Multinuclear NMR studies of V_2O_5–$Cs_2S_2O_7$ melts

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Abstract

^{133}Cs, ^{17}O and ^{51}V static and MAS NMR spectra have been obtained on the solid and molten $Cs_2S_2O_7$–V_2O_5 catalyst model system in the composition range $X_{V_2O_5} = 0$–0.5 and at temperatures up to 550°C. In addition ^{133}Cs and ^{51}V NMR spectra of several vanadates and oxosulfatovanadates(V) are reported. The results indicate that monomeric, dimeric and polymeric V(V) complexes, possibly $VO_2SO_4^-$, $(VO)_2O(SO_4)_4^{4-}$ and $(VO_2SO_4)_n^{n-}$, are formed in the system by increasing mole fraction $X_{V_2O_5}$. For the first time the ^{51}V NMR spectra of V_2O_5 dissolved in molten pyrosulfates are reported.

Keywords: Caesium; Multinuclear NMR studies; NMR studies; Oxosulphatovanadates(V); Vanadia

1. Introduction

This paper represents our first joint study of the $M_2S_2O_7$–V_2O_5 (M = alkali metals) systems. It is a part of our continued efforts to characterize the complexes responsible for the activity of the vanadium based catalysts for SO_2 oxidation. Several studies of these and related systems such as potentiometric, cryoscopic, spectrophotometric, conductometric, calorimetric, X-ray, ESR, infrared and Raman spectroscopic investigations have been made previously by us [1–10] in order to obtain information on the complex formation of vanadium in pyrosulfate melts and the compounds isolated here from. In spite of these efforts detailed information on the chemical nature of the complexes existing in the melts has not yet been obtained, and more information is necessary for the understanding of these systems. Recently

solid-state and high-temperature NMR has proven to be very informative for the studies of vanadium oxide catalysts and related systems [11]. Studies of the $Cs_2S_2O_7$–V_2O_5 system are important owing to the use of Cs as promoter in modified industrial catalysts for SO_2 oxidation. Here we present the ^{51}V, ^{133}Cs and ^{17}O NMR results obtained for the $Cs_2S_2O_7$–V_2O_5 system at room temperature and in the molten state in the temperature range from 380 to 550°C.

2. Experimental

NMR spectra were measured on a Bruker MSL-400 spectrometer. The magnetic field was 9.4 T and the resonance frequency 52.4 MHz for ^{133}Cs, 105.2 MHz for ^{51}V and 54.2 MHz for ^{17}O resonance. For solid samples, pulse durations were 2 μs and for melts they were 30 μs for ^{17}O spectra and 40 μs for ^{133}Cs and ^{51}V spectra. The delay

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times between pulses were for solid samples 1 s and 0.5 s for the ^{133}Cs and ^{51}V, respectively, and for melts 0.1 s for ^{133}Cs, ^{51}V and ^{17}O. The chemical shifts in the ^{133}Cs spectra were measured relative to a 0.1 M aqueous solution of $CsNO_3$, while the ^{51}V NMR spectra were referenced to the signal from $VOCl_3$. The ^{17}O spectra were measured relative to the signal from H_2O.

The high temperature measurements were performed by use of a high-temperature probe head which allowed studies up to 550–600°C. In these experiments the chemical shifts were measured relative to the lines of the standards measured at room temperature.

Magic angle spinning (MAS) was performed in plastic Andrew–Beams rotors at frequencies of about 4 kHz. The measurements of the NMR spectra were performed on samples with natural abundance of the isotopes (100% for ^{133}Cs, 99.97% for ^{51}V, 0.04% for ^{17}O).

Cs_2SO_4 from Novosibirsk Chemical Plant (Pure, 99%) was used after recrystallization. Pure $Cs_2S_2O_7$ was prepared by thermal decomposition of $Cs_2S_2O_8$ at 300°C in a stream of dry nitrogen as described earlier [8]. V_2O_5 was from Cerac (Pure, 99,9%) and used without additional treatment. All preparations took place in a nitrogen filled glove box with a water content less than 5 ppm.

For the NMR measurements, the $Cs_2S_2O_7$–V_2O_5 mixtures were contained in quartz tubes of 10 mm o.d. and ca. 100 mm length and sealed under 0.5 atm O_2 in order to prevent the possible autoreduction of V(V) to paramagnetic V(IV) at high temperatures.

