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Solvent–Solute Interaction. Solvent and Supporting Electrolyte Effects in Non-aqueous Electrochemistry of Tris(acetylacetonato)iron(III)

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Tris(acetylacetonato)iron(III) has been studied in acetonitrile, propylene carbonate, acetone, N,N-dimethylformamide, N,N-dimethylacetamide, dimethylsulfoxide, N,N-diethylformamide, methanol and ethanol employing polarographic and cyclic voltammetric methods Reversible or nearly reversible one-electron waves were registered in all these solvents containing $(C_2H_5)_4NClO_4$, $KClO_4$, $NaClO_4$ *and* $LiClO_4$ *as background electrolytes The polarographic half-wave potentials were found to vary with the nature of electrolyte cation, it has been observed that correlations between* $E_{1/2}$ *values and the reciprocal of cationic radius exist Their slopes are dependent on the properties of solvents and correlate with the appropriate values of Gutmann donor numbers All these observations are discussed in terms of the donor–acceptor concept for solvent–solute interaction*

Recent studies on the polarographic behaviour of the acetylacetonato complexes of Mn(III) [1] and Cu(II) [2] have shown that their characteristics are affected by both the properties of solvents and by the nature of supporting electrolytes This work was undertaken to learn more on the electrochemistry of tris(acetylacetonato)iron(III) in non-aqueous media

The mechanism of the polarographic reduction of $Fe(acac)_3$ has been examined with great care in acetonitrile solutions [3–5] Murray *et al* [3, 4] have found that under these conditions the reduction potential of the depolarizer is shifted toward a more positive direction by addition of $LiClO_4$ to the tetraethylammonium perchlorate supporting electrolyte Precise investigations have shown that this phenomenon is caused by coordinative relaxation of $Fe(acac)_3^-$ (it is the electroreduction product) in which an acetylacetonato ligand becomes transferred to the Li^+ ion Very similar results were obtained in N,N-dimethylformamide solutions, under these conditions also the coordinative relaxation occurs [6] Moreover, the polarographic properties of $Fe(acac)_3$ have been studied in acetone [7], but in this case the effect of electrolytes was not investigated.

It was the aim of this study to learn whether the reduction potential of $Fe(acac)_3$ may be influenced by the properties of various solvents Employing polarographic and cyclic voltammetric techniques, we have studied the reduction processes of the mentioned compound in the solvents acetonitrile (ACN), N,N-dimethylformamide (DMF), N,N-dimethylacetamide (DMA), dimethylsulfoxide (DMSO), N,N-diethylformamide (DEF), methanol and ethanol The perchlorates of $(C_2H_5)_4N^+$, K^+, Na^+ and Li^+ were used as background electrolytes

Experimental

The polarographic and cyclic voltammetric measurements (scan rate 50 mV s^{-1}) were made by means of a Radelkis OH-102 apparatus (three electrode system) The cell solutions were connected to an aqueous saturated calomel electrode The bridge solution was a solvent and electrolyte exactly as in the polarographic vessel The working electrode was either a mercury drop electrode characterized by a drop time of 2 0 s (a drop timer was used throughout experiments) or a hanging mercury drop electrode [8] of 0 80 mm diameter Coulometric measurements were carried out with a Radelkis OH-404 apparatus The u v –visible electronic absorption spectra were registered with a Specord spectrophotometer

$Fe(acac)_3$ was prepared as in ref [9] Tetraethylammonium perchlorate was obtained from $(C_2H_5)_4NBr$ and $HClO_4$ [10], recrystallized from triply distilled water and dried *in vacuo* at 60 °C Other perchlorates of AR grade were used without purification, $NaClO_4$ and $KClO_4$ were dried at 120 °C, $LiClO_4$ at 180 °C over P_2O_5 under reduced pressure. The solvents were dried and purified immediately before use according to the standard procedures [11]

The water content in the solvents, analysed by the Karl Fisher method, was about 10^{-3} *M*.

All experiments were run at 20 °C with freshly prepared solutions. Before electrochemical measurements the solutions were deoxygenated with solvent-presaturated pure argon. The concentrations of depolarizer and supporting electrolyte were 1.0 m*M* and 0.10 *M*, respectively.

