to correlate closely with ligand polarizability, as well as with the apparent magnitudes of the $h^+(2,q)$ crystal field components. This can be interpreted as due to intensity "borrowing" by the $^7F_0 \leftarrow {}^5D_0$ transition from the $^7F_2 \leftarrow {}^5D_0$ transition via crystal field induced mixings between the $^7F_0$ and $^7F_2$ (and $^5D_0$ and $^5D_2$) multiplet states. To first order, such mixings would arise from the $h^+(2,q)$ components of the crystal field potential.

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Raman Spectroscopic and Spectrophotometric Study of the System $K_2S_2O_7$–$KHSO_4$ in the Temperature Range 200–450 °C

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A series of Raman and near-infrared absorption spectra of molten $K_2S_2O_7$–$KHSO_4$ mixtures was obtained at 430 °C in the mole fraction range $X_{K_2S_2O_7} = 1.0000$–0.1000 and under the equilibrium vapor pressure of water. For molten $KHSO_4$, series of Raman and near-infrared absorption spectra were recorded in the temperature range 200–450 °C. The spectra could best be explained by the presence of the three species involved in the temperature-sensitive equilibrium $2HSO_4^- \rightleftharpoons S_2O_7^{2-} + H_2O$. The structure of $S_2O_7^{2-}$ in the melts was found to be most probably C_{2v} while HSO_4^- presumably has C_s symmetry. No intermediate compound of the three main species was found. Hydrogen bonding between the species seems, however, to be characteristic of the melts. This accounts also for the previously observed low vapor pressure of water. The infrared spectra of $K_2S_2O_7$ in KBr at 25 °C were measured; the spectra agreed well with results obtained by others.

Introduction

Previously[1] we have examined the complex formation of vanadium(V) in pyrosulfate melts as the first step in our attempts to explore the chemistry of melt systems that are idealized examples of the catalyst used for sulfuric acid production. The present investigation is only concerned with the solvent systems based on molten $K_2S_2O_7$–$KHSO_4$ mixtures. The densities of this molten salt system in the whole composition range have been measured previously.[2] The vapor pressures and the phase diagram have been examined[3] (a eutectic was found at 10 mol % $K_2S_2O_7$ with a melting point of 203.5 °C). There seems to be no intermediate compound formed in the system. The remarkable variation in the published melting point for $K_2S_2O_7$ (213–440 °C)[4,5] indicates that the hygroscopic $K_2S_2O_7$ used is in fact partly hydrolyzed to $KHSO_4$. Therefore many investigations have been made on undefined mixtures of the two components. The Raman spectrum of pure molten $K_2S_2O_7$ has as far as we know not been published before. However, Raman bands observed[6] for molten $KHSO_4$ at 300–700 °C were ascribed to $S_2O_7^{2-}$ having C_2 symmetry. The symmetry of $S_2O_7^{2-}$ in the solid state in $K_2S_2O_7$ was found to be C_{2v} on the basis of X-ray data[7] and Raman and IR measurements.[8] The autodissociation reaction $S_2O_7^{2-} \rightleftharpoons SO_4^{2-} + SO_3$ (or perhaps better as $2S_2O_7^{2-} \rightleftharpoons SO_4^{2-} + S_3O_{10}^{2-}$) is up to ca. 500 °C shifted far to the left[9,10] and therefore need not be taken into consideration in connection with the present investigation.

Molten hydrogen sulfates are in many respects different from most ionic salts presumably due to hydrogen bonding. Viscosity and conductance measurements[11] show a high degree of structuralization of the melt, and there is a great tendency to glass formation[12,13] with preservation of the structure in the melt. The published melting point of $KHSO_4$ varies between 207 and 212 °C. This is a much smaller range than the variation mentioned above for the melting point of $K_2S_2O_7$, indicating that commercial $KHSO_4$ probably has a more uniform composition than commercial $K_2S_2O_7$. A significant problem in working with molten bisulfates is the thermal instability of the melt. Above 300 °C an appreciable amount of water is lost possibly due to the decomposition reaction[6]

$$2HSO_4^- \rightleftharpoons H_2O + S_2O_7^{2-} \qquad (1)$$

and above 500 °C SO_3 is lost due to decomposition[6]

$$S_2O_7^{2-} \rightleftharpoons SO_3 + SO_4^{2-} \qquad (2)$$

Therefore much previous work performed above 300 °C in open cells is probably affected by decomposition.[14] The decomposition up to 500 °C and loss of water can be prevented by applying a fixed vapor pressure of water above the melt.[13,15] In this way the value for the ionic product $[H_2SO_4][SO_4^{2-}]$ related to the self-dissociation reaction

$$2HSO_4^- \rightleftharpoons H_2SO_4 + SO_4^{2-} \qquad (3)$$

in molten $KHSO_4$ at 220 °C and $P_{H_2O} = 0.041$ atm was estimated[13] to be $10^{-2.5}$ mol^2 kg^{-2}. The Raman spectroscopic investigation[6] mentioned above on molten $KHSO_4$ was interpreted in accordance with eq 1. Raman bands ascribed to HSO_4^- decreased while the bands ascribed to $S_2O_7^{2-}$ increased with increasing temperature in the range 300–500 °C. As far as we know, the absorption spectra of molten $KHSO_4$ in the