3. Results and discussion

The ^{133}Cs NMR spectra are presented in Figs. 1–4 and their parameters are collected in Table 1. Fig. 1-1 shows the ^{133}Cs NMR MAS spectrum of $Cs_2S_2O_7$ at room temperature. The line in the static spectrum, which is not presented here, is broadened due to dipole, quadrupole interactions and chemical shift anisotropy. The magic angle spin-

Table 1
^{133}Cs isotropic chemical shift values in ppm relative to 0.1 M$CsNO_3$ in water and quadrupole constants e^2qQ/h for cesium sulfates, vanadates, oxosulfatovanadates(V) and $Cs_2S_2O_7$–V_2O_5 mixtures

Compound	Type of Cs site [a]	δ_{iso} [b]	e^2qQ/h [c]
Cs_2SO_4	Cs_1	109	
	Cs_2	74	
$Cs_2S_2O_7$	Cs_1	60	3.3
	Cs_2	40	2.6
	Cs_3	18	2.4
	Cs_4	−3	3.3
$CsLiSO_4$		42	
Cs_3VO_4		−8	
$Cs_4V_2O_7$	Cs_1	−8	
	Cs_2	−25	
$CsVO_3$		−25	
$Cs_2V_6O_{16}$		−55	
$Cs_2V_4O_{11}$		−72	
$CsVO(SO_4)_2$		−5	
$Cs_4(VO)_2O(SO_4)_4$	Cs_1	32	
	Cs_2	20	
	Cs_3	5	
	Cs_4	−17	
$Cs_3VO_2(SO_4)_2$	Cs_1	79	
	Cs_2	−20	
	Cs_3	−62	
$4Cs_2S_2O_7 \cdot V_2O_5$	Cs_1	32	
	Cs_2	20	
	Cs_3	5	
	Cs_4	−17	
	Cs_5	60	
	Cs_6	40	
	Cs_7	18	
	Cs_8	−3	
$2Cs_2S_2O_7 \cdot V_2O_5$	Cs_1	32	
	Cs_2	20	
	Cs_3	5	
	Cs_4	−17	
$Cs_2S_2O_7 \cdot V_2O_5$		−8	

[a] For compounds with two or more non-equivalent Cs atoms, they are indicated as Cs_1, Cs_2 etc.
[b] Isotropic chemical shift δ_{iso} values in ppm obtained from MAS spectra, second order quadrupole correction included.
[c] Quadrupole coupling values in MHz obtained from simulated spectra with anisotropy parameter $\eta \approx 0$.

ning removes the dipole broadening and decreases the second-order quadrupole splitting thus allowing more precise information on the value of the isotropic chemical shift, δ_{iso}, and quadrupole coupling constant e^2qQ/h. Simulation of the ^{133}Cs MAS NMR spectra by use of the full set of spectral parameters shows that four non-equivalent Cs
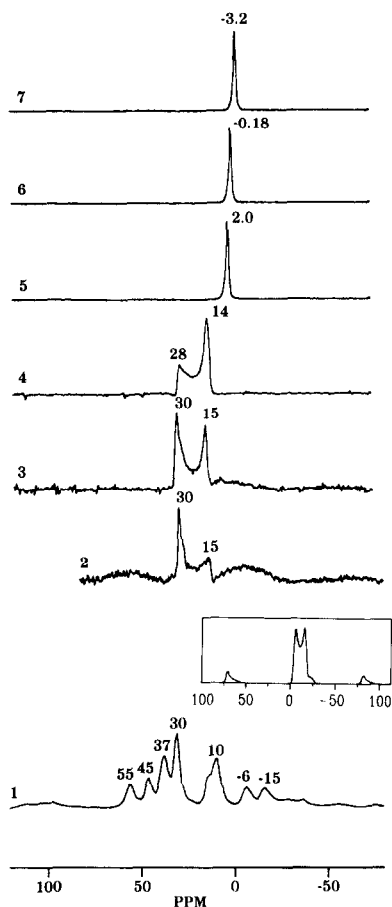
Fig. 1. ^{133}Cs NMR spectra of Cs$_2$S$_2$O$_7$ at different temperatures: 1 – MAS spectrum at 20°C, rotation frequency 4 kHz; 2 – 415°C, 3 – 426°C, 4 – 447°C, 5 – 468°C, 6 – 507°C, 7 – 547°C. Insert: An example of 52.4 MHz ^{133}Cs NMR spectra simulation (central transition) for one Cs site (Cs$_4$) with parameters close to those given in Table 1. Rotation frequency 4 kHz, quadrupole constant 3.3 MHz, axial symmetry, $\delta_\parallel = -61$ ppm, $\delta_\perp = 29$ ppm.

