon tank of transformer oil. The temperature of the bath was found to vary no more than ±0.002° during the course of a determination.

The resistances of the cells were extrapolated to resistances at zero frequency. The plot of f^2 *vs.* R proved to be linear up to 4000 c.p.s.

Procedure.—The cells were cleaned, dried and weighed. Pure solvent was distilled into the cell under an atmosphere of dry CO_2-free nitrogen. After weighing, the cell was brought to constant temperature. Solute was then added from small weighed cups or from the tared syringes. All small weighings were done using a Mettler microbalance. By use of the syringe, 1-ml. portions of the solution could be added containing 3 to 10 mg. of the solute. The solutions were stirred until the resistance became constant, a somewhat lengthy procedure due to the high viscosity of the solvent.

Bridge and Accessories.—The bridge used was a Jones type, Leeds and Northrup No. 4666, modified according to the circuit described by Luder[6] and enclosed in a grounded aluminum case. The oscillator was a standard Heathkit audio generator. The bridge output was amplified by a Leeds and Northrup two-stage amplifier and detected by an oscilloscope.

Discussion

The limiting conductances reported by Briscoe and Dirkse[3] for a series of quaternary ammonium compounds in anhydrous ethanolamine are much too high to be explained by any presently accepted theory of conductance. Moreover, their results would suggest that in this solvent the Kohlrausch law of independent migration and the Walden rule are not even approximately true. Close inspection of the original article and the thesis manuscript on which it is based failed to reveal any mention of measurements of the conductance of the pure solvent, despite details regarding its purification. Our measurements on the pure anhydrous ethanolamine show a relatively high specific conductance, indicating a high degree of autoionization. Failure to correct conductances of salt solutions for the high solvent conductance would account for the abnormally high limiting conductances reported by Briscoe and Dirkse.

The dielectric constant of ethanolamine, 37.72, is high enough to cause the phoreograms to be linear over an appreciable concentration range. This linear concentration range may be expected to be about the same as that observed with solutions of salts in dimethylformamide (dielectric constant = 36.71). The data from the present study verify this expectation. In addition, the extremely high viscosity 0.19346 poise at 25.00° would allow one to predict on a basis of Walden's rule that the limiting conductance values for most compounds should lie between 5 and 10. In Table I are listed the Λ_0 values obtained. Λ_0(I) refers to values obtained by graphical extrapolation of the phoreograms and Λ_0(II) refers to values from the Fuoss–Shedlovsky extrapolation procedure. These values are thus in line with expectations based on relative viscosities. The phoreograms are all catabatic, deviating only slightly from the theoretical Onsager value.

In all cases the solvent correction, a value which proved stable and reproducible, was subtracted from the conductance of the solution. Because the solvent correction is large, the precision of the measurements of the conductance of a solution decreases in the very dilute region where the conductance due to the solute itself was often less than 10% of the total solution conductance. In no case did the solvent correction become less than 10% of the total conductance. Thus, even in the most concentrated solution, the solvent correction is still important, a situation which contrasts sharply with that found by Sears and Dawson[7] in methylacetamide, where the solvent correction was never more than 3% of the total conductance.

These conditions existing in ethanolamine are intolerable for work of the highest precision and almost certainly account for the fact that the recent extrapolation procedure of Fuoss[8] showed too much scatter to be of value. Attempted extrapolation by a modification of the Fuoss method involved the use of the equations

$$\Lambda' = \Lambda + S\sqrt{C} - Ec \log c$$
$$\Lambda_K = \Lambda' - Jc$$
$$\Lambda_K = \Lambda_0 - K_A c f^2 \Lambda$$

J was approximated by use of values of A ranging from $3\text{-}4 \times 10^{-8}$ and Λ_K plotted against $cf^2\Lambda$. The plots resulted in curves unsuitable for the evaluation of Λ_0 or K_A. The data were then extrapolated by the method of Fuoss and Shedlovsky,[9] and the values of $1/K_D$, where K_D is the dissociation constant, are shown in Table I.