Results

We have previously found [2, 12] that the molecules of bis(acetylacetonato)copper(II) are able to interact in solutions both with the molecules of solvents and with alkali metal cations. The interaction with a solvent has been attributed to the transformation of planar $Cu(acac)_2$ structure into the square-pyramidal molecule $Cu(acac)_2 \cdot solv$ [2]. In this respect it was of interest to obtain information on the influence of solvent and supporting electrolyte on the electronic spectra of $Fe(acac)_3$. Thus, we have registered these spectra in all solvents with and without the respective electrolyte. In all the cases, however, we have found three electronic transition bands characterized by wavenumbers about 36500, 28200 and 22200 cm^{-1} and by log ϵ (ϵ stands for molar absorptivity) about 4.5, 3.5 and 3.5, respectively. Bands with these same characteristics were also observed in benzene (for theoretical considerations see ref. [13]). Thus, it becomes clear that there is no specific influence of a solvent and electrolyte on peak positions and molar absorptivities of $Fe(acac)_3$. Therefore it can be deduced that the octahedral symmetry of $Fe(acac)_3$ [9] is preserved in all the media under investigation.

One cathodic wave was registered in all solvents and electrolytes during the investigations of $Fe(acac)_3$ on a dropping mercury electrode. Measurements of the wave height as a function of depolarizer concentration (in the range 0.10 to 1.20 m*M*) and as a function of the square root of the mercury height indicated that limiting currents are controlled by diffusion. The number of electrons participating in the electrode reaction was measured by means of coulometry. Large scale electrolysis, carried out on a mercury pool cathode, yielded one for the number of electrons in all solvents and electrolytes studied. Semi-logarithmic analysis yielded $\Delta E/\Delta \log\{i/(i_d - i)\}$ values in the range 60–68 mV/log unit, while the corresponding theoretical value for a reversible one-electron process is about 60 mV. The diffusion current constants, the half-wave potentials and the values for the slope of the semi-logarithmic analysis determined in solutions containing 0.10 *M* tetraethylammonium perchlorate as supporting electrolyte are summarized in Table I.

TABLE I. Essential Characteristics of the Polarographic Wave of Tris(acetylacetonato)iron(III) in Various Solvents containing 0.10 *M* $(C_2H_5)_4NClO_4$ as Supporting Electrolyte.

Solvent[a]	I_d[b]	$-E_{1/2}$, V	Slope[c], mV
ACN	3.20	0.69	65
PC	2.33	0.69	64
AC	3.42	0.66	66
DMF	2.10	0.64	62
DMA	1.88	0.65	63
DMSO	1.26	0.65	62
DEF	1.94	0.64	60
MeOH	2.44[d]	0.48[d]	67[d]
EtOH	1.71[d]	0.53[d]	68[d]

[a] For abbreviations see Experimental part. [b] $I_d = i_d/m^{2/3} t^{1/6} C$ in $\mu A\ mg^{-2/3} s^{1/2}\ mM^{-1}$. [c] Slope of the plot of E *vs.* log $i/(i_d - i)$. [d] The value has been measured in saturated solution of electrolyte (below 0.1 *M*).

TABLE II. Effect of Alkali Metal Cations on the Polarographic Half-wave Potential of 1.0 m*M* $Fe(acac)_3$. Concentrations of supporting electrolytes: 0.10 *M*.

Solvent	$-E_{1/2}$, V		
	$KClO_4$	$NaClO_4$	$LiClO_4$
ACN	0.57[a]	0.49	0.30
PC	0.58	0.52	0.35
AC	0.56[a]	0.48	0.37
DMF	0.57	0.51	0.46
DMA	0.60	0.57	0.51
DMSO	0.58	0.55	0.50
DEF	0.62	0.56	0.53
MeOH	0.45[a]	0.42	0.36
EtOH	0.51[a]	0.48	0.44

[a] The value has been measured in saturated solution of electrolyte (below 0.1 *M*).

A distinct effect has been observed for the half-wave potential upon changing the supporting electrolyte from tetraethylammonium- to alkali metal cation perchlorates. As seen from Table II these values are shifted toward the more positive direction when the cationic radius decreases.

The $Fe(acac)_3$ complex was also studied by cyclic voltammetric method and a corresponding pair of cathodic and anodic peaks was observed in all solvents and electrolytes under investigation. A typical curve is reproduced in Fig. 1.

