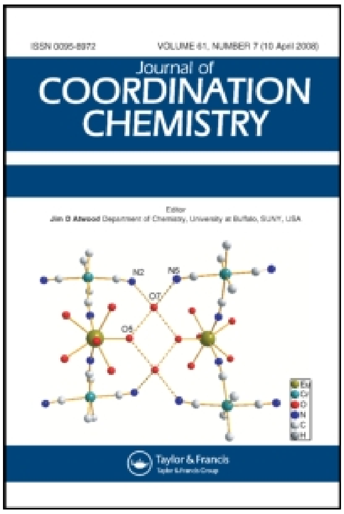

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POLAROGRAPHIC INVESTIGATIONS ON SOLVATOCHROMIC AND THERMOCHROMIC NICKEL(II) COMPLEXES IN NONAQUEOUS SOLUTIONS

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Reduction and oxidation potentials have been measured at different temperatures for solvatochromic and thermochromic mixed Ni(II) complexes with tetramethylethylenediamine and benzoylacetonate in dichloroethane (DCE), nitroethane (NE), *N*,*N*-dimethylformamide (DMF) and dimethylsulfoxide (DMSO). In DCE and NE square planar complexes are present, whereas octahedral coordination is found in DMF and DMSO. The results show that the entropy related temperature coefficients of the half wave potentials of the ligands depend strongly upon the coordination to the Ni-central atom, whereas the temperature coefficients of the Ni-potentials are invariant towards changes of the solvent. Isokinetic behaviour is found for all the ligand half wave potentials. The question is raised as to how the isokinetic temperatures are related to Raman active vibration frequencies.

Keywords: Nickel, electrochemistry, diketones, amines, isokinetic relationship

INTRODUCTION

Interest in investigating the electrochemistry of mixed Ni(II) complexes with tetramethylethylenediamine (tmen) and β-diketones (β-dik) like acetylacetonate (acac), benzoylacetonate (bzac), dibenzoylmethanate (dbzm) has been stimulated by their solvatochromic and thermochromic behaviour.[1-7] This behaviour has been interpreted as due to the reaction

$$\underset{\text{red, square planar}}{[\mathrm{Ni(tmen)}(\beta\text{-dik})]^+} + 2\mathrm{L} \rightarrow \underset{\text{blue, octahedral}}{[\mathrm{Ni(tmen)}(\beta\text{-dik})\mathrm{L}_2]^+} \tag{1}$$

in which L represents a solvent molecule. The equilibrium constants vary strongly with both the donor properties of L and the temperature. Spectral analysis has shown[1,2] that in dichloroethane (DCE) and in nitroethane (NE) the square-planar form is present, whereas in *N*,*N*-dimethylformamide (DMF) and in dimethylsulfoxide (DMSO) the octahedral form is predominant. It is obvious that the free energies of both the coordination centre and the ligands are changed in the course of reaction (1). In order to obtain information about the entropic and enthalpic contributions to these changes, the reduction and the oxidation potentials of both for the free and the coordinated ligands have been measured as a function of temperature and of solvent.

EXPERIMENTAL

For the preparation of $\mathrm{Ni(tmen)(bzac)BPh_4}$ the method of Fukuda[1] was slightly modified:. $\mathrm{Ni(NO_3)_2 \cdot 6H_2O}$ was dried over P_2O_5 for 15 hours under reduced pressure.

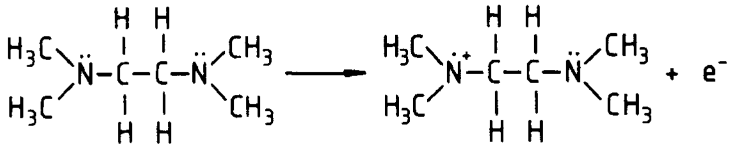
200 cm^3 of a 0.5 molar solution of tmen and the equimolar amount of bzac in dry DCE was added dropwise to 100 cm^3 of a 0.1 molar solution of the Ni compound in dry ethanol. After addition of anhydrous Na_2CO_3, the solution was refluxed for 3 hours, the aqueous phase removed and DCE evaporated. After recrystallisation from DCE, sodiumtetraphenylborate was added to the solution of Ni(tmen)(bzac)NO_3 in DCE until a colour change occurred from greenish-blue to red. The solvent was evaporated and Ni(tmen)(bzac)BPh_4 was recrystallized twice from DCE. The solvents used were purified according to standard procedures.[8-10] According to Karl-Fischer titration the water content was less than 30 mg dm^{-3}.