TABLE I

CONSTANTS DERIVED FROM CONDUCTANCE DATA IN ETHANOLAMINE

Compound	Λ_0(I)	Λ_0(II)	$1/K_D$	Onsager slope Theor.	Onsager slope Exptl.
LiCl	5.53	5.51	5.4	7.82	9.90
NaCl	6.59	6.54	6.6	8.55	10.87
KCl	7.41	7.40	15.5	9.11	13.20
NaBr	6.47	6.44	5.4	8.47	10.25
KBr	7.24	7.23	5.5	9.00	10.43
NaI	6.21	6.20	6.2	8.29	9.45
KI	7.10	7.07	7.5	8.90	10.98
Bu_4NI	4.86	4.85	6.6	7.36	9.62
$NaNO_2$	7.14	7.07	15.8	8.93	13.84
KNO_2	7.88	7.77	25.1	9.44	17.36
$AgNO_2$	6.52	6.51	6.5	8.50	9.96
$NaNO_3$	7.04	6.93	27.9	8.86	16.37
KNO_3	7.79	7.63	31.5	9.37	19.71
NaCNS	6.80	6.78	7.6	8.69	10.50
KCNS	7.74	7.68	12.8	9.34	12.92

Table II shows the differences in limiting equivalent conductances for the six pairs of sodium and

---

(5) J. F. J. Dippy and F. R. Williams, *J. Chem. Soc.*, Pt. I, 161 (1934).

(6) W. F. Luder, THIS JOURNAL, **62**, 89 (1940).

(7) L. R. Dawson, E. D. Wilhoit and P. G. Sears, *ibid.*, **78**, 1569 (1956).

(8) R. M. Fuoss, *ibid.*, **79**, 3301 (1957).

(9) R. M. Fuoss and T. Shedlovsky, *ibid.*, **57**, 489 (1935).

potassium salts studied. It will be seen that in all cases that the limiting conductance for the sodium salt is below that of the potassium analog and that the constancy of the difference indicates the validity of the Kohlrausch law within experimental error. These results are not in agreement with those recently reported by Muniyapan and Anjanejalu,[10] who measured conductances at various concentrations of sodium, potassium and silver nitrites in ethanolamine at 30°. Working at concentrations well above ours, they report conductance values for $KNO_2 < NaNO_2 < AgNO_2$, an order which is exactly opposite to that observed in our study. In addition, their phoreograms are not linear and if extrapolated would give values well in excess of ours and not in agreement with the prediction of Walden's rule. They report a solvent conductance of 30×10^{-6}, three times that of the present work. This higher value is almost certainly due to the fact that their solvent was distilled at atmospheric pressure, where ethanolamine is known to undergo slight decomposition to give ammonia and water among its decomposition products. Muniyapan and Anjanejalu mention also that their solution of silver nitrite was brown as a result of reduction of silver ion to metallic silver. This is found to occur upon the addition of ethanolamine to silver nitrite. However, if the nitrite is added slowly to the stirred solvent, no noticeable decomposition takes place. For these reasons and the good agreement of the alkali nitrite results with the Kohlrausch differences found for the other alkali salts, we believe our results to be correct.

TABLE II

KOHLRAUSCH DIFFERENCES FOR POTASSIUM AND SODIUM SALTS WITH COMMON ANIONS

Salts	$\Lambda_0(K^+) - \Lambda_0 Na^+$
KBr–NaBr	0.77
KCl–NaCl	.82
KNO_2–$NaNO_2$	.74
KCNS–NaCNS	.94
KI–NaI	.89
KNO_3–$NaNO_3$	.75

The order of cationic conductance is seen to be $K^+ > Na^+ > Ag^+ > Li^+ > Bu_4N^+$. For the three alkali metals conductance is directly related to the crystallographic ionic radius. This suggests that the smallest alkali cations are more highly solvated, presumably through ion-dipole forces. Since Ag^+ is nearly the same size as K^+, the large difference in conductance must be due to the fact that Ag^+ strongly coördinates ethanolamine to form the $Ag(NH_2CH_2CH_2OH)_2^+$ ion (the salt, $(Ag(NH_2C_2H_4OH)_2)NO_2$ has been isolated by Muniyapan and Anjanejalu[10]). Because of the stability of the covalent silver–nitrogen bond, the complex cation would be expected to migrate as a unit through the solvent. This complex cation, having only two solvent molecules attached (s-p hybridization) would be smaller than the covalent $(C_4H_9)_4N^+$ and should thus be more mobile than the latter. The experimental results confirm this expectation.

