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THERMODYNAMICS OF COMPLEX FORMATION REACTIONS IN NON-AQUEOUS SOLVENTS.

PART I. REACTIONS OF SILVER(I) WITH PYRIDINE AND RELATED LIGANDS IN ACETONE

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ABSTRACT

Log β_i, ΔH_i and ΔS_i values have been determined in acetone solution at 25°C using the entropy titration procedure for the stepwise formation of AgL_2^+ where L = pyridine, α-picoline, quinoline and 2,2′-bipyridine. The complexes formed under these conditions are all enthalpy stabilized, except for the $Ag(bipyr)^+$ complex which is both enthalpy and entropy stabilized.

INTRODUCTION

Organic solvents such as acetone and acetonitrile are extensively used as media for the preparation of metal complexes. In such a solvent, which shows reduced coordinating strength towards a metal ion, the enthalpy of complexation could be sufficiently exothermic to provide the driving force for the reaction. Very little is known, however, about the thermodynamics of complex-formation reactions in non-aqueous organic solvents. It was therefore decided to start a research project with the specific aim of obtaining quantitative thermodynamic data for complex-formation reactions in non-aqueous solvents. The silver(I)/L system with acetone as solvent, where L = pyridine (pyr), α-picoline (pic), quinoline (quin) and 2,2′-bipyridine (bpyr), was chosen as the model system. The entropy titration method [1] was used to evaluate the thermodynamic constants.

EXPERIMENTAL

Materials

$AgClO_4 \cdot H_2O$, was obtained from Fluka. The $AgClO_4 \cdot H_4O$ was dehydrated under vacuum at 70°C and then stored in a P_2O_5 desiccator. Acetone

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(Merck, pro analysi) was used as solvent without any further purification. Solutions for titration (± 0.01 mol dm^{-3}) were prepared by dissolving the $AgClO_4$ in acetone. Standardisation of the stock solution was done by potentiometric titration of the silver solution using a standard chloride solution. A Metrohm model 636 Titroprocessor, with a combined Ag/AgCl electrode, was used as measuring equipment.

The ligands pyridine, α-picoline and quinoline were obtained from Fluka and purified by means of distillation under nitrogen. The 2,2′-bipyridine (pro analysi) was obtained from Merck and used without further purification. Stock solutions of the ligands (± 1.0 mol dm^{-3}) were prepared by dissolving the required amount in acetone.

Calorimetry

The entropy titrations were conducted in a Tronac model 450 isoperibol solution calorimeter. The temperature of the water bath was controlled with a PTC-40 precision temperature controller at the preselected temperature, 25 °C, to an accuracy of ± 0.0003 °C. A precision buret of 2 cm^3 capacity and 0.1% accuracy was used for the titrations. Titrations were performed on 50 cm^3 of 0.01 mol dm^{-3} Ag(I) solutions. The heats of dilution of the ligands were determined by titrating the ligand solution into 50 cm^3 of acetone.

Data acquisition and calculations

The calorimeter was interfaced with an Apple II europlus microcomputer using a Prema model 5000 integrating digital multimeter, which served as the analog-to-digital converter. The multimeter was equipped with an IEEE 488 bus interface (as a standard feature) which provided the linkage with the micro-computer. Data were collected at one point per second, an average of 400 points per titration.

Calibration runs

At least three runs, were made to determine the heat capacity of the reaction vessel and contents prior to titration by introducing a constant current through a resistance heater, 100.0 ± 0.1 ohm, over a measured period of time. The difference in temperature was corrected for non-electrical heat contribution. The calibration procedure was repeated after the titration. Calculation of the heat liberated at each data point was carried out as described in the literature [2].

Calculation of the β_i and ΔH_i values from the experimental data was accomplished by means of the process which is described in the literature [1,2]. A least-squares program based on the Gauss–Newton method of analysis was used to calculate the β_i and ΔH_i values. ΔH_i values obtained in such a manner refer to the overall enthalpy of formation of the complex in solution, i.e., ΔH_1 (298.15 K) refers to the reaction:

$$Ag^{+}(solv) + pyr(solv) \rightleftharpoons Ag(pyr)^{+} + solv$$

and ΔH_2(298.15 K) refers to

$$Ag^{+}(solv) + 2pyr(solv) \rightleftharpoons Agpyr_2^{+} + solv$$

The Newton–Raphson method was used to estimate the free-ligand concentration for each set of β values.

RESULTS AND DISCUSSION

The values of log β_i, ΔH_i, ΔG_i and ΔS_i for the step-wise formation of the complexes are listed in Table 1. The distribution diagrams of species present in the calorimeter at each point are given in Figs. 1–4. Only a few experimental points are shown in the figures to illustrate the correlation obtained.

