it has been shown[6] that the percentage of B isomer drops in this same ratio in going from alcohol to chloroform.

TABLE II

		Solvent	$\bar{\nu}$, cm.$^{-1}$	$\bar{\nu}'$, cm.$^{-1}$	$\bar{\nu}'/\bar{\nu}$	ϵ'/ϵ
1	Fluorescein	Dil. alkali	20400	35100	1.72	0.144
2	Rhodamine B	Dil. alkali	18000	32300	1.80	.137
3	Crystal violet (A)	Ethanol	16940	32900	1.94	.258
4	Michler's hydrol	Gl. acetic acid	16670	33300	2.00	.165
5	Malachite green	Ethanol	16000	31700	1.98	.197
6	Methylene blue	Ethanol	15200	30700	2.02	.109
7	Capri blue	Ethanol	15100	32750	2.17	.153
8	Methylene blue (D^1H^{++})	$3M$ H_2SO_4	13500	29500	2.20	.110

This is a remarkable series in which ϵ'/ϵ is always large and $\bar{\nu}'/\bar{\nu}$ increases almost regularly with increasing wave length of the x band. This is just the trend that was predicted from our potential curve.

In the course of a number of investigations it has been shown how the absorption spectra of dyes are affected by acid, basic and amphoteric addition,[5] by isomerism[6,7] and by polymerization.[8] In three cases[6,9,10] the spectrum of the interesting isomer of the phosphorescent state has been studied. It has been shown how subsidiary vibrational bands may be recognized[8] and how y bands may be distinguished from x bands,[3,4] by studying, with polarized light, molecules that are oriented either by photochemical processes in a rigid solvent, or by excitation to the fluorescent state. In the present paper we have found the second order x bands of dyes and by the use of such data as are given in Tables I and II we can predict the approximate position of these x' bands in similar dyes. We believe that by these various means it is possible to classify all of the bands commonly found for dyes in the infrared, the visible, and the near ultraviolet. Thus it will be possible with greater security to attack the main problem of ascertaining the laws that relate color to chemical constitution.

Summary

Additional second order x bands have been sought and found in the absorption spectra of the cyanines and numerous dyes. In the latter group it has been necessary to make use of an extended potential diagram for electronic oscillations. In this group, the diagram leads to the conclusion that the ratio of the second order frequency to the first order frequency should increase as the first order frequency diminishes. This has been found to be true experimentally.

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[6] Lewis, Magel and Lipkin, THIS JOURNAL, **64**, 1774 (1942).

[7] Lewis, Magel and Lipkin, *ibid.*, **62**, 2973 (1940).

[8] Lewis, Goldschmid, Magel and Bigeleisen, *ibid.*, **65**, 1150 (1943).

[9] Lewis, Lipkin and Magel, *ibid.*, **63**, 3005 (1941).

[10] Lewis and Lipkin, *ibid.*, **64**, 2801 (1942).

[CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY AND PHYSICS, ILLINOIS INSTITUTE OF TECHNOLOGY]

Raman Spectra of Solutions of Silver Perchlorate in Toluene and in Water

BY M. J. MURRAY AND FORREST F. CLEVELAND

In a previous investigation[1] the Raman spectrum of a saturated solution of benzene in concentrated aqueous silver perchlorate showed that the vibrations of benzene most affected were those involving the carbon–carbon bonds. This was interpreted as indicating a coördination of the silver ion with the aromatic nucleus, in agreement with the ideas of Winstein and Lucas.[2] The behavior of toluene could not be tested in the same manner because this hydrocarbon has only slight solubility in the aqueous perchlorate. However, toluene, in contrast to benzene, is a remarkably potent solvent for anhydrous silver perchlorate even at room temperature. The saturated solution at 25° contains 50.3% of this salt.[3] It was hoped that the Raman spectrum of this solution would give an opportunity for checking independently the relation of the aromatic nucleus to the silver perchlorate without the disturbing influence of water.

