Inorganica Chimica Acta, 39 (1980) 129–136
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Stopped-flow Fourier-transform NMR and NMR Line Broadening Studies of the Rates of Dimethyl Sulphoxide Exchange with the Hexakis(dimethylsulphoxide) Complexes of Aluminium(III), Gallium(III) Ions in Nitromethane Solution

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Received July 25, 1979

Stopped-flow Fourier-transform NMR and conventional NMR line broadening experiments have been used to determine rate data for dimethyl sulphoxide (DMSO) exchange with the $[M(DMSO)_6]^{3+}$ *ions (M = Al(III), Ga(III)) in nitromethane-*d_3 *solution over a temperature range of 105 K (Al(III)) and 112 K (Ga(III)). Data previously reported for* $[Al(DMSO)_6]^{3+}$ *ion have been extended to higher temperatures and a correction made to the published results. At 298.2 K, rate parameters associated with the exchange of a single solvent molecule are: for* $[Ga(DMSO)_6]^{3+}$ *ion,* $k^I_{ex} = 1.87 \pm 0.05\ s^{-1}$, $\Delta H^* = 72.52 \pm 0.48\ kJ\ mol^{-1}$, $\Delta S^* = +3.51 \pm 1.54\ JK^{-1}\ mol^{-1}$; *and for* $[Al(DMSO)_6]^{3+}$ *ion,* $k^I_{ex} = 0.302 \pm 0.017\ s^{-1}$, $\Delta H^* = 82.64 \pm 1.16\ kJ\ mol^{-1}$, $\Delta S^* = 22.31 \pm 3.64\ JK^{-1}\ mol^{-1}$. *The exchange rates are independent of the un-coordinated DMSO concentration, and dissociative mechanisms are postulated in both cases. For* $[In(DMSO)_6]^{3+}$ *ion the rate of solvent exchange is too fast to measure accurately with a 60 MHz spectrometer even at low temperatures.*

Introduction

Rates of solvent exchange between solvates of diamagnetic and paramagnetic metal ions and uncoordinated solvent are widely measured by NMR line broadening methods [1], and it is well known that whereas values of ΔG^* obtained in this way are usually fairly accurate, it is often difficult to estimate values of ΔH^* and ΔS^* with as much precision, and values of ΔS^* are notoriously unreliable in many cases. The problem is especially pronounced for paramagnetic ions as was recently discussed for $[Ni(CH_3CN)_6]^{2+}$ ion [2]. One way of trying to improve the accuracy of ΔH^* and ΔS^* measurements is to extend the temperature range over which rate data are obtained, although for diamagnetic metal ions this is impossible if only line broadening experiments are used, since rate constants are difficult to estimate accurately in the limits of slow and fast exchange. One way of obtaining rate data more accurately in the slow exchange limit is to make use of stopped-flow Fourier-transform NMR (SF-NMR) as described recently for the $[Al(DMSO)_6]^{3+}$ ion [3]. By mixing this ion with an excess of deuterated dimethyl sulphoxide ($[^2H]_6$-DMSO) in nitromethane solution the exchange rate can be measured directly at low temperatures:

$$[M(DMSO)_6]^{3+} + 6[^2H]_6\text{-DMSO} \rightarrow [M([^2H]_6\text{-DMSO})_6]^{3+} + 6DMSO \qquad (1)$$

In this way the temperature range over which rate data may be obtained is considerably extended, and the activation parameters are easier to establish with precision. The good agreement between results from the NMR line-broadening and SF-NMR methods is also gratifying, and shows that any isotope effect associated with reaction (1) is negligible.

In the present study we have extended the study of reactions (1) to M = Ga(III), but attempts to study In(III) were thwarted by the greater rapidity of the reaction which precluded even line-broadening studies at low temperatures. Studies of Al(III) were extended to higher temperatures, by working in $[^2H]_3$-nitromethane solution under conditions where the free and bound DMSO resonances were comparable in magnitude, and these results show that previously reported [3, 4] values of the rate constants in both nitromethane and DMSO solution were incorrectly calculated. A correction has been made to the published values, and the activation parameters re-estimated with the inclusion of the new data reported here.

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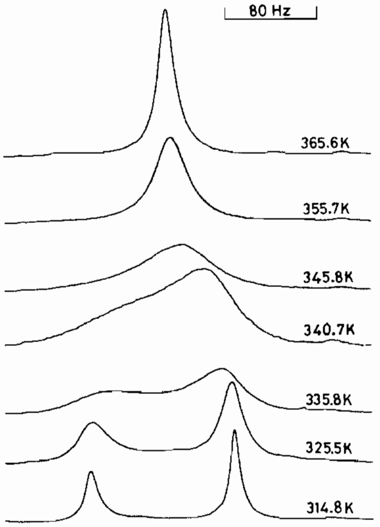

Fig. 1. Variable temperature 60 MHz ^1H NMR spectra of $[Ga(DMSO)_6](ClO_4)_3$ (1.14×10^{-2} molal) and DMSO (7.67×10^{-2} molal) in $[^2H]_3$-CH_3NO_2 solution.

