by the steric requirements of the hetero ligands. To answer this question, it will be necessary to establish the structures of selected macrocyclic complexes having the same formula but containing lanthanides of appreciably different sizes; efforts to obtain suitable crystals for this purpose are in progress.

Acknowledgment. This work was supported in part by the U.S. National Institutes of Health (Grant No. RO1-CA30148). The cooperative project was carried out under the sponsorship of NATO (Research Grant 184/84).

Registry No. Lu($C_{22}H_{26}N_6$)(CH_3COO)(OH)(ClO_4)(CH_3OH)(H_2O)$_{0.5}$, 100447-95-8; 2,6-diacetylpyridine, 1129-30-2; 1,2-diaminoethane, 107-15-3.

Supplementary Material Available: Tables of anisotropic thermal parameters for non-hydrogen atoms, calculated hydrogen positions, least-squares planes, and structure factors (23 pages). Ordering information is given on any current masthead page.

Contribution from Laboratoire de Dynamique et Thermophysique des Fluides, Associe au CNRS,
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Complex Formation in Pyrosulfate Melts. 2. Calorimetric Investigations of the Systems V_2O_5–$K_2S_2O_7$, $V_2O_5{\cdot}K_2S_2O_7$–K_2SO_4, $V_2O_5{\cdot}2K_2S_2O_7$–K_2SO_4, and $V_2O_5{\cdot}3K_2S_2O_7$–K_2SO_4 at 430 °C

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The enthalpies of mixing of solid V_2O_5 and liquid $K_2S_2O_7$ have been measured in the whole liquidus range at 430 °C. The maximum concentration of V_2O_5 was found to be in the mole fraction range $X_{V_2O_5}$ = 0.502–0.509. On the basis of the results the liquid–liquid enthalpies of mixing of liquid V_2O_5 and $K_2S_2O_7$ could be calculated. ΔH_{mix} was found to be strongly exothermic, and the data may indicate the formation of dimeric and polymeric complexes such as $(VO_2)_2(SO_4)_2S_2O_7^{4-}$ and $(VO_2SO_4)_n^{n-}$, respectively. Also, the enthalpies of mixing of solid K_2SO_4 and the liquid mixtures $V_2O_5{\cdot}K_2S_2O_7$, $V_2O_5{\cdot}2K_2S_2O_7$, or $V_2O_5{\cdot}3K_2S_2O_7$, contained in a calorimeter at 430 °C, were measured. The liquid–liquid enthalpies of mixing could be calculated on the basis of data obtained for the V_2O_5–$K_2S_2O_7$ system and the calculated heat of fusion of K_2SO_4 at 430 °C. Also in this case dimeric and polymeric complexes seem to be formed (possibly $(VO_2)_2(SO_4)_3^{4-}$ and $(VO_2(SO_4)_2)_n^{3n-}$). Structures for all the complexes are proposed. The importance of the results in relation to the catalytic oxidation of SO_2 to SO_3 is discussed.

Introduction

This paper concerning $K_2S_2O_7$–K_2SO_4–V_2O_5 molten mixtures is one of a series describing our attempts to explore the chemistry of the catalyst used for the oxidation of sulfur dioxide (i.e. the contact process utilized for the production of sulfuric acid). Earlier papers[2,3] describe the equilibria in the pure solvent melts $K_2S_2O_7$–$KHSO_4$–K_2SO_4 and also the complex formation of V(V) in dilute solutions obtained by addition of V_2O_5 to these melts. The methods of investigation, which are all useful for the study of dilute and transparent systems, were spectrophotometry, Raman spectroscopy, cryoscopy, and potentiometry. In order to study the dark and very viscous melts with a high concentration of V_2O_5 analogous to the concentration in the catalytic melts, other methods must be applied. This work involves the first calorimetric study of the complex formation of V(V) in the binary system $K_2S_2O_7$–V_2O_5 at 430 °C and in the ternary system $K_2S_2O_7$–K_2SO_4–V_2O_5 also.

The phase diagram of the $K_2S_2O_7$–V_2O_5 system has been studied by several authors in the past,[4-7] giving rise to rather different diagrams. Discrepancies also arise in the number of different compounds it has been claimed possible to isolate from the melts. These compounds, the so-called pyrosulfovanadates, are often distinguished only by the adduct formula $V_2O_5{\cdot}nK_2S_2O_7$, and the existence of different compounds corresponding to the n values 1, 1.25, 1.5, 2, 3, and 6 has been reported.[4-9] Some further characterization has been carried out[6-8] on the compounds with the n values 1, 2, and 3, i.e. $V_2O_5{\cdot}K_2S_2O_7$, $V_2O_5{\cdot}2K_2S_2O_7$, and $V_2O_5{\cdot}3K_2S_2O_7$, which seem to have incongruent melting points at 400, 380, and 330 °C, respectively. On the basis of the IR spectra[7] of the solids, bidentate (bridging or chelating) coordinate SO_4^{2-} groups appear to be present in all of these compounds, and furthermore, the compounds with n = 2 and 3 seem to contain the $S_2O_7^{2-}$ group also. The formulas KVO_2SO_4, $K_4(VO_2)_2(SO_4)_2S_2O_7$, and $K_3VO_2SO_4S_2O_7$ have been suggested for the compounds.

