Formation of Complex Compounds between Uranyl Nitrate and the Nitrates of the first Group Elements

The Systems:
(a) Uranyl Nitrate—Lithium Nitrate—Water
(b) Uranyl Nitrate—Sodium Nitrate—Water
(c) Uranyl Nitrate—Potassium Nitrate—Water
(d) Uranyl Nitrate—Ammonium Nitrate—Water

(Conductivity, pH and Spectrophotometry)

By S. S. GUPTA and C. S. PANDE

With 8 figures

Summary

Experiments with the systems: Uranyl nitrate — Lithium nitrate — Water, Uranyl nitrate — Sodium nitrate — Water, Uranyl nitrate — Potassium nitrate — Water, Uranyl nitrate — Ammonium nitrate — Water, viz., conductivity, pH and spectrophotometry revealed that in the first system there is no compound formation, in the second system only one complex compound is formed in the (1 : 1) molecular artio whereas in the last two systems two complexes are observed individually in the (1 : 1) and (1 : 2) molecular ratios respectively.

Introduction

The survey of literature brought to light that the uranyl nitrate has got a great tendency for the formation of complex compounds especially with the nitrates of the alkali metals as is reported in the previous communication by the authors. This work has especially been taken due to the classical work done by SAMUEL GLASSTONE, HAROLD NICHOLAS and SAUNDERS[1]). The zeal and encouragement which we got is mainly due to the inspiration derived from the valuable researches of J. RIGGS[2]), G. MALQUOSI[3]), K. LAYBOURN

[1]) S. GLASSTONE, H. NICHOLS and SAUNDERS, J. chem. Soc. **123**, Vol. 2, 2134 (1923).

[2]) S. GLASSTONE and E. J. RIGGS, J. chem. Soc. **127**, 2, 2846 (1925).

[3]) G. MALQUOSI, Gazetta **58**, 203—208 (1928); **59**, 355—362 (1929); Atti R. Accad. Lincei (1929), (Vi); 9, 231—233.

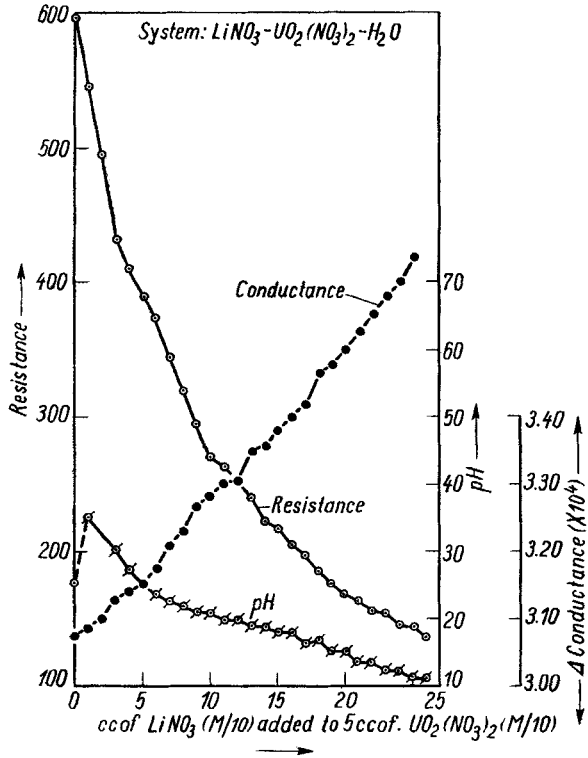
System: $LiNO_3$-$UO_2(NO_3)_2$-H_2O
Conductance
Resistance
pH
Resistance
pH
Δ Conductance (X10⁴)
ccof $LiNO_3$ (M/10) added to 5ccof. $UO_2(NO_3)_2$ (M/10)