Results

A comparison of data obtained for the $[Ga(DMSO)_6]^{3+}$ ion in $[^2H]_3$-nitromethane solution by the line-broadening and SF-NMR methods is shown in Figs. 1 and 2 respectively. The line-broadening results were fitted by complete line shape analysis to the equations summarised by Lincoln [1], using a non-linear least-squares computer program similar to that described previously [5]. The published program was modified to allow for different transverse relaxation times, T_{2a} and T_{2b}, for the free and bound DMSO resonances respectively, and to include a non-sloping baseline correction. Values of the chemical shift separation, $\delta\omega$, in the slow exchange region between 270 and 335 K were estimated as one of the six parameters in the fitting procedure; these values varied between 30.78 Hz at 270.4 K and 32.63 Hz at 335.8 K, and were extrapolated to higher temperatures by fitting the calculated values to a quadratic function of the absolute temperature, T (equation 2):

$$\delta\omega = 43.65 - 0.1078\ T + (2.234 \times 10^{-4})T^2 \qquad (2)$$

Failure to allow for the variation of $\delta\omega$ with temperature leads to erroneous activation parameters (especially ΔS^*) and is illustrated by the dashed line in Fig. 3. Rate constants associated with the exchange of a single solvent molecule, k_{ex}^I (the total exchange rate = $6\ k_{ex}^I[M(DMSO)_6^{3+}]$), were calculated from the relationship $k_{ex}^I = P_a/\tau$, where P_a is the fractional population of the free solvent peak ($P_a + P_b = 1$) and τ the estimated relaxation time ($\tau^{-1} = \tau_a^{-1}/P_b = \tau_b^{-1}/P_a$). k_{ex}^I was found not to vary significantly with P_a (Table I). Values of k_{ex}^I obtained from the line-broadening experiments between 305.0 and 365.6 K and from the SF-NMR studies between 253.2 and 273.2 K are summarised in Table I. In the SF-NMR

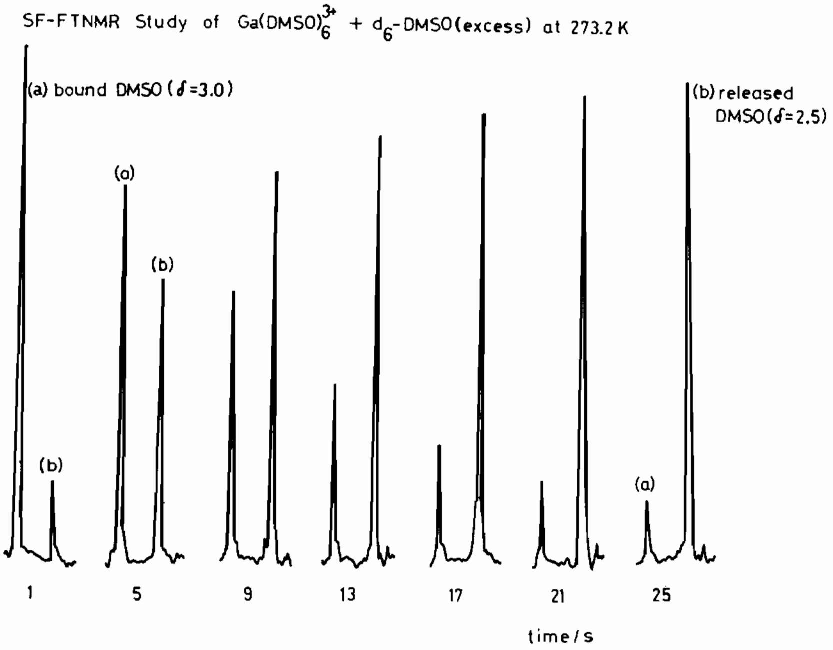

Fig. 2. Parts of successive 90 MHz ^1H NMR spectra obtained by SF-NMR; $[Ga(DMSO)_6](ClO_4)_3 = 1.0 \times 10^{-2}$ mol dm^{-3}, $[^2H]_6$-DMSO = 1.0 mol dm^{-3} in $[^2H]_3$-CH_3NO_2 solution at 273.2 K; (a) = co-ordinated DMSO at δ = 3.0 ppm, (b) = unco-ordinated DMSO at δ = 2.5 ppm.

TABLE I. Rate Constants for the Exchange of a Single Dimethyl Sulphoxide (DMSO) Molecule (k^I_{ex}) with the $[Ga(DMSO)_6]^{3+}$ Ion in $[^2H]_3$-nitromethane Solution.

