parent molecular weight at 0° was 178 (formula weight 160). Experiments on two separately prepared solutions containing 3 mole % of trimethylindium in dichloromethane yielded results of 168 and 184, also at 0°.

The apparent molecular weight was also determined by measuring the lowering of vapor pressure for solutions of the compound in benzene and in dichloromethane at room temperature. Results from five benzene solutions ranging in concentration from 3 to 24 mole % fell between 175 and 181 and showed no significant trend with changing concentration. The single experiment with dichloromethane was made with a 1.86 mole % solution and yielded an apparent molecular weight of 188.

Probably the chief source of error in these measurements was the procedure used to determine the amount of trimethylindium present in the solutions whose vapor pressures were studied. For each experiment the compound was sublimed into the sample bulb from a storage bulb which was weighed before and after the transfer. We suspect that during transfer some trimethylindium vapor may have condensed in a part of the vacuum line which could not conveniently be warmed, making the actual amount collected in the sample bulb slightly less than the value obtained from the weighings. This would produce artificially *high* values for the apparent molecular weight.

One of the referees suggested that the apparent molecular weight might be too low as a result of reaction of trimethylindium with traces of water adsorbed on glass surfaces. We tried to minimize such decomposition by thoroughly flaming out all parts of the vacuum line for which this was practicable. Moreover we found during preliminary experiments that the reaction with adsorbed water produced a nonvolatile deposit and also that addition of trimethylindium to solvent contaminated with water led to formation of a precipitate. This *insoluble* material was probably polymeric, but may have been $(CH_3)_2InOH$ or $CH_3In(OH)_2$; the latter is formed when excess water is used.[1] The by-product of hydrolysis, methane, would not have affected the measurements because the sample bulb was chilled and opened to the pump after transferring the trimethylindium. To sum up, the reaction with any moisture remaining despite our precautions would have reduced the amount of solute actually present, and this would have led, again, to an apparent molecular weight *larger* than the true value.

We conclude that trimethylindium dissolves as a monomer rather than as a tetramer in benzene, toluene, dichloromethane, and cyclopentane, although the accuracy of our work is too low to exclude a very slight degree of association. Trimethylindium thus behaves like triethyl- and tripropylindium, which were found to be monomeric in benzene solution.[8]

Acknowledgment.—This work was supported by grants G-5488 and G-17421 from the National Science Foundation.

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[8] F. Runge, W. Zimmermann, H. Pfeiffer, and I. Pfeiffer, *Z. anorg. Chem.*, **267**, 39 (1951).

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Absorption Spectra of Calcium–Ammonia Solutions

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Received May 31, 1963

Preliminary work on the absorption spectrum of calcium in liquid ammonia[1] suggested that, at concentrations around 0.02 *M*, calcium yields 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 ± 0.002 *M* at −64° and at 0.032 ± 0.003 *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 precooling 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 spectra of eleven calcium–ammonia solutions have been measured between 6,000 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 ref. 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 side-arm tube of the cell under argon in a dry bag. The calcium was added from the side arm to liquid ammonia in the make-up cell while the latter was immersed in a chlorobenzene slush (−45°).

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

TABLE I

EXTINCTION COEFFICIENTS OF Ca–NH_3 SOLUTIONS, −45°

Wave length, Å.	Concentration, m*M*										
	3.81	4.60	7.14	9.90	10.3	13.0	15.0	15.5	19.6	21.8	25.5
10,000	31,800	31,800	24,400	20,400	22,400	23,300	26,600	24,300	25,500	22,700	21,800
13,000	81,200	84,300	69,300	58,400	60,000	75,600	69,300	70,600	68,200	60,100	60,800
16,000	116,600	125,800	100,800	92,500	91,000	116,600	101,500	106,600	112,000	98,800	93,600
18,000	94,500	100,200	83,400	77,200	75,800	95,900	79,400	87,000	86,400	75,800	73,600
21,000	36,900	42,100	39,400	38,300	37,100	40,200	42,300	41,700	41,500	36,800	36,600
24,000	14,800	16,500	14,950	15,040	15,800	17,300	19,800	16,700	19,500	18,050	17,600
Peak	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_3 SOLUTIONS, −50°

Wave length, Å.	Concentration, m*M*					
	3.84	4.64	7.20	9.98	10.4	15.6
10,000	26,400	30,300	20,300	18,300	21,100	23,400
13,000	73,200	80,500	64,800	55,100	56,700	66,600
15,000	102,300	117,400	91,200	75,400	80,500	96,900
16,000	104,500	117,400	92,100	77,600	82,600	100,100
18,000	75,400	90,800	71,000	60,200	65,900	76,700
21,000	29,300	36,300	28,500	29,800	31,100	34,600
24,000	8,780	10,900	10,530	10,400	11,350	12,240
Peak	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

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 2° 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 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 per cent 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^{-2} showed a negative deviation from Beer's law, and the measured absorbances of the Ca solutions were corrected when applicable. A path length of 1.78×10^{-3} cm. best fit the CrO_4^{-2} solutions of low concentration, so this value was used in calculating molar extinction coefficients from the measured absorbances 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 wave lengths are give in Tables I and II.

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 wave lengths with the possible exception of 24,000 Å. At this wave length the extinction coefficients show a slight trend toward higher values with increasing concentration that is not seen at the other wave lengths.

The peak position shows no dependence on the absorbance at the maximum at either −45 or −50°. However, the spectral band is broadened and the peak shifts to higher wave length and absorbance when the temperature is raised from −50 to −45°. The average shift in peak position is -12 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 wave lengths except 24,000 Å., we conclude that two moles of solvated electrons are produced per gram-atom of calcium dissolved.

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 electron is not grossly affected by these processes. The model of Gold, Jolly, and Pitzer,[4] in which the ammoniated electron maintains its identity when monomer, dimer, and higher aggregates are formed, best fits this observation.

Acknowledgment.—This research was supported by the U. S. Atomic Energy Commission.

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

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