The size of Σ_E^2 for benzene, which is greater than the gas kinetic value of 21.9, is of interest principally because in the work of Bates and Taylor[20] this substance, when subjected to the action of excited mercury atoms, gave very little permanent gas. As was observed in that work the action of the mercury probably results for the most part in the removal of a hydrogen atom, which then recombines with other benzene molecules to form hydrobenzenes.

The author is indebted to the Research Laboratories of the General Motors Corporation for the pure hydrocarbons used in these measurements.

Summary

The quenching of mercury resonance radiation by nitric oxide, benzene, n-heptane, 2,2,3-trimethylbutane, 2-heptene and 3-heptene has been measured, and values of the effective cross sections of these molecules have been calculated. A general arrangement of molecules which correlates their effective cross sections and structure has been discussed.

[20] Bates and Taylor, THIS JOURNAL, 49, 2483 (1927).

PRINCETON, NEW JERSEY

SOLUBILITY OF THALLOUS CHLORIDE IN SOLUTIONS OF GLYCINE AND GLYCINE SALTS[1]

BY CRAWFORD F. FAILEY

The solubilities of salts in the presence of amino acids have been little investigated. Bjerrum[2] reported the solubility of dinitrotetramminecobaltinitrate $[Co(NH_3)_4(NO_2)_2]NO_3$ as about 8% greater in $N/10$ glycine than in water. Knowledge concerning the activity coefficients of strong electrolytes in the presence of amino acids would be valuable, however, in the determination of dissociation constants for amino acids themselves, it being necessary to calculate from the measured hydrogen-ion activity what concentration of free hydrogen or hydroxyl ion is present. Some assumption as to activity coefficients is therefore required. For example Birch and Harris[3] assumed γ_{H^+} and γ_{OH^-} to have the same value as in an ampholyte-free solution of identical salt concentration.

Experimental

The thallous chloride used in this investigation was a c. p. preparation recrystallized from distilled and from conductivity water. Theoretical nitrogen values were found for

[2] Bjerrum, Z. physik. Chem., 104, 147 (1923).
[3] Birch and Harris, Biochem. J., 24, 564 (1930).

the recrystallized glycine.   The nitric acid was distilled from silver nitrate, and sodium hydroxide from sodium was free from chloride and carbonate.

Approximately 10 g. of thallous chloride was shaken with the solvent to be used; the latter was then replaced by a fresh portion of about 200 ml. and the mixture rotated overnight in a water thermostat at a temperature of 25.00 ± 0.01°.   In weighed samples chlorides were determined gravimetrically as silver chloride, it having been shown that glycine did not interfere.   Each solubility recorded in Tables I and II is the average of at least two equilibrations, the duplicates usually agreeing within 0.1%.   In order to check the composition of the solid phase a sample was also removed from each of the most concentrated solvents and shown by analysis to consist of thallous chloride.

Discussion

Six determinations gave the solubility in water as 0.01617 ± 0.00002 mol per 1000 g. of water.   In Table I are shown the results for solvents

TABLE I

RESULTS FOR SOLVENTS WITH GLYCINE

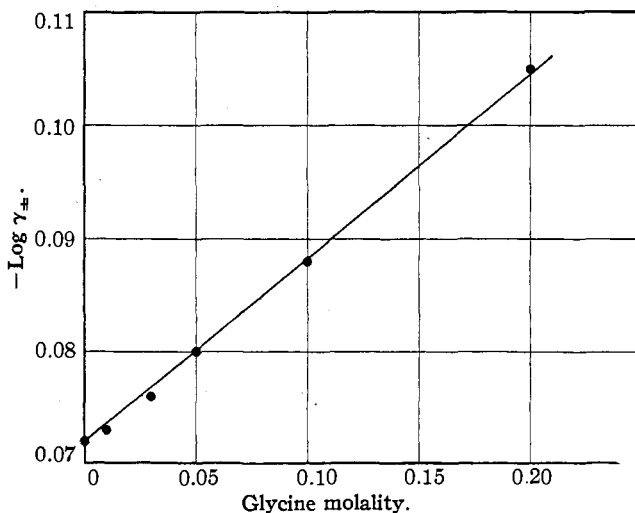| Glycine molality	Soly. $\times 10^5$	$-\log \gamma_\pm$	$\gamma_\pm$
0.000	1617	0.072	0.847
.010	1623	.073	.845
.030	1634	.076	.840
.050	1648	.080	.832
.100	1678	.088	.817
.200	1745	.105	.785

Fig. 1.

containing only glycine.   The first column indicates the solvent, the second thallous chloride solubility, the third values of $-\log \gamma_\pm$ calculated by means of the equation $-\log \gamma_\pm = \log 1/m_\pm{}^\circ \log 1/m_\pm$ on the assumption that log

$1/m_{\pm}{}^{\circ} = 1.8630.$[4]   In the fourth column are the activity coefficients. The compositions of the solutions are expressed as mols per 1000 g. of water *in vacuo.*

Figure 1, which is a plot of the above data with $-\log \gamma_{\pm}$ as ordinate and glycine molality as abscissa, shows that $-\log \gamma_{\pm}$ for thallous chloride is approximately a linear function of the glycine molality.