Fig. 1

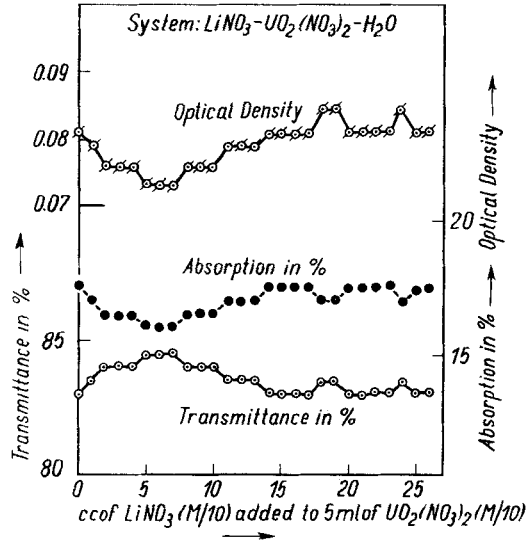
System: $LiNO_3$-$UO_2(NO_3)_2$-H_2O
Optical Density
Absorption in %
Transmittance in %
Transmittance in %
Absorption in %
Optical Density
ccof $LiNO_3$ (M/10) added to 5ml of $UO_2(NO_3)_2$ (M/10)

Fig. 2

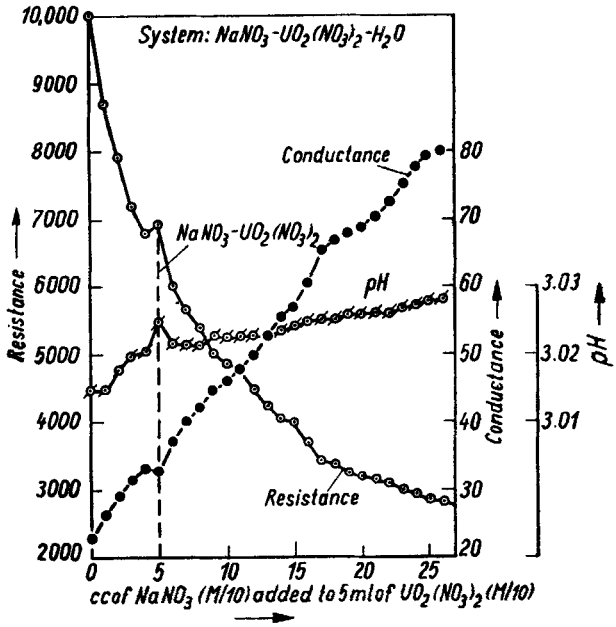
System: $NaNO_3$-$UO_2(NO_3)_2$-H_2O
Conductance
$NaNO_3$-$UO_2(NO_3)_2$
pH
Resistance
Resistance
Conductance
pH
10,000
9000
8000
7000
6000
5000
4000
3000
2000
80
70
60
50
40
30
20
3.03
3.02
3.01
0 5 10 15 20 25
ccof $NaNO_3$ (M/10) added to 5 ml of $UO_2(NO_3)_2$ (M/10)

Fig. 3

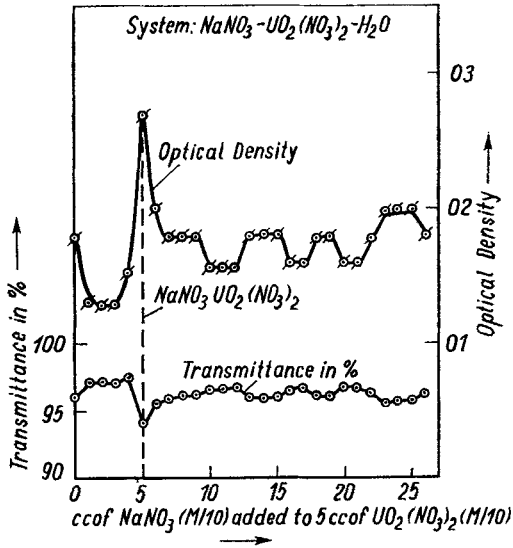
System: $NaNO_3$-$UO_2(NO_3)_2$-H_2O
Optical Density
$NaNO_3$ $UO_2(NO_3)_2$
Transmittance in %
Transmittance in %
Optical Density
03
02
01
100
95
90
0 5 10 15 20 25
ccof $NaNO_3$ (M/10) added to 5 ccof $UO_2(NO_3)_2$ (M/10)

Fig. 4

and W. M. MADGIN[4]), WILLIAM F. EHRET[5]), H. M. GLASS, K. LAYBOURN and W. M. MADGIN[6]), ARTHUR E. HILL and MATHAN KAPLAN[7]), M. A. PUSCHIN and M. RADOICIC[8]), NAYAR and PANDE[9]), on such class of compounds.

In this communication the systems explored are some investigated by previous workers as R. J. MAYER and F. WENDEL[10]), RIMBACH[11]), F. W. O.

