CXCIX.—*The Solubility of Silver Chloride, Silver Bromide, and Silver Iodide and the Normal Potentials of Chlorine, Bromine, and Iodine in Methyl Alcohol and Ethyl Alcohol.*

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IN a previous communication (J., 1928, 269) a method was described for determining the solution tension and normal potential of a metal in non-aqueous solvents, and by applying this method to the primary electrode Ag|$AgNO_3$, these properties of silver were evaluated in ten organic liquids. In the present paper some results are described for the secondary electrode Ag|AgX,NaX (where X = Cl, Br, or I) in methyl and ethyl alcohols, the same method being used in order to determine (1) the solubilities of the three silver halides and (2) the solution tensions and normal potentials of chlorine, bromine, and iodine in these solvents.

The *E.M.F.* of the cell, $\underset{\text{water}}{\text{Ag}|\text{AgX,NaX}} \,\vdots\, \underset{\substack{\text{non-aqueous}\\\text{solvent}}}{\text{NaX,AgX}|\text{Ag}}$, given by the Nernst formula is

$$E = (RT/nF) \,.\, \log_e (P_w/P_s)_{Ag} - (RT/nF) \,.\, \log_e (c_w)_{Ag}/(c_s)_{Ag} + e \quad (1)$$

where $(P_w/P_s)_{Ag}$ is the ratio of the solution tension of silver in water to that in the non-aqueous solvent, $(c_w)_{Ag}$ and $(c_s)_{Ag}$ are the concentrations (more strictly, activities) of the silver ion in water and in the non-aqueous solvent respectively, and e is the liquid-junction potential. If L_w, L_s are the respective solubility products of the salt AgX, and $(c_w)_X$, $(c_s)_X$ the respective concentrations of the halogen ion, $L_w = (c_w)_{Ag} \,.\, (c_w)_X$ and $L_s = (c_s)_{Ag} \,.\, (c_s)_X$, and (1) becomes $E = (RT/nF) \,.\, \log_e [(P_w/P_s)_{Ag} \,.\, (L_s/L_w)] + (RT/nF) \,.\, \log_e (c_w)_X/(c_s)_X + e$ and, deducing (as previously, *loc. cit.*) the ionic concentrations from conductivity data, we have

$$E = (RT/nF) \,.\, \log_e [(P_w/P_s)_{Ag} \,.\, (L_s/L_w) \,.\, (\Lambda_{\infty s}/\Lambda_{\infty w})] + (RT/nF) \,.\, \log_e \kappa_w/\kappa_s + e \quad . \quad . \quad . \quad (2)$$

where κ_w, κ_s are the specific conductivities and $\Lambda_{\infty w}, \Lambda_{\infty s}$ the molecular conductivities at infinite dilution of the salt NaX in water and in the non-aqueous solvent respectively.

The *E.M.F.* of the cell (see results) is a linear function of $\log_{10} \kappa_w/\kappa_s$, *i.e.*,

$$E = B + A \log_{10} \kappa_w/\kappa_s \quad . \quad . \quad . \quad . \quad (3)$$

(where A and B are constants), and on the assumption (*loc. cit.*) that when $E = 0$, $e = 0$, comparison of (2) and (3) yields

$$B = A \log_{10} [(P_w/P_s)_{Ag} \,.\, (L_s/L_w) \,.\, (\Lambda_{\infty s}/\Lambda_{\infty w})] \quad . \quad . \quad (4)$$

Since the values of $(P_w/P_s)_{Ag}$ have been determined previously (*loc. cit.*), those of $\Lambda_{\infty w}$ and $\Lambda_{\infty s}$ are known, and the constants A and B are determined in this investigation, (L_w/L_s) can be calculated.

EXPERIMENTAL.

The *E.M.F.* and conductivity apparatus and the purification of the alcohols have been described previously (J., 1927, 647; 1928, 524; *loc. cit.*).

Sodium chloride (Hopkin and Williams's " Puriss.") and sodium bromide (Kahlbaum) were purified by three recrystallisations from aqueous ethyl alcohol. Sodium iodide (B. D. H.) was similarly recrystallised from pure ethyl alcohol, which was distilled, but not dried, for this purpose. The salts were dried over phosphoric oxide in a vacuum.

TABLE I.

