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Solubilities of Tetraphenylphosphonium and Tetraphenylarsonium Perchlorate and Gravimetric Perchlorate Determination

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The solubilities of tetraphenylphosphonium and tetraphenylarsonium perchlorate in water were determined at various temperatures, between 5 °C and 100 °C. Tetraphenylphosphonium perchlorate is slightly less soluble than tetraphenylarsonium perchlorate. The concentrations of these substances in saturated solution at 20 °C are $(5.2 \pm 0.1) \times 10^{-5}$ and $(5.6 \pm 0.1) \times 10^{-5}$ mol dm^{-3}, respectively. The solubilities in aqueous sodium chloride and sodium sulfate at 20 °C were determined over a wide range of salt concentrations.

Gravimetric determination of perchlorate with tetraphenylphosphonium chloride on micro and semimicro scale is described. The details of the procedure are given and possible sources of error are discussed.

INTRODUCTION

Perchlorates react in aqueous solution with tetraphenylphosphonium and tetraphenylarsonium chloride to form sligthly soluble tetraphenyl'onium perchlorates. This has been used for gravimetric and precipitation — titrimetric determination of perchlorate.

Published data on the solubility product constant of tetraphenylarsonium perchlorate vary considerably[1-4]. Only one value has been reported for tetraphenylphosphonium perchlorate by T. Okubo, F. Oaki and T. Teraoka[3]. These authors determined the solubility of tetraphenylarsonium and tetraphenylphosphonium perchlorate and found the arsonium salt less soluble than the phosphonium salt. However, this was not observed in the gravimetric determination of perchlorate ions using corresponding salts precipitated under identical conditions.

Since these systems are of great concern to the analytical chemist, the present work has been undertaken with the aim to define them more precisely and in more detail.

EXPERIMENTAL

Apparatus

The temperature throughout the saturation was kept constant by a LAUDA ultra-thermostat type NB-S 15/12 Electronic. Absorbance measurements were made with a Beckman DU-2 spectrophotometer and 1-cm path length cells.

Preparation of Tetraphenylarsonium and Tetraphenylphosphonium Perchlorate

The tetraphenyl'onium perchlorate salts used in solubility determinations were prepared by precipitation. A solution of tetraphenylarsonium or tetraphenylphosphonium chloride ($c = 0.025$ mol dm^{-3}) was added slowly under stirring to an equal volume of hot, equimolar sodium perchlorate solution. The mixture was allowed to stand over night at room temperature. The precipitate was then filtered, washed with distilled water and dried in desiccator over silica gel. Part of the precipitate was dried at 110 °C.

Solubility Determination

Saturated solutions of tetraphenylarsonium and tetraphenylphosphonium perchlorate were obtained by equilibration of the salts with water or aqueous solution of sodium chloride and sodium sulfate. Each suspension was kept at constant temperature using a jacketed cell through which thermostated fluid was circulated. The mixtures were stirred continuously by magnetic stirrer. Solution samples taken for analysis were filtered by suction through a fine-porosity filter-stick joined to a volumetric flask in one compact assembly that enabled quick filtration and sampling at constant temperature. In solubility measurements at elevated temperature the saturated solution was sucked into a previously weighed volumetric flask, using a preheated filtration assembly. An appropriate ammount of saturated solution was taken and weighed and then suitably diluted to prevent supersaturation at room temperature. The concentration of salt in solution was determined by an extraction — spectrophotometric method[5]. 2 and/or 5 ml aliquots were taken for the analysis.

Recommended Procedure for Gravimetric Determination of Perchlorate

Pipete 1—5 ml of nearly neutral perchlorate solution ($c \approx 0.01$ mol dm^{-3}) into a weighed Schwarz-Bergkampf filtering beaker, capacity 10—15 ml. Warm the solution just to boiling, keeping the beaker in a protecting porcelain dish. Add 1—2 ml of tetraphenylphosphonium chloride solution ($c = 0.05$ mol dm^{-3}) dropwise and with agitation. Bring the contents again just to boiling. Allow the mixture to cool slowly to room temperature and then cool in a refrigerator to 5—10 °C. Filter by suction under water-pump vacuum. Wash the precipitate and beaker with four 1-ml portions of cold (5—10 °C) distilled water. Dry at 110 °C. 1 mg of $(C_6H_5)_4PClO_4$ corresponds to 0.2266 mg of ClO_4^-.

