[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

THE DISTRIBUTION OF AMMONIA BETWEEN TOLUENE AND AQUEOUS SILVER AMMONIA CHLORIDE AND HYDROXIDE, AND OF HYDROGEN CYANIDE BETWEEN BENZENE AND AQUEOUS HYDROGEN SILVER CYANIDE[1]

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Incidental to the experiments described in the previous paper,[2] we present the following values of the distribution ratio of ammonia between toluene and aqueous silver ammonia chloride and hydroxide at 25°. Column 1 gives the nature of the silver salt, Col. 2 its molality (mole per 1000 g. of water in vacuum), Col. 3 the molality of the total ammonia, Col. 4 the molality of the free NH_4OH based upon the formula $Ag(NH_3)_2^+$ for the complex ion (calculated molality of NH^+ deducted), and Col. 5 the mole fraction of NH_3 in the toluene layer.

TABLE I

DISTRIBUTION OF AMMONIA BETWEEN TOLUENE AND AQUEOUS SILVER AMMONIA CHLORIDE AND HYDROXIDE AT 25°

Silver salt	m $Ag(NH_3)_2$	m Σ base	$m(NH_4OH)$ free	$N(NH_3)$ in toluene	K_{mD}	log K_{mD}
None	.....	0.7347	0.7311	0.0004006	1825	3.261
None	.....	0.8394	0.8355	.0004629	1805	3.257
$Ag(NH_3)_2Cl$	0.0895	1.3039	1.1189	.0006085	1839	3.265
$Ag(NH_3)_2Cl$	.1628	2.1339	1.8007	.0009867	1825	3.261
$Ag(NH_3)_2Cl$	.2151	2.6400	2.2006	.0012054	1826	3.261
$Ag(NH_3)_2OH$	.07352	0.3155	0.09490	.0000520	1825	3.261
$Ag(NH_3)_2OH$	.07535	.3200	.09495	.0000592	1604	3.205
$Ag(NH_3)_2OH$	.07787	.3540	.1231	.0000787	1564	3.194
$Ag(NH_3)_2OH$	.05642[a]	.3392	.1699	.0000952	1784	3.251
$Ag(NH_3)_2OH$	.1525	.6519	.1945	.0001045	1861	3.270
$Ag(NH_3)_2OH$	.1582	.6767	.2021	.0001183	1708	3.232
$Ag(NH_3)_2OH$	.1623	.6950	.2082	.0001120	1859	3.269
$Ag(NH_3)_2OH$	.2033	.8673	.2574	.0001412	1822	3.261
$Ag(NH_3)_2OH$	.2225	.9518	.2841	.0001606	1769	3.248
$Ag(NH_3)_2OH$	.09731[a]	.5831	.2911	.0001660	1754	3.244
$Ag(NH_3)_2OH$	.2888	1.2304	.3642	.0001742	2091	3.320
$Ag(NH_3)_2OH$	.1363[a]	0.7921	.3833	.0002197	1744	3.242
$Ag(NH_3)_2OH$	.1783[a]	0.9691	.4341	.0002539	1710	3.233

[a] Not saturated with $Ag_2O(s)$.

If we assume the activity of the solvent as unity,[3] the constant of the reaction

$$NH_3(g) + H_2O \text{ (in } NH_4OH \text{ (aq.))} = NH_4OH \text{ (aq.)} \qquad (1)$$

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[1] Abridged paper; original received December 22, 1927.

[2] Randall and Halford, THIS JOURNAL, **52**, 178 (1930).

[3] See Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., New York, **1923, p. 558.**

is independent of the concentration of the ammonium hydroxide up to molal. At the small mole fractions of ammonia in the toluene layer, no great error can be made if we assume the activity of the NH_3 (in toluene) equal to its mole fraction. We therefore write

$$\text{NH}_3 \text{ (in toluene)} + \text{H}_2\text{O (in NH}_4\text{OH (aq.))} = \text{NH}_4\text{OH(aq.)};\ K_D = \gamma' m(\text{NH}_4\text{OH(aq.)})/\text{N}(\text{NH}_3 \text{ in toluene}) = \gamma' K_{mD} \quad (2)$$

where K_D, K_{mD} and γ' are the equilibrium constant, the ratio m/N and the combined activity coefficient of the aqueous ammonia and the water.