In the dilute solutions of V_2O_5 in $K_2S_2O_7$ in the range 410–450 °C the investigation[3] mentioned above has shown that the monomeric complex $VO_2SO_4^-$ and its solvated form ($VO_2SO_4S_2O_7^{3-}$) are most probably present in the melt; the existence of the unsolvated complex is also confirmed by others.[10]

The published phase diagrams of the binary system V_2O_5–K_2SO_4 show discrepancies.[8,11] These inconsistencies are illustrated by the different formulas, $V_2O_5{\cdot}K_2SO_4$, $5V_2O_5{\cdot}3K_2SO_4$, and $2V_2O_5{\cdot}K_2SO_4$, that have been claimed.[8,11,12] When the compounds are heated, SO_3 is liberated. When the mixture is cooled, $K_2O{\cdot}4V_2O_5$ has been posulated to be formed.[13]

No systematic investigation has been performed on the ternary system $K_2S_2O_7$–K_2SO_4–V_2O_5. One paper[13] deals with a system, $K_2O{\cdot}4V_2O_5$–$K_2S_2O_7$, that can be looked upon as the above-mentioned ternary system since K_2O and $K_2S_2O_7$ can combine to form K_2SO_4. However, in this investigation only one melt composition of the ternary system having the molar ratio

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$K_2S_2O_7$:K_2SO_4:V_2O_5 equal to 2:3:6 was examined. The spectra of the cooled melt showed bands similar to the bands in the spectra of the compound $V_2O_5 \cdot K_2S_2O_7$. Another paper[14] describes a more thorough investigation of the ternary system K_2O–V_2O_5–SO_3, which to some extent is analogous to the $K_2S_2O_7$–K_2SO_4 system investigated here. The investigation[14] showed that, besides the three above-mentioned compounds found[7] in the binary V_2O_5–$K_2S_2O_7$ system, the compound $K_3VO_2(SO_4)_2$ could also be isolated.

In $K_2S_2O_7$ solutions dilute with respect to K_2SO_4 and V_2O_5 it was found[3] that the complex $VO_2(SO_4)_2^{3-}$ is probably formed in the temperature range 410–450 °C.

One of the aims of this work is to obtain the molar enthalpies of liquid–liquid mixing (ΔH_{mix}) at 430 °C for the binary system V_2O_5–$K_2S_2O_7$ and for the ternary (or pseudobinary) systems $V_2O_5 \cdot K_2S_2O_7$–K_2SO_4, $V_2O_5 \cdot 2K_2S_2O_7$–K_2SO_4, and $V_2O_5 \cdot 3K_2S_2O_7$–K_2SO_4. The results might give information regarding complex formation in the binary system—often looked upon as the oxidized form of the catalyst—and furthermore tell if the three pyrosulfovanadates in the liquid state can combine with SO_4^{2-}.

Attempts to put forward reasonable structures for the complexes will be made, and their possible importance for the oxidation of SO_2 will be discussed.

Experimental Section

Materials. Handling of the hygroscopic $K_2S_2O_7$ and premixing of $K_2S_2O_7$ with V_2O_5 were performed in a glovebox with a dry argon atmosphere (dried continuously) with less than 2 ppm of water. Sufficently dry and pure $K_2S_2O_7$ seems not to be commercially available,[3] and it was therefore synthesized as earlier described[3] by thermal decomposition of $K_2S_2O_8$ (Merck, Pro Analysi, maximum 0.001% N). In this way $K_2S_2O_7$ was obtained with contamination by $KHSO_4$ and K_2SO_4, probably less than 1 and 2%, respectively.[2] In order to obtain convenient pieces of K_2SO_4, the pure salt (Merck, Suprapur, >99%) was heated to just above the melting point of 1069 °C, resolidified immediately, and crushed gently. A weight loss of 0.14% was found during the procedure of melting. This could not be attributed to loss of water since heating of K_2SO_4 to 130 °C for 4 h resulted in a weight loss of only 0.01%. The main contaminant of K_2SO_4 is probably $KHSO_4$, and a content of about 0.5% of this salt in K_2SO_4 could explain the weight loss found due to the decomposition reaction

$$2KHSO_4 \rightarrow K_2SO_4 + H_2SO_4 \qquad (1)$$

where gaseous H_2SO_4 is liberated. V_2O_5 in the form of granules from Cerac (Pure (99.9%)) was used without further purification. The nonhygroscopic compounds V_2O_5 and K_2SO_4 could be stored and handled outside the glovebox.

The Calorimeter. The Calvet microcalorimeter used has been described in detail earlier.[15] It contains two cavities—calorimetric cells—each surrounded by a thermopile consisting of several hundred thermocouples (Pt/Pt–10% Rh). The "hot" junctions are in contact with the surface of the calorimetric cells and the "cold" junctions are placed in the calorimetric block at constant temperature. The two thermopiles are connected in opposition, in this way eliminating thermal perturbations caused by drift of the temperature of the calorimeter or caused by other exterior means. The differential method gives rise to a very stable base line and enhances the sensitivity of the instrument considerably. The calorimetric furnace is regulated automatically, and the fixed experimental temperature is controlled by means of a thermocouple placed in the center of the calorimetric block.

