LXXI. — *The Absorption Spectra of Permanganates in Certain Solvents.*

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THE absorption spectra of the permanganates have been the subject of numerous investigations; a complete bibliography of the subject will be found in Kayser's "*Handbuch der Spectroscopie*," Vol. III., p. 415 (see also p. 116). In some respects the most important work is that of Ostwald (*Zeitsch. physikal. Chem.*, 1892, **9**, 579), who measured* the positions of the four least refrangible absorption bands in dilute aqueous solutions of thirteen different permanganates, and found that, within the limits of experimental error, the spectra were identical. From these results he concluded that in the dilute solutions the salts were completely dissociated, and that the colour was due to the free permanganion.

The object of the present investigation has been to examine the absorption spectra of permanganates in other solvents than water, in which the dissociation of the salt into ions would be less complete. Measurements have been made of the three least refrangible bands in the spectra of potassium, calcium, barium, and zinc permanganates, in water, acetone, acetic anhydride, acetonitrile, methyl acetate, pyridine, methyl alcohol, ethyl alcohol, and ethylene glycol, except in those cases where the reaction between the salt and solvent is too rapid for trustworthy measurements to be made.

EXPERIMENTAL.

In the case of solutions of permanganates, the well-defined nature of the bands enables measurements of the points of maximum absorption to be made visually with fairly concordant results, without having recourse to photometric methods. It was found that the cross wires of the telescope could be set on the point of maximum absorption with results which did not differ by more than ± 5 Ångström unit. The instrument used was a Hilger constant deviation type spectroscope, with which wave-lengths could be read off direct on a helical drum to ± 2 or ± 3 Ångström unit. For making measurements of absorption spectra, the slit was set to a suitable breadth, and the fiducial adjustment was made by setting the cross wires (by means of a screw movement in the eyepiece) to the middle of a standard bright line, the reading on the helical drum being previously set to the corresponding wave-length; this adjustment was performed whenever it was found desirable to alter the breadth of the slit. As a source of illumination, an ordinary electric filament lamp was used, the solutions

being contained in test-tubes placed in front of the slit of the spectroscope. The mean value of five or six determinations of the maximum of each absorption band was taken, and it is probable that the mean values given are correct to ± 3 Angström unit.

All permanganates react more or less rapidly with the organic solvents investigated. Of the salts used, the zinc salt was found to be the most active. The reaction, however, takes place much less rapidly at 0° , and the solvents were therefore cooled in a vessel of crushed ice and water before the solution was made up. Owing to the rapidity of oxidation, the solutions could not be made up to any known concentration, but, on the assumption that the intensity of colour is the same in all the solvents for the same concentration, a colorimetric estimate shows that the concentrations were of the order of $0.0006-N$.

The organic solvents were obtained from Kahlbaum. The methyl and ethyl alcohols were dried by treatment with calcium turnings, the acetone and pyridine with barium oxide, and the acetonitrile with phosphoric oxide. As in many cases the presence of a small quantity of water produces a marked change in physico-chemical properties, the effect of adding a drop of water to each solution was examined. The reduction of the permanganate usually took place much more rapidly, but no change in the absorption bands could be detected, and it is therefore probable that such traces of water as might have been present in the solvents produced changes in the absorption spectra which were well within the experimental error.

The measurements of the maxima are given in Angström units in the table on p. 639.

In every case, the position of the bands in a particular solvent is the same for the four different permanganates used, showing that the influence of the cation on the absorption lies within the limits of the experimental error of the determinations, although in some of the solvents, for example, methyl acetate, dissociation must have been far from complete.

No explanation can be offered of the change of position of the bands in different solvents. Kundt's law is not in accordance with the facts, there being no apparent connexion between the optical properties of the solvents and the position of the bands, and no connection has been found between the influence of the solvents and their behaviour in other respects.

In order to investigate further the influence of the state of the salt on the nature of the absorption, the position of the bands have been measured for a solid solution of potassium permanganate in potassium perchlorate, in which dissociation can hardly be supposed

Solute.	Solvent.	Observed wave-length.		
Potassium permanganate	Water.....	5719	5477	5256
Calcium ".....	".....	5718	5480	5257
Barium ".....	".....	5718	5478	5253
Zinc ".....	".....	5721	5474	5255
Potassium ".....	Acetone	5735	5496	5276
Calcium ".....	".....	5735	5493	5275
Barium ".....	".....	5737	5492	5272
Zinc ".....	".....	5737	5496	5277
Potassium ".....	Methyl acetate ...	5720	5480	5258
Calcium ".....	" ".....	5719	5479	5259
Barium ".....	" ".....	5720	5479	5258
Potassium ".....	Acetic anhydride	5719	5480	5260
Potassium ".....	Pyridine.....	5738	5490	5271
Calcium ".....	".....	5734	5493	5277
Barium ".....	".....	5735	5493	5275
Zinc ".....	".....	5733	5492	5275
Potassium ".....	Acetonitrile	5718	5478	5258
Calcium ".....	".....	5719	5477	5257
Barium ".....	".....	5719	5477	5257
Zinc ".....	".....	5721	5475	5258
Potassium ".....	Methyl alcohol...	5747	5505	5285
Calcium ".....	" ".....	5746	5505	5281
Barium ".....	" ".....	5748	5505	5282
Zinc ".....	" ".....	5749	5504	5282
Potassium ".....	Ethyl alcohol ...	5747	5503	5282
Calcium ".....	" ".....	5747	5503	5282
Barium ".....	" ".....	5746	5502	5284
Zinc ".....	" ".....	5747	5503	5281
Potassium ".....	Ethylene glycol	5730	5484	5267
Potassium ".....	{ Ethyl and amyl alcohols (equal volumes). }	5747	5504	5280

to occur. The general character of the spectrum is the same as in the case of a liquid solution, but the bands are shifted towards the violet end of the spectrum. The following results were obtained:

Mean wave-length: 5577, 5345, 5135.

The position of the bands in water is thus intermediate between the positions in the alcohols pyridine and acetone, and the positions in the solid solution.

It would seem, therefore, that the general nature of the absorption is due to the atomic grouping MnO_4 , and that it is influenced very little, if at all, by the nature of the cation or the extent of dissociation, the position of the points of maximum absorption being determined by the nature of the medium in which the salt is dissolved.

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