

INVESTIGATION OF URANYL NITRATE EXTRACTION FROM KETONE SOLUTIONS BY DIMETHYL SULFOXIDE

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Based on an analysis of low-temperature luminescence spectra ($T = 77$ K) of $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ solutions in acetone, the mechanisms of formation of a wide group of uranyl complexes in uranyl extraction from solutions by dimethyl sulfoxide are studied. It is shown that to increase the coefficient of uranyl distribution between the solution and solid phase (in the form of $\text{UO}_2(\text{NO}_3)_2 \cdot 2\text{DMSO}$) it is necessary to add sulfoxide in small amounts, of about 0.35–0.5 mole per mole of uranyl. One-time introduction of DMSO in amounts of 1–3 mole per mole of uranyl leads to the formation of a number of uranyl complexes that are well soluble in acetone, and to a corresponding decrease in the distribution coefficient. The role of entropy and enthalpy in improvement of the stability of chelate complexes of uranyl nitrate is evaluated.

Key words: luminescence, uranyl nitrate, extraction, donating ability.

Extraction methods have received wide acceptance for recent years. The number of organic compounds used in extraction has drastically increased. New extractants belonging to diverse classes of compounds make it possible to reach high selectivity and efficiency of separation of inorganic compounds. Extraction methods are widely adopted in nuclear fuel technology, in analytical chemistry, as well as in production of different inorganic compounds. Moreover, they are actively employed for investigation of the structure, composition, and properties of inorganic compounds [1], including those of uranyl.

One of the most important types of extraction is salt extraction into an organic phase, which occurs due to solvation or the formation of an uncharged chelate. How and by which mechanism does the extraction of uranyl salts proceed? This question is complicated and cannot be answered unambiguously, if for no other reason than the fact that several hundreds of various extractants are known for the uranyl ion, and effective extraction of the latter can proceed simultaneously by several mechanisms depending on many factors. Determination of the optimum extraction conditions and the search for new extractants and complexing agents are hindered by the absence of an adequate theory of extraction, which often makes searches ineffective, requires testing of a large number of different reagents, numerous concentration ratios of substances, and so on. As a rule, actual extraction processes are very complicated, and, therefore, in order to determine optimum extraction conditions it is necessary to carry out comprehensive studies.

In the present work, on the basis of an analysis of low-temperature luminescence spectra ($T = 77$ K) of $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ solutions in acetone we investigated the mechanisms of formation of a wide group of the complexes of uranyl in its extraction from solutions by dimethyl sulfoxide (DMSO). The role of entropy and enthalpy in the increased stability of chelate complexes of uranyl nitrate in hybrid solvents was evaluated.

The initial fragments of luminescence spectra of uranyl nitrate $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ solutions ($C = 0.02$ mole/liter) in acetone with added DMSO are shown in Fig. 1. The spectrum of a pure solution of uranyl nitrate in acetone (Fig. 1, curve 1) exhibits two rather narrow bands with the 20,769 and 19,864 cm^{-1} frequencies

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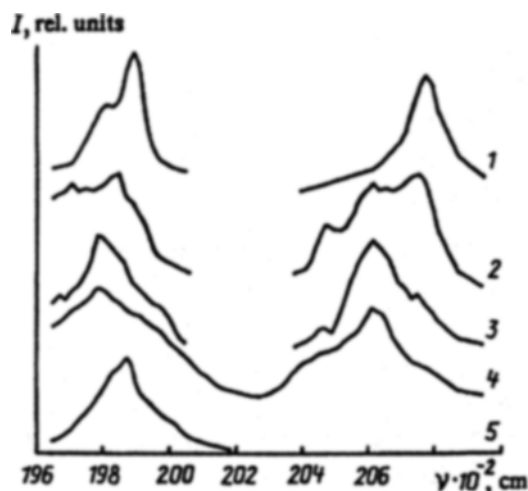


Fig. 1. Initial parts of luminescence spectra of $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ solutions in acetone with DMSO added. The $\text{DMSO}:\text{UO}_2^{2+}$ ratios are equal to: 1) 0; 2) 0.5; 3) 1; 4) 3; 5) 5.

