

ward trend of the conductance curve in the region of very low concentration is not felt to be real. The conductance of the solution in this region is almost entirely due to the solvent and the value for the soap is obtained only by taking the difference of two relatively large numbers. Neglecting the two values at high dilution, the soap exhibits a behavior characteristic of a strong electrolyte until the critical concentration is reached.

The change in slope in the equivalent conductance curve for potassium 9,10-dihydroxystearate at the critical concentration is not nearly as great as has been observed in the studies of sulfonates and other soaps in which the carbon chain does not contain substituted hydrophilic groups. This would indicate that the micelle formed is possibly somewhat smaller and of a different type as the result of the influence of the hydroxyl groups in the middle of the chain, and hence does not change the ionic characteristics of the soap as markedly.

In studying the conductance curve of potassium stearate, the critical concentration for micelle formation was not established. The soap behaved as a colloidal electrolyte throughout the concentration range investigated. It may be seen from Fig. 2 that the critical concentration must lie very close to 0.0005 *N* (the lower limit of the concentration range studied), in order that the curve for the stearate intersect the ordinate at a reasonable value of  $\Delta_0$ . Since measurements were not made below the critical concentration, as an approximation, a constant correction for the conductance of the solvent (the value of the conductance of the pure solvent) was applied in reducing the data.

Qualitative observations of the stearate solutions confirm the colloidal nature of the soap as indicated in the conductance measurements. All solutions were observed to be faintly opales-

cent whereas those of the dihydroxy compound were clear in dilute solution. The conductance curve obtained for potassium stearate is similar to that given by Bunbury and Martin,<sup>1</sup> if the fact that their measurements were made at 90° without repression of hydrolysis is considered.

While the critical concentration for the formation of micelles may be somewhat different in solutions not alkaline in character, the value indicated by these data is, without question, characteristic of the soap in the solvent used, and serves to evaluate the effect of the hydroxyl groups.

The change in density of solutions of the dihydroxystearate with concentration in the potassium hydroxide solvent presents an interesting contrast with that observed for potassium stearate. The density curves are illustrated in Fig. 1 and re-emphasize the pronounced effect of the hydroxyl groups in the molecule. It seems quite likely that the higher density observed for the potassium dihydroxystearate indicates association of water molecules by the hydroxyl groups.

### Summary

1. The electrical conductance and density of solutions of potassium 9,10-dihydroxystearate and potassium stearate in 0.001 *N* potassium hydroxide have been determined at 60°. A comparison of data for the two compounds reveals that the hydroxyl groups have considerable influence.

2. The critical concentration for the formation of micelles in 0.001 *N* potassium hydroxide is indicated at 0.0075 *N* for potassium 9,10-dihydroxystearate. The value for potassium stearate was not established but is probably in the vicinity of 0.0005 *N*.

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## The Solubility of Cesium and Rubidium Dichloroiodides in Hydrochloric Acid Solutions

BY PAUL BENDER AND ROGER A. STREHLOW

### Introduction

In the usual procedure for the purification of cesium or rubidium salts the repeated recrystallization of the dichloroiodide from hydrochloric acid solution is employed for the elimination of the other alkali metals. The quantity of material to be processed is ordinarily limited and the solubility of the complex salt appreciable, so that the attainment of efficiency in the purification process can be accomplished only through a quantitative knowledge of the solubility relationships involved. The present study was carried out to supply the required data which have not previously been available in the literature.

### Experimental

**Preparation of Materials.**—Cesium chloride of spectroscopic purity was prepared from Pollucite by the method of Wells.<sup>1</sup> Rubidium chloride was prepared from Lepidolite (from Pala, Calif.) essentially as described by Kennard and Rambo.<sup>2</sup> The five-fold recrystallization as rubidium acid tartrate recommended by Archibald<sup>3</sup> was carried out to ensure the removal of cesium. Other reagents employed were of analytical grade.

In the preparation of the dichloroiodides a slight excess of iodine was added to a hot hydrochloric acid solution of the alkali chloride and chlorine gas bubbled through the

(1) H. L. Wells, *Am. Chem. J.*, **26**, 265 (1901).

