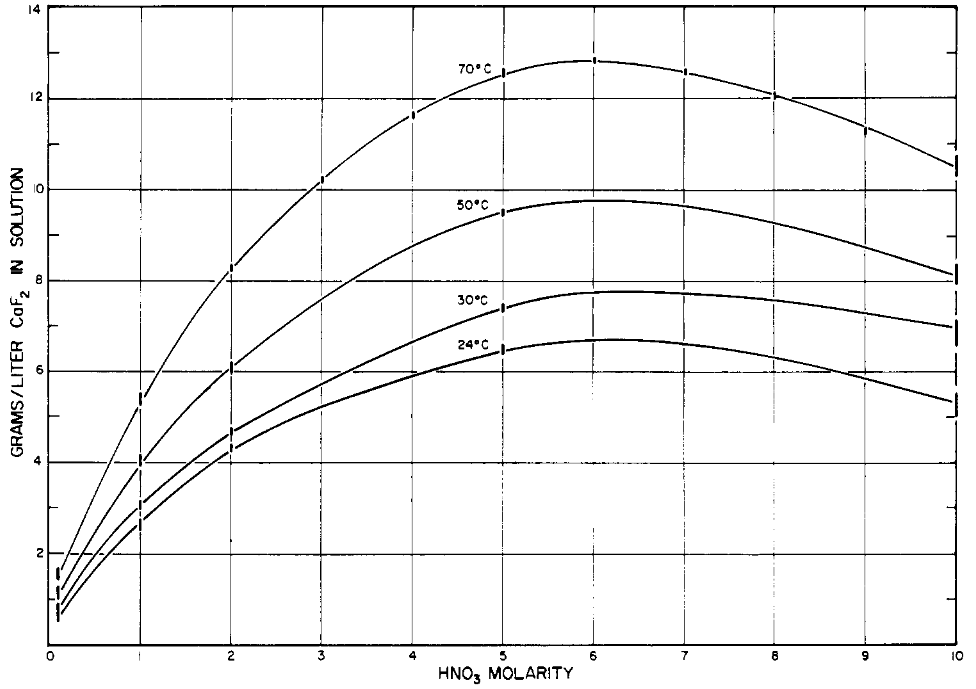

Figure 1. Solubility of CaF_2 in HNO_3 solution

cooling. The residues (undissolved solids) were oven-dried at 105° C. for 48 hours and weighed. The amount in solution was then determined by weight difference. Samples of the supernatant solutions were diluted tenfold to prevent reprecipitation of the dissolved solids, and were then analyzed for calcium by atomic absorption spectrometry.

RESULTS

The solubility isotherms for CaF_2 as a function of nitric acid concentration with temperature as a parameter are shown in Figure 1. These curves were drawn using average values obtained from triplicate samples. The deviations in the measurements are shown graphically in Figure 1. Additional results obtained by determining the concentration of calcium in solution agreed with the values obtained by weighing within ±5%.

Tests were also run at 70° C., using 3, 4, 6, 7, 8, and $9M$ HNO_3 to better define the maximum in the curve. The apparent maximum occurs at $6M$ HNO_3. The reason for the decreasing solubility with increasing acid concentration above $6M$ HNO_3 was not investigated, but was presumed to be due to a "salting-out effect," which is somewhat usual for solubilities involving concentrated electrolyte media.

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Stability Constants of Mn(II) and Zn(II) Acetylacetonates in 1-Propanol–Water Mixtures

AHMAD DADGAR[1] and RONALD DELORENZO
Lowell Technological Institute, Lowell, Mass. 01854

STABILITY constants of Ni(II) and Co(II) acetylacetonates have been determined in mixed solvent systems (*2*, *4*). The purpose of this work is to investigate in a similar manner the solvent effect on the stepwise formation of Mn(II) and Zn(II) acetylacetonates in 1-propanol–water solvent systems.

