XXXIX.—*The Solution Tension of Silver in Solvents other than Water.*

By FREDERICK KARL VICTOR KOCH.

THE Nernst formula for the electrode potential of a metal against a solution of its ions, $E = RT/nF.\log_e P/p$, does not explicitly involve any property of the solvent, but there is every reason to suppose that the tendency of the metal ion to go into solution (P) will vary with the solvent, just as the solubility of any chemical substance varies in different media (Brunner, *Z. Elektrochem.*, 1905, **11**, 415;

Carrara, "Elektrochemie nichtwässeriger Lösungen," Ahrens Samml., 1908, p. 31). The real origin of the electrolytic solution tension must, in fact, be sought in the existence of an attractive force between the dipole molecules of the solvent and the ions of the metal. Since the dipole character of the solvent is considered to run parallel to the dielectric constant, and as electrolytes are, in general, more highly ionised in solvents with high than in those with low dielectric constants, it might be considered that the attraction between ions and solvent molecules would increase with the dielectric constant. From this standpoint one would expect the solution tension to increase with increasing dielectric constant (compare Krüger, *Z. Elektrochem.*, 1911, **17**, 465; Kjellin, *Z. physikal. Chem.*, 1911, **77**, 210).

On the basis of the well-known Malmstrom–Krüger–Walden expression (Walden, "Elektrochemie nichtwässeriger Lösungen," p. 355), Baur (*Z. Elektrochem.*, 1906, **12**, 725) found that the solution tension should be proportional to the cube of the dielectric constant of the solvent, *i.e.*, $P = cD^3$, where c is a constant characteristic of the metal and independent of the solvent. It would follow that the difference between the normal potentials of a metal in two solvents A and B (*i.e.*, $E_A - E_B = 3RT/nF \, . \log_e D_A/D_B$) should be a constant with the same value for all metals. Sackur (*ibid.*, 1905, **11**, 387) actually showed, from the results of Carrara and D'Agostini (*Gazzetta*, 1905, **35**, 132), that the difference in normal potential for a number of metals in water and methyl alcohol was very nearly a constant. The value of this constant was, however, 0·11 volt, whilst the calculated figure is 0·032 volt.

An empirical relation between the dielectric constant and the electrode potential, of the form $E = A + B/D$ (A and B are constants), has been suggested by Ghosh, Chaudhuri, and Sen (*J. Ind. Chem. Soc.*, 1924, **1**, 189) and by Brodsky (*Z. physikal. Chem.*, 1926, **121**, 26). This formula is clearly incompatible with that of Baur, since it gives the electrode potential as a linear function of the reciprocal of the dielectric constant, whereas the latter gives it as a logarithmic function.

The experimental results recorded in the literature tell us little more than that the solution tension definitely varies with the solvent, and all workers (except Abegg and Neustadt, *ibid.*, 1909, **69**, 486) agree with this conclusion. A parallelism between the electrode potential and the dielectric constant is indicated by the researches of Luther (*ibid.*, 1896, **19**, 529), Mortimer and Pearce (*J. Physical Chem.*, 1917, **21**, 275), Ghosh, Chaudhuri, and Sen (*loc. cit.*) and Brodsky (*loc. cit.*), but the exact form of the relationship cannot be deduced from the experimental data so far obtained, The question whether the electrochemical series is the same in all solvents has apparently to be answered in the negative (Gates, *J. Physical Chem.*, 1911, **15**, 97; Ghosh, *ibid.*, 1915, **19**, 720).

The potentials given by many of the earlier workers cannot for various reasons be regarded as trustworthy, for they are not even in approximate agreement, some workers having omitted to take account of the degree of ionisation of the solute; and further, no satisfactory means has yet been found of overcoming the difficulty of the liquid junction potential.

