TABLE IV

VISCOSITIES OF THE HALOGENS

	Chlorine	Bromine	Iodine
Absolute viscosity at boiling point	0.00488	0.00717	0.01414
Abs. vis. divided by sq. rt. of density at b. p.	.00390	.00414	.00730
Constant "A" in the viscosity-temperature equation	.00588	.01226	.02183

curve also changes. Thus the constant A increases from 0.00588 for chlorine to 0.02183 for iodine.

The first two values given above increase much more rapidly from bromine to iodine than from chlorine to bromine. This is probably due to the fact that while both chlorine and bromine have association factors around 2 in the liquid state, iodine probably possesses a higher degree of molecular complexity.

Summary

The viscosities of liquid chlorine, bromine and iodine have been determined and the experimental methods described. The viscosity at the boiling point shows an increase with increasing atomic weight of the halogen, as would be expected from the Periodic Law.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

THE SEPARATION AND DETERMINATION OF THE ALKALI METALS, USING PERCHLORIC ACID. I. THE SOLUBILITIES OF THE PERCHLORATES OF THE ALKALI METALS IN MIXED ORGANIC SOLVENTS

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The quantitative separation and determination of the alkali metals is in general dependent upon the use of organic solvents. The most important separation in this group is that of potassium from sodium. The most common method involves the use of chloroplatinic acid and 80% ethyl alcohol but methods based on the use of perchloric acid have proved satisfactory in this as well as other separations of the alkali metals.[1] Improved methods of procedure in this group depend in part upon a thorough study of new organic solvents.[2] The present work is the first of a series of such studies.

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[1] (a) Smith, THIS JOURNAL, **45**, 2072 (1923). (b) Baxter and Rupert, *ibid.*, **42**, 2046 (1920). (c) Gooch and Blake, *Am. J. Sci.*, **44**, 381 (1917). (d) Morris, *Analyst*, **45**, 349 (1920); extensive bibliography.

[2] A list of organic solvents already studied in this connection includes *n*-butyl alcohol [Ref. 1 a; also Willard and Smith, THIS JOURNAL, **44**, 2816 (1922)]; *iso*butyl alcohol [Winkler, *Z. anal. Chem.*, **52**, 628 (1913)]; ethyl alcohol containing methyl

The solubility of the perchlorates of the alkali metals in water and numerous organic solvents, including alcohols and ethyl acetate, has been determined.[3] The nature of the solubility effect obtained using mixed solvents constitutes a marked advantage over the use of individual solvents. The data reported in this paper include the solubility of anhydrous sodium, potassium, rubidium, cesium ammonium perchlorates, sodium perchlorate monohydrate and lithium perchlorate trihydrate in mixtures of methyl, ethyl and *n*-butyl alcohols in various proportions with ethyl acetate. The data are discussed in relation to their application to quantitative analysis.

Introductory Considerations

Quantitative methods for separations in the alkali metal group consist of two types, precipitation and extraction processes. The separation of sodium and lithium by the method of Willard and Smith[2] is of the former type. The perchloric acid method for the separation of potassium and sodium is an extraction method. Sodium perchlorate would be more effectively separated from potassium perchlorate by extraction, using an organic solvent, if its solubility could be increased without increasing the solubility of the potassium salt. The selection of a mixture of solvents best suited to this end could be made only after an extended investigation, the results of which have been included in part in this paper.

Preparation of Materials

In a former paper[3] the opinion was expressed "that slight amounts of organic impurities, especially those similar in nature to the solvent used, would have no appreciable effect on the solubility results, but even traces of water have a large influence." An alcohol containing a small percentage of an isomeric alcohol or other members of its homologous series would fall under this classification of organic impurities. Such conditions would not hold for some mixtures of organic solvents such as esters contaminated with alcohols or alcohols with aldehydes.

The magnitude of the error resulting from the presence of a very small percentage of dissimilar organic impurity in a particular solvent is shown by the following example.

The solubility of anhydrous sodium perchlorate in a sample of ethyl acetate, the physical constants of which duplicated the best values to be found in the literature,[4] was shown to be 8.80% at 25°. The same ethyl acetate containing 0.13% of its volume of anhydrous ethyl alcohol, dis-

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alcohol, [Ref. 1 b]; ether and alcohol [Palkin, THIS JOURNAL, **38**, 2326 (1916)]; amyl alcohol [Gooch, *Am. Chem. J.*, **9**, 33 (1887)]; and pyridine [Kahlenberg and Krauskopf, THIS JOURNAL, **30**, 1104 (1908)].