	Methyl alcohol.			Ethyl alcohol.	
κ_w.	κ_s.	E (volt).	κ_w.	κ_s.	E (volt).
		Silver chloride.			
86·60	43·53	−0·046	86·60	1·925	−0·042
,,	6·067	−0·004	,,	0·2377	+0·007
,,	0·7720	+0·043	9·670	1·925	−0·092
9·670	43·53	−0·092	,,	0·2377	−0·050
,,	6·067	−0·052	1·114	1·925	−0·140
,,	0·7720	−0·008	,,	0·2377	−0·098
1·114	43·53	−0·137			
,,	6·067	−0·095			
,,	0·7720	−0·054			
		Silver bromide.			
75·63	41·62	−0·038	75·63	15·88	−0·072
,,	5·688	±0·000	,,	2·257	−0·031
,,	0·7298	+0·049	,,	0·2998	+0·013
8·417	41·62	−0·082	8·417	15·88	−0·126
,,	5·688	−0·040	,,	2·257	−0·082
,,	0·7298	+0·001	,,	0·2998	−0·037
1·031	41·62	−0·130	1·031	15·88	−0·170
,,	5·688	−0·087	,,	2·257	−0·122
,,	0·7298	−0·045	,,	0·2998	−0·083
		Silver iodide.			
86·80	51·57	−0·015	86·80	17·80	−0·045
,,	6·803	+0·027	,,	2·578	±0·000
,,	0·8433	+0·071	,,	0·3223	+0·047
9·541	51·57	−0·066	9·541	17·80	−0·092
,,	6·803	−0·020	,,	2·578	−0·056
,,	0·8433	+0·027	,,	0·3223	−0·005
1·019	51·57	−0·109	1·019	17·80	−0·142
,,	6·803	−0·070	,,	2·578	−0·102
,,	0·8433	−0·025	,,	0·3223	−0·052

The silver halides were prepared by precipitation from aqueous sodium halide solution with a slight excess of silver nitrate. The solution was boiled and the precipitated halide was washed repeatedly by decantation, filtered off, washed until free from silver nitrate, and dried first in a steam-oven and then over phosphoric oxide in a vacuum. Precautions were taken to prevent the action of light; there was no detectable discoloration. The *E.M.F.* measurements were carried out with the cells in a dark box, and each cell was protected by a thick opaque covering of black paper. No discoloration was observed after the measurements.

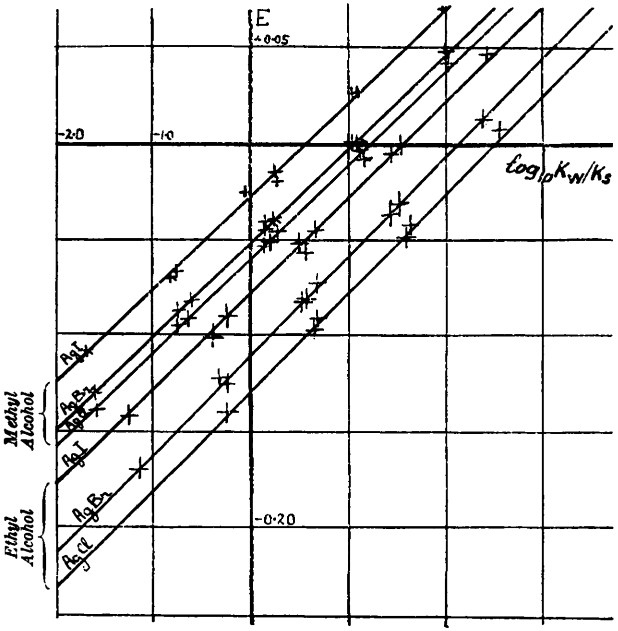
The solutions were approximately $N/10$, $N/100$, and $N/1000$ in water and the non-aqueous solvents, and by all possible combinations nine *E.M.F.*'s were measured. The solubility of sodium chloride in pure ethyl alcohol is not sufficiently great to give an $N/10$-solution, so only six *E.M.F.*'s were measured in this case. Two silver electrodes were inserted into each solution, which was saturated with the silver halide. The convention has been retained of giving the *E.M.F.* (E) the same sign as the non-aqueous electrode. The specific conductivities, κ_w, κ_s, in Table I are in mhos × 10^4/cm. measured at 25° ± 0·02°. The specific conductivity of the pure solvent has, as previously, been subtracted in all cases from that of the solution.

Discussion.