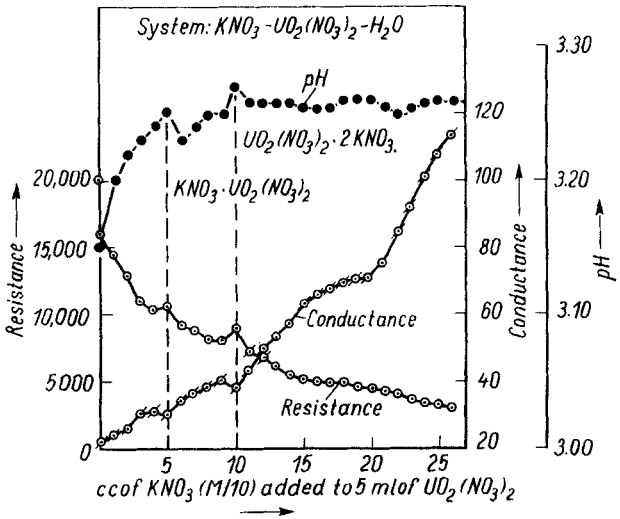

Fig. 5

DE CONINCK[12]), who were the first to examine the system alkali nitartes — uranyl nitrate — water. Since these systems have not been thoroughly dealt with so it was thought desirable to examine and investigate these systems. The physico — chemical properties like conductivity, pH and spectrophotometry were extensively used. The observed results are in good agreement and lead to the same conclusions.

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[4]) K. LAYBOURN and W. M. MADGIN, J. chem. Soc. **6**, 874–880; 1360–64 2582 bis 2589, (1932).

[5]) W. F. KHRET, J. Amer. chem. Soc. **54**, 3126–3134 (1932).

[6]) H. M. GLASS, K. LAYBOURN and W. M. MADGIN, J. chem. Soc. 199–202 (1953).

[7]) A. E. HILL and N. KAPLAN, J. Amer. chem. Soc. **58**, 1644–1645 (1936).

[8]) N. A. PUSCHIN and RADOICIC, Z. anorg. allgem. Chem. **233**, 41–46 (1937).

[9]) M. R. NAYAR and C. S. PANDE, Proc. Ind. Acad. Sci., Vol. XXVII, 1948, p. 284–292; Vol. XXVII, p. 293–299; Vol. XXVII, 1948, p. 343–348; Current Science, June 1948, 17, 187.

[10]) R. J. MEYER and F. WENDEL, Ber. dtsch. chem. Ges. **36**, 4055 (1903).

[11]) E. RIMBACH, ibid. **37**, 461 (1904).

[12]) A. SACHS, Zeitsch. Kryst. Min. **38**, 496 (1903).

Experimental

The stock solutions were prepared from the substances of A. R. B. D. H. quality. The purity of each salt was estimated before use by the usual standard methods. The stock solutions of all the nitrates were prepared in conductivity water and stored in thoroughly cleaned Jena glass bottles. The modus operandi was to keep the concentration of uranyl nitrate constant and to vary the concentration of other alkali nitrates respectively in each system

