

The Exchange of Water between Aqueous Chromic Ion and Solvent

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Citation: *The Journal of Chemical Physics* **18**, 757 (1950); doi: 10.1063/1.1747745

View online: <http://dx.doi.org/10.1063/1.1747745>

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presumably as vanadate, was extracted from the insoluble titanium oxide by repeated washings with cold water. To remove any Ca and Sc activities which may have been extracted with the V^{48} , the solution was acidified with HCl, 10 mg of Ca and Sc were added and precipitated from 1M Na_2CO_3 . The supernatant containing the V^{48} was neutralized with 12N HCl and evaporated to dryness. The V activity was separated from most of the NaCl by extraction with approximately 5 ml of 12N HCl. The HCl solution containing the activity and milligram amounts of NaCl was evaporated to dryness and diluted with water to give an isotonic saline solution of carrier-free V^{48} which was used in biological tracer studies.

The V^{48} was identified by the assigned³ 16-day half-life and by the 0.7-Mev positron and 1.33-Mev gamma-ray which have been reported.¹ Chemical separations with added Ca, Sc, Ti, and V carriers further identified the activity as V^{48} .

We are grateful to the staff of the 60-inch cyclotron for bombardments and to Professor G. T. Seaborg for his interest and helpful suggestions.

* This document is based on work performed under the auspices of the AEC.

† Lieutenant Colonel, U. S. Army, now stationed at Walter Reed Hospital, Washington, D. C.

¹ H. Walke, *Phys. Rev.* **52**, 777 (1937).

² G. T. Seaborg and I. Perlman, *Rev. Mod. Phys.* **20**, 585 (1948).

³ W. C. Peacock and M. Deutsch, *Phys. Rev.* **69**, 306 (1946).

X-Ray Patterns of Soaps

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February 27, 1950

THE x-ray diffraction patterns of solid soaps have been examined by many investigators using either single crystals or samples which have been described as powders. The single crystal patterns are not different in kind from those of other organic substances except for the fact that one of the unit cell axes is very long compared to the other two axes. Probably the most important difference is the appearance of a series of "long spacings" in the small angle region. These diffraction maxima can be called the (001) reflections if we label the long crystal axis a_3 . The length of the long axis is related to the thickness of the micellar layer. This micellar layer consists of a central layer of metal ions, not necessarily in a single plane, and of two fatty acid ion layers with the acid ions extending outward on both sides from the metal ion layer. The hydrocarbon end groups form the outer surface of the micellar layer. The values obtained for the long spacing indicate that the chains are tipped rather than perpendicular to the median plane. Such micellar layers presumably form in solution, probably starting as ion pairs or triplets, and the solids consist of a stacking of such micellar layers. The forces leading to the coalescence of such layers are the weak van der Waals forces between hydrocarbon chain ends.

The more common type of diffraction diagram, referred to as a powder diagram, is notorious for its apparent variability. These patterns for a given sample sometimes change with time, they change if the sample is heated and then restored to its original temperature, and they depend on the method of preparing the soap. These diagrams show a series of (001) long spacings at small angles and a broad diffraction band, with no resolved *sharp* lines, in the region $2\theta \approx 20^\circ$ (using copper x-rays). This broad band frequently shows broad sub-structure suggesting that it is the superposition of two or more broad peaks. Sometimes it is resolved into two or more broad peaks. Only very rarely are there additional broad peaks at larger scattering angles. Frequently there is a series of small narrow maxima extending out to $2\theta \approx 40^\circ$.

It is possible to account for these diagrams in terms of a disordered structure in which the micellar layers are superimposed with stacking disorder, together with some physically reasonable assumptions concerning disorder within a micellar layer. The

proposal that stacking disorder is present is certainly reasonable since the forces which would lead to an orderly arrangement are only the weak van der Waals forces of hydrocarbon chain ends. The central ion layers cannot exert strong interactions from one micellar layer to another.

