recrystallization, constitute fairly convincing evidence that the red product was a dimer of phenylacridine and dihydrophenylacridine. The formation of this substance may account for the peculiar double wave that was observed on the polarograms of phenylacridine in strongly acid medium, and the inconstancy of i_d/C, already mentioned, and this possibility is being further investigated.

The amounts of material prepared in the above experiments were limited to the order of a gram or less because the starting materials were fairly difficult to prepare and were available in only small amounts, but there is no evident reason why the method could not be applied to much larger scale preparations. Furthermore, the method need not be limited to the use of mercury working electrodes, but probably can also be applied with solid electrodes if the preliminary polarographic investigation is performed with microelectrodes of the same material.

Summary

The polarographic method has proved to be a valuable and convenient pilot technique to establish optimum conditions for carrying out electrolytic preparations at a controlled potential. In the present investigation this method of "polarographic synthesis" has been applied chiefly to the reduction of 9-(*o*-iodophenyl)-acridine, which served as a good test case because the reduction proceeds in two stages, first to 9-(*o*-iodophenyl)-dihydroacridine (I) and then to 9-phenyldihydroacridine (II) with elimination of iodine, and the reduction potentials of the two stages are separated by only about 0.3 v. at a mercury cathode. A cell and procedure have been described with which it was easily possible to prepare either compound I or II in a high state of purity, and with practically quantitative yield, by proper control of the potential of a working mercury cathode. From the experience gained thus far it appears that this method is capable of wide application in organic chemistry, and it should be particularly valuable whenever a selective oxidation or reduction of only one of two approximately equally reactive structures in a molecule is required.

CAMBRIDGE, MASSACHUSETTS RECEIVED MARCH 29, 1943

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF INDIANA UNIVERSITY]

The Activity and Osmotic Coefficients of Sodium Chlorate by an Isopiestic Method

BY JAMES HOMER JONES

The activity coefficients of sodium chlorate in aqueous solution at concentrations up to one molal have been determined by Scatchard[1] and co-workers from freezing point measurements. This investigation was undertaken to obtain the activity coefficients at 25° and to extend the experimentally determined activity coefficients to higher concentrations.

Experimental

Method and Apparatus.—The method employed was the isopiestic method, using an apparatus similar to that described by Phillips, Watson and Felsing.[2] The procedure was similar except that only six cups were employed at one time so that the time required to attain equilibrium would be shortened. Sodium chloride was chosen as the reference salt.

Purification of Materials: Sodium Chloride.—Reagent grade sodium chloride was dissolved in conductivity water and precipitated by hydrogen chloride gas. The salt was recrystallized from conductivity water, dried in platinum dishes at 300–400° and powdered in an agate mortar. The salt was stored in a vacuum desiccator over solid potassium hydroxide.

Sodium Chlorate.—Reagent grade sodium chlorate was recrystallized three times from conductivity water. The salt was partially dried at 100° in an oven. The lumps were broken up in an agate mortar and the salt finally dried in a vacuum desiccator at 100° with solid potassium hydroxide as desiccant.

Preparation of Solutions.—The dry salts were weighed by difference from weighing bottles into 125-ml. glass-stoppered Erlenmeyer flasks, and the calculated amount of water added. Frequent checks of concentration were made by evaporation of solution with concentrated sulfuric acid, igniting and weighing as sodium sulfate.

The solutions were weighed by difference into the weighed cups from weight burets. Samples ranged from 2.0 to 3.5 g. The precision in weighing was better than one part in 4000 for samples of two grams.

In order to test the apparatus, the isopiestic ratios of potassium chloride–sodium chloride were determined simultaneously with the sodium chloride–sodium chlorate ratios. The results agree within experimental error with the results of both Felsing[2] and Robinson.[3]

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(1) Scatchard, Prentiss and Jones, THIS JOURNAL, **56**, 805 (1934).

(2) Phillips, Watson and Felsing, *ibid.*, **64**, 244 (1942).

(3) Robinson, *Trans. Faraday Soc.*, **35**, 1217 (1939).

The Data Obtained

The isopiestic solutions investigated ranged from approximately 0.2 to 3.5 molal. The isopiestic concentrations are given in Table I. The column $M_0 - M_s$ gives the differences between the observed concentration of sodium chlorate and the value read from the smoothed curve through experimental points.

