

CCLXVI.—*The Constitution of Certain Salts and Acids in Solution as determined by Observations of Critical Solution Temperatures.*

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DURING the course of investigations on the behaviour of sulphur dioxide towards certain salts in acid solutions, the occurrence of complex formation with hydrogen chloride was frequently suspected. Thus, ferric chloride exhibited a far greater tendency than ferrous chloride to combine with hydrogen chloride (J., 1924, **125**, 1886), whilst cupric chloride only appeared to do so at acid concentrations above 7*N* (J., 1925, **127**, 505). Recent work by one of us (this vol., p. 1918) has indicated pronounced combination between hydrogen chloride and mercuric chloride [see also Abegg, "Handbuch der anorganischen Chemie," 1905, II, (2), 641], whilst the reaction between hydrogen chloride and sulphur dioxide or selenium dioxide is much less marked and probably only evident in high concentrations of acid.

It appeared that a study of the mutual miscibilities of liquids, as developed by Pfeiffer (*Z. physikal. Chem.*, 1892, **9**, 444), Timmermanns (*ibid.*, 1907, **58**, 128), and Patterson and his collaborators (*J. Physical Chem.*, 1925, **29**, 295; J., 1925, **127**, 624, 2544; 1926, 2787, 2791) might afford independent confirmation of such complex formation. We wished, however, to work at higher concentrations, if possible, and therefore it was necessary to test the applicability of the method in such cases, since recorded work has hitherto been restricted to the more dilute solutions.

The elevation of the critical solution temperature (*C.S.T.*) of a known mixture produced by each substance was determined separately and then the elevation due to the mixture of the substance with hydrogen chloride was observed. Any decrease from the theoretical elevation was assumed (when not accounted for by other means) to be due to complex formation. Two systems were employed: (1) water and phenol, and (2) water and *isobutyric acid*. The latter system, having a low *C.S.T.*, allows a considerable elevation before the boiling point is reached, and consequently a wide range of concentrations. It also has the advantage that the end-point is more easily determinable than is the case with phenol.

E X P E R I M E N T A L.

The determination of the *C.S.T.* was carried out in a test-tube fitted with a thermometer and glass stirrer. The apparatus was closed and provision was made for leading in a current of nitrogen

if required. The temperature was controlled by a water-bath and the *C.S.T.* in the case of *isobutyric acid* was observed by the appearance or disappearance of turbidity, as judged with a constant illuminant behind the tube, whilst for phenol, the apparent disappearance of the thermometer bulb was employed, as recommended by Patterson. Readings obtained in this way were reproducible to $\pm 0.02^\circ$.

The *isobutyric acid* with water gave a *C.S.T.* of 18.07° over a range of 26.8—28.6% of acid. Since this value is low compared with some of the values in the literature, a small amount of impurity is evidently present, but as this is probably *n-butyric acid* it is not likely to affect the results which follow.

In these results, *C* is the *molecular* concentration of salt per 1000 g. of total mixture (*i.e.*, water, organic solvent, and solute); *e* is the elevation of the *C.S.T.* in degrees; and *E* is the molecular elevation, *i.e.*, $E = e/C$. Table I gives the values of *e* for given concentrations of the separate constituents in the *isobutyric acid*-water system, as read from smoothed curves.

TABLE I.

<i>C</i>	0.02.	0.04.	0.06.	0.08.	0.10.	0.12.	0.16.	0.20.	0.24.
SeO ₂	0.52°	1.00°	1.48°	1.96°	2.40°	2.78°	3.56°	4.30°	5.08°
HCl	2.22	4.00	5.62	7.20	8.62	10.02	12.64	15.20	17.68
CuCl ₂	5.40	10.28	14.90	19.14	23.00	26.98	33.90	40.22	46.48
FeCl ₂	5.80	11.04	15.96	20.72	25.14	29.60	38.30	47.10	(55.90)
FeCl ₃	5.25	10.96	17.60	23.96	30.08	35.76	45.50	(52.90)	—
<i>C</i>	0.30.	0.40.	0.50.	0.60.	0.70.	0.80.	0.90.	1.00.	1.10.
SeO ₂	6.24°	8.24°	10.36°	12.80°	14.90°	17.22°	19.60°	21.96°	24.25°
HCl	21.18	26.20	31.50	36.30	40.80	45.10	49.04	52.78	56.20