RESULTS AND DISCUSSION

The few published values of the solubility of tetraphenylarsonium perchlorate are not in good agreement. The discrepancies originated probably in the methods applied for determination of salt in saturated solution. The different analytical methods vary in sensitivity and also in degree of accuracy and precision which can be achieved. It has been shown that the extraction — spectrophotometric method using vanadium-PAR complex[5] are very adequate for such systems.

In the present work the solubilities of tetraphenylarsonium and tetraphenylphosphonium perchlorate were determined using this method for final determination of salts in solution. Both solid salts were prepared under like conditions, and the other factors of importance in solubility determination, i. e. purity, temperature and equilibration were very carefully controlled. The time needed to reach the equilibrium state was determined by periodic sampling. Aliquots of solution were removed after 1, and 3 hours respectively, and after 24 hours at 20 °C. The solubilities at 20 °C were determined with equilibrium attained from both sides i. e. super-saturation and under-saturation side. At temperature above 20 °C the equilibrium was attained from the undersaturation side only. Under the conditions used, the period of 1 hour was always found sufficient for equilibration. The solubility values obtained with perchlorate salts dried at room temperature coincided with the ones obtained with the salts dried at 110 °C.

Onium salt concentrations in filtered saturated solution, or properly diluted solution (for solubilities at elevated temperatures) were determined by extraction — spectrophotometric method[5]. The absorbance of chloroform extracts were compared to the absorbance of extracts of known concentration in Ph_4AsCl or Ph_4PCl in the range $1 \times 10^{-6} — 3 \times 10^{-5}$ mol dm^{-3}. Calibration solutions were checked by adding sodium perchlorate and sodium chloride or sodium sulfate in concentrations used in solubility determinations. The added salts did not affect the absorbance of measured standard solutions.

Duplicate determinations carried out on aliquots of a single saturated solution agreed within $\pm 0.05 \times 10^{-5}$ mol dm^{-3}. The solubility values obtained on different succesive samples agreed to $\pm 0.1 \times 10^{-5}$ mol dm^{-3} in the range of temperature between 5 and 30 °C and to $\pm 0.2 \times 10^{-4}$ between 50 and 100 °C. Higher absolute and relative errors of solubility determination at elevated temperatures arose most probably from dilution error effects and high temperature coefficients of solubility.

Solubility product constants were calculated, assuming activity coefficients of unity and complete dissociation of salts in solution. The values obtained for 20 °C and 25 °C are given in Table I, along with the values reported in the literature. The best agreement has been found between our and Loach's value[2]. It is significant that Loach's value was obtained by a different approach (i. e. by precipitation study, measuring the molar detection limit for perchlorate ion in the presence of a known excess concentration of tetraphenylarsonium chloride).

TABLE I

Solubility Product Constants for Tetraphenylphosphonium and Tetraphenylarsonium Perchlorates at 20 °C and 25 °C Obtained in this Work and the Values Reported in Literature

K_s/mol^2 dm^{-6}		Analytical method used	References
Ph_4PClO_4	Ph_4AsClO_4		
2.7×10^{-9} (20 °C) 3.7×10^{-9} (25 °C)	3.1×10^{-9} (20 °C) 4.2×10^{-9} (25 °C)	Extraction spectrophotometric method, using V-PAR complex	this work
	1.2×10^{-8} (25 °C)	UV-spectrophotometry Absorbance of sat. solution measured at 270 nm	1
4.6×10^{-9} (20 °C)	2.6×10^{-9} (20 °C)	Absorbance of sat. solution measured at 268 and 264 nm respectively	3
	5.9×10^{-9} (25 °C)	Perchlorate determination by ion-selective electrode	4
	4.0×10^{-9} (25 °C)	Precipitation study. Estimation of molar detection limit for ClO_4 in presence of excess of Ph_4AsCl	2

The solubility values obtained at different temperature are presented in Figure 1. The smooth curve indicates good reliability of the results. The figure shows that the temperature coefficient of solubility for tetraphenylarsonium perchlorate is very similar to that of tetraphenylphosphonium perchlorate (which is to be expected from the close similarity of the two salts). Under identical conditions the arsonium salt is only slightly more soluble then the phosphonium. Somewhat larger differences were found at temperatures above 70 °C. Although at these high temperatures less precision can be attained, the difference is still noticeable.

