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Complex Formation in Pyrosulfate Melts. 4. Density, Potentiometry, Calorimetry, and Conductivity of the Systems $Cs_2S_2O_7$–V_2O_5, $Cs_2S_2O_7$–Cs_2SO_4, and $Cs_2S_2O_7$–Cs_2SO_4–V_2O_5 in the Temperature Range 340–550 °C

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Four different methods of investigation have been applied at 340–550 °C to solutions of V_2O_5 in $Cs_2S_2O_7$ or in the $Cs_2S_2O_7$–Cs_2SO_4 molten system. Fundamental physico-chemical data and evidence of complex formation in these catalytically important melts have been obtained in the temperature range of working industrial catalysts. From the potentiometric measurements the mole fractions of Cs_2SO_4 in molten $Cs_2S_2O_7$ saturated with Cs_2SO_4 at 470, 480, 490, and 500 °C were found to be 0.06844, 0.07550, 0.08244, and 0.09000, respectively. From these values the solubility products, $K_s(T)$, for Cs_2SO_4 have been obtained and $\Delta H° = 42.4(4)$, i.e. 42.4 ± 0.4 kJ/mol, for the dissolution process at 470–500 °C could be calculated. The potentiometric measurements of dilute solutions of V_2O_5, i.e. in the mole fraction range $X_{V_2O_5} = 0.007\,25$–$0.007\,55$, in the $Cs_2S_2O_7$–Cs_2SO_4 molten system at 470–500 °C, could best be explained by the reaction $(VO_2)_2(SO_4)_2S_2O_7^{4-}$ (or possibly formulated as $(VO)_2O(SO_4)_4^{4-}$) + $SO_4^{2-} \rightleftharpoons (VO_2)_2(SO_4)_3^{4-} + S_2O_7^{2-}$, where the equilibrium constant at 470 °C was found to be 46.4. Including more concentrated solutions of V_2O_5 in $Cs_2S_2O_7$, i.e. $X_{V_2O_5} = 0$–0.5, the measured densities and the previously measured conductivities have been fitted to the general polynomial $\rho = \sum_0^n A_n X^n + \sum_1^m B_m (t - 500)^m$ and $\kappa = \sum_0^n A_n X^n + \sum_1^m B_m (t - 450)^m + \sum_1^l C_l^R X^l (t - 450)$, respectively. The calculated excess molar volumes and molar conductivities exhibit a large deviation from ideality. Together with the observed strongly exothermic enthalpy of liquid–liquid mixing found by calorimetry, this shows that a pronounced interaction between the components in the molten binary $Cs_2S_2O_7$–V_2O_5 system takes place, probably leading to the formation of dimeric V(V) complexes such as $(VO_2)_2(SO_4)_2S_2O_7^{4-}$, (or$(VO)_2O(SO_4)_4^{4-}$) as in the dilute solutions and polymeric complexes like $(VO_4SO_4)_n^{n-}$.

Introduction

The molten system $M_2S_2O_7$–V_2O_5 (M = alkali metal) in the temperature range 400–600 °C is considered[2] a realistic model of the working industrial catalyst used for the production of sulfuric acid. In systems with cesium as the alkali metal an enhanced catalytic activity has been observed,[3–5] but virtually no fundamental physico–chemical data or data on the complex chemistry of the $Cs_2S_2O_7$–V_2O_5 or the $Cs_2S_2O_7$–Cs_2SO_4–V_2O_5 systems are available in the literature.

Very recently[6] we have examined the phase diagram of the $Cs_2S_2O_7$–V_2O_5 system on the basis of conductivity measurements in the temperature range 300–500 °C, i.e. covering both the solid and the liquid region. The present paper is concerned with density, potentiometric, and calorimetric measurements of the molten $Cs_2S_2O_7$–V_2O_5 system. On the basis of these data and the conductivity data measured earlier in the liquid region, the possible complex formation in the melts is discussed.

Our previous studies[6–9] using thermal, electrochemical, and spectroscopic methods of the molten $K_2S_2O_7$–V_2O_5 and $K_2S_2O_7$–K_2SO_4–V_2O_5 systems have proven useful in predicting complex formation in the melt. Thus vanadium oxo sulfato complexes such as $VO_2SO_4^-$, $VO_2SO_4S_2O_7^{3-}$, $VO_2(SO_4)_2^{3-}$, $(VO_2)_2(SO_4)_2S_2O_7^{4-}$, and $(VO_2)_2(SO_4)_3^{4-}$ and the polymeric complexes $(VO_2SO_4)_n^{n-}$ and $(VO_2(SO_4)_2)_n^{3n-}$ seem to be formed depending on the mole fraction, $X_{V_2O_5}$, of the mixture.

It has been claimed[10] that the compounds $CsVO_2SO_4$ and $Cs_4(VO_2)_2(SO_4)_2S_2O_7$ are formed by fusing V_2O_5 and $Cs_2S_2O_7$, indicating the possible existence of some of the above mentioned complexes in the melt. The conductivity of $Cs_2S_2O_7$–V_2O_5 mixtures has been reported.[11,12] However, these experiments are inconsistent and seem to be influenced by a considerable error, possibly due to contaminated chemicals (i.e. by $CsHSO_4$ in the $Cs_2S_2O_7$ used) or by errors in the experimental setup.

The work presented here involves the use of some of the few methods that can be applied to the study of these very dark, viscous, and hygroscopic melts.

Experimental Section

Materials. Pure and dry $Cs_2S_2O_7$ was obtained by thermal decomposition of $Cs_2S_2O_8$ synthesized in the laboratory.[6,13] V_2O_5 was from CERAC (pure, 99.9%), and Cs_2SO_4, from Merck (Pro Analysi, >99.5%). All handling of chemicals took place in a nitrogen- or an argon-filled glovebox with a measured water content of about 5 ppm and continuous gas purification by forced recirculation through external molecular sieves. The hygroscopic $Cs_2S_2O_7$ was kept in sealed ampules until used in the glovebox since contact with water leads to formation of $CsHSO_4$.