The polarographic and the cyclovoltametric measurements were performed using a standard polarographic and potentiostat-galvanostat system (Princeton Applied Research; Texas) based on a three electrode system. Mercury electrodes (either dropping or as a hanging drop) have been used. A nonisothermal cell arrangement[11,13] was used with a silver-wire reference electrode kept at constant temperature. The solution of 0.1 mM Ni(tmen)(bzac)BPh_4 and 0.1M NBu_4BPh_4 was placed in a thermostatted double-sided cell and pure nitrogen passed through the solution during the experiments. After the polarographic measurement bis(biphenyl)chromium(I)tetraphenylborate (BBCr) was added and its half wave potential used as reference.[13]

RESULTS AND DISCUSSION

The following reduction- and oxidation-steps[14-17] were investigated:

$$Ni^{2+} + 2e^- \longrightarrow Ni \qquad (2)$$



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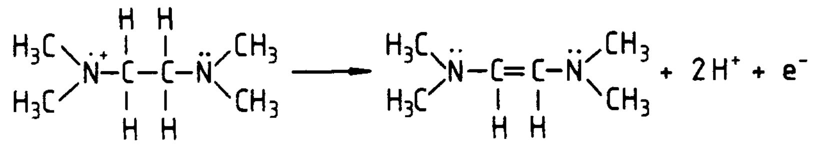

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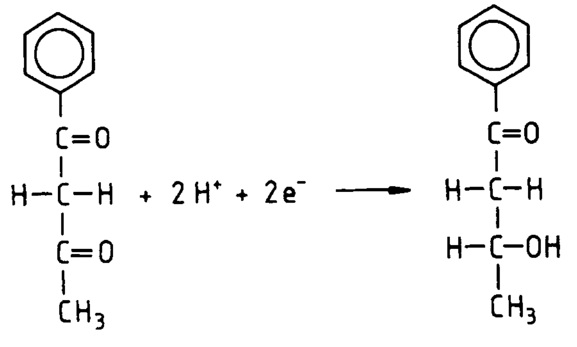

(5)

Figs. 1 and 2 show the cyclic voltamograms of the square-planar coordinated complex in DCE and the octahedral coordinated complex in DMSO, respectively. They were measured at a mercury electrode as no peaks were observed at a platinum electrode. Plots of peak current *vs* (sweep rate)$^{1/2}$ yielded straight lines which pass through the origin and with slopes in agreement with the number of electron transferred. The Ni^{2+} and the bzac reductions are irreversible on Hg in all used solvents with the exception of the bzac reduction in DMSO. The first oxidation step of tmen is irreversible in NE, slightly reversible in DCE and reversible in DMF. Such reversibility behaviour is found for the free and complexed ligands except for the second oxidation step of tmen, which is irreversible in NE and reversible in DCE, DMF and DMSO.

Table I gives the observed wave potential at 25°C. The changes due to complex formation with Ni^{2+} are much more pronounced for the oxidation potentials of tmen