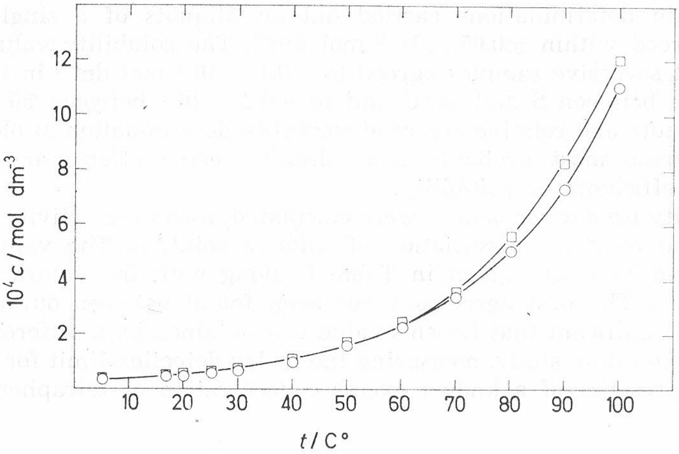

Figure 1. Solubilities of tetraphenylphosphonium and tetraphenylarsonium perchlorate in water as function of temperature. c means concentration of substance in saturated solution, and t Celsius'temperature.
○ Ph_4PClO_4; □ Ph_4AsClO_4.

Solubility of Tetraphenylphosphonium and Tetraphenylarsonium Perchlorate in Aqueous Solution of Sodium Chloride and Sodium Sulphate

Analytical methods based on precipitation of tetraphenylarsonium and tetraphenylphosphonium salts usually involve the addition of electrolytes to the medium. Added electrolytes have been reported to reduce the solubility, improve the coagulation and filterability and lower the tendency of the precipitate to adhere to the walls of the beaker. Sodium chloride has been commonly added[7-9].

In the present work the solubility of tetraphenylarsonium and tetraphenylphosphonium perchlorate were determined in aqueous solution of sodium chloride or sodium sulfate, over a wide concentration range. As generally expected, the increase of ionic strength of the solution decreases the activity coefficient of slightly soluble salt ions resulting with increase of solubility. For both salts at low and moderate ionic strength this has indeed been found. However, this effect is not large. The solubility increases by the factor of 1.12 only, when the ionic strength of the solution increases from zero to 0.5, independently of the kind of electrolyte. At high ionic strength (above 1) the solubility decreases significantly with the increase of the ionic strength of the solution. The magnitude of the effect is also dependent upon the type of electrolyte. The solubility of both tetraphenylarsonium and tetraphenylphosphonium perchlorate is lower in sodium sulfate than in sodium chloride solution for an equal ionic strength, as shown in Figure 2.

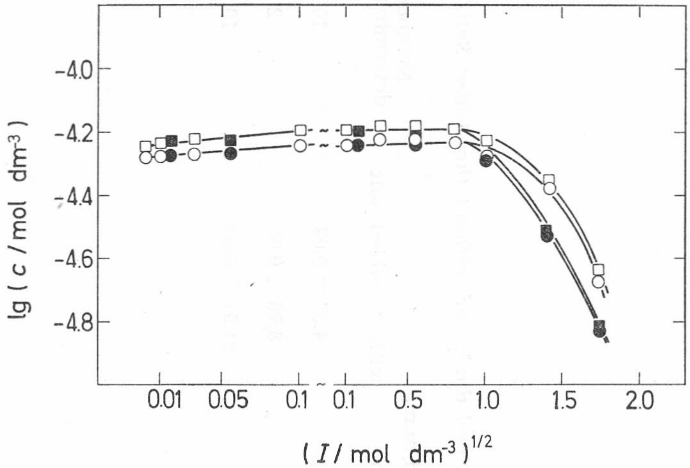

Figure 2. Solubilities of tetraphenylphosphonium and tetraphenylarsonium perchlorate in aqueous solutions of sodium chloride and sodium sulfate at 20 °C as function of ionic strength. c denotes concentration of substance in saturated solution.

○ $Ph_4PClO_4 + NaCl$; ● $Ph_4PClO_4 + Na_2SO_4$;
□ $Ph_4AsClO_4 + NaCl$; ■ $Ph_4AsClO_4 + Na_2SO_4$.

Gravimetric Determination of Perchlorate with Tetraphenylphosphonium Chloride

Results obtained in solubility determination, have shown that tetraphenylphosphonium perchlorate is somewhat less soluble than the arsonium perchlorate. The difference in solubility is small and without particular analytical significance. From the economic point of view, the determination of perchlorate by tetraphenylphosphonium salt has an advantage because Ph_4PCl is cheaper than Ph_4AsCl.

