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ABSORPTION SPECTRA OF CALCIUM-AMMONIA SOLUTIONS

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Preliminary work on the absorption spectrum of calcium in liquid ammonia[1] suggested that, at concentrations around 0.02 M, calcium yields

(1) M. Gold and W. L. Jolly, Inorg. Chem., 1, 818 (1962).

less than two moles of ammoniated electrons per gram atom of metal. However, two liquid phases formed during the make-up of some of the solutions, so no definite conclusions could be reached. In a continuing study of calcium-ammonia solutions, we have reached the point where we wish to report some preliminary results on liquid-liquid phase separation and the results of a more careful study of the spectra.

We wished to prepare solutions for spectral studies at concentrations as high as possible while avoiding liquid-liquid phase separation. Therefore we determined the boundary between the one-phase and two-phase regions on the ammonia-rich side of the Ca - NH_3 phase diagram. Conductivity measurements indicated that the bronze phase forms at 0.013 ± .002 M at -64° and at 0.032 ± .003 M at -45°. Thus we were able to measure the spectra of solutions as concentrated as 0.025 M at -45° without danger of phase separation. In earlier work[1], the solutions were cooled down to about -70°

before warming to -65°, at which temperature the initial spectral measurements were made. This pre-cooling procedure did not affect the alkali metal solutions (the second phase appears at concentrations of about 1 M at these temperatures in the case of the alkali metals), but some of the calcium solutions undoubtedly underwent phase separation. It is so difficult to get good mixing between the cell windows that even when the temperature was raised to -55° and -45°, it is doubtful that equilibrium was reachieved.

It is fortunate that spectra of single-phase solutions can be obtained at -45° so that direct comparison with the spectra of alkali metal solutions at this temperature can be made.

Experimental:

The absorption of spectra of eleven calcium-ammonia solutions have been measured between 6,000 Å and 25,000 Å at -45°. Spectra of some of the solutions were also obtained at -50° to see if any unusual temperature effects occurred.

Apparatus II of reference 1 and a Cary Model 14 spectrophotometer were used for all the measurements. The procedures were similar to those used previously. The calcium metal (United Mineral Co., 99.5% pure) was cut, cleaned and introduced into the sidearm tube of the cell under argon in a dry bag. The calcium was added from the sidearm to liquid ammonia in the make-up cell while the latter was immersed in a chlorobenzene slush (-45°). After the solution had become homogeneous, the cell was introduced into the cold box, where the temperature was kept around -45°. After slightly cooling the optical cell and allowing the solution to run into it, the cell was

cooled to a temperature two degrees below that at which the spectrum was to be obtained and then was warmed to the latter temperature. Analyses for the amounts of metal and NH_3 were made as previously described, and the density data of Cragoe and Harper[2] were used to calculate the solution

(2) C. S. Cragoe and D. R. Harper, Sci. Papers Bureau of Stds., No. 420, 287 (1921).

concentrations.

All the solutions whose spectra were determined showed 5 to 10% decomposition. Because the reproducibility of the spectra was considerably better than this, it was assumed that all the decomposition occurred during make-up, and we have used the final concentrations of calcium in all our calculations.

Some of the solutions of high concentration did not run cleanly into the optical cell section, and a small trace of bronze solution was observable in the make-up section after the spectrum was recorded. As pointed out in the earlier paper, this leads to calculated concentrations which are too low. However, the amount of material left in the make-up cell was so small that it is felt it only caused a few percent error in the calculated concentration.

The path length of the optical cell used in these measurements was determined using alkaline potassium chromate solutions. The absorbance of $CrO_4^{=}$ showed a negative deviation from Beer's law, and the measured absorbancies of the Ca solutions were corrected when applicable. A path length of 1.78×10^{-3} cm. best fit the $CrO_4^{=}$ solutions of low concentration,

so this value was used in calculating molar extinction coefficients from the measured absorbancies and concentrations.

Results:

The recorded spectra all consisted of a single broad band with a peak in the neighborhood of 15,800 Å. The extinction coefficients at several wavelengths are given in Tables I and II, and Figure 1 presents plots of absorbancy versus molarity of calcium at three wavelengths at -45°C.

Within the scatter of the data, Beer's law is obeyed, and the average values of the extinction coefficients at -45° are within ±4%, twice those of the alkali metal solutions at all wavelengths with the possible exception of 24,000 Å. At this wavelength the extinction coefficients show a slight trend toward higher values with increasing concentration that is not seen at the other wavelengths.

The peak position shows no dependence on the absorbancy at the maximum at either -45° or -50°. However, the spectral band is broadened and the peak shifts to higher wavelength and absorbancy when the temperature is raised from -50° to -45°. The average shift in peak position is 112 cm^{-1} $deg.^{-1}$. The spectra of alkali metal solutions showed a shift of -11.3 cm^{-1} $deg.^{-1}$ in the range -55° to -45°.

Conclusion:

Because the molar extinction coefficients of the calcium solutions are about two times those of the alkali metal solutions at all wavelengths except 24,000 Å, we conclude that two moles of solvated electrons are produced per gram atom of calcium dissolved.