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(1) Hansen, N. H.; Fehrmann, R.; Bjerrum, N. J. *Inorg. Chem.* **1982**, *21*, 744.
(2) Hansen, N. H.; Bjerrum, N. J. *J. Chem. Eng. Data* **1981**, *26*, 13.
(3) Hagisawa, H.; Takai, T. *Bull. Inst. Phys. Chem. Res. Tokyo* **1937**, *16*, 29.
(4) Wickert, K. *Brennst.-Wärme-Kraft* **1959**, *11*, 110.
(5) Spitsyn, V. I.; Meerov, M. A. *Zh. Obshch. Khim.* **1952**, *22*, 905.
(6) Walrafen, G. E.; Irish, D. E.; Young, T. E. *J. Chem. Phys.* **1962**, *37*, 662.
(7) Lynton, H.; Truter, M. R. *J. Chem. Soc.* **1960**, 5112.
(8) Simon, A.; Wagner, H. *Z. Anorg. Allg. Chem.* **1961**, *311*, 102.
(9) Flood, H.; Førland, T. *Acta Chem. Scand.* **1947**, *1*, 781.
(10) Durand, A.; Picard, G.; Vedel, J. *J. Electroanal. Chem. Interfacial Electrochem.* **1976**, *70*, 55.
(11) Rogers, S. E.; Ubbelohde, A. R. *Trans. Faraday Soc.* **1950**, *46*, 1051.
(12) Duffy, J. A.; Glasser, F. P., Ingram, M. D. *J. Chem. Soc. A* **1968**, 551.
(13) Ben Hadid, A.; Picard, G.; Vedel, J. *J. Electroanal. Chem. Interfacial Electrochem.* **1976**, *74*, 145.
(14) Ingram, M. D.; Duffy, J. A.; Forbes, S. M. *J. Appl. Electrochem.* **1971**, *1*, 53.
(15) Ben Hadid, A.; Picard, G.; Vedel, J. *J. Electroanal. Chem. Interfacial Electrochem.* **1976**, *74*, 157.

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near-infrared region have not previously been given in the literature.

Experimental Section

Materials. All handlings of chemicals were performed in a glovebox under a dry-nitrogen atmosphere (dried continuously by molecular sieves). $K_2S_2O_7$ was obtained by thermal decomposition of $K_2S_2O_8$ (Merck, Pro Analysi, maximum 0.001% N) under a dry-nitrogen atmosphere as earlier described[1] and kept in sealed glass ampules. The $KHSO_4$ used (Merck, Suprapure, 99%) was dried at 110 °C for 3 days and stored in the glovebox.

Raman Spectroscopy. The cells used for the Raman spectroscopic measurements were made of borosilicate tubes having a piece of square tubing added in one end with an inner opening of 5 by 5 mm and a height of around 10 mm. The square-tubing part diminishes glass reflections of the laser beam going through the melt. The cells were filled with chemicals in the glovebox and sealed (under vacuum) immediately after this procedure. The cells with $K_2S_2O_7$–$KHSO_4$ mixtures were equilibrated for 2–6 days in a rocking furnace at the measuring temperature before transference to a furnace especially designed as earlier[16] described for obtaining Raman spectra of samples at high temperatures (i.e. up to ca. 800 °C). The cell containing only $KHSO_4$ was placed directly in this furnace, and spectra were recorded from 2 to 24 h after each change of temperature without removal of the cell from the furnace. The Raman spectra were detected by a JEOL JRS-400D spectrometer with a cooled extended S-20 photomultiplier. A Coherent Radiation 4-W argon ion laser was the source of the 514.5-nm line (output 500–1000 mW) used for excitations of the melts. The signal due to the 90° scattered light giving rise to the polarized (||) and the depolarized (|⊥) spectra was amplified in a photon-counting system and recorded on paper tape for every 1 cm^{-1}. The spectra could consequently be smoothed (with use of either 9 or 25 neighboring points) and plotted conveniently via a central computer. The spectral resolution was typically 2 cm^{-1}.

Spectrophotometry. The cells used for measuring the absorption spectra were made of fused quartz (Ultrasil from Hellma or Spectrosil from Thermal Syndicate) with optical path lengths of 0.1–1 cm. As in the case of the Raman spectroscopic investigation the cells with $K_2S_2O_7$–$KHSO_4$ mixtures were loaded, sealed, and thereafter equilibrated in a rocking furnace for 2–6 days prior to transference to a furnace especially designed for the spectrophotometric measurements. The furnace[17] could be regulated to within ±0.1 °C. The temperature was measured with Pt resistance thermometers or calibrated chromel–alumel thermocouples. Those cells that contained only $KHSO_4$ were placed directly in this furnace and equilibrated for ca. 24 h at constant temperature without removal of the cell from the furnace.

The spectra were recorded with a Cary 14R spectrophotometer equipped with a Datex digital system for punching out spectral data on paper tape. As in the case of the Raman spectroscopic measurements this procedure made it possible to plot the spectra in the desired format using the central computer. The temperature of the $KHSO_4$ melts was increased stepwise from the lowest to the highest measured temperature. In this way equilibrium between H_2O in the gaseous and in the liquid phase was obtained faster than if the temperature was decreased stepwise.

General Considerations

The density of the $KHSO_4$–$K_2S_2O_7$ melts was obtained from the work by Hansen and Bjerrum.[2] The formality, C', of a compound is defined as the initial molar concentration of the compound added to the melt. The formal composition of the melt is given by the mole fractions X_{KHSO_4} or $X_{K_2S_2O_7}$. The absorptivity is defined as Al^{-1}, where A is the absorbance corrected for the absorbance of cell and solvent and l is the path length of the optical cell. The formal absorptivity of a compound is defined as $A(lC')^{-1}$.

