CCCLXIX.—*Miscibility Tests of Dilute Solutions of Chromic Chloride Hexahydrates.*

### By JOHN EDWARD HOWARD and WILLIAM HAMILTON PATTERSON.

IN the study of salt solutions by the change in the mutual miscibility temperature (M.M.T.) of two liquids, one of which acts as the salt solvent (water and phenol; Carrington, Hickson, and Patterson, J., 1925, **127**, 2544 : ethyl and methyl alcohols with paraffins; Howard and Patterson, preceding paper : water with butyric and *iso*butyric acids; Patterson, unpublished research), it was considered advantageous to deal separately with the chromic chloride hexahydrates.

The two isomerides considered are the violet salt, formulated by Werner and Gubser (*Ber.*, 1901, **34**, 1579) as hexa-aquochromic chloride, $[Cr(H_2O)_6]Cl_3$, and the green salt, dihydrated dichlorotetra-aquochromic chloride, $[Cr(H_2O)_4Cl_2]Cl,2H_2O$. These are hereafter referred to by their colours. The intermediate isomeride of this type, first prepared as a solid by Bjerrum (*Ber.*, 1906, **39**, 1597), was not used in making up solutions on account of its

instability. It appears probable, however, that it is present in solutions in equilibrium (compare Fig. 2) and that similar results may be deduced as in the case of the other isomerides.

Various preparations were used and it was shown that the violet solid could be kept in stoppered bottles for several months and still give the same results. Details of preparation and analysis will appear in a subsequent communication by Partington and Tweedy, whom we have to thank for the samples.

FIG. 1.
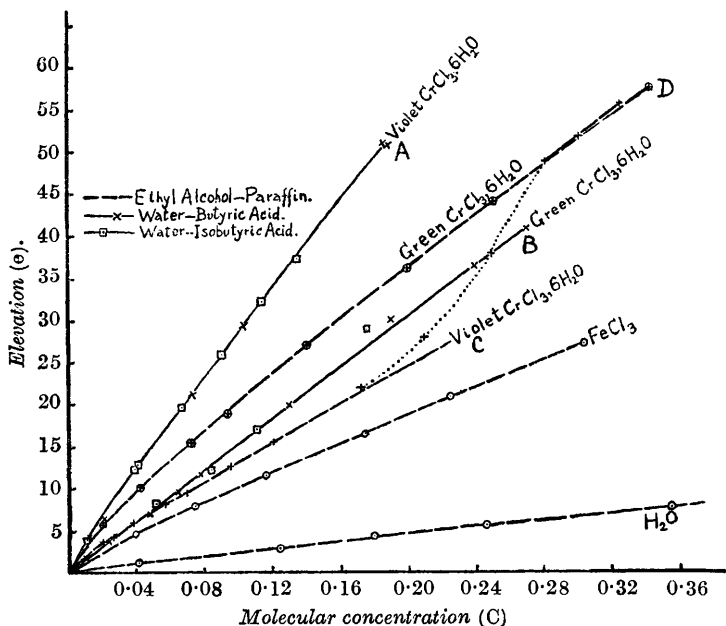
The liquid pairs used and their critical solution temperatures were :

(1) Water–butyric acid, 26% ; C.S.T. —1·2° to 1·05°.
(2) Water-*iso*butyric acid, 30% ; C.S.T. 17·50° to 17·95°.
(3) Water–phenol, 36·1% ; C.S.T. 66·0°.
(4) Ethyl alcohol–paraffin (b. p. 160—180°), equal parts by weight ; M.M.T. 20·0°.

[The range of C.S.T. in (1) and (2) represents a slow change which occurs in aqueous solutions of butyric and *iso*butyric acids during the course of several months, referred to elsewhere.] By use of these liquid pairs it is possible to study the state of salts in solution at temperatures above the respective C.S.T.'s.

In what follows, C is the concentration in g.-mols. of salt per 1000 g. of total aqueous or alcoholic solution (not total mixture), e is the rise in C.S.T. or M.M.T., at the time of the experiment, on dissolving the salt, and $E = e/C$. It has been shown in other cases that it is simpler to calculate concentrations on the salt solvent only; in the present case, in aqueous solution, the same rise is obtained working in butyric or *iso*butyric acid systems (over a temperature interval of 0—55°), indicating little change of hydration. The figures obtained for these systems, therefore, are classified together in the following table, where the values are interpolated for even concentrations, the actual observations being shown in the curves A and B in Fig. 1.

