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Note

THERMODYNAMICS OF COMPLEX FORMATION REACTIONS IN NON-AQUEOUS SOLVENTS. PART 2. REACTION OF SILVER(I) WITH *N,N,N′,N′*-TETRAMETHYLENE DIAMINE IN ACETONE, METHANOL AND ETHANOL

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Non-aqueous solvents such as acetone, ethanol and methanol are extensively used as media for the preparation of coordination complexes Reactions of these complexes, such as ligand exchange reactions, are normally carried out in non-aqueous solvents Very little is, however, known about the thermodynamics of complex formation reactions in non-aqueous solvents The thermodynamics of the reaction between silver(I) and pyridine as well as substituted pyridine ligands in acetone were reported recently [1] This study was continued and extended to include the effect of the solvent on the thermodynamics of the complex formation reaction The Ag^+/*N,N,N′,N′*-tetramethylene diamine (tmen) system was chosen as model for the investigation

EXPERIMENTAL

The experimental procedure, entropy titration method [2,3], was described previously [1] The ligand *N,N,N′,N′*-tetramethylene diamine (purum), was obtained from Fluka and used without further purification Stock solutions of the ligand (ca 1 0 mol dm^{-3}) were prepared by dissolving the required amount of ligand in the solvent Silver(I) solutions ranging from $2\ 0 \times 10^{-3}$ to $1\ 0 \times 10^{-2}$ mol dm^{-3}, were used Acetone, methanol and ethanol (Merck, pro analysi) were used without further purification

RESULTS AND DISCUSSION

The titration curves obtained by titrating a $1\ 0 \times 10^{-2}$ mol dm^{-3} silver(I) solution with 1 0 mol dm^{-3} tmen in acetone (curve B) and ethanol (curve A)

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are shown in Fig 1 The curve obtained using methanol as solvent was very similar to that obtained in ethanol The curves indicated that the silver and tmen react in a mole ratio 1 2 in both solvents The endpoint of the titration curve in acetone is much sharper than that obtained for ethanol This suggests larger formation constants for the reaction in acetone

The thermodynamic constants which were extracted from these curves are summarised in Table 1 The formation of $Ag(tmen)^+$ and $Ag(tmen)_2^+$ are enthalpy driven in all three solvents The values indicated that the reaction is more enthalpy driven in acetone than in methanol or ethanol The formation constants, log B_1, for the reaction

$$Ag^+(solv) + tmen(solv) \rightarrow Ag(tmen)^+ + solv$$

seems to decrease for the various solvents in the order acetone > ethanol > methanol