T/K	305.0	314.8	325.5	330.4	335.8
k^I_{ex}/s^{-1} [a]	3.72 ± 0.08	9.13 ± 0.06	24.28 ± 0.14	34.04 ± 0.17	54.09 ± 0.15
T/K	340.7	345.8	350.3	355.7	365.6
k^I_{ex}/s^{-1} [a]	79.53 ± 0.21	122.2 ± 0.6	178.2 ± 0.6	261.8 ± 1.1	541.6 ± 3.0
T/K	339.6	339.6	339.6		
k^I_{ex}/s^{-1} [a]	78.0 ± 0.9[b]	78.5 ± 1.3[b,c]	71.8 ± 0.4[d]		
T/K	273.2	263.2	258.2	253.2	
$10^2\ k^I_{ex}/s^{-1}$ [e]	9.05 ± 0.39	3.50 ± 0.08	2.05 ± 0.07	0.924 ± 0.027	

[a]Line broadening results with $P_a = 0.58$ unless specified. Ga(III) = 1.137×10^{-2} molal and $\delta\omega$ from equation (2). [b]Average of two separate estimations. [c]$P_a = 0.66$. [d]$P_a = 0.71$. [e]SF-NMR results.

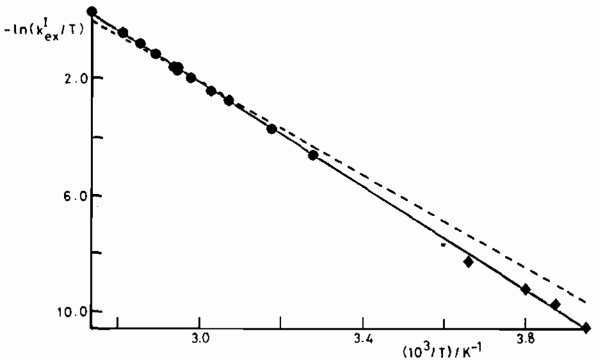

Fig. 3. Plot of $\ln(k^I_{ex}/T)$ against $1/T$ for $[Ga(DMSO)_6]^{3+}$ solvent exchange; (●) line broadening results (Fig. 1); (♦) SF-NMR results.

experiments k^I_{ex} was estimated from the slope of a plot of $\ln[h^b/(h^b + h^f)]$ *versus* time, where h^b and h^f are the heights of the bound and free solvent resonances respectively. Although in such an experiment the decaying bound solvent resonance corresponds to the disappearance of all six co-ordinated solvent molecules (equation 1), nevertheless the slope of a plot of $\ln[h^b/(h^b + h^f)]$ *versus* time gives $-k^I_{ex}$ directly and *not* $-6\ k^I_{ex}$ as was originally believed [3]. Proof of this is given in Appendix I. The good agreement between the line-broadening and SF-NMR results is illustrated in Fig. 3. The activation parameters are summarised in Table II.

Previous studies of solvent exchange with the $[Al(DMSO)_6]^{3+}$ ion include measurements of the broadening of the bound DMSO resonance in the slow exchange region in DMSO solution [4], and SF-NMR studies at lower temperatures in $[^2H]_3$-nitromethane and DMSO solutions [3]. The rates were not found to differ significantly in these two solvents [3]. In the present study extension of these results to higher temperatures has been carried out in $[^2H]_3$-nitromethane solution in the way described for the $[Ga(DMSO)_6]^{3+}$ ion. The values of k^I_{ex} are collected in Table III. These results show that previous estimates [3, 4] of k^I_{ex} are too small by a factor of six. The SF-NMR results are wrong for the reason explained in Appendix I; the results of Thomas and Reynolds are also wrong because they estimated the rates from the expression $k = \pi\delta/6$, where δ (Hz) is the increase in the linewidth of the bound DMSO resonance due to exchange broadening. We believe $k^I_{ex} = \pi\delta$ in the slow exchange region [1, 7], and it is clearly wrong to divide by six as explained by Thomas and Reynolds because "there are six protons per molecule" [4]. Therefore, all the values of k^I_{ex} in Table I of reference 3 are too small by a factor of six. The corrected rate constants are given in Table III, and the good agreement between the present results and the corrected rate constants is shown in Fig. 4. The activation parameters calculated from all the data in Table III are collected in Table II. The line-broadening results, in $[^2H]_3$-nitromethane solution between 334.0 K and 367.2 K alone gave $\Delta H^* = 83.1 \pm 1.3$ kJ mol^{-1} and $\Delta S^* = +23.0 \pm 3.7$ JK^{-1} mol^{-1} in good agreement with the combined results.

For the $[In(DMSO)_6]^{3+}$ ion it was not possible to measure k^I_{ex} accurately even at low temperatures. At room temperature, separate solutions of $[In(DMSO)_6]^{3+}$ ion and DMSO have resonances at $\delta = 3.06$ and 2.51 ppm respectively at low dilution in $[^2H]_3$-nitromethane solution, and a solution containing a mixture of 2.9×10^{-3} mol dm^{-3} $[In(DMSO)_6]^{3+}$ and 1.74×10^{-2} mol dm^{-3} of added (free) DMSO (mole fraction of free DMSO, $P_A = 0.53$) gave a single sharp resonance at $\delta = 2.75$ ppm indicating fast exchange under these conditions. However, upon successive dilution and cooling to *ca.* 220 K signs of significant line broadening were observed at concentrations of bound and free DMSO in the region of 10^{-3} mol dm^{-3}. At these concentrations, the amount of water and other impurities present could not be neglected, and so attempts to

Table II Rates and Activation Parameters at 298.2 K for Solvent Exchange with Al^{3+}, Ga^{3+}, In^{3+} and Sc^{3+} Ions in $[^2H]_3$-Nitromethane Solution Unless Specified.