	Systems. Water–butyric acid. Water–*iso*butyric acid.				System. Ethyl alcohol–paraffin.			
	Violet.		Green.		Violet.		Green.	
C.	e.	E.	e.	E.	e.	E.	e.	E.
0·01	3·6°	354°	1·85°	186°	1·9°	—	3·0°	—
0·02	6·4	326	3·2	—	3·4	171	5·5	277
0·04	12·4	306	6·1	156	6·0	151	9·6	237
0·06	17·7	293	9·0	152	8·3	140	13·4	221
0·08	23·1	286	12·0	,,	10·6	133	16·8	210
0·10	28·3	282	15·1	,,	13·0	130	20·2	202
0·12	33·6	280	18·3	,,	15·3	128	23·5	196
0·14	38·8	277	21·5	,,	17·6	127	26·7	191
0·16	44·0	275	24·6	,,	20·1	127	30·1	187
0·18	49·3	273	27·2	,,	Changes to brown		33·2	184
0·20	54·5	—	30·2	,,	solution at 40°;		36·2	181
0·24	—	—	36·2	,,	intermediate		42·15	176
0·28	—	—	(42·2)	,,	values to 67°;		48·1	172
0·32	—	—	—		then values for green.		54·05	169

The results show that in aqueous solution, up to $C = 0·05$, the rise in C.S.T. due to the violet is nearly double that due to the green. Above this concentration, the ratio becomes progressively less. No reason is known why the former should produce exactly double the effect of the latter, as the value for the complex ion in each case is unknown. The method, however, gives results more in accord with the Werner theory than do either freezing-point or conductivity measurements. The following values were found for chromic nitrate, $Cr(NO_3)_3,9H_2O$ (from Kahlbaum; containing some iron), in *iso*butyric acid :

C.	C.S.T.	e.	E.
0·0138	21·0°	3·1°	225°
0·0505	28·4	10·5	208
0·1207	42·0	24·1	200
0·1692	50·35	32·45	192

Investigation of other salts (*e.g.*, of cadmium) shows that nitrates

do not form complexes and also that the effect of the nitrate radical is much less than that of the chloride. The curve for chromic nitrate lies between the violet and the green, being nearer the latter in the approximate ratio of 5 : 3; hence the ion $[Cr(H_2O)_6]^{\cdots}$ has in aqueous solution nearly the same effect as the $Cr^{\cdots}$ ion, whilst the ion $[CrCl_2(H_2O)_4]^{\cdot}$ has a less effect. These relations are, however, only qualitative (Duckett and Patterson, *J. Physical Chem.*, 1925, **29**, 295). To make them quantitative, the change of hydration with temperature and concentration would have to be taken into account and also the nature of the opposed ion. Under similar conditions of temperature, the values for E are $Cl = 43$, $NO_3 = 11$. At $C = 0.05$, E for violet $= 300$, for green $= 154$; replacing $3Cl$ by $3NO_3$ in the violet gives $E = 300 - 129 + 33 = 204$ (Found, for nitrate : 208); replacing Cl by NO_3 in the green gives $154 - 43 + 11 = 122$: hence the effects of $Cr^{\cdots}$ and $CrCl_2(H_2O)_4^{\cdot}$ are in the ratio $175 : 111$.

Change in Aqueous Solution.

The method is convenient for investigating rate of change, especially in dilute solutions. As the influence of temperature is very marked, in some cases it is necessary to measure time in minutes, and in others in months.

The results are summarised to supplement those of other workers, who generally used more concentrated solutions, however (*e.g.*, Olie, *Z. anorg. Chem.*, 1906, **51**, 29).

Violet.—Change very slow below 40°, slow below 50°.

$C = 0.067$: no change measurable at 40° in 120 mins.

$C = 0.073$: 10% at 17° in 3 days; 100% at 95° in 65 mins.

$C = 0.188$: 59% at 82° in 22 mins.; 69% at 82° in 57 mins.

(At the ordinary temperature the last had reverted to 16.6% after 4 months, with intermediate values.)

$C = 0.188$: 16.6% at 65° in 35 mins.; 26.8% at 65° in 76 mins.; 6.1% at 50° in 47 mins.

