LXVII.—*Silver Nitrate Concentration Cells in Acetonitrile and Benzonitrile.*

By Frederick Karl Victor Koch.

The Nernst formula for concentration cells

$$E = 2(1 - n_k)RT/nF \cdot \log_e C_1/C_2 \quad . \quad . \quad . \quad . \quad (1)$$

(where n_k is the transport number of the kation for primary electrodes, and C_1 and C_2 are the concentrations of the ions in the two solutions) has received good confirmation for aqueous solutions. It was first tested for non-aqueous solutions by Kahlenberg (*J. Physical Chem.*, 1900, **4**, 709), who investigated concentration cells of silver nitrate and cadmium iodide in acetonitrile and pyridine. The discrepancies between the observed and the calculated *E.M.F.*'s were large, except for silver nitrate in acetonitrile, and Kahlenberg concluded that the Nernst formula was not applicable to non-aqueous solutions. It is known, however, that complex conditions exist both in solutions of cadmium iodide in acetonitrile (Koch, J., 1927, 647) and in solutions of silver nitrate in pyridine (Abegg and Neustadt, *Z. physikal. Chem.*, 1909, **69**, 486), although Sakhanov and Grünbaum (*J. Russ. Phys. Chem. Soc.*, 1916, **48**, 1794) found that the Nernst formula was obeyed in the latter case if the solutions were sufficiently dilute. Wilson (*Amer. Chem. J.*, 1906, **35**, 78) found that although solutions of silver nitrate in ethyl alcohol conformed to the Nernst formula, its solutions in methyl alcohol showed deviations from the theory. Grant and Partington (*Trans. Faraday Soc.*, 1923, **19**, 414), however, have shown that the theory is accurately obeyed in the latter solvent. The Nernst formula has further been confirmed for silver nitrate concentration cells in acetone (Roshdestwensky and Lewis, J., 1912, **101**, 2094), ethyl alcohol (Pearce and Farr, *J. Physical Chem.*, 1914, **18**, 729; Krumreich, *Z. Elektrochem.*, 1916, **22**, 446), and ammonia (Cady, *J. Physical Chem.*, 1905, **9**, 477).

The following results for silver nitrate concentration cells in acetonitrile and benzonitrile at 0° and 25° likewise support the Nernst formula, and show that the solution laws are obeyed in these solvents at least as nearly as in water.

EXPERIMENTAL.

Materials.—Acetonitrile and benzonitrile were purified as previously described (J., 1927, 647; this vol., p. 269); they had specific conductivities of 0·5—1·0 × 10^{-7} and 0·5 × 10^{-7} mho, respectively, at 25°. Atomic-weight silver nitrate was kindly supplied by Dr. H. F. Harwood. The most concentrated solution (*N*/10 approx.) was made up by weight and the others by volume-dilution.

Apparatus.—The conductivity apparatus was the same as that previously described (*loc. cit.*, 1927). The *E.M.F.*'s were measured by the usual Poggendorff compensation method. The bridge wire (10 m. long), which was of the drum type (Leeds and Northrup), was calibrated by the method of Strouhal and Barus. The standard Weston cell was checked against other standard cells during the course of the investigations. Since the *E.M.F.*'s were small, they were measured in series with the standard cell in order to throw the zero point on to the centre of the bridge. Owing to the high resistance of these non-aqueous solutions, it is necessary to employ a high-resistance null instrument. Mudford's electromagnetically shielded galvanometer, with a resistance of 10,000 ohms, proved quite satisfactory.

The special all-glass cell was similar to that described by Krumreich (*loc. cit.*), and could be entirely immersed in the thermostat. The electrodes were inserted by means of ground-in joints and the liquid–liquid junction bridge was made as short as possible in order to reduce the resistance of the cell to a minimum. The electrodes consisted of silver foil wound round glass tubing; they were coated with a compact layer of crystalline silver by plating in a concentrated aqueous solution of silver nitrate, an even deposit being obtained by surrounding the electrode with a cylinder of silver foil. A platinum wire, which was fused to the silver foil, was connected through the bottom of the glass tube to the mercury–copper contact within.

Limits of Accuracy.—The *E.M.F.*'s in benzonitrile could be reproduced to about 0·5 millivolt, but those in acetonitrile only to about 1·0 millivolt; they have, however, been reduced in both cases to the nearest millivolt. The results given are the most consistent of several series which were recorded. The specific conductivity of every solution used was determined at 0° and 25° and the errors which would otherwise be introduced by intra- or extrapolation were thus avoided. The conductivity readings may be considered accurate to 0·1%, and since in the calculation of the *E.M.F.*'s only the specific conductivities themselves are used, all errors inherent in weighings, determination of density, etc., are automatically eliminated.

Results and Discussion.

In the following tables Q_1 and Q_2 are the weights of solvent (in kg. per g.-mol. of silver nitrate), and κ_1 and κ_2 are the specific conductivities (in mhos) of the two electrode solutions.

Acetonitrile.

