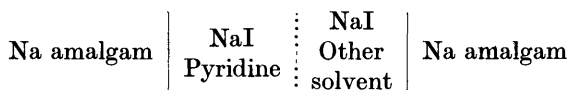


CXLVIII.—*The Solution Tension of Sodium in Solvents other than Water.*

By FREDERICK KARL VICTOR KOCH.

RESULTS previously obtained (J., 1928, 269) showed that there was no simple relationship between the solution tension of silver in ten organic solvents and the corresponding dielectric constant of the solvent. It seemed that this might possibly be due to the fact that the electronic configuration of the silver ion is not of the inert-gas type. To test this point a similar investigation has now been carried out on the sodium ion, since this is known to have such a structure.

The cells investigated were of the type



in which the concentration of sodium in the amalgam is the same on both sides of the cell. As previously shown (*loc. cit.*), the *E.M.F.* (*E*) of such cells may be expressed in the form

$$E = B + A \cdot \log_{10} \kappa_P / \kappa_S$$

where κ_P and κ_S are the respective specific conductivities of sodium iodide in pyridine and the other solvent, and *A* and *B* are constants such that (on the basis of the assumptions previously stated)

$$B = A \cdot \log_{10} P_P \Lambda_{\infty P} / P_S \Lambda_{\infty S}$$

where P_P and P_S are the solution tensions of sodium, and $\Lambda_{\infty P}$ and $\Lambda_{\infty S}$ are the molecular conductivities at infinite dilution of sodium iodide in pyridine and in the other solvent respectively. Since all the necessary quantities can be determined, the ratio P_P/P_S can be calculated.

EXPERIMENTAL.

The apparatus and the purification of the materials have been previously described (*loc. cit.*; J., 1928, 525; 1930, 1552, 2056). The Broca galvanometer (internal resistance 1000 ohms) was used as detecting instrument. Half elements of the type depicted in Fig. 1 were employed because they require the use of only small amounts of amalgam and permit rapid and easy manipulation.

Of the ten solvents previously investigated, aniline and phenyl-acetonitrile were not now used because of the very small solubility of sodium iodide therein; moreover, the latter solvent appeared to react with this salt. Sodium amalgam reacts with ethyl cyanoacetate, but since the *E.M.F.*'s were reasonably steady, measure-

ments were nevertheless carried out : these were made as rapidly as possible.

Sodium amalgam was prepared as follows. Nitrogen from a cylinder was passed through four large wash-bottles. The first was empty and served as a trap to prevent back suction of liquid into the cylinder, the next two contained pyrogallol solution, and the

FIG. 1.

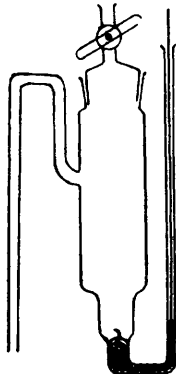
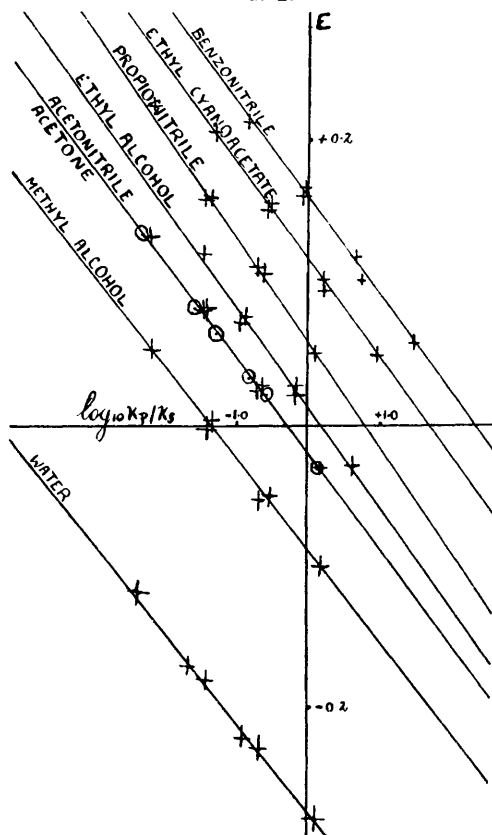


FIG. 2.



last concentrated sulphuric acid. The nitrogen then passed through a calcium chloride tube, about one yard long, and into a long-necked Jena-glass flask (about 300 c.c.) in which the amalgam was made. From this flask the nitrogen passed through another calcium chloride tube, about $\frac{1}{2}$ yard long, through another empty wash-bottle (to prevent back diffusion of air) and thence into the atmosphere. The mercury was purified by covering it with dilute nitric acid and bubbling air through it for 48 hours ; it was thoroughly

washed with distilled water and dried with filter paper, from which any loose bits had been previously removed. A suitable quantity was then thoroughly dried by being heated in the Jena flask (the neck of which was water-cooled) in a current of dry nitrogen, and after this had cooled, an amount of Kahlbaum's sodium, corresponding approximately to a 0.2% amalgam, was added. The amalgam so obtained was almost as bright as the original mercury. It was freshly prepared immediately before it was required and was used only once. A difference of as much as 10% between the concentrations of sodium in the amalgam on the two sides of the cell would produce an error of only 2.1 millivolts in the determined *E.M.F.* The *E.M.F.*'s were reproducible to within ± 5 mv.