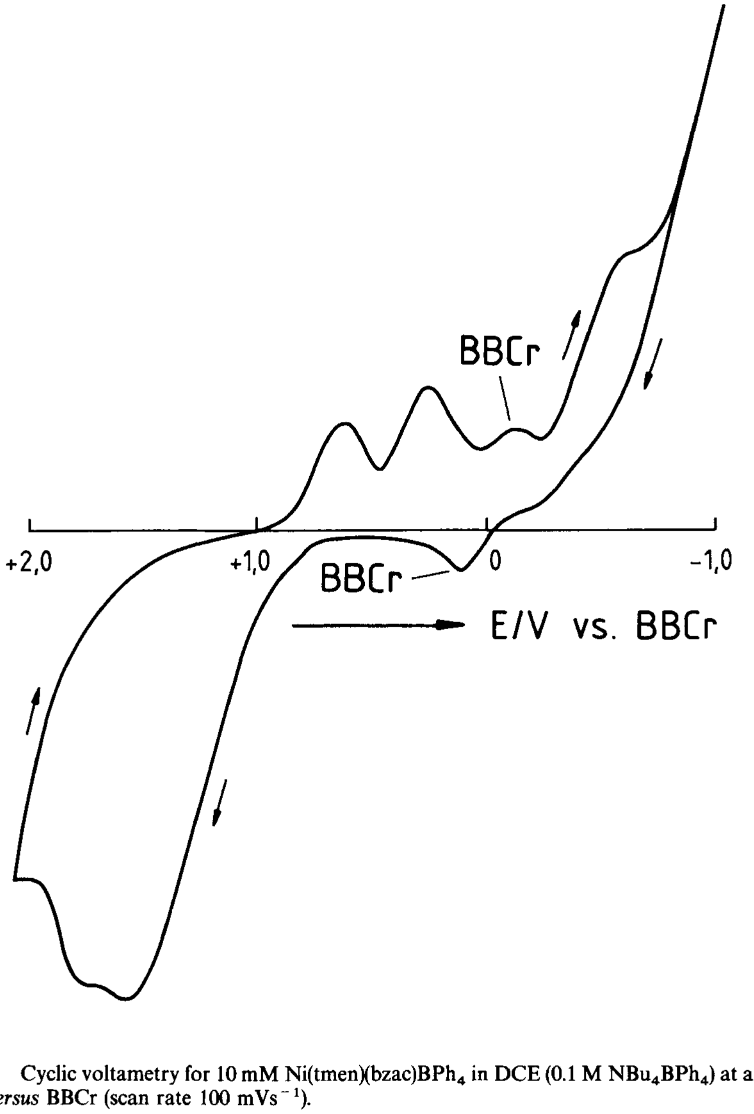

FIGURE 1 Cyclic voltametry for 10 mM Ni(tmen)(bzac)BPh_4 in DCE (0.1 M NBu_4BPh_4) at an Hg-drop electrode *versus* BBCr (scan rate 100 mVs^{-1}).

