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

THE TRANSFERENCE NUMBERS OF SODIUM AND POTASSIUM IN MIXED CHLORIDE SOLUTION

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In 1923, Schneider and Braley[1] published data on the transference numbers of sodium and potassium in mixed chloride solution from which they drew the conclusion that these salts formed complexes of such a nature that under some conditions the sodium ion was not transferred.

In 1925, MacInnes,[2] in discussing the results of Schneider and Braley, and Dewey,[3] reporting similar determinations, contended the results were in error in some instances, particularly those at a total normality of 0.2 with a potassium to sodium ratio of greater than 1. The results of the determinations by Dewey conformed in part with the calculated values on the basis of the following equation developed by MacInnes:[2] $T_K = (1 - N_{Na})N_K/[(N_K - N_{Na}) + (1 - N_K)/x]$, but did not seem entirely satisfactory, as part of them also fell on the curves as obtained from the data of Schneider and Braley.

Because of the conflicting evidence on the data available it seemed advisable to repeat again the determinations on those points at which the greatest discrepancies occurred, using the same method of transference that was used by Schneider and Braley, but with a more recent and more accurate method of analyzing the obtained portions. This has been done on the solutions of a total normality of 0.2.

Method of Analysis

The analytical procedure was the perchlorate method for sodium and potassium as reported by Smith,[4] but modified by the use of pure ethyl acetate as the extraction medium rather than the mixture of ethyl acetate and *n*-butyl alcohol. This method proved to give very accurate results on test solutions of varying concentration ratios. The details of the method are as follows.

A weighed portion of the solution containing the sodium and potassium chlorides was evaporated to dryness in the presence of a slight excess of perchloric acid in a 100cc. Pyrex beaker. The beaker was then heated with a free flame until all of the perchloric acid was apparently expelled. The resulting residue was then dissolved in water and again evaporated to dryness, thus expelling any perchloric acid which may have been occluded in the salt crystals. The sodium perchlorate was then extracted from the mixture with pure, anhydrous ethyl acetate, the rate of solution of the sodium salt being increased by gently warming the beaker. The mixture was filtered through a Monroe

[1] Schneider and Braley, THIS JOURNAL, **45,** 1121 (1923).

[2] MacInnes, *ibid.*, **47,** 1922 (1925).

[3] Dewey, *ibid.*, **47,** 1927 (1925).

[4] Smith, *ibid.*, **47,** 762 (1925). Smith and Ross, *ibid.*, **47,** 774 (1925).

crucible and washed with ethyl acetate. The potassium perchlorate, which is insoluble in the ethyl acetate, was then dried to constant weight at 350°. The ethyl acetate solution of the sodium perchlorate was evaporated to dryness and changed to sodium sulfate by treating with sulfuric acid and again evaporating to dryness and igniting to constant weight.

Results

The results obtained on the solutions of a total normality of 0.2 are given in Table I, which should be self-explanatory.

TABLE I

DETERMINED AND CALCULATED TRANSFERENCE NUMBER AT VARYING SODIUM AND POTASSIUM RATIOS

Total normality 0.2; temp., 25°

Mole fraction KCl	Mole fraction NaCl	Pole	Wt. of Ag in Coulom., g.	NaCl trans., g.	KCl trans., g.	T_{Na}	T_K	Calcd. by MacInnes eq. T_{Na}	Calcd. by MacInnes eq. T_K
0.798	0.202	A	1.8336	0.0657	0.4954	0.066	0.390	0.066	0.406
		C	1.8335	.0599	.4412	.060	.348		
.745	.254	A	1.1943	.0567	.3242	.088	.393	.084	.376
		C	1.1944	.0502	.2893	.080	.350		
.664	.336	A	1.6830	.1046	.3884	.114	.339	.113	.346
		C	1.6832	.0980	.3948	.107	.340		
.663	.337	A	1.6250	.0905	.3757	.104	.336	.113	.346
		C	1.6250	.0964	.3691	.109	.332		
.491	.509	A	1.2610	.1090	.2273	.160	.260	.178	.263
		C	1.2612	.1045	.2196	.153	.252		
.517	.493	A	1.9257	.1764	.3582	.169	.269	.171	.277
		C	1.9259	.1758	.3322	.168	.256		
.322	.678	A	1.6685	.2279	.1831	.252	.159	.248	.178
		C	1.6687	.2168	.1840	.239	.159		
.224	.776	A	1.8500	.2441	.1670	.243	.130	.286	.127
		C	1.8500	.2361	.1640	.235	.128		
.198	.802	A	1.5813	.2445	.1146	.285	.105	.297	.113
		C	1.5811	.2495	.1213	.291	.111		

Summary

These data seem to confirm the validity of MacInnes' equation to a greater degree than was done by the data of Dewey, and show that transference values are additive. They do not show the existence of complex ions, as first contended by Schneider and Braley. The only reason that can be offered for the erroneous data previously reported is that the chloroplatinate method of analysis used is not accurate for the variation of proportions which existed. Further discussion of the data will be given in a succeeding paper on the transference numbers of cesium and lithium chloride mixtures.

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