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POTENTIOMETRIC METHOD FOR THE DETERMINATION OF SODIUM IONS BY MEANS OF A GLASS ELECTRODE WITH A SODIUM FUNCTION

by

V. E. Goremykin

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Translated

from

IZVESTIYA AKADEMII NAUK S.S.S.R. 1957 (11), 1387

by

H. J. de Bruin

Sydney, July, 1958.

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Summary

It has been shown possible to determine the ionic concentration of natural waters by means of a glass electrode with a sodium function.

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The work by Nikolskiy and his school (1–4) on the theory of the glass electrode, and in particular the research by Schults on the glass electrode with a sodium function (S.G.E.) opened the way for its use in analytical applications. These possibilities were confirmed by subsequent research work on the stability and reproducibility of the EMF of the S.G.E. (5) and by the preliminary results of its use in the determination of the concentration of Na^+ in natural waters.

For the precise determination of Na^+ using the S.G.E., it appears to be important to establish the possibility of measuring the activity as well as the activity coefficients of the Na^+ ions, although it is known that strict thermodynamic theory deals only with the corresponding average values in the electrolyte. To measure a Na^+ according to the principles of the work by Harned (7) and Taylor (8), it is a condition to assume that $\gamma Na^+ = \gamma Cl^- = \gamma \pm NaCl$ in dilute NaCl solutions. The justification of this assumption, to a certain extent, is confirmed by measuring the EMF of the cells

Glass electrode | Soln. NaCl(m) || KCl sat | Hg_2Cl_2 | Hg (I)

Ag | AgCl | Soln. NaCl(m) || KCl sat | Hg_2Cl_2 | Hg (II)

Glass electrode | Soln. NaCl(m) || AgCl | Ag (III)

for different molalities of the standard solution of NaCl (table 1). From a graphical representation of the results of measurements of E in cell I and II as a function of $-\log a_{Na^+}$ and $-\log a_{Cl^-}$ respectively, straight lines are obtained in certain ranges, concentrations being equal to the gradients.

TABLE I

MEASUREMENT OF THE EMF OF A CELL WITH STANDARD SOLUTIONS.

m_{NaCl} in the cell.	E of the Cell			Δ E of the cell		
	I	II	III	I	II	III
0.1	+0.0433	−0.0467	−0.0024	0.0161	0.0161	0.0322
0.05	+0.0272	−0.0628	−0.0356	0.0383	0.0382	0.0765
0.01	−0.0111	−0.1010	−0.1121	0.0169	0.0170	0.0339
0.005	−0.0280	−0.1180	−0.1460			

To work out the possibilities of measuring the ion activity by means of cells with a liquid junction, mixtures of solutions of NaCl and $CaCl_2$ were investigated having a constant ionic strength $\mu = 0.1$. An equation was worked out using calibration measurements in standard NaCl solutions, to calculate the activities from measurements of E in cells with experimental solutions.

In Table 2 it is shown that cells with a liquid junction must be used to measure the empirical ionic activity, and also that the magnitudes of γ_{Na^+} and γ_{Cl^-} remain the same in given solutions of constant ionic strength identical to the magnitude of $\gamma \pm$ NaCl.

In natural waters both Cl^- and SO_4^{2-} ions are commonly present. We therefore attempted to compare γ_{Na^+} in Na_2SO_4 solutions with the magnitude of γ_{Na^+} in NaCl solutions over a wide range of ionic strengths.

TABLE 2

ACTIVITY COEFFICIENTS IN A SOLUTION OF NaCl AND $CaCl_2$

No. of the experiment.	Composition		γNa^+	$\gamma Cl-$	$\gamma \pm NaCl$
	^mNaCl	$^mCaCl_2$			
1	0.08998	0.003337	0.780	0.780	0.780
2	0.07499	0.008335	0.779	0.780	0.779
3	0.04998	0.01667	0.780	0.778	0.778
4	0.02500	0.02500	0.779	0.778	0.778

From Table 3 it follows that solutions of NaCl and Na_2SO_4 of ionic strength somewhat less than $\mu = 0.05$, may be considered to be the limit for which the magnitude of γ_{Na^+} does not depend on the composition of the solution, but only on the ionic strength. The discrepancy of the value of γ_{Na^+} in the combined solution of NaCl and Na_2SO_4, compared with that in a NaCl solution of $\mu = 0.05$ will be still smaller than that of the pure solution. The independence, therefore of γ_{Na^+} from the composition of natural chloride sulphate waters may, for practical purposes, be extended to an ionic strength $\mu = 0.05$.

TABLE 3

VALUE OF γ_{Na^+} IN Na_2SO_4 SOLUTION

No. of the experiment	$^mNa_2SO_4$	μ Na_2SO_4 Solution	γNa^+ found in a Na_2SO_4 Solution	γ_{Na^+} accepted for NaCl Solution	Deviation from accepted value in %
1	0.03333	0.1	0.736	0.778	−5.4
2	0.01666	0.05	0.813	0.823	−1.1
3	0.006666	0.02	0.877	0.875	+0.2
4	0.003333	0.01	0.904	0.904	±0.0
5	0.001666	0.005	0.929	0.929	±0.0
6	0.000666	0.002	0.951	0.953	−0.2
7	0.000333	0.001	0.966	0.966	±0.0

To calculate γ_{Na^+} for $\mu \leq 0.05$, we used the equation:

$$\log \gamma_{Na^+} = - \frac{0.506 \sqrt{\mu}}{1 + 1.316 \sqrt{\mu}} + 0.0521 \mu$$

according to Harned (9), based on calculations of $\gamma \pm NaCl$. To calculate the ionic strength of natural waters, the results of a brief water analysis could successfully be used.

TABLE 4

RESULTS OF THE DETERMINATION OF Na^+ ION CONCENTRATION IN NATURAL WATER, USING A GLASS ELECTRODE

No. of the experiment	Ionic strength of the water	$\frac{Ca^{2+} + Mg^{2+}}{Na^+}$	$\frac{SO_4^{2-}}{Cl^- + HCO_3^-}$	Concentration Na^+ in milli equiv/l.		Difference in %
				with glass electrode	zinc uranyl acetate Method	
1	0.2473	0.5	0.3	130.50	129.80	+0.5
2	0.0362	2.0	0.9	8.91	8.73	+2.1
3	0.5330	6.0	0.9	163.70	165.20	−0.9
4	0.0478	< 0.1	0.1	42.56	42.37	+0.5
5	0.0505	0.3	0.5	32.12	31.48	+2.0
6	0.0209	2.4	0.0	3.67	3.60	+2.0
7	0.0891	2.2	6.0	9.16	9.26	−1.1
8	0.0884	1.7	5.0	14.31	14.39	−0.6
9	0.1415	0.9	7.0	27.51	27.22	+1.2
10	0.1998	1.6	36.0	25.46	24.97	+2.0

The concentration of Na^+ ions by the potentiometric method was calculated from the equation

$$C_{Na^+} = \frac{a_{Na^+}}{\gamma_{Na^+}}$$

The results of Na^+ determinations by the potentiometric method were compared with those of the zinc uranyl acetate method (10) which was taken as a standard (table 4).

Some samples were diluted with distilled water (sample No. 1–10 times, No. 3–20 times, Nrs. 7 and 8 twice, No. 9 – three times and No. 10 – 4 times). The average deviation from the standard method was about ± 2.0%.

The given method was used for waters having a pH ≥6; more acid waters were neutralised by gaseous ammonia in the presence of an indicator – neutral red. In the waters investigated the ratio of equivalents $\frac{Ca^{2+} + Mg^{2+}}{Na^{+}}$ did not exceed 6.

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