The consequences of this proposal are that the (001) spectra are unaffected by the stacking disorder and are no different in sharpness or intensity from those given by a well-ordered layer sequence. An examination of published data and of unpublished data, very kindly provided by Professor R. D. Vold of this laboratory, shows that almost without exception all of the regular series of spacings past $2\theta \approx 20^\circ$ can be identified as high orders of the (001) series. Previously these were called "side spacings."

On the other hand, when h and k are not both zero, then random stacking disorder causes the index 1 to become meaningless. The resulting (hkl) reflections become broad (hk) diffraction maxima of the two-dimensional lattice of the micellar layer. The present case differs from that discussed by Warren¹ for carbon black in that here the layers are many atoms thick. Elementary considerations concerning the Fourier transform from crystal space to reciprocal space shows that the (hk) maxima for thick distributions are narrower in scattering angle range than for thin layers. This is observed to be true for soaps as compared to carbon black, whose layers are presumed to be one atom thick.

Within a micellar layer the fatty acid ions must approximate a hexagonal array. This requires that there can be only three different (hk) pairs (and their negatives) which give diffraction maxima near $2\theta \approx 20^\circ$. These are the (10), (01), and ($\bar{1}\bar{1}$) maxima. The (11) maximum should occur at a value of $\sin\theta$ which is $\sqrt{3}$ times that of (10), and that for (20) should have a value of $\sin\theta$ twice that for (10). If the net is not exactly hexagonal the (10), (01), and ($\bar{1}\bar{1}$) maxima occur at different but nearly equal angles, and the 20° peak may resolve.

If we assume that in a micellar layer the fatty acid ions are randomly oriented about their long axes, it can readily be shown that the only strong (hk) maxima should be (10), (01), and ($\bar{1}\bar{1}$), i.e., those at $2\theta \approx 20^\circ$.

These considerations permit a consistent and physically reasonable unification of the discordant observations. It is apparent that the great list of different diffraction patterns, which have been identified with different polymorphic forms, merely represent different conditions of ordering, and that probably only the single crystal specimens represent phases in the thermodynamic sense. A more complete report is in preparation.

¹ B. E. Warren, *Phys. Rev.* **59**, 693 (1941).

The Exchange of Water between Aqueous Chromic Ion and Solvent*

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March 10, 1950

A PROBLEM of interest in the chemistry of aqueous solutions is that of determining the formulas of the species which result upon the interaction of cations and water. With cations of one extreme type, including probably those of low charge and large radius, the complexes may be very labile, and the configuration even in the first sphere of coordination may be so indefinite, that it would be impossible to assign definite formulas to them. For other cations, of appropriate properties, it can be expected that a definite configuration with respect to water in the first sphere of coordination is maintained, and for these, in principle at least, meaningful formulas can be assigned to the complex consisting of the cation and directly bound water.

An indirect method which has been used to establish the coordination number of a cation for water in aqueous solution is to determine the maximum coordination number with respect to other ligands, the assumption being made that the coordination

TABLE I. Exchange of $\text{Cr}_{\text{aq}}^{+++}$ with H_2O .

<i>N</i> expresses the mole fraction $\frac{\text{H}_2\text{O}^{18}}{\text{H}_2\text{O}^{18} + \text{H}_2\text{O}^{16}}$ in the samples distilled from the solutions. From these, values of <i>N</i> for zero and infinite time (<i>N</i> ₀ exp. and <i>N</i> _∞ exp. respectively) are obtained by extrapolation. <i>N</i> ₀ ⁶ , <i>N</i> ₀ ⁷ , and <i>N</i> ₀ ⁸ are the calculated values of the mole fraction in the liquid for initial holdback by each Cr^{+++} of 5, 6, and 7 molecules of H_2O respectively. <i>N</i> _∞ calc. is the mole fraction calculated for random mixing in the liquid.					
Experimental					
Time, hours	0.30	18.3	18.9	401.3	
<i>N</i>	8.422	8.169	8.169	7.518	
Calculated results					
<i>N</i> ₀ exp.	<i>N</i> ₀ ⁶	<i>N</i> ₀ ⁶	<i>N</i> ₀ ⁷	<i>N</i> _∞ exp.	<i>N</i> _∞ calc.
8.427	8.307	8.474	8.653	7.517	7.582
<i>N</i> ₀ exp.	<i>N</i> ₀ ⁶	<i>N</i> ₀ ⁷	<i>N</i> ₀ ⁸	<i>N</i> _∞ exp.	<i>N</i> _∞ calc.
<i>N</i> _∞ exp.	<i>N</i> _∞ calc.	<i>N</i> _∞ calc.	<i>N</i> _∞ exp.	<i>N</i> _∞ exp.	<i>N</i> _∞ calc.
1.1211	1.1177	1.1412	1.0056		1.0087

