619. *The Stability Constants of the Silver Complexes of Some* NN-*Substituted 2-Hydroxyethylamines.*

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Stability constants for the silver complexes of the *NN*-dimethyl, *NN*-diethyl, and *NN*-di-isopropyl derivatives of 2-hydroxyethylamine have been obtained at 20° by electrode-potential and solubility measurements. In addition, the basic dissociation constants have been determined.

THERE being no published values for the dissociation constants of *NN*-dimethyl, *NN*-diethyl, and *NN*-di-isopropyl derivatives of 2-hydroxyethylamine, or for the stability of their silver complexes, we have remedied this deficiency.

EXPERIMENTAL

Dissociation Constants of the NN-*Substituted 2-Hydroxyethylamines at* 20°.—The compounds were purified by distillation under reduced pressure and characterised by measurement of refractive indices (Hilger–Chance Refractometer) and equivalent weight (see Table 1).

TABLE 1. *Properties of* NN-*substituted 2-hydroxyethylamines.*

	Dimethyl		Diethyl		Di-isopropyl	
	Found	Lit.	Found	Lit.	Found	Lit.
Purity (% as base)	98·7		99·7		99·9	
n_D^{20}	1·4296	1·4300 [1]	1·4412	—	1·4428	—
n_D^{25}	1·4276	—	1·4388	1·4400,[2] 1·4389 [3]	1·4408	—

Dissociation constants were determined by measuring the pH values set up during neutralisation of the base in the cell;

$$\text{Pt,H}_2\text{(1 atm.)} \,|\, \text{Base + HCl} \,|\, \text{Sat. KCl bridge} \,|\, \text{Sat. calomel}$$

Dilute solutions of the bases were titrated with hydrochloric acid at 20°, and from the measured e.m.f.s the pH values were calculated, where pH is defined by $\text{pH} = -\log\{\text{H}^+\}$ (braces denote activities). The calomel electrode potential was taken [4] as 0·2476 v at 20°. Titration data are

TABLE 2. *Dissociation constants at* 20° *of* NN-*substituted 2-hydroxyethylamines.*

Dimethyl			Diethyl			Di-isopropyl		
HCl (ml.)	pH (obs.)	p*K*	HCl (ml.)	pH (obs.)	p*K*	HCl (ml.)	pH (obs.)	p*K*
(i) 50 ml. *of* 0·0505M-*base titrated with* 0·497M-HCl			(i) 50 ml. *of* 0·0504M-*base titrated with* 0·497M-HCl			(i) 50 ml. *of* 0·487M-*base titrated with* 0·497M-HCl		
1·00	9·96	4·87	1·00	10·52	4·29	1·00	10·72	4·07
1·50	9·74	4·86	1·50	10·31	4·29	1·50	10·50	4·07
2·00	9·56	4·86	2·00	10·12	4·29	2·00	10·32	4·07
2·50	9·39	4·86	2·50	9·96	4·29	2·50	10·14	4·08
3·00	9·23	4·85	3·00	9·79	4·29	3·00	9·97	4·07
3·50	9·03	4·87	3·50	9·61	4·29	3·50	9·77	4·08
4·00	8·81	4·87	4·00	9·38	4·30	4·00	9·51	4·09
	Mean	4·86		Mean	4·29		Mean	4·08
(ii) 50 ml. *of* 0·0101M-*base titrated with* 0·105M-HCl			(ii) 50 ml. *of* 0·101M-*base titrated with* 0·105M-HCl			(ii) 50 ml. *of* 0·00974M-*base titrated with* 0·0998M-HCl		
1·00	9·88	4·88	1·00	10·40	4·33	1·00	10·60	4·11
1·50	9·66	4·87	1·50	10·20	4·31	1·50	10·41	4·10
2·00	9·48	4·86	2·00	10·03	4·31	2·00	10·24	4·09
2·50	9·30	4·86	2·50	9·85	4·31	2·50	10·07	4·10
3·00	9·11	4·87	3·00	9·67	4·31	3·00	9·87	4·10
3·50	8·90	4·87	3·50	9·46	4·31	3·50	9·68	4·11
	Mean	4·87		Mean	4·31		Mean	4·10

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[1] Knorr and Mathes, *Ber.*, 1901, **34**, 3482.
[2] Horne and Schriener, *J. Amer. Chem. Soc.*, 1932, **54**, 2928.
[3] Headlee, Collet, and Lazzell, *J. Amer. Chem. Soc.*, 1933, **55**, 1066.
[4] Bates, " Electrometric pH Determinations," Chapman & Hall, London, 1954, p. 201.