MATERIALS

Acetylacetone (Eastman Kodak Co., white label) was standardized by the method of Smith and Mitchell (*7*) and found to be 98.7% pure. An infrared spectrum was taken and the peaks corresponded to those reported in the literature (*6*). A gas chromatograph analysis resulted in two peaks, the smaller being 1.3% of the total area of both peaks, indicating one impurity, which was found to be water. Attempts to distill the acetylacetone for further purification were not successful, and since minor impurities were not considered to be significant sources of error (*2*), the acetylacetone was used without further purification. Solutions of acetylacetone were made up in recognition of the fact that it was 98.7% pure.

Manganese perchlorate and zinc perchlorate (G. Frederick Smith Chemical Co.) were standardized according to the standard methods. The specifications of the other chemicals

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[1] Present address, Department of Chemistry, Arya-Mehr University of Technology, Tehran, Iran.

The stability constants of Mn(II) and Zn(II) acetylacetonates in 1-propanol–water have been measured at three different temperatures (0°, 25°, and 40° C.). Linear relationships were shown when log K_1 or log K_2 was plotted vs. 1/D. Also, the data have been compared with similar data previously obtained for Ni(II) and Co(II) acetylacetonates in the same solvent system.

used in this work were the same as those given in a previous report (*4*). National Bureau of Standards buffers were used in all pH meter calibrations. These buffers were accurate to the third decimal place.

APPARATUS

All pH measurements were made with a Beckman research pH meter in conjunction with a Beckman glass electrode (No. 41263) and a Beckman frit junction reference electrode (No. 39071). The pH range of the glass electrode was 0 to 11 and the temperature range was −5° to +80° C.

A Wilkens-Anderson refrigerated constant-temperature bath was used for the constant-temperature studies. This bath had a temperature range from −10° to +65° C. and maintained a constant temperature within ±0.1° C. A National Bureau of Standards certified thermometer was used to check the temperature periodically.

EXPERIMENTAL

The experimental procedure used in the present work for the determination of the stability constants of metal acetylacetonates has been described elsewhere (*4*).

RESULTS

Stability constant data determined for Mn(II) and Zn(II) acetylacetonates are given in Table I. The symbols used are as follows: 1/D is the reciprocal of dielectric constant. The terms K_1', K_2', and β' are the first, second, and over-all concentration stability constants, respectively. The same symbols without the prime correspond to the thermodynamic stability constants. When log $K (K = K_1$ or $K_2)$ was plotted against 1/D, linear relationships were obtained. The equations for these lines, as determined by the method of least squares (*3*), are given in Table II. The average error for log K was 0.03 log unit.

SOLVENT EFFECT ON CHELATION

In Figure 1, log K_1 data are plotted against 1/D for Mn(II) and Zn(II) acetylacetonates in 1-propanol–water solvent system at 25° C. Similar data for Co(II) and Ni(II) acetylacetonates obtained previously (*2, 4*) are also shown in Figure 1. One can conclude that in 1-propanol–water (D range, 30 to 80) log K_1 *vs.* 1/D data for metal ions of similar basicity give parallel lines with nearly the same slope. It follows that one would have been able to obtain, for example, the Zn(II) data simply by getting the log K_1 value for Zn(II) acetylacetonate at 25° C. in water and then to draw a line parallel to the lines obtained for other metal chelates in the same solvent system. The above conclusion also follows when log K_2 data are plotted against 1/D.

The log K for Ni(II) acetylacetonate was plotted against the reciprocal of the dielectric constant in different solvent systems (*4*). The log K data in 1-propanol–, 2-propanol–, and dioxane–water systems showed only one linear relationship. On the basis of this observation, it was concluded that these solvent systems may be placed in one group with respect to their solvent effect on metal chelation. Therefore, it seems reasonable to expect that log K data for these metal ions or other metal ions (with similar

Table I. Stability Constants for Mn(II) and Zn(II) Acetylacetonates in 1-Propanol–Water Systems at 0°, 25°, and 40° C.

