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THE NEAR-ULTRAVIOLET, VISIBLE, AND INFRARED SPECTRA OF

MOLTEN KSCN AND NaSCN

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ABSTRACT

It has been shown that sulfur dissolves in alkali-halides and alkali-thiocyanate melts. These solutions of sulfur have a characteristic blue color. To identify the species responsible for this color, the visible and infrared absorption spectra of NaSCN and KSCN were studied. The visible absorption can be characterized as a continuum with a band peak at 558 mμ. The infrared range covered was from 2 to 15μ. Absorption by the sulfur was observed to occur at about 14.5μ. A comparison of the continuum observed in the visible region with that observed for sulfur vapor in the range of 300° to 700° C shows that the sulfur species in solution is most probably S_4.

It has been shown that sulfur dissolves in LiCl-KCl, LiBr-KBr, and KSCN to give a characteristic blue solution.[1] The correspondence between the behavior of sulfur in alkali halides and alkali thiocyanates is not surprising since the cyanide ion very closely approximates the properties of the chloride ion. Since the thiocyanates melt at lower temperatures and since sulfur is released by decomposition (as opposed to the more difficult introduction of sulfur into the alkali halides by distillation),

[1] J. Greenberg, B. R. Sundheim, D. M. Gruen, J. Chem. Phys. 29 461 (1958)

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the near-ultraviolet, visible, and infrared absorptions of the alkali thiocyanate systems were measured in an attempt to identify the sulfur species present. The infrared spectra were obtained by use of the platinum-screen technique.[2] The near-ultraviolet and visible spectra were obtained by use of Vycor cells.

The samples were prepared by using reagent grade materials that were heated gradually under vacuum to 10° C above the melting point. On melting, the systems appeared water white. When bubbling in the melts had ceased, the samples were removed from the vacuum line and filtered through Pyrex glass wool. Infrared data were obtained by using a Perkin-Elmer model 13 with a NaCl prism. In this region, the platinum-screen cell was used. The cell was maintained at 10 mm Hg by continuous pumping. The temperature of the screen was controlled to within ±2° C by use of a relay-type proportional controller. The controller had a Pt-Pt 13 percent Rh thermocouple sensor, which was attached to the center of the screen. The upper limit to the use of this cell was approximately 400° C. Above this temperature, the evaporation of the sulfur destroyed the film. The near-ultraviolet and visible regions were covered by use of a Perkin-Elmer model 350 with a fused silica prism. This instrument is designed to cover the region from the near-infrared region to the near-ultraviolet region. For this purpose, lead sulfide and photomultiplier detectors in conjunction with tungsten- and hydrogen-lamp light sources were used. For convenience, Vycor cells wrapped with Nichrome wire and heated by the

[2] J. Greenberg, L. J. Hallgren, Rev. Sci. Inst. 31 444 (1960)

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proportional controller were used in this region. The thermocouple sensor was inserted into the cell by a tube sealed into the cell.

In both cases, the samples were run against air. To balance the instruments, the reference beams had to be attenuated by 50 percent. The data are therefore reported as relative transmission. From density and area considerations, the thickness of the thiocyanate melt on the platinum screen was estimated to be 0.05 mm. The Vycor cells used in the visible region had a 1-cm light path.

Care had to be taken that no large thermal gradient was present in the platinum screen or Vycor cell. If such a gradient was present, sulfur would distill out of solution. To prevent this, the width of the platinum screen was kept to a minimum - approximately 5 mm wide. At 400° C, the emission of the heated salts did not pose any experimental problem.

Figure I shows the infrared absorption spectra of KSCN at 250° and 400° C and of NaSCN at 300° and 400° C. The infrared spectra of these salts in the range of 2 to 15μ are almost identical since the absorption is primarily due to the thiocyanate ion. The cation coupling is not observed in this range. Table I gives the peak positions for the bands observed. These positions are in good agreement with those reported for solid KSCN.[3] The $2\nu_1$ assignment for NaSCN was not found; however, a peak was observed at about 3225 cm^{-1} that can be attributed to the presence of the hydroxyl ion. In both cases, there was a distinct temperature broadening of the bands. No appreciable shift in peak position was observed as a function of temperature. Where shifts did

[3] L. H. Jones, J. Chem. Phys. 25 1069 (1956)

occur, no uniform trend was observable. The absorption at $\lambda > 14.5\ \mu$ may be attributed to the presence of sulfur.

The near-ultraviolet and visible absorption spectra for KSCN at 250° and 400° C shown in Figure 2 are characterized by short wavelength cutoffs at 0.28 and 0.35μ, respectively, and by a strong absorption maximum at 0.56μ for the 400° C melt. The short wavelength absorption edge can be attributed to sulfur absorption and not to the absorption of either cyanide or the thiocyanate ion. This was shown by observing a distinct shift in the absorption edge with the increase in intensity of the 0.56μ peak. The shift of this absorption edge toward longer wavelengths was directly related to the intensity of the band peak and could not be related to the temperature broadening of the cyanide or thiocyanate ion.