The practical problem has previously been to determine the potential (e_1) in a cell of the type

$$\text{Metal} \underset{e_1}{|} \text{Non-aqueous solution} \underset{e}{|} \text{Aqueous solution} \underset{e_2}{|} \text{Standard electrode}$$

in which e_2 is known. The two difficulties are then: (1) To determine the ionic concentration of the non-aqueous solution, without which the value of e_1 is meaningless; and (2) either to estimate or to eliminate the liquid junction potential (e).

The ionic concentration has usually been obtained from conductivity measurements. This is well-known to be unsatisfactory, but there is at present no better alternative.

The difficulty of the liquid junction potential is more formidable, and in many cases it has been neglected. Several methods, all having certain disadvantages, have been employed; the chief of these are (*a*) the dropping electrode; (*b*) the electrocapillary method; (*c*) the calculation of the liquid junction potential by Henderson's or some other formula; and (*d*) its elimination by the insertion of concentrated intermediate solutions of potassium chloride or ammonium nitrate. Even in the first two methods there appears to be some uncertainty as to the interpretation of the results, and it was therefore considered advisable to proceed on new lines, now to be described.

EXPERIMENTAL.

In order to investigate the effect of the solvent upon the solution tension (or electrode potential), it is advisable to select an electrode which (1) will give constant and reproducible potentials, (2) is a primary electrode, (3) has only one valency, (4) has a corresponding salt which is soluble in a large number of solvents. The electrode which was used as best fulfilling these conditions was $Ag|AgNO_3$.

Purification of Materials.—The pure silver nitrate employed, which had been originally intended for work on atomic weights, was kindly supplied by Dr. H. F. Harwood.

Pure acetonitrile was prepared as described in a previous paper

(J., 1927, 647), its specific conductivity being $\kappa_{25^\circ} = 0{\cdot}5$—$1{\cdot}0 \times 10^{-7}$ mho. Propionitrile (B.D.H.) was purified in the same manner as the acetonitrile, and then had $\kappa_{25^\circ} = 1{\cdot}7 \times 10^{-7}$ mho.

Benzonitrile (B.D.H.) was steam-distilled, washed with aqueous sodium carbonate solution, and extracted with ether. The extract was dried over calcium chloride, filtered, and the ether removed on the steam-bath. The benzonitrile was then distilled in a vacuum, and the constant-boiling fraction (b. p. 73°/6 mm.) was kept for about 2 days over calcium chloride and then redistilled under low pressure. The distillate was shaken with a little phosphoric oxide, and after being again distilled had specific conductivity $\kappa_{25^\circ} = 0{\cdot}5 \times 10^{-7}$ mho.

Phenylacetonitrile (B.D.H.) was shaken with potassium carbonate to remove phenylacetic and hydrocyanic acids. After filtration on a Buchner funnel, it was distilled in a vacuum at 110° (b. p. 231°/760 mm.), a large first fraction being rejected in order to ensure the removal of the last traces of benzyl chloride (b. p. 126°/760 mm.). The distillate which had come over at a constant temperature was further purified in the same way as the phenylacetonitrile and then had $\kappa_{25^\circ} = 0{\cdot}5 \times 10^{-7}$ mho.

Ethyl cyanoacetate (B.D.H.) was shaken with calcium chloride for ½ hour and distilled in a vacuum at 96° (b. p. 206°/760 mm.), a large first fraction being rejected : $\kappa_{25^\circ} = 2{\cdot}5 \times 10^{-7}$ mho.

Pyridine (Hopkin and Williams's " Pure ") was dried over solid potash and distilled at atmospheric pressure (b. p. 114—115°); it was protected by soda–lime tubes : $\kappa_{25^\circ} = 1{\cdot}7 \times 10^{-7}$ mho.

Aniline (Hopkin and Williams's " Redistilled ") was dried over solid potash and distilled in a vacuum at 76° (b. p. 184·4°/760 mm.). Dry nitrogen was passed through the bubbler instead of dry air. Precautions were taken, as in the case of pyridine, to prevent contamination by atmospheric carbon dioxide. The pure aniline was colourless, and had a specific conductivity lower than that of any of the other solvents, *viz.*, $2{\cdot}5 \times 10^{-8}$ mho. This was fortunate, since the specific conductivities of the silver nitrate solutions were also exceptionally low.

