

Short Communication

Influence of Tetraalkylammonium Ions on Structure of Nonaqueous Solvents

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Summary. The half-wave potentials of the redox system $[\text{Co}(\text{en})_3]^{3+}/[\text{Co}(\text{en})_3]^{2+}$ have been influenced by the tetraalkylammonium cation of the supporting electrolyte used. This was explained with the specific interactions (solvation) of the tetraalkylammonium ion with the nonaqueous solvent.

Keywords. Solvation of tetraalkylammonium ions; Half-wave potential; Thermodynamics; Nonaqueous solvents.

Einfluß von Tetraalkylammoniumionen auf die Struktur nichtwäßriger Lösungsmittel (Kurze Mitt.)

Zusammenfassung. Das Halbwellenpotential des Redoxsystems $[\text{Co}(\text{en})_3]^{3+}/[\text{Co}(\text{en})_3]^{2+}$ wird von Tetraalkylammonium-Ionen des Stützelektrolyten beeinflusst. Dies wird durch die spezifischen Wechselwirkungen (Solvatation) der Ionen mit dem nichtwäßrigen Lösungsmittel erklärt.

Solvent–solvent and ion–solvent interactions with ions as structure makers or structure breakers influence the solvation thermodynamics mainly from the entropic point of view [1–4].

It seems that tetraalkylammonium ions (TAA^+) used as supporting electrolytes show important specific interactions with nonaqueous solvents. It is known from literature that TAA^+ ions have a strong “structure making” influence on water [5]. It was observed, however, that the Me_4N^+ ion breaks up the structure of water despite it is solvated in some nonaqueous solvents [6]. Kay and coworkers [7] found that in aqueous solutions Pr_4N^+ , Bu_4N^+ , and Am_4N^+ ions are excellent structure makers, while for the Et_4N^+ ion the two effects appear to cancel. Et_4N^+ has a size between these ions, and therefore will not interact with the solvent like Me_4N^+ (smaller) or like Pr_4N^+ , Bu_4N^+ , and Am_4N^+ ions (larger).

Similar effects of TAA^+ ions (influence on the structure of the nonaqueous solvent) were observed when the redox properties of the system $[\text{Co}(\text{en})_3]^{3+}/[\text{Co}(\text{en})_3]^{2+}$ (C^{3+}/C^{2+}) in a series of nonaqueous solvents with supporting electrolytes containing TAA^+ ions was studied. All values of the half-wave potentials, $E_{1/2}$, of the one-electron reversible reduction of the redox system in the nonaqueous

Table 1. Half-wave potentials of the redox system $[\text{Co}(\text{en})_3]^{3+}/[\text{Co}(\text{en})_3]^{2+}$ (reference BB $\text{Cr}(\text{I})/\text{BB}\text{Cr}(\text{0})$ couple) in nonaqueous solvents with the supporting electrolytes Et_4NClO_4 and Bu_4NClO_4 and the corresponding changes in the standard entropies

Solvent	Et_4N^+	Bu_4N^+	$\Delta E_{1/2}^{\text{a}}$ [V]	$\Delta\Delta S^{\text{o b}}$ [JK $^{-1}$ mol $^{-1}$]
	$E_{1/2}$ [V]	$E_{1/2}$ [V]		
<i>NM</i>	0.63	0.62	-0.01	-3.2
<i>AN</i>	0.52	0.46	-0.06	-19.4
<i>PDC</i>	0.47	0.44	-0.03	-9.7
<i>AC</i>	0.38	0.23	-0.15	-48.5
<i>MeOH</i>	0.48	0.46	-0.02	-6.5
<i>DMF</i>	0.19	0.18	-0.01	-3.2
<i>DMA</i>	0.17	0.16	-0.01	-3.2
<i>DMSO</i>	0.14	0.12	-0.02	-6.5
<i>HMPT</i>	0.11	0.10	-0.01	-3.2

$$\text{a } \Delta E_{1/2} = E_{1/2}(\text{Bu}_4\text{N}^+) - E_{1/2}(\text{Et}_4\text{N}^+)$$

$$\text{b } \Delta\Delta S^{\text{o}} = (nF/298) \Delta E_{1/2}$$

solvents with Et_4ClO_4 were greater than with Bu_4ClO_4 used as supporting electrolytes (Table 1).

The observed phenomena may be explained as follows: In solvents with a particular structure the solvation entropy change is smaller than in solvents without any structure. The desolvation of the cations at the polarographic reduction is entropically less advantageous in the solvent with structure than without that. From the expressions

$$\Delta G^{\text{o}} = \Delta H^{\text{o}} - T\Delta S^{\text{o}} \quad (1)$$

and

$$\Delta G^{\text{o}} = -nFE^{\text{o}} \cong -nFE_{1/2} \quad (2)$$

follows: the more negative ΔH^{o} and positive ΔS^{o} , the more positive E^{o} or $E_{1/2}$. Because the enthalpy changes, ΔH^{o} , will not influence the half-wave potential, the differences between the half-wave potentials of the redox system $\text{C}^{3+}/\text{C}^{2+}$ measured in the presence of the two different TAA^+ ions have to be explained by different entropy changes, ΔS^{o} .

The result of the structure making influence on the solvation of the TAA^+ ions is the decrease of ΔS^{o} and hence, the shift of $E_{1/2}$ to more negative values (Table 1). The $E_{1/2}$ values of the redox system $\text{C}^{3+}/\text{C}^{2+}$ in nonaqueous solvents with Bu_4N^+ are smaller than with Et_4N^+ . The observed results could be expected from the behavior of the TAA^+ ions in aqueous solutions [7], where the Bu_4N^+ ion had a greater influence on the solvent structure compared to Et_4N^+ .

On the basis of these results, we can conclude that the observed differences of the $E_{1/2}$ values of the redox system $\text{C}^{3+}/\text{C}^{2+}$ in nonaqueous solvents with different supporting electrolytes are entropic in character. This suggests that the Bu_4N^+ ion influences the structure of the nonaqueous solvents to a greater extent than Et_4N^+ .

Experimental Part

[Co(en)₃](ClO₄)₃ was prepared from [Co(en)₃]Cl₃ [8] by an anion exchange and neutralizing the resulting hydroxide with perchloric acid. The preparation of bisbiphenylchromium(I) iodide (BBCrI) has been described [9]. The supporting electrolytes Et₄NClO₄ and Bu₄NClO₄ have been prepared by neutralizing Et₄NOH and Bu₄NOH, respectively, with perchloric acid.

The used solvents nitromethane (NM), acetonitrile (AN), propanediol-1,2-carbonate (PDC), acetone (AC), methanol (MeOH), dimethylformamide (DMF), dimethylacetamide (DMA), dimethylsulfoxide (DMSO), and hexamethylphosphoric acid triamide (HMTP) were dried and purified according to standard procedures [10].

Electrochemical measurements were performed in three-electrode constitution in nitrogen atmosphere at 25°C. The working electrode was a dropping mercury electrode, the reference electrode was a saturated calomel electrode (SCE), and the auxiliary electrode was Pt-wire. The reference electrode was separated from the measured solution by a specially constructed salt bridge in order to prevent leakage of water from the reference electrode to the solution under investigation.

The measured half-wave potentials of the studied redox system were referred to the half-wave potentials of the bisbiphenylchromium (I/0) couple [BBCr(I)/BBCr(0)] in the respective solvents.

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