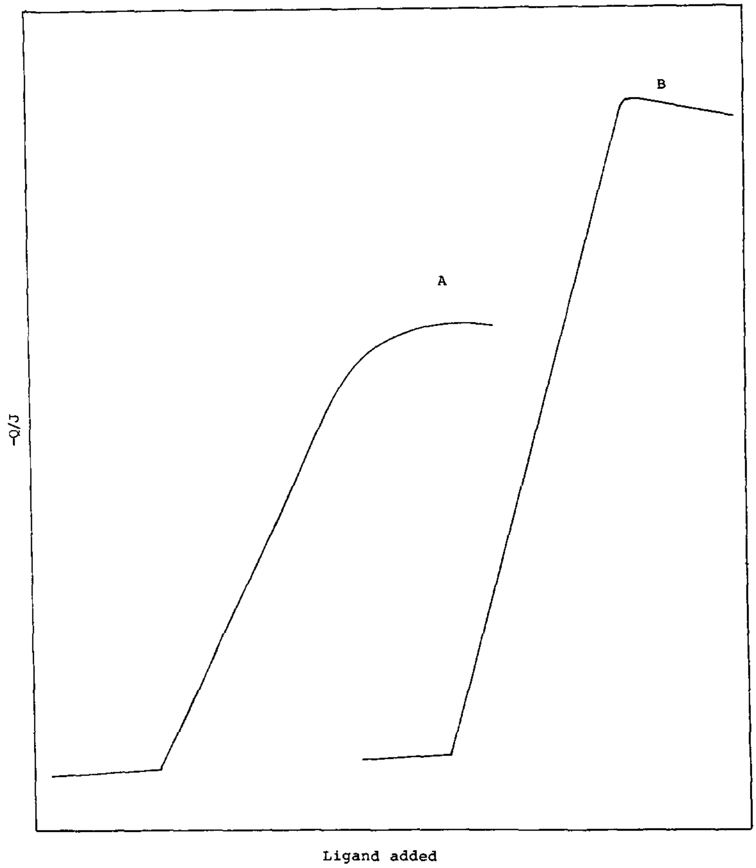

Fig 1 The titration curves of silver(I) ($1\ 0 \times 10^{-2}$ mol dm^{-3}) with tmen ($1\ 0$ mol dm^{-3}) in A, ethanol, B, acetone

TABLE 1

Thermodynamic constants for the silver(I)/N,N,N',N'-tetramethylene diamine system in different solvents Concentrations silver(I) = 0 01 mol dm^{-3} and tmen = 1 00 mol dm^{-3}

Thermodynamic parameters	Acetone	Methanol	Ethanol
log B_1	4 03	3 74	3 82
log B_2	8 00	8 09	8 09
ΔG_1 (kJ mol^{-1})	−23 02	−21 33	−21 82
ΔG_2 (kJ mol^{-1})	−45 69	−46 19	−46 17
ΔH_1 (kJ mol^{-1})	−75 11	−39 82	−25 30
ΔH_2 (kJ mol^{-1})	−198 07	−97 39	−88 24
ΔS_1 (J mol^{-1} K^{-1})	−174 71	−62 02	−11 67
ΔS_2 (J mol^{-1} K^{-1})	−511 08	−171 72	−141 10

An interesting aspect was that ΔH_1 seems to be dependent on the initial Ag^+ concentration ($[Ag^+]_i$) It increased from a value of −75 11 kJ mol^{-1} for $[Ag^+]_i = 9\ 334 \times 10^{-3}$ mol dm^{-3} to −36 56 kJ mol^{-1} for $[Ag^+]_i = 4\ 667 \times 10^{-3}$ mol dm^{-3} Such a change in ΔH_1 was not observed when the reaction was carried out in ethanol and methanol This could be due to either simultaneous equilibria during the initial stages of the reaction, since no rigorous measures were employed to exclude water from the reaction, or the fact that the ionic strength was not controlled during the titration

The degree of formation of Ag(tmen)$^+$ was very similar at different concentrations in acetone, however in methanol and ethanol it was found that the degree of formation of Ag(tmen)$^+$ increased (Table 2)

The formation constant, B_2 was found to be very similar for the reaction in all three solvents (Table 1) at a $[Ag^+]_i \cong 1\ 0 \times 10^{-2}$ mol dm^{-3} Using more dilute Ag^+ solutions did not change the value significantly when acetone and ethanol were used as solvents A value of log $B_2 = 6\ 82$ was, however, obtained when methanol was used as solvent

It is clear from the above results that very interesting thermodynamic data can be extracted from the reactions taking place in non-aqueous media,

TABLE 2

The degree of formation of Ag(tmen)$^+$ found in the various solvents

Degree of AgL$^+$ (%)	Initial $[Ag^+]$ (mol dm^{-3})	log B_1	Solvent
33 8	$9\ 334 \times 10^{-3}$	4 03	Acetone
29 4	$4\ 667 \times 10^{-3}$	4 02	Acetone
19 5	$1\ 065 \times 10^{-2}$	3 74	Methanol
52 1	$5\ 325 \times 10^{-3}$	3 77	Methanol
22 9	$1\ 071 \times 10^{-2}$	3 82	Ethanol
40 7	$5\ 356 \times 10^{-3}$	4 19	Ethanol

using the entropy titration method Important differences and similarities exist for the reaction in the various solvents A detailed study is in progress and a full report will appear later

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