

CHAPTER III

EXPERIMENTAL



3.1 Materials

3.1.1 Ion-exchanger: Ammonium 12-molybdophosphate (AMP) was prepared by the following method. 1 ml. of concentrated nitric acid and 0.5 gm. of ammonium nitrate in about 7 ml. of distilled water were added to a solution containing 6 mg. of phosphate as ammonium dihydrogen orthophosphate. 3 ml. of 10% ammonium molybdate were added and placed in a water bath at 80°C for 20 minutes. The yellow precipitate was separated by filtering through a Büchner funnel, on a Whatman filter paper No. 1, under the slightly reduced pressure and was washed with distilled water until all excess acid was removed.

This preparation method was found to be used widely since it yields the AMP with a particle size suitable for the use as an inorganic ion exchanger. The molecular formula and the molecular weight of the resulting AMP are $(\text{NH}_4)_3 \text{PMo}_{12}\text{O}_{40}$ and 1880 respectively.

3.1.2 Electrolytes: All electrolytes employed in the study of the ion exchange properties of AMP were purchased from BDH Chemical Limited and used directly without further purification. They are tabulated with their minimum assay and some of their physical properties as shown in the Table 3.1.

Table 3.1

Physical properties of electrolytes

Chemicals	Formula	Minimum assay (%)	Physical properties		
			Molecular weight	Melting point ^c	Solubility in H ₂ O 100 gm. at 30 ^o C
AR Barium chloride	BaCl ₂ ·2H ₂ O	99.0	244.28	-2H ₂ O, 100	38.2
AR Calcium chloride	CaCl ₂ ·2H ₂ O	72.0	147.02	772	102.0
AR Caesium chloride	CsCl	99.9	167.367	646	197.3
AR Potassium chloride	KCl	99.8	74.557	776	37.0
* Rubidium chloride	RbCl	120.937	715	97.6
AR Sodium chloride	NaCl	99.9	58.448	800.4	36.3
AR Strontium chloride	SrCl ₂ ·6H ₂ O	98.5	266.62	-4H ₂ O, 61	198
** Thallium (I) chloride	TlCl	99.0	239.847	430	0.42
AR Thallium (I) sulphate	Tl ₂ SO ₄	99.5	504.80	115d ^{***}

* spectroscopic pure

** laboratory reagents

*** decompose

3.2 Study of the ion exchange equilibrium

Principle of the method

Equilibration of the ion exchange with a solution was achieved by placing the ion exchanger in the electrolyte solution with continuous stirring to ensure complete and uniformly mixing. Stoppered

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bottles were used in order to avoid concentration changes by evaporation of the solvent. The time of contact with the solution was varied from 15 minutes with, usually, 15 minutes interval up to a period of time that was long enough for attainment of equilibrium. After each contacting time, the ion exchanger must be separated from the solution. The bulk solution was readily filtered off and its composition was analysed. The counter ion concentration of the ion exchanger was found to increase while the counter ion of the electrolyte solution decreased in the filtrate. The procedure was repeated until the composition remained unchanged with time while in contact with the ion exchanger. The ion exchanger was regarded as to be in equilibrium with the contacting electrolyte solution.

Typical procedure adopted for this work can be described as follows: 0.25 gm. of ammonium 12-molybdophosphate (AMP) and 30 ml. 0.015 M. of an aqueous solution containing a cationic counter ion were filled in a 60 ml. polyethylene bottle. The bottle was set in a Lab-Line instruments mechanical shaker Model 3575-1. For the interval of time, the precipitate was filtered on a Whatman filter paper No. 42. The cation in the filtrate, except for a thallium ion, were analysed for their concentrations using the Varian-Techtron Atomic Absorption Spectrometer Model AA5. Iodometric titration was the principle method used for the determination of thallium ion concentration whereas ammonium ion concentration was obtained with the aid of the Perkin-Elmer double beam grating spectrophotometer Model 124. All pH measurements were carried out by using a Radiometer pH meter type PHM 28 coupled with a pair of glass and calomel electrodes.

3.3 Concentration determination

3.3.1 Determination of cation concentrations by atomic absorption spectrometer

A series of standard solutions was prepared. A suitable volume of the filtrate obtained from section 3.2 was diluted making a 50 ml. unknown sample. Experimental conditions were given in the Table 3.2.