(2) T. G. Kennard and A. I. Rambo, *Am. J. Sci.*, **28**, 102 (1934).

(3) E. H. Archibald, "The Preparation of Pure Inorganic Substances," John Wiley and Sons, New York, N. Y., 1932.

solution until the last of the iodine had dissolved. The salt which separated on cooling was recrystallized four times before use. Analysis of the air dried products gave the following result in terms of % ICl: CsCl<sub>2</sub>I, calcd. 49.11, found 49.19; RbCl<sub>2</sub>I, calcd. 57.28, found 57.32.

**Solubility Measurements.**—Standard procedures were followed in the solubility determinations. The thermostat temperature was maintained at 25.00 ± 0.02° and 0.00 ± 0.02° for the two series of measurements; the thermometers employed were calibrated before use. Duplicate determinations were run at each hydrochloric acid concentration to provide a check on the attainment of equilibrium.

**Analytical Methods.**—Samples of the saturated solutions were transferred to the weighing flasks by air pressure. Glass wool plugs were used as filters in the delivery tubes. Approximately 50-cc. samples of the cesium dichloroiodide solutions were taken, and 25-cc. samples of the rubidium dichloroiodide solutions. The analysis was made by evaporating the weighed sample to dryness, igniting lightly to drive off the ICl, and weighing the residual cesium or rubidium chloride. Due precautions were taken to ensure complete removal of the iodine chloride. Hydrochloric acid solutions used were standardized by means of silver chloride. Calibrated weights

TABLE I  
THE SOLUBILITY OF CESIUM DICHLOROIODIDE IN HYDROCHLORIC ACID SOLUTIONS

A. at 25°		
m HCl	G. salt/100 g. solution	G. salt/100 cc. solution
0.8805	9.059	9.805
1.998	8.274	9.052
2.989	7.470	8.236
4.909	6.097	6.824
6.987	5.057	5.746
8.989	4.455	5.142
10.75	4.139	4.841
12.48	3.964	4.697
15.29	3.894	4.700
B. at 0°		
m HCl	G. salt/100 g. solution	G. salt/100 cc. solution
0.8805	3.623	3.783
1.998	3.524	3.745
2.989	3.321	3.577
4.909	2.890	3.187
6.987	2.553	2.877
8.989	2.343	2.691
10.75	2.231	2.604
12.48	2.189	2.591
15.29	2.195	2.652

TABLE II  
THE SOLUBILITY OF RUBIDIUM DICHLOROIODIDE IN HYDROCHLORIC ACID SOLUTIONS

A. at 25°		
m HCl	G. salt/100 g. solution	G. salt/100 cc. solution
1.998	44.02	64.92
4.909	28.73	38.20
8.989	17.51	22.17
12.48	13.58	17.16
B. at 0°		
m HCl	G. salt/100 g. solution	G. salt/100 cc. solution
1.998	25.20	31.68
4.909	17.51	21.50
8.989	10.66	12.98
12.48	8.75	10.83

were used in all determinations. Weld specific gravity bottles were used in the density measurements required for the conversion of the results to the volume concentration basis.

### Results

In Tables I and II are summarized the results of the solubility determinations. The accuracy of the data is estimated at 0.2% for the cesium dichloroiodide, and 0.3% for the rubidium dichloroiodide.

### Discussion

Solubility measurements were not carried out at higher temperatures because the high temperature coefficient of solubility permits the volume of solvent employed to be adjusted simply on the basis of convenience in the filtration following crystallization. Precautions must of course be taken to avoid loss of iodine chloride from the hot solutions. The use of approximately nine molal hydrochloric acid as solvent is recommended as giving minimum inconvenience from hydrogen chloride in the vapor while retaining nearly the maximum advantage of the cosolute effect.

### Summary

The solubility of cesium and rubidium dichloroiodides in hydrochloric acid solutions has been measured at 0 and 25°.

MADISON, WISCONSIN

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