atoms exist in the structure of Cs$_2$S$_2$O$_7$ with the NMR parameters given in Table 1. Four lines in the spectrum of this sample indicate non-equivalence of Cs atoms in the structure of Cs$_2$S$_2$O$_7$ or alternatively that the sample contained several crystal modifications of Cs$_2$S$_2$O$_7$. The crystal structure of Cs$_2$S$_2$O$_7$ has however not been published. Increasing the temperature, changes the spectrum (Fig. 1, spectra 2–7). The spectrum at 415°C exhibits broadened outer lines and a central pattern which is typical for axial anisotropy of the chemical shift. This is most probably due to increased mobility of the Cs$^+$ ions at elevated temperatures. Its motion at these conditions seems

to be anisotropic and is associated with the motion between several selected sites in the structure of the Cs$_2$S$_2$O$_7$ crystal. It is interesting that the shape of the anisotropic line changes upon temperature. This indicates the change of the character of the motion and probable appearance of the new types of motion. More studies of this behavior are necessary to derive a detailed model of the motion of Cs$^+$ ion at temperatures below the melting point. For molten Cs$_2$S$_2$O$_7$ (m.p. 461°C [14]) only a single line, with a chemical shift which is different from the value averaged over different sites in the crystal, is observed. This corresponds to Cs$^+$ ions moving randomly in the melt and not localized in some specific crystal sites. The ^{133}Cs NMR line slightly shifts to high field by increase of the temperature.

Unlike Cs$_2$S$_2$O$_7$, the quadrupole splitting of the second order is not observed in the spectrum of Cs$_2$SO$_4$ where two lines at $\delta = 109$ ppm and $\delta = 74$ ppm (Table 1) are in agreement with two chemically non-equivalent sites in the structure of this compound [15]. Similar values of the chemical shifts for this compound have been reported previously [16].

Five vanadates are known to exist in the V$_2$O$_5$–Cs$_2$O system [17]. Those are orthovanadate Cs$_3$VO$_4$; pyrovanadate Cs$_4$V$_2$O$_7$, metavanadate CsVO$_3$; vanadate Cs$_2$V$_4$O$_{11}$ and vanadate Cs$_2$V$_6$O$_{16}$. We have measured their ^{133}Cs NMR spectra (Fig. 2A) which show that each Cs–vanadate has its characteristic chemical shift with a tendency in accord with the expected decreased attraction between Cs$^+$ and the anion having decreased negative charge density in the series from sample 1 to 5. The quadrupole coupling constants are small; due to this the spectra are not complicated by the quadrupolar effects. Fig. 2B illustrates the ^{51}V spectra of Cs vanadates. They show that by increased vanadium to oxygen ratio the environment of V changes from about regular tetrahedral in ortho- and pyrovanadates to distorted tetrahedral in metavanadate. Further increase of the V/O ratio results in the appearance of distorted octahedral V environment in Cs$_2$V$_4$O$_{11}$ which exists along with tetrahedral V