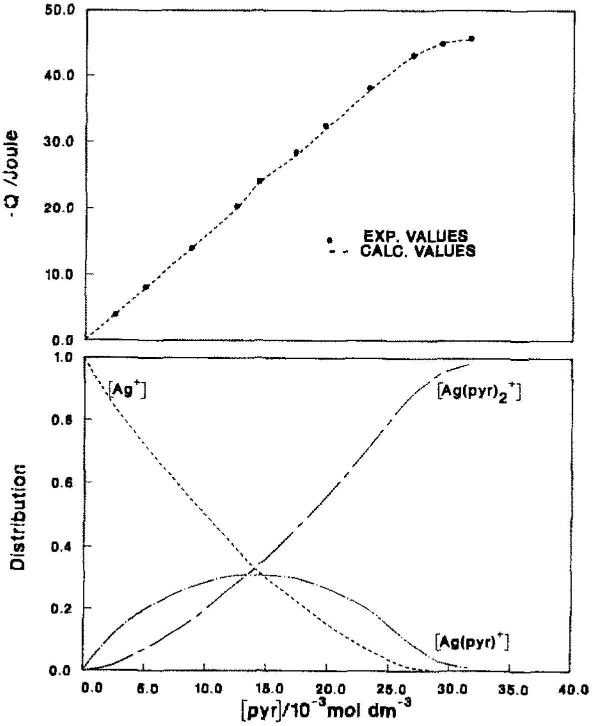

Fig. 1. Enthalpimetric titration curve and distribution diagram for the silver(I)/pyridine system.

TABLE 1

Thermodynamic data for silver(I) reactions with various ligands in acetone

Ligand	log β_1	log β_2	ΔG_1	ΔG_2	ΔH_1	ΔH_2	ΔS_1	ΔS_2
			(kJ mol^{-1})				(J mol^{-1} K^{-1})	
pyr	4.02	8.10	−22.93	−46.22	−31.77	−64.62	−29.64	−61.75
bpyr	4.91	8.26	−28.02	−47.13	−17.45	−57.09	+35.46	−33.42
quin	5.19	8.16	−29.61	−46.56	−39.71	−88.62	−33.88	−141.14
pic	5.16	8.32	−29.44	−47.47	−35.81	−89.16	−21.37	−139.89

Ag^+/pyr system

The results indicate that the $Ag(pyr)^+$ species forms only to a maximum of 31% but remains at this concentration for the duration of the titration. From the diagram it can also be seen that the various species, i.e., Ag^+, $Ag(pyr)^+$ and $Ag(pyr)_2^+$, were all present for most of the time of the titration. This is in contrast with the other systems studied in which the

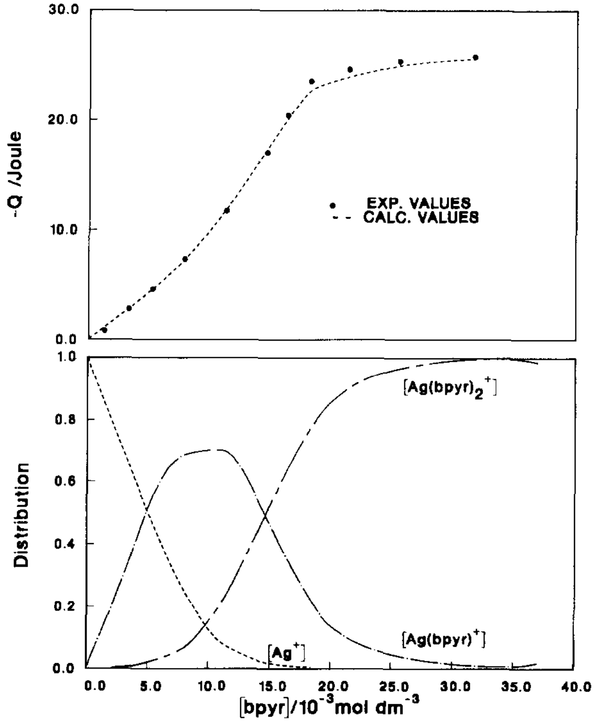

Fig. 2. Enthalpimetric titration curve and distribution diagram for the silver(I)/bipyridine system.