TABLE 3. *Solubility of silver hydroxide at 20° in* NN-*substituted 2-hydroxyethylamines.*

Dimethyl			Diethyl			Di-isopropyl		
Base (10^{-2}M)	AgOH (10^{-4}M)	log β_2	Base (10^{-2}M)	AgOH (10^{-4}M)	log β_2	Base (10^{-2}M)	AgOH (10^{-4}M)	log β_2
10·1	7·1	3·88	10·1	18·6	4·64	4·3	1·2	3·93
15·1	12·1	3·89	15·1	28·3	4·59	6·5	1·7	3·82
20·2	16·1	3·85	20·1	44·5	4·66	8·6	2·4	3·78
25·2	20·3	3·82	25·2	56·3	4·64		Mean	3·84
30·3	24·5	3·80	30·2	68·1	4·63			
35·3	29·0	3·79	35·2	80·1	4·62			
40·4	33·8	3·79	40·3	90·5	4·59			
	Mean	3·83		Mean	4·62			

TABLE 4. *Titration of* NN-*substituted 2-hydroxyethylamines* (50 ml. *portions*) *with silver nitrate at* 20° *in presence of* HNO$_3$ (10 ml.).

Dimethyl				Diethyl				Di-isopropyl			
AgNO$_3$ (ml.)	pH (obs.)	pAg (obs.)	log β_2	AgNO$_3$ (ml.)	pH (obs.)	pAg (obs.)	log β_2	AgNO$_3$ (ml.)	pH (obs.)	pAg (obs.)	log β_2
Base 0·0503M; HNO$_3$ 0·0508M; AgNO$_3$ 0·0100M				Base 0·0496M; HNO$_3$ 0·0508M; AgNO$_3$ 0·0100M				Base 0·0424M; HNO$_3$ 0·101M; AgNO$_3$ 0·0050M			
3·00	9·73	4·261	3·85	3·00	10·32	5·047	4·71	2·00	10·18	4·561	4·12
4·00	9·71	4·100	3·82	4·00	10·31	4·907	4·71	2·50	10·17	4·550	4·11
5·00	9·70	3·993	3·82	5·00	10·31	4·794	4·71	3·00	10·17	4·343	4·08
6·00	9·70	3·903	3·83	6·00	10·29	4·684	4·69	3·50	10·17	4·270	4·08
7·00	9·69	3·828	3·83	7·00	10·28	4·605	4·69	4·00	10·17	4·211	4·08
8·00	9·69	3·762	3·83	8·00	10·27	4·533	4·69	4·50	10·17	4·161	4·09
9·00	9·68	3·707	3·84	9·00	10·26	4·466	4·69	5·00	10·16	4·122	4·10
10·00	9·68	3·654	3·84	10·00	10·25	4·409	4·70			Mean	4·09
11·00	9·67	3·606	3·85	11·00	10·25	4·353	4·70				
12·00	9·67	3·561	3·85	12·00	10·25	4·308	4·70				
		Mean	3·84			Mean	4·70				
Base 0·201M; HNO$_3$ 0·102M; AgNO$_3$ 0·050M				Base 0·199M; HNO$_3$ 0·200M; AgNO$_3$ 0·050M				Base 0·0849M; HNO$_3$ 0·101M; AgNO$_3$ 0·0100M			
3·00	10·12	4·739	3·77	6·00	10·30	5·122	4·61	2·00	9·76	4·211	4·03
4·00	10·11	4·585	3·75	8·00	10·30	4·968	4·61	2·50	9·76	4·105	4·02
5·00	10·10	4·464	3·74	10·00	10·28	4·842	4·62	3·00	9·75	4·025	4·03
6·00	10·09	4·372	3·75	12·00	10·26	4·731	4·63	3·50	9·75	3·953	4·03
7·00	10·08	4·290	3·75	14·00	10·25	4·631	4·63	4·00	9·75	3·891	4·03
8·00	10·07	4·224	3·76	16·00	10·23	4·534	4·63	4·50	9·74	3·840	4·04
9·00	10·06	4·158	3·76	18·00	10·21	4·448	4·63	5·00	9·74	3·795	4·04
10·00	10·06	4·099	3·76	20·00	10·19	4·370	4·64			Mean	4·03
11·00	10·04	4·032	3·75			Mean	4·63				
12·00	10·03	3·982	3·75								
		Mean	3·75								