In calculations of the melt compositions the amount of $KHSO_4$ decomposed in accordance with eq 1 to give the equilibrium pressure of water above the melt could be neglected. In the worst case (i.e. the experiment with maximum gas to melt volume) this amounted to 0.06% by weight based on extrapolated vapor pressure data[3] of $KHSO_4$ at the highest measured temperature, i.e. 450 °C.

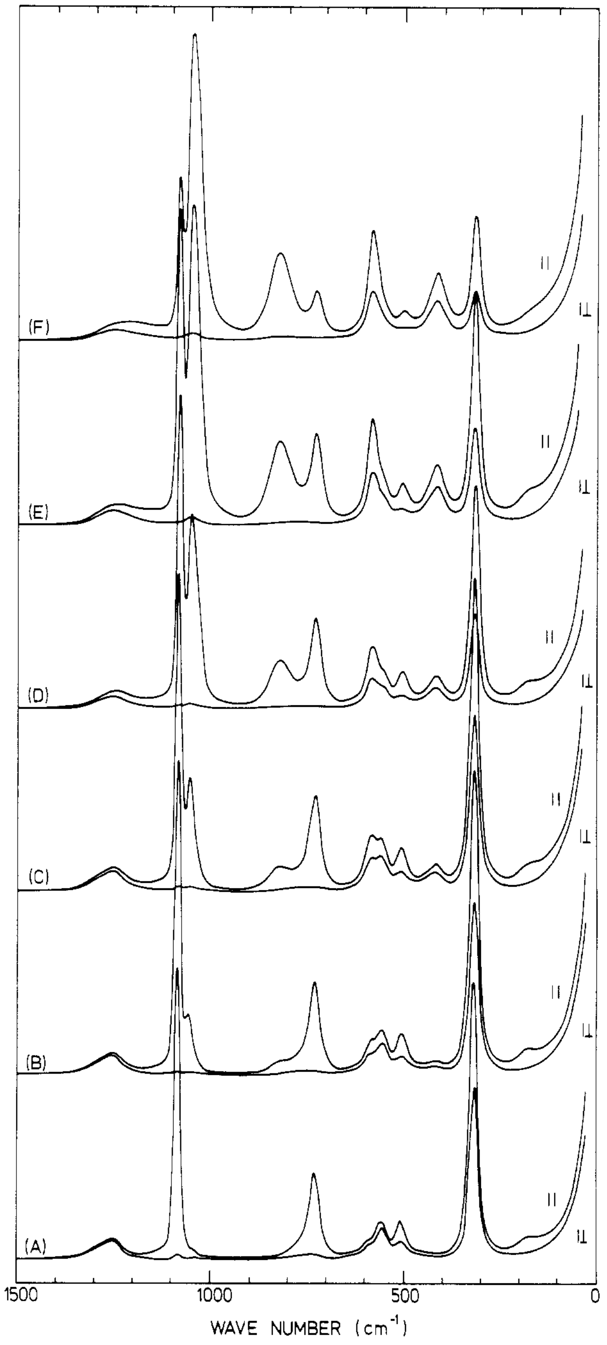

Figure 1. Raman spectra of molten $K_2S_2O_7$–$KHSO_4$ mixtures at 430 °C. The mole fractions of $KHSO_4$ were as follows: (A) 0.0000; (B) 0.2003; (C) 0.4005; (D) 0.5998; (E) 0.7502; (F) 0.9000. || and |⊥ denote polarized and depolarized spectra, respectively.

Raman and Infrared Spectra

Experimental Results. In Figure 1 is shown a series of Raman spectra of molten $KHSO_4$–$K_2S_2O_7$ mixtures at 430 °C. The composition of the melt is changed from 100% $K_2S_2O_7$ (A) to 10% $K_2S_2O_7$ (F). In Figure 2 are shown the Raman spectra of 100% $KHSO_4$ at temperatures in the range 205 °C (subcooled liquid) to 450 °C.

It is seen from spectrum A in Figure 1 that strong polarized bands are found for molten $K_2S_2O_7$ at 1085, 730, and 318 cm^{-1} and weaker polarized bands at 760, 506, and 174 cm^{-1}. The depolarized bands are found at 1250 and 556 cm^{-1}, and furthermore, a weak depolarized band seems to be present around

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[16] Berg, R. W.; von Winbush, S.; Bjerrum, N. J. *Inorg. Chem.* **1980**, *19*, 2688.

[17] Fehrmann, R.; Bjerrum, N. J.; Andreasen, H. A. *Inorg. Chem.* **1975**, *14*, 2259.

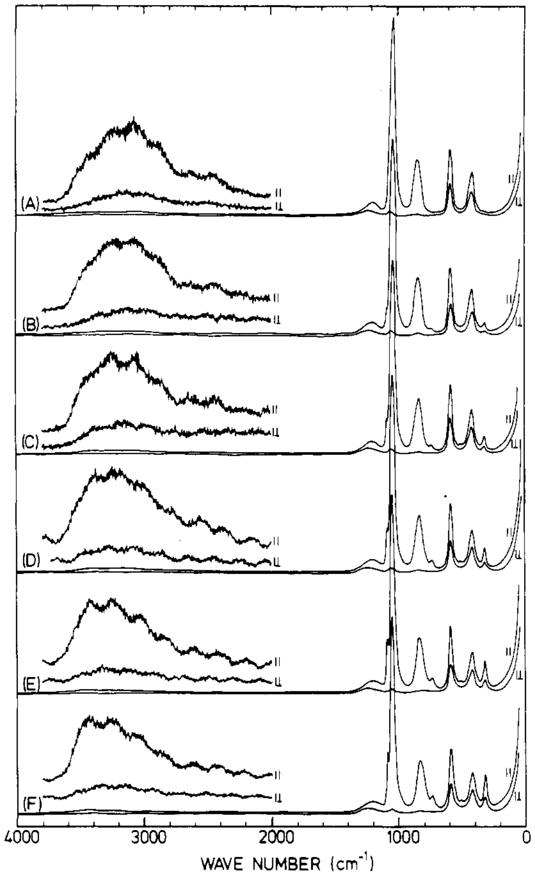

Figure 2. Raman spectra of molten $KHSO_4$ in the temperature range 205–450 °C. The temperatures were as follows: (A) 205 °C; (B) 250 °C; (C) 300 °C; (D) 350 °C; (E) 400 °C; (F) 450 °C. $\|$ and $|\perp$ denote polarized and depolarized spectra, respectively.

