

1008. The Stabilities of the Silver Complexes of Some 2-Hydroxypropylamines.

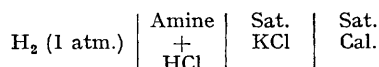
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Dissociation constants of the primary, secondary, and tertiary 2-hydroxypropylamines have been obtained at 20° from pH measurements. Stability constants at 20° of the complexes formed by them with silver ions have been determined from solubility and electrode-potential measurements.

No values have been reported for the dissociation constants of the 2-hydroxypropylamines or for the stability constants of the silver complexes of these bases.

EXPERIMENTAL

Dissociation Constants of the 2-Hydroxypropylamines at 20°.—The mono-, di-, and tri-2-hydroxypropylamines were fractionally distilled under reduced pressure of nitrogen. Their purities were estimated by titrating their dilute aqueous solutions, prepared by weight, with hydrochloric acid. They were also characterised by refractive index (Hilger–Chance Refractometer) (see Table 1). Dissociation constants were determined by hydrogen electro-titrations at 20° in dilute aqueous solutions of the bases with hydrochloric acid, using the cell:



From the measured e.m.f.'s pH's were calculated, pH being $-\log \{H^+\}$, where braces denote activities. The potential of the calomel half-cell was taken as 0.2476 v.¹ For the equilibrium $B + H_2O \rightleftharpoons BH^+ + OH^-$ (B = base) the constant K is defined by $K = \{BH^+\}\{OH^-\}/\{B\}$, where $\{BH^+\} = ([HCl] - [H^+] + [OH^-])f_{\pm}$, and $\{B\} = ([\text{Total base}] - [HCl] + [H^+] - [OH^-])f_{\pm}$ (square brackets denoting concns. in mole/l.). The mean activity coefficients of the

TABLE 1.
Properties of 2-hydroxypropylamines.

	Mono		Di		Tri	
	Found	Lit. ²	Found	Lit. ²	Found	Lit. ²
Purity (% as base)	99.8	—	99.6	—	99.9	—
n_D^{20}	1.4483	1.4488	Solid		Solid	
n_D^{60}	1.4336	1.4335	1.4516	1.4512	1.4555	1.4543

univalent ionic species in solution were calculated from $-\log f_{\pm} = 0.505\sqrt{I}/(1 + \sqrt{I})$, where I = ionic strength.³ The activity coefficient of the un-ionised, uncombined base was taken as unity. Temperature control was $\pm 0.1^\circ$. The titration data, together with the new calculated pK 's for the mono-, di-, and tri-hydroxypropylamines at 20°, are in Table 2.

Solubilities of Silver Oxide in Aqueous Solutions of 2-Hydroxypropylamines.—Silver oxide was precipitated from silver nitrate solution by addition of the stoichiometric amount of sodium hydroxide and washed completely free from other ions; excess of moisture was removed by suction filtration. Excesses of the still moist silver oxide were added to standard aqueous solutions of the hydroxyamines in dark bottles under nitrogen and the mixtures agitated at 20°. The equilibrated mixtures were filtered from undissolved silver oxide and the clear filtrates analysed for silver by Volhard's thiocyanate method (Table 3).

Titrations of Aqueous Solutions of 2-Hydroxypropylammonium nitrate–Silver Nitrate Mixtures at 20° with Sodium Hydroxide.—Addition of silver nitrate to aqueous solutions of the free

¹ Hitchcock and Taylor, *J. Amer. Chem. Soc.*, 1937, **59**, 1812.

² Shell Chemical Company, Technical Bulletin GC/25/1.

³ Guggenheim and Schindler, *J. Phys. Chem.*, 1934, **38**, 539.

TABLE 2.
Dissociation constants at 20° of 2-hydroxypropylamines.