Complex[a]	Concentration ranges/mol dm^{-3} of metal ion : free solvent	Temperature Range/K	k^I_{ex}/s^{-1}	ΔH^*/ kJ mol^{-1}	ΔS^*/ JK^{-1} mol^{-1}	NMR nucleus	Refs.
$[Al(H_2O)_6]^{3+}$	2.26[c] : 50	273-413	16	65.3	0	^{17}O	b
$[Al(DMSO)_6]^{3+}$	(0.013-0.138) : (0.11-14.08)	262-367	0.30 ± 0.02	82.6 ± 1.2	+22.3 ± 3.7	^1H	d
$[Al(TMP)_6]^{3+}$	(0.10-0.13) : (0.348-15.0)	320-331	0.36	87	+35	^1H	e
	0.2 : (0.64-2.8)	310-330	0.38 ± 0.02	98.3 ± 6.3	+76.2 ± 20.9	^{21}Al	f
	0.2 : 1.2	303-366	0.78 ± 0.16	85.0 ± 4.3	+38.2 ± 12.8	^1H	g
$[Al(DMF)_6]^{3+}$	0.1 : 0.64	330-366	0.05 ± 0.01	93.2 ± 2.5	+42.6 ± 7.5	^1H	g,h
$[Al(DMMP)_6]^{3+}$	(0.095-0.19) : (0.93-1.70)	306-326	5.1 ± 0.1	83.7 ± 6.3	+47.7 ± 20.9	^1H	f
	0.15 : (0.45-0.73)	283-306	5.0 ± 0.3	74.9 ± 2.5	+18.4 ± 7.9	^{27}Al	f
$[Al(DMHP)_6]^{3+}$	(0.43-0.84) : (1.89-5.18)	301-318	1.3 ± 0.1	82.8 ± 6.7	+28.9 ± 25.1	^1H	f
$[Al(HMPA)_4]^{3+}$	(0.071-0.073) : (0.018-0.044)	248-278	4.8×10^3 [i]	32.2 ± 2.1	-42.7 ± 6.3	^{27}Al	f
$[Ga(H_2O)_6]^{3+}$	1.50[j] : 50	243-355	760	69.0	+42	^{17}O	b,j
$[Ga(DMSO)_6]^{3+}$	0.014 : (0.095-0.206)	253-366	1.87 ± 0.05	72.5 ± 0.5	+ 3.5 ± 1.6	^1H	k
$[Ga(TMP)_6]^{3+}$	(0.0915-0.209) : (0.593-1.153)	292-319	5.0 ± 0.2	87.9 ± 3.3	+63.2 ± 5.0	^1H	l
		284-349	6.4 ± 0.5	74.1 ± 2.6	+19.2 ± 8.3	^1H	g
$[Ga(DMF)_6]^{3+}$	0.035 : 0.19	303-346	1.67 ± 0.20	85.7 ± 3.3	+46.4 ± 10.0	^1H	g
$[In(H_2O)_6]^{3+}$	(1.865-2.639) : 50	278-358	4.0×10^4 [i]	19.2 ± 4.2	-96	^{17}O	m
$[In(TMP)_6]^{3+}$	(0.102-0.198) : (0.609-1.196)	284-330	7.2 ± 0.3[i]	35.6 ± 2.1	-109	^1H	l
			33.9 ± 1.7[i]	29.4 ± 2.0	-117 ± 7	^1H	g
$[In(DMSO)_6]^{3+}$	0.001 : 0.006	250-300	very rapid			^1H	n
$[In(DMF)_6]^{3+}$	0.001 : 0.006	250-300	very rapid			^1H	g
$[Sc(TMP)_6]^{3+}$	(0.0044-0.125) : (0.0315-0.892)	300-340	51.3 ± 1.8[i]	26.0 ± 0.9	-126 ± 3	^1H	p,s
$[Sc(DMMP)_6]^{3+}$	(0.0261-0.166) : (0.124-1.042)	300-340	13.7 ± 0.5[i]	29.7 ± 1.1	-124 ± 3	^1H	q,s
$[Sc(TMU)_6]^{3+}$	(0.00145-0.124) : (0.0108-0.682)	300-340	0.26 ± 0.03	91.2 ± 2.3	+47.8 ± 6.7	^1H	r,s
$[Sc(DMA)_6]^{3+}$	(0.0071-0.0415) : (0.0390-0.357)	300-340	4.6 ± 0.3	30.3 ± 2.0	-132 ± 6	^1H	r,s
			and 112 ± 3[i]	26.0 ± 0.6	-119 ± 2	^1H	t,s
$[Sc(DMF)_6]^{3+}$		> 180[u]	very rapid			^1H	r
$[Sc(DMSO)_6]^{3+}$		> 245	very rapid			^1H	r