TABLE III

CONDUCTANCE DATA FOR SOLUTIONS IN ETHANOLAMINE AT 25°

$C \times 10^4$	Λ	$C \times 10^4$	Λ	$C \times 10^4$	Λ
Sodium bromide		Potassium bromide		Sodium nitrate	
3.935	6.268	4.519	7.053	5.539	6.659
8.092	6.185	10.577	6.868	8.246	6.600
14.684	6.070	17.922	6.807	15.380	6.370
25.340	5.956	26.033	6.709	23.260	6.244
34.549	5.58	43.058	6.582	28.723	6.156
46.687	5.765	55.864	6.472	41.205	5.982
56.926	5.701	67.122	6.383	56.961	5.826
69.420	5.620				
Potassium nitrate		Sodium chloride		Potassium chloride	
2.438	7.445	2.132	6.460	2.456	7.256
5.175	7.355	5.821	6.286	4.559	7.200
6.293	7.290	10.168	6.239	7.723	6.886
8.465	7.244	15.466	6.169	12.110	6.928
13.468	7.085	22.947	6.068	16.678	6.846
15.877	6.975	34.850	5.947	22.024	6.820
18.026	6.947	50.382	5.816	27.668	6.745
21.672	6.884			33.462	6.660
28.852	6.727			38.519	6.571
36.382	6.585			46.590	6.514
Sodium iodide		Potassium iodide		Sodium nitrite	
2.732	6.051	2.088	6.936	3.806	6.862
6.036	5.984	5.347	6.851	8.362	6.751
7.775	5.945	8.727	6.792	13.799	6.639
9.958	5.923	11.933	6.738	19.441	6.533
12.967	5.875	15.114	6.673	25.709	6.441
13.726	5.860	24.105	6.554	40.520	6.255
24.946	5.723	38.151	6.411	62.426	6.044
40.159	5.585	53.560	6.300		
58.430	5.474	68.546	6.203		
72.355	5.403				
Potassium nitrite		Sodium thiocyanate		Potassium thiocyanate	
2.254	7.580	1.558	6.663	3.113	7.510
6.501	7.453	2.617	6.635	8.633	7.370
10.882	7.326	3.248	6.585	15.270	7.242
15.036	7.222	5.462	6.547	22.335	7.127
19.161	7.133	8.370	6.489	29.120	7.045
33.865	6.867	9.645	6.482	35.897	6.965
49.973	6.642	14.452	6.388	42.547	6.895
71.028	6.411	19.595	6.335	70.792	6.660
		30.265	6.220		
		41.039	6.124		
Tetra-*n*-butylammonium iodide		Lithium chloride		Silver nitrite	
3.257	4.691	5.429	5.299	3.109	6.353
5.453	4.638	12.089	5.199	7.098	6.251
14.847	4.491	20.388	5.082	12.356	6.185
24.386	4.380	30.728	4.985	17.827	6.099
30.839	4.327	41.068	4.895	23.411	6.034
41.501	4.240	51.074	4.815	42.800	5.865
63.172	4.102	60.976	4.758	64.761	5.717
		71.240	4.708		

The alkali metal cations on the other hand should form more labile and less stable solvates through ion-dipole interactions. The formation of such solvates is opposed by the obviously strong intermolecular forces between the solvent molecules,

---

[10] T. Muniyapan and B. Anjanejalu, *Proc. Ind. Acad. Sci.*, **45B**, 454 (1957).

which produce the very high solvent viscosity and boiling point. The weakly solvating alkali metal cations would then be expected to be relatively mobile, the mobility increasing with increasing crystallographic radius of the cation. Moreover the lability of the cation-to-solvent bonds involving the larger alkali metals may allow these solvated cations to move not as distinct solvated units, but with continual exchange of solvent molecules so that the cation moves with respect to even its innermost solvation sheath. Such a process is favored by the strong intermolecular forces between the ethanolamine molecules, since these forces resist the motion of solvent molecules relative to each other.

The $1/K_D$ values lend support to the above statements. The similar values for $AgNO_2$ and Bu_4NI suggest that in the case of Ag^+ the solvated cation is considerably larger than its crystallographic radius of Ag^+, and that the strongly coordinated solvent molecules hinder the close approach of anions to form stable ion pairs. All sodium salts have higher dissociation constants than the potassium analogs and in the case of the alkali chlorides the order of $1/K$ values is $Li < Na < K$, suggesting again that the over-all solvated cation radius and the energy of solvation increases from K to Li. With increasing strength of alkali cation–solvent bond, close approach of the anion is increasingly hindered.

