chloride ion.[3] The high peak at 261 mμ does not coincide with any of the other known maxima of the polyhalide ion and is, therefore, probably due to the I_2Cl^- ion.

Another interesting bit of information given by Table I is that there is not much difference in the absorption spectra of the polyhalides in acetonitrile and in ethylene dichloride. However, from the study of electrical conductances of these complexes in the two solvents,[4] it is known that while the polyhalides are strong electrolytes in acetonitrile, they are considerably associated in ethylene dichloride, the dissociation constants being of the order of 1×10^{-4}. Therefore in ethylene dichloride they are present primarily as ion pairs. It can be concluded that the absorption spectra of the polyhalide ions are not appreciably affected by the ion-pair formation.

[3] It is evident that in view of high absorption at 360 mμ the 338 peak of ICl_2^- will be masked.

[4] (a) A. I. Popov and N. E. Skelly, THIS JOURNAL, **76**, 5309 (1954); (b) A. I. Popov and N. E. Skelly, *ibid.*, **77**, 3722 (1955).

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The Diffusion Coefficient of Nickel(II) in Sodium Perchlorate Solutions

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In connection with other work the diffusion coefficient of Ni(II) was determined in both dilute and concentrated sodium perchlorate at 25°. The capillary cell technique essentially as employed by Wang[1] was used with Ni^{66} as the radiotracer. The solutions were slightly acid to prevent hydrolysis, and the nickel concentration was approximately 3 millimolar to make specific adsorption on the capillary walls negligible.

Experimental.—Ni^{66} tracer was produced by the bombardment of Bi_2O_3 powder with 340 Mev. protons. Ni carrier was added, and the nickel fraction of the target was taken and purified by standard methods, lastly being weighed as the dimethylglyoximate. The Ni precipitate was then dissolved in hot concentrated HNO_3, the solution was evaporated to dryness and the nickel converted to the perchlorate with concentrated $HClO_4$. The salt formed on evaporating this solution was then recrystallized twice from aqueous solution, and finally was dissolved in a known quantity of the perchlorate solution to be studied. This solution was used as the stock solution for the capillary cells. An identical solution for the large diffusion bath was prepared using non-radioactive nickel perchlorate.

The capillary cells used were about 7 cm. long and 2 mm. in diameter to allow the use of fairly large samples, for the radioisotope was difficult to prepare with high specific activity.

The capillary cells were filled with tracer solution and placed in the diffusion bath previous to total immersion for about 20 minutes to allow them to come to the temperature of the constant temperature bath, which was maintained at 25.00 ± 0.03°. Stirring in the diffusion bath was not deemed necessary for the accuracy that was desired. Diffusion was allowed to take place for about 2.5–3 days, at which time the cells were removed from the diffusion bath and the entire contents taken and sampled.

It was found that with large quantities of $NaClO_4$ on the counting plate, reproducible counts could not be obtained, necessitating the following sampling scheme, which was applied to both the stock tracer solution and the contents of the cells after diffusion.

The nickel in the samples was extracted in a centrifuge cone with dimethylglyoxime dissolved in chloroform, the succeeding extracts being removed with a transfer pipet into a weighed 25-ml. glass-stoppered erlenmeyer flask. Each time the $CHCl_3$ was evaporated with a heat lamp, and, after a sufficient number of extractions, the dimethylglyoximate was destroyed with hot concentrated HNO_3. The resulting solution was concentrated under the heat lamp, and a weighed portion was taken and placed on a platinum counting plate and evaporated.

The samples were then counted with a thin mica window Geiger–Müller tube in conjunction with a scaler on each of three succeeding days. The 56-hour Ni^{66} is in equilibrium with the 5-minute Cu^{66} which decays to stable Zn^{66}. The 2.63 Mev. β-rays from the Cu^{66} primarily are those being counted, with a small contribution from the weak betas from the Ni^{66}. A total of at least 100,000 counts was taken in each case to reduce the probable statistical deviation to about 1%, and each count was corrected for coincidences and background. Since Ni^{66} has a 56-hour half-life, and in some cases the size of the samples necessitated a counting period of up to 300 minutes, each count was also corrected for decay during the counting period. All counts were then extrapolated to the same time, chosen as the middle of the counting period in the entire experiment. The ratio of the average concentration after diffusion to the initial concentration was then determined for each cell. From these ratios the diffusion coefficient was found by successive approximations to the equation

$$\frac{C_{av}}{C_0} = \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \exp\left[\frac{-(2n+1)^2\pi^2 DT}{4L^2}\right]$$

where C_{av} is the averaged concentration after diffusion, C_0 is the initial concentration, D is the diffusion coefficient in cm.²/sec., T is the total diffusion time in seconds, and L is the length of the cell in centimeters.

Results.—In each experiment four cells were used. The average values obtained for the diffusion coefficients in the solutions studied are given in Table I.

TABLE I

$NaClO_4$, M	$HClO_4$, M	$Ni(ClO_4)_2$, M	$D \times 10^5$, cm.²/sec.
0.1	0.001	0.00323	0.60 ± 0.06
3.0	.001	.00360	.56 ± .06

The values of the diffusion coefficients are seen to be reasonable when compared with the limiting value of 0.69×10^{-5} obtained from conductance data.[2] They suggest that there has been no change in the nickel species in going to the more concentrated solution. It is also of interest to note that the value 0.60×10^{-5} cm.²/sec. fits our unpublished polarographic data in 0.1 M $NaClO_4$ to within 2% when the improved diffusion current equation of Lingane and Loveridge[3] is used.

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[1] J. H. Wang, THIS JOURNAL, **74**, 1182 (1952).

[2] I. M. Kolthoff and J. J. Lingane, "Polarography," 2nd Edition, Vol. 1, Interscience Publishers, New York, N. Y., 1952, p. 52.

[3] Reference 2, p. 63.