1300 cm^{-1}. The very weak bands around 1035 and 600 cm^{-1} could possibly be due to a small contamination by HSO_4^- in the melt since strong bands appear at these wavenumbers when increasing amounts of $KHSO_4$ are added (see spectra B–F). Here bands at 417, 823, and ca. 1200 cm^{-1} further characterize the spectra with high content of $KHSO_4$. However, the bands at 1035 and 600 cm^{-1} in spectrum A are depolarized in contrast to the polarized bands found at similar frequencies in the melts containing $KHSO_4$. It therefore seems probable that $S_2O_7^{2-}$ has bands at these wavenumbers. With increasing additions of $KHSO_4$ all bands ascribed to $S_2O_7^{2-}$ decrease with the same fraction compared to the other bands in the spectra in accordance with the gradual decrease in the pyrosulfate ion concentration. The bands assigned to $S_2O_7^{2-}$ are given in Table I.

In the Raman spectrum of subcooled molten $KHSO_4$ at 205 °C (spectrum A in Figure 2) the bands ascribed to HSO_4^- completely dominate and only very weak traces of the $S_2O_7^{2-}$ bands can be seen. On the basis of this spectrum it seems likely that a weak depolarized band located at 1240 cm^{-1} can be ascribed to HSO_4^-. A very broad and weak group of bands are located around 3000 cm^{-1} as can be seen from the enlarged part of the spectrum. These bands are not due to HSO_4^- but are probably due to water formed by the decomposition of $KHSO_4$ described by eq 1. This matter will be discussed later. The bands assigned to HSO_4^- are given in Table I.

The infrared spectrum of $K_2S_2O_7$ in KBr at 25 °C shows 13 bands. The frequencies and the relative intensities are given in Table II.

Table I. Raman Shifts (cm^{-1}) and Polarizations of Bands for the Observed Spectra[a]

this work	polarizn	Walrafen et al.[6]	polarizn
	$S_2O_7^{2-}$		
1300 w	dp	1295	dp
1250 m	dp	1250	p
		1200	p
		1135	p
1085 vs	p	1080	p
1035 w	dp	1050–1060	dp
		825	dp
		790	dp
760 w	p	765	p
730 s	p	730	p
600 w	dp	590	dp
556 m	dp	555	p
506 m	p	505	p
		455	p
		420	dp
318 vs	p	320	p
174 m	p	170	dp
		90	dp
	HSO_4^-		
417 s	p	420	dp
585 s	p	590	dp
823–844 s	p	840	p
1046 vs	p	1050	p
1205 m	p	1230	dp
1240 w	dp	1360–1390	dp

[a] Key: w, weak; m, medium; s, strong; v, very; dp, depolarized; p, polarized.

Table II. Frequencies (cm^{-1}) for the Observed Infrared Spectra of Solid $K_2S_2O_7$ in KBr at 25 °C[a]

this work	Walrafen et al.[6]	Simon and Wagner[8]	$KHSO_4$[18]
	1325 w		1325 w
1302 s	1295 s	1289–1302 s	1280 s
1262 s	1250 s	1267 s	
	1200 w		
	1140 w		1160 s
1096 s	1097 s	1108 m	
1050 s	1050–1060 s	1059 s	1065 s
			1005 s
			877 s
857 w	850 m		848 s
			820 w
780 s	790 s	800 s	
	775 w		
738 m	738 m	750 m	
652 m	646 w	655 s	
		618 w	
585 s	590 s	589 s	
563 m	560 s	563 w	
527 m	515 m	526 m	
467 m	458 m	467 w	
	437 w		
340 m	335 w		

[a] Key: w, weak; m, medium; s, strong.

Table III. Possible Symmetry and Calculated Number of Expected Raman- and Infrared-Active Fundamentals Due to Vibrations of $S_2O_7^{2-}$

	no. of fundamentals						
	D_{3h}	D_{3d}	D_3	C_{2v}	C_2	C_s	C_1
Raman, total	10	6	11	21	21	21	21
Raman, p	7	6	11	7	11	13	21
Raman, dp	3	0	0	14	10	8	0
infrared	7	7	10	17	21	21	21

Structure of $S_2O_7^{2-}$. In Table III are shown the expected number of Raman- and IR-active fundamentals of the point groups corresponding to the most probable structures of $S_2O_7^{2-}$. The structures of the dihedral point groups require a linear S–O–S bridge while the cubic groups contain a nonlinear S–O–S bridge.