For comparison with the spectrum of the non-aqueous solution, spectra of aqueous solutions of silver perchlorate and of mercuric perchlorate were also obtained.

Experimental

Toluene (purified by repeated extraction with concentrated sulfuric acid and by distillation) was saturated with silver perchlorate which had been prepared according to the method of Hill.[4] Turbidity in the solution was very effectively removed by centrifuging. Four-hour excitation by Hg 4358 Å. yielded a number of Raman lines without producing excessive continuum on the spectrogram.

An almost saturated aqueous solution of mercuric perchlorate was prepared by dissolving mercuric oxide in 70% perchloric acid. After adding a little water and a slight excess of perchloric acid the solution was filtered repeatedly through a sintered glass funnel. Spectrograms obtained for this solution were remarkably free of background.

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[1] Taufen, Murray and Cleveland, THIS JOURNAL, **63**, 3500 (1941).

[2] Winstein and Lucas, *ibid.*, **60**, 836 (1938).

[3] Hill and Miller, *ibid.*, **47**, 2702 (1925).

[4] Hill, *ibid.*, **43**, 254 (1921).

Discussion of Results

The data obtained in the present work are summarized in Table I. The spectrum of the toluene solution of silver perchlorate is seen to be almost a superposition of the spectra of pure toluene and of silver perchlorate in water with the following notable exceptions:

TABLE I

RAMAN SPECTRA OF TOLUENE AND OF SOLUTIONS OF SILVER PERCHLORATE IN TOLUENE AND IN WATER

Toluene[a]		Saturated solution of silver perchlorate in toluene		Concentrated aqueous silver perchlorate	
Δν cm.⁻¹	I	Δν cm.⁻¹	I	Δν cm.⁻¹	I
		167	3b		
219	5b	233	3b		
340	1	339	1		
		461	1b	459	3
522	7	520	4		
621	4	618	4[b]	625	4
788	9	785	8		
		916	7	929	10[c]
1006	10	1000	10		
1031	6	1028	3		
				1106	1vvb
1156	2	1158	2		
1181	1	1181	1		
1210	8	1210	5		
1381	3	1382	3		
1586	2	1574	2		
1606	6	1596	5		
2854	1	2854	1		
2872	1	2874	1		
2918	7	2920	6		
3032	4	3032	3		
3058	10b	3058	10b		

[a] One hour exposure. Longer exposures would have brought out weaker lines that had no counterpart in the observed spectrum of the toluene in the solution. [b] Intensity enhanced by coincidence of perchlorate and toluene lines. [c] This frequency has the same value in 20% solution.

1. The appearance of a prominent band at 167 cm.$^{-1}$ which has no distinct counterpart in the spectrum of silver perchlorate dissolved in water.
2. The shift of the 219 cm.$^{-1}$ band of toluene to 233 cm.$^{-1}$ in the solution.
3. A shift of the symmetrical vibration of the perchlorate from 929 cm.$^{-1}$ in water solution to 916 cm.$^{-1}$ in toluene.
4. The shift of the 1586–1606 cm.$^{-1}$ doublet of toluene to 1574–1596 cm.$^{-1}$ in the solution.

The 167 cm.$^{-1}$ band which appears so plainly on the spectrograms of the silver perchlorate in toluene has not been reported by other observers for aqueous solutions of monovalent metal perchlorates,[5] nor for various perchlorates in alcohols, acetone, ether or ethyl acetate,[6] nor for the crystalline perchlorates thus far examined.[7] Its presence on the spectrograms of the aqueous silver salt in the present investigation is extremely doubtful.

The presence of a line near 167 cm.$^{-1}$, recently reported by Manzoni-Ansidei,[8] for aqueous solutions of divalent metal perchlorates was verified in the present work.

The lines at 459, 625, 929 and 1106 cm.$^{-1}$ represent the Raman-active vibrations of the perchlorate group with T_d symmetry. No other fundamentals would be expected in the aqueous silver perchlorate nor in other ionized perchlorates. In this case the 167 cm.$^{-1}$ band could be accounted for as a difference tone ($625 - 459 = 166$). However, since the existence of this band in aqueous silver perchlorate (ionized) is doubtful even on a spectrogram in which the other bands of the perchlorate group are strong, it seems that this explanation can hardly be correct.