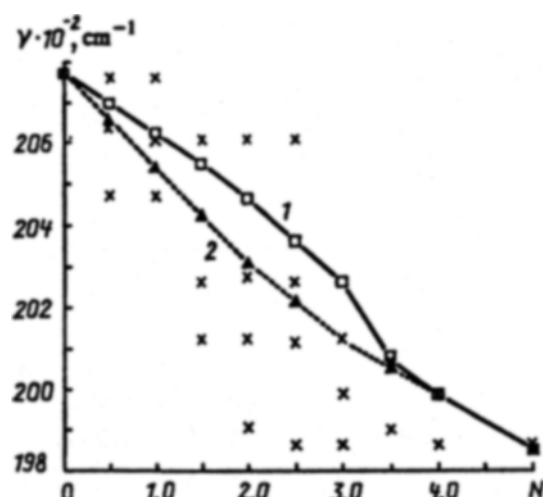


Fig. 2. Frequencies of purely electronic transitions in uranyl complexes versus the number of added DMSO molecules with the initial substitution in $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, respectively, of: 1 - nitrate groups and 2 - water molecules; \times - experimental points.

corresponding to purely electronic and vibronic transitions to a vibrational level (symmetrical) of the ground state of an uranyl-ion. With DMSO added to this solution in an amount of 0.5 molecule per uranyl ion ($\text{DMSO}:\text{UO}_2^{2+} = 0.5:1.0$), the spectrum undergoes considerable changes (Fig. 1, curve 2). The maxima of the bands are shifted toward the longwave part and become broadened, and some new bands emerge. These facts are indicative of the appearance of new complexes in the solution, the composition of which contains DMSO molecules. Here, attention should be paid to the degree of mixing of the solution. As experience shows, for good reproduction of spectra of different samples mixing must be done for no less than 3 min. This can be explained by the fact that the rate of substitution of some ligands for others is limited by that of diffusional transfer of molecules from the volume of the solvent to the ion-complexing agent, and, as this rate is finite, a certain interval of time or corresponding mixing is required to reach equilibrium in the system.

With an increase of the amount of DMSO molecules in the solution (1:1), the position of bands in the spectrum is shifted toward the longwave part even more, and in this case the halfwidth of the bands slightly decreases (Fig. 1, curve 3). With a further increase the amount of DMSO molecules in the solution (Fig. 1, curve 4), the position of the shortwave band is almost unchanged, but its intensity drastically decreases, while in the longer-wave region ($20,250\text{--}20,000\text{ cm}^{-1}$) the spectrum is distorted. This fact testifies to the successive formation of new types of complexes.

When DMSO molecules are added to the solution in amounts up to the ratios $\text{DMSO}:\text{UO}_2^{2+} = 1.5:4.0$, the spectrum changes mainly in the longwave region, while the shortwave band does not displace and gradually decreases with respect to the intensity. In this concentration interval little precipitation is observed in the solution.

With a further increase in the concentration of DMSO molecules (5:1), the bands of purely electronic transitions in the shortwave spectrum almost disappear, while in the longwave region (Fig. 1, curve 5) only one, rather broad, luminescence band is observed. With a considerable increase in the DMSO concentration, the position of this band remains practically unchanged; only its form and intensity change. The band becomes narrower and more symmetrical.

To determine the composition of the first coordination sphere of the complexes, we will analyze the dependence of the position of bands in the spectrum on the type of ligands entering the complexes. For this, we used

TABLE 1. Positions of Bands ν_{00} and $\nu_{00}-\nu_1$ (cm^{-1}), Their Halfwidth (cm^{-1}) and Relative Intensities I (rel. units) in Luminescence Spectra of Uranyl Nitrate Solutions as Functions of the Number N of Added DMSO Molecules and the Tentative Composition of the First Coordination Sphere of an Uranyl Ion

