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

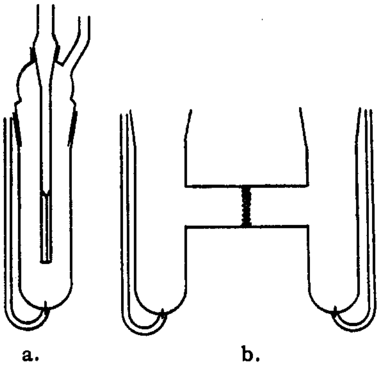
Polarography in Liquid Ammonia. I. The Alkali Metals

BY H. A. LAITINEN AND C. J. NYMAN

Up to the present time, no research has been carried out on polarographic measurements in liquid ammonia, although the dropping mercury electrode has been used in this solvent. Murtazaev[1] has measured electrocapillary curves of salts in liquid ammonia and has shown that chloride, bromide and iodide ions are adsorbed at the mercury–solution interface, causing shifts in the electrocapillary maximum similar to those observed in aqueous solution. Pleskov and Monosson[2] have measured the potential of the electrocapillary maximum in 0.1 normal ammonium nitrate solution at −35° and found it to be 0.386 v. more positive than the potential of a lead electrode in 0.1 normal lead nitrate solution. Dropping amalgam electrodes were used by Pleskov[3] and by Pleskov and Monosson,[4] in their determination of the standard electrode potentials of the alkali metals in liquid ammonia. Since it was known that the dropping mercury electrode would function in liquid ammonia, a polarographic study of the reduction of the alkali metal ions was undertaken.

Experimental

The electrolysis cell shown in Fig. 1a was used for all the experiments in this investigation unless otherwise specified. A platinum wire was sealed through the bottom of the cell so that the mercury pool could be used as the non-polarizable electrode. A conventional H-type cell, as shown in Fig. 1b, was used when it was desired to have the anode and cathode compartments separated; a sintered glass disc prevented mixing of the solutions in the two sides of the cell. When using this cell, two connections to the drying system (Fig. 2) were necessary.



a. b.

Fig. 1.—Electrolysis cells.

Using the apparatus shown in Fig. 2, the following procedure was carried out in the preparation of air-free anhydrous liquid ammonia solutions. The cell was connected to the drying system as shown at A after a weighed sample had been introduced into it. Ampules B and B′ each contained a small piece of sodium metal, approximately 1 g., in order to dry the ammonia. The system was evacuated through tube C, and after ampule B was cooled with a Dry Ice and acetone-bath, gaseous ammonia was allowed to enter the system through tube D. When 35 to 40 cc. had condensed, the ammonia was distilled from ampule B to B′, and then into the electrolysis cell until the desired volume was obtained. Stopcock E was then closed, and the bath surrounding the cell was brought to −36° by the addition of warm acetone. The solution was allowed to stand for one hour to be certain that the indifferent electrolyte had reached solubility equilibrium. Occasional stirring was achieved by opening stopcock E and evaporating ammonia into ampule B′, which was cooled with a Dry Ice and acetone-bath. In this evaporation, small bubbles formed which stirred the solution, but which did not cause any splattering on the walls of the cell.

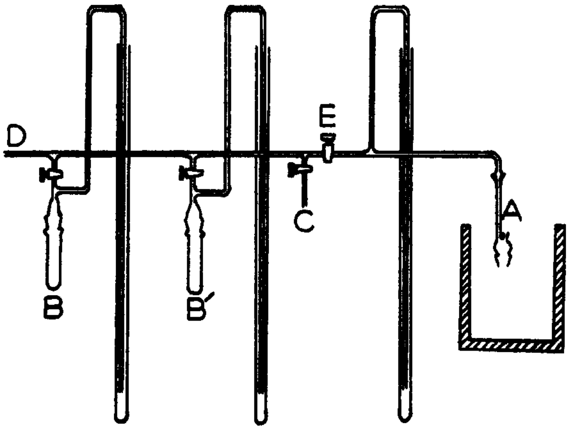


Fig. 2.—Drying system for the preparation of anhydrous liquid ammonia solutions.