There is a possibility, inasmuch as a solid compound of toluene with silver perchlorate has been isolated,[3] that a bond between the molecules could be the source of a frequency in this region. Since, however, a band is present at the same position in the spectrum of aqueous mercuric perchlorate, this seems also to be ruled out.

It appears most likely that the band near 167 cm.$^{-1}$ arises when a heavy atom is attached covalently to the perchlorate group. In the aqueous solutions of divalent metal perchlorates, incomplete dissociation in the second stage of ionization is indicated. If the vibration in question is of the linear type for both silver and mercuric perchlorate, it is strange that it should appear with the same frequency for both compounds, since Raman shifts are very sharply dependent on the mass of the vibrating atoms. Furthermore, it is not clear why attaching heavy atoms to the perchlorate group should not affect the inner vibrations of this group to a greater extent than is observed.

The highest value, approximately 950 cm.$^{-1}$, for the totally symmetrical frequency of the perchlorate group is found in the spectra of various solid perchlorates. The frequency drops to 930 cm.$^{-1}$ for solutions of perchlorates in water, alcohols and acetone.[6] In toluene the same vibration is found in the present work to have a value of 916 cm.$^{-1}$. This is the lowest frequency for this vibration that appears to have been reported for any perchlorate and indicates that toluene has a definite effect on this group unless the solid silver perchlorate itself has an unexpectedly low value.

Although the nuclear carbon–carbon frequencies in toluene are affected by the presence of silver perchlorate, coördination of the silver to the aromatic ring seems to play a somewhat less important role than it did in the benzene–aqueous silver perchlorate solution where the shift in frequency

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(5) Magat, "Tables annuelles des constantes et données numériques," Hermann et Cie., Paris, 1937, Vol. XII, Sec. 26, p. 24.

(6) Goubeau, *Z. physik. Chem.*, **B36**, 45 (1937).

(7) Krishnamurti, *Indian J. Phys.*, **5**, 633 (1930).

(8) Manzoni-Ansidei, *Atti accad. Italia, Rend. classe sci. fis., mat. nat.*, [7] 1, 459 (1940).

was somewhat greater and where it was the only major change observed.

Summary

The Raman spectrum of a concentrated solution of silver perchlorate in toluene shows a band at 167 cm.$^{-1}$ which has no distinct counterpart in the spectrum of aqueous solutions of the same salt. Concentrated aqueous mercuric perchlorate also shows a band at this same position. It is suggested that this band may arise because of covalency between the metal atom and the perchlorate group.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF NEW YORK UNIVERSITY]

A Study of Bredig Platinum Sols

BY JOSEPH MINDEL AND CECIL V. KING

With the exception of the early work of Bredig,[1] Svedberg[2] and Benedicks,[3] studies of Bredig sols have emphasized composition and properties rather than mechanism of formation. Furthermore, the early investigators minimized the specific chemical reactions of the metals involved and correlated such physical properties as heats of fusion and heat conductivities of the metals, the characteristics of the electrical circuit, etc., with the distribution of particle size and the effectiveness of the arc in dispersing the metal.

The present work is a study of some of the processes involved in the formation of Bredig platinum sols. It is well known that stable platinum sols can be prepared by passing an arc under conductivity water. During arcing, the conductivity of the liquid increases.[4] The colloidal particles themselves carry only a small fraction of the current. Pennycuick[5] showed that the conductivity was due to the presence of hexahydroxyplatinic acid. He postulated,[6] on the basis of conductimetric titrations, that the colloidal micelle consisted of a platinum core, whose surface was covered with platinic oxide and hexahydroxyplatinic acid, while the intermicellar fluid was a solution of the acid. One of us[7] showed by direct analysis that the colloidal particles were not pure platinum. Pennycuick,[8] on the basis of a thorough analytical investigation, has proposed a formula for the micelle: 3.9 Pt, 1.16 PtO_2, 1.0 $H_2Pt(OH)_6$.