[a] DMSO = $(CH_3)_2SO$; TMP = $(CH_3O)_3PO$; DMF = $(CH_3)_2NCHO$; DMMP = $(CH_3O)_2(CH_3)PO$; DMHP = $(CH_3O)_2HPO$; HMPA = $[(CH_3)_2N]_3PO$; TMU = $[(CH_3)_2N]_2CO$; DMA = $(CH_3)_2NCOCH_3$. [b] J. W. Neely, *Ph.D. Thesis,* University of Berkeley, 1971; these data update those of D. Fiat and R. E. Connick, *J. Am. Chem. Soc., 90,* 608 (1968); the previously reported data were for Al(III), ΔH^* = 113 kJ mol^{-1}, ΔS^* = +117 JK^{-1} mol^{-1} and for Ga(III) ΔH^* = 26.4 kJ mol^{-1}, ΔS^* = −92 JK^{-1} mol^{-1}. [c] Approximate molality of Al^{3+}_3; *ca.* 0.55 molal Mn^{2+} was also present. [d] From the data in Table III. [e] Ref. 7. [f] Ref. 6. [g] C. Ammann and A. E. Merbach, unpublished results. [h] W. A. Movius and N. A. Matwiyoff, *Inorg. Chem., 6,* 847 (1967) report ΔH^* = 74 kJ mol^{-1}, ΔS^* = +5.0 JK^{-1} mol^{-1}; a correction to k^I_{ex} by a factor of six has been made by L. S. Frankel and E. R. Danielson who report k^I_{ex} = 0.34 s^{-1}, ΔH^* = 74 kJ mol^{-1}, ΔS^* = −9.6 JK^{-1} mol^{-1} (Ref. 7). [i] Second-order rate constant/ dm^3 mol^{-1} s^{-1}. [j] Approximate molality of Ga^{3+}; *ca.* 0.60 molal Mn^{2+} was also present. [k] From the data in Table I. [l] L. Rodehüser, P. R. Rubini and J.-J. Delpuech, *Inorg. Chem., 16,* 2837 (1977). [m] Data for the hydrolysed complex are also given by J. W. Neely (footnote b). [n] This work. [p] D. L. Pisaniello, S. F. Lincoln and E. H. Williams, *Chem. Comm.,* 1047 (1978); *J. Chem. Soc. Dalton* 1473 (1979). [q] D. L. Pisaniello and S. F. Lincoln, *Inorg. Chim. Acta, 36,* 85 (1979). [r] D. L. Pisaniello and S. F. Lincoln, *J. Chem. Soc. Dalton,* (in press); in the case of DMA these data refer to k_1 where $k^I_{ex} = k_1 + k_2$ [DMA]. [s] Data also reported in $[^2H]_3$ acetonitrile solution, with very different results in most cases. [t] These data refer to k_2 where $k_{obs} = k_1 + k_2$ [DMA]. [u] In $[^2H]_2$-dichloromethane solution.

TABLE III. Rate Constants for the Exchange of a Single Dimethyl Sulphoxide (DMSO) Molecule (k^I_{ex}) with the $[Al(DMSO)_6]^{3+}$ Ion (in $[^2H]_3$-nitromethane Solution Unless Specified).

T/K	334.0	338.8	344.0	349.1	353.6
k^I_{ex}/s^{-1} [a]	10.5 ± 0.1	16.7 ± 0.1	26.3 ± 0.1	40.2 ± 0.1	60.9 ± 0.2
T/K	358.6	363.2	367.2		
k^I_{ex}/s^{-1} [a]	94.0 ± 0.2	140.3 ± 0.3	201.1 ± 0.4		
T/K	262.2	273.2	283.2	293.2	297.2
$10^3 k^I_{ex}/s^{-1}$ [b]	3.12 ± 0.18	12.0 ± 0.6	44.4 ± 1.2	106.8 ±3.0	330.0 ±20.0
T/K	313.2	318.2	323.2	328.2	333.2
k^I_{ex}/s^{-1} [c]	1.79 ± 0.10	3.02 ± 0.02	5.56 ±0.13	9.02 ±0.02	12.2 ±0.4
T/K	338.2				
k^I_{ex}/s^{-1} [c]	21.4 ± 0.6				

[a] Line-broadening results with $P_a = 0.61$, [Al(III)] 1.1×10^{-2} molal and $\delta\omega = 75.19 - 0.2878\,T + (4.7275 \times 10^{-4})T^2$ (T = absolute temperature). [b] SF-NMR results (Ref. 3) multiplied by six (see text). [c] Line-broadening results in DMSO solution (Ref. 4) multiplied by six (see text) [Al(III)] varied between 0.052 and 0.138 mol dm^{-3}.