Methyl alcohol (Kahlbaum) had been kept over lime for some months. It was shaken with fresh lime and distilled at atmospheric pressure first from lime and then from dry silver nitrate. It was found that standing over anhydrous copper sulphate did not improve the product : $\kappa_{25^\circ} = 1{\cdot}5 \times 10^{-6}$ mho.

Ethyl alcohol (Burrough's " Absolute ") was purified in the same way as the methyl alcohol : $\kappa_{25^\circ} = 1{\cdot}0 \times 10^{-7}$ mho.

Acetone (Hopkin and Williams's " Redistilled ") was dried over calcium chloride and distilled at atmospheric pressure over metallic calcium which had been scraped so as to present a fresh surface: $\kappa_{25^\circ} = 1{\cdot}3 \times 10^{-6}$ mho.

The Solutions.—Solutions of three concentrations (approximately $N/10$, $N/100$, and $N/1000$) were made in water and in the non-aqueous solvent, except those in pyridine ($N/100$, $N/500$, $N/1000$, $N/2000$), aniline ($N/100$, $N/500$, $N/1000$), and acetone ($N/90$, $N/540$, $N/1000$). All the solutions were stable except those in ethyl cyanoacetate, which decomposed, giving a brown coloration and a slight white precipitate within 24 hours of preparation. The measurements with these solutions were therefore all made on one day. Silver nitrate reacts with phenylacetonitrile, forming silver cyanide, slowly at 100° but immediately at the boiling point; at room temperature, however, the reaction is negligible.

The solutions of silver nitrate in pyridine (Werner, *Z. anorg. Chem.*, 1897, **15**, 1; Abegg and Neustadt, *loc. cit.*) and aniline (Getman and Gibbons, *Amer. Chem. J.*, 1911, **46**, 117) undoubtedly contain complexes. Since these are likely to break up with dilution, only dilute solutions (below $N/100$) were used. There is, nevertheless, some uncertainty in the deduction of ionic concentrations from conductivity measurements of these solutions, although it is to be noted that Sakhanov and Grünbaum (*J. Russ. Phys. Chem. Soc.*, 1916, **48**, 1794) found that the Nernst formula held for silver nitrate concentration cells when the solutions were very dilute. Measurements in pyridine and aniline were made in spite of the uncertainties mentioned, because it was considered that on account of their ammoniacal character they would probably yield interesting results.

Apparatus, etc.—The same conductivity and *E.M.F.* apparatus was used as that described in a previous paper (J., 1927, 647). All specific conductivities (which may be considered accurate to within 0·1%) were determined at 25° (±0·01°) in spite of the fact that the *E.M.F.*'s were measured at room temperature, because (as will be seen later) it is only the *ratio* of the specific conductivities of the two solutions which is required, and this will be very nearly the same at 25° as at room temperature, as is apparent from the fact that the difference of *E.M.F.* of the cells at 25° and at room temperature is only very slight. The specific conductivities of the pure solvents have in all cases been subtracted from the observed specific conductivity of the solution.

Two electrodes were inserted into each solution, and since measurements were made with and against the standard cell, a total of 8 readings was obtained for each *E.M.F.*; the average of these values was taken. Two independent series of *E.M.F.* determinations were made with each organic solvent, fresh solutions being used and the electrodes replated when necessary. The values given, which are the most consistent of these, may be considered accurate to within 1—2 millivolts. The convention has been adopted of giving the *E.M.F.* the same sign as the electrode in the non-aqueous solution.