[3] Willard and Smith, THIS JOURNAL, **45**, 286 (1923).

[4] Solvent 13, of Ref. 3.

solved 10.74%, an increase of over 22%. From these data it would seem probable that ethyl acetate containing as little as one part of ethyl alcohol in 20,000 parts would dissolve anhydrous sodium perchlorate to the extent of 1% in excess of the true value.

As a result of such considerations the solvents used for this work were those of a previous stock which had been carefully purified[3] or carefully selected and compared with the former. Solubility determinations were repeatedly made in establishing the purity of any given solvent. The identity of the samples of the same solvent was established if comparable solubility results were obtained. Solubility data for the pure solvents used are given in Ref. 3.

Ethyl Acetate.—Solvent 13 in Table I of Ref. 3 was used in the case of all solubility determinations except those of potassium, rubidium and cesium perchlorates. These were determined using a very pure anhydrous product obtainable in quantity from the usual sources. This material without further treatment was found to dissolve 9.11% of anhydrous sodium perchlorate at 25°. This corresponds to a purity of 99.98%, assuming the only impurity to be ethyl alcohol.

Methyl Alcohol.—An anhydrous material purchased in quantity from the usual sources was found to correspond with Solvent 2 in Table I of Ref. 3. It was found to dissolve 6.42% of ammonium perchlorate and 34.33% of anhydrous sodium perchlorate as compared with 6.41% and 33.93% for the pure solvent. Technical methyl alcohol, dried over stick potassium hydroxide and distilled, dissolved 42.2% of anhydrous sodium perchlorate.

Ethyl Alcohol.—Ninety-three per cent. alcohol dehydrated with lime to 99.6% was made anhydrous by reaction with a slight excess of metallic calcium. Its boiling range was 78.29–78.31° (corr.); d^{25}_{4} 0.78515, corr. to vacuum. The undried alcohol was found by density determination to be 93.1% pure.

***n*-Butyl Alcohol.**—This was the same as Solvent 10 in Table I of Ref. 3.

Perchloric Acid.—This material was prepared as described in Ref. 1a.

Lithium, Sodium, Ammonium, Potassium, Rubidium and Cesium Perchlorates.—These were the same materials as those described in Ref. 3. The latter three slightly soluble perchlorates were recrystallized from their solution in perchloric acid at the boiling point by cooling to 0° with the object of obtaining fine crystals which required no grinding before testing their solubility. The crystals thus obtained were known to have occluded a small amount of perchloric acid. This fact did not alter solubility data in the organic solvents used, as in no case were the resulting solutions acid. This phenomenon of acid occlusion as exhibited by potassium, rubidium and cesium perchlorates is the subject of the second paper of this series.

Lithium Perchlorate Trihydrate.—The material used was the same as that described in Ref. 3.

Sodium Perchlorate Monohydrate.—This substance was prepared by crystallization of sodium perchlorate from water below 50°. The material thus obtained was filtered centrifugally and dried at room temperature in contact with an excess of anhydrous sodium perchlorate. Analysis of the product gave 12.87% of water of crystallization as compared to a calculated value of 12.82%.

Apparatus and Methods

The experimental manipulations were carried out essentially as reported in Ref. 3, pp. 290–293, inclusive. All determinations involving potassium, rubidium and cesium perchlorates were carried out using from 80–100 cc. of the saturated solution in question with conversion of the dissolved perchlorates to sulfates as a means of determination. All determinations were made in duplicate and the strict concordance of the values obtained with those of previously reported determinations[3] is significant.

Solubility Data

The solubilities in percentage by weight of anhydrous sodium perchlorate, hydrated sodium and lithium perchlorates and ammonium perchlorate in the various mixtures of solvents, are listed in Table I.