On the basis of the number of depolarized bands assigned to $S_2O_7^{2-}$ in the observed spectra the structures corresponding to the dihedral groups and the point group C_1 can be excluded. None of the structures C_{2v}, C_s, or C_2 can be ruled out exclusively on the basis of the observed number of polarized and depolarized bands. However, a Raman spectrum of fine powdered $K_2S_2O_7$ at 25 °C shows bands at approximately the same frequencies and with the same relative intensities as is observed in the spectra of the melt. The factor group splitting of some of the bands in the solid state is of course taken into considereation. Therefore, the C_{2v} structure of $S_2O_7^{2-}$ in the melt seems to be the most probable, since C_{2v} is the structure of $S_2O_7^{2-}$ found by the X-ray investigation[7] of $K_2S_2O_7$. The $S_2O_7^{2-}$ in $K_2S_2O_7$ was in that study shown to have a bent bridge with a S–O–S angle of 124° and with eclipsed SO_3 groups. Thus this conformation seems to be retained in the melt despite the fact that the C_s or C_2 structure with staggered SO_3 groups appears to be somewhat more energetically favorable.

From Table I it can be seen that more bands are ascribed to $S_2O_7^{2-}$ by Walrafen et al.[6] than in the present work. However, the spectrum[6] used to identify the bands of $S_2O_7^{2-}$ was obtained by heating $KHSO_4$ to 620 °C, with the assumption that the bisulfate decomposes completely into pyrosulfate and water (i.e., according to eq 1). The weak bands found at 420, 825, and 1200 cm^{-1} and assigned to $S_2O_7^{2-}$ seem to be due to traces of HSO_4^-. The complete absence of these bands in spectrum A of Figure 1 supports this interpretation. Most of the intensity of the 1050- and 590-cm^{-1} bands might furthermore be caused by HSO_4^-. Other bands found by Walrafen et al.[6] at 90, 455, 790, and 1135 cm^{-1} and assigned to $S_2O_7^{2-}$ seem to be so weak that they might be spurious. Therefore, the actual number of bands due to $S_2O_7^{2-}$ most likely are considerably smaller than the number given by Walrafen et al.[6] The polarization found previously[6] and found in the present work seems to be in agreement for eight bands. However, this is not the case for the bands at 556 and 1250 cm^{-1}, which obviously are depolarized, and for the band at 174 cm^{-1}, which is polarized. The conclusion by Walrafen et al.[6] that $S_2O_7^{2-}$ has C_2 symmetry in the melt must therefore be considered very doubtful.

Assignments of the bands of $S_2O_7^{2-}$ to certain vibrations are speculative and are omitted since only half of the theoretically expected number of bands are observed and since some of the bands might further be combinations or overtones.

In Table II the results of the solid-state infrared investigation of $K_2S_2O_7$ are compared with the results of Walrafen et al.[6] and Simon and Wagner[8] and with observed frequencies of $KHSO_4$.[18] There seems to be good agreement between our frequencies and those observed by the other authors. The number of bands observed by Walrafen et al.[6] is, however, 18 and thus exceeds ours by 5 and Simon and Wagner's[8] by 6 bands. But some of the bands—for example at 1325 and 1140 cm^{-1}—might be due to the presence of residual HSO_4^-. Therefore, a C_{2v} structure for $S_2O_7^{2-}$ in solid $K_2S_2O_7$ giving rise to 17 infrared-active fundamentals is certainly not to be excluded on the basis of the infrared spectra. Similarly the C_s structure cannot be excluded, but it is in contradication with the X-ray investigation[7] and seems therefore less probable. The conclusion by Walrafen et al.[6] that $S_2O_7^{2-}$ has C_2 symmetry in the solid state must therefore also be considered very doubtful. The infrared spectra also exclude a possible dihedral symmetry for $S_2O_7^{2-}$ in the solid state since the maximum number of bands expected for dihedral symmetry is only 10 (Table III).

Structure of HSO_4^-. The observed frequencies assigned to HSO_4^- are shown in Table I. Five of the bands remain approximately constant in all spectra while the frequency shifts for one band in the range 823–844 cm^{-1} are dependent on the temperature (i.e. the lower the temperature, the higher the frequency). This band is assigned to the totally symmetric stretching involving the S–OH group, and the temperature dependencey is possibly due to changes in hydrogen bonding between this group and other species in the melt.[6] Although the authors did not notice it, this change in frequency can be seen by a close look at the spectra of molten $KHSO_4$ at 290–620 °C reported by Walrafen et al.[6] In aqueous solutions of HSO_4^- this band is found[19] at 885 cm^{-1}. In such solutions the hydrogen bonding should occur between HSO_4^- and H_2O, but in the low-temperature melts of $KHSO_4$ hydrogen bonding is also possible between HSO_4^- ions. At elevated temperatures the hydrogen bonds might be formed between HSO_4^- and $S_2O_7^{2-}$. There is rather good agreement between the other measured frequencies of HSO_4^- and those found by Walrafen et al.[6] except for the broad band at 1360–1390 cm^{-1}, which was not observed by us. Furthermore, we found a polarized and a depolarized band around 1200 cm^{-1} while only one depolarized band was found previously[6] in this region. The bands found at 1046 cm^{-1} and around 840 cm^{-1} are highly polarized in agreement with previous work.[6] The bands found in the present work at 417 and 585 cm^{-1} are weakly polarized, the depolarization ratio being around $^1/_2$. Previously[6] these bands have been characterized as depolarized. The C_s symmetry of HSO_4^- is obviously the most probable structure giving rise to 12 Raman-active fundamentals.