Q_1.	Q_2.	$\kappa_1 \times 10^3$.	$\kappa_2 \times 10^3$.	E (obs.).	n_k.	E (calc.).
			At 25° ± 0·01°.			
487	8·21	0·2672	5·970	0·086	0·461	0·087
,,	16·4	,,	3·775	0·075	0·449	0·074
,,	32·8	,,	2·332	0·059	0·470	0·061
,,	65·7	,,	1·387	0·047	0·445	0·046
,,	121	,,	0·7958	0·030	0·465	0·031
,,	243	,,	0·4444	0·012	(0·540)	0·014
				Mean	0·458	
			At 0° ± 0·01°.			
487	8·21	0·2082	4·992	0·083	0·445	0·082
,,	16·4	,,	3·139	0·068	0·467	0·070
,,	32·8	,,	1·919	0·056	0·464	0·057
,,	65·7	,,	1·124	0·044	0·445	0·043
,,	121	,,	0·6339	0·029	0·446	0·029
,,	243	,,	0·3491	0·012	(0·506)	0·013
				Mean	0·453	

Benzonitrile.

Q_1.	Q_2.	$\kappa_1 \times 10^4$.	$\kappa_2 \times 10^4$.	E (obs.).	n_k.	E (calc.).
			At 25° ± 0·01°.			
640	10·0	0·3295	4·823	0·076	0·451	0·074
,,	20·0	,,	2·948	0·061	0·459	0·060
,,	40·0	,,	1·880	0·049	0·468	0·048
,,	80·0	,,	1·237	0·036	0·467	0·036
,,	160	,,	0·7716	0·023	0·474	0·024
,,	320	,,	0·5217	0·012	0·475	0·013
				Mean	0·466	
			At 0° ± 0·01°.			
640	10·0	0·2221	3·134	0·069	0·446	0·067
,,	20·0	,,	1·963	0·056	0·450	0·055
,,	40·0	,,	1·274	0·045	0·457	0·044
,,	80·0	,,	0·8459	0·034	0·462	0·034
,,	160	,,	0·5194	0·021	0·473	0·022
,,	320	,,	0·3521	0·011	0·475	0·012
				Mean	0·461	

The assumption has been made that the ionic concentration may be deduced from conductivity measurements. We then have

$$C_1/C_2 = \alpha_1 N_1/\alpha_2 N_2 \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where α_1, α_2 are the degrees of ionisation and N_1, N_2 are the normalities of the two solutions, respectively.

$$\left.\begin{array}{ll}\text{But} & \alpha_1 = \Lambda_1/\Lambda_\infty\,,\ \alpha_2 = \Lambda_2/\Lambda_\infty \\ \text{and} & \Lambda_1 N_1 = \kappa_1,\ \Lambda_2 N_2 = \kappa_2\end{array}\right\} \quad . \quad . \quad . \quad . \quad (3)$$

where Λ_1 and Λ_2 are the molecular conductivities corresponding to the normalities N_1 and N_2, and Λ_∞ is the molecular conductivity at infinite dilution. By inserting (3) in (2) and (2) in (1)

$$E = 2(1 - n_k)RT/F \,.\, \log_e \kappa_1/\kappa_2 \quad . \quad . \quad . \quad . \quad (4)$$

for a silver nitrate concentration cell ($n = 1$).

We have thus eliminated Λ_∞ and require only the values of the specific conductivities of the two solutions and that of the transport number in order to calculate the *E.M.F.*'s. The transport number of the silver ion for silver nitrate solutions in acetonitrile has been found by Schlundt (*J. Physical Chem.*, 1903, **6**, 189), using the direct Hittorf method, to be 0·448 and 0·471 for $N/11$- and $N/35$-solutions, respectively; but H. H. Morgan (in this laboratory; unpublished) obtained the values 0·442 and 0·448 at the same concentrations, showing a considerably smaller variation with dilution. Since no values of the transport number of the silver ion in benzonitrile are recorded in the literature, a determination was made for an $N/10$-solution by the usual method and found to be 0·396 (mean of 0·392 and 0·400). Determinations in more dilute solutions are untrustworthy owing to the high electrical resistance. The figures for n_k in the sixth column of the tables were deduced by comparing the observed *E.M.F.* with the *E.M.F.* calculated on the basis of the formula $E = RT/F \,.\, \log_e \kappa_1/\kappa_2$. The mean value of n_k was then used to obtain E (calc.) by formula (4).

It will be observed that the values of n_k for acetonitrile lie near to those obtained by Schlundt and Morgan, and those for benzonitrile, although higher than the value obtained by the direct method for an $N/10$-solution, are nearly the same as n_k for acetonitrile. It has in fact been shown by Walden [" Elektrochemie Nichtwässeriger Lösungen, 1924, p. 185; see also Carrara, *Gazzetta*, 1903, **33**, (ii), 241], on the basis of the expression $u\eta = k$ (where u is the mobility of an ion, η the viscosity of the solvent, and k a constant), that the transport number of an ion in a given salt should be independent of the solvent.

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