recorded in Table 2, where K refers to the equilibrium $\text{B} + \text{H}_2\text{O} \rightleftharpoons \text{BH}^+ + \text{OH}^-$, being defined by $K = \{\text{BH}^+\}\{\text{OH}^-\}/\{\text{B}\}$, where $\{\text{BH}^+\} = ([\text{HCl}] - [\text{H}^+] + [\text{OH}^-])f_{\pm}$, and $\{\text{B}\} = ([\text{Total base}] - [\text{HCl}] + [\text{H}^+] - [\text{OH}^-])\,f_{\pm}$(square brackets denote concentrations in mole/l.). The mean activity coefficients of the univalent ionic species in solution were calculated from the relation[5] $-\log f_{\pm} = 0{\cdot}505\sqrt{I}/(1 + \sqrt{I})$, where I = ionic strength. The activity coefficient of the un-ionised, uncombined base was taken as unity. Temperature control was maintained within ±0·1°. The basic dissociation constants of the *NN*-substituted 2-hydroxyethylamines recorded in the present investigation are new.

Solubility of Silver Hydroxide in Aqueous Solutions of the NN-*Substituted 2-Hydroxyethylamines at* 20°.—Silver hydroxide was prepared by precipitation from 0·1M-silver nitrate by addition of the stoicheiometric amount of 0·1M-sodium hydroxide (carbonate free). It was washed free from extraneous ions. An excess of the moist silver hydroxide was added to standard aqueous solutions of the bases and equilibrated at 20° under air-free conditions in black bottles. The solutions were filtered from silver hydroxide and analysed for their total silver contents by Volhard's thiocyanate method (see Table 3).

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[5] Guggenheim and Schindler, *J. Phys. Chem.*, 1934, **38**, 539.

Titration of Aqueous Solutions of NN-*Substituted 2-Hydroxyethylamines with Silver Nitrate.*—To prevent the immediate precipitation of silver hydroxide in this titration, known volumes of standard nitric acid were added to amine solutions of given concentration so as suitably to adjust their initial pH values. These solutions were then progressively titrated with standard solutions of silver nitrate at 20°. The titrations were carried out in a black beaker, since the complexes were light-sensitive.

A glass electrode was used to record the pH values, and silver iodide electrodes for the pAg values during titration of the base in the cell:

$$\text{Ag}\,|\,\text{AgI Glass elec.}\,|\,\text{Base} + \text{HNO}_3 + \text{AgNO}_3\,|\,\text{Sat. KNO}_3\text{ bridge}\,|\,\text{Sat. calomel}$$

Silver electrodes were unsuitable, as they did not function reversibly in these solutions. Silver iodide electrodes have been employed by other workers[7] to determine $\{Ag^+\}$. Nitrogen was bubbled through the whole to effect mixing and exclude carbon dioxide. The pH and pAg values of the silver iodide–calomel cell, together with the calculated stability constants, are recorded in Table 4.