Experimental Technique. All experiments concerning measurements of the heat of mixing were performed by addition of a solid (V_2O_5 or K_2SO_4) to a liquid ($K_2S_2O_7$ or $K_2S_2O_7$–V_2O_5 mixtures). This addition was made by the "indirect drop method", one of several addition methods that have been described earlier.[15] However, in connection with these experiments a modified experimental setup was constructed as shown in Figure 1. The outer quartz tube (B) has an outer diameter of 18 mm and is 600 mm long; the lower 100-mm part fits very closely to the alumina walls of the calorimetric cavity in order to secure an optimized horizontal heat conductivity. The standard-taper joint of borosilicate glass (A) at the top is connected to the quartz tube outside the calorimeter by a taper joint. A gentle gas flow is maintained through the system before and during the experiment. Through the taper joint, two Pyrex or quartz tubes lead into the calorimetric cavity. The inner tube (C) (outer diameter 6 mm) is equipped with a small funnel at the top outside the calorimeter and a hole in the wall just above the smoothly ground end of the glass rod inside the calorimeter. The end of the glass rod also acts as a stopper (E) in the reservior of the outer tube, which is well tightened to the taper joint (A) by conventional fittings consisting of a screw and a silicon packing. Just below the reservoir and in close contact with it, the crucible (F), containing the melt, is found. This quartz or borosilicate crucible has outer dimensions close to the inner dimensions of the tube (B) to optimize the horizontal heat flow. The experiments concerning the heat of mixing were performed as follows: The crystalline V_2O_5 or K_2SO_4 was weighed with an accuracy of 10^{-2} mg. The final weight of the crystals was measured after the dust had been removed from their surface by several drops from about 50 cm. The deviation between the last two preliminary weighings was less than a few hundredths of a milligram before the crystals were accepted as dust free. A crystal, typically with a mass of 10–30 mg, was dropped through the funnel of the tube (C) into the reservoir (D), and the thermal disturbance was registered on a recorder and fed to a system for automatic integration. After the base line was reestablished—usually within 20 min—the tube (C) was raised about 2 cm by manipulation from the outside, allowing the crystal to drop from the reservior into the melt below. The possible thermal effect could be integrated manually from the recorder or—usually—directly by the connected integrator. In both cases calibration was performed by dropping five small gold bullets, with known weights and thermal effects similar to the ones in the experiments, directly into the melt. In order to check the indirect-drop method, experiments with a two-step drop of gold bullets were also performed. No thermal effect could be registered in any case by the final drop of the chemically inert gold bullets from the reservior to the melt. However, different thermal effects were found by dropping gold bullets into the reservior instead of directly into the melt, a consequence of the inhomogeneity of the thermopile system. Values corresponding to the direct drop were therefore applied.

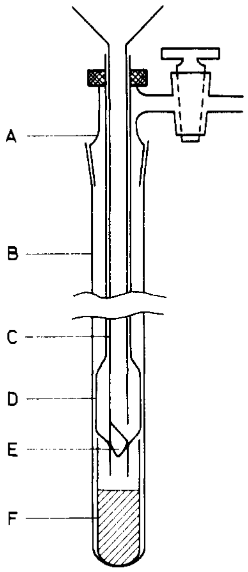

Figure 1. Microcalorimetric device used for the "indirect drop method": A, standard-taper joint; B, outer tube; C, inner tube with funnel at top; D, tube with reservoir; E, stopper connected to inner tube; F, crucible with melt.

Up to 15 additions were made to the same melt in experiments lasting up to 24 h. Each series was usually terminated by weighing the solidified melt in the crucible, in order to check that all the added crystals had reached the melt. In this way the possible escape of volatile components (SO_3 or H_2SO_4) during the experiment could also be checked. For the V_2O_5–$K_2S_2O_7$ system an average loss of 0.6% by weight was found. For the series concerning the ternary system V_2O_5–$K_2S_2O_7$–K_2SO_4 the average weight loss was found to be 0.05%. An experimental series was usually terminated when the point of saturation (indicated by no thermal effect) of the melt was reached. The solidified melt was usually crushed in order to recover the final crystal and thus confirm that saturation was in fact reached.

Sometimes the crystal in the reservoir stuck to the wall, presumably due to a reaction with tiny amounts of volatile compounds from the crucible. In these cases—which occurred frequently when K_2SO_4 crystals were added—the tubes (C and D) were removed, the reservoir was cleaned, and the tubes were remounted in the calorimeter. The experimental series could thereafter be continued when a stable base line was again obtained.

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General Considerations

In the present case, where a solid (B) is dropped into a liquid (A), both at the same temperature, T, the molar enthalpy of liquid–liquid mixing, ΔH_{mix} (at the temperature T), is given by

$$\Delta H_{mix} = \Delta H_{exptl} - X_B(H_{B(l),T} - H_{B(s),T}) \qquad (2)$$

Here ΔH_{exptl} is the molar heat evolved at constant pressure during the experiment, X_B is the mole fraction of the solid, and the term $H_{B(l),T} - H_{B(s),T}$ is the molar heat of fusion of the solid at the temperature T. This molar heat of fusion at 430 °C was by extrapolation found to be 61.84 kJ/mol for V_2O_5 (mp 670 °C) and 49.18 kJ/mol for K_2SO_4 (mp 1069 °C), on the basis of the data in the tables in ref 16.

In the case of the ternary system V_2O_5–$K_2S_2O_7$–K_2SO_4 where the liquid, A, has the composition $V_2O_5{\cdot}nK_2S_2O_7$ (n = 1, 2, or 3), the molar enthalpy of liquid–liquid mixing, ΔH_{mix}, at the temperature T is given by

$$\Delta H_{mix} = \Delta H_{exptl} + \Delta H_{premix} - X_B(H_{B(l),T} - H_{B(s),T}) \qquad (3)$$

where the term ΔH_{premix} is the enthalpy of mixing found for n = 1, 2, or 3 in the binary system V_2O_5–$K_2S_2O_7$. The spread (uncertainty) in the value of the heat of mixing for a particular drop was around ±2%. However, the deviation between the measured value and the true value is probably ±5%.[17] The uncertainty in the temperatures is ±1 °C.