The solutions of sodium iodide in pyridine were approximately *N/10*, *N/100*, and *N/1000* and had specific conductivities (κ_F) at $25^\circ \pm 0.02^\circ$ of 1.052×10^{-3} , 1.849×10^{-4} , and 3.298×10^{-5} mho/cm. respectively. The benzonitrile solutions were approximately *N/100* and *N/1000*, having respective specific conductivities (κ_S) of 2.334×10^{-4} and 3.409×10^{-5} mho/cm. The solutions in the remaining seven solvents were approximately *N/10* and *N/100*, and the corresponding specific conductivities (κ_S) in mho/cm. $\times 10^4$ are tabulated below :

Conc.	H ₂ O.	MeOH.	Aceto- nitrile.	Acetone.	EtOH.	Propio- nitrile.	Ethyl cyano- acetate.
<i>N/10</i>	87.61	51.42	75.48	56.03	18.02	51.48	6.877
<i>N/100</i>	9.624	6.769	7.650	9.247	2.593	8.392	1.150

The specific conductivity of the pure solvent has been subtracted from the observed specific conductivity of the solution in every case.

In the following table are recorded the *E.M.F.*'s (in volts) of the cells. They have been given the opposite sign to the electrode in the pyridine solution.

Solvent.	<i>N/10</i> NaI	<i>N/100</i> NaI in pyridine.	<i>N/1000</i> NaI in pyridine.
Water	<i>N/10</i> NaI	- 0.222	- 0.173
	<i>N/100</i> "	- 0.283	- 0.230
Methyl alcohol	<i>N/10</i> "	- 0.054	- 0.003
	<i>N/100</i> "	- 0.102	- 0.055
Acetonitrile	<i>N/10</i> "	+ 0.033	+ 0.080
	<i>N/100</i> "	- 0.031	+ 0.020
Acetone.....	<i>N/10</i> "	+ 0.022	+ 0.080
	<i>N/100</i> "	- 0.029	+ 0.028
Ethyl alcohol	<i>N/10</i> "	+ 0.019	+ 0.068
	<i>N/100</i> "	- 0.030	+ 0.025
Propionitrile.....	<i>N/10</i> "	+ 0.109	+ 0.166
	<i>N/100</i> "	+ 0.047	+ 0.104
Ethyl cyanoacetate.....	<i>N/10</i> "	+ 0.094	+ 0.149
	<i>N/100</i> "	+ 0.047	+ 0.102
Benzonitrile	<i>N/100</i> "	+ 0.114	+ 0.161
	<i>N/1000</i> "	+ 0.055	+ 0.098

Discussion.

Solution Tensions and Normal Potentials.—The values of the constants A and B deduced from the linear graphs of E against $\log_{10} \kappa_P / \kappa_S$ (see Fig. 2) are tabulated below.

Solvent.	A .	B .	Solvent.	A .	B .
Water	- 0.065	- 0.282	Ethyl alcohol	- 0.067	+ 0.010
Methyl alcohol ...	- 0.065	- 0.095	Propionitrile ...	- 0.064	+ 0.059
Acetonitrile	- 0.069	- 0.023	Ethyl cyano-		
Acetone	- 0.067	- 0.023	acetate	- 0.069	+ 0.113
			Benzonitrile ...	- 0.069	+ 0.156

The values of Λ_∞ for sodium iodide in water, methyl alcohol, and ethyl alcohol have been obtained from the mobilities of the individual ions given by Ulich (*Trans. Faraday Soc.*, 1927, **23**, 390), and the values for the other solvents have been calculated by means of the Walden rule, $\Lambda_\infty \eta = \text{constant}$; for this purpose, the average of the two values of Λ_∞ for sodium iodide at 25° in benzonitrile given by Martin (J., 1929, 3282) were taken, together with the same figures for the viscosities (η) as previously (*loc. cit.*, p. 279). In the following table are given the values of

$$P_w/P_s = (P_w/P_P) \cdot (P_P/P_s),$$

where P_w is the solution tension of sodium in water. The normal potentials (e_0) have been calculated from the formula $e_0 = -2.713 + 0.058 \log_{10} P_w/P_s$, in which the numerical value of the normal potential of sodium in water (*i.e.*, 2.713) is that given by Lewis and Randall ("Thermodynamics," 1923, p. 433).