1/D	log K_1'	log K_2'	log β'	log K_1	log K_2	log β	1/D	log K_1'	log K_2'	log β'	log K_1	log K_2	log β
Mn(II), 0° C.							Zn(II), 0° C.						
0.0113	4.18	3.04	7.22	4.27	3.13	7.40	0.0113	5.07	3.90	8.97	4.16	3.99	9.15
0.0131	4.38	3.18	7.56	4.50	3.30	7.80	0.0131	5.28	4.18	9.46	5.40	4.30	9.70
0.0160	4.69	3.45	8.14	4.86	3.62	8.48	0.0160	5.54	4.47	10.01	5.71	4.64	10.35
0.0182	4.90	3.62	8.52	5.11	3.83	8.94	0.0182	5.73	4.74	10.47	5.94	4.95	10.89
0.0212	5.16	3.85	9.01	5.42	4.11	9.53	0.0212	5.97	4.96	10.93	6.23	5.22	11.45
0.0248	5.96	4.13	9.59	5.79	4.46	10.25	0.0248	6.32	5.29	11.61	6.65	5.62	12.27
0.0297	5.91	4.51	10.42	6.33	4.93	11.26	0.0297	6.81	5.72	12.53	7.23	6.14	13.37
Mn(II), 25° C.							Zn(II), 25° C.						
0.0127	4.01	2.85	6.86	4.12	2.96	7.08	0.0127	4.88	3.75	8.63	4.99	3.86	8.85
0.0149	4.28	3.02	7.30	4.42	3.16	7.58	0.0149	5.18	4.10	9.28	5.32	4.24	9.56
0.0183	4.67	3.35	8.02	4.87	3.55	8.42	0.0183	5.57	4.54	10.11	5.77	4.74	10.51
0.0213	4.87	3.53	8.40	5.11	3.77	8.88	0.0213	5.70	4.77	10.47	5.94	5.01	10.95
0.0247	5.20	3.80	9.00	5.49	4.09	9.58	0.0247	6.02	5.03	11.05	6.31	5.32	11.63
0.0294	5.55	4.13	9.68	5.93	4.51	10.44	0.0294	6.34	5.25	11.59	6.72	5.63	12.35
0.0352	6.08	4.50	10.58	6.58	5.00	11.58	0.0352	6.96	5.69	12.65	7.46	6.19	13.65
Mn(II), 40° C.							Zn(II), 40° C.						
0.0137	4.00	2.76	6.76	4.11	2.87	6.96	0.0137	4.86	3.67	8.53	4.97	3.78	8.75
0.0159	4.31	3.01	7.32	4.46	3.16	7.62	0.0159	5.14	4.04	9.18	5.29	4.19	9.48
0.0199	4.70	3.37	8.07	4.92	3.59	8.51	0.0199	5.60	4.49	10.09	5.82	4.71	10.53
0.0230	4.93	3.57	8.50	5.19	3.83	9.02	0.0230	5.78	4.81	10.59	6.04	5.07	11.11
0.0269	5.21	3.88	9.09	5.52	4.19	9.71	0.0269	6.08	5.03	11.11	6.39	5.34	11.73
0.0323	5.53	4.11	9.64	5.93	4.51	10.44	0.0323	6.53	5.35	11.88	6.93	5.75	12.68
0.0392	6.14	4.60	10.74	6.67	5.13	11.80	0.0392	7.17	5.77	12.94	7.70	6.30	14.00

Table II. Linear Equations for the First and Second Chelation of Mn(II) and Zn(II) with Acetylacetone Determined by the Method of Least Squares

First Chelation	Second Chelation
Mn(II)	
$\log K_1 = 116.4\ (1/D) + 2.95$ at 0° C.	$\log K_2 = 97.5\ (1/D) + 2.04$ at 0° C.
$\log K_1 = 106.5\ (1/D) + 2.84$ at 25° C.	$\log K_2 = 90.8\ (1/D) + 1.83$ at 25° C.
$\log K_1 = 95.6\ (1/D) + 2.92$ at 40° C.	$\log K_2 = 85.4\ (1/D) + 1.81$ at 40° C.
Zn(II)	
$\log K_1 = 110.2\ (1/D) + 3.93$ at 0° C.	$\log K_2 = 109.0\ (1/D) + 2.92$ at 0° C.
$\log K_1 = 104.9\ (1/D) + 3.73$ at 25° C.	$\log K_2 = 83.7\ (1/D) + 3.22$ at 25° C.
$\log K_1 = 102.8\ (1/D) + 3.65$ at 40° C.	$\log K_2 = 79.6\ (1/D) + 3.18$ at 40° C.