Solubilities in solutions of nitric acid and of sodium hydroxide are recorded in the first eight rows of Table II.   The last eight rows represent the same solvents except that one-tenth mole of glycine has been added per 1000 g. of water.   The first, second, third and fourth columns are as in Table I.   Column five is the square root of the ionic strength, the latter being taken as the sum of thallous chloride plus acid or base.

TABLE II

SOLUBILITIES IN OTHER SOLVENTS

Solvent	Soly. $\times 10^5$	$-\log \gamma_{\pm}$	$\gamma_{\pm}$	$\sqrt{\mu}$
$HNO_3\ M = 0.025$	1734	0.102	0.791	0.206
.050	1821	.123	.753	.261
.075	1887	.139	.726	.307
.100	1945	.152	.705	.346
$NaOH\ M = 0.025$	1777	.113	.771	.207
.050	1896	.141	.723	.263
.075	1995	.163	.687	.308
.100	2086	.182	.658	.346
Glycine $M/10 + HNO_3\ M = 0.025$	1794	.117	.764	.207
.050	1868	.134	.735	.262
.075	1925	.147	.713	.307
.100	1979	.159	.693	.346
Glycine $M/10 + NaOH\ M = 0.025$	1810	.121	.757	.208
.050	1902	.142	.721	.263
.075	1978	.159	.693	.308
.100	2051	.175	.668	.347

Figure 2 taken from Table II has as coördinates $-\log \gamma_{\pm}$ and $\sqrt{\mu}$. It may be seen that the points for any series of solvents, for example the series of nitric acid alone, or the series of nitric acid containing in addition one-tenth mole of glycine per 1000 g. of water, fall approximately on a straight line.   These lines are not parallel.   The activity coefficient of thallous chloride is depressed to a greater extent by tenth molal sodium hydroxide alone than by a similar solution to which glycine has been added.   This may be due to formation of un-ionized thallous hydroxide in the more alkaline solution, for a plot of the conductivity of thallous hydroxide[5] according to the method of Onsager[6] indicates a considerable amount of association.

[4] "International Critical Tables," Vol. VII, p. 319.

[5] "International Critical Tables," Vol. VI, p. 243.

[6] Onsager, *Physik. Z.,* **28,** 277 (1927).

Solutions of glycine as strong as tenth molal depress the activity co-efficient of thallous chloride by about 0.03. A change of this magnitude in γ_{H^+} or γ_{OH^-} would affect a pK calculation appreciably only in very acid or in very alkaline solutions, and since most titration curves are determined in ampholyte solutions more dilute than tenth molal, one may conclude that, at least for glycine, this factor is negligible.
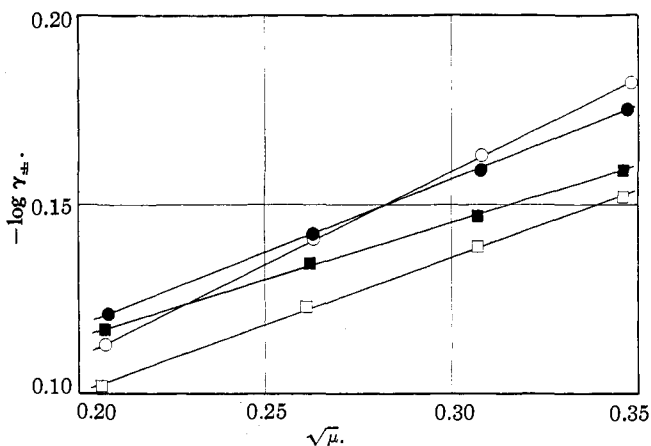

Fig. 2.—□, HNO₃; ○, NaOH; ■, glycine $M/10$ + HNO₃; ●, glycine $M/10$ + NaOH.

Summary

The solubility of thallous chloride has been measured at 25° in the presence of glycine, of nitric acid, of sodium hydroxide, and of glycine to which acid or base has been added. The negative logarithm of the activity coefficient of thallous chloride is approximately a linear function of the glycine molality. It is approximately a linear function of the square root of the ionic strength in the solutions containing electrolytes as well.

NEW YORK, N. Y.