If these values of *e* and *C* be plotted graphically, the curves, with the exception of that of selenium dioxide, deviate from straight lines, giving a curvature which is concave towards the concentration axis. This is in accordance with the decreased ionisation to be expected at the higher concentrations.

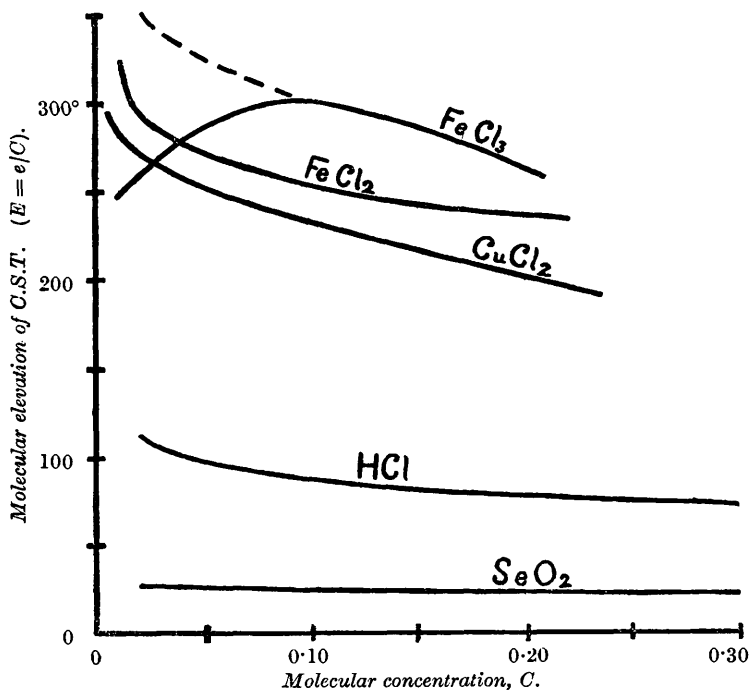
Ferric chloride gives a curvature near the origin which is slightly different from the remainder. These effects are much more clearly shown by plotting *E* against *C* (see Fig. 1).

For a normal substance such as hydrogen chloride, *E* increases with diminishing concentration as the result of ionisation. In the case of ferric chloride the increase ceases at $C = 0.09$ and *E* falls rapidly with further dilution. Since hydrolysis begins to be appreciable at about the same stage, it probably affords an explanation (Goodwin, *Z. physikal. Chem.*, 1896, **21**, 15).

An interesting series of curves is obtained by plotting $\log e$ against $\log C$. They approximate to parallel straight lines over a fair

range of concentration, the exception being that of ferric chloride, which crosses those of cupric and ferrous chlorides. The straight lines are in accordance with the equation $\log e = m \log C + b$, which gives the relation $e = AC^m$, proposed by Carrington, Hickson, and Patterson (J., 1925, 127, 2548). The numerical value of the constant in our case gives $m = 0.92$ for the system *isobutyric acid-water*, whilst the previous authors obtained $m = 0.84-0.87$ for phenol-water.

FIG. 1.



The regularity of the results obtained on plotting C against e and E , and $\log C$ against $\log e$, as well as of the results for the mixtures still to be described, suggests that the principles developed by Patterson in the more dilute solutions are also valid for the higher concentrations.

Mixtures of Salts with Hydrogen Chloride.

The possibility of complex formation was investigated, the concentration of the salt being kept approximately constant whilst that of the hydrogen chloride was varied over a fairly wide range. The theoretical elevation of the C.S.T., denoted by "Mean e calc.,"

is half the sum of the elevations for *double* the concentration of each constituent, as described by Patterson (J., 1925, 127, 626). This rule can be applied when the values of e for the salt and hydrogen chloride do not vary considerably, but for differences greater than 20° it is not so accurate.