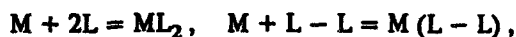
N	ν_{00}	$\Delta\nu$	I	$\nu_{00}-\nu_1$	$\Delta\nu$	I	Composition
0	20,769	130	62	19,894	160	100	$2\text{NO}_3^- \cdot 2\text{H}_2\text{O}$
0.20	20,740	230	100	19,844	290	100	$2\text{NO}_3^- \cdot 2\text{H}_2\text{O}$
0.35	20,760						$2\text{NO}_3^- \cdot 2\text{H}_2\text{O}$
		260	43	19,844	280	100	
	20,660						$2\text{NO}_3^- \cdot \text{H}_2\text{O} \cdot \text{DMSO}$
	20,460		12				$2\text{NO}_3^- \cdot 2\text{DMSO}$
0.50	20,760						$2\text{NO}_3^- \cdot 2\text{H}_2\text{O}$
		390	42	19,860	270	100	
	20,644						$2\text{NO}_3^- \cdot \text{H}_2\text{O} \cdot \text{DMSO}$
	20,465		23				$2\text{NO}_3^- \cdot 2\text{DMSO}$
1.00	20,760		35				$2\text{NO}_3^- \cdot 2\text{H}_2\text{O}$
	20,607	205	65	19,784	270	100	$2\text{NO}_3^- \cdot \text{H}_2\text{O} \cdot \text{DMSO}$
	20,470		13				$2\text{NO}_3^- \cdot 2\text{DMSO}$
1.45	20,590	200	50	19,784	420	100	$2\text{NO}_3^- \cdot \text{H}_2\text{O} \cdot \text{DMSO}$
	20,260		25				$2\text{NO}_3^- \cdot 2\text{DMSO}$
	19,905		80				5DMSO
1.75	20,590	220	52	19,784	420	100	$2\text{NO}_3^- \cdot \text{H}_2\text{O} \cdot \text{DMSO}$
	19,904		85				5DMSO
2.10	20,607		50	19,784	480	100	$2\text{NO}_3^- \cdot \text{H}_2\text{O} \cdot \text{DMSO}$
	20,275		40				$2\text{NO}_3^- \cdot 2\text{DMSO}$
	19,904	480	110				5DMSO
2.50	20,607		35				$2\text{NO}_3^- \cdot \text{H}_2\text{O} \cdot \text{DMSO}$
	19,860	430	100				5DMSO
3.50	20,060		60				$4\text{DMSO} \cdot \text{H}_2\text{O} + 3\text{DMSO} \cdot 2\text{H}_2\text{O}$
	19,900		125	19,092		100	5DMSO

correlation dependences [2-4] of the position of the purely electronic transition in an uranyl ion on the total number of ligands entering the first coordination sphere. The calculated dependences of the position of the purely electronic transition on the number of DMSO molecules added are given in Fig. 2. The points on curve 1 correspond to the case when DMSO molecules are at first substituted for water molecules of the first coordination sphere of uranyl and then for nitrate ions. The points on curve 2 stand for the reverse sequence of substitution. Results of processing of the spectra and possible forms of the complexes formed in the solution in the course of adding DMSO are given in Table 1. An analysis of the graphs and the results contained in the table reveals that in the case of adding DMSO in small amounts, water molecules are replaced first. The $\text{UO}_2(\text{NO}_3)_2 \cdot 2\text{DMSO}$ complexes formed are almost insoluble in acetone; therefore, very fine crystals are formed in the solution and are suspended for some time in the latter. In this DMSO concentration range ((0.35-1.00):1), the intensity of the luminescence bands ($\nu_{00} = 20,475 \text{ cm}^{-1}$) assigned to these complexes at first increases and then decreases. In the case of high concentrations ((1-4):1), crystals rapidly grow and soon precipitate. Simultaneously, uranyl complexes free of nitrate groups are formed in the solution (see Table 1). After substitution of DMSO molecules for nitrate ions, the complexes again become acetone-soluble.

In connection with the fact that the donating ability, characterized (according to Gutman [5]) by the donation number (DN), is much lower for a nitrate ion than for H_2O and DMSO ($DN(NO_3^-) \approx 12$, $DN(H_2O) = 17-18$, $DN(DMSO) = 29.8$), the coordination stability of nitrate ions with respect to uranyl and the easier initial substitution of DMSO molecules for water molecules could be attributed only to the chelate effect, since a nitrate ion is a bidentate ligand.

To elucidate the role of the chelate effect in the stability of the nitrate complexes of uranyl, we consider in brief the nature of this effect. The latter, though it has long been known in chemistry, is still debatable. Its essence lies in the fact that ligands with two or more donor groups arranged so that they are capable, upon metal ion coordination, of forming five- or six-member rings, form complexes with considerably higher stability constants as compared to the corresponding monodentate ligands.

Quantitatively, the chelate effect is evaluated by the logarithmic difference between the stability constants of the following reactions:



$$\log \beta_{\text{chel}} = \log \beta_{1 \text{ } M(L-L)} - \log \beta_{2 \text{ } ML_2}.$$

Hence, it is seen that the chelate effect represents an equilibrium constant of the reaction



As

$$-RT \ln K = \Delta_{\text{chel}} G^0 = \Delta_{\text{chel}} H^0 - T \Delta_{\text{chel}} S^0,$$

the causes of increased chelate stability are usually treated by analyzing the changes in the entropy and enthalpy components of the Gibbs energy.