The possible correlations between S–O vibrational frequencies of SO_4^{2-} (T_d) and HSO_4^- (C_s) are given by Walrafen et al.[6] Their interpretation of the 417-cm^{-1} band to show "accidental degeneration" of one polarized and one depolarized fundamental and the 585-cm^{-1} band to include two polarized and one depolarized fundamental might obtain support from the odd depolarization ratios found in the present work for these bands. The expected[6] polarized and depolarized fundamentals at 1230 and 1340 cm^{-1} do not agree with the observation by Walrafen et al.[6] of both bands being depolarized. However, the bands found at 1205 cm^{-1} (polarized) and 1240 cm^{-1} (depolarized) in the present work might be due to these fundamentals. The band at 1340 cm^{-1} is not found in the present work, and it seem difficult to detect it in the spectra given previously.[6] It might therefore turn out to be spurious.

The bands of the S–O–H bending modes might be missing because they are too weak or too broad to be detected. They are expected[6] to occur in the 1200-cm^{-1} region, and they could be enhanced by certain types of hydrogen bonding. In this region intermolecular vibrations are also considered to be found as a result[20] of intermolecular hydrogen bonding forming network structures in the melt. This might account for the broad features of the Raman spectrum found in the frequency area 1100–1300 cm^{-1}, which are seen especially clearly in the spectra of melts with high contents of $KHSO_4$ (e.g. spectrum F, Figure 1).

H_2O in the Melts. In accordance with eq 1, H_2O should be formed when HSO_4^- decomposes at elevated temperatures. Indeed the bands located in the region 3000–3500 cm^{-1} in Figure 2 support this: Three bands found at 3630 cm^{-1} ($\nu_3(b_1)$), 3450 cm^{-1} ($\nu_1(a_1)$), and 3225 cm^{-1} ($2\nu_2(a_1)$, Fermi resonance) are characteristic[21] of the Raman spectrum of H_2O. These three bands seem to be located at a frequency ca. 200 cm^{-1} lower in the melt than in water. The lowest frequency band of these ($2\nu_2(a_1)$) located around 3050 cm^{-1} has the highest relative intensity at 205 °C (spectrum A) and decreases gradually with increasing temperature (A–F) relative to the two other bands found at around 3250 and 3450 cm^{-1}. This behavior is probably[22] due to a gradual decrease in the strength

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[18] Miller, F. A.; Wilkins, C. H. *Anal. Chem.* **1952**, *8*, 1253.

[19] Walrafen, G. E.; Dodd, D. M. *Trans. Faraday Soc.* **1961**, *57*, 1286.

[20] Walrafen, G. E. *J. Chem. Phys.* **1963**, *39*, 1479.

[21] Walrafen, G. E. *J. Chem. Phys.* **1962**, *36*, 1035.

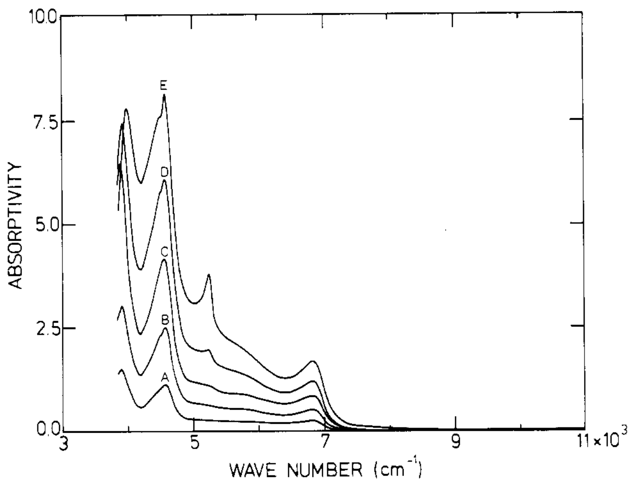

Figure 3. Spectra of molten $K_2S_2O_7$–$KHSO_4$ mixtures at 430 °C. The mole fractions of $KHSO_4$ were as follows: (A) 0.1999; (B) 0.4000; (C) 0.6010; (D) 0.8000; (E) 1.0000.

of the hydrogen bonds of the water molecules at elevated temperatures. This agrees well with the observed shift of the ~840-cm^{-1} band of HSO_4^- mentioned earlier and interpreted as weakening of O···H–OSO_3 bonds. This shift is also observed[21] in pure water with increasing temperature.

Possible Equilibria in the Melts. In molten $K_2S_2O_7$ the possible dissociation equilibrium (eq 2) seems to be of no importance in the temperature range investigated, i.e. up to 450 °C. Thus no Raman band is detected at 980 cm^{-1}, which is the position[23] of the $\nu_1(a_1)$ band of SO_4^{2-} in molten $K_2S_2O_7$ at 500 °C saturated with respect to K_2SO_4. The detection limit corresponds to around 2 mol % of sulfate.

In the $KHSO_4$ melts from 200 to 450 °C none of the intense polarized bands characteristic[6,19] of SO_4^{2-}, H_2SO_4, $HS_2O_7^-$, or $H_2S_2O_7$ are found in the region 900–1000 cm^{-1}. Furthermore, a calculation of the sulfate concentration in molten $KHSO_4$ at 220 °C and P_{H_2O} = 0.041 atm based on the estimated value[13] for the product $[H_2SO_4][SO_4^{2-}]$ shows that the melt contains as a maximum around 1 mol % of sulfate. This indicates that the self-dissociation reaction of $KHSO_4$ (eq 3) is unimportant for the present investigation. It therefore seems probable that the dominating species present in the melts investigated are $S_2O_7^{2-}$, HSO_4^-, and H_2O over the entire temperature range investigated.

The above conclusion is further supported by the observation that the frequencies of most of the Raman bands assigned to these species are preserved independently of temperature or composition of the melts. However, the relative concentrations of these species change as for example can be seen from Figure 2 (A–F), where the bands of $S_2O_7^{2-}$ are increased relative to the bands of HSO_4^- with increasing temperature. This is in accordance with the expected shift of eq 1 to the right. This equilibrium seems to be the only important one in the molten systems investigated.