At the temperatures involved in these experiments, sulfur is known to exist as a high-molecular-weight, yellow polymer.[4] It is therefore a possibility that the sulfur species responsible for the blue color might be a lower-molecular-weight polymer with an odd electron. Since sulfur is known to polymerize further in the presence of hydroxyl groups, NaOH was added to the blue melt. A yellow sulfur precipitate was formed. The formation of a precipitate of the high-polymer sulphur at these temperatures would tend to indicate that the blue sulfur species in solution was itself a low molecular-weight species.

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[4] R. C. Brasted, Comprehensive Inorganic Chemistry, Vol. 8, D. Van Nostrand Co. Inc., Princeton, New Jersey, 1961

An examination of the visible absorption spectra of sulfur vapor in the range of 300° to 700° C shows that the absorption of the S_4 species is almost identical to that of the blue sulfur species present in the alkali thiocyanate melts. The absorption spectra of S_4 in the vapor is a continuum with its maximum at 510 mμ. The fact that the band peak is shifted to lower energies in the melt is not unexpected because of the influence of dipole forces.

The close resemblance of the absorption characteristics of S_4 vapor to that of the sulfur species in the melt along with the fact that S_8 absorbs in the untraviolet and S_6 and S_2 are known to be yellow[5] indicates that the species present in the fused salts is S_4. It is interesting to note that the blue color in liquid oxygen is due to the presence of O_4.

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[5]Von H. Braune and E. Steinbacher, Z. Naturforsch. 7a 486 (1952)

TABLE I. - PEAK POSITIONS FOR MOLTEN KSCN AND NaSCN

KSCN		NaSCN		Solid KSCN[3]	
νcm^{-1}(250° C)	νcm^{-1}(400° C)	νcm^{-1}(300° C)	νcm^{-1}(400° C)	νcm^{-1}	Assignment
4000	4000	----	----	4087	$2\nu_1$
2740	2740	2762	2770	2788	$\nu_1 + \nu_3$
2020	2020	2020	2041	2053	--------
1721	1709	1718	1718	1709	$\nu_3 + 2\nu_{2a}$
1385	1408	1406	1408	1452	$3\nu_{2a}$
1272	1202	1255	1268	1227	$\nu_3 + \nu_{2a}$
935	935	935	930	951	$\nu_{2a} + \nu_{2b}$
743	738	745	741	748.7	ν_3

