and 50°C. for the alkyl chlorides. Under the conditions employed (helium at 40 ml. per minute), compounds VI and V had retention times of 2.2 and 4.0 minutes, respectively. Similarly, III and II had retention times of 5.0 and 8.2 minutes. Prepared mixtures of the isomeric alcohols and chlorides were used to calibrate the procedure.

ACKNOWLEDGMENT

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Solubility and Spectra of Cadmium in Dilute Cadmium Chloride–Molten Salt Mixtures

D. A. WENZ
Chemical Engineering Division, Argonne National Laboratory, Argonne, Ill.   60439

The solubility of cadmium in dilute mixtures of cadmium chloride with LiCl, 59 mole % LiCl–41 mole % KCl, and 50 mole % MgCl₂–30 mole % NaCl–20 mole % KCl was measured at 500° and 650° C. Absorption spectra of the species produced when cadmium dissolves in the three salt systems are reported.

THE solution of cadmium metal in cadmium chloride has been the subject of a large amount of investigation. Older work, reviewed by Bredig (2) and Corbett (3), and a recent e.m.f. study (6) indicate that cadmium dissolves by a reaction with cadmium chloride to form the cadmium (I) species, Cd_2^{2+}, perhaps solvated by an unknown number of cadmium (II) chloride entities. Other research (4, 5, 8) has shown that Cd_2^{2+}, unsolvated by cadmium chloride, is produced when cadmium dissolves in aluminum chloride-based salts containing cadmium chloride. Several workers have studied the effects on the cadmium solubility of diluting cadmium chloride with other chlorides (7, 9–12). The present work reports an investigation of cadmium solubility in dilute mixtures of cadmium chloride in several molten salts. The absorption spectra of the dissolved cadmium subchloride species in these systems are presented.

EXPERIMENTAL

Purification of Materials. Cadmium metal sticks of 99.99% purity (American Smelting and Refining Co.) were cleaned with dilute nitric acid, distilled water, and acetone, and then vacuum sublimed at about 1 micron pressure and 450° C. Immediately before use, the cadmium was filtered through a coarse fritted quartz disk on a vacuum line to remove any insoluble impurities. Anhydrous cadmium chloride (Mallinckrodt AR grade) was

purified by sparging at 650° C. first with chlorine gas for about 1 hour, then with hydrogen chloride for about 2 hours, and finally filtering the purified salt after the system was evacuated. The solvent chloride salts, LiCl, 59 % LiCl–41 mole % KCl, and 50 mole % MgCl₂–30 mole % NaCl–20 mole % KCl, were prepared from the individual reagent grade alkali metal chlorides and from anhydrous magnesium chloride. These salts were purified by bubbling hydrogen chloride through the molten salts at 500° to 650° C. for about 3 to 4 hours, removing dissolved hydrogen chloride under vacuum, and filtering. The purified salts were sealed in quartz ampoules and then transferred to a glovebox containing a purified helium atmosphere. All manipulations involving the purified reagents were performed either in the helium-filled glovebox or on a vacuum line.

Measurements. Spectral measurements were made using a Cary Model 14 Recording Spectrophotometer equipped with a high temperature furnace similar to that described by Young and White (13). The absorbance of a solution of solvent salt and cadmium chloride was measured as the base line, then cadmium metal in excess of its solubility was added and the absorbance measured again. An inert argon atmosphere was maintained in the cells during these operations. Air was the reference in both cases. The absorption cells had a path length of 1 cm., but an 8-mm. insert was used in some cases to shorten the light path. The absorbance due to dissolved cadmium was obtained by

Table I. Absorption Maxima of Solutions of Cadmium in Cadmium Chloride–Salt Mixtures

Solvent Salt	Temp., °C.	λ_{max}, A.
LiCl	650	3050
59 mole % LiCl-41 mole % KCl	650	3350
	500	3000
50 mole % MgCl$_2$-30 mole % NaCl-20 mole % KCl	650	3600
	500	3300