number will be the same for water.¹ Another indirect method is to carry out a variety of double decomposition reactions, analyzing the solid phases to learn whether a particular cation/water ratio recurs. This method involves the assumption that the configuration in the solid is retained in solution, and, unless the structure of the solid is known, an additional assumption about the disposition of the water molecules in the solid. A direct method of counting the positions occupied by water associated with a cation in water is based on studying the exchange of bound water with solvent water, using a tracer such as O^{18} for H_2O .² A condition for the success of this method is that the exchange be slow enough so as not to be completed by the time the first and succeeding samplings of the solvent are made. The fact that for some cations the rate of substitution of water by other ligands is measurably slow encouraged the hope that replacement of water by water would also prove slow enough in some cases to make the exchange method applicable. The present note reports some results which have been obtained with chromic ion,³ a cation which does fulfill the condition of slow exchange of bound water for solvent water.

The experiments were conducted by mixing a known amount of solution of known composition containing $\text{Cr}(\text{ClO}_4)_3$ and HClO_4 dissolved in ordinary water with a known amount of water enriched in O^{18} . Aliquots were taken at intervals, a portion of the water removed by distillation, and the isotopic composition determined by equilibrating the distillate with CO_2 , measuring the ratio $\text{O}^{18}/\text{O}^{16}$ in CO_2 by means of a mass spectrometer. The results obtained using a solution 1.47 molal in $\text{Cr}(\text{ClO}_4)_3$ and 0.13 molal in HClO_4 at 25° are presented in Table I.

The data of Table I show that a slow exchange of water takes place in the system. In other experiments, we have found that there is no initial holdback (within a time of sampling even as short as 2 minutes) by H^+ or ClO_4^- ; furthermore, that the exchange of H_2O with ClO_4^- or the glass containers is negligible under the conditions of these experiments. The exchange effects observed must therefore be attributed to Cr^{+++} . From the total change in *N* during the experiment, and the composition of the solution, the initial holdback per Cr^{+++} is calculated as 6.2 ± 0.2 (compare *N*₀ exp./*N*_∞ exp., *N*₀⁶/*N*_∞ calc., *N*₀⁷/*N*_∞ calc. in Table I). This value is based on the assumption that the mixing of H_2O^{18} and H_2O^{16} in the final solution is random. If allowance is made for the slight preference of the ions for H_2O^{18} over H_2O^{16} indicated by other results obtained in these studies, the holdback per Cr^{+++} is reduced by 0.1 to 0.2. The initial holdback per Cr^{+++} can also be obtained by comparing the values of *N*₀ exp. with the values of *N*₀ calculated from the composition for assumed values of the initial holdback. If the data are used in this way, allowance has to be made for the fractionation which takes place on the distillation of samples of water from the solution. *N*₀⁶/*N*₀ exp. is 1.0056, which is very nearly the ratio of *N*_{liq}/*N*_{vap} for a distillation under otherwise identical conditions using water. The second method leads to a value of 6.0 ± 0.2 as the initial holdback of H_2O for each chromic ion. If the initial holdback is interpreted as due to

water held in the first sphere of coordination, the experiments show the coordination number of Cr^{+++} for H_2O in water to be 6. Other experiments under similar conditions not reported in detail support this value.