The peak currents were controlled by diffusion and the ratios of i_{pa}/i_{pc} were equalled to the unity, independently of the nature of solvents and of the properties of supporting electrolytes. The $(E_{pa} - E_{pc})$ values are listed in Table III; it must be pointed

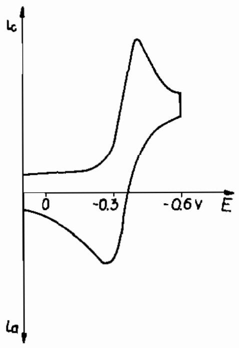

Fig. 1. Cyclic voltammetric curve of 1.0 m*M* tris(acetylacetonato)iron(III) in propylene carbonate containing 0.10 *M* $(C_2H_5)_4NClO_4$ as background electrolyte. Scan rate 50 mV s^{-1}.

out that these values are uncorrected for the ohmic drop.

TABLE III. Separation of Anodic and Cathodic Peak Potentials from Cyclic Voltammetric Curves of 1.0 m*M* $Fe(acac)_3$. Scan rate 50 mV s^{-1}, concentration of electrolyte 0.10 *M*.

Solvent	$E_{pa} - E_{pc}$, mV			
	$(C_2H_5)_4NClO_4$	$KClO_4$	$NaClO_4$	$LiClO_4$
ACN	75	80	105	160
PC	90	80	110	125
AC	100	120[a]	90	125
DMF	70	70	80	100
DMA	65	65	70	90
DMSO	70	65	70	80
DEF	75	70	90	100
MeOH	170[a]	180[a]	90	95
EtOH	160[a]	180[a]	80	95

[a] The value has been determined in saturated solution of electrolyte (below 0.1 *M*).

Discussion

As seen from Tables I and II the half-wave potential of $Fe(acac)_3$ varies considerably with the nature of the solvent and of the cation of supporting electrolyte. Thus, it was of interest to ascribe quantitatively the dependence of $E_{1/2}$ to the parameters characterizing the properties of both these species. We will first consider the data describing the influence of alkali metal ions on the half-wave potentials determined in a given solvent.

As evidently follows from Tables I and II the $E_{1/2}$ values of $Fe(acac)_3$ depend upon the crystallographic (unsolvated) radius of the cation. Plots of the half-wave potential *versus* $1/r_{M^+}$ (here r_{M^+} is the cationic radius) give linear relationships in all the solvents studied. This means that in order to ascribe the dependence of $E_{1/2}$ to the nature of the cation the empirical equation in the form

$$E_{1/2} = E^{\circ}_{1/2} + \mu \times 1/r_{M^+} \qquad (1)$$

should be offered, similarly as in the case of the ion pairing affecting electroreduction of organic compounds [16]. Thus, $E^{\circ}_{1/2}$ and μ may be simply treated as an intercept and a slope of regression line, respectively. Consequently, μ-parameter is considered as the measure of the sensitivity of half-wave potential to the effects of electrolyte cations in a given solvent. The values of μ corresponding to the

TABLE IV. Parameters of Eqn. (1) Calculated by Least Squares Method[a] and Solvent Characteristics.

Solvent	D[b]	Dipole moment[c]	DN[d]	$-E^{\circ}_{1/2}$, mV[e]	μ[e]	r[f]	F[g]
ACN	37	3.92	14.1	786 ± 10	289 ± 9	0.999	507.4
PC	69.1	4.98	15.1	772 ± 14	250 ± 13	0.998	195.1
AC	20.9	2.71	17.0	722 ± 21	216 ± 19	0.996	62.8
DMF	36.7	3.82	26.6	672 ± 29	134 ± 27	0.980	12.2
DMA	38.9	3.79	27.8	680 ± 6	103 ± 5	0.999	215.8
DMSO	45	3.96	29.8	673 ± 22	109 ± 21	0.982	13.5
DEF			30.9	674 ± 14	84 ± 13	0.988	20.9
MeOH	32.6	1.70	19(25.7)	513 ± 7	90 ± 7	0.997	82.9
EtOH	24.6	1.69	20(31.5)	555 ± 8	69 ± 8	0.993	37.9

[a] Values of the ionic radii of alkali metal and tetraethylammonium cations are taken from ref. [14] and ref. [15], respectively. [b] D = dielectric permittivity. [c] In Debye, 1 Debye = 3.3356×10^{-30} C m. [d] Gutmann's donor number taken from ref. [17], values shown in parentheses are from ref. [18]. [e] Errors are standard deviations. [f] Correlation coefficient. [g] Snedecor's F-test.