The thermostat consisted of a one-gallon Dewar flask filled with acetone, a copper cooling coil, a cone drive stirrer and a toluene expansion udder for controlling the temperature. The toluene expanded against a mercury filled U-tube outside the bath forcing the mercury into a capillary. Electrical contact was made through the bottom of the U-tube and through the capillary. A leveling device for controlling the amount of mercury was sealed into the bottom of the U-tube. As the temperature rose and contact was made through the mercury in the U-tube, a mercury relay switch was actuated starting the pump which circulated cold acetone through the cooling coil. This thermostat held the temperature at a constant value of −36.0 ± 0.2°.

Dropping mercury electrode 1 had the following characteristics in a saturated solution of tetrabutylammonium iodide in liquid ammonia at −36°. At a pressure of 20 cm., the drop time was 6.4 seconds (open circuit), and the value of m was 0.844 mg./sec. Under similar conditions, electrode 2 had an m of 1.184 mg./sec., and a drop time of 5.1 seconds (open circuit). As a comparison, electrode 1 had the following characteristics in air-saturated water at 25°. At a pressure of 20 cm., the drop time was 7.1 seconds (open circuit), and the value of m was 1.14 mg./sec.

The polarograph used was a Sargent Model XX. The calibration of this instrument was checked by inserting

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[1] A. Murtazaev, *Acta Physicochim. U. R. S. S.*, **12**, 225 (1940).

[2] V. A. Pleskov and A. M. Monosson, **2**, 621 (1935).

[3] V. A. Pleskov, **6**, 1 (1937); **21**, 235 (1946).

[4] V. A. Pleskov and A. M. Monosson, *ibid.*, **2**, 615 (1935).

a known resistance in place of the electrolysis cell and measuring accurately the applied potential. With these data, the current flowing through the circuit could be calculated and compared with that indicated by the recorder. All applied potential values were checked by means of a student type potentiometer.

The ammonia used in these investigations was obtained from the Matheson Company and was dried as previously described before use. The alkali metal salts were C. P. materials of commerce and were dried at 110° before use. The tetrabutylammonium iodide was prepared by a slight modification of the method used by Cox, Kraus and Fuoss,[5] as previously described by Laitinen and Wawzonek.[6] That this material was free of alkali metal ions was indicated by the fact that the residual current curve showed no wave at potentials corresponding to their reduction.

Data and Discussion

The expression

$$E_{\text{d.e.}} = E_{1/2} - \frac{RT}{nF} \ln i/(i_{\text{d}} - i)$$

is the equation of the current–voltage curve obtained for the reduction of a metal ion at the dropping mercury electrode when the metal is soluble in mercury.[7] $E_{\text{d.e.}}$ is the potential of the dropping mercury electrode; $E_{1/2}$ is the half-wave potential; i_{d} is the diffusion current; and i is the current which flows at a potential $E_{\text{d.e.}}$. A plot of $E_{\text{d.e.}}$ *versus* log $i/(i_{\text{d}} - i)$ should be a straight line with a slope of $-2.303RT/nF$, if the reduction process is reversible. The half-wave potentials of the alkali metal ions were obtained from a plot of this type by determining the potential at which log $i/(i_{\text{d}} - i)$ was zero. Typical polarograms are shown in Fig. 3 and Fig. 4.