Results and Discussion

The Binary System V_2O_5–$K_2S_2O_7$. The enthalpies of mixing at 430 °C of solid V_2O_5 with liquid $K_2S_2O_7$ (mp 419 °C) were measured for 55 different compositions of the binary system in the liquidus range. In all, seven different experimental series were carried out. In order to reduce the systematic experimental error in a series, some series had initial compositions with different V_2O_5 mole fractions. In this way premixing of V_2O_5 and $K_2S_2O_7$ to the desired initial composition was performed in the drybox before the dropping experiments were carried out. The enthalpy of mixing of the premixed melt was then found by linear interpolation between the two neighboring values found from other experimental series. This value was used in the calculation of the enthalpy of mixing of the series concerned. Thus, all experimental series were related to the same reference composition (i.e. pure molten $K_2S_2O_7$ and V_2O_5). The observed enthalpies (corrected by the calculated heat of fusion of V_2O_5 at 430 °C to obtain the enthalpy of liquid–liquid mixing) are given in Table I in the supplementary data. The initial compositions of the series where premixing was performed are also given. The last addition corresponding to the highest concentration of V_2O_5 in this table (i.e. to $X_{V_2O_5}$ = 0.5176) showed no thermal effects (i.e. the behavior observed with the chemically inert gold bullets). A piece of solid V_2O_5 was also recovered after cooling and crushing of the melt. The calculated solid straight line in Figure 2 at greater values of $X_{V_2O_5}$ will therefore be followed in the composition range from saturation to $X_{V_2O_5}$ = 1. This is a consequence of saturation, resulting in a two-phase system. The positions for the three compounds found in the solid state by the phase diagram investigation[7] mentioned earlier are shown by dashed lines.

The shape of the curve indicates that, at $X_{V_2O_5}$ = 0.33, a complex may be formed while there is no sharp "break" indicating complex formation at $X_{V_2O_5}$ = 0.25 (corresponding to $V_2O_5{\cdot}3K_2S_2O_7$). Progress from pure $K_2S_2O_7$ to the point of saturation with respect to V_2O_5 might therefore be described as follows: In the dilute part of the V_2O_5–$K_2S_2O_7$ system the earlier investigation[3] showed that the monomeric complexes $VO_2SO_4S_2O_7^{3-}$ and $VO_2SO_4^-$ are probably formed. The present investigation at higher concentrations of vanadium shows a local minimum for ΔH_{mix} at $X_{V_2O_5}$ = 0.33, indicating a relatively low entropy at this composition. Such behavior, indicating a high "structural" order in the melt, is probably caused by the formation of a complex achieving its maximum concentration at the molar ratio V_2O_5:$K_2S_2O_7$ = 1:2. When $X_{V_2O_5}$ = 0.33 is exceeded, a steep decrease in ΔH_{mix} is observed, and ΔH_{mix} achieves its lowest value at the point of saturation (i.e. $X_{V_2O_5}$ = 0.502–0.509). This value is in good accordance with the value 0.508 ± 0.003 for the liquidus point at 430 °C obtained from the phase diagram of Glazyrin et al.[7] This further decrease in entropy of the molten mixture indicates an increased "structural order" of the melt.

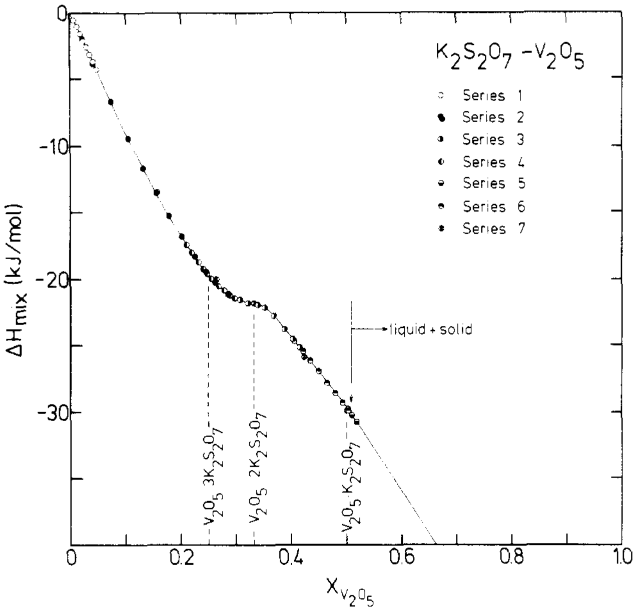

Figure 2. Molar enthalpy of liquid–liquid mixing for the binary system $K_2S_2O_7$–V_2O_5 at 430 °C. The indicated compounds are found by phase diagram studies as described in ref 7.

Due to the large decrease in entropy and the apparently high viscosity and tendency to glass formation of these concentrated melts (i.e. $X_{V_2O_5} \rightarrow 0.5$), polymeric complexes are most probably formed. It is worthwhile here to mention that the break found at $X_{V_2O_5}$ = 0.33 *cannot* be due to a crossing of the liquidus curve of the phase diagram. This can be seen from the work of Glazyrin et al.,[7] but it is also clear on the basis of recent conductivity and density measurements[18] performed in the concentration and temperature ranges $X_{V_2O_5}$ = 0–0.50 and 380–480 °C, respectively.

The partial enthalpy of V_2O_5 at infinite dilution in $K_2S_2O_7$ at 430 °C could be calculated. In the composition range $X_{V_2O_5}$ = 0–0.05 the partial enthalpy was found to be $\Delta H_{V_2O_5} = -91.5 \pm 0.4$ kJ/mol (average of 10 measurements; see supplementary material, Table I). This high negative value adds support to the impression that a chemical reaction takes place on mixing liquid $K_2S_2O_7$ and V_2O_5.

The Ternary System V_2O_5–$K_2S_2O_7$–K_2SO_4. Previously[3] it was found that vanadium sulfato complexes were formed in the V_2O_5–$K_2S_2O_7$ system at low values of $X_{V_2O_5}$ when K_2SO_4 was added. We therefore decided to investigate the possible formation of these types of complexes also at higher values of $X_{V_2O_5}$. This was done by measuring the enthalpies of mixing of solid K_2SO_4 with the molten premixed compositions $V_2O_5{\cdot}K_2S_2O_7$, $V_2O_5{\cdot}2K_2S_2O_7$, and $V_2O_5{\cdot}3K_2S_2O_7$ in the whole liquidus range at 430 °C. As shown by eq 3 the estimation of ΔH_{mix} involves experimentally observed values of ΔH_{mix} from the binary V_2O_5–$K_2S_2O_7$ system. These values are obtained by linear interpolation of the data in Table I (supplementary material). For the compositions $V_2O_5{\cdot}K_2S_2O_7$, $V_2O_5{\cdot}2K_2S_2O_7$, and $V_2O_5{\cdot}3K_2S_2O_7$ the values 30.0, 21.9, and 19.8 kJ/mol are found, respectively. Thus the experimental results given in Table II in the supplementary data correlate the ternary fraction $X_{K_2SO_4}$ with the molar heat of mixing of liquid $K_2S_2O_7$ with V_2O_5 and K_2SO_4 (extrapolated liquid states)