Near-Infrared Spectra

Experimental Results. Near-infrared spectra of various melts were recorded in the wavenumber range (3.8–11.0) × 10^3 cm^{-1}. A series of 12 spectra were measured in this range of molten $KHSO_4$–$K_2S_2O_7$ mixtures at 430 °C, but for convenience only every second spectrum is shown in Figure 3. The spectrum of $K_2S_2O_7$ (X_{KHSO_4} = 0.000) shows no absorption in the wavenumber range investigated. This spectrum has been used as background and is subtracted from all spectra of melts containing $KHSO_4$. The composition is changed from X_{KHSO_4} = 0.1999 (A) to X_{KHSO_4} = 1.000 (E) with steps of 0.2 in mole fraction. By proper choice of path lengths of the optical cells absorbance above 0.7 were avoided. This ensured[23,24] that emission of melt and furnace in the investigated wavenumber area and temperature range was not serious with respect to the accuracy of the measured absorbances. Thus a calculation at 4.5 × 10^3 cm^{-1} and for a measured absorbance of 0.7 of a 430 °C melt shows that the absorbance obtained is correct within ca 0.5%. Since all bands increase with increasing mole fraction of $KHSO_4$, the absorption bands are most clearly seen in spectrum E. Strong bands are found at 3.9 × 10^3, 4.6 × 10^3, 5.3 × 10^3, and 6.8 × 10^3 cm^{-1} while weaker bands are found at 4.4 × 10^3 and 5.8 × 10^3 cm^{-1}. The positions of the bands are not changed in this series with the exception of the band at 3.9 × 10^3 cm^{-1}, which changes to 4.0 × 10^3 cm^{-1} in spectrum E. However, the relative intensity of the bands changes. Further there seems to be internal correlation between the bands at 3.9 × 10^3, 4.4 × 10^3, and possibly 5.8 × 10^3 cm^{-1} and between the bands at 4.6 × 10^3, 5.3 × 10^3 and 6.8 × 10^3 cm^{-1}.

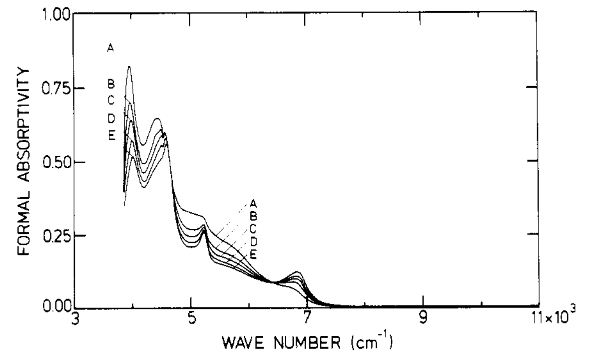

Figure 4. Spectra of molten $KHSO_4$ in the temperature range 200–450 °C. The temperatures were as follows: (A) 200 °C; (B) 300 °C; (C) 350 °C; (D) 400 °C; (E) 450 °C.

In Figure 4 is shown a series of spectra of molten $KHSO_4$ from 200 °C (subcooled) to 450 °C. As in Figure 3 the bands are due to O–H vibrations. The same bands and the same correlations are also observed in this case, and furthermore, a temperature-related isosbestic point is found at 6.4 × 10^3 cm^{-1}.

Discussion. In order to identify the species present in the melts, the obtained spectra were compared with a spectrum of H_2O at 25 °C.[23] This spectrum had strong bands at 5.2 × 10^3 and 6.9 × 10^3 cm^{-1} and a weak band at 5.6 × 10^3 cm^{-1}. The positions, shapes, and relative intensities of these water bands correspond well with the bands found at 4.6 × 10^3, 5.3 × 10^3, and 6.8 × 10^3 cm^{-1} in the melts, and they may therefore be attributed to H_2O. The shift toward somewhat lower wavenumber is analogous to the shift found for the water bands in the Raman spectra of the melts. A spectrum of H_2O saturated with $KHSO_4$ at 25 °C shows the appearance of a band at 6.8 × 10^3 cm^{-1}, and this lends support to the impression that the water bands are shifted to lower wavenumbers when H_2O is hydrogen bonded to HSO_4^- or perhaps also when it is bonded to $S_2O_7^{2-}$. The concentration of HSO_4^- is too low in this case to give information about the position of the HSO_4^- bands. Therefore a saturated (20 mol %) solution of K_2SO_4 in 96% H_2SO_4 (giving rise to HSO_4^- quantitatively) was examined spectrophotometrically and the spectrum was compared with that of 96% H_2SO_4. Weak bands at 4.5 × 10^3, 5.0 × 10^3, and 5.6 × 10^3 cm^{-1} could be ascribed to HSO_4^-. These bands may correspond to the bands found at 3.9 × 10^3, 4.4 × 10^3, and 5.8 × 10^3 cm^{-1} in the melts. The low intensity

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(22) Busing, W. R.; Hornig, D. F. *J. Phys. Chem.* **1961**, *65*, 284.

(23) Hansen, N. H. Thesis, Chemistry Department A, The Technical University of Denmark, 1979.

(24) Morrey, J. R. Voiland, E. E. *Spectrochim. Acta* **1962**, *18*, 1175.

of the first two bands relative to that of the last band compared with the high relative intensity found for these bands in the melt could be due to a change in the character of the hydrogen bonding, which might affect especially the intensity of bending modes.