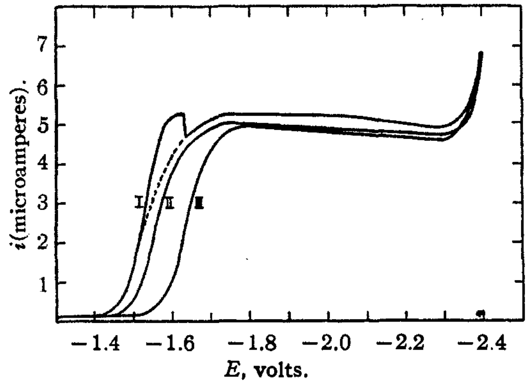

Fig. 3.—Polarograms of sodium, potassium and rubidium iodides in saturated tetrabutylammonium iodide: curve I, 9.8 × 10^{-4} *M* RbI; curve II, 1.00 × 10^{-3} *M* KI; curve III, 1.04 × 10^{-3} *M* NaI.

It is possible to evaluate the half-wave potentials theoretically either by an equation derived by Lingane[8] or by one derived by von Stackelberg.[9]

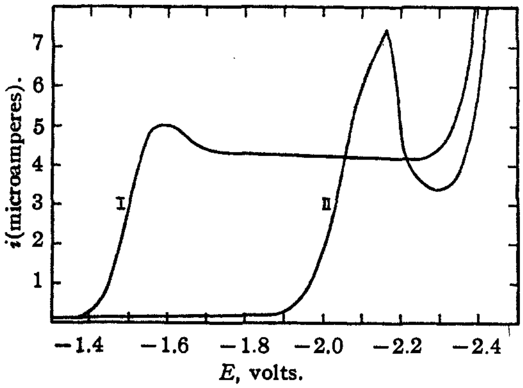

Fig. 4.—Polarograms of cesium and lithium chlorides in saturated tetrabutylammonium iodide: curve I, 8.1 × 10^{-4} *M* CsCl; curve II, 1.01 × 10^{-3} *M* LiCl.

The latter is more convenient in the case of the alkali metals, as the standard electrode potentials of the metals are not necessary. The half-wave potential as measured polarographically is equal to the potential of an amalgam electrode in the cell

$$\text{M(Hg)}_x\ (C_a)\ |\ \text{M}^+\ (C_s)\ |\ \text{Ref. elect.}$$

when the concentration of metal ion in the solution is equal to the concentration of metal in the amalgam. For the dropping mercury electrode to have the same potential as the amalgam electrode in the above cell, the diffusion coefficients of the ion in solution and the metal in the amalgam must be equal. The potential E of the amalgam electrode in the above cell is given by the equation

$$E = E_{1/2} - \frac{RT}{nF} \ln \frac{C_a}{C_s}$$

where C_a is the concentration of metal in the amalgam and C_s is the concentration of metal ion in the solution. The data necessary for calculation of the half-wave potentials are available, since Pleskov and Monosson[3,4] have made such measurements in the evaluation of the standard electrode potentials of the alkali metals in liquid ammonia. A lead electrode in 0.1 normal solution of lead nitrate was used by these authors as a reference electrode. In the experimental determination of the half-wave potentials, a mercury pool in a saturated solution of tetrabutylammonium iodide was used as the reference electrode. In order to relate the two reference electrodes, the following cell was prepared. The dropping mercury electrode and a quiet mercury pool were placed in one compartment of the cell shown in Fig. 1b. The solution in this compartment was 0.001 molar with sodium iodide and saturated with tetrabutylammonium iodide. The other compartment contained a lead electrode in 0.1 normal lead nitrate solution. Since the half-wave potential of sodium ion must be a constant, it was determined against each electrode, and the difference between the two values must be equal to the difference of potential between the two reference electrodes. The mercury

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(5) N. L. Cox, C. A. Kraus and R. M. Fuoss, *Trans. Faraday Soc.*, **31**, 749 (1935).

(6) H. A. Laitinen and S. Wawzonek, THIS JOURNAL, **64**, 1765 (1942).

(7) J. Heyrovsky and D. Ilkovic, *Coll. Czech. Chem. Commun.*, **7**, 198 (1935).

(8) J. J. Lingane, THIS JOURNAL, **61**, 2099 (1939).