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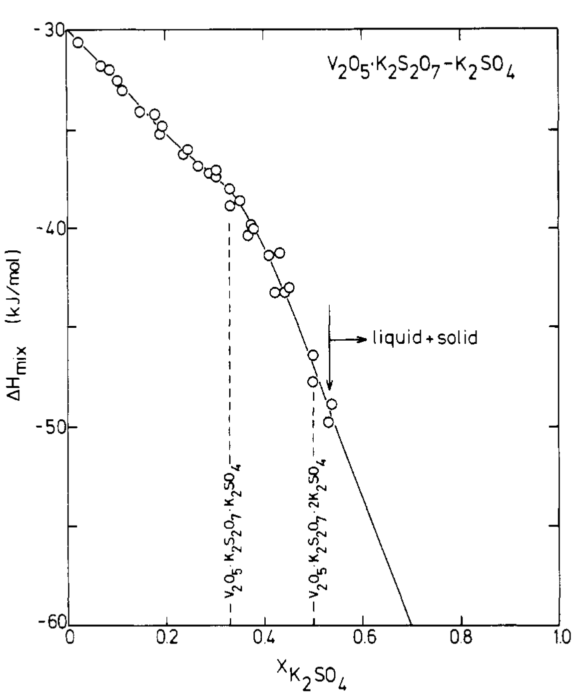

Figure 3. Molar enthalpy of liquid–liquid mixing for the ternary (or pseudobinary) system $V_2O_5{\cdot}K_2S_2O_7-K_2SO_4$ at 430 °C. The compositions of possible compounds formed in the melt are shown by dashed lines.

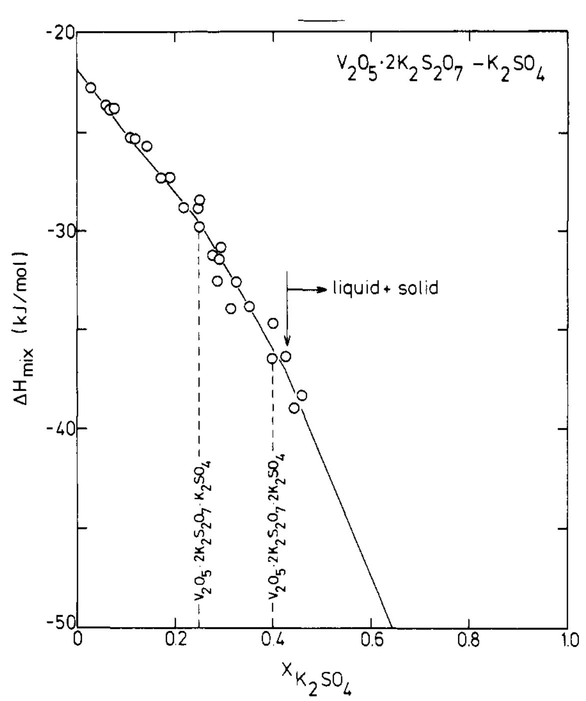

Figure 4. Molar enthalpy of liquid–liquid mixing for the ternary (or pseudobinary) system $V_2O_5{\cdot}2K_2S_2O_7-K_2SO_4$ at 430 °C. The compositions of possible compounds formed in the melt are shown by dashed lines.

at 430 °C. Contrary to the case of the binary $V_2O_5-K_2S_2O_7$ system, all of the experimental ternary series were carried out with molten $V_2O_5{\cdot}nK_2S_2O_7$ (n = 1, 2, or 3) and molten K_2SO_4 as reference composition (i.e. $X_{K_2SO_4} = 0$ initially for all series).

Prior to these experiments an attempt to estimate the heat of mixing of K_2SO_4 in molten $K_2S_2O_7$ at 430 °C failed. This was apparently due to the low solubility[2] ($X_{K_2SO_4(satd)} = 0.0425$) of K_2SO_4 in the melt, giving rise to a dissolution reaction of the crystalline K_2SO_4 too slow to make the heat exchange detectable. Therefore, the observed rather fast dissolution of K_2SO_4 in $K_2S_2O_7$ melts containing V_2O_5 is probably caused by complex formation in the melt, discussed as follows.

A plot of the data for the $V_2O_5{\cdot}K_2S_2O_7-K_2SO_4$ system is given in Figure 3. Around $X_{K_2S_2O_7} = 0.33$ a "break" is found for the exothermic heat of mixing, indicating that a local minimum might occur at this composition (corresponding to $V_2O_5{\cdot}K_2S_2O_7{\cdot}K_2SO_4$). However, this minimum is not very well pronounced due to the occurrence of the even more exothermic heat of mixing in the range $X_{K_2SO_4} = 0.33-0.50$, where the melt becomes saturated with respect to K_2SO_4. The saturation is confirmed by the absence of a thermal effect above $X_{K_2SO_4} = 0.50$ (two points) and the recovery of crystals of K_2SO_4 from the solidified melt. The solid line above $X_{K_2SO_4} = 0.50$ represents extrapolation of the observed ΔH_{mix} values as a consequence of saturation. The arrow indicates the higher limit for the composition at which saturation takes place.