In Table I are recorded the *E.M.F.* of each cell and the specific conductivity of each solution. As will be seen in the sequel, the *E.M.F.* of the cell stands in a simple relation to the ratio of the specific conductivities of the two electrode solutions, and hence the values of κ are tabulated throughout, κ_w and κ_s being the specific conductivities of the aqueous and non-aqueous solutions, respectively. In each case the three aqueous solutions ($N/10$, $N/100$, and $N/1000$) were run against non-aqueous solutions of the three dilutions (four in the case of pyridine) specified on p. 273.

TABLE I.

Pyridine.

$\kappa_w \times 10^4$.	$\kappa_s \times 10^5$.	*E.M.F.* (volt).
106·5	38·59	−0·453
,,	10·49	−0·492
,,	5·923	−0·503
,,	3·278	−0·509
12·46	38·59	−0·389
,,	10·49	−0·424
,,	5·923	−0·445
,,	3·278	−0·452
1·330	38·59	−0·353
,,	10·49	−0·366
,,	5·923	−0·369
,,	3·278	−0·384

Aniline.

$\kappa_w \times 10^4$.	$\kappa_s \times 10^7$.	*E.M.F.* (volt).
107·3	33·34	−0·327
,,	10·44	−0·343
,,	6·805	−0·372
12·52	33·34	−0·259
,,	10·44	−0·283
,,	6·805	−0·299
1·357	33·34	−0·194
,,	10·44	−0·237
,,	6·805	−0·253

Acetonitrile.

$\kappa_w \times 10^4$.	$\kappa_s \times 10^4$.	*E.M.F.*
105·3	67·78	−0·106
,,	12·99	−0·148
,,	1·849	−0·200
12·23	67·78	−0·047
,,	12·99	−0·095
,,	1·849	−0·149
1·319	67·78	+0·019
,,	12·99	−0·030
,,	1·849	−0·097

Propionitrile.

$\kappa_w \times 10^4$.	$\kappa_s \times 10^5$.	*E.M.F.*
106·6	300·5	−0·049
,,	60·45	−0·095
,,	9·365	−0·152
12·31	300·5	+0·014
,,	60·45	−0·033
,,	9·365	−0·089
1·332	300·5	+0·069
,,	60·45	+0·028
,,	9·365	−0·025

Phenylacetonitrile.

$\kappa_w \times 10^4$.	$\kappa_s \times 10^5$.	*E.M.F.*
106·7	35·20	+0·008
,,	7·575	−0·031
,,	1·061	−0·088
11·97	35·20	+0·057
,,	7·575	+0·022
,,	1·061	−0·027
1·294	35·20	+0·113
,,	7·575	+0·078
,,	1·061	+0·026

Ethyl cyanoacetate.

$\kappa_w \times 10^4$.	$\kappa_s \times 10^5$.	*E.M.F.*
106·5	36·44	+0·013
,,	8·122	−0·020
,,	1·407	−0·072
12·42	36·44	+0·062
,,	8·122	+0·027
,,	1·407	−0·020
1·345	36·44	+0·121
,,	8·122	+0·086
,,	1·407	+0·042

TABLE I (*cont.*).

Benzonitrile.

$\kappa_w \times 10^4$.	$\kappa_s \times 10^5$.	*E.M.F.*
106·3	45·79	+0·004
,,	9·603	−0·036
,,	2·262	−0·073
12·44	45·79	+0·058
,,	9·603	+0·021
,,	2·262	−0·016
1·307	45·79	+0·119
,,	9·603	+0·079
,,	2·262	+0·047

Methyl alcohol.

$\kappa_w \times 10^4$.	$\kappa_s \times 10^4$.	*E.M.F.*
105·6	38·30	+0·092
,,	7·189	+0·041
,,	1·003	+0·006
12·41	38·30	+0·149
,,	7·189	+0·103
,,	1·003	+0·050
1·333	38·30	+0·205
,,	7·189	+0·157
,,	1·003	+0·113

Ethyl alcohol.