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Density. The densities of the $Cs_2S_2O_7$–V_2O_5 molten salt system have been measured by two experimental methods: In dilute solutions ($X_{V_2O_5} \leq 0.2$), the "automated float method"[14,15] was used. It is based on magnetic detection of quartz floats with iron cores as they pass a differential transformer. The densities of the floats used were calculated on the basis of 10 or more determinations at room temperature and corrected for the thermal expansion of quartz at the measuring temperature. Two different temperatures were obtained depending on whether the float sank (during heating of the melt) or it rose (during cooling). From these two temperatures, the density of the float, and the distance the float had to move to reach the magnetic detector, the temperature at which the float and melt had the same density could be obtained with a standard error of 0.5 °C. The furnace and its regulation has been described in detail earlier.[14] Unfortunately this method is inadequate when the viscosity of the liquid is high. For the present system this limit is reached when the mole fraction of V_2O_5 is greater than 0.2. In the second experimental method the densities were obtained from the Archimedian principle by measuring the apparent weight of a spherical platinum bob dipped into a quartz crucible containing the melt as described earlier.[7] The density was obtained from the expression

$$\rho_t = \Delta m / V_t \quad (\mathrm{g/cm^3}) \tag{1}$$

where Δm is the weight difference in grams of the bob in argon and in the melt and V_t is the volume of the bob at the temperature t. After each series of measurements the weight of the contents of the crucible was measured. The weight loss did not exceed 1%. This loss is possibly due to decomposition of $Cs_2S_2O_7$ into SO_3 and Cs_2SO_4.

The density and specific conductivity of molten V_2O_5 in the extrapolated liquid state below the melting point of 670 °C was found from the data of Pantony and Vasu.[16] A least-squares fit gave[7] for t in °C the expressions $\rho_t = 3.453 - 1.702 \times 10^{-3}t$ and $\kappa_t = 4919 \exp(-10933/(t + 273.2))$ for the density and conductivity of molten V_2O_5, respectively.

The excess molar volume of the melt, V_t^E, could then be calculated from the densities of the components of the melt and the measured densities.

The densities of the melts containing Cs_2SO_4 were calculated assuming that the mixtures of Cs_2SO_4 with the other components behave ideally (i.e. assuming the densities to be additive). The density of Cs_2SO_4 in the extrapolated liquid state was obtained from ref 17.

Potentiometry. The electrochemical cell has been described in detail earlier.[8] It was made of Pyrex and the two chambers were separated by a borosilicate filter with low porosity. The gold electrodes were sealed vacuum-tight through the cell walls by means of very thin gold foil (15 μm). All additions of chemicals to the cell were made by cutting the stems open in the glovebox. Thereafter the cell was sealed under 0.4 atm of O_2 (equal to around 1 atm at the measuring temperature) and transferred to an aluminum block furnace regulated to within ±0.1 °C as earlier described.[14] Equilibrium was reached slowly, sometimes after up to 30 days, indicated by a stable potential (±0.05 mV/day).

The potentials of electrochemical concentration cells of the following compositions were measured:

Au I	1 atm O_2	solution I $Cs_2S_2O_7$-Cs_2SO_4 or $Cs_2S_2O_7$-Cs_2SO_4-V_2O_5	Pyrex filter	solution II $Cs_2S_2O_7$-Cs_2SO_4 saturated with Cs_2SO_4	1 atm O_2	Au II

The electrode process at each electrode is considered to be $O_2 + 4e^- \rightleftharpoons 2O^{2-}$. The cell potential is given by[18]

$$\Delta E = (1/F)\int_{\mathrm{I}}^{\mathrm{II}} \sum_i t_i(-z_i^{-1}\mathrm{d}\mu_i - {}^2/_4\mathrm{d}\mu_{O^{2-}}) \tag{2}$$

where t_i, z_i, and μ_i are the transference number, charge, and chemical potential of the ith ion, respectively. Since the oxygen pressure and therefore the oxygen activity is the same in both compartments and since the main component of solutions I and II is $Cs_2S_2O_7$, eq 2 can be simplified to

$$\Delta E = -\frac{RT}{2F}\ln\frac{[O^{2-}]_{\mathrm{II}}}{[O^{2-}]_{\mathrm{I}}} \tag{3}$$

as earlier described.[8] On the basis of the calculations given in ref 8, the error by this simplification has been estimated to be around 2 mV in the worst case. As this value is small compared to the measured potentials it is neglected in the present work.

From the equilibrium $2SO_4^{2-} \rightleftharpoons S_2O_7^{2-} + O^{2-}$ with the equilibrium constant $K = [S_2O_7^{2-}][O^{2-}]/[SO_4^{2-}]^2$, where $[S_2O_7^{2-}]$ to a good approximation is constant, a substitution into eq 3 leads to the expression

$$\mathrm{p}SO_4^{2-}(\mathrm{I}) = -(F/(RT\ln 10))\Delta E + \mathrm{p}SO_4^{2-}(\mathrm{II}) \tag{4}$$

where $\mathrm{p}SO_4^{2-}$ is the negative logarithm of the sulfate concentration (mol/L).

When V_2O_5 is added to the measuring compartment, the average experimental coordination number, $\bar{n}$, of SO_4^{2-} to V(V), may be calculated from

$$\bar{n} = \frac{C'_{Cs_2SO_4} + [SO_4^{2-}]_{\mathrm{dec}} - [SO_4^{2-}]_{\mathrm{I}}}{C_{V(V)}} \tag{5}$$

where $C'_{Cs_2SO_4}$ is the concentration of sulfate due to the added Cs_2SO_4, $[SO_4^{2-}]_{\mathrm{dec}}$ is a small correction due to the decomposition of the solvent, and $[SO_4^{2-}]_{\mathrm{I}}$ is the measured sulfate concentration obtained from eq 4.

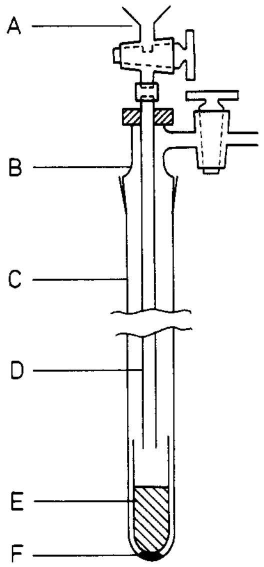

Figure 1. Microcalometric device for the "direct drop method": A, funnel with stopcock for making additions; B, standard taper joint; C, outer tube; D, inner tube; E, crucible with melt; F, kaowool plug.

Calorimetry. The experimental setup used for the "direct drop" calorimetric measurements is outlined in Figure 1. The experimental procedure deviates somewhat from the "indirect drop method" applied earlier on the $K_2S_2O_7$–V_2O_5 system.[9] $Cs_2S_2O_7$ (in some cases premixed with V_2O_5) was weighed into the Pyrex crucible (E) in the glovebox. The outer tube (C) (diameter 18 mm, length 600 mm) was closed with a standard taper joint connected to a funnel (A) through which additions could be made first to a cavity in the barrel of a modified stopcock and later to the melt by turning the barrel. The large tube was evacuated and flushed with argon through another stopcock and then placed in the Calvet calorimeter which was held at a constant temperature of 470 °C. Addition to the crucible of preweighed dust-free V_2O_5 granules through the inner tube (D) was as already mentioned made by turning the modified stopcock. It took between $^1/_2$ and 1 h for equilibrium to be reestablished. In all up to nine additions could be made in an experimental series. Integration of the signal proportional to the evolved/absorbed heat was performed by computer. Calibration was carried out in each series by the addition of preweighed gold pieces to the melt.