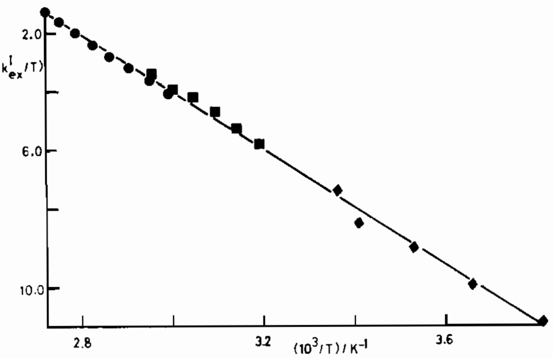

Fig. 4. Plot of $\ln(k^I_{ex}/T)$ against 1/T for $[Al(DMSO)_6]^{3+}$ solvent exchange; (●) line broadening results at high temperatures in $[^2H]_3$-CH_3NO_2 solution; (■) line broadening results in the slow exchange region – data from ref. 4 multiplied by six; (◆) SF-NMR results from ref. 3 multiplied by six.

measure k^I_{ex} were abandoned. Work at a higher field strength under strictly anhydrous conditions will be necessary for reliable estimates of k^I_{ex} in this case.

Discussion

A comparison of the rates and activation parameters for solvent exchange with Al^{3+}, Ga^{3+}, In^{3+} and Sc^{3+} ions is shown in Table II. Some of these data have been obtained over a narrow temperature range of less than 30 K (sometimes only 11 K) and the results are less reliable for that reason. Nevertheless, the pattern emerges that for Al^{3+} ions, with the exception of the four-co-ordinate $[Al(HMPA)_4]^{3+}$ ion and possibly $[Al(H_2O)_6]^{3+}$ ion for which conflicting data are reported (Table II), values of ΔS^* are always significantly positive, and the rates determined in $[^2H]_3$-nitromethane solution are independent of the free solvent concentration. For the sterically crowded $[Al(HMPA)_4]^{2+}$ ion, the opposite type of behaviour has been found, with ΔS^* significantly negative and the reaction first-order in the concentration of free HMPA [6]. A switch in mechanism from a dissociative process for the six-co-ordinate complexes, to an associative process for the four-co-ordinate $[Al(HMPA)_4]^{3+}$ ion, has been postulated and seems very reasonable [6]. For the six-co-ordinate complexes two mechansims, I_d or D, can be proposed to account for the observed first-order rate law (M = metal ion, S = solvent molecule):

$$\textit{D-mechanism} \quad [MS_6]^{3+} \xrightarrow{k} [MS_5]^{3+} + S$$

$$[MS_5]^{3+} + S^* \xrightarrow{\text{rapid}} [MS_5S^*]^{3+} \qquad (3)$$

$$\textit{I}_d\textit{ mechanism} \quad [MS_6]^{3+} + S^* \underset{\text{rapid}}{\overset{K_o}{\rightleftharpoons}}$$

$$[MS_6]^{3+}, S \xrightarrow{k_1} [MS_5S^*]^{3+} + S \qquad (4)$$

For the I_d mechanism, rapid outer-sphere association is followed by rate-determining solvent interchange with M–S bond breaking more important than M–S* bond making. In this case,

$$d[MS_5S^*]/dt = k_1K_o[MS_6][S^*]/(1 + K_o[S^*]) \qquad (5)$$

where [S*] is the free solvent concentration. To account for the observed independence of k^I_{ex} with decreasing [S*], one must then postulate $K_o[S^*] \gg 1$ such that saturation of the outer-sphere of $[MS_6]^{3+}$ has occurred and from (5), $k^I_{ex} = k_1$. Since for $[Al(DMSO)_6]^{3+}$ ion this is true when [S*] is as low as 0.11 mol dm^{-3}, and similarly for $[Al(TMP)_6]^{3+}$ ion when $[S^*] > 0.348$ mol dm^{-3}, such a mechanism requires $K_o > 10$ dm^3 mol^{-1}. This is feasible for a trivalent metal ion reacting with a neutral molecule in nitromethane solution, values of K_o in the range 87 to 1250 having been estimated for reactions of $[Al(DMSO)_6]^{3+}$ ion with planar aromatic ligands like 1,10-phenanthroline and 2,2′-bipyridine in this solvent [3]. For a solvent exchange process in an inert diluent like nitromethane, it seems likely that symbiosis will cause aggregation of free and bound solvent molecules, and values of K_o in excess of 10 dm^3 mol^{-1} seem reasonable for a small trivalent metal ion like Al^{3+} (ionic radius 51–53 pm). Nevertheless, it is not possible to rule out the alternative D-mechanism for $[Al(DMSO)_6]^{3+}$ ion on the basis of the present results, and at least one group favours a D-mechanism for $[Al(TMP)_6]^{3+}$ ion [7]. The close similarity between the rates and activation parameters observed for $[Al(DMSO)_6]^{3+}$ and $[Al(TMP)_6]^{3+}$ ions makes it unlikely that they react by different mechanisms, and further work is needed to try to resolve this dichotomy. We are presently determining values of ΔV^* for $[Al(S)_6]^{3+}$ ion (S = DMSO, TMP, DMF) to give further insight into the mechanisms of these reactions [12].