$\kappa_w \times 10^4$.	$\kappa_s \times 10^5$.	*E.M.F.*
105·6	107·3	+0·088
,,	21·84	+0·054
,,	3·484	+0·000
11·97	107·3	+0·143
,,	21·84	+0·104
,,	3·484	+0·054
1·291	107·3	+0·195
,,	21·84	+0·161
,,	3·484	+0·114

Acetone.

$\kappa_w \times 10^4$.	$\kappa_s \times 10^5$.	*E.M.F.*
105·6	11·50	+0·104
,,	2·360	+0·067
,,	1·592	+0·045
12·45	11·50	+0·163
,,	2·360	+0·126
,,	1·592	+0·104
1·340	11·50	+0·223
,,	2·360	+0·185
,,	1·592	+0·163

Discussion.

When the experimental figures recorded in Table I are plotted as in Figs. 1, 2, and 3, it is found that the value of E is a linear function of $\log_{10} \kappa_w/\kappa_s$; moreover, the slopes of the different lines for each organic solvent coupled with water are nearly equal.

This general result may be put in the form $E = A \log_{10} \kappa_w/\kappa_s + B$, and Table II gives the values of the constants deduced for each case.

TABLE II.

Solvent.	*A.*	*B.*
Pyridine	−0·065	−0·352
Aniline	−0·065	−0·092
Acetonitrile	−0·064	−0·091
Propionitrile	−0·066	−0·012
Phenylacetonitrile	−0·057	+0·088
Ethyl cyanoacetate	−0·057	0·095
Benzonitrile	−0·060	0·087
Methyl alcohol	−0·059	0·117
Ethyl alcohol	−0·057	0·145
Acetone	−0·063	0·227

Now, on the basis of the Nernst theory, the *E.M.F.* of the cell $Ag|AgNO_3$(aqueous)$|AgNO_3$ (non-aqueous)$|Ag$ is given by

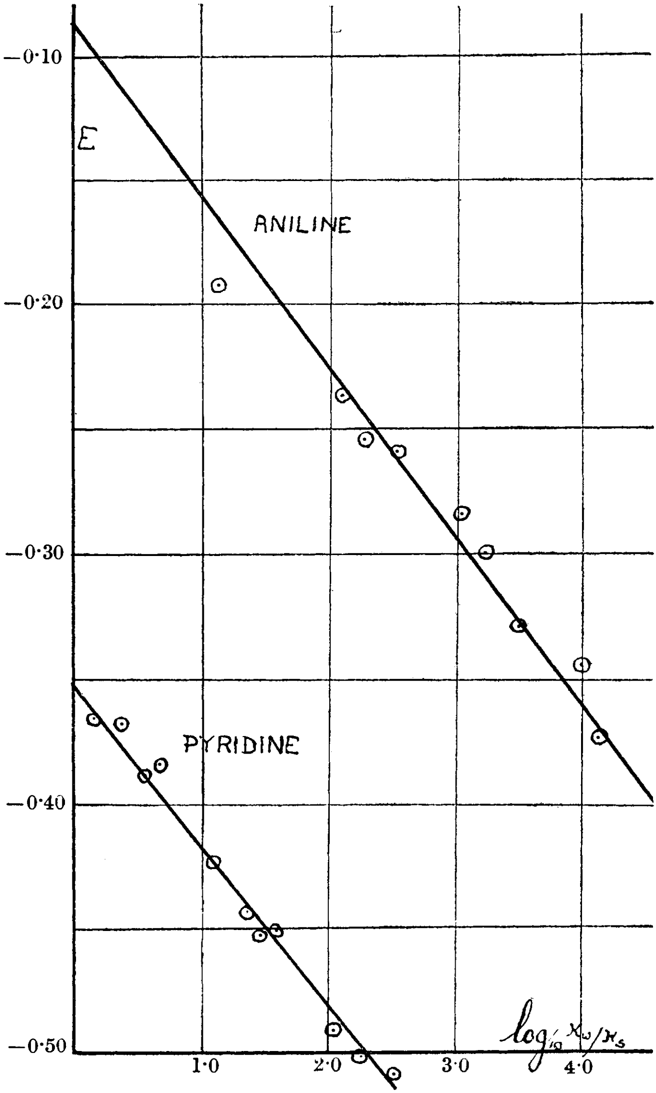
$$E = RT/F \,.\, \log_e P_w/rc_w - RT/F \,.\, \log_e P_s/rc_s + e$$
$$= RT/F \,.\, \log_e P_wc_s/P_sc_w + e.$$