A slight decomposition of $Cs_2S_2O_7$ was observed. After each series the crucible was weighted to ensure that the weight loss due to decomposition was low, i.e. less than 1% (w/w). In the last two experimental series the crucible was crushed in order to recover V_2O_5 crystals, as the point of saturation had been reached (indicated by no

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thermal effect other than the heating of the crystal from room temperature to the experimental temperature). The Calvet microcalorimeter used has been described in detail earlier.[19]

The molar enthalpy of liquid–liquid mixing, ΔH_{mix}, when a solid (B) at room temperature, T_{amb}, is dropped into a liquid (A) at temperature T, is given by eq 6, where Δh_{exp} is the heat evolved or absorbed at constant

$$\Delta H_{\text{mix}} = \frac{\Delta h_{\text{exp}} - n_{\text{B}}\int_{T_{\text{amb}}}^{T} C_p(\text{B})(\delta T) - n_{\text{B}}[\Delta H_f(\text{B},T)]}{n_{\text{A}} + n_{\text{B}}} \qquad (6)$$

pressure during the experiment, n_A and n_B are the number of moles of A and B, respectively, $C_p(\text{B})$ is the heat capacity of B, and $\Delta H_f(\text{B},T)$ is the molar enthalpy of fusion of B extrapolated to the temperature T. The molar heat of fusion at 470 °C was found to be 62.06 kJ/mol for V_2O_5 (mp 670 °C) based on extrapolation from the data in ref 20.

When a premix of $Cs_2S_2O_7$–V_2O_5 was used, the initial value of ΔH_{mix} was calculated from the previous experiments. The uncertainty in the value of the heat of mixing for a particular drop was around ±2%. The uncertainty in the temperature was ±1 °C.

Conductivity. All experimental details concerning the conductivity measurements have been given previously,[6] and the measured values are tabulated in the supplementary material of that paper.

The conductivity of ionic melts is usually exponentially related to the temperature by the equation

$$\kappa = A_\kappa e^{-E_\kappa/RT} \qquad (7)$$

where κ is the conductivity, A_κ is a constant, E_κ is the activation energy necessary to promote the ionic migration, and R and T have their usual meanings. The equivalent conductivity Λ of a conducting species present in the molar concentration C is given by the following classic equations:

$$\Lambda = (\kappa/C)1000 \qquad (8)$$

$$\Lambda = A_\Lambda e^{-E_\Lambda/RT} \qquad (9)$$

The experimental molar conductivity, Λ_{exptl}, at a given composition and temperature is expressed by

$$\Lambda_{\text{exptl}} = \kappa V^{\text{M}} \qquad (10)$$

where V^{M} is the molar volume of the melt calculated from the composition and the measured density of the melt.

As previously,[7] in order to discuss possible complex formation in the melt, Λ_{exptl} should be compared to a calculated value for "simplest solutions" (Delimarskii and Markov[21]):

$$\Lambda_{\text{calc}} = X_1\Lambda_1 + X_2\Lambda_2 + 2X_1X_2\Lambda_1 \quad (\Lambda_1 < \Lambda_2) \qquad (11)$$

where X_1 and X_2 are the mole fractions and Λ_1 and Λ_2 are the molar conductivities of the components, respectively.

Results and Discussion

Density Measurements of the Molten $Cs_2S_2O_7$–V_2O_5 System. The experimental densities and temperatures of the $Cs_2S_2O_7$–V_2O_5 system are given in Table A of the supplementary material. Eight different compositions have been investigated; the highest measuring temperature was 552 °C, and the lowest temperature was 436 °C. The highest composition investigated, $X_{V_2O_5} = 0.499$, is close to the solubility limit according to the phase diagram.[6] A comparison of the values of the density obtained from the two experimental methods can be made for the pure $Cs_2S_2O_7$ melt and for the mixture with the composition $X_{V_2O_5} = 0.1$. Figure 2 shows good agreement between the two methods.

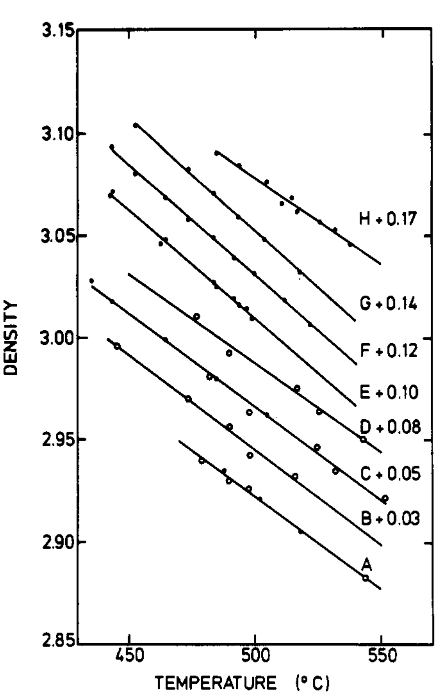

Figure 2. Density of the molten $Cs_2S_2O_7$–V_2O_5 system for the following compositions $X_{V_2O_5}$: A, 0.000; B, 0.050; C, 0.100; D, 0.200; E, 0.300; F, 0.349; G, 0.397; H, 0.499. Filled circles: Archimedian method. Open circles: Automated float method. For clarity, the data (except for composition A) are offset on the ordinate by the specified values.

Table I. Linear Density Equations[a] and Excess Molar Volumes of the Molten $Cs_2S_2O_7$–V_2O_5 System

$X(V_2O_5)$	$A(X)$, g/mL	$10^3B(X)$, g/mL	SD, g/mL	V^E at 500 °C, mL/mol
0.000	2.9222(15)	–0.907(28)	0.001	0.000
0.050	2.9149(30)	–0.936(57)	0.002	–0.02(18)
0.100	2.9151(25)	–0.927(22)	0.002	–0.42(31)
0.200	2.9074(32)	–0.879(60)	0.002	–0.85(58)
0.300	2.9094(17)	–1.078(26)	0.002	–1.75(86)
0.349	2.9106(11)	–1.102(14)	0.001	–2.2(10)
0.397	2.9126(10)	–1.118(18)	0.001	–2.7(11)
0.499	2.9090(23)	–0.852(46)	0.002	–3.3(14)

[a] $\rho = A(X) + B(X)(t - 500)$.