TABLE I

SOLUBILITIES OF SODIUM, LITHIUM AND AMMONIUM PERCHLORATES IN ETHYL ACETATE CONTAINING VARIOUS PROPORTIONS OF METHYL, ETHYL AND *N*-BUTYL ALCOHOLS AT 25° ± 0.1°

Vol.-% of alcohol		0	5	10	20	30	40
Vol.-% of ethyl acetate		100	95	90	80	70	60
Solute	Alcohol used						
$NaClO_4$	Methyl	8.80	...	19.39	23.37	25.85	27.81
$NaClO_4$	Abs. Ethyl	8.80	13.83	16.05	18.55	19.66	20.08
$NaClO_4$	93% Ethyl	8.80	14.12	16.92	20.00	21.75	22.79
$NaClO_4$	*N*-Butyl	8.80	...	12.34	13.16	...	12.82
$NaClO_4$	*N*-Butyl[a]	8.80	11.97	13.00	14.32	14.75	14.71
$NaClO_4.H_2O$	Abs. Ethyl	26.32	...	29.32	31.16	32.44	33.26
$LiClO_4.3H_2O$	Abs. Ethyl	26.35	...	31.05	33.59	35.10	36.51
NH_4ClO_4	Methyl	0.029	...	0.135	0.550	1.27	2.31

Vol. % of alcohol		50	60	70	80	90	95	100
Vol. % of ethyl acetate		50	40	30	20	10	5	0
Solute	Alcohol used							
$NaClO_4$	Methyl	29.38	30.50	31.61	32.56	33.44	...	34.33
$NaClO_4$	Abs. Ethyl	20.07	19.67	18.78	17.53	15.82	14.80	12.83
$NaClO_4$	93% Ethyl	23.30	23.39	22.73	21.92	20.96	21.31	20.60
$NaClO_4$	*N*-Butyl	11.99	10.54	...	6.70	4.35	...	2.19
$NaClO_4$	*N*-Butyl[a]	13.98	13.09	11.66	9.85	7.87	6.97	4.27
$NaClO_4.H_2O$	Abs. Ethyl	33.63	33.61	33.20	32.56	31.56	31.10	29.80
$LiClO_4.3H_2O$	Abs. Ethyl	37.96	38.58	39.79	40.84	41.77	...	42.16
NH_4ClO_4	Methyl	3.47	4.35	5.08	5.67	6.12	...	6.42

[a] The same alcohol reported in Ref. 1 a.; b. p., 112–118°; d_4^{25}, 0.8065.

The percentages by volume of the mixed solvents used for the solubilities of each vertical column are given in the first two horizontal rows. The solute used giving the data of each remaining horizontal row is given in the first vertical column. Likewise, the alcohol mixed with the ethyl acetate giving the solubilities contained in each horizontal row is listed in the second vertical column.

The data of Table I are represented graphically in Fig. 1, for the purpose of ready comparison. The solubility in weight-percentages of a given solute is plotted as ordinate. The mixed solvent proportions are plotted as abscissas. The volume-percentages of alcohol from 0 to 100 are plotted, reading from left to right. Those of ethyl acetate are plotted on the same axis from 0 to 100 reading from right to left.

Discussion

From Table I and Fig. 1 it is obvious that the solubilities of the anhydrous solutes are much higher in the mixed solvents than would be predicted from a knowledge of the solubility of the same solute in each individual solvent. Such a predicted series of solubilities would be represented as a straight-line function connecting the first and last point of each curve given. The abnormalities found based on such a consideration range from 100%, or even more, down.