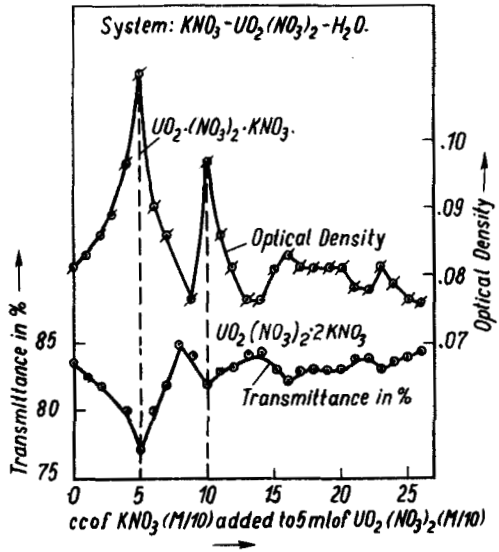

Fig. 6

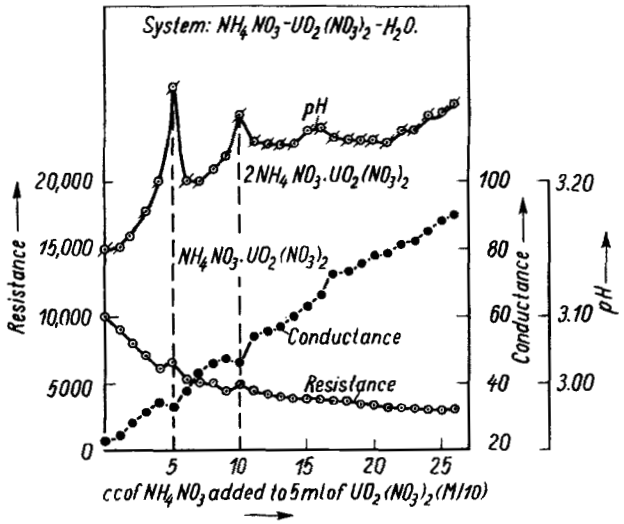

Fig. 7

separately following NAYER and PANDE'S mono-variation method[13]). In all the solutions the concentration of uranyl nitrate was kept constant (i. e. M/100) while that lithium, sodium, potassium or Ammonium nitrate varied systematically from 0.0 M to 0.052 M and as such 27 mixed solutions were prepared. The composition of these solutions is shown in table No. 1.

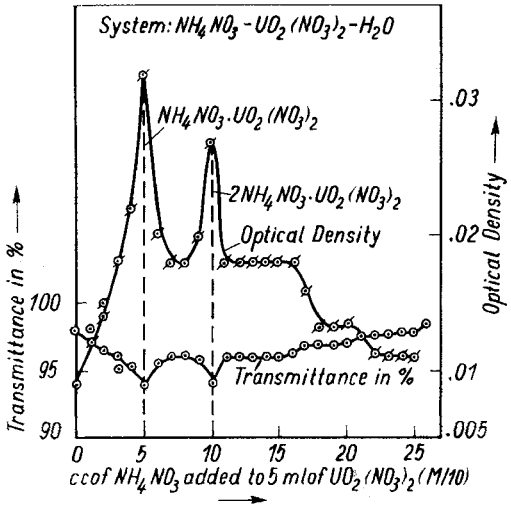

Fig. 8

Conductivity

Conductivity measurements were made by the conductivity — assembly Electronic Magic-eye (Phillips Model G. M. 4249). A pyrex glass conductivity cell with platinum electrodes was used in conductivity measurements. The cell was platinized and washed by following all the details given in Findlay: Practical Physical Chemistry. The cell was rinsed several times with the solution used. At least three readings were taken for each solution. The temperature of the thermostat was maintained at 35 °C. Each solution was placed in the cell and kept in the thermostat for at least half an hour before observations were recorded.

pH Measurements

The pH measucments of the solutions were made by using a Phillips G. M. 4494/Model using a glass electrode, at 35 °C. The values are recorded according to the tables.

Spectrophotometry

Measuremts of per cent transmission, per cent absorption and optical density were made by using a Baush and Lomb 50 cycles spectrophotometer.

[13]) F. W. O. DE CONINCK, Bull. Acad. roy. Belg. 1909, p. 744.

Table 1
The System: $M(NO_3)-UO_2(NO_3)_2-H_2O$
(M = Li, Na, K, or. NH_4)
Composition of the Solutions

Soln. No.	Total Volume of the Soln. cc	cc of $UO_2(NO_3)_2$ M/10 added.	Conc. of the $UO_2(NO_3)_2$ soln. M	CC of M (NO_3) M/10 added.	Conc. of M (NO_3) Soln. added.	Ratio of the Constituents.
1.	50	5	0.01	0.0	0.000	5/0
2.	50	5	0.01	1.0	0.002	5/1
3.	50	5	0.01	2.0	0.004	5/2
4.	50	5	0.01	3.0	0.006	5/3
5.	50	5	0.01	4.0	0.008	5/4
6.	50	5	0.01	5.0	0.010	5/5 or 1 : 1
7.	50	5	0.01	6.0	0.012	5/6
8.	50	5	0.01	7.0	0.014	5/7
9.	50	5	0.01	8.0	0.016	5/8
10.	50	5	0.01	9.0	0.018	5/9
11.	50	5	0.01	10.0	0.020	5/10 or 1 : 2
12.	50	5	0.01	11.0	0.022	5/11
13.	50	5	0.01	12.0	0.024	5/12
14.	50	5	0.01	13.0	0.026	5/13
15.	50	5	0.01	14.0	0.028	5/14
16.	50	5	0.01	15.0	0.030	5/15 or 1 : 3
17.	50	5	0.01	16.0	0.032	5/16
18.	50	5	0.01	17.0	0.034	5/17
19.	50	5	0.01	18.0	0.036	5/18
20.	50	5	0.01	19.0	0.038	5/19
21.	50	5	0.01	20.0	0.040	5/20 or 1 : 4
22.	50	5	0.01	21.0	0.042	5/21
23.	50	5	0.01	22.0	0.044	5/22
24.	50	5	0.01	23.0	0.046	5/23
25.	50	5	0.01	24.0	0.048	5/24
26.	50	5	0.01	25.0	0.050	5/25 or 1 : 5
27.	50	5	0.01	26.0	0.052	5/26