Table II. Cadmium Solubilities in Salts Containing Cadmium Chloride

Solvent Salt	Temp., °C.	X_{CdCl_2}	X_{Cd}
LiCl	650	0.0523	6.8×10^{-4}
		0.0599	7.2×10^{-4}
		0.32	$\sim 1.1 \times 10^{-2}$
59 mole % LiCl-41 mole % KCl	650	0.0334	7.0×10^{-5}
		0.0605	1.4×10^{-4}
		0.0823	3.7×10^{-4}
		0.106	5.9×10^{-4}
	500	0.104	1.0×10^{-4}
		0.149	2.0×10^{-4}
		0.236	6.6×10^{-4}
		0.275	1.3×10^{-3}
50 mole % MgCl$_2$-30 mole % NaCl-20 mole % KCl	650	0.0327	6.4×10^{-4}
		0.0540	1.0×10^{-3}
		0.0620	1.0×10^{-3}
		0.0915	2.3×10^{-3}
		0.103	1.9×10^{-3}
		0.116	2.2×10^{-3}
	500	0.0545	3.5×10^{-4}
		0.0620	3.3×10^{-4}
		0.118	9.4×10^{-4}
		0.160	1.9×10^{-3}

uncertainties in the subtraction of two large absorbances to obtain the net spectrum preclude drawing any conclusions concerning possible asymmetry on the low wave length side of some of the absorption maxima. The wave lengths of the absorption maxima, having half-band widths of approximately 700 A., are given in Table I.

The molar absorptivities of the lower valent cadmium species at the maxima, estimated to be of the order of 10^4 liter mole.$^{-1}$ cm.$^{-1}$, were too high to calculate accurately since the concentrations of dissolved cadmium that gave observable absorbances were too low to be measured by hydrogen evolution. The changes in wave length of the cadmium subchloride absorption maximum with temperature and solvent composition are greater than those reported by Barnes (1) for AlCl$_3$-CdCl$_2$-Cd mixtures, suggesting that the absorption mechanism may be different in the two sets of salts.

The results of measurements of the amount of cadmium dissolved in salt mixtures containing cadmium chloride in equilibrium with cadmium metal are presented in Table II. The concentrations are in units of atom fraction, x_{Cd}, and mole fraction, x_{CdCl_2}. The data show that at the same temperature and mole fraction of cadmium chloride in the three solvent salts, the cadmium solubility increases in the order LiCl-KCl-CdCl$_2$ < LiCl-CdCl$_2$ < MgCl$_2$-NaCl-CdCl$_2$. These solubilities compare reasonably well with those in the literature for similar systems at higher cadmium chloride concentrations (7, 9–12). The information obtained in the present research can be used to determine whether Cd$_2^{2-}$ (presumably the reduced species in such solutions) is solvated by cadmium chloride in these solvents if activity coefficients for the necessary components of the salt-cadmium solutions can be measured.

a point by point subtraction of the base line absorbance from the total absorbance after addition of cadmium metal to the salt.

Solutions of cadmium chloride were equilibrated with excess cadmium metal while stirring under an argon atmosphere. Samples of the salts containing dissolved cadmium were taken at the temperature of the experiment (500° or 650° C.). Temperatures were measured to within $\pm 1°$ C., using a Pt-Pt, 10% Rh thermocouple. Quartz containers, stirrers, and sampling tubes were used.

The concentration of cadmium metal dissolved in the salts was determined by hydrolyzing the salt samples with 1 to 3N hydrochloric acid in a platinum crucible and collecting the hydrogen evolved from the reduction of HCl by the lower valent cadmium species. The amount of hydrogen evolved was determined by gas chromatography with a standard deviation of 5 to 10%. The cadmium chloride concentration was determined by titration of an aqueous solution of the sample with EDTA using Eriochrome Black T as an indicator. The solvent salt concentration was calculated by difference. The standard deviation in the concentrations of the salt components is about 2%. Salt densities were estimated assuming additivity of volumes upon mixing.

RESULTS AND DISCUSSION

The absorption spectra of the species produced by the reaction of cadmium with solutions of about 0.005 mole fraction cadmium chloride in the molten salts were determined by subtracting the solvent absorption, which is intense below about 3000 A., from the total absorption of solvent plus dissolved cadmium. A single broad maximum in the ultraviolet region was observed in every case. The

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