TABLE I

ISOPIESTIC CONCENTRATION OF SODIUM CHLORIDE AND CHLORATE SOLUTIONS

M_{NaCl}	M_{NaClO_3}, (obs.)	$M_0 - M_s$
0.2180	0.2209	−0.0031
.4073	.4193	− .0004
.4347	.4473	− .0003
.7576	.7951	+ .0003
.9759	1.0360	± .0000
1.0164	1.0804	− .0003
1.4578	1.5910	+ .0004
1.5472	1.6953	+ .0022
1.7553	1.9410	− .0021
2.0508	2.3057	− .0011
2.3475	2.6774	− .0007
2.6825	3.1226	+ .0075
2.8782	3.3716	− .0020

The differences in column three are well within the estimated over-all error of ±0.2%.

Treatment of Data

From the observed isopiestic molalities, the isopiestic ratios $M_{(NaCl)}/M_{(NaClO_3)}$ were determined. These ratios were then plotted against the molalities of the reference salt. The isopiestic ratios at rounded concentrations of sodium chlorate were calculated from the smoothed curve passing through the origin. These ratios are given in Table II.

The method of calculation of the activity coefficients of sodium chlorate is that outlined by Robinson and Sinclair,[4] using the equation

$$\log \gamma_x = \log \gamma_r + \log \frac{M_r}{M_x} + \frac{2}{2.3026} \int_0^{a_r^{1/2}} \frac{\left(\frac{M_r}{M_x} - 1\right) da_r^{1/2}}{a_r^{1/2}}$$

The subscript r denotes the reference salt and subscript x denotes sodium chlorate. The values of the reference salt were those obtained by Scatchard, Hamer and Wood.[5]

The value of the integral up to 0.2 M was made by assuming the value of the activity coefficient at 0.2 M from the freezing point data of Scatchard and co-workers.[1] The value of this integral up to 0.2 M is very small (0.0050). Extrapolation of the integral to infinite dilution yielded a maximum value for the integral of 0.0056. The value 0.0056 for the integral will yield a value of the activity coefficient at 0.2 M that is 0.12% higher than the given value. This is still well within the estimated error of ±0.20% claimed.

The values of the osmotic coefficient for sodium chlorate were based on the values of Scatchard, Hamer and Wood[5] for sodium chloride using the relation

$$\phi(\text{NaClO}_3) = \frac{\phi_{(\text{NaCl})} M_{(\text{NaCl})}}{M_{(\text{NaClO}_3)}}$$

TABLE II

ACTIVITY AND OSMOTIC COEFFICIENTS OF SODIUM CHLORATE

M_{NaClO_3}	Ratio $\frac{NaCl}{NaClO_3}$	ϕ	$\gamma_{25°}$	$\gamma_{0°}$[a]
0.2	0.9862	0.9130	0.720	0.710
.3	.9792	.9038	.687	.674
.4	.9731	.8974	.663	.645
.5	.9673	.8930	.644	.621
.6	.9617	.8895	.630	.602
.7	.9565	.8866	.616	.585
.8	.9513	.8845	.605	.570
.9	.9459	.8828	.595	...
1.0	.9409	.8812	.586	.544
1.2	.9306	.8785	.566	↑ not determined ↓
1.4	.9205	.8758	.557	
1.6	.9107	.8743	.547	
2.0	.8917	.8725	.529	
2.5	.8693	.8743	.516	
3.0	.8477	.8785	.506	

[a] From Scatchard's freezing point measurements.

I wish to thank the International Nickel Company for the nickel from which the cups were pressed; and Mr. Benson of the Chemistry and Chemical Engineering Shop of the University of Texas for pressing the seamless cups.

Summary

The isopiestic ratios of sodium chloride–sodium chlorate were experimentally determined over the approximate concentration range 0.2 to 3.5 molal.

From the observed molalities and ratios, the activity and osmotic coefficients were determined by comparison with sodium chloride.

BLOOMINGTON, INDIANA RECEIVED APRIL 1, 1943

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[4] Robinson and Sinclair, THIS JOURNAL, **56**, 1830 (1934).

[5] Scatchard, Hamer and Wood, *ibid.*, **60**, 3069 (1938).