NUCLEAR MAGNETIC RESONANCE AND SPECTROPHOTOMETRIC STUDIES OF THE BINDING OF MUREXIDE WITH LITHIUM, SODIUM AND POTASSIUM IONS IN BINARY DIMETHYLSULFOXIDE-ACETONITRILE MIXTURES

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Abstract

The complexation reactions between murexide and Li^+ , Na^+ and K^+ ions in different dimethylsulfoxide-acetonitrile mixtures were studied by both spectrophotometric and ^7Li -NMR methods at 25 °C. The stoichiometry of the complexes was found to be 1:1. The formation constants of the resulting complexes, determined by both experimental techniques used, were found to be in satisfactory agreement. In all solvent mixtures studied, the stability of murexide complexes varied in the order $\text{Na}^+ > \text{K}^+ > \text{Li}^+$. There is an inverse relationship between the complex formation constants and amount of dimethylsulfoxide in the mixed solvent. A linear relationship was observed between $\log K_f$ for all complexes and the mole fraction of acetonitrile in solvent mixtures.

Introduction

Although the alkali and alkaline earth ions possess profound influences upon biological and materials sciences,^{1,2} their coordination chemistry, especially with classical ligands, has received very little attention, as compared to transition metal ions.³ Perhaps the most important reason for the delayed interest in this area of research is the quite weak interactions of conventional ligands with alkali and alkaline earth cations which are often beyond the sensitivities of most physicochemical techniques. However, due to the urgent need for understanding the vital role of cations like Na^+ , K^+ , Mg^{2+} and Ca^{2+} ions in biological systems, on the one hand, and the discovery of new macrocyclic ligands such as crown ethers⁴ and cryptands⁵ in the late 1960's, on the other, a new era in the coordination chemistry of alkali and alkaline earth cations has opened during the past decades.⁶⁻⁸

Since, in the process of complex formation, the ligand must compete with solvent molecules for the cation, any variation in solvent properties is expected to change the apparent binding strength of the resulting complexes. Thus, an interesting possibility for understanding the nature of interactions between alkali and alkaline earth cations and conventional ligands in solution is the use of nonaqueous solvent of lower solvating abilities and dielectric constants than water.

Murexide, the ammonium salt of purpuric acid (I), has been frequently used as a suitable metallochromic indicator for a large number of metal ions over a wide range of experimental conditions.⁹⁻¹³ In most cases, the ligand forms 1:1 complexes with mono-di- and trivalent metal cations in aqueous, nonaqueous and mixed solvents. The metal binding of murexide is accompanied by a relatively strong shift of its absorption band, with $\lambda_{\text{max}} = 522 \text{ nm}$ in aqueous solution, towards shorter wavelengths. Due to the very rapidly established equilibrium between metal ions and murexide in solution,^{14,15} the indicator has been successfully used in the competitive study of the thermodynamics¹⁶⁻²⁰ and kinetics^{16,21-24} of a variety of metal ion complexes. We have previously reported the spectrophotometric study of murexide complexes with alkali,²⁵ alkaline earth²⁶ and transition metal ions^{27,28} in nonaqueous media. In this paper we report the complexation of Li^+ , Na^+ and K^+ ions in different binary dimethylsulfoxide-acetonitrile mixtures by both nuclear magnetic resonance and spectrophotometry.

Experimental

Reagent grade murexide, lithium perchlorate, sodium perchlorate and potassium nitrate (all from Merck) were of the highest purity available and used without any further purification except vacuum drying over P_2O_5 . Reagent grade acetonitrile (AN, Merck) and dimethylsulfoxide (DMSO, Merck) were purified and dried by previously described methods.²⁹ Different DMSO-AN solvent mixtures were prepared by weight.

All nuclear magnetic resonance measurements were made on a JEOL FX90Q FT-NMR Spectrometer with a field strength of 21.13 kG. At this field, lithium-7 resonates at 33.74 MHz. A 4.0 M aqueous LiCl solution was used as external reference and the reported lithium-7 chemical shifts refer to this solution. The paramagnetic (downfield) shift from the reference is designated as being positive. All chemical shift measurements were carried out at a probe temperature of 25.0 ± 0.1 °C.