Ph_4PCl was first used for precipitation of perchlorate with both gravimetric and volumetric finishes by Willard and Perkins[7]. The precipitation was carried out in the presence of 2—3 M sodium chloride. Hutton and Stephen[10] avoided the addition of the salt. They used a stronger reagent solution and precipitation at elevated temperature. Fuhrman[9] carried out the precipitation at elevated temperature and in the presence of sodium chloride.

In this work, the experiments were undertaken to find out optimal conditions for the gravimetric analysis on micro- and semimicro scale. As the precipitate is not very insoluble and also has a tendency to adhere to the walls, some precautions must be taken to obtain satisfactory analytical results. It was found that accurate and reproducible results can be obtained by carrying out all steps of the procedure, from precipitation to weighing, in a single vessel of the Schwarz-Berkampf type. Using this technique, the loss of the precipitate by adsorption on the walls is eliminated. Moreover the solubility-loss is also lower, because the volume of the needed washing solution is significantly smaller than the volume required when the precipitate has to be quantitatively transfered to a separate filtering device.

TABLE II

Precipitation of Perchlorate in Presence of Na_2SO_4 or NaCl (I = 0.3 mol dm^{-3}) and without the Added Salts

ClO_4^- taken	Ph_4PClO_4 calcd.	Ph_4PClO_4 found/m/mg			Number of determinations
m/mg	m/mg	Na_2SO_4 present	NaCl present	without added salt	
0.993	4.38	4.37 ± 0.02	4.36 ± 0.02	4.37 ± 0.02	10
1.986	8.76	8.73 ± 0.02	8.75 ± 0.03	8.76 ± 0.03	2
4.965	21.91	21.91 ± 0.03	21.92 ± 0.03	21.91 ± 0.03	10

Precipitation of tetraphenylphosphonium perchlorate in the presence of large concentration of electrolyte reduces the solubility and gives a precipitate with better settling behaviour as well. However, very large salts concentrations are generally undesirable in gravimetric procedures. It was found that moderate salt concentrations (or even no added salts) gave precipitates with satisfactory settling behavior under the conditions described in the Recommended procedure. The crystals obtained were smaller, but the data presented in Table II show, that there was no difference between the results obtained in the presence or absence of added salts. The precipitant must be added slowly and in more than 100% excess, to a hot solution. Prolonged digestion was found to be without effect on the results. Cooling before filtration to 5—10 °C and washing with water of equal temperature slightly improve the results, due to lower solubility of the precipitate. The presence of a number of foreign anions does not influence the results, as shown in Table III. Iodide, molybdate, permanganate and tungstate ions interfere.

TABLE III

Determination of Perchlorate in the Presence of Equimolar Amount of Foreign Anion. 0.990 mg of ClO_4^- taken. Precipitant Added in 100% Excess.

Anion added	Ph_4PClO_4/m/mg	
	Calcd.	Found[a]
ClO_3^-	4.37	4.36 ± 0.02
BrO_3^-		4.36 ± 0.01
JO_3^-		4.35 ± 0.03
Br^-		4.34 ± 0.03
CrO_4^{2-}		4.36 ± 0.02
NO_3^-		4.36 ± 0.01
CH_3COO^-		4.36 ± 0.01
HPO_4^{2-}		4.35 ± 0.02

[a] Results are means of at least two determinations.

It is interesting to note that the same procedure, using sodium perchlorate solution as a precipitant, may be applied in turn for the determination of tetraphenylphosphonium or tetraphenylarsonium soluble salts.

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SAŽETAK

Topljivost tetrafenilfosfonij- i tetrafenilarsonij-perklorata i gravimetrijsko određivanje perklorata

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Određena je topljivost tetrafenilfosfonij- i tetrafenilarsonij-perklorata u vodi pri različitim temperaturama između 5 °C i 100 °C. Tetrafenilarsonij-perklorat neznatno je topljiviji od tetrafenilfosfonij-perklorata. Koncentracija zasićene otopine pri 20 °C iznosi za tetrafenilfosfonij perklorat $(5.2 \pm 0.1) \times 10^{-5}$ mol dm^{-3}, a za tetrafenilarsonij perklorat $(5.6 \pm 0.1) \times 10^{-5}$ mol dm^{-3}. Također je određena topljivost ovih spojeva u otopinama natrij-klorida i natrij-sulfata različite ionske jakosti.

Opisan je postupak za mikro- i semimikro-gravimetrijsko određivanje perklorata taloženjem s tetrafenilfosfonij kloridom.

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