In this expression, e is the liquid junction potential, which may be positive or negative, P_w and P_s are the electrolytic solution tensions of silver in water and in the organic solvent respectively, c_w and c_s are the ionic concentrations of the two solutions respectively, and r is a factor to convert concentration to pressure terms.

Further, on the classical view, $c_s/c_w = \kappa_s\Lambda_{\infty\, w}/\kappa_w\Lambda_{\infty\, s}$ so that

$$E = RT/F \,.\, \log_e P_w\Lambda_{\infty\, w}/P_s\Lambda_{\infty\, s} - RT/F \,.\, \log_e \kappa_w/\kappa_s + e \quad . \quad . \quad (1)$$

FIG. 1.

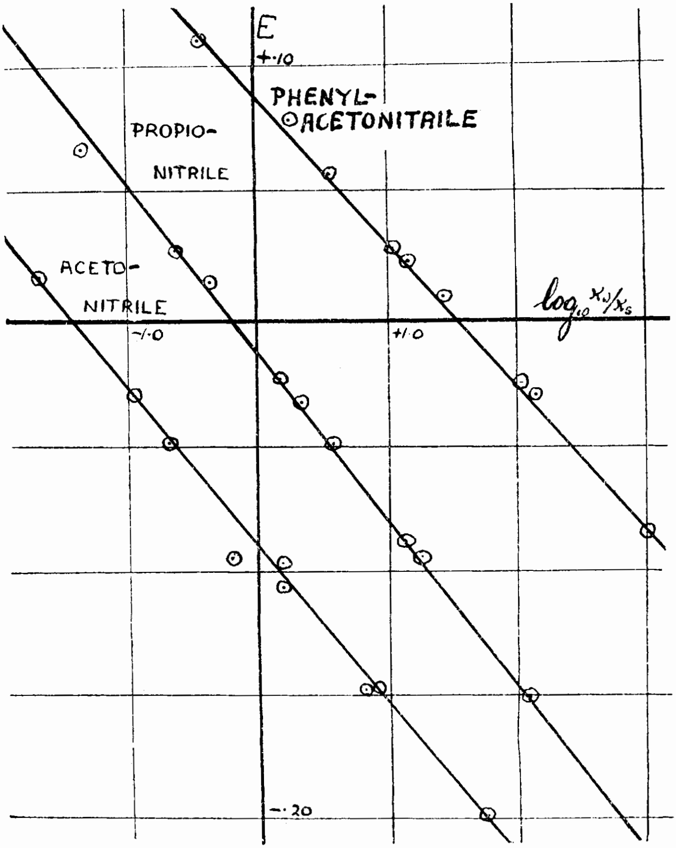


If this theoretical relationship is compared with the general empirical result of this investigation, *viz.*, $E = A \log_{10} \kappa_w/\kappa_s + B$, it appears that e must be expressible as the sum of two terms, one a constant and the other involving $\log_{10} \kappa_w/\kappa_s$. Hence (1) assumes the form

$$E = b \log_{10} P_w\Lambda_{\infty\, w}/P_s\Lambda_{\infty\, s} - a \log_{10} \kappa_w/\kappa_s$$

and therefore $a = -A$, and $b \log_{10} P_w\Lambda_{\infty\, w}/P_s\Lambda_{\infty\, s} = B$. Since B has been determined in the present research, and the values of Λ_∞ in water and in the organic solvents can be obtained, the last equation would provide a means of calculating P_w/P_s if the value of b could be ascertained. This difficulty cannot be surmounted unless either e is known or some assumption is made regarding it. The latter course has been adopted, and it is assumed that when $E = 0$, $e = 0$ (compare Baur, *Z. physikal. Chem.*, 1923, **103**, 39; *Trans. Faraday Soc.*, 1924, **19**, 718). On this basis, from (1),