For each composition investigated (using all the data obtained), a linear equation[14] $\rho = A(X) + B(X)(t - 500)$ fits the experimental points well. The values of the coefficients $A(X)$ and $B(X)$ are given in Table I for each value of $X_{V_2O_5}$ investigated. In Figure 2 the experimental densities are plotted versus temperature and compared with the linear analytic expressions given in Table I. For general use an empirical equation for the density at all temperatures and compositions in the ranges investigated is also calculated. This equation is of the same form as the one used for the $K_2S_2O_7$–V_2O_5 system, i.e. $\rho = \sum_0^n A_n X^n + \sum_1^m B_m(t - 500)^m$. The most satisfactory equation for the density in the temperature range 430–540 °C was found to be $\rho = 2.9221 - 0.1302X + 0.453X^2 - 0.459X^3 - 9.813 \times 10^{-4}(t - 500)$ g/mL with SD = 0.0030 g/mL.

As an example, the excess molar volumes at 500 °C of the molten $Cs_2S_2O_7$–V_2O_5 system as a function of the composition are given in Table I and shown in Figure 3. The densities of the melt at each composition are taken from Table I, and the density of V_2O_5 is calculated as described in the Experimental Section. The excess molar volume has about the same magnitude as that found in the molten $K_2S_2O_7$–V_2O_5 system[7] but the $X_{V_2O_5}$ value of the minimum is different. For the $K_2S_2O_7$–V_2O_5 system the minimum was found at around $X_{V_2O_5} = 0.33$ while in the present $Cs_2S_2O_7$–V_2O_5 system the minimum is found at a higher mole fraction of $X_{V_2O_5}$. Unfortunately it is not possible to measure the density at 500 °C at $X_{V_2O_5} > 0.5$ according to the phase diagram.[6] The increased deviation from ideality up to $X_{V_2O_5} = 0.5$ points to an increasing extent of complex formation taking place in the melt in this composition range.

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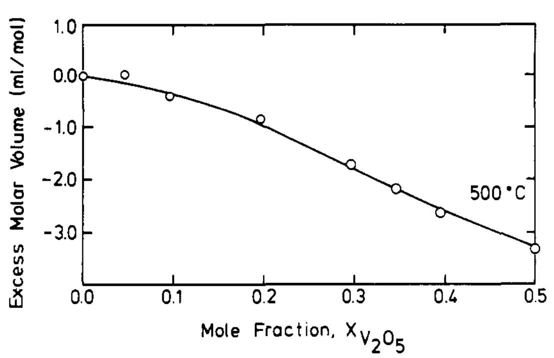

Figure 3. Excess molar volume isotherm for the molten $Cs_2S_2O_7$–V_2O_5 system.

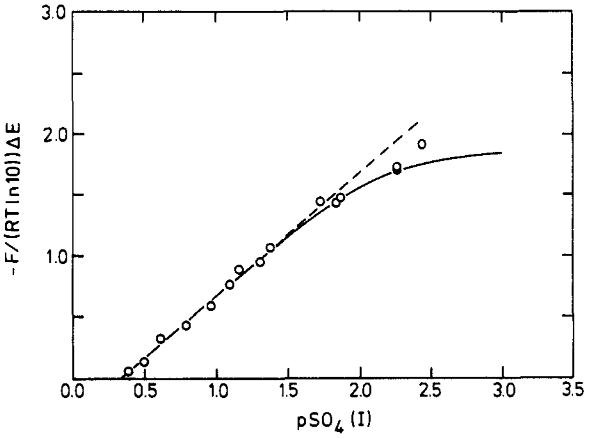

Figure 4. Measured potential as a function of the concentration of sulfate in the measuring chamber at 470 °C. The curve is drawn on the basis of a value of p*K* = 5.24 for the decomposition reaction of $Cs_2S_2O_7$.

Table II. Compositions of Saturated $Cs_2S_2O_7$–Cs_2SO_4 Melts in the Temperature Range 470–500 °C[a]

temp, °C	mol fracn $X_{Cs_2SO_4}$	pSO_4^{2-}	$[SO_4^{2-}]$, mol/L	$[Cs^+]$, mol/L	K_s, $(mol/L)^3$
470	0.06844	0.3327	0.4648	13.582	85.737
480	0.07550	0.2906	0.5122	13.568	94.297
490	0.08244	0.2528	0.5588	13.556	102.682
500	0.08999	0.2150	0.6095	13.545	111.823

[a] $K_s = [Cs^+]^2[SO_4^{2-}]$.

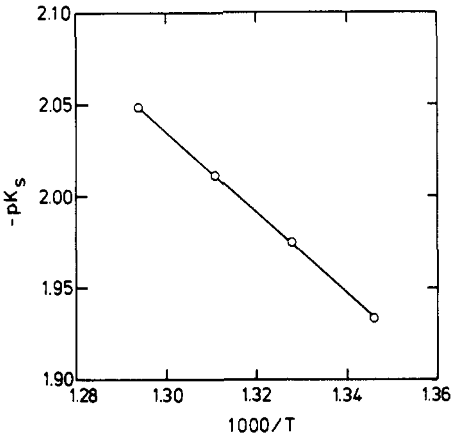

Figure 5. $-pK_s$ vs $1/T$ for the dissolution reaction $Cs_2SO_4(s) \rightleftharpoons 2Cs^+ + SO_4^{2-}$ in $Cs_2S_2O_7$.

