

mono-*n*-hexyl ether (hexyl Cellosolve) from Carbide and Carbon Chemical Co., and *sym*-trioxane from Celanese Chemical Co.

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Metal Complexing by Phosphorus Compounds

Solubilities of Magnesium Soaps of Linear Carboxylic Acids

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CALCIUM and magnesium are the two common cations contributing to water hardness. These cations participate in a number of undesirable reactions, one of which is soap precipitation. One way to soften the water is to "sequester" the cations with complexing agents, which in most cases are members of the polyphosphate family.

It is well known in the soap industry that water hardness caused by magnesium is more easily sequestered by polyphosphates than that caused by the presence of calcium. Yet, it has been shown recently (3, 4) that the formation constants of magnesium polyphosphate complexes are only slightly higher than the corresponding calcium complexes (1). Since sequestration against precipitation is dependent on the insolubility of the precipitate as well as the stability of the complex formed, measurement of solubilities of magnesium soaps is of interest and is reported in this paper. In a previous publication, the solubilities of calcium soaps of linear carboxylic acids were reported (2).

EXPERIMENTAL

Purity of the chemicals and the complexometric procedure for determining solubility of precipitates were the same as previously (2) described for calcium soaps. Here again, the precipitation of magnesium soap at pH 12 was

made to compete against complexing of magnesium by the tripolyphosphate anion.

RESULTS AND DISCUSSION

Raw data (Table I) show the amount of 0.1M Mg(NO₃)₂ solution that must be added to a solution containing tripolyphosphate and linear carboxylate anions to reach a point of incipient precipitation. The individual experimental numbers in Table I are averages of two or more runs. When duplicates did not agree within the experimental error (± 0.03 ml.), more checks were made to establish the values more precisely.

Since all the experimental data were collected at pH 12, the concentration of acidic complexes is negligible (3, 4). At the nephelometric endpoint, the material balance of magnesium is

$$YZA = (\text{Mg}^{-2}) + (\text{MgP}_3\text{O}_{10}^{-3}) + (2\text{Mg}_2\text{P}_2\text{O}_7^{-4}) \quad (1)$$

where *A* is the volume of solution in ml., *Z* and *Y* are the molar concentration and ml. of magnesium solution to reach the nephelometric endpoint, respectively, and parenthesis represent concentration. In reference 2, there are two misprints: Table II shows logs of the formation constants rather than the negative log. Also, Equation 5 in Reference

Table I. Summary of Data for the $Mg^{+2}-P_3O_{10}^{-5}$ -Linear Carboxylate Systems^a

Temp., °C.	Tripolyphosphate, M., ($C_1 \times 10^3$)	Linear Carboxylate, M., (C_2)	Cc. of 0.1M $Mg(NO_3)_2^b$	
			0.1	1.0
Laurate				
25	3.56	6×10^{-2}	7.23	8.07
	3.56	11×10^{-2}	4.80	6.90
Tridecylate				
25	2.60	2×10^{-2}	3.10	...
	3.56	8×10^{-3}	7.30	...
	3.56	1.2×10^{-2}	6.02	7.22
	3.56	1.6×10^{-2}	...	6.93
37	3.56	1.6×10^{-2}	6.98	...
	3.56	1.8×10^{-2}	6.20	...
Myristate				
25	2.32	1×10^{-3}	4.47	4.68
		2×10^{-3}	2.65	3.76
37		2×10^{-3}	4.42	...
		3×10^{-3}	3.98	...
50		4×10^{-3}	5.60	...
		5×10^{-3}	5.54	...
Palmitate				
25	3.56	8×10^{-5}	5.92	...
		1.2×10^{-4}	4.02	4.72
		2×10^{-4}	1.25	3.34
37		1.2×10^{-4}	6.58	...
		2×10^{-4}	5.02	...
5		2×10^{-4}	7.82	...
		2.8×10^{-4}	7.14	...
Stearate				
25	2.32	2×10^{-5}	2.25	4.70
		4×10^{-5}	0.80	3.40
37	3.56	2×10^{-5}	5.02	...
		4×10^{-5}	2.75	...
50	3.56	2×10^{-5}	7.10	...
		4×10^{-5}	5.00	...

^a Total volume of solution was always 250 ml.