The values of the constant B deduced from the linear plots of E against $\log_{10} \kappa_w/\kappa_s$ [see Fig. 1 and equation (3)] are tabulated below.

	AgCl.	AgBr.	AgI.
Methyl alcohol	−0·062	−0·052	−0·028
Ethyl alcohol	−0·128	−0·110	−0·080

FIG. 1.



The slope of all the lines (A) is very nearly the same and equal to + 0·050.

In order to calculate the solubility ratios ($\sqrt{L_w/L_s}$) the values of $(P_w/P_s)_{Ag}$ previously determined have been used. These are 81·1 for methyl alcohol and 150 for ethyl alcohol. The following values for Λ_∞ at 25° have been derived from the ionic mobilities given by Ulich (*Trans. Faraday Soc.*, 1927, **23**, 390) for water and ethyl alcohol and by Hartley and Raikes (*ibid.*, p. 394) for methyl alcohol :

	NaCl.	NaBr.	NaI.
Water	127·6	129·4	128·0
Methyl alcohol	97·0	101·2	106·7
Ethyl alcohol	43·3	44·4	48·2

There is some uncertainty in these values, but an error of 10% in the ratio $\Lambda_{\infty w}/\Lambda_{\infty s}$ corresponds to an error of only 2·1 millivolts in B, so that small differences in Λ_∞ have only a negligible effect on the results.

The ratios of the solubilities of the silver halides in water to those in the two alcohols, calculated by equation (4), are given below (the solubility of a sparingly soluble salt is equal to the square root of its solubility product) :

	AgCl.	AgBr.	AgI.	Theoretical (Walden).
Water/methyl alcohol	33	26	16	12·2
Water/ethyl alcohol	136	90	47	33·5
Methyl alcohol/ethyl alcohol	4·3	3·5	2·9	2·7

The solubility ratios for water/methyl alcohol deduced from *E.M.F.* measurements of a different type by Buckley and Hartley (*Phil. Mag.*, 1929, **8**, 334) are 43, 33, and 13 respectively.

The solubility of silver chloride, bromide, and iodide in water being taken as $1·3 \times 10^{-5}$, $7·8 \times 10^{-7}$, and $1·0 \times 10^{-8}$ mol./litre, the corresponding figures in methyl alcohol are $3·9 \times 10^{-7}$, $3·0 \times 10^{-8}$, $6·2 \times 10^{-9}$, and in ethyl alcohol, $9·6 \times 10^{-8}$, $8·7 \times 10^{-9}$, $2·1 \times 10^{-10}$ respectively.

Ionic Distribution Coefficients and Normal Potentials.—Michaelis and Fujita (*Z. physikal. Chem.*, 1924, **110**, 268) have shown on the basis of Nernst's theory of specific ionic distribution coefficients (*ibid.*, 1892, **9**, 132) that the following thermodynamic relationship holds for the distribution equilibrium of a completely ionised salt (composed of two ions) between two solvents 1 and 2 : (The result may be generalised to include miscible solvents by imagining the two solutions to be separated by a membrane which is permeable only to the ions but not to the two solvents.)

$$\gamma_C \cdot \gamma_A = (P_1/P_2)_C \cdot (P_1/P_2)_A = (c_1/c_2)^2 \quad . \quad . \quad (5)$$

where c_1 and c_2 are the concentrations of the salt, γ_C and γ_A are the ionic distribution coefficients, and $(P_1/P_2)_C = \gamma_C$, $(P_1/P_2)_A = \gamma_A$ are the ratios of the solution tensions of the kation and anion respectively. The ionic distribution coefficient is identically equal to the ratio of the solution tensions. For a sparingly soluble salt, c_1 and c_2 may be replaced by the solubilities s_1 and s_2; hence

$$\gamma_C \cdot \gamma_A = (s_1/s_2)^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

Hence if γ_C and (s_1/s_2) are known, γ_A can be calculated. The solubility product of a sparingly soluble salt composed of two ions in a given solvent is proportional to the product of the solution tensions of its constituent ions in that solvent.

From the solubility ratios given on p. 1554 and the values of γ_{Ag} of 81·1 for water/methyl alcohol and 150 for water/ethyl alcohol, the values of γ_A given in Table II were obtained. The normal potentials were then calculated from the equation e_n(alcohol) = e_n(water) − 0·058 $\log_{10} \gamma_A$, the normal potentials in water given by Lewis and Randall (" Thermodynamics," p. 433) being used. The author's figures for silver (*loc. cit.*) are also included.