As we increase the size of the central metal ion the tendency to change from a dissociative to an associative mechanism is expected as it becomes easier for the metal ion to increase in co-ordination number. The ionic radii [8] of Ga^{3+} (62 pm) In^{3+} (79–81 pm) and Sc^{3+} (73–81 pm) ions are such that one might expect a change in mechanism for the larger In^{3+} and Sc^{3+} ions, especially when steric crowding by the co-ordinated solvent molecules is not too serious. Sc^{3+} ion is known to form complexes with higher co-ordination numbers (7, 8 and 9) [9], and the large negative ΔS^* values observed for solvent exchange (except with $[Sc(TMU)_6]^{3+}$ ion in $[^2H]_3$-nitromethane solution) [10] are consistent with an associative (I_a or A) mechanism. For the sterically crowded $[Sc(TMU)_6]^{3+}$ ion a dissociative mechanism is postulated in $[^2H]_3$-nitromethane solution [10] (ΔS^* = +47.8 JK^{-1} mol^{-1}). For an I_a mechanism, reaction sequence (4) and equation (5) are again valid, but bond-making is expected to be more important than bond-breaking in the rate determining (k_1) step. The order of the reaction depends, as before, on the magnitude of the outer-sphere association constant (K_o), and a distinction between I_d and I_a mechanisms is not possible simply from the rate law. However, values of k_1 might be expected to vary more widely for an I_a mechanism with changes in the solvent nucleophilicity, and the very rapid rates of solvent exchange observed for $[M(S)_6]^{3+}$ ion (M = In^{3+}, Sc^{3+}; S = DMSO, DMF) compared with that measured for $[M(TMP)_6]^{3+}$ ions (M = Sc^{3+}, In^{3+}) is an indication that k_1 is varying and that associative mechanisms are involved. The large negative ΔS^* values observed for solvent exchange with $[M(TMP)_6]^{3+}$ ions (M = In^{3+}_3 and Sc^{3+}) is also consistent with associative mechanisms in these cases too.

In contrast, for $[Ga(S)_6]^{3+}$ ions (S = DMSO, TMP, DMF) the rates and activation parameters are not very different, and values of ΔS^* are positive in all cases (the earlier report of a negative ΔS^* value for $[Ga(H_2O)_6]^{3+}$ ion has been corrected to +42 JK^{-1} mol^{-1} in a recent review) [11]. Therefore, it seems reasonable to postulate that hexakis-solvates of Ga^{3+} ion will normally react with a dissociative mechanism, and preliminary results show that values of ΔV^* are positive for $[Ga(S)_6]^{3+}$ ions (S = DMSO, TMP and DMF) in accord with this view [12].

Conclusion

For solvent exchange with $[M(S)_6]^{3+}$ ions a dissociative mechanism (I_d or D) normally occurs when M is Al^{3+} or Ga^{3+}, whereas for the larger In^{3+} and Sc^{3+} ions associative mechanisms are expected to be found more frequently, especially when the solvent (S) is a good nucleophile (*e.g.* DMSO or DMF) which is not extremely bulky. When very bulky solvents such as HMPA or TMU are involved different behaviour is to be expected since steric crowding will hinder associative attack by the incoming solvent and accelerate solvent dissociation from the crowded inner-sphere of the metal ion. In some cases solvent crowding produces a reduction in the normal co-ordination number, especially with a small ion like Al^{3+} (*e.g.* $[Al(HMPA)_4]^{3+}$), and this lowering of the co-ordination number results in change from a normally dissociative mechanism with the six-co-ordinate species to associative behaviour with the four-co-ordinate complex [6]. When a larger metal ion like Sc^{3+} is involved, the normally associative behaviour observed with less bulky solvents like H_2O, TMP, DMF and DMSO appears to switch over to a dissociative mechanism when a bulky solvent is involved (*e.g.* $[Sc(TMU)_6]^{3+}$ ion) [10].

Experimental

$[M(DMSO)_6](ClO_4)_3$ (M = Al, Ga, In) were prepared by dissolving fairly dry samples of the hydrated salts (10^{-3} mol) in ethanol (25 cm^3), filtering if necessary, and this solution was dehydrated by stirring with triethyl orthoformate (10 cm^3) for 2 h under dry nitrogen. Dry DMSO (1 cm^3) was then added dropwise, and the white crystalline product collected by filtration under dry nitrogen, washed with dry ether (5 × 10 cm^3) and recrystallised from dry nitromethane containing DMSO (10%). ^1H NMR showed the samples to be pure and free from residual water.