Potentiometric Measurements of the Systems $Cs_2S_2O_7$–Cs_2SO_4 and $Cs_2S_2O_7$–Cs_2SO_4–V_2O_5 in the Temperature Range 470–500 °C. The main purpose of these measurements was to investigate the possible coordination of SO_4^{2-} to vanadium in molten $Cs_2S_2O_7$. Thus, it was necessary to know pSO_4^{2-}(II), i.e. the sulfate concentration in the saturated reference melt at the desired temperatures. Table B of the supplementary material shows the potentials measured at 470, 480, 490, and 500 °C between the saturated reference chamber (II) and the measuring chamber (I) to which increasing amounts of Cs_2SO_4 have been added. A small correction for the Cs_2SO_4 initially present in the $Cs_2S_2O_7$ was made, obtained by an iterative procedure (as earlier described in detail[8]) leading to a straight line plot of the measured potentials (i.e. a $-(F/RT \ln 10))\Delta E$) versus the concentration of sulfate added in total to the melt (i.e. as $-\log C'_{Cs_2SO_4}$ or pSO_4^{2-}(I)) up to $pSO_4^{2-}(I) = 1.5$. However, at low concentrations of SO_4^{2-} (i.e. $pSO_4^{2-}(I) > \sim 1.5$) deviation from the straight line behavior is observed. This is due to the solvent dissociation equilibrium ($S_2O_7^{2-} \rightleftharpoons SO_4^{2-} + SO_3$) which at low $[SO_4^{2-}]$ gives a considerable contribution to the total sulfate concentration of the melt. At 470 °C values of 0.00492 mol/L ($X_{Cs_2SO_4} = 0.000\,737$) and 5.24 (average of four experimental series) were found for the initial $[SO_4^{2-}]$ and the p*K* value of the solvent dissociation reaction, respectively. The purity of the synthesized $Cs_2S_2O_7$ is therefore higher than 99.9%. For convenience only the data at 470 °C are shown in Figure 4. The slope of the line is 1.007(38), i.e. very close to the value of 1 expected from eq 4. The average of the slopes of the lines at all temperatures was found to be 0.995(8). Employing lines with the slope of 1 at all temperatures gives by extrapolation to $\Delta E = 0$ the concentration of sulfate in the saturated melt, pSO_4^{2-}(II), as shown in Table II. The calculated pK_s values versus $1/T$, for the dissolution process $Cs_2SO_4(s) \rightleftharpoons 2Cs^+ + SO_4^{2-}$ in molten $Cs_2S_2O_7$, are shown in Figure 5. From the slope of the straight line, found by linear regression, a value of 42.4(4) kJ/mol is found for the heat of dissolution of Cs_2SO_4 in $Cs_2S_2O_7$. No values with which to compare are found in the literature; however, a value of 36.7(7) is found[22] for the heat of fusion of Cs_2SO_4 (where the solvent is Cs_2SO_4). The difference might be attributed to the different solvents and the error in ΔH_{fus} of Cs_2SO_4 due to extrapolation from the melting point of Cs_2SO_4 of 1010 °C to the range 470–500 °C. The values of the equilibrium constant (p*K*) for the solvent dissociation reaction at 480, 490, and 500 °C were found to be 5.22, 5.14, and 5.06, respectively. They are however to be taken as tentative values since they are calculated on the basis of only a few measured points at high pSO_4(I). No values to compare with are found in the literature, but they compare well with the value of 5.49 found earlier[8] for molten $K_2S_2O_7$ at 430 °C.

All the measured cell potentials, compositions, and temperatures of the $Cs_2S_2O_7$–Cs_2SO_4–V_2O_5 system contained in the measuring chamber are shown in Table III. The reference chamber contained the molten system $Cs_2S_2O_7$–Cs_2SO_4 saturated with Cs_2SO_4. Values of the average experimental coordination number, $\bar{n}$, of SO_4^{2-} to vanadium have been calculated at all temperatures. The coordination number shows very small variations with temperature, and therefore only the data at 470 °C are shown in Figure 6 for convenience. One cell gave, for the last addition, around $pSO_4^{2-} = 0.9$, an unlikely high value for $\bar{n}$, and trying to reproduce the result, a new cell gave a value close to 0. Both cells were presumably leaking, and the points are therefore omitted in Figure 6. The value of $\bar{n}$ increases from 0.04 to 0.5 with increasing sulfate content of the melt (i.e. decreasing pSO_4^{2-}) up to the limit of saturation. A maximum value of 0.5 for $\bar{n}$ will indicate the presence of dimeric vanadium complexes in the melt coordinating only one SO_4^{2-} ion. A similar picture might be found[8] in the $K_2S_2O_7$–K_2SO_4–V_2O_5 system if the points near K_2SO_4 saturation are considered to be in error to a small extent.

The curve B, shown in Figure 6, is calculated for the equilibrium including dimeric V(V) species

$$(VO_2)_2(SO_4)_2S_2O_7^{4-} + SO_4^{2-} \rightleftharpoons (VO_2)_2(SO_4)_3^{4-} + S_2O_7^{2-} \quad (12)$$

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(22) Deniélou, L.; Fournier, Y.; Petitet, J.-P.; Téqui, C. *Rev. Int. Hautes Temper. Refract.* **1971**, *8*, 119.

Table III. Compositions[a,b] Cell Potentials and Average Coordination Number[c] for the Molten $Cs_2S_2O_7$–Cs_2SO_4–V_2O_5 System in the Temperature Range 470–500 °C

		temp, °C							
		470		480		490		500	
$X_{Cs_2S_2O_7}$	$X_{Cs_2SO_4}$	ΔE, mV	$\bar{n}$	ΔE, mV	$\bar{n}$	ΔE, mV	$\bar{n}$	ΔE, mV	$\bar{n}$
0.911 64	0.000 809	289.2	0.043	293.0	0.039	296.8	0.040	300.6	0.041
0.989 17	0.003 296	240.7	0.13	247.0	0.12	253.4	0.12	260.0	0.12
0.983 73	0.008 782	177.5	0.30	185.3	0.30	192.7	0.30	200.3	0.29
0.976 43	0.016 10	126.2	0.43	132.1	0.41	140.0	0.41	147.4	0.41
0.948 60	0.044 15	39.8	0.50	46.1	0.48	52.6	0.48	50.6	0.49

[a] [V(V)] = 0.10 M. $X_{Cs_2SO_4}$ has been corrected for the sulfate content initially present in the $Cs_2S_2O_7$. $X_{V_2O_5}$ can be found from the mole fractions of the other two components. [c] $\bar{n}$ has been calculated from eq 5.

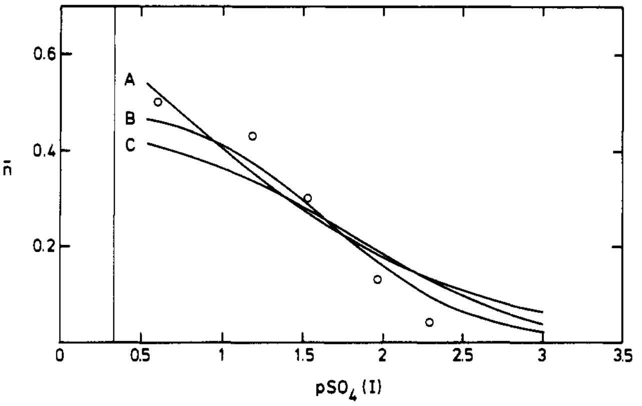

Figure 6. Average experimental coordination number, $\bar{n}$, of sulfate to vanadium in the $Cs_2S_2O_7$–Cs_2SO_4–V_2O_5 system at 470 °C as a function of the concentration of sulfate in the measuring chamber. The calculated curves are for the reactions (A) $VO_2SO_4^- + SO_4^{2-} \rightleftharpoons VO_2(SO_4)_2^{3-}$, (B) $(VO_2)_2(SO_4)_2S_2O_7^{4-} + SO_4^{2-} \rightleftharpoons (VO_2)_2(SO_4)_3^{4-} + S_2O_7^{2-}$, and (C) $2VO_2SO_4^- + SO_4^{2-} \rightleftharpoons (VO_2)_2(SO_4)_3^{4-}$. [V(V)] = 0.10 M. The vertical line indicates the Cs_2SO_4 saturation limit.

where the sulfate neutral dissolution process

$$V_2O_5 + 2S_2O_7^{2-} \rightarrow (VO_2)_2(SO_4)_2S_2O_7^{4-} \qquad (13)$$

is considered to occur initially. The variances for the model equilibria A–C were found to be 0.0045, 0.0022, and 0.0075, respectively, showing that the dimer–dimer equilibrium, eq 12, gives the best—however not significantly the best—fit to the data.