Recording all electronic spectra and the absorbance measurements at fixed wavelengths were carried out on a Shimadzu model UV-263 spectrophotometer, equipped with a Shimadzu CPS controller model 260 thermostat at 25.0 ± 0.1 °C.

Results

Spectrophotometric Studies

The absorption spectra of murexide (2.0×10^{-5} M) and its complexes with Li^+ , Na^+ and K^+ ion in various DMSO-AN mixtures were recorded. Sample visible spectra for titration of murexide with Na^+ ion in 7% AN at 25 °C are shown in Fig. 1. As it was pointed out before,^{10,27,30} all the resulting complexes are distinguished by a strong and ion specific blue shift (~ 20 – 60 nm), reasons of which are discussed elsewhere.^{25,26,31} The stoichiometry of the complexes in different DMSO-AN mixtures was examined by the method of continuous variations.^{32,33} Samples of the resulting plots are shown in Fig. 2. In all cases, the metal ion to ligand mole ratio in the alkali-murexide complexes was found equal to 1:1. Moreover, the existence of a well-defined isosbestic point in the spectra of murexide upon titration with alkali cations (Fig. 1) is also a good indication for a simple 1:1 complexation equilibrium.

To determine the formation constants of the resulting 1:1 complexes in various DMSO-AN solutions, the spectra of solutions containing a constant amount of murexide (2.0×10^{-5} M) and varying excess amounts of the alkali cations were obtained (cf. Fig. 1). The plots of $1/(\epsilon_A - \epsilon_{\text{Mu}})$ vs. $1/C_M$ gave straight lines, in accordance to equation (1):^{25,34}

$$\frac{1}{\epsilon_A - \epsilon_{\text{MMu}}} = \frac{1}{\epsilon_{\text{MMu}} - \epsilon_{\text{Mu}}} \left(1 + \frac{1}{K_f C_M} \right) \quad (1)$$

where $\epsilon_A = A/C_{\text{Mu}}$, A is the absorbance of the solution, C_{Mu} is the total concentration of alkali metal ion and ϵ_{Mu} and ϵ_{MMu} are the molar absorptivities of the ligand and complex, respectively.

Sample linear plots of $1/(\epsilon_A - \epsilon_{\text{Mu}})$ vs. $1/C_M$ for the murexide- Li^+ system in different DMSO-AN mixtures are shown in Fig. 3. The K_f values evaluated from the slopes and intercepts of the resulting plots are summarized in Table I.

Nuclear Magnetic Resonance Studies

Lithium-7 chemical shifts of 0.005 M solutions of Li^+ ion in different DMSO-AN mixtures in the absence and presence of 0.005 M of Na^+ and K^+ ions were measured as a function of the mole ratio of murexide to lithium ion. In all cases, only one population-average resonance was observed, indicating that the exchange rate of the cation between the bulk solution and the complexed site is fast on the NMR time scale. The resulting mole ratio data are shown in Fig. 4. As it is seen, in all solvent mixtures, addition of murexide to the Li^+ ion solutions (curves number 1 in Fig. 4) causes an almost linear paramagnetic shift which begins to level off at mole ratios greater than unity. The slope of the corresponding mole ratio plots changes significantly at the point where the ligand-to-cation mole ratio is equal to one, emphasizing the formation of a relatively stable 1:1 complex. On the other hand, as it is obvious from Fig. 4 (curves number 2 and 3), unlike the case involved in the formation of 1:1 murexide- Li^+ complex in which the

change in chemical shift with murexide/ Li^+ mole ratio is quite linear at mole ratios < 1 , the ^7Li chemical shift shows a curved relationship for murexide/ Li^+ mole ratios between 0 and 2. However, in all cases, a plateau in chemical shift is reached at mole ratios greater than two. This is obviously indicative of the quantitative formation of 1:1 complexes of murexide with all cations used, which is in support of the results obtained spectrophotometrically.