The heat of mixing of around −37 kJ/mol at $X_{K_2SO_4} = 0.33$ is rather high and indicates that higher "order" (decreased entropy) is obtained in the melt. However, at $X_{K_2SO_4}$ exceeding 0.33 further increase of the negative heat of mixing is observed, indicating an even higher "order" in the melt reaching its maximum value at the saturation point (i.e. very close to $X_{K_2SO_4} = 0.50$, corresponding to $V_2O_5{\cdot}K_2S_2O_7{\cdot}2K_2SO_4$).

In the saturated melt $X_{K_2SO_4(satd)} = 0.5005-0.5328$. However, since more than 90% of the K_2SO_4 crystals were recovered from the saturated melt with the high mole fraction, the value for $X_{K_2SO_4(satd)}$ is probably close to 0.50.

A plot of the data for the pseudobinary $V_2O_5{\cdot}2K_2S_2O_7-K_2SO_4$ system is given in Figure 4. In this system a "break" might be present at $X_{K_2SO_4} = 0.25$, which would correspond to the formation of a complex with a molar ratio of vanadium to added sulfate of 2:1.

A further look at Figure 4 shows that also in this system ΔH_{mix} is increasingly exothermic going from $X_{K_2SO_4} = 0.25$ to the saturation value found to be in the range 0.4000–0.4277. The arrow indicates the higher of these limits. Also, here the solid line above the saturation point reflects the values that ΔH_{mix} attains, as a consequence of saturation. Again pieces of K_2SO_4 crystals could be isolated from the saturated melt, indicating that the true saturation value is close to 0.4.

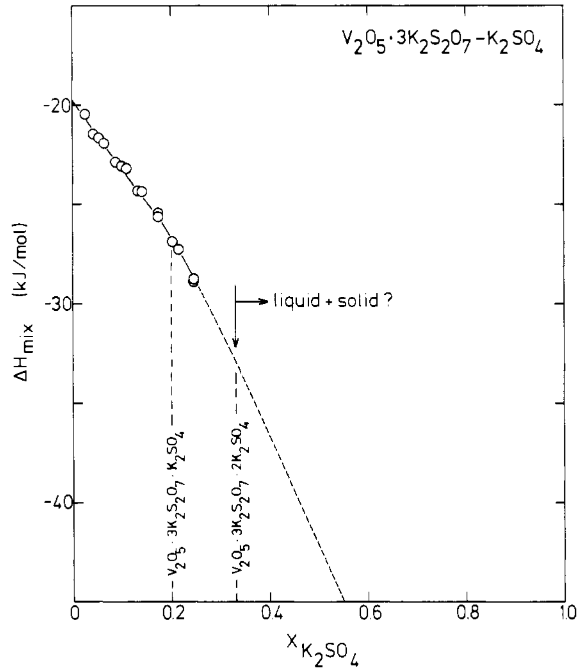

Figure 5. Molar enthalpy of liquid–liquid mixing for the ternary (or pseudobinary) system $V_2O_5{\cdot}3K_2S_2O_7-K_2SO_4$ at 430 °C. The compositions of possible compounds formed in the melt are shown by dashed lines.

A plot of the data for the pseudobinary $V_2O_5{\cdot}3K_2S_2O_7-K_2SO_4$ system is given in Figure 5. Unfortunately, in this case no experimental values could be obtained above $X_{K_2SO_4} = 0.25$ since the dissolution reaction became too slow (more than 2 h) to give rise to a detectable enthalpic effect. The true saturation point might however be at $X = 0.33$, corresponding to the formation

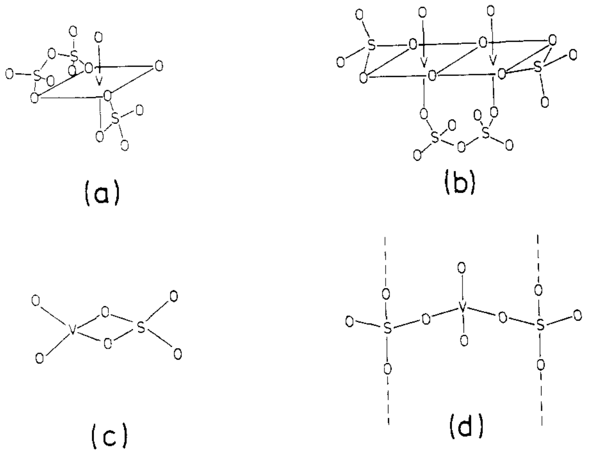

Figure 6. Possible structures of complexes formed in the binary system V_2O_5–$K_2S_2O_7$ at 430 °C: (a) $VO_2SO_4S_2O_7^{3-}$; (b) $(VO_2)_2(SO_4)_2S_2O_7^{4-}$; (c) $VO_2SO_4^-$; (d) $(VO_2SO_4)_n^{n-}$.

of the same species as in the previous systems.

The molar heat of mixing of around −27 kJ/mol at $X_{K_2SO_4} = 0.2$ in the $V_2O_5{\cdot}3K_2S_2O_7$–K_2SO_4 system should be compared with the corresponding values of −30 and −37 kJ/mol in the $V_2O_5{\cdot}2K_2S_2O_7$–K_2SO_4 and $V_2O_5{\cdot}K_2S_2O_7$–K_2SO_4 systems, respectively. This might be due to more pyrosulfate being present in the form of uncoordinated $S_2O_7^{2-}$ ions, thus giving rise to a relatively high entropy.

Possible Complex Structures. The structures of the vanadium(V) complexes that may be formed in the binary V_2O_5–$K_2S_2O_7$ and the ternary V_2O_5–$K_2S_2O_7$–K_2SO_4 systems have not been discussed earlier.