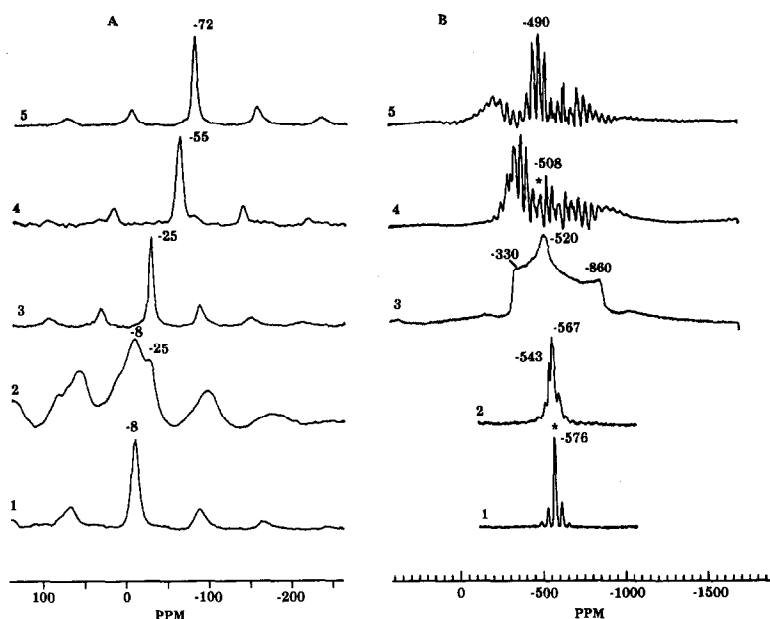Fig. 2. A – ^{133}Cs NMR MAS spectra of Cs vanadates at 20°C: 1 – Cs_3VO_4, 2 – $Cs_4V_2O_7$, 3 – $CsVO_3$, 4 – $Cs_2V_6O_{16}$, 5 – $Cs_2V_4O_{11}$. Rotation frequency 3–4 kHz. B – ^{51}V NMR MAS spectra of Cs vanadates: 1 – Cs_3VO_4, 2 – $Cs_4V_2O_7$, 3 – $CsVO_3$ (static spectrum), 4 – $Cs_2V_6O_{16}$, 5 – $Cs_2V_4O_{11}$.

in this sample. At higher contents of V in the sample ($Cs_2V_6O_{16}$) only V in distorted octahedral environment is present. This trend follows from the general crystallochemical considerations and agrees with results obtained for a number of alkali metal vanadates as pointed out previously [11–13]. The line shape of the ^{51}V NMR spectra in these vanadates also changes from a symmetry typical for V in regular tetrahedra, to a fully anisotropic, typical for V in distorted tetrahedra and to the axially anisotropic, usually observed for distorted octahedral environment of V atoms [11]. For $Cs_2V_4O_{11}$ the superposition of the line with axial anisotropy from V in distorted octahedra and the line from V in nearly regular tetrahedra is observed in the spectrum (Fig. 2B, spectrum 5).

The room temperature ^{51}V and ^{133}Cs NMR spectra of the $Cs_2S_2O_7$–V_2O_5 mixtures, which were prepared at 500°C, are illustrated in Fig. 3. The ^{51}V and ^{133}Cs NMR spectra, static as well as the magic angle spinning spectra, appeared to be very characteristic.

Our previous studies of a large number of V compounds with well defined structure have showed that anisotropy of ^{51}V chemical shift tensor could be used for characterization of the local environment of the V nuclei [11]. In particular, V in isolated tetrahedral sites has chemical shift anisotropies less than 100 ppm, i.e. $\delta_1 \approx \delta_2 \approx \delta_3$; V in slightly distorted tetrahedra demonstrates $\Delta\delta = 100$–300 ppm ($\delta_1 = \delta_2 \neq \delta_3$); V in strongly distorted tetrahedra has $\Delta\delta = 400$–600 ppm ($\delta_1 \neq \delta_2 \neq \delta_3$); V in distorted octahedra produces very broad spectra with $\Delta\delta = 600$–1400 ppm ($\delta_1 \approx \delta_2 \neq \delta_3$).