Fig. 1. Visible spectra for titration of murexide (2.0×10^{-3} M) with Na^+ ion in 15% AN at 25°C . Respective concentrations of the Na^+ ion (M) in different solutions are: 1, 0.0; 2, 1.0×10^{-3} ; 3, 2.0×10^{-3} ; 4, 3.0×10^{-3} ; 5, 4.0×10^{-3} ; 6, 5.0×10^{-3} ; 7, 6.0×10^{-3} ; 8, 7.0×10^{-3} ; 9, 8.0×10^{-3} ; 10, 9.0×10^{-3} .

Fig. 2. Continuous variations plots for different M^+ -murexide systems in DMSO solution.

Fig. 3. Linear plots of $1/(\epsilon_A - \epsilon_{\text{Mu}})$ vs. $1/C_M$ for Li^+ -murexide in different solvent mixtures: (1) 0% AN; (2) 7% AN; (3) 15% AN; (4) 23% AN.

Fig. 4. Lithium-7 chemical shifts as a function of murexide/Li⁺ mole ratio in the absence (1) and presence of K⁺ (2) and Na⁺ (3) ions in different solvent mixtures: (A) 0% AN; (B) 7% AN; (C) 15% AN; (D) 23% AN.

TABLE I. Formation constants of the murexide-Li⁺, -Na⁺ and -K⁺ complexes in different DMSO-AN mixtures at 25 °C^a

wt% AN	Method	log K _f		
		Li ⁺	Na ⁺	
0	NMR Spect.	2.15	2.47	2.19
		2.05	2.55	2.25
		1.99 ^b	2.58 ^b	2.18 ^b
7	NMR	2.41	2.75	2.53
	Spect.	2.37	2.72	2.51
15	NMR	2.68	2.91	2.76
	Spect.	2.58	2.84	2.79
23	NMR	2.82	3.09	2.92
	Spect.	2.81	3.13	2.98

^aSD on log K_f values is at the most ±0.05.

^bData taken from Ref. 25.

The formation constants of 1:1 murexide-Li⁺ complex in different solvent mixtures were calculated from the variation of the ⁷Li chemical shift with the murexide/Li⁺ mole ratio. It has been shown previously that the observed chemical shift is given by:³⁵

$$\delta_{\text{obs}} = \left\{ [K_f C_M - K_f C_{\text{Mu}} - 1] + (K_f^2 C_{\text{Mu}}^2 + K_f C_M^2 - 2K_f C_{\text{Mu}} C_M + 2K_f C_{\text{Mu}} + 2K_f + 2K_f C_M + 1)^{1/2} \right\} (\delta_M - \delta_{\text{MMu}}) / 2K_f C_M + \delta_{\text{MMu}} \quad (2)$$

where δ_M and δ_{MMu} are the respective chemical shifts of the free and complexed lithium ion. A non-linear least-squares curve fitting program KINFIT³⁶ was used to evaluate K_f and δ_{MMu} values for the resulting complex, by fitting the δ_{obs} , vs. C_{Mu} data (at constant $C_{\text{Li}} = 0.005$ M). A sample computer fit of the ⁷Li

chemical shift-mole ratio data is shown in Fig. 5A, and the calculated $\log K_f$ values are also given in Table I. A fair agreement between the observed and calculated chemical shifts shown in Fig. 5A further the formation of a complex with 1:1 stoichiometry between Li^+ and murexide.

Fig. 5. Computer fit of lithium-7 chemical shift vs. murexide/ Li^+ mole ratio in 23% AN at 25 °C in the absence (A) and presence (B) of Na^+ ions: (x) experimental point; (o) calculated point; (=) experimental and calculated points are the same within the resolution of the plots.

The competitive complexation equilibria for the case of 1:1 complexation between murexide and Li^+ ions (i.e. Na^+ and K^+ ions) can be written as:

The charges are omitted for simplicity. The free murexide concentration, $[\text{Mu}]$, is then obtained from equation (5):

$$K_f K_f' [\text{Mu}]^3 - \{K_f K_f' (C_{\text{Mu}} - C_{\text{Li}} - C_{\text{M}}) - K_f - K_f'\} [\text{Mu}]^2 - \{K_f (C_{\text{Mu}} - C_{\text{Li}}) + K_f' (C_{\text{Mu}} - C_{\text{M}}) - 1\} [\text{Mu}] - C_{\text{Mu}} = 0 \quad (5)$$