TABLE II.

Ionic distribution coefficients and normal potentials.

	Water.	Methyl alcohol.		Ethyl alcohol.	
	e_n	γ_A	e_n	γ_A	e_n
Chlorine	+1·3594	13·2	+1·294	123	+1·238
Bromine	+1·0659	8·6	+1·012	54	+0·966
Iodine	+0·5357	3·0	+0·508	15	+0·468
Silver	+0·7995	81·1	+0·910	150	+0·926

The values of log γ_A found by Bjerrum and Larsson (*Z. physikal. Chem.*, 1927, **127**, 368) for the chloride, bromide, iodide, and silver ions for the solvent pair water–ethyl alcohol are 2·5, 1·8, 1·4, and 2·1 respectively, and are in reasonably good agreement with those found in this investigation, *viz.*, 2·1, 1·7, 1·2, and 2·2.

Isgarischew (*Z. Elektrochem.*, 1913, **19**, 491) estimated the liquid-junction potential by means of Henderson's formula and found that the normal potential of silver in methyl alcohol was + 0·91 volt, which is in exact agreement with the above value.

The normal potentials of chlorine, bromine, iodine, and silver in methyl alcohol referred to H = 0 in methyl alcohol, as given by Buckley and Hartley (*loc. cit.*), are + 1·128, + 0·849, + 0·369, and + 0·764 respectively. On subtracting these figures from those of this investigation, the differences are seen to be + 0·166, + 0·163, + 0·139, and + 0·146. Hence it follows that the normal potential of hydrogen in methyl alcohol is + 0·15(3) ± 0·014 volt.

Electrode Potential and Dielectric Constant.—Theoretical calculation of the difference of normal potential in two solvents. Born (*Z. Physik*, 1920, **1**, 45) has calculated the free energy of solvation, A_T, of an ion on the assumptions (1) that the ion is a rigid sphere and (2) that it is transferred from a vacuum into a continuous medium of dielectric constant ε. Thus $A_T = 1{\cdot}194 \times 10^{-11} Ne^2 z^2(1 - 1/\varepsilon)/r_i$ kg.-cals., where $e = 4{\cdot}774 \times 10^{-10}$ *e.s.u.*, $N = 6{\cdot}06 \times 10^{23}$ is the Avogadro number, z is the valency, and r_i the radius of the ion. The free energy of transference of an ion from one solvent (ε_1) to another (ε_2) is therefore

$$A_T = 1{\cdot}194 \times 10^{-11} Ne^2z^2(1/\varepsilon_1 - 1/\varepsilon_2)/r_i$$

and if e_n is the theoretical difference in normal potential in the two solvents, $\Delta A_T = 23{\cdot}074\Delta e_n$ and hence

$$\Delta e_n = 1{\cdot}194 \times 10^{-11} Ne^2z^2(1/\varepsilon_1 - 1/\varepsilon_2)/23{\cdot}074r_i \quad . \quad (7)$$

The ionic radii of the chloride, bromide, iodide, and silver ions, deduced by Goldschmidt (*Trans. Faraday Soc.*, 1929, **25**, 282) from an X-ray examination of crystal structure, are 1·81, 1·96, 2·20, and 1·13 Å.U. respectively. The dielectric constants of water, methyl alcohol, and ethyl alcohol have been taken as 81·7, 35·4, and 25·4 respectively.

Since in actual fact ions are not rigid (compare Fajans, *Z. Elektrochem.*, 1928, **34**, 502) and solvents are not continuous dielectric media, Born's formula can never give an exact interpretation of the experimental results. Nevertheless, it is of interest to see how closely the differences of normal potential calculated from this formula agree with the corresponding values obtained from the experimental results of this investigation. These data are therefore compared in Table III.

TABLE III.

Differences in normal potential.