Solvent.	Dielectric constant.	Λ_∞ for NaI at 25°.	P_w/P_s .	e_0 .
Water	81.7	128	1.0	[- 2.713]
Methyl alcohol	35.4	107	6.3×10^2	- 2.551
Pyridine	12.4	65.8	1.1×10^4	- 2.478
Ethyl alcohol	25.4	48.2	1.2×10^4	- 2.477
Acetonitrile	36.4	170	1.3×10^4	- 2.474
Acetone.....	21	186	1.4×10^4	- 2.472
Ethyl cyanoacetate.....	27.7	23.5	1.7×10^5	- 2.408
Propionitrile.....	27.5	142	2.0×10^5	- 2.404
Benzonitrile	26.3	47.8	1.5×10^6	- 2.357

The value of the normal potential of sodium in methyl alcohol, referred to $e_0(\text{H}_2) = 0$ in methyl alcohol, deduced from *E.M.F.* measurements of a different type by Buckley and Hartley (*Phil. Mag.*, 1929, **8**, 336), is - 2.728. If the normal potential of hydrogen in methyl alcohol [referred to $e_0(\text{H}_2) = 0$ in water] be taken as + 0.15(3) (Koch, J., 1930, 1555), this value becomes - 2.57(5) when referred to $e_0(\text{H}_2) = 0$ in water.

It appears from the above results for the sodium ion that the dielectric constant is not the only property of the solvent of which the solution tension (or normal potential) is a function, but that it

depends, even in the case of an ion of inert-gas structure, on specific ionic-molecular forces. Further, when the solvents are arranged in the order of decreasing solution tension of sodium, then the sequence is quite different from that previously found for silver (*loc. cit.*).

Free Energies of Complex Formation.—The above experimental results may be subjected to the same theoretical analysis as that previously applied to those for the silver ion (see Koch, *Phil. Mag.*, 1930, **10**, 559).

If it be assumed that the sodium ion behaves as a *rigid* sphere in a *continuous* medium of dielectric constant ϵ , then its free energy of transference (A_T) from a vacuum to a pure solvent is given by Born's formula (*Z. Physik*, 1920, **1**, 45) as

$$A_T = (z^2 \cdot e^2 \cdot N) \cdot (1 - 1/\epsilon)/(r \cdot J) \text{ kg.-cals.}$$

where z is the valency and r the radius of the ion, e is the electronic charge, N the Avogadro number, and J a factor to convert electrostatic units to kg.-cals. The values of A_T have been calculated by taking the usual values of the universal constants and the value of $r = 0.98 \text{ \AA.U.}$ for the sodium ion, deduced by Goldschmidt (*Trans. Faraday Soc.*, 1929, **25**, 282) from an X-ray examination of crystal structure.

The absolute free energy of transference of an ion from a vacuum to a solvent cannot be determined experimentally, but only the free energy of transference, ΔA_E , from one solvent to another, *i.e.*, $\Delta A_E = n \cdot F \cdot \Delta e_0$, where Δe_0 is the difference in normal potential of the ion in the two solvents. Since, however, the solution tension of sodium and the solubility of sodium iodide are less in benzonitrile than in any of the other solvents, A_E has been arbitrarily taken as equal to A_T in this particular case. The "experimental" values of the free energies A_E have thus been obtained by adding on the differences ΔA_E . Although A_E can never be exactly equal to A_T , it is possible that these values of A_E are not appreciably less than the absolute values.

Now the free energy, A_T , given by the Born formula may be regarded as that corresponding to an *ideal* state of ionic-molecular interaction which may be called "ionic solvation" (*i.e.*, ionic-molecular electrovalency). In all *actual* cases there will, however, be an additional expenditure of energy due to a change in shape of the ion and one or more orientated solvent molecules. This extra energy A_C is given by the difference $A_C = A_E - A_T$ and has been termed "the free energy of complex formation," since it indicates a state of "ionic-molecular complex formation" (*i.e.*, ionic-molecular covalency).

The values of A_C (in kg.-cals. per g.-ion) given in the following table must, of course, be regarded as only approximate. (0.1 Kg.-cal. corresponds to about 4 mv.) The figures previously obtained (*ibid.*) for the silver ion are also included.

Solvent.	A_E .	A_T .	A_C (Na ⁺).	A_C (Ag ⁺).
Pyridine	164.4	154.4	10.0	17.5
Acetone.....	164.2	159.9	4.3	[0.0]
Water	169.9	166.0	3.9	(- 0.2)
Methyl alcohol	166.1	163.3	2.8	(- 0.3)
Ethyl alcohol	164.4	161.4	3.0	0.8
Acetonitrile	164.3	163.3	1.0	3.8
Propionitrile.....	162.7	161.7	1.0	3.4
Ethyl cyanoacetate.....	162.8	162.1	0.7	2.2
Benzonitrile	[161.6]	161.6	[0.0]	2.3

From these data it appears that the sodium ion is similar to the silver ion in its affinity for the pyridine molecule, but differs from it by having a greater affinity for molecules containing ketonic or hydroxyl groups than for those containing nitrile groups.

Summary.

The solution tensions and normal potentials of sodium in eight organic liquids have been determined by a method previously described. The results show that the solution tension (or normal potential) depends, not only upon the dielectric constant, but also (even in the case of an ion of inert-gas structure) upon specific ionic-molecular forces. The nature of these forces has been investigated theoretically.

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