In this case, the observed ^7Li chemical shift is obtained from equation (6):³⁴

$$\delta_{\text{obs}} = P_{\text{Li}} \delta_{\text{Li}} + P_{\text{LiMu}} \delta_{\text{LiMu}} \quad (6)$$

where P_{Li} and P_{LiMu} are the mole fractions of free and complexed Li^+ ion, respectively. By substitution from equation (3) and the mass balance equation $C_{\text{Li}} = [\text{Li}^+] + [\text{Li-Mu}]$, equation (6) can be written as:

$$\delta_{\text{obs}} = \{\delta_{\text{Li}} + \delta_{\text{LiMu}} [\text{Mu}] K_f\} / \{1 + K_f [\text{Mu}]\} \quad (7)$$

The K_f values were evaluated by obtaining the free murexide concentration, $[\text{Mu}]$, from equation (5) and fitting the chemical shift-mole ratio data to equation (7), by using the KINFIT program.

A sample computer fit of the mole ratio data for a ternary Li^+ -Mu- K^+ system is shown in Fig. 5B and the resulting K_f values for murexide complexes with Na^+ and K^+ complexes are also included in Table I. Our assumption of 1:1 stoichiometry of both Li^+ -murexide and M^+ -murexide complexes seem reasonable in the light of fair agreement between the observed and calculated chemical shifts.

Discussion

From the data given in Table I, it is immediately obvious that, in the case of all metal ion-murexide complexes in different DMSO-AN mixtures, the K_f values obtained with both NMR and spectrophotometric techniques (and those previously reported in pure DMSO) are in satisfactory agreement. It is also seen that, in all solvent mixtures used, the stability of the complexes vary in the order $\text{Na}^+ > \text{K}^+ > \text{Li}^+$. A similar order has already been reported in the literature.²⁵

Fig. 6. Variation of average $\log K_f$ values for different murexide complexes with X_{AN} : (1) Na^+ ; (2) K^+ ; (3) Li^+ .

The reported crystalline structures for the Li^+ ³⁷ and K^+ ³⁸ complexes of murexide show that the two approximately planar barbiturate rings of the ligand are not coplanar, the interaction between neighboring carbonyl groups causing torsion about the central nitrogen-carbon bonds. Thus, the highest stability observed for Na^+ complex among the alkali ions used is probably due to the proper ionic size of this cation, which could favor a suitable spatial fit with the flexible donating atoms of murexide in solution (i.e. the bridging nitrogen atom and neighboring oxygens). However, it should be noted that the thermodynamic stability is not just a measure of the absolute metal ion-ligand interaction, but is a measure of relative strength as compared to ionic solvation of all charged species involved in the complexation reaction (i.e. metal ion and murexide). Thus, the highest stability observed for the sodium-murexide complex results from a balance between the binding and solvation energies.

The data given in Table I clearly revealed that the solvent properties play a fundamental role in the complex formation processes. In all cases, the stability of resulting 1:1 complexes increases with increasing amount of AN in the mixed solvent. It is well known that the Gutmann donating ability of solvent, DN ,³⁹ plays a key role in different complexation reactions.^{6,7,19,20,25,26,28} DMSO is a solvent of high solvating ability ($\text{DN} = 29.8$) which can strongly compete with murexide for the metal ions. Thus, it is not surprising that addition of AN as a solvent of relatively low donor number ($\text{DN} = 14.1$) to DMSO will increase the stability of murexide complexes. It should be noted that the somewhat lower dielectric constant of AN (38.0) in comparison with that of DMSO (45.0) would also cause the electrostatic contribution to the bond formation to increase with increasing amount of AN in the solvent mixture.

It is interesting to note that there is actually a linear relationship between $\log K_f$ of the murexide complexes and the mole fraction of AN (X_{AN}) in the mixed solvent (Fig. 6). The same trend has already

been reported for various complexes in different mixtures.^{20,21,22,23,24} It has been reasonably assumed that the preferential solvation of cations by DMSO is mainly responsible for such a monotonic dependence of the overall stability of the murexide complexes on the solvent composition.

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