Experimental

The first phase of the present investigation was a study of the variation of the composition of the sol particles with changes in the nature of the dispersion medium and of the gas atmosphere.

The sols were prepared by arcing between platinum wires 2 mm. in diameter, using a source of direct current of 220 volts and 4 amperes. Water, hydrochloric acid (0.0001–0.0007 *N*) and nitric acid (0.0001–0.0004 *N*) were used as dispersion media, and air, oxygen and nitrogen as stirring gases. The arcing vessel was immersed in an ice-bath.

The sols were evaporated whole or coagulated by freezing to provide the dry residue for analysis. The evaporation was carried out at 50–60° and atmospheric pressure in tared beakers; freezing was accomplished by an ice–salt mixture and after thawing the coagulum was transferred to tared beakers and dried at 50–60°. The analysis was carried out in the beakers, platinum being determined as potassium chloroplatinate. Test analyses made on weighed samples of pure platinum agreed with the taken weights to within 1%.

Sols were allowed to stand for twenty-four hours before samples were taken for analysis. The coarse sludge that settled out in that time was separated and its platinum content determined.

The minimal concentrations of potassium chloride that coagulated the sols in twenty-four hours were determined to serve as rough estimates of stability. No attempt was made to study in detail the action of electrolytes.

Table I summarizes the results, the type of sol being denoted by the gas used for stirring and by the dispersion medium.

In any one series of analyses, the scattering of experimental values was greater than the systematic error of the method of determination, indicating a considerable degree of variation in the composition of each type of sol. It is evident that, despite the variation in the oxidative capacity of the gaseous atmosphere and of the dispersion medium in which the sols were prepared, the range of platinum content is relatively small.[9]

TABLE I

COMPOSITION AND STABILITY OF PLATINUM SOLS AS A FUNCTION OF GAS ATMOSPHERE AND DISPERSION MEDIUM

Type of sol	Per cent. of platinum in sol particles	Per cent. of platinum in sludge	Coagulation concn. of KCl (*M*)
Air–water	89.9 ± 2.4[10]	98.6 ± 0.6[10]	0.0054–0.0056
Oxygen–water	91.9 ± 2.6	98.8 ± 0.4	0.0034–0.0038
Nitrogen–water	89.5 ± 3.5	98.9 ± 0.9	0.0038–0.0042
Air–HCl	87.6 ± 3.0	98.5 ± 0.8	
Air–HNO_3	86.7 ± 6.5	97.1 ± 1.2	

In properties, too, the sols are similar. All are black, contain negatively charged particles, are stable for years

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[1] G. Bredig, *Z. angew. Chem.*, **11**, 951 (1898).

[2] T. Svedberg, "The Formation of Colloids" (Churchill, London, (1921)). This book contains references to previous papers.

[3] C. Benedicks, (a) *Kolloid-Beihefte*, **4**, 229 (1913); (b) *Kolloid-Z.*, **11**, 263 (1912).

[4] H. T. Beans and H. E. Eastlack, THIS JOURNAL, **37**, 2667 (1915).

[5] S. W. Pennycuick, (a) *J. Chem. Soc.*, 2108 (1928); (b) 2600 (1927).

[6] S. W. Pennycuick, (a) *Kolloid-Z.*, **49**, 407 (1929); (b) *J. Chem. Soc.*, 618 (1929).

[7] C. V. King, THIS JOURNAL, **60**, 144 (1938).

[8] S. W. Pennycuick. *ibid.*, **61**, 2234 (1939).

[9] The analysis of a few sols made by arcing in water in an atmosphere of hydrogen showed the particles to be 98.7 ± 0.9% platinum. These hydrogen–water sols were not noticeably less stable than the others. The nature of these sols is considered in the Discussion.

[10] Pennycuick's formula for the colloidal micelle corresponds to 89.3% platinum. He also found[8] that the sludge was practically pure platinum.