An explanation of the entropy nature of the chelate effect is given by G. Schwarzenbach [6]. He has suggested that chelation is a stepwise process: at first a bidentate ligand adheres to a metal cation by one donor atom and then coordination of the second donor atom occurs. The probability of coordination of the second donor atom must be proportional to its effective concentration in the immediate vicinity of a metal cation. In a dilute solution, this effective concentration of donor atoms of the chelate ligand near a metal cation considerably exceeds the mean ligand concentration in the entire volume of the solution, since the second donor atom of the ligand, being already connected by one end to the metal cation, is confined in a relatively small volume of the solution surrounding this metal cation.

It can be inferred from our experimental results that in more dilute solutions uranyl complexes exhibit better stabilization of the chelate group NO_3^- as compared to monodentate ligands, i.e., water molecules. And, on the contrary, the chelate effect slowly decreases with an increasing concentration of DMSO molecules in the solution and remains virtually insignificant at a concentration of DMSO: UO_2^{2+} of more than (3-4):1. A similar result is observed if solutions with a higher uranyl concentration (0.5 mole/liter) are taken.

With variation of the composition of the solvent, the contributions of rotational and translational components of entropy of the reaction remain, apparently, constant, while the contributions due to solvation of reagents change. However, resolution of a complex ion can change the length of the cation-donor atom bond of both the neutral ligand and acidoligand [7] and influence the entropy component of the Gibbs energy.

A change in the composition of the first coordination sphere in a mixed solvent can entail not only a change in the exchange rates of solvent molecules but also a change in the nature of the second coordination-sphere complex. This occurs due to the fact that replacement of water molecules in the first coordination sphere by, e.g., DMSO, dimethyl acetamide, etc. leads to the formation of a hydrophobic sphere around the complexing ion, and to a decrease in the possibility of formation of hydrogen bonds with solvent molecules of the second coordination sphere.

The main contribution to enthalpy in the formation of $\text{UO}_2(\text{NO}_3)_2 \cdot \text{H}_2\text{O} \cdot \text{DMSO}$ and $\text{UO}_2(\text{NO}_3)_2 \cdot 2\text{DMSO}$ complexes is mainly made by the difference in the energies of breaking of uranium-oxygen bonds of water molecules and newly formed uranium-oxygen bonds of DMSO molecules. These differences in enthalpies can be calculated if the donation numbers of ligands are known (see above). Enthalpy changes in the solvation of ligands and complex ions with the solvent composition are somewhat different. Therefore, the solvation component of enthalpy of chelation will also change. Chelate ring closure occurs rapidly, which is explained by a high statistical gain, since for a monodentate ligand this process is bimolecular while for bidentate ligand this is a monomolecular process. Naturally, the change in enthalpy in the latter case will be minimal (the donation ability of mono- and bidentate-coordinated nitrate groups is approximately the same).

Here it is pertinent to note that if even a comparatively small amount of DMSO molecules (1:1-1:2) is at once added, then simultaneously complexes of the type $\text{UO}_2(\text{NO}_3)_2 \cdot \text{H}_2\text{O} \cdot \text{DMSO}$, $\text{UO}_2(\text{NO}_3)_2 \cdot 2\text{DMSO}$, $\text{UO}_2^{2+} \cdot 2\text{H}_2\text{O} \cdot 3\text{DMSO}$, and $\text{UO}_2^{2+} \cdot 3\text{H}_2\text{O} \cdot 2\text{DMSO}$ are formed in the solution. Thus, from the viewpoint of implementing extraction of the $\text{UO}_2(\text{NO}_3)_2 \cdot 2\text{DMSO}$ complex from a solution, the addition of a large amount of DMSO at once is not rational. From the aforesaid it follows that for an increasing distribution coefficient, DMSO should be added in small amounts, i.e., (0.35-0.50):1.00.

In conclusion it should be noted that though in the modern chemical literature the discussions of the nature and estimates of the chelate effect sometimes cast doubt on the existence of the effect itself, in our case this is of great importance. It is also worth noting that if several compounds are formed in a solution, usually chemical analysis fails to give an adequate picture of the processes involved. But use of the dependences of the position of purely electronic transitions on total DN [2-4] makes it possible to elucidate in detail the mechanisms of complexation of uranyl compounds in different heterogeneous media. The results obtained can be employed in development of methods of quantitative determination of uranyl in various media.

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