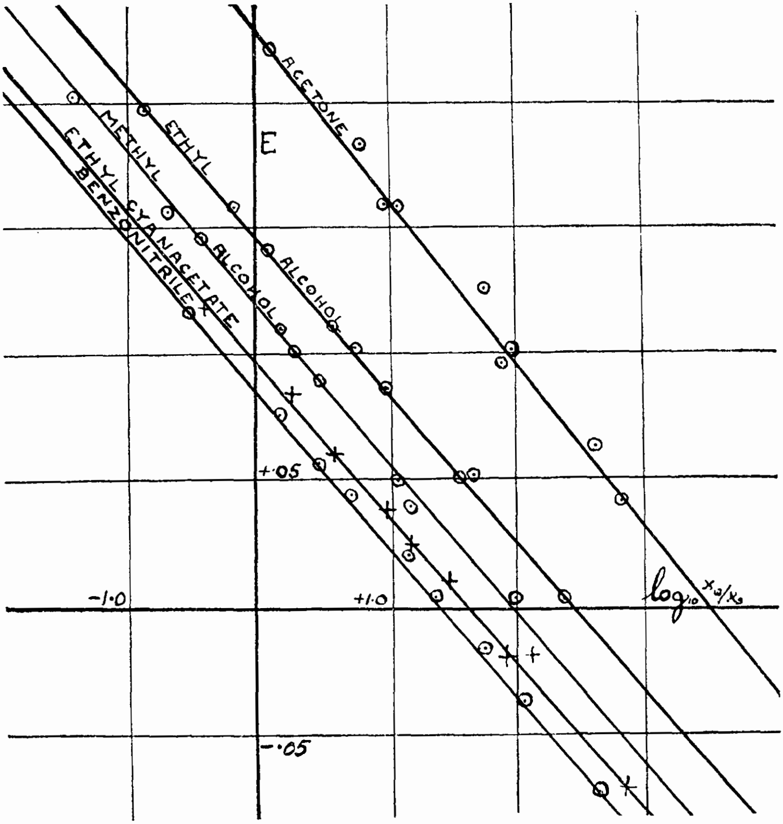
FIG. 2.



$\log_{10} P_w\Lambda_{\infty\,w}/P_s\Lambda_{\infty\,s} = \log_{10} \kappa_w/\kappa_s$, and $B = -A \log_{10} \kappa_w/\kappa_s = -A \log_{10} P_w\Lambda_{\infty\,w}/P_s\Lambda_{\infty\,s}$.

The values of A and B are known for each solvent from the graphs (see Table II). The value of Λ_∞ for silver nitrate in water at 25° is taken as 134 (Harkins, *J. Amer. Chem. Soc.*, 1911, **33**, 1819), and the values of Λ_∞ for silver nitrate in the various organic solvents have been obtained by taking as a starting point the value of $\Lambda_\infty = 113$ in methyl alcohol (Frazer and Hartley, *Proc. Roy. Soc.*, 1925, **109**, *A*, 362) and calculating the others therefrom with the help of the Walden rule: $\Lambda_\infty \times \eta = \text{constant}$.* The figures employed for the viscosity (η) of the different solvents (taken either from Walden, *op. cit.*, or from the Landolt–Börnstein Tabellen) are

FIG. 3.