(9) M. von Stackelberg, *Z. Elektrochem.*, **45**, 466 (1939).

pool was found to be 0.318 v. more positive than the lead electrode.

Table I contains the values of the half-wave potentials calculated from the data of Pleskov and Monosson, as well as the values observed with the dropping mercury electrode in 0.001 molar metal iodide solution with a saturated solution of tetrabutylammonium iodide as indifferent electrolyte. The observed values have been corrected for the iR drop through the solution. The slopes of the plots of $E_{\text{d.e.}}$ *versus* $\log i/(i_d - i)$ are also recorded.

TABLE I

$E_{1/2}$ IN LIQUID AMMONIA AT −36° *versus* Pb | $Pb(NO_3)_2$ (0.1 *N*)

Ion	E, v.	C_a, m./l.	C_s, m./l.	$E_{1/2}$ (calcd.), v.	$E_{1/2}$ (obs.), v.	Slope of $E_{\text{d.e.}}$ vs. $\log i/(i_d - i)$
Li^+	−1.658	0.351	0.1	−1.632	−1.67	−0.058
Na^+	−1.337	.564	.1	−1.302	−1.31	− .057
K^+	−1.287	.770	.1	−1.245	−1.24	− .056
Rb^+	−1.229	.367	.1	−1.202	−1.21	− .061
Cs^+	−1.078	.192	.01	−1.018	−1.15	− .065

In the case of lithium, a large maximum (see Fig. 4) approximately equal to the diffusion current was observed, and smaller maxima were observed with rubidium and cesium ions. All of these maxima decreased when the concentration of the reducible ion was lowered to 2×10^{-4} molar, and they practically disappeared in the case of rubidium and cesium ions. Attempts to eliminate the lithium maximum by the use of gelatin did not succeed, and the problem was not investigated further.

It is seen that there is a reasonable agreement between the observed and calculated values of the half-wave potentials, and that the slope of $E_{\text{d.e.}}$ *vs.* $\log i/(i_d - i)$ plot approaches the reversible value −0.047, but in no case was a reversible slope obtained.

The half-wave potentials of the alkali metal ions become more positive as the atomic number increases. There are two reasons why this inverse order of reduction might be expected. The solvation energy of the smaller ions is greater than for the larger ions, and, therefore, more energy must be supplied to the smaller ions to reduce them. The free energy of amalgamation of the metals, as indicated by the difference of potential between the metal and its amalgam, shows a tendency to increase as the atomic number increases. These two factors are working in the same direction, and, therefore, an inverse order of the ease of reduction is a logical one.

The diffusion currents of the alkali metal ions, as measured in liquid ammonia at −36°, are recorded in Table II. A saturated solution of tetrabutylammonium iodide served as the supporting electrolyte. As a comparison, theoretical values were calculated by means of the Ilkovic equation[10,11]

$$i_d = 605nCD^{1/2}m^{2/3}t^{1/6}$$

which relates the diffusion current i_d (microamperes) of an ion to n, the number of faradays of electricity required per mole of electrode reaction, to its concentration C (millimoles per liter), to its ionic diffusion coefficient D (cm.²/sec.), and to the capillary characteristics m (mg./sec.) and t (sec.). The ionic diffusion coefficient D can be evaluated by means of the expression[12,13]

$$D = RT\lambda^0/zF^2$$

where R is 8.317 volt-coulombs per degree, T is the absolute temperature, λ^0 is the equivalent conductance of the ion at infinite dilution (ohm^{-1}-cm.^{2}-equiv.$^{-1}$), z is the charge of the ion, and F is 96,500 coulombs. The remaining terms in the Ilkovic equation are experimental quantities which are easily obtained.