The sample with $Cs/V = 1$ has a ^{51}V spectrum which is very different from the spectra of the samples with other Cs/V molar ratios (Fig. 3A – spectra 1, 1′). The spectrum exhibits a pattern that is typical for a fully anisotropic δ-tensor and could be attributed to V atoms in a distorted octahedral environment by oxygen atoms with one V–O bond that is considerably shorter than others, as indicated by a value of $\delta_\parallel = -1200$ ppm. The relatively large difference between δ_1 and δ_2 (170 ppm) reflects a non-equivalence of oxygen atoms in the equatorial plane. The ^{133}Cs NMR MAS spectrum shows a single line with $\delta = -8$ ppm and indicates that only one type of Cs sites exists
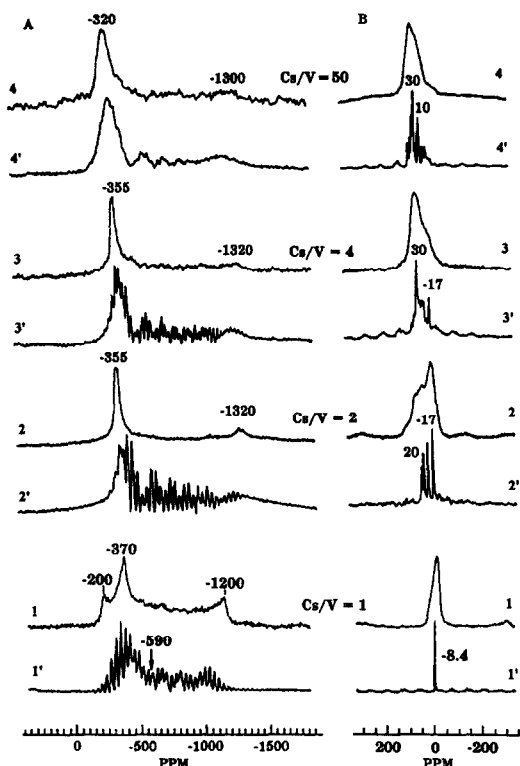
Fig. 3. A – ^{51}V NMR static (1–4) and MAS (1′–4′) spectra of Cs$_2$S$_2$O$_7$–V$_2$O$_5$ mixtures measured at ambient temperature and different Cs/V ratios. The samples were prepared at 500°C. 1, 1′ – Cs/V = 1; 2, 2′ – Cs/V = 2; 3, 3′ – Cs/V = 4; 4, 4′ – Cs/V = 50. B – ^{133}Cs NMR static (1–4) and MAS (1′–4′) spectra of Cs$_2$S$_2$O$_7$–V$_2$O$_5$ mixtures measured at ambient temperature and different Cs/V ratios. The samples were prepared at 500°C. 1, 1′ – Cs/V = 1; 2, 2′ – Cs/V = 2; 3, 3′ – Cs/V = 4; 4, 4′ – Cs/V = 50.

in this sample (Fig. 3B, spectra 1, 1′). The observations of single resonances from V and Cs atoms with NMR parameters different from those for the parent materials (V$_2$O$_5$, Cs$_2$S$_2$O$_7$) clearly reveals the formation of the chemical compound with 1:1 ratio corresponding to a chemical formula CsVO$_2$SO$_4$. Attempts to grow crystals of this compound, suitable for X-ray investigations, are in progress.

For the sample with Cs/V = 2 both ^{51}V and ^{133}Cs NMR spectra are quite different from those for the previous sample (Fig. 3, spectra 2, 2′). The ^{51}V NMR spectrum exhibits a shape which is typical for axial anisotropy of the chemical shift tensor and could be attributed to V in distorted octahedral environment (symmetry C_{2v}). The ^{133}Cs spectrum shows four lines with chemical

shifts in the range from 32 to −17 ppm and is indicative for four non-equivalent Cs sites in this sample. Thus ^{51}V and ^{133}Cs NMR spectra suggest formation of a chemical compound with the composition 2Cs$_2$S$_2$O$_7$·V$_2$O$_5$. The crystal structure of this compound has been reported recently [6] and the formula found to be Cs$_4$(VO)$_2$O(SO$_4$)$_4$, a dimeric vanadium salt. According to the X-ray determination there are indeed four non-equivalent Cs atoms in the structure of this compound having V in distorted octahedral environment, in good agreement with the present ^{133}Cs and ^{51}V NMR data.

The sample with Cs/V = 4 exhibits a ^{51}V spectrum similar to Cs/V = 2 and a ^{133}Cs MAS spectrum which appears to contain superposition of the lines from Cs$_2$S$_2$O$_7$ and the compound with Cs/V = 2 (Fig. 3, spectra 3, 3′). Thus the compounds formed in the sample with Cs/V = 4 are most probably Cs$_4$(VO)$_2$O(SO$_4$)$_4$ as found for Cs/V = 2 and Cs$_2$S$_2$O$_7$.

The dilute sample with Cs/V = 50 has a ^{51}V NMR spectrum also corresponding to V in an octahedral coordination, but broadened due to a glassy state of this sample (Fig. 3-A, spectra 4, 4′). The ^{133}Cs NMR spectrum of this mixture is characterized mostly by Cs$_2$S$_2$O$_7$, the compound that dominates at this molar ratio.