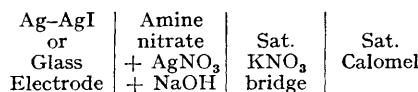
Mono			Di			Tri		
HCl (ml.)	pH (obs.)	pK	HCl (ml.)	pH (obs.)	pK	HCl (ml.)	pH (obs.)	pK
(i) 50 ml. of 0.0507M-base titrated with 0.501M-HCl			(i) 50 ml. of 0.05029M-base titrated with 0.501M-HCl			(i) 50 ml. of 0.05232M-base titrated with 0.501M-HCl		
0.50	10.55	4.59	0.50	9.95	5.20	—	—	—
1.00	10.22	4.59	1.00	9.62	5.20	1.00	8.65	6.19
1.50	10.00	4.59	1.50	9.39	5.20	1.50	8.42	6.20
2.00	9.80	4.61	2.00	9.20	5.20	2.00	8.24	6.20
2.50	9.65	4.60	2.50	9.03	5.21	2.50	8.07	6.20
3.00	9.48	4.60	3.00	8.87	5.20	3.00	7.90	6.21
3.50	9.28	4.61	3.50	8.67	5.21	3.50	7.73	6.21
4.00	9.07	4.60	4.00	8.46	5.20	4.00	7.52	6.21
4.50	8.72	4.62	4.50	8.11	5.21	4.50	7.25	6.21
Mean 4.60			Mean 5.20			Mean 6.20		
(ii) 50 ml. of 0.01046M-base titrated with 0.101M-HCl			(ii) 50 ml. of 0.0132M-base titrated with 0.101M-HCl			(ii) 50 ml. of 0.01026M-base titrated with 0.101M-HCl		
0.50	10.46	4.61	—	—	—	—	—	—
1.00	10.17	4.61	1.00	9.60	5.20	1.00	8.60	6.20
1.50	9.98	4.59	1.50	9.40	5.21	1.50	8.38	6.19
2.00	9.80	4.59	2.00	9.19	5.20	2.00	8.18	6.20
2.50	9.62	4.61	2.50	9.03	5.19	2.50	8.02	6.19
3.00	9.47	4.59	3.00	9.86	5.19	3.00	7.84	6.20
3.50	9.28	4.60	3.50	9.68	5.19	3.50	7.65	6.21
4.00	9.07	4.60	4.00	8.45	5.20	4.00	7.45	6.21
4.50	8.78	4.61	4.50	8.13	5.21	4.50	7.11	6.21
Mean 4.60			Mean 5.20			Mean 6.20		

TABLE 3.
Solubility of silver hydroxide at 20° in 2-hydroxypropylamines.

Mono			Di			Tri		
Base (10 ² M)	AgOH (10 ³ M)	log β_2	Base (10 ² M)	AgOH (10 ³ M)	log β_2	Base (10 ² M)	AgOH (10 ³ M)	log β_2
4.97	9.77	6.79	5.01	3.883	5.72	5.08	0.8275	4.27
9.84	19.78	6.78	10.16	8.198	5.72	10.05	1.635	4.26
14.90	30.51	6.78	15.60	12.47	5.71	15.25	2.561	4.28
20.11	41.48	6.77	20.77	17.04	5.71	20.09	3.370	4.27
25.04	51.84	6.78	25.20	20.21	5.71	25.14	4.470	4.27
Mean 6.78			Mean 5.71			Mean 4.27		

hydroxyamines immediately precipitated silver oxide. To prevent this, the amines were converted into propylammonium salts by addition of stoichiometric amounts of nitric acid. Known amounts of silver nitrate solution were added and the resulting mixtures progressively titrated at 20° with carbonate-free sodium hydroxide solution. Nitrogen was bubbled through to mix the solutions and exclude carbon dioxide.

After each known addition of alkali, pH was measured by means of a glass electrode and pAg values derived from silver-silver iodide electrode measurements,⁴ these titrations being carried out in the cell:



The use of the saturated potassium nitrate bridge was assumed to eliminate diffusion potentials. Results are in Table 4, with calculated values for the formation stability constants of the complex species present in solution.

⁴ Grunwald and Purlee, *J. Chem. Phys.*, 1957, **27**, 990.

TABLE 4.

Titration of 2-hydroxypropylammonium nitrate-silver nitrate mixtures with sodium hydroxide at 20°.