Green.—The change is quite appreciable, even at the ordinary temperature. The figures at higher temperatures in the table were obtained by extrapolating the curves shown in Fig. 2 to zero concentration. Equilibrium is practically attained in 2 hours at 40°, 3 hours at 35°, or 24—72 hours at 25°. The position of this equilibrium lies about half-way between the green and the violet up to $C = 0.17$ and is almost independent of temperature within this range. At higher concentrations and temperatures, it lies much nearer the green curve. At the ordinary temperature it reverts, during several months, towards the violet. The main results are shown graphically in Fig. 2.

The figures obtained for the system water–phenol, on dissolving the green salt, give $E = 271$—$204°$, over the temperature range 68—$79°$ and $C = 0·00845$—$0·065$. Evidently these values correspond to a mixture; also some reaction with the phenol must be allowed for.

A measurement with the violet in *iso*butyric acid gave $E = 227°$ for $C = 0·2587$. Change in hydrolysis must also be considered:

Fig. 2.

Green to violet.   Time in minutes.
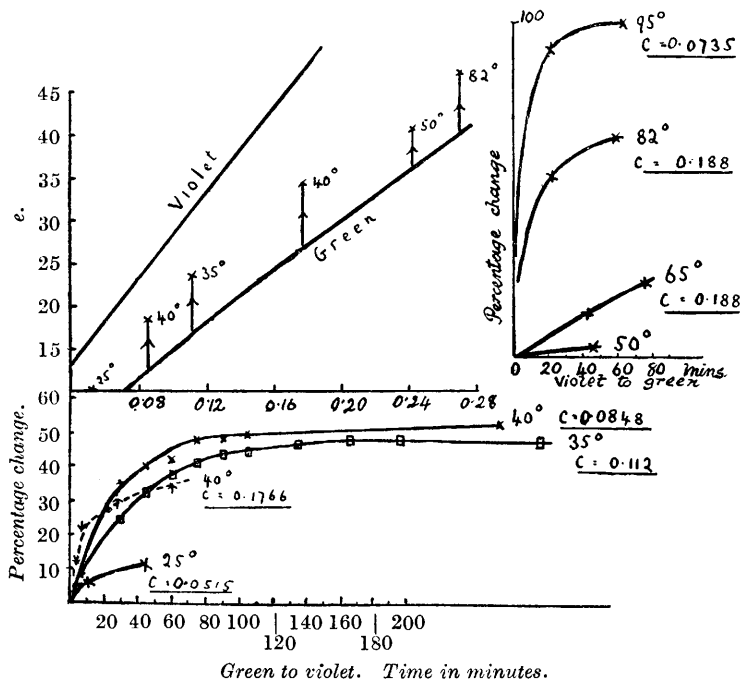
although this will not greatly alter the M.M.T., it has been shown to influence the velocity of change.

Solutions in Ethyl Alcohol.

The broken lines in Fig. 1 represent ethyl-alcoholic solutions. The order of salts in ethyl-alcoholic solution has been shown to be nearly the reverse of that in aqueous solution, *e.g.*, salts of tervalent metals have a smaller effect than salts of univalent metals.

The curve C (Fig. 1) for violet up to $e = 20°$ (or a temperature of $40°$) lies below that of the green. The dotted line represents a mixture (brown solution) up to $e = 48°$ (or $68°$), at which point the curve becomes identical with that of the green, D. It was not

5 c

possible to study the kinetics of change in this system.   The curve for ferric chloride is given for comparison, as it has been shown that this salt consists of the non-associated molecule $FeCl_3$ in ethyl alcohol, and it is believed that the curve for normal chromic chloride should be very near it.

The molecular influence of water on this system is shown by the bottom line, which has no curvature.   It is to be expected that the two molecules of water of hydration in the green isomeride would enter the alcohol and give the corresponding rise of M.M.T.   The difference between the two curves varies from 4 to 2 mols. of water. As in aqueous solution, the effect of the complexes is uncertain and it is not to be expected that the difference should be exactly that of 2 mols. of water.   The possibility of alcoholate formation also must not be overlooked.   The position of the violet curve shows how strongly the water is held in the co-ordinated complex.

The results both in aqueous and in alcoholic solution support the Werner theory and are at variance with the views of Britton (J., 1925, **127**, 2128), who postulates the existence in the green solution of basic aggregates essentially colloidal in nature.   Moreover, the effect of colloids on C.S.T. has been shown to be exceedingly small.

EAST LONDON COLLEGE,
      UNIVERSITY OF LONDON.