Thus it appears that both ^{51}V and ^{133}Cs NMR spectra are very sensitive to the chemical composition of the samples and therefore NMR can be used to monitor the compound formation in these systems. Accordingly the ^{133}Cs and ^{51}V NMR could be used for monitoring of the state of the active component in real catalysts. It has been claimed that the compounds CsVO$_2$SO$_4$ and Cs$_4$(VO$_2$)$_2$(SO$_4$)$_2$S$_2$O$_7$ and probably Cs$_3$VO$_2$(SO$_4$)$_2$ are formed in the Cs$_2$S$_2$O$_7$–V$_2$O$_5$ or Cs$_2$S$_2$O$_7$–Cs$_2$SO$_4$–V$_2$O$_5$ systems [17]. Density, potentiometry, calorimetry and conductivity measurements [10] of the molten systems supported the concept of complex formation of vanadium in the melts. At low V concentrations most probably the monomeric VO$_2$SO$_4^-$ and dimeric (VO)$_2$O(SO$_4$)$_4^{4-}$ complexes are present while at the composition typical for vanadium catalysts in

addition the polymeric species $(VO_2SO_4)_n^{n-}$ are formed. Comparison of ^{51}V NMR chemical shift parameters for the oxosulfatovanadates(V) formed by $Cs_2S_2O_7$ and V_2O_5 [11] with those for the $Cs_2S_2O_7$–V_2O_5 mixtures measured in this work (Table 2) shows that the corresponding values are very close to each other, thus supporting the formation of chemical compounds with Cs/V ratio 1 and 2, respectively also in this system.

The ^{133}Cs NMR spectra measured at 470°C for the series of $Cs_2S_2O_7$–V_2O_5 melts, show a shift of the ^{133}Cs line by increase of the V concentration (Fig. 4). The data in Fig. 4 suggests an interaction of the Cs^+ cations with oxosulfatovanadate(V) anions in the melt. An exchange reaction between Cs^+ and negatively charged oxosulfatovanadate(V) anions probably takes place in the melt:
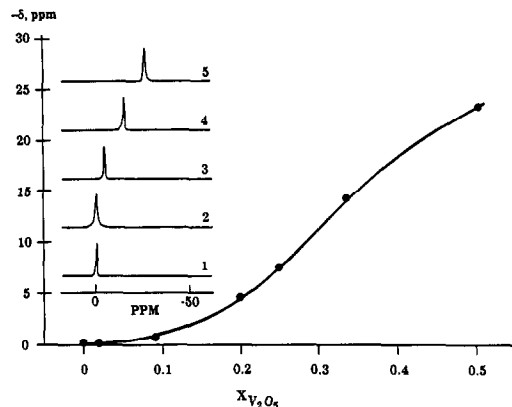
$$V_xO_yS_z^{n-} + Cs^+ \rightleftharpoons V_xO_yS_zCs^{(n-1)-} \qquad (1)$$

Fig. 4. ^{133}Cs NMR spectra of $Cs_2S_2O_7$–V_2O_5 melts measured at 470°C as a function of sample composition, 1 – $Cs_2S_2O_7$, 2 – Cs/V = 50, 3 – Cs/V = 4, 4 – Cs/V = 2, 5 – Cs/V = 1 and a plot of the chemical shift of the ^{133}Cs NMR line of $Cs_2S_2O_7$–V_2O_5 melt at 470°C as a function of sample composition.

The rate of this reaction should be more than the difference in the chemical shifts of Cs in the cationic state and in the complexes with oxosul-

Table 2
Components of ^{51}V chemical shift tensor in ppm (± 10 ppm), relative to $VOCl_3$, for cesium vanadates, oxosulfatovanadates(V) and $Cs_2S_2O_7$–V_2O_5 mixtures