The half-life for the exchange of H_2O between $\text{Cr}(\text{H}_2\text{O})_6^{+++}$ and water under the conditions of our experiments is ca. 40 hours. Further work on this exchange, and on the exchange of water with other hydrated cations, will be presented for publication later. A detailed account of experimental procedure, calculations, and further discussion is therefore deferred.

The authors wish to express their appreciation to Dr. Samuel Epstein for help in the analysis of samples, to Dr. Harold C. Urey for the use of his precise mass spectrometer, and to Dr. Lewis Friedman of the Brookhaven National Laboratories for making the mass-spectrometer analyses of preliminary samples.

* This work was supported in part by funds from the ONR under contract N6-ori-02026.

† AEC Predoctoral Fellow.

¹ N. Bjerrum (Zeits. f. anorg. chem. 118, 131 (1921)) has shown that the ions $\text{Cr}(\text{CNS})_6^{3-}$ can be formed in water solution. More recently, Hall and Eyring (Ph.D. Thesis "Isomers of chromic salts," 1948, University of Utah, Howard Tracy Hall) have used the reagent $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ to count coordination positions unoccupied by other complex groups.

² H. W. Crandall, J. Chem. Phys. 17, 602 (1949) using this method has shown that UO_2^{++} exists as a distinct species in water.

³ Concurrently with, and independently of the work reported here, experiments on the $\text{Cr}_{\text{aq}}^{+++}$ - H_2O exchange sponsored by F. A. Long have been in progress in the Department of Chemistry, Cornell University.

Raman Spectrum of Ethylene

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February 27, 1950

RECENTLY, a new assignment has been prepared for ethylene;^{1,2} the following comments may be of interest.

(a) The Raman line at 3075 cm^{-1} is attributed to be a breakdown of selection rules in the liquid state, causing the appearance of the B_{2u} fundamental. The infra-red gas frequency of the latter is 3105 cm^{-1} . No liquid-vapor shift as large as 30 cm^{-1} has been reported previously, even in polar molecules (excepting hydrogen bonding*).

(b) The force constants for the two alternative assignments for the B_{1g} and B_{2u} bending modes, using unnormalized coordinates and factoring out the stretching modes, are as follows:

	(1)	(2)
B_{1g}	1050	1236
B_{2u}	995	810.3 cm^{-1}
δ	0.0993	0.1417
d	0.0993	0.1417
		0.1376
		$0.0940 \times 10^6 \text{ dynes/cm}$

In (2), bending is more difficult in the B_{1g} than in the B_{2u} mode; no satisfactory physical explanation can be given for this, while repulsions between the non-bonded hydrogen atoms would account for the reverse order in (1). There is some evidence for an exaggerated repulsion of this type in tetra-chloro-ethylene.³

(c) The 995 cm^{-1} band seems too strong to be a Coriolis-perturbed fundamental of a normally inactive species; this is probably not true of the band centered at $\sim 810 \text{ cm}^{-1}$.

It is also of interest that in both the combinations $B_{1g}(1)B_{2u}(2)$, $B_{1g}(2)B_{2u}(1)$ the force constants are practically the same in both modes; this would be so if the $\text{H} \cdots \text{H}$ forces were negligible (though the $\text{H} \cdots \text{C}$ forces could still be important). The first combination leaves 995 cm^{-1} to be explained, the second, 810 cm^{-1} ; in view of (c) above, the first seems unlikely.

Finally, the Raman line at 1236 cm^{-1} can be accounted for by several triple combinations:

$$\begin{cases} 3019 - 949 - 825 = 1245(B_{1g}) \\ 1623 + 943 - 1342 = 1224(B_{2g}) \\ 3105 - 1050 - 825 = 1230(B_{3g}) \end{cases}$$

(using Herzberg's assignment). Since no separating Fermi reso-