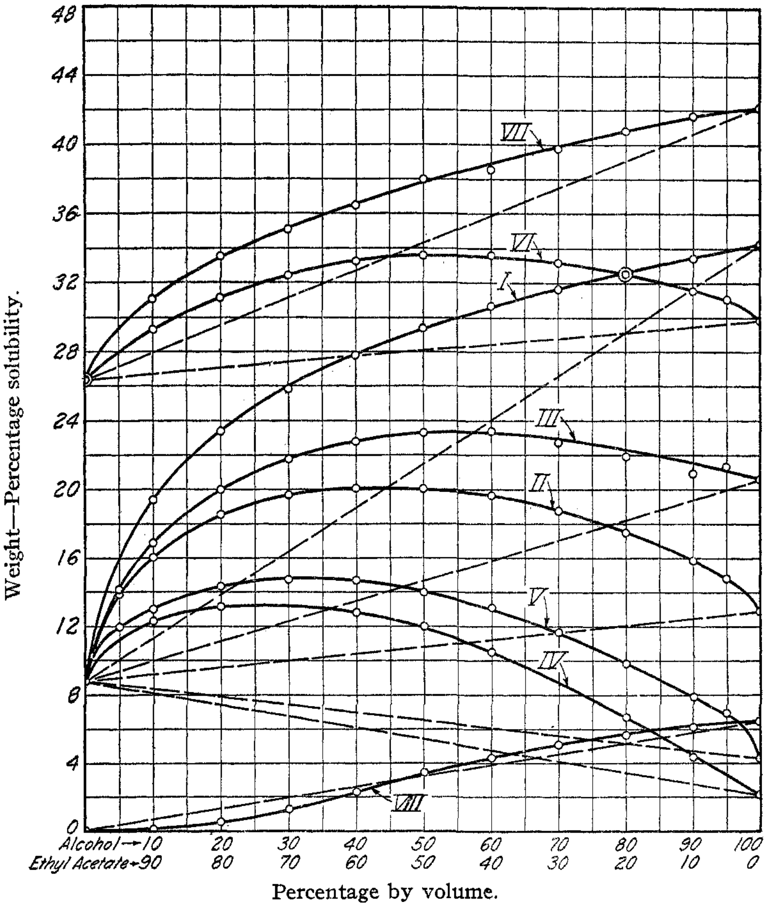

Fig. 1.—Curves I, II, III, IV and V. Solubility of $NaClO_4$ in methyl, abs. ethyl, 93% ethyl and *n*-butyl alcohol mixtures with ethyl acetate, respectively. Curve VI, $NaClO_4.H_2O$ in abs. ethyl alcohol; Curve VII, $LiClO_4.3H_2O$ in abs. ethyl alcohol; Curve VIII, NH_4ClO_4 in methyl alcohol mixtures with ethyl acetate.

To select a specific example, consider the solubility of anhydrous sodium perchlorate in a mixture of 20 parts of anhydrous ethyl alcohol and 80 parts of ethyl acetate; 18.55% by weight of the solution saturated at 25° is found to be sodium perchlorate while 9.6% would be predicted. In this case and that of mixtures of *n*-butyl alcohol with ethyl acetate, the individual solvents could be used as the basis of an extraction process for the separation of potassium and sodium. The advantage of the increased solubility of sodium perchlorate in the mixed solvents is at once apparent. The use of mixed solvents offers no advantage over individual solvents in the case of the extraction of lithium perchlorate. From the data already given, together with the solubility determinations following, a choice of a mixture of solvents to be used for any given separation can be made.

Mixed alcohols give rise to normal solubility effects. This was determined using absolute ethyl alcohol and *n*-butyl alcohol, and a straight-line solubility curve was found. Mixtures of ethyl acetate and acetone give only very slightly abnormal values. The substitution of acetone for ethyl acetate gives only very slightly abnormal solubilities when mixed with alcohols. Mixtures of ethyl acetate with alcohols are thus seen to be the most practicable.

The abnormal solubility results just described could be obtained as a result of two plausible conditions, namely, interaction between the solvents of the mixture, or interaction between the anhydrous solute and one or both solvents. The former condition is indicated through the elimination of the latter as the result of experiment.

Lithium and sodium perchlorates form hydrates. If these solutes in their anhydrous form were dissolved in alcohols it is possible that "alcoholates" instead of hydrates might be formed. In such case the solubility of these modified solutes in alcohols and ethyl acetate might be greater than that of the anhydrous salts. The abnormal results obtained would thus be explained.

Accordingly the solubility of lithium perchlorate trihydrate in mixtures of ethyl alcohol and ethyl acetate was determined (Curve VII, Fig. 1). Its solubilities in both solvents are less than those of the anhydrous solute. Only slightly abnormal solubilities were obtained in the mixed solvents. Both circumstances fit the assumptions. With sodium perchlorate monohydrate, however, the solubility in the individual solvents is greater than that of the anhydrous salt and the abnormal solubilities are less pronounced (Curve VI, Fig. 1)

If the tendency to form "alcoholates" is associated with the formation of hydrates for a given solute, and the former condition gives rise to the abnormal solubility effects obtained in mixed solvents, normal results should be obtained using solutes for which hydrates are not known. The solubility of ammonium perchlorate, representing such an example, in mixtures of methyl alcohol and ethyl acetate was determined (Curve VIII, Fig. 1). Here added abnormality was found. For small percentages of alcohol a marked depression of its solubility over the predicted value was obtained. Interaction of solute and solvent is probably therefore not an explanation for the results obtained.