Compound	Type of vanadium sites [a]	δ_1	δ_2	δ_3	δ_{iso} [b]	$\Delta\delta$ [c]
V_2O_5		−310	−310	−1270	−610[†]	960
Cs_3VO_4		−520	−580	−626	−576[†]	106
$Cs_4V_2O_7$	V_1				−543[†]	
	V_2				−567[†]	
$CsVO_3$		−330	−522	−863	−583[†]	533
$Cs_2V_6O_{16}$		−296	−296	−953	−508[†]	657
$Cs_2V_4O_{11}$	V_1^{oct}	−190	−220	−1120	−510	930
	V_2	−445	−455	−825	−575[†]	380
[d] $CsVO_2SO_4$		−284	−340	−1010	−544	726
[d] $CsVO(SO_4)_2$		−220	−263	−1530	−671	1289
[e] $Cs_4(VO_2)_2(SO_4)_2S_2O_7$		−365	−365	−1340	−690	975
[d] $Cs_3VO_2(SO_4)_2$		−201	−297	−1180	−559	931
$50Cs_2S_2O_7$–V_2O_5, glass		−320	−320	−1325	−655	1005
$10Cs_2S_2O_7$–V_2O_5, glass		−320	−320	−1300	−650	980
$4Cs_2S_2O_7$–V_2O_5, cryst.		−355	−355	−1320	−680[†]	965
$3Cs_2S_2O_7$–V_2O_5, glass		−325	−325	−1280	−643	955
$2Cs_2S_2O_7$–V_2O_5, cryst.		−355	−355	−1320	−680[†]	965
$Cs_2S_2O_7$–V_2O_5, cryst.		−200	−370	−1200	−590[†]	905

[a] If a compound has two or more non-equivalent V atoms, they are indicated as V_1, V_2 etc.
[b] For the isotropic chemical shift δ_{iso} the superscript sign † indicates values obtained from isotropic spectra or from MAS spectra. The values of δ_{iso} that are not marked with this sign were calculated as $\delta_{iso} = 1/3(\delta_1 + \delta_2 + \delta_3)$.
[c] Anisotropy of the chemical shift $\Delta\delta$ was measured as $\Delta\delta = |\delta_\perp - \delta_\parallel|$ or $\Delta\delta = |\delta_1 - \delta_3|$ for fully anisotropic spectra, or estimated as the line width at half-height for broadened isotropic spectra.
[d] Values taken from [19]. $CsVO_2SO_4$ was probably not crystalline.
[e] Values taken from [11]. The compound is most probably $Cs_4(VO)_2O(SO_4)_4$ as shown recently by X-ray investigations [6].
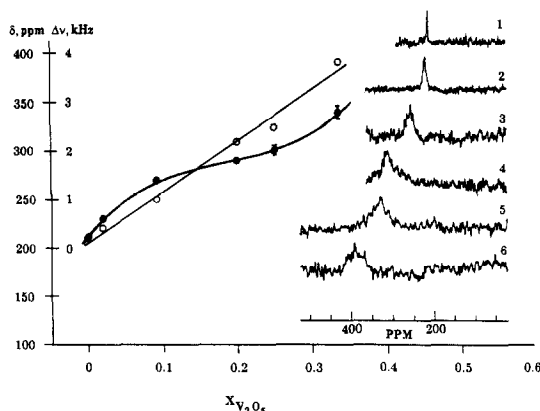
Fig. 5. ^{17}O NMR spectra of $Cs_2S_2O_7$–V_2O_5 melts measured at 500°C as a function of sample composition, 1 – $Cs_2S_2O_7$, 2 – Cs/V = 50, 3 – Cs/V = 10, 4 – Cs/V = 4, 5 – Cs/V = 3, 6 – Cs/V = 2 and a plot of the chemical shift (○) and line width (●) of the ^{17}O NMR line of $Cs_2S_2O_7$–V_2O_5 melts at 500°C as a function of sample composition.

fatovanadate(V) anions, i.e. more than 10^3 Hz at 470°C. Different $V_xO_yS_z^{n-}$ species exist in the melt as it follows from the continuous decrease of the ^{133}Cs chemical shift by increase of the mole fraction of V_2O_5 (Fig. 4). Indeed the δ vs. $X_{V_2O_5}$ plot for the ^{133}Cs NMR spectra indicates complex equilibria takes place in the melt, sensitive to the composition. Probably, the interaction of Cs^+ with monomeric $(0 < X_{V_2O_5} < 0.1)$, dimeric $(0.1 < X_{V_2O_5} < 0.3)$ and polymeric $(0.3 < X_{V_2O_5})$ vanadium species are responsible for the spectral changes. This result is in a good agreement with the previous indications, that by increasing the V content several charged anions, namely, monomeric $VO_2SO_4^-$, dimeric $(VO)_2O(SO_4)_4^{4-}$ and polymeric $(VO_2SO_4)_n^{n-}$ species could be formed, the latter existing at high vanadium concentrations [1,2,4,10,11,14].