Calorimetric Measurements of the Binary System $Cs_2S_2O_7$–V_2O_5 at 470 °C. The enthalpies of mixing at 470 °C of V_2O_5 with liquid $Cs_2S_2O_7$ (mp 461 °C [6]) were measured at 62 different compositions in the liquidus range of the binary system. The observed enthalpies for all 9 series, corrected for the heat of fusion of V_2O_5 at 470 °C, are given in Table C of the supplementary material including the initial compositions of the series 4–9 of premixed melts. The measured data are displayed in Figure 7. The arrow indicates the composition, $X_{V_2O_5} = 0.4981$, above which no thermal effect other than the heating of the V_2O_5 granule from room temperature to the experimental temperature was observed. Furthermore in series 8 and 9, ending above $X_{V_2O_5} = 0.5$, granules of V_2O_5 were recovered from the crucible after the experiments, supporting the finding that the liquidus point at 470 °C of the binary system indeed is located close to $X_{V_2O_5} = 0.5$. At greater values than $X_{V_2O_5} = 0.5$ the data therefore follows the calculated solid line which ends at $-\Delta H_{fus}$ of V_2O_5 at 470 °C, i.e. at −62.06 kJ/mol, for $X_{V_2O_5} = 1$. The shape of the curve in Figure 7 is very similar to what was found previously[9] for the $K_2S_2O_7$–V_2O_5 binary system. The interpretation of the measurements is therefore also very similar: The increasingly large negative heat of mixing observed in the whole range, $X_{V_2O_5} = 0$–0.5, indicates a strong interaction of the two components by mixing, most probably due to the formation of complexes in the melt. At low values of $X_{V_2O_5}$ the monomeric complexes $VO_2SO_4^-$ and $VO_2SO_4S_2O_7^{3-}$ seem to be formed on the basis of the previous[8] potentiometric, cryoscopic, and spectrophotometric measurements of the molten $K_2S_2O_7$–V_2O_5 system. At higher values of $X_{V_2O_5}$, dimeric complexes like $(VO_2)_2(SO_4)_2S_2O_7^{4-}$ (or the stoichiometrically analogous $(VO)_2O(SO_4)_4^{4-}$ [23] seem to be formed reaching their maximum concentration at $X_{V_2O_5} = 0.33$ corresponding to the reaction

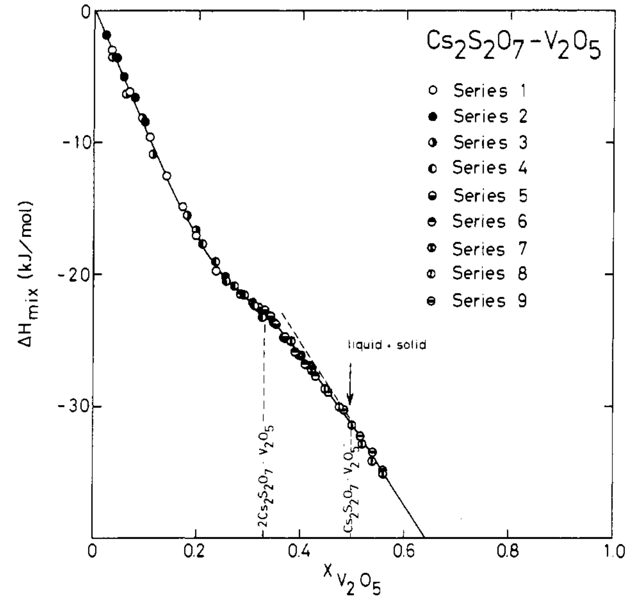

Figure 7. Molar enthalpy of liquid–liquid mixing for the binary system $Cs_2S_2O_7$–V_2O_5 at 470 °C. The indicated compounds are found by phase diagram studies as described in ref 6.

$$V_2O_5 + 2S_2O_7^{2-} \rightarrow (VO_2)_2(SO_4)_2S_2O_7^{4-} \text{ (or } (VO)_2O(SO_4)_4^{4-}) \qquad (14)$$

The formation of this complex probably leads to the tendency toward a local minimum for ΔH_{mix} at $X_{V_2O_5} = 0.33$ as observed in Figure 7. Further addition of V_2O_5 to the melt beyond $X_{V_2O_5} = 0.33$ leads to a rather steep decrease of ΔH_{mix}, indicating an especially strong interaction of the components in this region up to the point of saturation at $X_{V_2O_5} = 0.5$. In addition the high viscosity and the strong tendency[6] to glass formation of the melt by solidification in this region also points to a strong association in the melt probably due to the polymerization reaction

$$(n/4)V_2O_5 + (n/4)(VO_2)_2(SO_4)_2S_2O_7^{4-} \rightleftharpoons (VO_2SO_4)_n^{n-} \qquad (15)$$

This polymeric complex is expected to be formed to a maximum extent at $X_{V_2O_5} = 0.5$, i.e. for V_2O_5:$Cs_2S_2O_7$ = 1:1, corresponding to the reaction

$$nV_2O_5 + nS_2O_7^{2-} \rightarrow 2(VO_2SO_4)_n^{n-} \qquad (16)$$

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(23) To be submitted for publication.

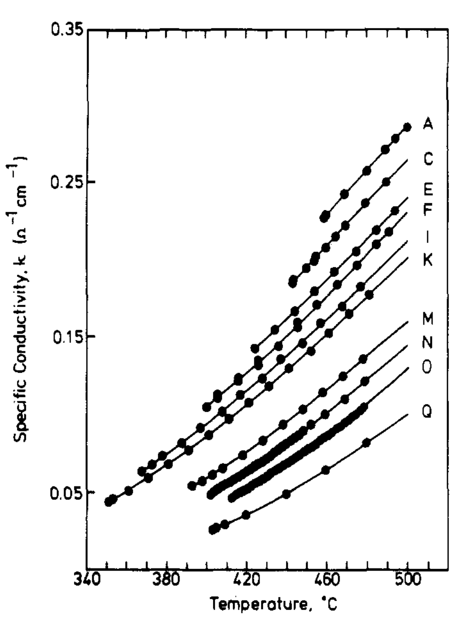

Figure 8. Conductivity of the molten $Cs_2S_2O_7$–V_2O_5 system for the following compositions $X_{V_2O_5}$: A, 0.0000; C, 0.0542; E, 0.0998; F, 0.1149; I, 0.1496; K, 0.1749; M, 0.2534; N, 0.2899; O, 0.3332; Q, 0.4100. Capital letters refer to compositions as in ref 6. Some compositions are omitted for clarity. Polynomials and standard deviations for all the compositions are given in supplementary Table D.