DMSO was refluxed under vacuum over calcium hydride for 1 h and then vacuum distilled. Nitromethane was dried with anhydrous calcium chloride and distilled and stored over activated 4A molecular sieves. Commercial $[^2H]_3$-nitromethane was also stored over 4A molecular sieves before use.

NMR line-broadening experiments were carried out at 60 MHz with a Bruker WP-60 FTNMR spectrometer and $[^2H]$ internal nitromethane lock. 100–1000 scans (8 K data points, sweep width 720 Hz) were used, more scans being taken near to the coalescence point. A trace of TMS was added as a measure of field inhomogeneity, and adjustment of T_{2a} and T_{2b} made by comparison of the widths of the free and bound DMSO resonances with that of TMS in the limit of very slow exchange. Temperatures were measured (±0.3 K) with a callibrated platinum resistance thermometer in an identical tube to the sample (by substitution after each experiment). SF-NMR experiments were carried out at 90 MHz with a Bruker WH-90 as described previously [3].

Acknowledgements

P.M. thanks the Ciba-Geigy Fellowship Trust for a Senior Fellowship and the Science Research Council (UK) for a grant to develop stopped-flow FTNMR. A.E.M. thanks the Swiss National Science Foundation for financial support (grant No 2.189-0-78).

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Appendix I

In a SF-NMR experiment in which a solvated metal ion MS_6 is mixed with an excess of deuterated solvent, S^*, if k represents the rate constant for the exchange of a *single* solvent molecule, neglecting any isotope effects the following reaction sequence occurs with overall rate constants as shown:

$$\begin{array}{llll}
MS_6 & + S^* & \xrightarrow{6k} & MS_5S^* + S \\
MS_5S^* & + S^* & \xrightarrow{5k} & MS_4S_2^* + S \\
MS_4S_2^* & + S^* & \xrightarrow{4k} & MS_3S_3^* + S \\
\vdots & & & \vdots \\
MSS_5^* & + S^* & \xrightarrow{k} & MS_6^* + S
\end{array}$$

Let h^b represent the height of the bound solvent resonance at time t, and p a proportionality constant which relates the height of a single solvent resonance to a concentration. If all the mixed solvento-species $MS_{6-n}S_n^*$ have the same chemical shift:

$$h^b/p = 6[MS_6] + 5[MS_5S^*] + 4[MS_4S_2^*] + \ldots + [MSS_5^*] \qquad \text{(i)}$$

The rate laws for the individual reaction steps are:

$$\left.\begin{array}{l}
-d[MS_6]/dt = 6k[MS_6] \\
-d[MS_5S^*]/dt = 5k[MS_5S^*] - 6k[MS_6] \\
-d[MS_4S_2^*]/dt = 4k[MS_4S_2^*] - 5k[MS_5S^*] \\
\quad\vdots \qquad\qquad\qquad \vdots \\
-d[MSS_5^*]/dt = k[MSS_5^*] - 2k[MS_2S_4^*]
\end{array}\right\} \text{(ii)}$$

From (i), the total rate of disappearance of the bound solvent resonance is given by equation (iii):

$$-d[h^b/p]/dt = -6\,d[MS_6]/dt - 5\,d[MS_5S^*]/dt - 4\,d[MS_4S_2^*]/dt \ldots - d[MSS_5^*]/dt \qquad \text{(iii)}$$

Combining (ii) and (iii):

$$\begin{aligned}
-d[h^b/p]/dt = {} & 36k\,[MS_6] - 30k\,[MS_6] + \\
& 25k\,[MS_5S^*] - 20k\,[MS_5S^*] + \\
& 16k\,[MS_4S_2^*] - 12k\,[MS_4S_2^*] + \\
& 9k\,[MS_3S_3^*] - 6k\,[MS_3S_3^*] +
\end{aligned}$$

$$4\,k\,[\mathrm{MS_2S_4^*}] - 2\,k\,[\mathrm{MS_2S_4^*}] +$$

$$k\,[\mathrm{MSS_5^*}]$$

$$= k\,(6[(\mathrm{MS_6}] + 5[\mathrm{MS_5S^*}] +$$

$$4[\mathrm{MS_4S_2^*}] + \ldots + [\mathrm{MSS_5^*}])$$

$$= \mathrm{k}h^{\mathrm{b}}/p$$

Hence $\ln(h^{\mathrm{b}}/h^{\mathrm{b}}_{\mathrm{o}}) = -kt$ where $h^{\mathrm{b}}_{\mathrm{o}}$ is the height of the bound solvent resonance at time $t = 0$. Since $h^{\mathrm{b}}_{\mathrm{o}} = h^{\mathrm{b}} + h^{\mathrm{f}}$ where h^{f} is the height of the free solvent resonance ($h^{\mathrm{f}} = 0$ when $t = 0$), it follows that a plot of $\ln[h^{\mathrm{b}}/(h^{\mathrm{b}} + h^{\mathrm{f}})]$ *versus* time, t, has a slope of $-k$ and *not* $-6k$ as was originally proposed [3].