TABLE II

DIFFUSION CURRENTS OF THE ALKALI METAL IONS IN LIQUID AMMONIA AT −36°

Ion	λ_0, ohm^{-1}-cm.^{2} equiv.$^{-1}$	$D \times 10^5$, cm.^{2}-sec.$^{-1}$	$m^{2/3}t^{1/6}$, mg.$^{2/3}$-sec.$^{-1/2}$	C, mm./l.	i_d (calcd.), micro-amperes	i_d (obs.), micro-amperes	% Diff.
Li^+	122	2.59	0.893	1.01	2.78	3.11	12
Na^+	135	2.86	1.256	1.04	4.23	4.84	14
K^+	174	3.69	1.262	1.00	4.64	4.71	2
Rb^+	179	3.80	1.262	0.98	4.62	5.06	10
Cs^+	180	3.82	1.273	0.81	3.83	4.21	10

Table II contains the data necessary for and the results of such calculations. The values for the equivalent ionic conductance at infinite dilution were obtained by interpolation between the data of Pleskov and Monosson[14] at −40° and data which they recalculated for −33.5° from the work of Franklin and Kraus.[15] Since no values were available for rubidium and cesium at −33.5°, the same correction which was applied to potassium was used to correct the values for these ions from −40 to −36°.

The diffusion currents calculated from the Ilkovic equation are lower than the observed values. The discrepancy can largely be attributed to the failure to obtain complete suppression of the migration current. The concentration of indifferent electrolyte was 0.0057 molar ±5% and, therefore, the ratio of indifferent electrolyte to reducible ion was about 6 to 1. Assuming as a first approximation the mobilities of all ions to be equal, the migration current would represent 7% of the total current.

Another cause for the observation of abnormally high diffusion currents lies in the failure of Ilkovic equation at excessively rapid drop rates. At the potentials at which the diffusion currents of the alkali metal ions were measured, the drop time was 1.0 to 2.2 seconds. Lingane and Lover-

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[10] D. Ilkovic, *Coll. Czech. Chem. Commun.*, **6**, 498 (1934).

[11] D. MacGillavry and E. K. Rideal, *Rec. trav. chim.*, **56**, 1013 (1937).

[12] W. Nernst, *Z. physik. Chem.*, **2**, 613 (1888).

[13] I. M. Kolthoff and J. J. Lingane, THIS JOURNAL, **61**, 825 (1939).

[14] V. A. Pleskov and A. Monosson, *Z. physik. Chem.*, **156**, 176 (1931).

[15] E. C. Franklin and C. A. Kraus, *Am. Chem. J.*, **23**, 277 (1900); THIS JOURNAL, **27**, 191 (1905).

idge[16] and Buckley and Taylor[17] have observed abnormally high values of the quantity $i_d/Cm^{2/3}t^{1/6}$ at drop times less than three seconds unless a suppressor, such as gelatin, was present.

The use of some other supporting electrolyte with a higher solubility was not attempted because of the difficulty involved in finding one which was not reduced at very negative potentials and which could also be freed easily from traces of the alkali metal ions. In all probability, better agreement between the observed and calculated values of the diffusion current would be obtained if higher ratios of non-reducible to reducible ion were to be used.

Summary

The half-wave potentials of the alkali metal ions in liquid ammonia were found to agree with those calculated theoretically, and the reduction process appeared to be reversible.

The diffusion currents of the alkali metal ions were measured and compared with those calculated from the Ilkovic equation.

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[16] J. J. Lingane and B. A. Loveridge, THIS JOURNAL, **66**, 1425 (1944).

[17] F. Buckley and J. K. Taylor, *J. Research Nat. Bur. Standards*, **34**, 97 (1945).