	Water–methyl alcohol.		Water–ethyl alcohol.		Methyl alcohol–ethyl alcohol.	
	Found.	Calc.	Found.	Calc.	Found.	Calc.
Cl	−0·065	−0·063	−0·121	−0·109	−0·056	−0·044
Br	−0·054	−0·058	−0·100	−0·100	−0·046	−0·041
I	−0·028	−0·052	−0·068	−0·089	−0·040	−0·036
Ag	+0·110	+0·102	+0·126	+0·173	+0·016	+0·070

Since the difference in normal potential of a given element in two solvents is given by b' $(1/\varepsilon_1 - 1/\varepsilon_2)$ (where, by equation 7, b' is a constant), the normal potential itself is given by a formula of the type $e_n = a + b/\varepsilon$, where a and b are constants characteristic of the ion and independent of the solvent. This formula has been put forward by Brodsky (*Z. physikal. Chem.*, 1926, **121**, 1) and confirmed for the electrodes Hg|HgX,KX (where X = Cl, Br, or I) in water, methyl alcohol, ethyl alcohol, and binary mixtures of these liquids. He has recently derived this formula in the above manner from that of Born (*Physikal. Z.*, 1929, **30**, 665). Considering Brodsky's formula as another form of that of Born, it can be expected to be strictly valid only under the same conditions, *i.e.*, for a rigid ion in a continuous dielectric medium. It appears that these conditions are approximately fulfilled by the three halogen ions and the silver ion in the three solvents now investigated. Measurements for the silver ion in ten organic liquids of diverse chemical character (Koch, *loc. cit.*) have, however, shown that, in general, the dielectric constant is not the only property of the solvent which determines the electrode potential. The measure of agreement between theory and experiment exhibited by Table III and by the results of Brodsky must therefore be attributed to the fact that the two alcohols and water are chemically similar, and that any specific ionic–molecular interaction is negligibly small compared with the experimental inaccuracy.

The Walden relation. According to Baur, Krüger, and Walden (Walden, "Elektrochemie Nichtwässerige Lösungen," 1924, pp. 355, 443), the distribution coefficients of *all* ions for a given pair of solvents should be the *same* and equal to $(\varepsilon_1/\varepsilon_2)^3$, where ε_1 and ε_2 are the dielectric constants. Hence by equation (6), $s_1/s_2 = (\varepsilon_1/\varepsilon_2)^3$, that is, the solubility of a sparingly soluble salt is proportional to the cube of the dielectric constant of the solvent.

The theoretical figures based on this supposed relation are given in the last column of the table on p. 1554. There is no agreement, except for the case of silver iodide, which is probably fortuitous, and the fact that the ratios are different for all three silver halides is in itself a sufficient contradiction.

The Walden figures for γ_A in Table II are 12·2 for water/methyl alcohol and 33·5 for water/ethyl alcohol. There is again no agreement. The ratios γ_A for methyl alcohol/ethyl alcohol for the chloride, bromide, iodide, and silver ions are 9·6, 6·3, 5·0, and 1·8 respectively, whereas Walden's value is 2·7.

On the same basis, the difference in normal potential in two solvents 1 and 2 should be a constant with the *same* value for *all* elements, *i.e.*, $\Delta e_n = (3RT/nF) \, . \log_e \varepsilon_1/\varepsilon_2$. The values of this constant for univalent ions for the solvent pairs water–methyl alcohol, water–ethyl alcohol, and methyl alcohol–ethyl alcohol are 0·063, 0·089, and 0·025 volt respectively. Comparison with Table III shows that there is no agreement.

Summary.

(1) The solubilities of silver chloride, silver bromide, and silver iodide have been determined in methyl and in ethyl alcohol by an electrochemical method previously described.

(2) The results are in disagreement with the Walden relation,

which states that the solubility is proportional to the cube of the dielectric constant of the solvent.

(3) The distribution coefficients of the three halogen ions for the solvent pairs water–methyl alcohol and water–ethyl alcohol have been calculated from the results, whence have been deduced the normal potentials in these solvents.

(4) The differences in normal potential of chlorine, bromine, iodine, and silver for pairs of these solvents have been calculated by a formula of Born and found to be in reasonably good agreement with the experimental values.

(5) It is shown that in cases where the specific ionic–molecular interaction is negligibly small, Brodsky's formula, *viz.*, $e_n = a + b/\varepsilon$ (where e_n is the normal potential, ε the dielectric constant of the solvent, and a and b are constants), is valid. The theoretical foundation of this formula is derived from Born's equation, which assumes that the ion is a rigid sphere located in a continuous dielectric medium. These conditions are, apparently, approximately fulfilled for the chloride, bromide, iodide, and silver ions in water, methyl alcohol, and ethyl alcohol.

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