Beyond $X_{V_2O_5} = 0.5$, the liquidus temperature seems to rise steeply according to the phase diagram,[6] indicating that V_2O_5 unwillingly dissolves. This is in agreement with the present investigation and possibly due to the absence of $S_2O_7^{2-}$ in the melt above $X_{V_2O_5} = 0.5$, in accordance with eq 16.

The Ternary System $Cs_2S_2O_7$–Cs_2SO_4–V_2O_5. Ongoing calorimetric measurements at 470 °C of the heat of mixing of Cs_2SO_4 and the molten $Cs_2S_2O_7$–V_2O_5 systems with the composition 2:1 $Cs_2S_2O_7$:V_2O_5 and 1:1 $Cs_2S_2O_7$:V_2O_5, respectively, show a highly exothermic effect and a high solubility above at least the molar ratio 1:1 Cs_2SO_4:V_2O_5. Similarly, spectrophotometric measurements of the ternary system at 470–490 °C confirm the high solubility of Cs_2SO_4 in the melt up to at least the molar ratio 2:1 Cs_2SO_4:V_2O_5 and large changes in the vis/near-IR absorption spectra are observed. This supports the conclusion of the potentiometric measurements and is consistent with the earlier calorimetric measurements[9] of the ternary system $K_2S_2O_7$–K_2SO_4–V_2O_5, which indicate the formation of dimeric and polymeric V(V)-sulfato complexes in the melts.

Conductivity Measurements of the Molten $Cs_2S_2O_7$–V_2O_5 System. The conductivity of the $Cs_2S_2O_7$–V_2O_5 system has been measured[6] at 17 different compositions in the mole fraction range $X_{V_2O_5} = 0$–0.4100. We have fitted the experimental data for the liquid region to polynomials of the type $\kappa = A(X) + B(X)(t - 450) + C(X)(t - 450)^2 + D(X)(t - 450)^3$, where κ is the conductivity in Ω^{-1} cm^{-1} and t is the temperature in °C. In Table D of the supplementary materials, the coefficients are given for the different compositions along with the standard deviations, and in Figure 8, these polynomials are plotted for the different compositions investigated. However, for clarity some compositions are not shown.

In addition, for general use, an empirical equation for the conductivity of the form

$$\kappa = \sum_{0}^{n} A_n X^n + \sum_{1}^{m} B_m (t - 450)^m + \sum_{1}^{l} C_l X^l (t - 450)$$

has been calculated from all the measured conductivities, temperatures, and compositions. The most satisfactory equation was found to be $\kappa = 0.21470 - 0.3811X - 0.4755X^2 + 1.1518X^3 + 1.4551 \times 10^{-3}(t - 450) + 1.8759 \times 10^{-6}(t - 450)^2 - 1.6558 \times 10^{-3}X(t - 450)$ Ω^{-1} cm^{-1} with SD = 0.0016 Ω^{-1} cm^{-1} for the temperature range from the liquidus temperature (see ref 6) to 500 °C and for $0.0000 \leq X_{V_2O_5} \leq 0.4100$.

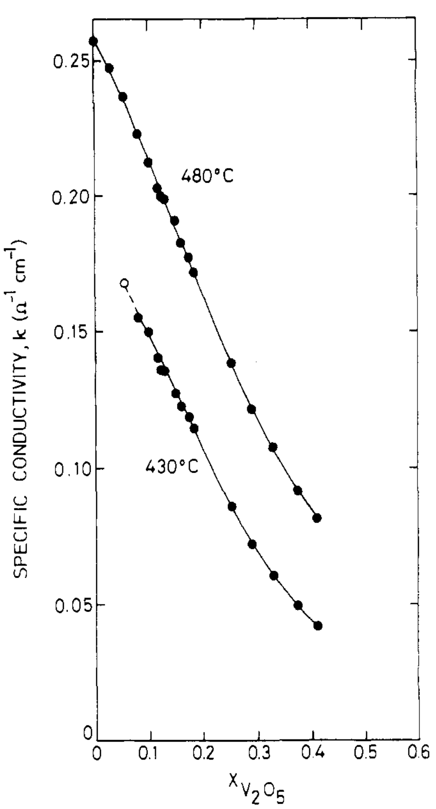

Figure 9. Conductivity isotherms for the molten $Cs_2S_2O_7$–V_2O_5 system. The open circle indicates an extrapolated liquid state.

In Figure 9 plots of the conductivity, κ, vs the composition of the molten part of the $Cs_2S_2O_7$–V_2O_5 system at 430 and 480 °C are shown. Generally the conductivity decreases with decreasing temperature—as should be expected—and with increasing amount of V_2O_5 added to the melt. The conductivity of V_2O_5 in the extrapolated liquid state can be calculated from the polynomial given in the Experimental Section to 8.7×10^{-4} Ω^{-1} cm^{-1} at 430 °C and 2.4×10^{-3} Ω^{-1} cm^{-1} at 480 °C. Thus, the conductivity is indeed expected to decrease steeply with increasing mole fraction of $X_{V_2O_5}$ as is seen in Figure 9. The rather sharp break found[7] in the conductivity isotherm of the molten $K_2S_2O_7$–V_2O_5 system at $X_{V_2O_5} = 0.33$ is, however, not observed in Figure 9.

The conductivity of the $Cs_2S_2O_7$–V_2O_5 system is lower than found previously[7] in the $K_2S_2O_7$–V_2O_5 system. The steep decrease in the conductivity, found by addition of V_2O_5, is similar to the behavior in the $K_2S_2O_7$–V_2O_5 system but in complete disagreement with the earlier measurements at 450 °C of the $Cs_2S_2O_7$–V_2O_5 system,[12] where a *maximum* for the conductivity was found at $X_{V_2O_5} = 0.08$. The conductivity of $Cs_2S_2O_7$ at 450 °C is found to be 0.215 Ω^{-1} cm^{-1} in the present investigation by extrapolation to the subcooled region. This value is not in agreement with the value of around 0.09 Ω^{-1} cm^{-1}, which can be read from the diagram in the earlier work.[12] It compares, however, well with the value of 0.23 Ω^{-1} cm^{-1} which was found in another work.[11] The discrepancies might be due to the use of $Cs_2S_2O_7$ contaminated with $CsHSO_4$ [11] or to the use of electrodes with surface tension-dependent—and thereby also composition-dependent—areas.[12]