[CONTRIBUTION FROM THE DEPARTMENT OF PHYSICAL CHEMISTRY, HARVARD MEDICAL SCHOOL]

Mechanical Properties of Substances of High Molecular Weight. IV. Rigidities of Gelatin Gels; Dependence on Concentration, Temperature and Molecular Weight[1]

BY JOHN D. FERRY

Earlier measurements[2] have shown that the rigidity of a gelatin gel is approximately proportional to the square of the concentration, and it is well-known that the rigidity decreases with increasing temperature[3] or with degradation.[4] Previous work has, however, been confined to samples of unknown molecular weight. The series of degraded gelatins described by Scatchard, Oncley, Williams and Brown[5] has now afforded the opportunity of studying samples of known average molecular weight and molecular size distribution. The method of propagation of transverse vibrations[6] permits absolute measurements of rigidity to be made conveniently at concentrations lower than those usually employed by previous investigators. This paper reports rigidity measurements by the transverse vibration method on certain of the gelatin samples studied by Scatchard, Oncley, Williams and Brown, together with several other gelatins from different sources.

Materials and Method

The following gelatin samples were employed: four of the series of degraded ossein gelatins,[5] originally furnished through the kindness of Dr. D. Tourtellotte of the Knox Gelatin Company; one sample each of ossein (A-O), porkskin (A-P), and calfskin (A-C) gelatin, furnished by the Atlantic Gelatin Company; and one calfskin gelatin (EK-120), purchased from the Eastman Kodak Company. Table I lists the values of number-average molecular weight, M_n, derived from osmotic pressure and viscosity measurements.[7] Values of α, the fraction of bonds broken in the parent molecule, and M_w, the weight-average molecular weight, as calculated from the statistics of degradation,[5] are also included for the degraded series. They are omitted for the other samples because it is not certain that the details of the statistical treatment are applicable to those.

TABLE I

MOLECULAR WEIGHTS OF GELATIN SAMPLES

Sample	α	$M_n \times 10^{-3}$	$M_w \times 10^{-3}$
	Degraded Series (Ossein)		
L1–00	0.00125	45	74
L1–80	.00235	29	53
L1–180	.00345	22	41
P7–180	.00470	17	33
	Additional Samples		
A-P		47	
A–C		47	
A–O		39	
EK–120		37	

The degraded samples were furnished as sterile stock solutions, at a concentration of about 60 g./l., in 0.15 *M* sodium chloride at *p*H 7; the others, furnished in solid form, were dissolved in 37° and adjusted to the same *p*H and salt concentration, unless otherwise specified. Stock solutions were kept at 0°, except for occasional brief warming to 37° to withdraw samples, with sterile precautions. From studies of the rate of degradation,[5,7] no perceptible change in molecular weight would be expected for several years under these conditions. The measurements described here were completed in less than two years. Recent unpublished measurements on similar samples indicate that there is no change after five years.

The stock solutions, after warming at 37° for one hour, were diluted with 0.15 *M* sodium chloride (unless otherwise specified) to the desired concentrations and transferred to rectangular glass cells provided with clamps[8] to hold the

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[1] Part of this work was carried out under contract, recommended by the Committee on Medical Research, between the Office of Scientific Research and Development and Harvard University. Presented in part at meetings of the Society of Rheology, New York, N. Y., Oct. 30, 1943, and Nov. 17, 1944.

[2] A. Leick, *Ann. Physik*, **14**, 139 (1904); S. E. Sheppard and S. S. Sweet, THIS JOURNAL, **43**, 545 (1921).

[3] M. L. Sheely, *Ind. Eng. Chem., Anal. Ed.*, **2**, 348 (1930); J. C. Derksen, Thesis, Amsterdam, 1935.

[4] E. T. Oakes and C. E. Davis, *J. Ind. Eng. Chem.*, **14**, 708 (1922).

[5] G. Scatchard, J. L. Oncley, J. W. Williams and A. Brown, THIS JOURNAL, **66**, 1980 (1944).

[6] J. D. Ferry, *Rev. Sci. Instruments*, **12**, 79 (1941); THIS JOURNAL, **64**, 1323 (1942).

[7] Unpublished measurements by Drs. G. Scatchard and A. Brown, Massachusetts Institute of Technology.

[8] Designed by Dr. S. H. Armstrong, Jr.