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* The values of Λ_∞ obtained by the above method are as comparable as those given by different observers. Moreover, the data given in the literature are scanty and not always trustworthy.

given in the second column of Table III, whilst the values of Λ_∞ derived, except for water and methyl alcohol, as stated above, are tabulated in the third column. The fourth column contains the values of P_w/P_s, and the fifth the normal potentials of silver calculated from the equation $\epsilon_n = 0{\cdot}7995 + 0{\cdot}058 \log_{10} P_w/P_s$, in which the normal potential of silver in water is taken as + 0·7995 (Lewis and Randall, "Thermodynamics," p. 414).

TABLE III.

Solvent.	η.	Λ_∞ for $AgNO_3$ at 25°.	P_w/P_s.	ϵ_n.
Pyridine	0·00894	71·4	$2{\cdot}05 \times 10^{-6}$	+0·470
Aniline	0·0374	17·1	$4{\cdot}90 \times 10^{-3}$	+0·666
Acetonitrile	0·00345	185·0	$5{\cdot}24 \times 10^{-2}$	+0·725
Propionitrile	0·00413	154·6	0·759	+0·799
Phenylacetonitrile	0·0193	33·1	8·64	+0·853
Ethyl cyanoacetate	0·0250	25·5	8·82	+0·854
Benzonitrile	0·0123	51·9	10·9	+0·860
Methyl alcohol	0·00565	113·0	81·1	+0·910
Ethyl alcohol	0·0111	57·5	150·0	+0·926
Acetone	0·00316	202·0	6043·0	+1·019

The values of P_w/P_s support the generally accepted view that the electrolytic solution tension of a metal varies with the solvent, but are in conflict with the attempted correlation of solution tension and dielectric constant (compare p. 270).

The suggestion has been made (Brodsky, *loc. cit.*) that the solution tension of a metal in different solvents should run parallel with the solubility of a given salt of the metal in these liquids, and with the object of testing this relationship the solubilities of silver nitrate in pyridine, aniline, propionitrile, phenylacetonitrile, and ethyl cyanoacetate have been roughly determined at room temperature (18°). Figures for the other solvents have been taken from Walden's book. In Table IV the various solvents are arranged in the order of diminishing solution tension, whilst the corresponding dielectric constants (*D.C.*) and solubilities (in g. per 100 g. of solvent) are set out in the second and third columns.

TABLE IV.

Solvent.	*D.C.*	Solubility.	Solvent.	*D.C.*	Solubility.
Pyridine	12·4	27	Ethyl cyanoacetate	27·7	35
Aniline	6·85	22	Benzonitrile	26·3	105
Acetonitrile	36·4	290	Methyl alcohol	35·4	3·7
Propionitrile	27·5	180	Ethyl alcohol	25·4	3·1
Water	81·7	270	Acetone	21	0·3
Phenylacetonitrile	15	75			

The results of the present investigation show that the solution tension of silver is definitely greater in pyridine, aniline, and acetonitrile than in water, a relationship which is in conflict with the formulation of Baur and others (see p. 270). Altogether, there is an absence of any kind of order in the dielectric constants when the solvents are arranged in order of decreasing solution tensions as above, and there is also no obvious relation between the solubility of silver nitrate and the solution tension of the silver ion. It seems that the existence of specific attractive forces between the solvent molecules and the metal ion would account best for the observed effects, the high solution tension of silver in pyridine being due to this solvent's pronounced ammoniacal character.

Summary.

(1) The solution tensions and normal potentials of silver in various solvents at room temperature have been deduced by a new method.

(2) The results show that there is no relation at all between the solution tension (or normal potential) and the dielectric constant of the solvent.

(3) An explanation is sought in the action of specific attractive forces between the metal ion and the solvent molecule. Molecules containing groups of an ammoniacal or nitrile character are shown to have, in general, a greater affinity for the silver ion than those containing hydroxylic or ketonic groups.

In conclusion, the author desires to acknowledge his debt to Professor J. C. Philip, F.R.S., for the interest and valuable suggestions with which he has furthered this work.

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