Solubilities of Lithium Chloride, Mercury(II) Chloride, and Their Mixtures in Ethylenediamine–Water Mixtures

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At 25° C., the solubility, y (grams per 100 grams of mixed solvent), of lithium chloride in ethylenediamine-water mixtures containing between 0.06 and 0.6% of water is given by $y = 1.26_4 + 0.66_0x \pm 0.019$, where 100 grams of solvent contains x grams of water. The solubility, z, of mercury(II) chloride in ethylenediamine-water mixtures containing between 0.06 and 1.25% of water is given by $z = 0.35_0 + 0.27_3x \pm 0.015$. In solutions that are saturated with both solids, the solubility of mercury(II) chloride is about four times greater than in the absence of lithium chloride. The solubility of lithium chloride is not greatly affected by the presence of mercury(II) chloride at saturation level. Less extensive solubility determinations at 20° and 30° C. of the solids and of their mixtures are also reported.

THE ELECTROCHEMISTRY of solutions in ethylenediamine (*5*) and uses of this solvent in the titration of very weak acids (*6, 7, 8*) have been recently reviewed. Bruckenstein and Mukherjee (*1*) have studied the relative dissociation constants of silver salts and alkali metal halides in ethylenediamine (EDA), while Schaap and his coworkers (*5*) have measured a number of polarographic half-wave potentials and potentiometric electrode potentials in this solvent.

A reference electrode of stable and reproducible potential is essential in fundamental studies. Schaap and his coworkers (*5*) introduced an electrode consisting of saturated two-phase zinc amalgam in contact with EDA that is saturated with (or else 0.25*M* in) lithium chloride and also saturated with respect to zinc chloride. The reference electrode used by Bruckenstein and Mukherjee (*1*) consists of a mercury pool in contact with EDA that is saturated with both mercuric chloride and lithium chloride.

EDA readily absorbs water and carbon dioxide from the atmosphere. In the case of systems based on saturated solutions, changes in the solubilities of the potential-determining compounds may alter the value or the stability of the electrode potential. As part of a study of such effects, the solubilities of lithium chloride, mercuric chloride, and mixtures of these have been determined at three temperatures in distilled EDA and in EDA-water mixtures of low water content.

EXPERIMENTAL

Chemicals. Ethylenediamine (Eastman, 98%) was allowed to stand over sodium hydroxide pellets for 24 hours and was then distilled at 23 mm. through a 60-cm. vacuum-jacketted column packed with 2-mm. glass helices. After rejection of the forecut, the material was distilled directly into 15-ml. wide-stemmed ampoules normally containing approximately 0.5 gram of lithium chloride or mercury(II) chloride. These solids (Baker reagent grade) were dried in batches of a few grams at 150° C. and transferred while still hot to the ampoules. Karl Fischer titration of random samples at ice-salt-temperature (*1*) gave 0.058 ± 0.010 gram of water per 100 grams of distilled EDA. The average water contents of dried lithium chloride and mercury(II) chloride were 0.10% and 0.04%, respectively.

Procedure. After the introduction of approximately 8 grams of distillate, the ampoules were sealed under vacuum when possible. Otherwise, the ampoules were quickly capped, weighed, and sealed at atmospheric pressure after water had been introduced from a microburet. After rotation in a thermostat bath maintained to within 0.1° C. of the specified temperature for one week, the sealed ampoules were opened just before withdrawal of a sample of the solution for analysis. Lithium chloride was determined gravimetrically as silver chloride. Mercury(II) chloride was determined by coulometric titration of mercury(II) with thioglycollate ion (*3*). Samples weighed in stoppered 0.6-ml. bottles were introduced into the cell containing deoxygenated and pretitrated buffered mercury(II) thioglycollate solution and titrated successively. Some mercury(II) chloride in EDA solutions were analyzed both coulometrically and gravimetrically as silver chloride. Solutions containing both lithium chloride and mercury(II) chloride were analyzed by coulometric titration of mercury(II) and gravimetric determination of total chloride as silver chloride. The procedures were checked by the analysis of standard aqueous solutions containing mercury(II) chloride or lithium chloride (or both) and EDA in the approximate ratios encountered in the solubility measurements.

Table I. Solubility at 25.0 ± 0.1° of Lithium Chloride in EDA–Water Mixtures

100 Grams of Mixed Solvent		100 Grams of Mixed Solvent	
H_2O^a, G.	LiCl, G.	H_2O^a, G.	LiCl, G.
0.168	1.41	0.656	1.89
0.171	1.37	0.753	1.99
0.185	1.34	0.776	1.87
0.261	1.44	0.794	1.64
0.270	1.48	0.831	1.80
0.330	1.48	0.964	1.88
0.430	1.54	1.100	2.31
0.466	1.61	1.202	2.25
0.503	1.63	1.231	2.42
0.520	1.60	1.304	2.25
0.545	1.66		

[a] Corrected for the water content of the EDA used.