Mono-2-hydroxypropylamine.						Mono-2-hydroxypropylamine.					
NaOH (ml.)	pH (obs.)	pAg	10 ² I	log K ₁	log K ₂	NaOH (ml.)	pH (obs.)	pAg	10 ² I	log K ₁	log K ₂
(i) 50 ml. of 0.1012M-amine nitrate + 25 ml. of 0.01M-AgNO ₃ with 0.10M-NaOH						(ii) 50 ml. of 0.0510M-amine nitrate + 15 ml. of 0.01M-AgNO ₃ with 0.10M-NaOH					
1.00	6.99	2.687	6.988	3.04	3.74	1.00	7.32	2.885	4.091	3.18	3.60
1.50	7.14	2.760	6.942	3.16	3.62	1.50	7.53	3.024	4.060	3.28	3.50
2.00	7.26	2.840	6.897	3.22	3.56	2.00	7.70	3.165	4.030	3.30	3.48
2.50	7.38	2.934	6.865	3.26	3.52	2.50	7.88	3.359	4.00	3.25	3.53
3.00	7.49	3.037	6.809	3.25	3.53	3.00	8.06	3.589	3.971	3.32	3.46
3.50	7.60	3.154	6.764	3.35	3.43	3.50	8.23	3.830	3.941	3.20	3.58
			Mean	3.21	3.57				Mean	3.25	3.53
Dihydroxypropylamine.						Dihydroxypropylamine.					
(i) 50 ml. of 0.1032M-amine nitrate + 20 ml. of 0.01M-AgNO ₃ with 0.10M-NaOH						(ii) 50 ml. of 0.0504M-amine nitrate + 10 ml. of 0.01M-AgNO ₃ with 0.10M-NaOH					
1.00	6.57	2.679	7.548	2.99	2.72	1.00	7.13	3.037	4.295	2.84	2.87
1.50	6.78	2.751	7.496	2.66	3.05	1.50	7.34	3.162	4.261	2.72	2.99
2.00	6.95	2.827	7.444	2.77	2.94	2.00	7.52	3.298	4.225	2.96	2.75
2.50	7.09	2.922	7.393	2.90	2.81	2.50	7.67	3.430	4.192	2.97	2.74
3.00	7.20	2.991	7.342	2.90	2.81	3.00	7.78	3.550	4.159	2.99	2.72
3.50	7.30	3.078	7.292	2.95	2.76	3.50	7.92	3.71	4.126	2.99	2.72
4.00	7.42	3.186	7.242	2.93	2.78	4.00	8.00	3.81	4.094	3.00	2.71
			Mean	2.87	2.84				Mean	2.78	2.93
Trihydroxypropylamine.						Trihydroxypropylamine.					
(i) 50 ml. of 0.1016M-amine nitrate + 5 ml. of 0.01M-AgNO ₃ with 0.10M-NaOH						(ii) 50 ml. of 0.0504M-amine nitrate + 4 ml. of 0.01M-AgNO ₃ with 0.10M-NaOH					
1.5	6.26	3.242	9.082	2.06	2.21	1.5	6.62	3.355	4.612	2.26	2.01
2.0	6.39	3.298	9.001	2.21	2.06	2.0	6.76	3.410	4.571	2.30	1.97
2.5	6.52	3.350	8.922	2.24	2.03	2.5	6.88	3.465	4.532	2.32	1.95
3.0	6.62	3.410	8.846	2.29	1.98	3.0	6.96	3.510	4.491	2.34	1.93
3.5	6.70	3.460	8.769	2.31	1.96	3.5	7.05	3.553	4.451	2.31	1.96
4.0	6.77	3.510	8.695	2.34	1.93	4.0	7.12	3.600	4.414	2.34	1.93
			Mean	2.24	2.03	5.0	7.26	3.666	4.339	2.28	1.99
									Mean	2.31	1.96

DISCUSSION

The hydroxypropylamine solutions when saturated with silver oxide, gave rise in all cases to highly alkaline solutions containing excesses of the hydroxyamines, and since the hydroxyamines themselves could not cause this, it was assumed that the silver in solution was present as strong, complex bases^{5,6} of the type AgB_nOH (where B represents the ligand, here the 2-hydroxypropylamines) thus $\text{AgOH} + n\text{B} \rightleftharpoons \text{AgB}_n\text{OH} \rightleftharpoons \text{AgB}_n^+ + \text{OH}^-$. The complex cation AgB_n^+ must necessarily be in equilibrium with silver ions $\text{AgB}_n^+ \rightleftharpoons \text{Ag}^+ + n\text{B}$, its stability constant being defined by $\beta_n = \{\text{AgB}_n^+\}/\{\text{Ag}^+\}\{\text{B}\}^n$.

If the original concentration of the base is C mole/l., the amount of silver found by analysis is S mole/l., and f is the activity coefficient (calc.) of the univalent ions, then $Sf = \{\text{AgB}_n^+\} = \{\text{OH}^-\}$. The excesses of the ligands can be assumed to be present as the free base, B, since none of the base can be present as the conjugate acid BH^+ at these high pH's. Thus, the activity coefficient being assumed to be unity, $(c - nS)$ mole/l., is the concentration, and hence the activity of the un-ionised, uncombined hydroxyamine base, B. The solution conditions must also satisfy the solubility product relation for silver hydroxide⁷ at 20°, viz., $K_s = \{\text{Ag}^+\}\{\text{OH}^-\} = 1.413 \times 10^{-8}$, since the solutions were saturated with silver hydroxide. Hence it follows that $\beta_n = (fS)^2/K_s(c - nS)^n$.

⁵ Alner and Lansbury, *J.*, 1961, 619, 3169.

⁶ Alner, *J.*, 1962, 649, 3282.

⁷ Alner and Smeeth, *J.*, 1958, 852, 4207.