The solutions were maintained at 35 °C by placing them in a thermostat at that temperature. Before recording the observations, the adjustment was made with a blank solvent used in the preparation of solutions. The spectrophotometric observations are recorded according to the Tables attached.

Observation and Conclusion

When these values of resistance, conductivity, pH, % transmittance, % absorption and optical density of the solutions were plotted against the vo-

Table 2

The System: $UO_2(NO_3)_2$–$LiNO_3$–H_2O

(conductivity, pH and spectrophotometry)

Cell constant 1.474 Temp. 35° ± 0.5°C

Soln. No.	cc of $LiNO_3$ M/10 added to 5 cc of $UO_2(NO_2)$ M/10	Resistance in ohms	Conductance × 10^4 in Mhos	pH	% transmittance	% Absorption	Optical density
1.	0.0 cc	596	16.78	3.15	83.0	17.0	0.0810
2.	1.0 cc	545	18.35	3.25	83.5	16.5	0.0785
3.	2.0 cc	495	20.20	3.23	84.0	16.0	0.0760
4.	3.0 cc	430	23.25	3.20	84.0	16.0	0.0760
5.	4.0 cc	410	24.39	3.17	84.0	16.0	0.0760
6.	5.0 cc	390	25.64	3.15	84.5	15.5	0.0735
7.	6.0 cc	372	26.88	3.14	84.5	15.5	0.0735
8.	7.0 cc	345	28.98	3.13	84.5	15.5	0.0735
9.	8.0 cc	320	31.25	3.12	84.0	16.0	0.0760
10.	9.0 cc	295	33.89	3.12	84.0	16.0	0.0760
11.	10.0 cc	270	37.03	3.11	84.0	16.0	0.0760
12.	11.0 cc	262	38.16	3.11	83.5	16.5	0.0785
13.	12.0 cc	250	40.00	3.10	83.5	16.5	0.0785
14.	13.0 cc	240	41.66	3.09	83.5	16.5	0.0785
15.	14.0 cc	222	45.04	3.09	83.0	17.0	0.0810
16.	15.0 cc	218	45.88	3.08	83.0	17.0	0.0810
17.	16.0 cc	206	48.54	3.08	83.0	17.0	0.0810
18.	17.0 cc	198	50.50	3.07	83.0	17.0	0.0810
19.	18.0 cc	189	52.91	3.05	83.5	16.5	0.0785
20.	19.0 cc	174	57.47	3.05	83.5	16.5	0.0785
21.	20.0 cc	170	58.82	3.03	83.0	17.0	0.0810
22.	21.0 cc	164	60.97	3.03	83.0	17.0	0.0810
23.	22.0 cc	158	63.29	3.02	83.0	17.0	0.0810
24.	23.0 cc	152	65.79	3.02	83.0	17.0	0.0810
25.	24.0 cc	148	67.57	3.01	83.5	16.5	0.0785
26.	25.0 cc	142	70.42	3.01	83.0	17.0	0.0810
27.	26.0 cc	136	73.53	3.01	83.0	17.0	0.0810

lume of all these nitrates added to a fixed volume of uranyl nitrate, we obtained the curves according to the figures. It will be noticed that in the case of lithium nitrate there is no definite break in the regular curves indicating there by that no complex compound is formed. In the case of Sodium nitrate one break is observed showing the formation of one complex compound in the 1 : 1 molecular ratio were as in the case of potassium nitrate and ammonium nitrate two complexes are detected individually. The ratio of these two nitrates to uranyl nitrate at these points is (1 : 1) and (1 : 2) respectively.