On the basis of the measured conductivities and the densities from the general polynomial given above and under the assumption that Cs^+ is carrying all the current, the equivalent conductivity of the cesium ion, Λ_{Cs^+}, can be calculated by applying eq 8. This has been done for each composition in the range $X_{V_2O_5} = 0$–0.4100 and for all temperatures above the liquidus temperatures.[6] Since

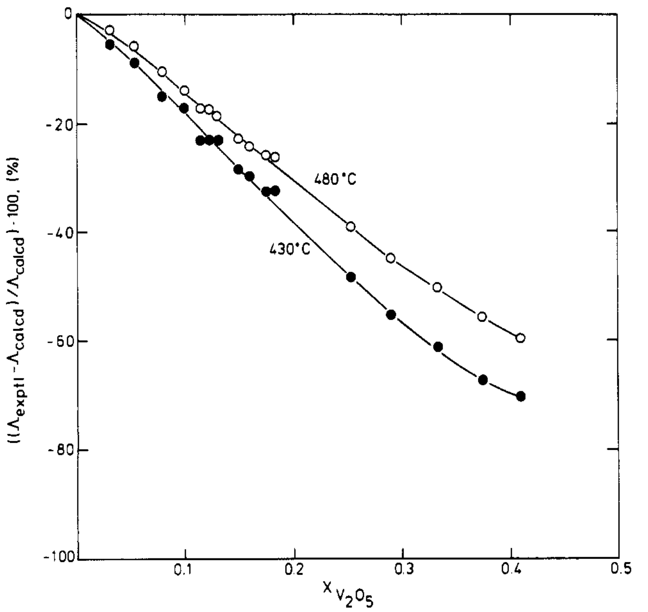

Figure 10. Deviation (%) between the experimental and calculated molar conductivity of the molten $Cs_2S_2O_7$–V_2O_5 system at 430 and 480 °C.

ln Λ_{Cs^+} shows a linear relationship with $1/T$ at all the compositions, it seems reasonable that the cesium ion indeed carries the major part of the current. On the basis of the slope and intercept of these lines and eq 9, E_{Λ,Cs^+} and A_{Λ,Cs^+} can be calculated for each composition as shown in Table E of the supplementary material.

In this table, Λ_{exptl} is also given at two temperatures for each composition, calculated from eq 10. From the conductivities of the pure components, the ideal values of the molar conductivities, Λ_{calcd}, have furthermore been obtained by applying eq 11. The deviation $((\Lambda_{exptl} - \Lambda_{calcd})/\Lambda_{calcd})$ in % is also given in Table E and shown in Figure 10. A large negative deviation from ideality is seen—larger than the 5% which usually[21] is considered a limit for the formation of complexes. The greater the mole fraction of V_2O_5, the greater the deviation, indicating increased formation of complexes with increased amounts of V_2O_5 added to the melt possibly reaching a maximum deviation at $X_{V_2O_5} = 0.5$, where the polymeric complexes, such as $(VO_2SO_4)_n^{n-}$, reach the maximum concentration. Also, the deviation becomes greater as the temperature decreases. This is probably due to an increase in the viscosity due to a larger degree of complex polymerization at lower temperatures.

It is also seen in Table E that the activation energy, E_{Λ,Cs^+}, for the migration of the cesium ion rises as the mole fraction of V_2O_5 is increased. This supports the concept that the formation of polymeric complexes and the viscosity increases in the melt as the V_2O_5 concentration is increased.

Conclusions

All the applied methods of investigation strongly support the concept of complex formation of vanadium in the binary $Cs_2S_2O_7$–V_2O_5 and the ternary $Cs_2S_2O_7$–Cs_2SO_4–V_2O_5 systems. In the melts with low concentrations of vanadium, monomeric and dimeric V(V)–oxo–sulfato complexes like $(VO_2)_2(SO_4)_2S_2O_7^{4-}$ (or the stoichiometric analogue $(VO)_2O(SO_4)_4^{4-}$) and $(VO_2)_2(SO_4)_3^{4-}$, most probably dominate. In melts with compositions that apply to the industrial sulfuric acid catalysts, i.e. for $X_{V_2O_5} > 0.2$, in addition to the dimeric complexes also polymeric complexes like $(VO_2SO_4)_n^{n-}$ are formed to an increasing extent up to $X_{V_2O_5} = 0.5$. These findings compare well with our previous investigations of the analogous K-systems and with the recent phase diagram and compound investigation on the $Cs_2S_2O_7$–V_2O_5 system. However, in the molten $Cs_2S_2O_7$–V_2O_5 system the equilibrium

$$(n/2)(VO_2)_2(SO_4)_2S_2O_7^{4-} \rightleftharpoons (VO_2SO_4)_n^{n-} + (n/2)S_2O_7^{2-} \quad (17)$$

involving the dimeric and polymeric complexes might be shifted to the right to a relatively larger extent than in the $K_2S_2O_7$–V_2O_5 system. Thus the expected breaks on the conductivity curves and the expected minimum of the excess molar volume at $X_{V_2O_5} = 0.33$ might be smeared out. The analogue complex chemistry of V(V) in the molten $K_2S_2O_7$–V_2O_5 and $Cs_2S_2O_7$–V_2O_5 systems is in good agreement with the observation of a very similar catalytic activity of industrial sulfuric acid catalysts, promoted by K or Cs, at relatively high temperatures, where the degree of reduction of V(V) to V(IV) is low.[5] The superior activity of Cs-promoted catalysts observed at lower temperatures[5,13] seems therefore to be caused by a difference in the complex chemistry and compound formation of V(IV) formed by the increased reduction of V(V) by SO_2 at lower temperatures.[24]

Acknowledgment. The Danish Technical Research Council, The Danish Natural Science Research Council, and Myhrwolds Foundation have supported this investigation.

Supplementary Material Available: Table A, listing all measured densities of the $Cs_2S_2O_7$–V_2O_5 system, Table B, listing all measured cell potentials at 470, 480, 490, and 500 °C for 16 different compositions of the molten $Cs_2S_2O_7$–Cs_2SO_4 system, Table C, listing all measured molar enthalpies of liquid–liquid mixing of the $Cs_2S_2O_7$–V_2O_5 system, Table D, giving empirical equations for the specific conductivities measured at 17 different compositions of the molten $Cs_2S_2O_7$–V_2O_5 system in the mole fraction range $X_{V_2O_5} = 0$–0.41, and Table E, listing the experimental and calculated molar conductivities and the parameters for the temperature dependency of the equivalent conductivity of the cesium ion for the 17 different compositions investigated of the molten $Cs_2S_2O_7$–V_2O_5 system (7 pages). Ordering information is given on any current masthead page.

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[24] Work in progress.