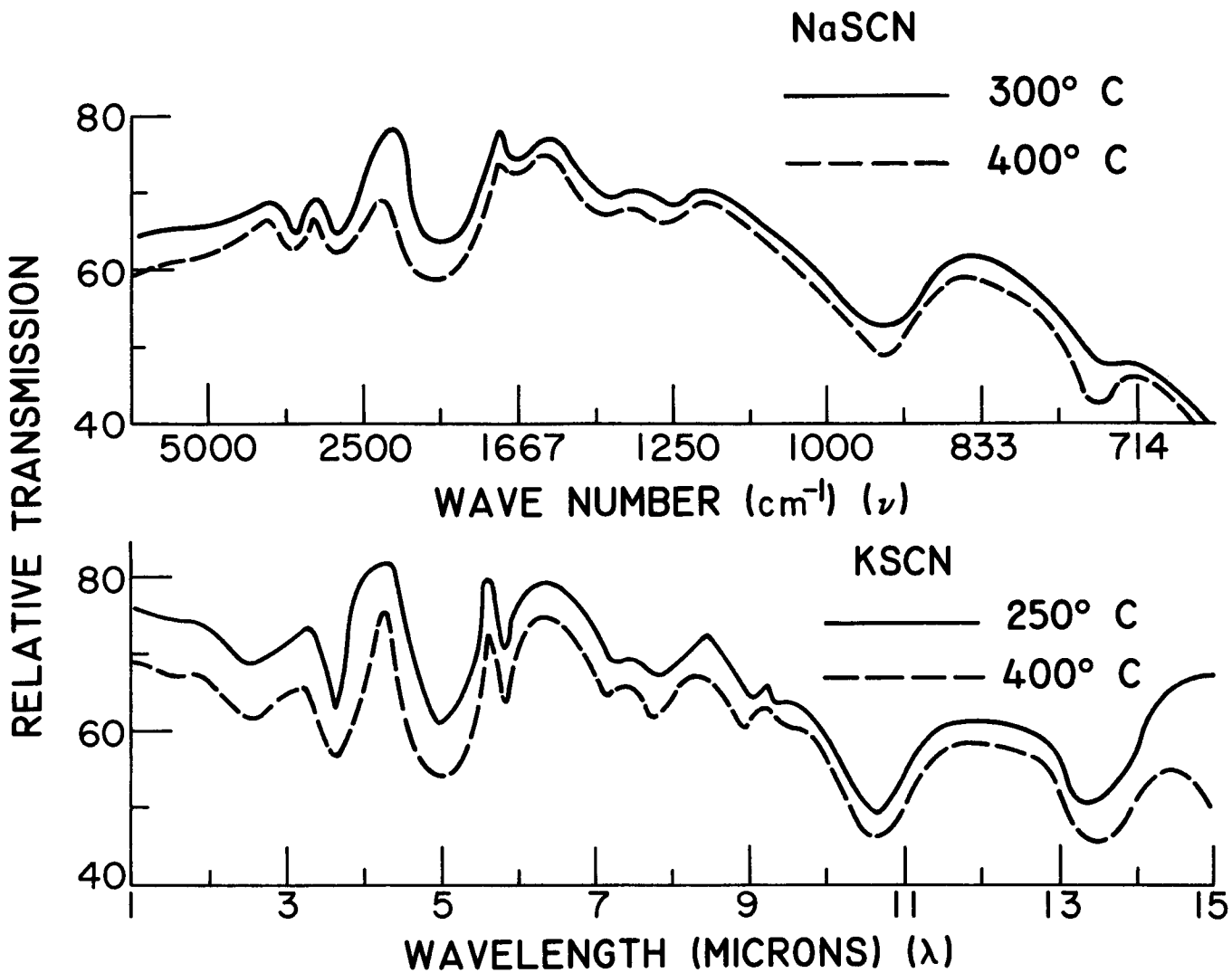

Figure 1. - Infrared absorption spectra of molten NaSCN and KSCN platinum screen cell in Vacuo.

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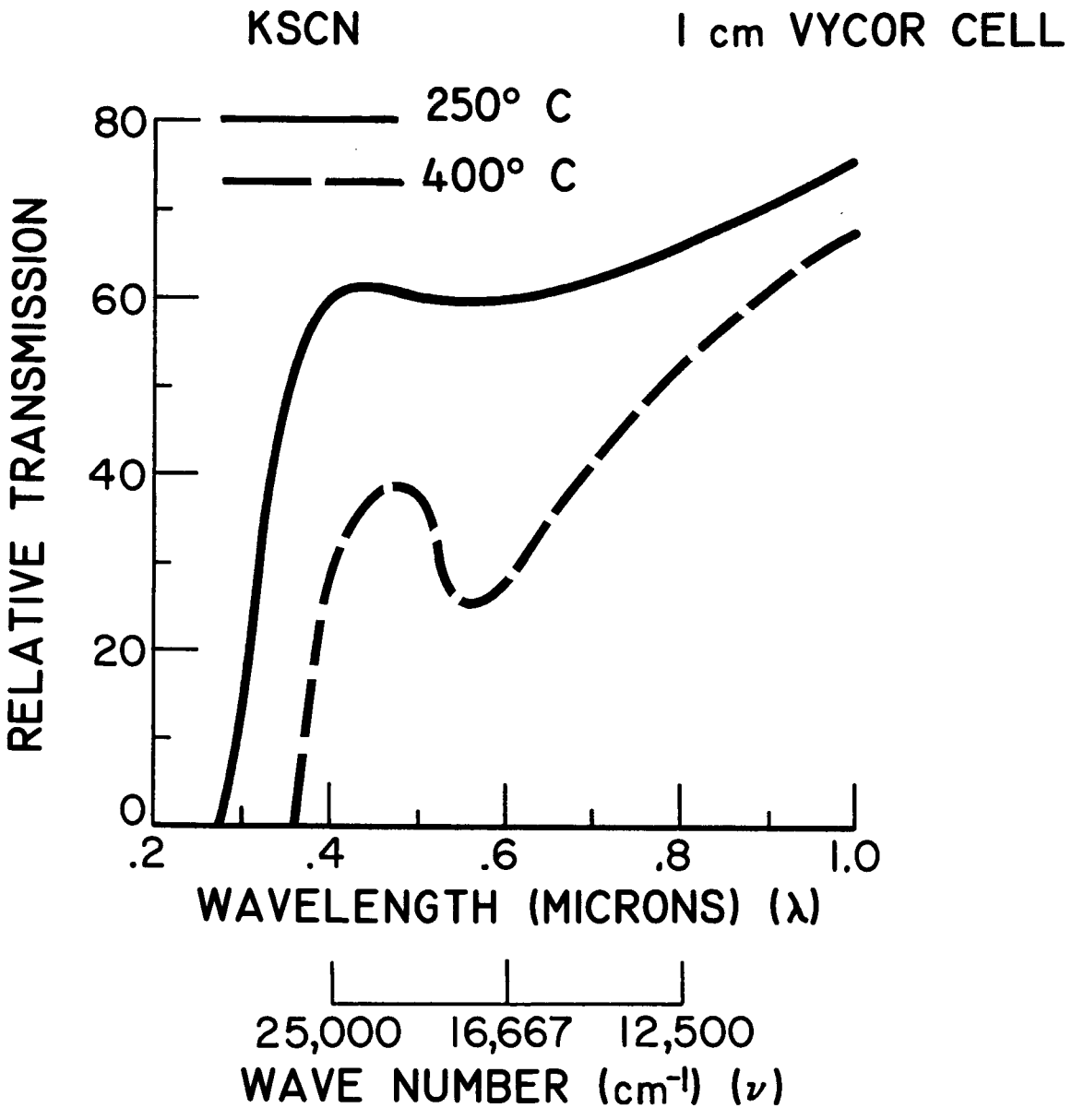

Figure 2. - Visible absorption spectra of molten KSCN.