Table II. Solubility at 25.0 ± 0.1° of Mercury(II) Chloride in EDA–Water Mixtures

100 Grams of Mixed Solvent		100 Grams of Mixed Solvent	
H_2O^a, G.	$HgCl_2$, G.	H_2O^a, G.	$HgCl_2$, G.
0.153	0.403	0.784	0.564
0.211	0.431	0.910	0.614
0.288	0.424	0.921	0.629
0.309	0.449	0.935	0.556
0.401	0.502	1.045	0.636
0.426	0.467	1.176	0.664
0.511	0.527	1.240	0.722
0.563	0.509	1.253	0.642
0.656	0.512		

[a] Corrected for the water content of the EDA used.

Results. Six solubility determinations at 25.0° C. gave a mean value and a standard deviation of 1.30 grams and 0.01 gram, respectively, of lithium chloride per 100 grams of distilled EDA. This mean value and those obtained from solutions containing not more than 0.6% of added water (Table I) give the relationship

$$y = 1.26_4 + 0.66_0 x \pm 0.019$$

where y and x are the weights (grams) of lithium chloride and of water, respectively, per 100 grams of EDA–water solvent. No correction has been applied for the water content of lithium chloride. If all of the water contained in the solid passed into the solution, each amount of water would be raised by 0.006 gram. Preliminary solubility determinations at 20.0° and 30.0° C. gave 1.04 ± 0.04 grams and 2.18 ± 0.05 grams, respectively, of lithium chloride per 100 grams of distilled EDA.

Eleven coulometric solubility determinations at 25.0° C. gave a mean value and a standard deviation of 0.35_7 gram and 0.013 gram, respectively, of mercury(II) chloride per 100 grams of distilled EDA. This mean value and all of those obtained from solutions containing added water (Table II) give the relationship

$$z = 0.35_0 + 0.27_3 \pm 0.015$$

where z is the weight (grams) of mercury(II) chloride per 100 grams of solvent. The correction (maximum, + 0.002 gram) for the water content of the solid has been ignored. Preliminary solubility determinations at 20.0° and 30.0° C. gave 0.40 ± 0.02 gram of mercury(II) chloride per 100 grams of distilled EDA at both temperatures.

Solubility determinations were made in distilled EDA that was saturated with both lithium chloride and mercury(II) chloride. Table III shows the effect of water content on the saturation values at 20.0, 25.0, and 30.0° C. The correction (maximum ~+0.008 gram) for the water contained in the solids has been ignored. Extrapolation of the results obtained at 25.0° C. gives 1.27 grams of lithium chloride and 1.56 grams of mercury(II) chloride per 100 grams of anhydrous EDA.

DISCUSSION

According to Isbin and Kobe (2), the separate solubilities, at 25° C., of lithium chloride and mercury(II) chloride are 1.39 grams and 0.4 gram, respectively, per 100 grams of EDA. These results, each about 10% higher than the values applicable to anhydrous EDA obtained by short extrapolation of the authors' data, approximate the authors' results obtained with EDA containing about 0.15% water. Isbin and Kobe did not determine the water content of their solvent, which was pretreated by the method of Putnam and Kobe (*4*). The latter workers give 99.83 and 99.80 as the percentages of EDA in the middle fractions of their distillate. If the principal impurity was water, the results of Isbin and Kobe are in line with the present results.

Table III. Solubilities of Lithium Chloride and Mercury(II) Chloride When Present Together in EDA–Water Mixtures

	100 Grams of Mixed Solvent		
° C.	H_2O^a, G.	LiCl, G.	$HgCl_2$, G.
20.0	0.058[b]	1.13	1.53
	0.613	1.45	2.35
	0.621	1.55	2.47
	1.213	1.99	3.42
	1.221	2.12	3.14
25.0	0.058[b]	1.32	1.66
	0.621	1.79	2.43
	0.669	1.80	2.39
	1.203	2.38	3.21
	1.208	2.43	3.24
30.0	0.058[b]	2.23	3.11
	0.651	2.59	3.48
	0.659	2.91	3.67
	1.213	2.99	4.08
	1.234	3.16	4.26

[a] Corrected for the water content of the EDA used.
[b] No water added.

The concentrations of lithium chloride in lithium chloride–mercury(II) chloride systems, determined by a difference method, are less certain than the concentrations of mercury(II) chloride. It is, however, obvious that the solubility of lithium chloride is affected but slightly by the presence of mercury(II) chloride at saturation level. The approximately fourfold increase in the solubility of mercury(II) chloride, caused by the presence of lithium chloride at saturation level, is presumably due to the formation of chloromercury(II) anions.

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