Table 3.2

Experimental condition for the determination
of cation concentration

Element	Ba	Ca	Cs	K	Na	Rb	Sr
Concentration of the standard stock solution (ppm)	5000	100	5000	100	100	100	100
Volume of the filtrate used for the analysis	20	2	10	2	0.2	2	1
Monochromator wavelength (nm)	553.5	422.7	852.1	766.5	589.0	780.0	460.7
Lamp current (mA)	10	3	20	3	7	15	6

Percent of transmission of the standard and the unknown solutions were read. The concentration were then calculated and reported in parts per million. They are shown in Table 4-1

3.3.2 Determination of the thallium ion concentration

a) Iodometric titration A 25 ml. of the filtrate solution, 60 ml. of concentrated hydrochloric acid and about 5 ml. of carbon tetrachloride were added into a 250 ml. conical flask. This mixture was kept at room temperature and the standard 0.025 M. potassium iodate⁽⁶⁾, from a burette was ran in, until the solution, which at first was strongly coloured with iodine, became pale brown. The flask was then stoppered and vigorously stirred with a magnetic stirrer, until the purple colour due to iodine was transferred to the organic layer. The titration was continued, and the flask was vigorously shaken after each addition of the iodate solution until the organic layer was very faintly violet. This was continued until the last trace of violet was losed and had only a very pale-yellow colour. The thallium content of the solution was calculated via the known volume and the concentration of the iodate solution in the usual way.

b) Radiotracer technique 0.25 gm. AMP and 30 ml. of 0.015 M. thallium (I) sulphate solution labelled with Tl-204 were placed in a polyethylene bottle which was then shaken in a mechanical shaker. The solution was filtered off after each desired contacting time. The count rate of 10 ml. of this solution and the same volume of the original labelled Tl_2SO_4 solution were both measured via a Mullard MX 124 liquid G.M. tube used in conjunction with a 123A Baird Atomic counter. The concentration of the thallium ion in the solution was calculated simply by the comparison of the countrate of the unknown sample with the known correlation of the countrate and the concentration of

the thallium ion in the labelled standard Tl_2SO_4 solution.

3.3.3 Determination of the ammonium ion concentration

0.02674 gm. of ammonium chloride was dried at $100^{\circ}C$, dissolved in deionized water to get a 100 ml. solution. The solution contained 5.0×10^{-6} mole per milliliter was resulted. Standard solution were prepared by adding 1 ml. of Nessler's reagent,⁽⁶⁾ to a series of 50 ml. volumetric flasks, which each contained 0.5, 1, 1.5, 2, 2.5 ml. of the ammonium chloride solution respectively and the volume was then made up to the mark with deionized-water. The content was allowed to stand for 10 minutes, to obtain a permanent yellow colour. The ammonium ion concentration was determined by the spectrometric technique.

The wavelength of the Perkin-Elmer Spectrophotometer was selected at 374.045 nm. The calibration curve was constructed under exactly the same conditions of temperature and reaction time as adopted for the sample. The absorbance was regarded from which the concentrations of ammonium ion in each samples were calculated and reported in Table 4-3 to 4-10.

3.3.4 Determination of the hydrogen ion concentration

Buffer solutions of various pHs e.g. 4, 7, 9 were used to standardize the pH meter each time prior to the measurement of the hydrogen ion concentration in the solution.

3.4 Reversibility of the exchanging process of the AMP

0.25 gm. of the AMP and 30 ml. of the electrolyte solution were equilibrated. The AMP precipitate was filtered off, dried for an hour at 80°C and cooled in a desiccator. 0.125 gm. of the precipitate was then mixed with 15 ml. of 0.015 M. NH_4Cl and was shaken overnight. The new equilibrium solution was separated and analysed for the ammonium ion concentration by colorimetric method.

Note. All of the measurements reported above have almost always been carried out singly since the primary aim of this work is to do qualitative study of the order and the type of equilibria existing in the exchange process. Hence in the following chapters neither a confident limit of the data obtained are shown nor quantitative interpretations of the rate and the order of the reactions are offered.