The order of anion conductances for the alkali salts is quite unique, being $NO_2^- > NO_3^- > CNS^- > Cl^- > Br^- > I^-$. This order for the halides is exactly the reverse of that obtained with the solvents dimethylformamide and N-methylacetamide studied by French and Glover.[11] This may be partly due to the different tendency toward solvation existing in the two types of solvent systems. The order of $1/K$ values, however, is $Cl > I > Br$ for both sodium and potassium salts, though the differences between iodide and bromide are small and may not be significant.

The over-all order of anion mobility is difficult to explain in detail due to the differences in the structure of the anions. Factors such as size, charge, dipole moment and symmetry would all be expected to affect the anion–solvent attraction and, therefore, the ionic conductances and ion pair formation. If the anions are slightly solvated, then their relative sizes may be the chief factor affecting the mobilities, and the greater conductance of nitrite than nitrate and the decreasing order of conductance for chloride, bromide and iodide can be understood.

[11] C. M. French and K. H. Glover, *Trans. Faraday Soc.*, **51**, 1427 (1955).

BLOOMINGTON, INDIANA

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

The Mechanism of Oxidative Scission in Natural Rubber[1]

BY A. V. TOBOLSKY AND A. MERCURIO[2]

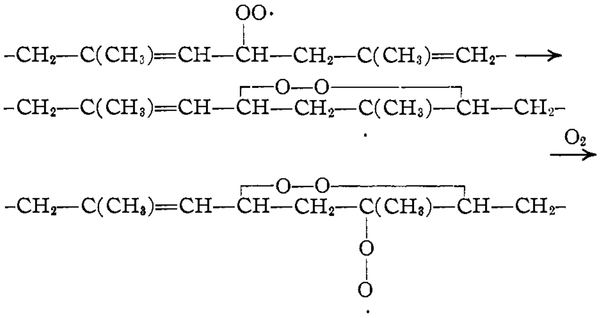
RECEIVED JANUARY 14, 1959

The free radical producers 2-azobisisobutyronitrile, di-*t*-butyl peroxide and benzoyl peroxide have been used to initiate the oxidation of natural rubber in dilute benzene solutions at 60–80°. Quantitative comparisons are made between the measured rate of scission of natural rubber and the known rate of initiation of oxidation chains (in the kinetic sense) by these agents under these conditions. We find that one scission occurs for each initiating radical produced. This is interpreted to mean that scission occurs in the termination step of the radical chain reaction. A possible chemical mechanism for the oxidative scission of natural rubber is discussed.

Natural rubber oxidation by molecular oxygen involves a radical chain reaction[3] very similar to the mechanism proposed to explain the oxidation of ethyl linoleate.[4] In the case where an external initiator (a free radical source) is used, the following mechanism applies at intermediate or high oxygen pressure

$$\begin{array}{lll}
\text{(a)} & \text{Initiator} \longrightarrow 2R'\cdot & \multirow{2}{*}{\text{Initiation}} \\
\text{(a}'\text{)} & R'\cdot + RH \longrightarrow R\cdot + R'H & \text{Initiation} \\
\text{(b)} & R\cdot + O_2 \longrightarrow RO_2\cdot & \text{Propagation} \\
\text{(c)} & RO_2\cdot + RH \longrightarrow ROOH + R\cdot & \text{Propagation} \\
\text{(d)} & RO_2\cdot + RO_2\cdot \longrightarrow \text{Termination products} & \text{Termination}
\end{array}$$

In the above equations RH represents natural rubber $(-CH_2-CH{=}C(CH_3)CH_2-)_n$. Radicals originating from the external initiator interact with the rubber in step (a′) to form R· either by the abstraction of an α-methylenic hydrogen atom or by attack at the double bond. A side reaction occurring in propagation is the intramolecular reaction of $RO_2\cdot$ as[5]



A very noticeable consequence of the oxidation is scission of polyisoprene chains. In this paper, we have associated the scission reaction with a

---

[1] This article is based upon a dissertation submitted by A. Mercurio in partial fulfillment of the requirements for the degree of Doctor of Philosophy at Princeton University.

[2] Thiokol Chemical Corporation Fellow 1957–1958.

[3] Reviewed in N. Grassie, "The Chemistry of High Polymer Degradation Processes," Interscience Publishers, Inc., New York, N. Y., 1956, Chapter 4.

[4] J. Bolland and G. Gee, *Trans. Faraday Soc.*, **42**, 236 (1946).

[5] J. Bolland and H. Hughes, *J. Chem. Soc.*, 492 (1949).