DISCUSSION

The mechanism for complex formation between the *NN*-disubstituted 2-hydroxyethylamines and silver hydroxide has been represented[6] in terms of the formation of strong complex bases of the type AgB_nOH, where B is the ligand; thus $AgOH + nB \rightleftharpoons AgB_nOH = AgB_n^+ + OH_C^-$. The complex cation AgB_n^+ must be in equilibrium with silver ions $AgB_n^+ \rightleftharpoons Ag^+ + nB$, its stability constant being defined by $\beta_n = \{AgB_n^+\}/\{Ag^+\}\{B\}^n$. The uncombined base present in the complex solution will ionise ($B + H_2O \rightleftharpoons BH^+ + OH_B^-$); and the solution conditions must also satisfy the solubility product relation for silver hydroxide at 20°, *viz.*, $K_s = \{Ag^+\}\{OH^-\}_{B+C}$, since the solution was saturated with respect to silver hydroxide. The subscripts B and C denote the source of the hydroxyl ions. From the solubility product relation the activity of the silver ions in the equilibrium mixture may be calculated, provided $\{OH^-\}_{B+C}$ is known.

If s equiv./l. represents the concentration of silver found by analysis we can equate this to the concentration of the complex cation AgB_n^+, since under the experimental conditions (where large excesses of the base were present) dissociation of the complex cation could be assumed to be negligibly small. If c equiv./l. represents the initial concentration of base, then the concentration of the uncombined, un-ionised base in the equilibrium solution is $(c - ns - [OH^-]_B)$. The stability constant expression becomes:

$$\beta_n = \frac{sf^2[OH^-]_{B+C}}{K_s(c - ns - [OH^-]_B)}, \tag{1}$$

where f represents the mean activity coefficient, and the activity coefficient of the un-ionised base is taken as unity

The hydroxyl-ion concentration arising from the ionisation of the base was calculated from a knowledge of the respective dissociation constant, *i.e.*,

$$K = \{BH^+\}\{OH^-\}_{B+C}/\{B\} \tag{2}$$

Since $[BH^+] = [OH^-]_B = x$ (say), and $[AgB_n^+] = [OH^-]_C = s$, equation (2) becomes

$$K = \frac{xf^2(x + s)}{(c - ns - x)}. \tag{3}$$

A first approximation for the value of the activity coefficient was calculated on the assumption that the ionic strength was equal to the concentration of the complex base AgB_nOH. Substitution of this value into equation (3) enabled the quadratic in x to be solved, on the assumption that $n = 2$. Corrected values for the ionic strength $I = (s + x)$ and for the activity coefficient were evaluated, and successive approximations

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[6] Alner and Smeeth, *J.*, 1958, 852, 4207.

[7] Antikainen, Heitanen, and Sillén, *Acta Chem. Scand.*, 1960, **14**, 95.

were repeated until constant values for f and x were obtained. Substitution of these values into equation (1) permits calculation of the stability constant, it being assumed that $n = 2$. It was shown that n possessed this value by graphically representing $f\sqrt{s(s + x)}$ values against $(c - 2s - x)$ values: straight lines passing through the origin were obtained. Values for log β_2 calculated from equation (1) are recorded in Table 3. The value for K_s was taken [6] as $1{\cdot}413 \times 10^{-8}$ at 20°.

Throughout the titrations with silver nitrate, a large excess of base was present, justifying the assumption that the complexes were present in solution in their limiting forms, AgB_2^+. pAg measurments were taken as representing activities of the free silver ions in the equilibrium solutions.

If s equiv./l. represents the total silver concentration (as before), and $[Ag^+]$ the concentration of free silver ions calculated from the pAg values and mean activity coefficients, the concentration of the complex is $(s - [Ag^+])$ and that of the uncombined, un-ionised base is $\{c - 2(s - [Ag^+]) - [OH^-]\}$. Thus the stability constant expression becomes:

$$\beta_2 = \frac{(s - [Ag^+])}{\{c - 2(s - [Ag^+] - [OH^-]\}[Ag^+]}, \qquad (4)$$

since activity coefficients cancel. Table 4 records the calculated values of log β_2 for the complexes investigated, determined by direct substitution of the experimental results into equation (4).

For each complex, the values of the stability constant obtained by the two methods were in good agreement.

The dissociation constants demonstrate the order of basic strengths to be di-isopropyl > diethyl > dimethyl, but the stability values of the complexes do not show the same regular gradation.

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