^b Soln. (y) to nephelometric endpoint at ionic strengths.

Table II. Solubility Products of Magnesium Soaps

Magnesium Soap	Temp., °C.	Neg. Log. Solubility Product at Ionic Strength of		
		0.1	1.0	0.0 ^a
Laurate	25	7.56 ± 0.04	7.20 ± 0.08	7.73 ± 0.1
Tridecylate	25	9.19	9.02	9.27
	37	8.89
Myristate	25	11.17	10.96	11.27
	37	10.47
	50	10.06
Palmitate	25	13.63	13.56	13.66
	37	13.01
	50	12.21
Stearate	25	15.29	14.51	15.64
	37	14.92
	50	14.44

^a Infinite dilution, extrapolated.

2 should be $Mg + MgL \rightleftharpoons Mg_2L$, rather than $2Mg + L \rightleftharpoons Mg_2L$.

Moreover,

$$\beta_1 = \beta_{MgP_3O_{10}} = \frac{(Mg^{+2})(P_3O_{10}^{-5})}{(MgP_3O_{10}^{-3})} \quad (2)$$

$$\beta_2 = \beta_{Mg_2P_3O_{10}} = \frac{(Mg^{+2})^2(P_3O_{10}^{-5})}{(Mg_2P_3O_{10}^{-1})} \quad (3)$$

$$K_{sp} = (Mg^{+2})(C_2)^2 \quad (4)$$

where K_{sp} is the apparent solubility product and C_2 is the molarity of the linear carboxylate.

Combining Equations 1, 2, and 3:

$$\frac{YZ}{A} = (Mg^{+2}) \left[1 + \frac{(P_3O_{10}^{-5})}{\beta_1} \times \left(1 + (Mg^{+2})\beta_1 \right) \right] \quad (5)$$

Since β_1/β_2 is $10^{2.13}$ at unit ionic strength (3, 4) and from Equation 4 and the conditions of our experiments (Mg^{+2}) is about 10^{-5} , the term $(Mg^{+2})\beta_1/\beta_2$ is much less than one. Hence, combination of Equations 4, 5, and the material balance for tripolyphosphate reduces to the simple equation:

$$K_{sp} = \frac{\beta_1 C_2^2}{(C_1 A - YZ - 1)} \quad (6)$$

where C_1 is the tripolyphosphate concentration. In other words, under the conditions in Table I, the formation of 2 to 1 complexes can be ignored.

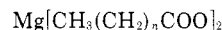
The value of $p\beta_1$ at unit ionic strength was previously reported (3, 4) to be 5.81 at 25°, and fairly independent of temperature. At an ionic strength of 0.1, $p\beta_1$ has been found to be 5.70. Using these values of β_1 , the data in Table I were interpreted with Equation 6 to give the apparent solubility products tabulated in Table II. The uncertainties shown as \pm are 95% confidence limits, obtained by statistical treatment of the experimental data. Changes in the ratio of tripolyphosphate to carboxylate concentration did not affect the values of K_{sp} , establishing that the data represent true equilibria.

The solubility products at infinite dilution, $[K_{sp}]_\infty$, were estimated by using the Debye-Hückel equation, and were found to fit the semiempirical least-squares equation:

$$p[K_{sp}]_\infty = -7.76 + 1.32 \times (\text{no. of carbons})$$

$$\text{in the linear carboxylate anion} = -7.76 + 1.32(n + 2) \quad (7)$$

where n is the integer in the soap formula



The solubilities of magnesium soaps with $n < 10$ or with unsaturation in the chain for $18 > n > 10$ were too high to be accurately measured with this technique because of unfavorable competition with the tripolyphosphate anion.

The solubility products of magnesium soaps are $10^{3.5}$ to 10^5 times the values for the corresponding calcium soaps (2), so that their molar solubilities are higher by no less than a factor of ten. This explains the ease of sequestering magnesium as compared to calcium in the presence of soaps.

From the temperature dependence of the solubility products at 0.1 ionic strength the following apparent enthalpy values were calculated: for the dissolution of magnesium tridecylate 10.6 kcal. per mole, for magnesium myristate 19.6 ± 5 kcal. per mole, for magnesium palmitate 24.9 ± 3 kcal. per mole and for magnesium stearate 15.5 ± 3 kcal. per mole.

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