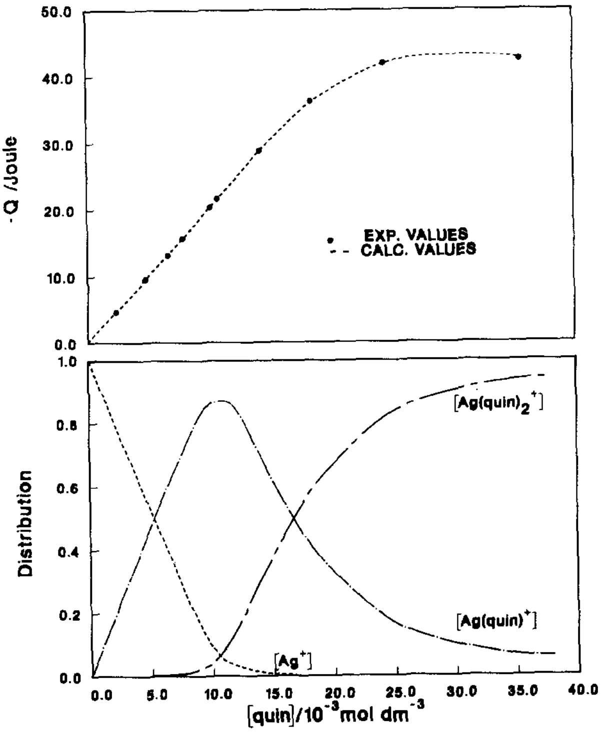

Fig. 3. Enthalpimetric titration curve and distribution diagram for the silver(I)/quinoline system.

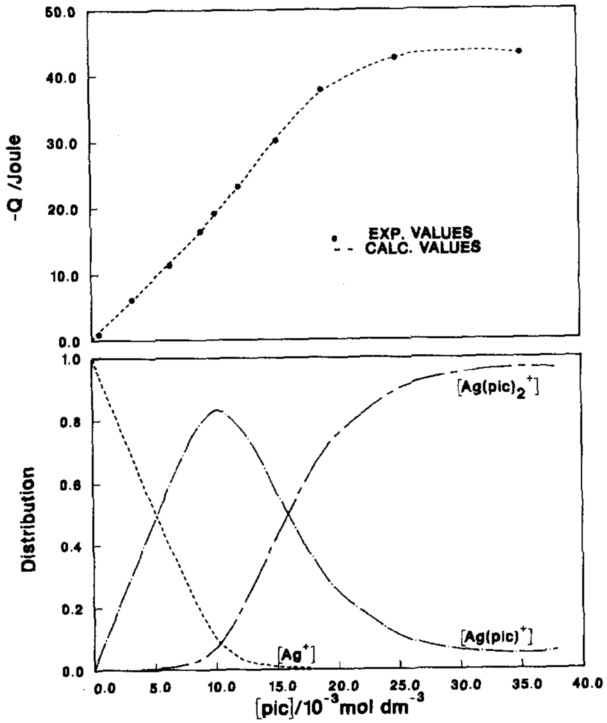

Fig. 4. Enthalpimetric titration curve and distribution diagram for the silver(I)/α-picoline system.

concentration of the species AgL^+ peaks at approximately half-way through the titration, i.e., at a mole ratio of ligand: Ag^+ of 1 : 1.

Ag^+/bpyr system

The formation of the $Ag(bpyr)^+$ complex was found to be enthalpy as well as entropy driven, $\Delta H_1 = -17.45$ kJ mol^{-1} and $\Delta S_1 = +35.5$ J mol^{-1} K^{-1}. The formation of the second complex, $Ag(bpyr)_2^+$ is, however, only enthalpy driven. The enthalpy of formation for $Ag(bpyr)_2^+$, $\Delta H_2 = -57.09$ kJ mol^{-1}, is more than three times greater than ΔH_1. This is clearly reflected in the titration curve as a change (increase) in the slope at a mole ratio, L:Ag^+, of 1 : 1. Although Ag^+ is known to form linear AgL_2^+ complexes with bidentate ligands [3], the positive ΔS_1 value obtained for the formation of AgL^+ could be due to a chelate action of the ligand during the initial stages of the reaction.

Ag^+/quin and Ag^+/pic systems

These systems were found to be very similar. An important difference for these systems, as compared to the pyridine and bipyridine systems, is the larger log β_1 values obtained. This is also illustrated in the distribution diagrams which indicate that the degree of formation of both $Ag(quin)^+$ and $Ag(pic)^+$ is more than 80%; 86% for $Ag(quin)^+$ and 83% for $Ag(pic)^+$. This is perhaps due to steric factors which favour the formation of the AgL^+ species over that of AgL_2^+.

CONCLUSIONS

It was illustrated that by obtaining thermodynamic data of complex-formation reactions in a non-aqueous solvent of reduced coordinating properties, important differences regarding the ligand can be observed. The entropy titration method is a very suitable method to use in obtaining these data.

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