Table I. Extinction Coefficients of Ca-NH_3 Solutions, -45°

Wavelength	Concentration (Millimoles/liter)										
	3.81	4.60	7.14	9.90	10.3	13.0	15.0	15.5	19.6	21.8	25.5
10,000 Å	31,800	31,800	24,400	20,400	22,400	23,300	26,600	24,300	25,500	22,700	21,800
13,000 Å	81,200	84,300	69,300	58,400	60,000	75,600	69,300	70,600	68,200	60,100	60,800
16,000 Å	116,600	125,800	100,800	92,500	91,000	116,600	101,500	106,600	112,000	98,800	93,600
18,000 Å	94,500	100,200	83,400	77,200	75,800	95,900	79,400	87,000	86,400	75,800	73,600
21,000 Å	36,900	42,100	39,400	38,300	37,100	40,200	42,300	41,700	41,500	36,800	36,600
24,000 Å	14,800	16,500	14,950	15,040	15,800	17,300	19,800	16,700	19,500	18,050	17,600
Peak, Å	15,800	15,720	15,850	15,870	15,910	15,800	15,850	15,850	15,800	15,750	15,800
ε at peak	119,500	128,300	102,300	93,800	91,600	117,400	101,800	107,300	113,200	99,900	94,400

Table II. Extinction Coefficients of Ca-NH_4, -50°

Wavelength	Concentration (Millimoles/liter)					
	3.84-	4.64	7.20-	9.98-	10.4-	15.6-
10,000 Å	26,400	30,300	20,300	18,580	21,300	23,900
13,000 Å	73,200	80,500	64,800	56,000	57,200	67,900
15,000 Å	102,300	117,400	91,200	76,500	81,500	98,900
16,000 Å	104,500	117,400	92,100	78,800	83,400	102,200
18,000 Å	75,400	90,800	71,000	61,100	66,600	78,300
21,000 Å	29,300	36,300	28,500	30,300	31,400	35,300
24,000 Å	8,780	10,900	10,530	10,570	11,440	12,480
peak, Å	15,570	15,650	15,600	15,700	15,690	15,650
ϵ at peak	106,100	118,800	92,900	78,800	83,100	101,200

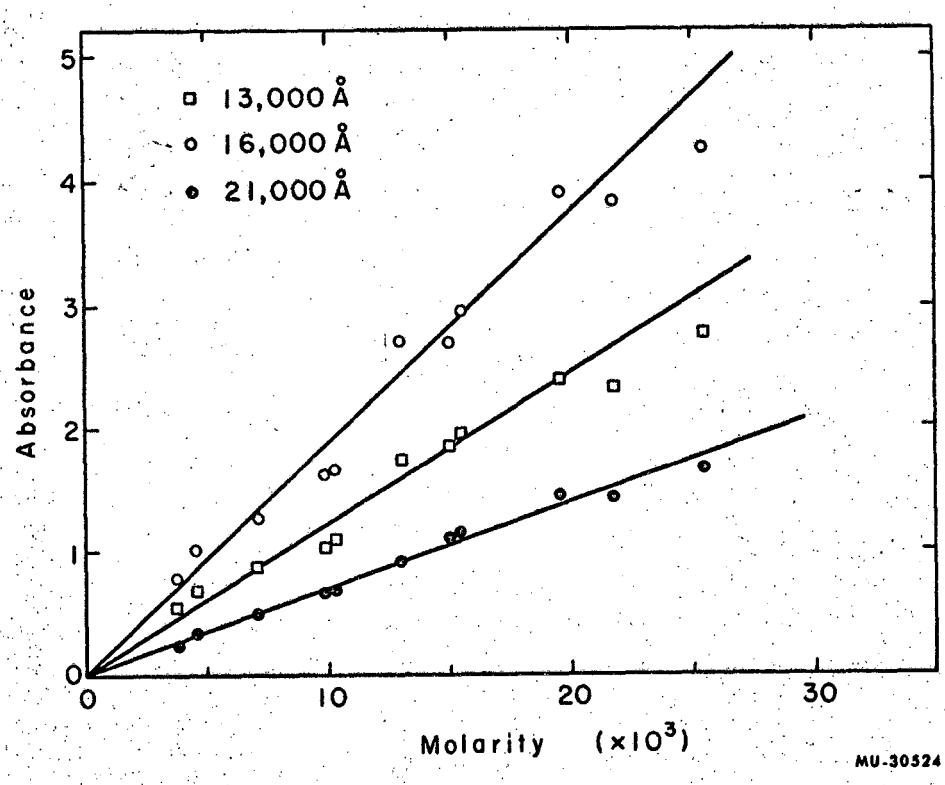

Figure 1. Absorbance vs. Molarity for Calcium-Ammonia Solutions at -45°.

The similarity of the spectra of calcium solutions and all the alkali metal solutions over the concentration range in which considerable aggregation and electron pairing occur[3] indicates that the environment of the

(3) S. Freed and N. Sugarman, J. Chem. Phys., 11, 354 (1943).

electron is not grossly affected by these processes. The model of Gold, Jolly and Pitzer[4], in which the ammoniated electron maintains its identity

(4) M. Gold, W. L. Jolly and K. S. Pitzer, J. Am. Chem. Soc., 84, 2264 (1962).

when monomer, dimer and higher aggregates are formed, best fits this observation.

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