TABLE II.

SeO ₂ + HCl.				CuCl ₂ + HCl.					
	<i>C.</i>	<i>e</i> calc.	Mean <i>e</i> calc.	<i>e</i> obs.		<i>C.</i>	<i>e</i> calc.	Mean <i>e</i> calc.	<i>e</i> obs.
SeO ₂	0.681	30.58°	} 39.70°	39.63°	CuCl ₂	0.103	41.20°	} 36.42°	36.75°
HCl	0.438	48.80			CuCl ₂	0.241	31.65		
SeO ₂	0.347	14.78	} 26.66	27.87	CuCl ₂	0.090	37.20	} 30.47	30.83
HCl	0.312	38.54			CuCl ₂	0.168	23.75		
FeCl ₂ + HCl.				SO ₂ + HCl.					
FeCl ₂	0.105	48.95	} 33.30	33.60	FeCl ₂	0.0716	35.20	} 36.65	36.29
HCl	0.116	17.65			FeCl ₂	0.307	38.10		
FeCl ₂	0.0703	34.60	} 31.20	31.08	FeCl ₂	0.0681	33.80	} 26.49	26.47
HCl	0.205	27.80			FeCl ₂	0.128	19.81		
						Mean <i>e</i> calc.			
SO ₂	(0.4)						<i>e</i> obs.		
HCl	0.550					33.0°	34.2°		

No consistent lowering of e is thus observed for the mixtures SeO₂ + HCl, FeCl₂ + HCl, and CuCl₂ + HCl. The actual concentration of sulphur dioxide was not determined, since the same stock solution was used in making up both the SO₂ and the SO₂ + HCl mixtures for the determination of e . Only a slight increase in e is observed, and in view of the experimental errors involved, this may be interpreted as evidence of no combination between sulphur dioxide and hydrogen chloride at these concentrations.

Ferric Chloride and Hydrogen Chloride.—It was evident that some kind of reaction was taking place. When the ferric chloride alone was in the mixture of *isobutyric* acid and water, it imparted a dark brown colour to the organic layer. On addition of hydrogen chloride, this became lighter, assuming a light yellow colour when the ratio HCl : FeCl₃ reached 6 : 1. The concentration of ferric chloride was kept at *ca.* 0.08 whilst that of hydrogen chloride was varied from 0.08 to 0.50, and in these circumstances depressions of e were observed as shown in Table III.

The consistent appreciable decrease in e is evidence of complex formation, and since the greatest percentage decrease occurs when HCl : FeCl₃ = 3 : 1, it appears probable that the compound FeCl₃.3HCl exists in solution.

The complex ferric compounds which are formed by carboxylic

TABLE III.

C.		e calc.		Mean			Decrease
FeCl ₃ .	HCl.	FeCl ₃ .	HCl.	e calc.	e obs.	Diff.	in e, %.
0.0766	0.0790	43.65°	13.00°	28.33°	29.36°	+1.03°	—
0.0824	0.1715	46.42	27.40	34.91	33.33	-1.58	4.6
0.0836	0.2446	46.80	31.42	39.11	36.63	-2.48	6.5
0.0844	0.2625	47.20	32.72	39.96	37.08	-2.88	7.5
0.0869	0.2770	48.20	34.10	41.15	37.98	-3.17	8.0
0.0815	0.3145	46.10	37.65	41.87	39.77	-2.10	5.1
0.0764	0.4370	44.00	48.10	46.05	43.51	-2.54	5.7

acids, such as acetic acid, might be expected to explain the anomalous behaviour of ferric chloride in *isobutyric acid* :

$3\text{FeCl}_3 + 6\text{CH}_3\cdot\text{CO}_2\text{H} + 2\text{H}_2\text{O} \rightleftharpoons [\text{Fe}_3(\text{OH})_2(\text{CH}_3\cdot\text{CO}_2)_6]\text{Cl} + 8\text{HCl}$
 (Weinland, "Complex-Verbindungen," 1919, pp. 345 *et seq.*). The brown coloration may then be satisfactorily attributed to the coloured complex, whilst the subsequent addition of hydrochloric acid leads to the repression of complex formation and a consequent fading of colour.