A general feature[7] of the compounds identified from the V_2O_5–$K_2S_2O_7$ system seems to be the presence of the VO_2^+ unit and bidentate coordinate ligands. Furthermore, the VO_2^+ unit, and not the VO^{3+} unit as previously proposed,[19] seems to be stabilized[20,21] in strongly acid aqueous solutions of vanadates. The VO_2^+ unit may therefore be stable in Lewis acid solutions in general (e.g. molten pyrosulfates). The idea of stability of the VO_2^+ unit where the V–O bonds have considerable π-character and where there is a cis arrangement of the oxygen ligands is supported by considerations of metal–ligand orbital interactions[21] and NMR investigations[20,22] on acid aqueous solutions. Tetrahedral and octahedral geometries seem to be the most important states of the V(V) complexes.[21]

In the molten V_2O_5–$K_2S_2O_7$ system at 410–450 °C the monomeric complex $VO_2SO_4^-$ and the solvated form, $VO_2SO_4S_2O_7^{3-}$, seem[3] to be present in dilute solutions (i.e. at low $X_{V_2O_5}$). In the more concentrated part of the binary V_2O_5–$K_2S_2O_7$ system (i.e. at high $X_{V_2O_5}$) the present work indicates that complexes are formed at the molar ratios V_2O_5:$K_2S_2O_7$ = 1:2 and 1:1.

The corresponding reactions may be

$$V_2O_5 + 2S_2O_7^{2-} \rightarrow (VO_2)_2(SO_4)_2S_2O_7^{4-} \quad (4)$$

and

$$V_2O_5 + S_2O_7^{2-} \rightarrow 2VO_2SO_4^- \quad (5)$$

In these concentrated melts the $VO_2SO_4^-$ species is probably present as the polymer $(VO_2SO_4)_n^{n-}$. This accounts for the relatively low entropy and high viscosity observed. The complexes can be looked upon as the anionic part of two of the compounds isolated[7] from V_2O_5–$K_2S_2O_7$ melts. The complex corresponding to the anionic part of the third compound, $VO_2SO_4S_2O_7^{3-}$, or a polymer of this seems not to be very stable at the stoichiometric equivalent composition (i.e. $X_{V_2O_5} = 0.25$). This complex in the monomeric form is, however, stable in more dilute melts (i.e. $X_{V_2O_5} < 0.05$ as mentioned above). That the melt at 430 °C is almost saturated for $X_{V_2O_5} = 0.50$ might in accordance with eq 5 be taken as an indication that V_2O_5 can only dissolve due to a reaction with the solvent.

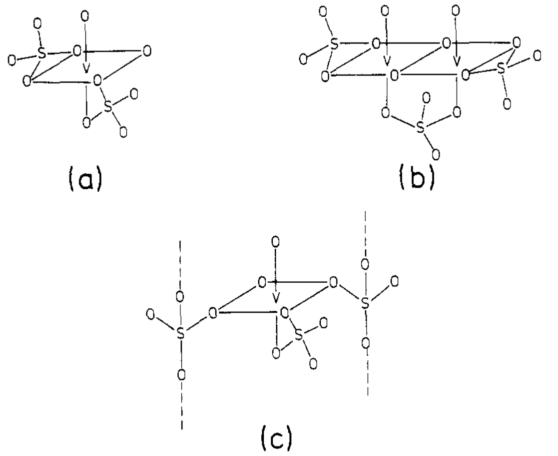

Figure 7. Possible structures of complexes formed in the ternary V_2O_5–$K_2S_2O_7$–K_2SO_4 system at 430 °C: (a) $VO_2(SO_4)_2^{3-}$; (b) $(VO_2)_2(SO_4)_3^{4-}$; (c) $(VO_2(SO_4)_2)_n^{3n-}$.

The most reasonable structures of the above-mentioned complexes are shown in Figure 6, where bidentate coordination by sulfate and pyrosulfate ligands make the preferred 4- and 6-coordinate V(V) complexes possible. For the dimeric complex $(VO_2)_2(SO_4)_2S_2O_7^{4-}$, a structure with two oxygens of the two *cis*-dioxo groups as bridging ligands gives rise to a very compact arrangement where bidentate $S_2O_7^{2-}$ and SO_4^{2-} ligands make a coordination number of 6 possible for both vanadium atoms. If no pyrosulfate is present in the solution (i.e. at high $X_{V_2O_5}$) achievement of this high coordination number might be impossible. Therefore the polymeric structure of $(VO_2SO_4)_n^{n-}$ shown in Figure 6, where sulfate and VO_4 tetrahedra are linked together by sharing corners, is not unreasonable.

In the ternary system with high mole fractions of V_2O_5 and K_2SO_4 studied at present, complexes corresponding to the mole ratios of V_2O_5:K_2SO_4 = 1:1 and 1:2 seem to be formed. Possible reactions giving rise to the formation of these complexes are

$$(VO_2)_2(SO_4)_2S_2O_7^{4-} + SO_4^{2-} \rightleftarrows (VO_2)_2(SO_4)_3^{4-} + S_2O_7^{2-} \quad (6)$$

and

$$VO_2SO_4^- + SO_4^{2-} \rightleftarrows VO_2(SO_4)_2^{3-} \quad (7)$$

The latter reaction is identical with the one proposed in the molten ternary system V_2O_5–$K_2S_2O_7$–K_2SO_4 dilute with respect to V_2O_5 and K_2SO_4.[3] In the concentrated system the relatively low entropy and high viscosity observed at high concentrations of vanadium and sulfate indicate that polymerization could take place also in this system, giving rise to $(VO_2(SO_4)_2)_n^{3n-}$.

The complexes formed in the V_2O_5–$K_2S_2O_7$–K_2SO_4 system could very well have the structures proposed in Figure 7. As in the V_2O_5–$K_2S_2O_7$ system the dimer in this ternary system might "open up", forming chains where sulfato groups link together the vanadium atoms. The coordination number for the central atom might reach 6 by bidentate coordination of the added sulfate group.