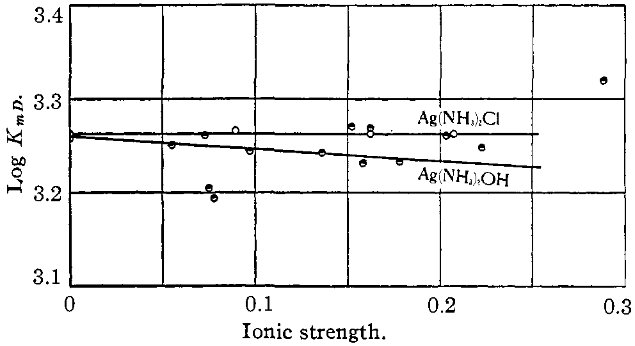

Fig. 1.—Distribution of ammonia between toluene and aqueous silver ammonia chloride or hydroxide.

The values of K_{mD} and of log K_{mD} are given in Cols. 6 and 7 of Table I. The values of log K_{mD} are plotted in Fig. 1 against the ionic strength, μ, which is taken as the molality of the silver salt. The values with silver ammonia hydroxide are less concordant than the others because of difficulty of determining the small amount of ammonia in the toluene layer.

From Equation 2

$$\log \gamma' = \log K_D - \log K_{mD} \quad (3)$$

Since the curves of Fig. 1 are approximately straight lines, the logarithm of the activity coefficient of the ammonia is approximately proportional[4] to the ionic strength.

In the case of ammonia in the presence of silver ammonia chloride, we may take log γ' equal to zero. In the case of the silver ammonia hydroxide, the value of $(\log \gamma')/\mu = 0.136$ is about that which would be predicted from that of the chloride and of other substances as given by Randall and Failey.[4]

The assumption that log γ' is a measure of the combined effect of salting out of the ammonia and the lowering of the activity of the water implies that ammonia in the toluene layer is not hydrated. Complete hydration in the toluene layer would eliminate the activity coefficient of the water from the constant of Equation 1. By combining the data of Hantzsch and

[4] **See Randall and Failey,** *Chem. Reviews*, **4,** 271, 285, 291 (1927).

Vogt[5] on the distribution of ammonia between air and toluene with data on the vapor pressure of aqueous ammonia, the distribution ratio K_{mD} has been calculated for the case in which hydration is impossible. The distribution ratio obtained in this manner is in agreement with our own as given in Table I, and justifies the assumption that the activity coefficient of the water is included in γ'.

If in calculating the distribution coefficient, we employ the mole fraction of ammonium hydroxide in the aqueous phase instead of the molality, we find a positive salting out effect. The calculation of an activity coefficient based on these quantities would not be significant since the activity coefficient is defined as the ratio of the activity to the molality rather than to the mole fraction. Since the activity of the ammonium hydroxide is determined by the mole fraction of ammonia in the toluene layer, it is, of course, independent of the units of concentration employed in the aqueous phase.

The values for the distribution of hydrogen cyanide between benzene and aqueous hydrogen silver cyanide are given in Table II. There is no trend in the values of the distribution coefficient and we may assume that at these low concentrations of the complex acid the activity coefficient of the aqueous hydrogen cyanide may be taken as unity.

TABLE II

DISTRIBUTION OF HYDROGEN CYANIDE BETWEEN BENZENE AND AQUEOUS HYDROGEN SILVER CYANIDE AT 25°

m HCN(aq.)	m $HAg(CN)_2$	N(HCN) in benzene	K_{mD}	m HCN(aq.)	m $HAg(CN)_2$	N(HCN) in benzene	K_{mD}
0.1016	0.00204	0.00228	44.6	0.3625	0.00331	0.00830	43.7
.1234	.00216	.00283	43.6	.1780	.00367	.00401	44.4
.1596	.00245	.00365	43.6	.4230	.00400	.00922	45.9
.2124	.00292	.00492	43.3	.2775	.00425	.00617	44.8
.1825	.00296	.00412	44.3	.4465	.00427	.01065	41.9
.2325	.00316	.00545	42.7	.4830	.00462	.01158	41.6

Summary

The activity coefficient of ammonia in aqueous silver ammonia chloride and of hydrogen cyanide in aqueous hydrogen silver cyanide is unity at 25°. The quotient $(\log \gamma')/\mu$ for ammonia in aqueous silver ammonia hydroxide is 0.136 at 25°.

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[5] Hantzsch and Vogt, *Z. physik. Chem.*, **38**, 701 (1901).