SOLVATION AND REDOX PROPERTIES OF $[Co(en)_3]^{3+}$–$[Co(en)_3]^{2+}$ SYSTEM

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The solvation effect of a number of nonaqueous polar solvents was studied on the oxidation-reduction properties of the $[Co(en)_3]^{3+}$–$[Co(en)_3]^{2+}$ system. Interactions of these ions with the solvent molecules are discussed in terms of their coordination, which is accompanied by a specific interaction of the Lewis acid–base type, namely formation of a hydrogen bond between the interacting particles. This is the main controlling factor of the redox properties of the studied system.

Many authors have been concerned with the solvation of ions in nonaqueous media during last decades. Their results showed that the behaviour of ions in these media cannot be in most cases characterized by electrostatic concepts about ion solvation. Ion–solvent interactions can include considerable contributions of covalent bonds which cannot be explained by purely electrostatic concepts.

In contrast, the coordination chemical concept about ion solvation involves the coordination of solvent molecules to the solute ions resulting in specific interactions of the Lewis acid–base type between the interacting particles. In such cases, the dielectric constant ceases to be an adequate measure of the solvation capability since specific interactions are usually energetically more important and determine the behaviour of ions in solution.

EXPERIMENTAL

$[Co(en)_3](ClO_4)_3$ was prepared from $[Co(en)_3]Cl_3$ (ref.[1]) by exchange of anions on an ion exchanger and recrystallized for several times. Bis(biphenyl)chromium iodide (BBCrI) was prepared according to literature[2]. Tetraethylammonium perchlorate (TEAP) was prepared by neutralization of Et_4NOH with perchloric acid and recrystallized from water.

The solvents — nitromethane (NM), acetonitrile (AN), propanediol 1,2-carbonate (PDC), acetone (AC), methanol (MeOH), N,N-dimethylformamide (DMF), N,N-dimethylacetamide (DMA), dimethyl sulphoxide (DMSO), and hexamethylphosphortriamide (HMPT) were purified according to standard procedures[3]. N,N-dimethylthioformamide (DMTF) was prepared[4] from DMF and P_4S_{10} and suitably purified[5]. The water content in the purified solvents was determined by the Karl-Fischer method and was in all cases under the determination limit (10^{-4}M).

Polarographic measurements were carried out on a Model 174 A polarographic analyser with a three-electrode system consisting of a dropping mercury electrode, a platinum wire counter electrode, and a saturated Ag/AgCl reference electrode. The latter was separated from the measured solution by specially modified porous glass diaphragms[6] which prevented contamination of the measured solution with water. All measurements were done at 25°C in nitrogen atmosphere, the concentration of the supporting electrolyte was 0·1M. The depolarizer concentration was in the range $5 . 10^{-4}$—$5 . 10^{-3}$M.

RESULTS

The polarographic reduction of the complex ion $[Co(en)_3]^{3+}$ to $[Co(en)_3]^{2+}$ in the above-mentioned solvents is reversible according to the logarithmic analysis and the test according to Tomeš. The limiting current is controlled by diffusion as follows from the dependence of the wave height on the depolarizer concentration and on the square root of the height of mercury column. The half-wave potential is independent of the drop time.

For the purpose of mutual comparison, the half-wave potentials of the reversible one-electron reduction of $[Co(en)_3]^{3+}$ ions in the mentioned solvents are referred to the $E_{1/2}$ value of the redox system [BBCr(I)]/[BBCr(0)] in the same media[7-9] (Table I). This method of the internal standard eliminates the unknown liquid junction potentials between the aqueous reference and nonaqueous indicator electro-

TABLE I

Half-Wave Potentials for $[Co(en)_3]^{3+}/[Co(en)_3]^{2+}$ Redox System on the [BBCr(I)]/[BBCr(0)] Scale, Donor Numbers (DN) of Solvents[10] and their Dielectric Constants

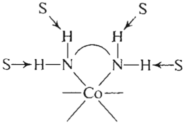
Solvent	$E_{1/2}$, V	DN	ε
NM	0·63	2·7	35·9
DMTF	0·51	11·5[a]	51·2
AN	0·52	14·1	36·4
PDC	0·47	15·1	64·4
AC	0·38	17·0	20·7
MeOH	0·48	19·0	32·6
DMF	0·19	26·6	38·3
DMA	0·17	27·8	37·8
DMSO	0·14	29·8	46·4
HMPT	0·11	38·8	30·0

[a] Value calculated from the correlation between the the donor numbers of the solvents and the corresponding $E_{1/2}$ values[6].

de. Table I shows also the donor numbers and dielectric constants of the solvents. The $E_{1/2}$ values show marked changes in dependence on the donor (base) character of the solvents.

DISCUSSION

The mentioned shift of the $E_{1/2}$ values for the redox system $[Co(en)_3]^{3+}/[Co(en)_3]^{2+}$ in dependence on the donor number of the solvent is best elucidated by the concept about coordination of the solvent molecules to the redox pair ions. With both complex ions, the H atoms bound to nitrogen of the ethylenediamine group have an acidic character and can function as acceptors with respect to the nonaqueous solvent molecules as donors with the formation of a hydrogen bond:



The half-wave potentials for the reversible one-electron reduction of the $[Co(en)_3]^{3+}$ ions are shifted to more negative values with increasing donor number DN (Table I).

In the analysis of the mentioned facts, we take into account that the studied redox system consists of a reduced form whose H atoms have weaker acceptor properties and will not interact too much with the solvent, and from the oxidised form whose H atoms are strong acceptors. The higher positive charge of the oxidised form leads to an increased polarization of the N—H bonds and as a result of this it is more stabilized, *i.e.*, it interacts more specifically with the solvent molecules than the reduced form. Donor–acceptor interactions of the solvent with this complex ion are therefore mainly responsible for the observed phenomena. With increasing donor capability of the solvent, this interaction is proportionally increased, *i.e.*, the stability of the solvate – an outer-sphere complex – increases and the half-wave potential is shifted to more negative values.

An exception from the observed dependence is methanol, in the medium of which a upper $E_{1/2}$ value was measured than would correspond to the donor property of methanol determined against $SbCl_5$ as acceptor. This result can be interpreted in terms of certain properties of methanol, which is the only protic solvent of the studied group. It is known that methanol has a "structure" formed from small clusters of several molecules bonded with a hydrogen bond[11–13]. These interactions between the solvent molecules are probably energetically more favourable than those with the polarized H atoms of ethylenediamine and for this reason methanol functions seemingly as a weaker donor. In reality, as could be observed on the obtained results, the effective donor power of the associated solvent is a function of the acceptor capability of the selected acid. In such cases the observed deviations from the assumed behaviour can serve as a means for better understanding of the ion–solvent interactions.

No general relation between the change of the $E_{1/2}$ value for the studied redox system and the dielectric constant of the solvents used was observed. For the studied solvents, the dielectric constant alone is not an adequate measure of solvation of the studied ions and it is unimportant for the description of the solvation properties of the solvents. The specific ion–solvent interactions (hydrogen bond) have a decisive and main influence on the behaviour of the studied ions in these solvents.

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