It is interesting to note that an equilibrium between HSO_4^-, H_2O, and $S_2O_7^{2-}$ (i.e. eq 1) could give rise to temperature-related isosbestic points. However, it should be emphasized that the existence of the temperature-related isosbestic point at 6.4×10^3 cm^{-1}, shown in Figure 4, is not a proof for the involvement of eq 1, especially since internal linearity of the spectra is not found over the entire wavelength range measured.

An extensive computer calculation on the basis of the observed spectra and of the type described earlier[1,25] of species concentrations and thermodynamic data is not justified due to the large variation in solvent composition, ionic strength, temperature, and vapor pressure.

Conclusion

Both the Raman spectra and the absorption spectra of molten $KHSO_4$–$K_2S_2O_7$ mixtures can be interpreted in accordance with eq 1. The dominating species formed in the temperature range investigated are HSO_4^-, H_2O, and $S_2O_7^{2-}$. Parameters that influence the relative concentration of these species are the initial compositions of the melts, the temperature, and the vapor pressure of water, which in the present investigation is equal to the equilibrium pressure at the actual temperature. The structure of $S_2O_7^{2-}$ in the melt most probably corresponds to the point group C_{2v}. The structure of HSO_4^- is most likely C_s. Different types of hydrogen bonding probably occur between the three main species in the melt depending on the temperature. Due to the rather low vapor pressures of the melts also at elevated temperatures, the water molecules must be associated strongly to the sulfur-containing species. Such an association possibly involves either three hydrogen bonds or two hydrogen bonds and a third bond (e.g. a electrostatic (dipole–dipole) bonding between a lone pair on the oxygen atom and a pyrosulfate ion).

Unfortunately, due to the many unknown parameters involved, the spectra cannot be used for quantitative estimations of, for example, species concentrations and equilibrium constants. However, the intensity of the Raman bands of HSO_4^- compared with the intensities of $S_2O_7^{2-}$ bands at 430 °C might be used to estimate the initial composition of any melt composed of $KHSO_4$ and $K_2S_2O_7$ under the assumption that the melt is examined at the equlibrium pressure.

An extended knowledge of these molten mixtures is useful in the study of redox equilibria, complex formation, and solubility of solute vanadium species, as will be shown in a later paper.[26]

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Registry No. $K_2S_2O_7$, 7790-62-7; $KHSO_4$, 7646-93-7; $S_2O_7^{2-}$, 16057-15-1; HSO_4^-, 14996-02-2.

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(25) Fehrmann, R.; Bjerrum, N. J.; Pedersen, E. *Inorg. Chem.* **1982**, *21*, 1497.

(26) Fehrmann, R.; Hansen, N. H.; Bjerrum, N. J.; Philipsen, J.; Pedersen, E., to be sumitted for publication.

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Resonance Raman Enhancement of Imidazole Vibrations via Charge-Transfer Transitions of Pentacyanoiron(III) Imidazole and Imidazolate Complexes

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Modest enhancement is observed for Raman modes of the bound imidazole (ImH) in $[(ImH)Fe(CN)_5]^{2-}$ upon laser excitation in a broad, weak absorption band at ~480 nm, which is assignable, on the basis of excitation profiles, to overlapping charge-transfer transitions from the two highest ImH π orbitals to the Fe^{III} d_π vacancy. Similar enhancement is seen for Im^- modes in $[(Im)Fe(CN)_5]^{3-}$ upon excitation in a weak band at ~650 nm and a strong band at ~440 nm, which are suggested to be the two π CT transitions, the π orbitals being split by the bonding alterations accompanying deprotonation of the bound ImH. The Fe–imidazole stretching vibration is weak or absent in these spectra, consistent with the nonbonding character of the Fe terminal orbital. Detection of ring modes of ImH or Im^- bound to low-spin Fe^{III} in heme proteins may require a concentration of ~25 mM if similar CT transitions can be located and excited. Detection limits might be lower if the CT dipole strengths are increased in the proteins via favorable orientations of the imidazole rings.

Introduction

Transition-metal ions are commonly bound to proteins via histidine side chains, due to the σ donor strength of the imidazole and the moderate pK_a (~7) of the imidazolium ion.[1] Spectroscopic probes of bound imidazole are therefore useful in studying metalloproteins. The vibrational modes of bound imidazole can in principle be monitored by Raman spectroscopy. To attain adequate sensitivity, however, and, more importantly, to discriminate against unbound imidazole, it is necessary to employ resonance enhancement[2] via selective excitation of electronic transitions involving the bound imidazole. Charge-transfer (CT) transitions from imidazole to the metal ion or vice versa are attractive in this regard.

Heme proteins are of particular interest, because at least one of the heme axial ligands is usually imidazole. However, CT transitions are difficult to locate because the absorption spectrum is dominated by the intense porphyrin π-π^* transitions. We have observed large enhancements of bound pyridine (py) modes in $(py)_2Fe^{II}(MP)$ (MP = mesoporphyrin IX) via a transition at ~490 nm assigned to Fe^{II} $(d_\pi) \rightarrow$ py(π^*) CT.[3] Since the π^* orbitals of imidazole (ImH) are higher in energy than those of Py, analogous Fe^{II} $(d_\pi) \rightarrow$

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(1) Sundberg, R. J.; Martin, R. B. *Chem. Rev.* **1974**, *74*, 471.

(2) Spiro, T. G.; Stein, P. *Annu, Rev. Phys. Chem.* **1977**, *28*, 501.

(3) Wright, P. G.; Stein, P.; Burke, J. M.; Spiro, T. G. *J. Am. Chem. Soc.* **1979**, *101*, 3531.

0020-1669/83/1322-4014$01.50/0