Table 3

The System: $UO_2(NO_3)_2$–$NaNO_3$–H_2O

(Conductivity, pH and Spectrophotometry)

Cell constant 22.93 Temp. 35° ± 0.5 °C

Soln. No.	cc of $K(NO_3)$ M/10 added to 5 cc of $UO_2(NO_3)_2$ M/10	Resistance in ohms $\times 10^3$	Conductance $\times 10^4$ in Mhos	pH	% transmittance	% Absorption	Optical density
1.	0.0 cc	10.00	20.93	3.150	96.0	4.0	0.0180
2.	1.0 cc	8.70	26.35	3.150	97.0	3.0	0.0130
3.	2.0 cc	7.90	29.02	3.180	97.0	3.0	0.0130
4.	3.0 cc	7.20	31.85	3.200	97.0	3.0	0.0130
5.	4.0 cc	6.80	33.72	3.200	96.5	3.5	0.0155
6.	5.0 cc	6.90	33.23	3.240	94.0	6.0	0.0270
7.	6.0 cc	6.05	37.90	3.220	95.5	4.5	0.0200
8.	7.0 cc	5.66	40.51	3.220	96.0	4.0	0.0180
9.	8.0 cc	5.40	42.46	3.220	96.0	4.0	0.0180
10.	9.0 cc	5.00	45.86	3.225	96.0	4.0	0.0180
11.	10.0 cc	4.90	46.80	3.230	96.5	3.5	0.0155
12.	11.0 cc	4.80	47.77	3.230	96.5	3.5	0.0155
13.	12.0 cc	4.50	50.39	3.230	96.5	3.5	0.0155
14.	13.0 cc	4.20	53.95	3.220	96.0	4.0	0.0180
15.	14.0 cc	4.00	56.61	3.235	96.0	4.0	0.0180
16.	15.0 cc	4.00	57.32	3.240	96.0	4.0	0.0180
17.	16.0 cc	3.70	61.14	3.245	96.5	3.5	0.0155
18.	17.0 cc	3.45	66.46	3.250	96.5	3.5	0.0155
19.	18.0 cc	3.40	67.44	3.250	96.0	4.0	0.0180
20.	19.0 cc	3.35	68.04	3.255	96.0	4.0	0.0180
21.	20.0 cc	3.30	69.48	3.260	96.5	3.5	0.0155
22.	21.0 cc	3.20	71.65	3.260	96.5	3.5	0.0155
23.	22.0 cc	3.10	73.97	3.260	96.0	4.0	0.0180
24.	23.0 cc	3.00	76.43	3.260	95.5	4.5	0.0200
25.	24.0 cc	2.92	78.52	2.700	95.5	4.5	0.0200
26.	25.0 cc	2.90	79.06	2.700	95.5	4.5	0.0200
27.	26.0 cc	2.85	80.45	2.280	96.0	4.0	0.0180

There is excellent similarity in the curves with respect to all physicochemical properties investigated and, therefore, there is no question about the genuineness of the phenomenon. The break occurs at exact stoichiometric ratio of concentrations corresponding to the compounds stated above. Thus the existence of these compounds become unequivocal when such dissimilar properties like conductivity, pH and spectrophotometric measurements yield similar results.

Table 4

The System: $UO_2(NO_3)_2$—KNO_3—H_2O

(Conductivity, pH and Spectrophotometry)