The occurrence of complex formation causes solubility of the ferric chloride in both liquids instead of in the water alone, and this would tend to decrease the *C.S.T.*, especially for higher concentrations of ferric chloride. Since, however, the abnormalities in *C.S.T.* are mainly observed at the lower concentrations of ferric chloride, and in the opposite sense, we consider that the extent of interaction between the ferric chloride and *isobutyric acid* must be relatively small.

For the remaining examples, the phenol-water system was found more convenient.

Mercuric Chloride and Hydrogen Chloride.—Mercuric chloride is soluble both in phenol and in *isobutyric acid*, but the former solvent was found to be more suitable to work with. The *C.S.T.* was depressed and *e* was negative (Table IV).

TABLE IV.

C	0.05	0.10	0.15	0.20	0.25
-e for HgCl ₂	1.72°	3.58°	5.58°	7.72°	9.85°
+e for HCl.....	3.58	6.50	9.02	11.38	13.60
C	0.30	0.35	0.40	0.50	0.60
-e for HgCl ₂	12.00°	14.10°	—	—	—
+e for HCl.....	15.80	17.50	19.18	22.20	(24.7)

The graph of $\log C$ against $\log e$ for mercuric chloride is a straight line and its slope indicates $m = 1.1$. This differs from the normal value, 0.87, for ordinary substances insoluble in phenol.

The concentration of mercuric chloride was kept nearly constant and that of hydrogen chloride varied; the results obtained are given in Table V, and afford an example of the *C.S.T.* being raised by a

TABLE V.

C_{HgCl_2} .	C_{HCl} .	Mean e calc.	e obs.	Increase.
0.248	0.108	-4.2°	- 3.5°	0.7°
0.243	0.168	-1.5	+ 0.1	1.6
0.245	0.250	+1.05	+ 4.79	3.74
0.249	0.278	+1.55	+ 6.81	5.26
0.244	0.456	+6.20	+15.20	9.0
0.244	0.479	+6.65	+15.84	9.2
0.226	0.595	+9.75	+21.66	11.9

mixture. It is raised to an extent greater than would be expected from the simple mixture, and the effect increases with relative increase in the ratio HCl/HgCl_2 . Since one of the constituents, mercuric chloride, is soluble in the phenol layer, it shows that a complex is being formed which is insoluble in phenol.

Cuprous Chloride and Hydrogen Chloride.—The value “Mean e calc.” = (25°) is an approximation and indicates a lower limit, since “ e calc.” has been estimated by analogy with the chlorides of univalent metals. If cuprous copper exerts a higher valency as in the double formula Cu_2Cl_2 a still higher value would result. In either case, the low value of e obs. is thus in accordance with complex formation.

(Phenol-water system.)

	C .	e calc.	Mean e calc.	e obs.
HCl	0.422	35°	(25°)	22.2°
CuCl	0.0836	(15)		

Summary.

The elevation of critical solution temperature has been employed in order to study complex formation in hydrogen chloride solutions.

The values of e for various salts and acids have been determined in the system *isobutyric acid*-water, and for mercuric chloride in the phenol-water system.

Values of e and E obtained for these salts are regular, except in the case of ferric chloride, in which hydrolysis probably occurs.

The constant m approximates to 0.92 in the equation $e = AC^m$ for *isobutyric acid*-water.

No complex formation has been found between hydrogen chloride and sulphur dioxide, selenium dioxide, or ferrous and cupric chlorides, but considerable complex formation occurs between hydrogen chloride and ferric, mercuric, or cuprous chloride in the concentrations used.

The concentrations are considerably higher than those used hitherto, but the principles are still applicable.