The Solubilities of Potassium, Rubidium and Cesium Perchlorates in Mixed Alcohols and Ethyl Acetate

As will be demonstrated in the subsequent papers of this series, the presence of free perchloric acid during the extraction of the soluble from the insoluble alkali perchlorates using mixed solvents is a pronounced disadvantage. The addition of perchloric acid for its common-ion effect to mixed solvents containing ethyl acetate as the major constituent fails of its purpose. The solubilities considered in this section, therefore, omit the effect of small amounts of perchloric acid and are reported in Table II.

TABLE II

THE SOLUBILITIES OF POTASSIUM, RUBIDIUM AND CESIUM PERCHLORATES IN MIXED ALCOHOLS AND ETHYL ACETATE AT 25°

Solute	$KClO_4$			$RbClO_4$			$CsClO_4$			
Vol.-% of alc.	10	15	20	10	15	20	10	15	10	
Vol.-% of EtAc	90	85	80	90	85	80	90	85	90	
Alc. used										
Methyl	0.35	0.52	0.55	0.24	..	0.43	0.50	..	0.56	$\times 10^{-2}$
Abs. Ethyl	.16	.26	.33	.16	..	.10	.13	..	.23	
93% Ethyl	.28	.44	.50	..	..	.27	..	..	.40	
n-Butyl	.24	.20	.25	.11	..	.13	.09	..	.12	

The description of Table I already given serves likewise for Table II. The values reported in Table II cannot be considered of greater accuracy than approximately 0.5 mg. All errors accumulating throughout the process of their determination tend to give high results. The data represent saturated solutions, a condition not obtained in practical applications. Predictions based upon the data given in Table II may be somewhat liberally interpreted.

The solubility of potassium perchlorate in pure ethyl acetate[3] is 1.3 mg. in 100 cc. at 25°. Rubidium and cesium perchlorates are insoluble in ethyl acetate. Ethyl acetate should therefore be the wash solution in all cases. If one extraction was found sufficient, 20 cc. of extractant, representing one-fifth the solubilities given in Table II, would give the maximum error through solubility. Working at less than 25°, which is ordinary practise, would decrease this error. Any of the combinations of Table II could then be employed. If two extractions were found necessary, approximately 30 cc. of extractant would be required and the higher values of Table II would represent too great errors.

Mixtures of absolute ethyl alcohol and ethyl acetate give the best values if the figures of Table I are also considered; 93% ethyl alcohol can be substituted for absolute alcohol with but small decrease in accuracy. Mixtures of *n*-butyl alcohol and ethyl acetate give the lowest solubilities and could probably be used in all proportions.

The data of the present paper are thus seen to be a practical guide to the selection of the most probably favorable conditions for any of the separations involved. Exact choices depend upon a more thorough study of each case.

Summary

1. The solubility of the alkali perchlorates in various mixtures of methyl, ethyl and *n*-butyl alcohols with ethyl acetate have been determined.
2. The solubility data thus obtained were shown to represent conditions advantageous in the separation and determination of the alkali metals by the extraction process.
3. An attempt was made to interpret the abnormal solubility results and to point out their analytical significance.
4. Solubility determinations were shown to be of value in establishing the purity of the solvents employed.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF WISCONSIN]

THE SEPARATION OF SELENIUM AND TELLURIUM BY SULFUR DIOXIDE IN HYDROCHLORIC ACID SOLUTION

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Although the use of sulfur dioxide as a precipitating agent for selenium and tellurium was known to Berzelius, the possibility of its utility in the presence of concd. hydrochloric acid as a means of separating these elements was first suggested by Divers and Shimose.[1] The method has come into the copper industry under the name of Keller[2] who has contributed certain details to the procedure. Lenher[3] has suggested that when large amounts of tellurium are present, selenium and tellurium are coprecipitated and Keller has confirmed this observation and has recommended that the quantity of hydrochloric acid should be a hundred times that of the tellurium. This suggestion is, however, only part of the case. We have had in this Laboratory, where the method has had extended use, such widely varying results that the method has been carefully studied and important details have been suggested.

The concentration of the hydrochloric acid is a very important factor. The specific gravity of the acid used by Keller was 1.175. In our experi-

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[1] Divers and Shimose, *Chem. News*, **49**, 26 (1884).

[2] Keller, THIS JOURNAL, **19**, 771 (1897); **22**, 241 (1900).

[3] Lenher, *ibid.*, **21**, 347 (1899).