Of course the structures put forward here are speculative though reasonable. Attempts to obtain more direct information about the coordination compounds are in progress. NMR, IR, and X-ray investigations on solids and solutions are appropriate to these highly colored, hygroscopic, and viscous melts.

Application to Catalysis. Research concerning the catalytic oxidation of sulfur dioxide has been reviewed.[23,24] Very little is known about the complex formation and redox chemistry of vanadium in the catalyst under operating conditions, and the reaction mechanism is still unresolved. The molten system V_2O_5–$K_2S_2O_7$

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in the mole fraction range $X_{V_2O_5} = 0.22-0.33$ is considered a realistic description of the catalyst. However, the temperature of the melt should be in the range 400–500 °C, and furthermore the melt should be in contact with an $SO_2/O_2/SO_3$ gas mixture in order to correspond to the conditions of operation. Even in the absence of this redox mixture the complexes of vanadium(V) in the $V_2O_5-K_2S_2O_7$ binary system might very well be analogous to the complexes formed during operation of the catalyst. The present results show that the dominating vanadium(V) complex in solution in the mole fraction range $X_{V_2O_5} = 0.22-0.33$ is probably the dimer $(VO_2)_2(SO_4)_2S_2O_7^{4-}$. Furthermore, the results for the ternary $V_2O_5-K_2S_2O_7-K_2SO_4$ system show that the $S_2O_7^{2-}$ group is labile and that a ligand exchange forming $(VO_2)_2(SO_4)_3^{4-}$ can take place. This lability might lead to an exchange of $S_2O_7^{2-}$ with SO_2 during the catalytic reaction, giving rise to the formation of the complex $(VO_2)_2(SO_4)_2SO_2^{2-}$ as the initial step in the catalytic cycle. In this complex a two-electron transfer from SO_2 to the vanadium central atoms forming SO_3 and possibly a V(IV) complex might take place simultaneously.

The redox and complex chemistry of vanadium in similar melts is under investigation.[25-27] Furthermore, an extended calorimetric study involving temperatures other than 430 °C in the range 400–450 °C is under way;[28] conductivity and density measurements are in progress.[18]

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Registry No. KVO_2SO_4, 67163-79-5; $K_4(VO_2)_2(SO_4)_2S_2O_7$, 76569-58-9; $K_3VO_2SO_4S_2O_7$, 76569-57-8; V_2O_5, 1314-62-1; $K_2S_2O_7$, 7790-62-7; K_2SO_4, 7778-80-5.

Supplementary Material Available: Listings of experimental values of molar liquid–liquid enthalpies of mixing for the system $V_2O_5-K_2S_2O_7$ at 430 °C (Table I) and for the three different pseudobinary compositions of the ternary system $V_2O_5-K_2S_2O_7-K_2SO_4$ at 430 °C (Table II) (5 pages). Ordering information is given on any current masthead page.

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Aromatic and Antiaromatic Thiazyl Heterocycles. Comparison of the Structural, Spectroscopic, and Cycloaddition Properties of 1,3,2,4-Benzodithiadiazine, $C_6H_4S_2N_2$, and 1,3,5,2,4-Benzotrithiadiazepine, $C_6H_4S_3N_2$

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Preparative routes to 1,3,2,4-benzodithiadiazine, $C_6H_4S_2N_2$, 1,3,5,2,4-benzotrithiadiazepine, $C_6H_4S_3N_2$, and their respective norbornadiene adducts $C_6H_4S_2N_2 \cdot C_7H_8$ and $C_6H_4S_3N_2 \cdot C_7H_8$ are described. The molecular structures of $C_6H_4S_2N_2$ and the two adducts have been determined by X-ray crystallography. The structural differences between $C_6H_4S_2N_2$ and $C_6H_4S_3N_2$ are related to MNDO molecular orbital calculations on their ground-state electronic structures. The aromatic/antiaromatic characters of the two compounds are discussed in relation to their electronic and ^1H NMR spectra, their electrochemical behavior, and the ease of dissociation of their norbornadiene adducts. Crystal data for $C_6H_4S_2N_2$: monoclinic, space group *Pc*, $a = 5.616$ (1) Å, $b = 3.896$ (1) Å, $c = 15.434$ (3) Å, $\beta = 102.23$ (2)°, $V = 330.0$ Å^3, $Z = 2$ at −115 °C, $R = 0.040$ for 634 reflections with $I > 3\sigma(I)$. Crystal data for $C_6H_4S_2N_2 \cdot C_7H_8$: orthorhombic, space group *Pbca*, $a = 10.230$ (3) Å, $b = 19.922$ (7) Å, $c = 11.221$ (6) Å, $V = 2309$ Å^3, $Z = 8$ at 20 °C, $R = 0.044$ for 1175 reflections with $I > 3\sigma(I)$. Crystal data for $C_6H_4S_3N_2 \cdot C_7H_8$: orthorhombic, space group *Pbca*, $a = 10.571$ (2) Å, $b = 11.914$ (2) Å, $c = 20.027$ (3) Å, $V = 2522$ Å^3, $Z = 8$ at 21 °C, $R = 0.040$ for 2034 reflections with $I > 3\sigma(I)$.

Introduction

The electronic structures of planar binary sulfur–nitrogen rings and related derivatives have been the subjects of many theoretical studies,[2] most of which have focused attention on the structural consequences of the occupation of antibonding π orbitals[3] and on the interpretation of their electronic[4] and MCD[5] spectra. One intriguing question regarding these compounds concerns the relevance of the term aromaticity in discussing their chemical properties. The preponderance of planar cyclic $4n + 2$ π-systems, e.g. $S_5N_5^+$, $S_4N_4^{2+}$, $S_4N_3^+$, $S_3N_3^-$, S_2N_2, provides an appealing argument for the applicability of the Hückel rule. However, more detailed studies of the potential analogies between these inorganic

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