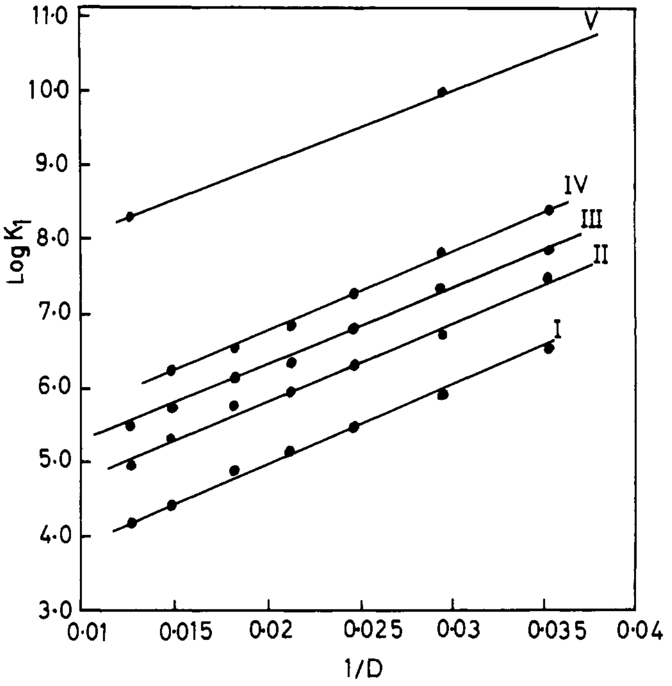

Figure 1. Log K_1 of metal acetylacetonates *vs.* 1/D in 1-propanol–water system at 25° C.

I. Mn(II) III. Co(II)
II. Zn(II) IV. Ni(II)
V. Cu(II)

basicity) with acetylacetone should be a function of the dielectric constant only, and independent of the nature of the solvent (D range, 30 to 80).

Although the data for Cu(II) acetylacetonate in dioxane-water (Figure 1) follow this argument, the present literature data for Co(II), Mn(II), and Ni(II) acetylacetonates in dioxane-water fail to follow the parallel relationship. This failure may well be due to some uncertainty in the data obtained from the literature. The data reported in the literature are only for three solvent systems (water, 50%, and 75% dioxane), and in addition, the standard state and the ionic strength are not always clearly defined in the work reported.

Calvin and Wilson (*1*) pointed out that it is possible to put a series of ligands in one group on the basis of their stability constant with a particular metal ion—i.e., Cu^{+2}. It was reported (*5*) that in mixed solvent systems (D range 30 to 80) of similar solvent effect on metal chelation, the factors influencing the chelation of acetylacetone with such metal ions as Cu(II), Ni(II), Co(II), and Zn(II) are the same as those affecting the chelation of these metal ions with dimethylglyoxime and salicylaldehyde. If we accept that the main factor influencing chelation is the dielectric constant of the media, and also recognize that some ligands have common properties on chelation, then for a given range of dielectric constant, plots of log *K* for a series of metal ions with different ligands, having similar properties on chelation, should give parallel lines with nearly the same slope. Plots of this nature can be of great value for determining the stability constant data without recourse to the experimental work.

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CORRECTION

In the article "Some New Silicon-Containing Secondary and Tertiary Acetylenic Alcohols" by John Samuel Adams, Jr. [J. CHEM. ENG. DATA **15**, 203 (1970)], the following material was omitted: The boiling points (° C/mm) for the last two compounds in Table I are 86–88/0.2 and 89.5—92/12. These compounds are liquids at room temperature so that no melting points were determined.