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For silver, the most probable value for n is 2 and the expression simplifies to $fS = K'(c - 2S)$, where $K' = \sqrt{(\beta_n K_s)}$. Graphs of fS against $(c - 2S)$ gave straight lines all passing through the origin, demonstrating that the measured values satisfied $n = 2$. Substitution of the experimental results enabled β_2 to be evaluated; its constancy is evidence for the correctness of writing the complex cation as AgB_2^+ . The mean values for $\log \beta_2$ for the silver complexes of the primary, secondary, and tertiary hydroxypropylamines were found to be 6.78, 5.71, and 4.27 respectively. The close agreement between the values of $\log \beta_2$ obtained from solubility data (Table 3) with those computed from $\log k_1 k_2$ obtained from titration data (Table 4) strongly supports the correctness of the assumptions made in the treatment of the solubility data, *viz.*, that in the presence of excesses of the hydroxyamines the silver ions were present wholly as their limiting complexes AgB_2^+ .

During the titrations of the 2-hydroxypropylammonium nitrate–silver nitrate mixtures with alkali, as long as some silver nitrate remained it could be assumed that complex formation occurred in a stepwise reversible manner,⁸ $\text{Ag}^+ + \text{B} \rightleftharpoons \text{AgB}^+$; $\text{AgB}^+ + \text{B} \rightleftharpoons \text{AgB}_2^+$, the respective formation stability constants being $K_1 = \{\text{AgB}^+\}/\{\text{Ag}^+\}\{\text{B}\}$; $K_2 = \{\text{AgB}_2^+\}/\{\text{AgB}^+\}\{\text{B}\}$; $\beta_2 = K_1 K_2 = \{\text{AgB}_2^+\}/\{\text{Ag}^+\}\{\text{B}\}^2$. Since all the ionic species concerned were univalent, activity coefficients cancel and the above expressions may be correctly rewritten in terms of concentrations instead of activities.

If T_{Ag} (mole/l.) represents the total silver concentration (free and combined), and $[\text{Ag}^+]$ the concentration (moles/l.) of free silver ions, we can write for the total silver content of the solution $T_{\text{Ag}} - [\text{Ag}^+] = [\text{AgB}^+] + [\text{AgB}_2^+]$. Substituting values for $[\text{AgB}^+]$ and $[\text{AgB}_2^+]$ given by the expressions for K_1 , K_2 , and β_2 , and eliminating k_2 , we obtain $K_1 = (T_{\text{Ag}} - [\text{Ag}^+])/[\text{Ag}^+][\text{B}] - \beta_2[\text{B}]$. Also for the condition of electroneutrality to apply during the additions of alkali we can write $[\text{BH}^+] + [\text{Na}^+] + [\text{H}^+] + [\text{Ag}^+] + [\text{AgB}^+] + [\text{AgB}_2^+] = [\text{NO}_3^-] + [\text{OH}^-]$ from which $[\text{BH}^+]$, the concentration of hydroxypropylammonium ions, can be computed, since $[\text{Ag}^+] + [\text{AgB}^+] + [\text{AgB}_2^+] = T_{\text{Ag}}$. Application of the relation $\text{pOH} = \text{p}K + \log [\text{BH}^+]/[\text{B}]$ and $\text{p}K_w = 14.17$,⁹ enables $[\text{B}]$, the concentration of free hydroxypropylamine, to be calculated. Values for $[\text{Ag}^+]$ were derived from the silver–silver iodide potential measurements, assumed to give $\{\text{Ag}^+\}$ values, which were converted into the corresponding $[\text{Ag}^+]$ values by means of calculated activity coefficients. T_{Ag} was known and also β_2 from the solubility data measurements. Substitution of these values into the expression for K_1 , gave values for the formation constants K_1 , of the respective AgB^+ species, and from these, those for K_2 corresponding to the respective AgB_2^+ species were derived from the relation $K_2 = \beta_2/K_1$. Mean values found for K_1 and K_2 respectively were, for the primary hydroxypropylamine $\log K_1 = 3.21\text{--}3.25$; $\log K_2 = 3.53\text{--}3.57$; for the secondary hydroxypropylamine $\log K_1 = 2.78\text{--}2.81$; $\log K_2 = 2.84\text{--}2.93$, and for the tertiary hydroxypropylamine $\log K_1 = 2.24\text{--}2.31$; $\log K_2 = 1.96\text{--}2.03$.

These new results show that the order of the strengths of the hydroxyamines as bases was mono- > di- > tri-hydroxypropylamine, and the order of the complexing abilities with silver ions at 20° was analogous, the silver complex of the monohydroxypropylamine being the most stable and that of the trihydroxypropylamine the least.

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- ⁸ Bjerrum, "Metal Ammine Formation in Aqueous Solution," Haase, Copenhagen, 1941.
- ⁹ Harned and Hamer, *J. Amer. Chem. Soc.*, 1933, 2194, 4496.