Cell constant 34.65 Temp. 35° ± 0.5 °C

Soln. No.	cc of $K(NO_3)$ M/10 added to 5 cc of $UO_2(NO_3)_2$ M/10	Resistance in ohms $\times 10^3$	Conductance $\times 10^4$ in Mhos	pH	% transmittence	% Absorption	Optical density
1.	0.0 cc	16.0	22.93	3.15	83.0	17.0	0.0810
2.	1.0 cc	14.4	24.06	3.20	82.5	17.5	0.0835
3.	2.0 cc	13.0	26.65	3.22	82.0	18.0	0.0860
4.	3.0 cc	11.0	31.50	3.23	87.5	18.5	0.0890
5.	4.0 cc	10.5	33.00	3.24	80.0	20.0	0.0970
6.	5.0 cc	10.8	32.00	3.25	77.0	23.0	0.1140
7.	6.0 cc	9.6	36.00	3.23	80.0	20.0	0.0970
8.	7.0 cc	9.0	38.50	3.24	82.0	18.0	0.0860
9.	8.0 cc	8.7	39.83	3.25	85.0	15.0	0.0710
10.	9.0 cc	8.6	40.30	3.25	84.0	16.0	0.0760
11.	10.0 cc	9.0	38.50	3.27	82.0	20.0	0.0870
12.	11.0 cc	7.8	44.42	3.26	83.0	18.0	0.0860
13.	12.0 cc	7.0	49.50	3.26	83.0	17.0	0.0810
14.	13.0 cc	6.4	54.14	3.26	84.0	16.0	0.0760
15.	14.0 cc	5.8	59.74	3.26	84.0	16.0	0.0760
16.	15.0 cc	5.6	64.16	3.25	83.0	17.0	0.0810
17.	16.0 cc	5.3	65.37	3.25	82.5	17.5	0.0810
18.	17.0 cc	5.1	67.93	3.25	83.0	17.0	0.0810
19.	18.0 cc	5.0	69.30	3.26	83.0	17.0	0.0810
20.	19.0 cc	4.9	70.71	3.26	83.0	17.0	0.0810
21.	20.0 cc	4.8	71.50	3.26	83.0	17.0	0.0810
22.	21.0 cc	4.4	78.70	3.35	83.5	16.5	0.0785
23.	22.0 cc	4.0	86.62	3.25	83.5	16.5	0.0785
24.	23.0 cc	3.7	93.64	3.25	83.0	17.0	0.0810
25.	24.0 cc	3.4	101.32	3.26	83.5	16.5	0.0785
26.	25.0 cc	3.2	108.30	3.26	84.0	16.0	0.0760
27.	26.0 cc	3.0	115.50	3.26	84.5	15.5	0.0735

Table 5
The System: $UO_2(NO_3)_2$—NH_4NO_3—H_2O
(Conductivity, pH and Spectrophotometry)

Cell constant 22.93 Temp. 35° ± 0.5 °C

Soln. No.	cc of $NH_4(NO_3)$ M/10 added to 5 cc $UO_2(NO_3)_2$ of M/10	Resistance in ohms $\times 10^3$	Conductance $\times 10^4$ in Mhos	pH	% transmittence	% Absorption	Optical density
1.	0.0 cc	10.00	22.93	3.15	98.0	2.0	0.0090
2.	1.0 cc	9.20	24.77	3.15	97.0	3.0	0.0130
3.	2.0 cc	8.05	28.41	3.16	96.5	3.5	0.0155
4.	3.0 cc	7.35	31.18	3.18	96.0	4.0	0.0180
5.	4.0 cc	6.70	34.17	3.20	95.0	5.0	0.0220
6.	5.0 cc	6.75	33.94	3.22	93.0	7.0	0.0320
7.	6.0 cc	5.80	39.44	3.20	95.5	4.5	0.0200
8.	7.0 cc	5.50	41.74	3.20	96.0	4.0	0.0180
9.	8.0 cc	5.00	54.86	3.21	96.0	4.0	0.0180
10.	9.0 cc	4.80	47.69	3.22	95.5	4.5	0.0200
11.	10.0 cc	4.85	47.24	3.25	94.0	6.0	0.0270
12.	11.0 cc	4.30	53.20	3.23	96.0	4.0	0.0180
13.	12.0 cc	4.05	57.32	3.23	96.0	4.0	0.0180
14.	13.0 cc	3.90	58.69	3.23	96.0	4.0	0.0180
15.	14.0 cc	3.80	60.32	3.23	96.0	4.0	0.0180
16.	15.0 cc	3.60	63.52	3.24	96.0	4.0	0.0180
17.	16.0 cc	3.45	66.27	3.24	96.0	4.0	0.0180
18.	17.0 cc	3.30	69.47	3.23	96.5	3.5	0.0155
19.	18.0 cc	3.17	72.23	3.23	97.0	3.0	0.0130
20.	19.0 cc	2.95	77.73	3.23	97.0	3.0	0.0130
21.	20.0 cc	2.90	79.06	3.23	97.0	3.0	0.0130
22.	21.0 cc	2.87	79.69	3.23	97.0	3.0	0.0130
23.	22.0 cc	2.77	82.77	3.24	97.5	2.5	0.0110
24.	23.0 cc	2.67	85.76	3.24	97.5	2.5	0.0110
25.	24.0 cc	2.60	88.28	3.25	97.5	2.5	0.0110
26.	25.0 cc	2.52	90.80	3.25	97.5	2.5	0.0110
27.	26.0 cc	2.50	91.72	3.26	98.5	2.0	0.0090

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