The ^{17}O NMR spectra and a plot of the NMR parameters as a function of the mole fraction $X_{V_2O_5}$ of the $Cs_2S_2O_7$–V_2O_5 melt at 500°C are shown in Fig. 5. These results were obtained for ^{17}O in the presence of O_2 (0.5 atm at room temperature in the sample tube). It follows from these spectra that an increase of the V content in the melt leads to a shift of the ^{17}O NMR line to low field and to a large increase of the line width. The changes in the $\Delta\nu_{1/2}$ and δ plots vs. $X_{V_2O_5}$ also indicate a different interaction of oxygen atoms of

the sulfate and pyrosulfate anions with V in the melt. It can be seen that the change of δ and $\Delta\nu_{1/2}$ vs. $X_{V_2O_5}$ is analogous to what was found for the ^{133}Cs spectra; this is therefore also in accord with the presence of monomeric, dimeric and polymeric V species in the melt. Similar results have been obtained earlier for the $K_2S_2O_7$–V_2O_5 system [18] and they were interpreted as the coordination of pyrosulfate anions with V. A similar dependence in the $Cs_2S_2O_7$–V_2O_5 system indicates that the chemistry of both systems is very close to that of the other and that in the $Cs_2S_2O_7$–V_2O_5 system sulfate and/or pyrosulfate anions are coordinated to V. The alternative explanation of the shift and broadening of the ^{17}O NMR line could be the effect of a small amount of paramagnetic V^{4+} species which possibly are formed by the addition of V_2O_5 to the melt. However, this possibility can be ruled out in the present case since the preparation of samples and NMR measurements of the melts have been performed in oxygen atmosphere. Data on the chemical shifts of ^{17}O of sulfate or pyrosulfate oxygen in the $Cs_2S_2O_7$–V_2O_5 system (still not available) are necessary to make conclusions on the structure of the complexes.

Fig. 6 illustrates the first published ^{51}V NMR spectrum of the molten $Cs_2S_2O_7$–V_2O_5 system, in fact of any V_2O_5–alkali pyrosulfate melt. The spectra of the Cs/V = 4 sample were measured at 380°C and at ambient temperature. Previous attempts to record the ^{51}V NMR spectra of the $K_2S_2O_7$–V_2O_5 system failed presumably due to an

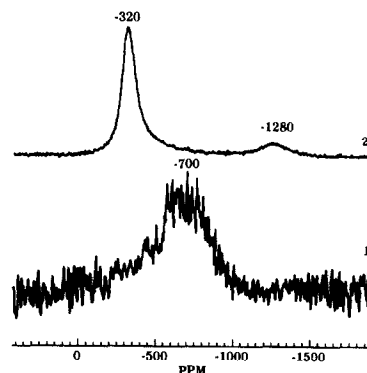Fig. 6. ^{51}V NMR spectrum of the molten $4Cs_2S_2O_7 \cdot V_2O_5$ mixture measured at 380°C – 1 and the spectrum of the same sample (glass) at room temperature – 2.

extremely large line width [11]. It was estimated that the line width should be more than 30 kHz because of a fast relaxation of the V nuclei in large polymeric species having a relatively long correlation time ($\approx 10^{-7}$–10^{-8} s). The chemical shift of the line in the melt is ca. -700 ppm, a value which coincides within the experimental error with $\delta_{iso} = 1/3(2\delta_\perp + \delta_\parallel)$, obtained for the solid crystalline sample (Table 2). The line width for the $4Cs_2S_2O_7 \cdot V_2O_5$ sample was found to be about 60 kHz. This shows, indeed, that the size of the complexes in the melt is large and suggests association of monomeric vanadium complexes most probably forming the dimer ion $(VO)_2O(SO_4)_4^{4-}$. Another aspect of this result is the conclusion that the large line width of the ^{51}V NMR line in the $M_2S_2O_7$–V_2O_5 melts (M = K, Cs) is indeed caused by the low and probably anisotropic mobility of complexes in the melt and not by the effect of paramagnetic tetravalent vanadium. Although a long accumulation time (of several hours) is needed for the registration of the very broad ^{51}V NMR line in these highly viscous and conductive melts, this, the first observation of ^{51}V NMR in the molten state opens new possibilities to study the chemistry of the catalytically important $M_2S_2O_7$–V_2O_5 systems.

Acknowledgements

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