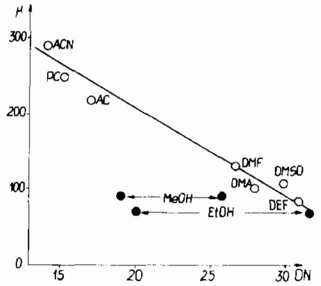

Fig. 2. Plot of the μ-value of eqn. (1) *vs.* donor number of solvents. Correlation coefficient for all points (with DN values 25.7 and 31.5 for methanol and ethanol, respectively) is r = 0.966. For the points proper for non-proton-releasing solvents (empty points) r = 0.984.

solvents applied by us are listed in Table IV. This also contains some solvent characteristics.

Now, it is of particular interest to interpret the solvent effect on the redox behaviour of $Fe(acac)_3$. Obviously, the half-wave potentials collected in Tables I and II cannot be compared with solvent characteristics, because the corresponding liquid junction potentials are unknown. Therefore, we have investigated whether μ values from Table IV can be correlated with solvent parameters. Plots of μ values *versus* the dipole moment or the dielectric permittivity showed no correlations, whereas a linear relationship was found with the solvent donor number (Fig. 2). It should be noted that as for donor number of ethanol, both 20 [17] and 31.5 [18] are indicated in Fig. 2, but 31.5 is fitted better than 20. Similarly, the correlation is visibly improved, when 25.7 [18] is chosen instead of 19 [17] for donor number of methanol.

The lack of correlations with the dipole moment and the dielectric permittivity indicates that a purely electrostatic approach fails in the interpretation of our experimental results. As seen in Fig. 2 the interpretation can be obtained on the basis of the donor–acceptor concept proposed by Gutmann for solvent–solute interaction [17]. As follows from Fig. 2 an increase in donor properties of solvents leads to a decrease in μ-value, once more similarly as in the case of ion pair formation in organic electrochemistry [19].

As first pointed out by Murray *et al.* [3, 4] the electroreduction mechanism of $Fe(acac)_3$ may be represented by the following scheme

$$Fe(acac)_{3\,solv} + e \rightleftharpoons Fe(acac)^-_{3\,solv} \tag{2}$$

$$Fe(acac)^-_{3\,solv} + (M^+)_{solv} \rightleftharpoons Fe(acac)_{2\,solv} + M(acac)_{solv} \tag{3}$$

where molecules and ions in solvated form are marked by the supscript solv. Accordingly, the electron transfer step proceeds reversibly, whereas coordinative relaxation (reaction (3)) is not fully reversible. Generally speaking, this is a reason of moderate deviations from reversibility of the polarographic and voltammetric waves of $Fe(acac)_3$ in the media investigated by us.

Neglecting this small irreversibility, coordinative relaxation can be formally treated as a phenomenon accompanied by desolvation of $Fe(acac)_3^-$ and M^+ and then by solvation of newly formed species, *viz.* $Fe(acac)_2$ and M(acac). Thus, in order to form $Fe(acac)_2$ and M(acac) in solution, the inequality

$$\Delta G^\circ_{form}\{Fe(acac)_2\} + \Delta G^\circ_{form}\{M(acac)\} + \Delta G^\circ_{solv}\{Fe(acac)_2\} + \Delta G^\circ_{solv}\{M(acac)\} < \Delta G^\circ_{solv}(M^+) + \Delta G^\circ_{solv}\{Fe(acac)_3^-\} \tag{4}$$

must be fulfilled (here ΔG°_{form} and ΔG°_{solv} stand for free enthalpy of formation and solvation, respectively). Obviously, all these terms are influenced upon changing the solvent, but these changes cannot generally be separated. Therfore, let us note only that among the species participating in reaction (3), M^+, $Fe(acac)_2$ and $Fe(acac)_3^-$ are able to undergo specific interaction with solvents. The anion $Fe(acac)_3^-$ possesses electron donating (Lewis-basic) properties, whereas M^+ and $Fe(acac)_2$ are Lewis-acidic (electron pair acceptor) agents. As a consequence, it is sufficient to take into account only the properties of M^+ and $Fe(acac)_2$ in order to explain the nature of the relationship presented in Fig. 2.

On the basis of ref. [20] one may anticipate the tendency of bis(acetylacetonato)iron(II) to undergo interaction with the molecules of electron donating solvents. Although the energetic aspects of this interaction were not until now studied, it is very probable that Lewis acidity of alkali metal cations is much stronger. In this light $\Delta G^\circ_{solv}(M^+)$ value from inequality (4) seems to be the chief contributor to the half-wave potential of $Fe(acac)_3$. We suppose also that this same term plays a decisive role in nonaqueous electrochemistry of the other complex compounds which are reversibly reduced with coordinative relaxation.

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