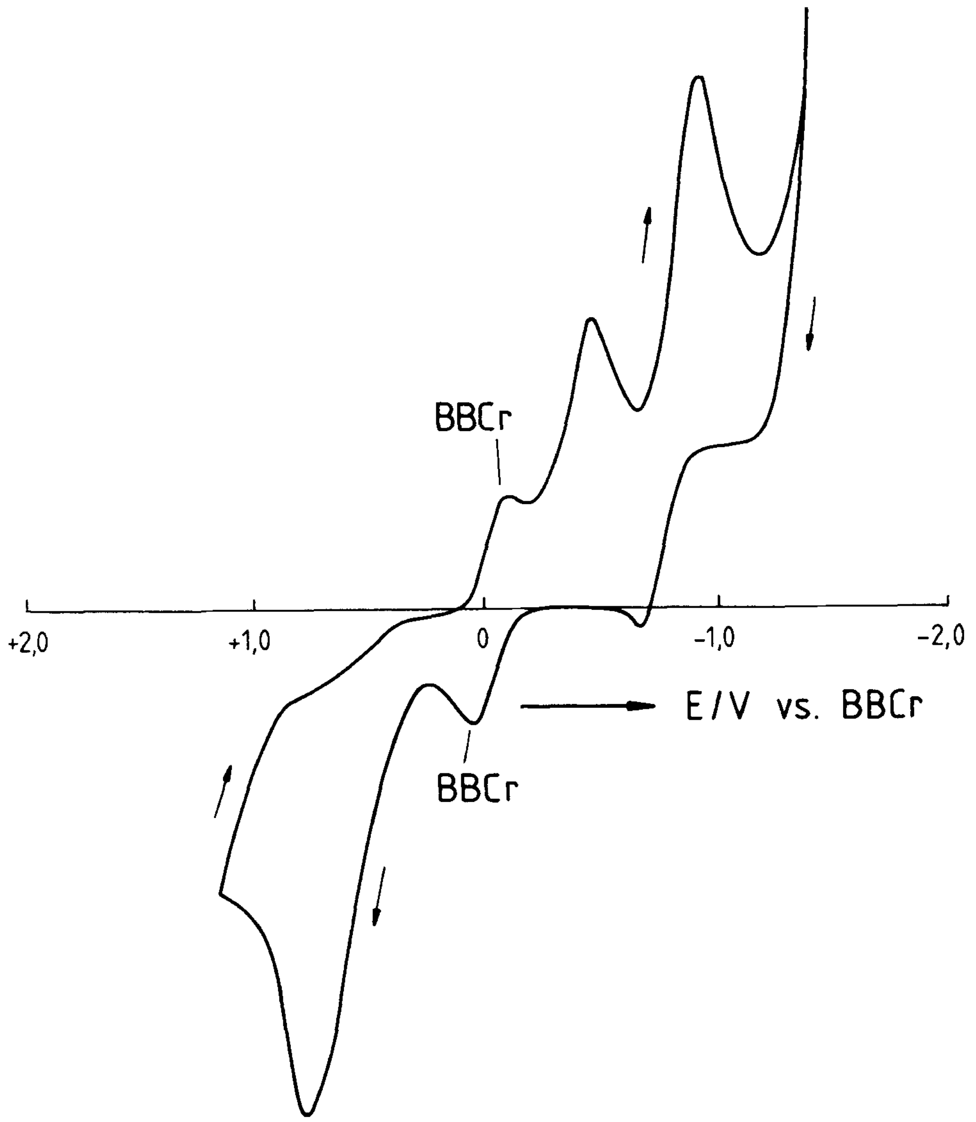

FIGURE 2 Cyclic voltametry for 10 mM Ni(tmen)(bzac)BPh_4 in DMSO (0.1 M NBu_4BPh_4) at an Hg-drop electrode *versus* BBCr. (scan rate 200mVs^{-1}).

than for the reduction potentials of bzac. As the solvent is changed, $E_{1/2}$-values of the ligands are less effected than the Ni^{2+}. The former correlate linearly with the solvent acceptor numbers[18] (AN), whereas apart from NE the latter show linear dependence with the donor numbers (DN). With increasing AN the ligands undergo more readily redox reactions, whereas increasing DN leads to a stabilization of the Ni-coordination centre. One would expect different values for the square-planar complexes (in DCE and NE) and for the octahedral complexes (in DMF and DMSO). From this point of view the potential in NE is surprisingly high. This may be due to strong π-interactions of NE with the coordinated bzac by which the coordination

TABLE I

Half wave potentials, $E_{1/2}$, in mV, for the Ni central atom (Ni-red), the two oxidation steps of free and complexed tetramethylethylenediamine (tmen-ox$_1$ and tmen-ox$_2$) and of (free and complexed) the reduction of benzoylacetonate (bzac-red) in different solutions at 25°C

Solvent		Ni-red	tmen-ox$_1$	tmen-ox$_2$	bzac-red
DCE	free		825	1260	−1095
	complexed	−471	955	1430	−1080
NE	free		780	1240	
	complexed	61	1095	1582	
DMF	free		743		−982
	complexed	−647			−987
DMSO	free		713		−860
	complexed	−727			−862

centre would become less stable. In fact, the reduction potential of bzac could not be measured within the potential range of the solvent.

Table II summarizes the temperature-dependent and temperature-independent parts of $E_{1/2}$ assuming a linear dependence of $E_{1/2}$ *versus* T according to common thermodynamics. The correlation coefficients show that this is a reasonable assumption. All half-wave potentials of the ligands show strong changes of the temperature coefficient $dE_{1/2}/dT$, when free ligands and coordinated ligands are compared. With

TABLE II

Temperature dependent and temperature independent parts of $E_{1/2}$

Solvent	reaction	$\frac{dE_{1/2}/dT}{\text{mVK}^{-1}}$	$\frac{E_{1/2}(T=0)}{\text{mV}}$	m[a]	r[b]
		free ligands			
DCE	tmen-ox$_1$	1.43	410	4	0.998
	tmen-ox$_2$	1.50	811	5	0.995
	bzac-red	0.96	−811	4	0.995
NE	tmen-red$_1$	1.49	335	6	0.983
	tmen-red$_2$	−1.32	1973	5	0.955
DMF	tmen-ox$_1$	2.50	−7.05	5	0.997
	bzac-red	−3.34	−0.315	4	0.999
DMSO	tmen-ox$_1$	2.39	−3.49	4	0.999
		Ni complexes			
DCE	Ni-red	−2.48	−338	4	0.995
	tmen-ox$_1$	−3.45	1987	4	0.997
	tmen-ox$_2$	−0.384	1550	5	0.900
	bzac-red	−2.48	−339	4	0.94
NE	Ni-red	−0.52	219	5	0.913
	tmen-ox$_1$	−4.52	2440	5	0.999
	tmen-ox$_2$	1.37	832	6	0.974
DMF	Ni-red	1.49	3.35	6	0.983
	bzac-red	−0.20	−895	5	0.902
DMSO	Ni-red	−0.4	−609	4	0.997

[a] Number of data sets (different temperatures). [b] Correlation coefficients for linear regression of $E_{1/2}$ *versus* T.

exception of the values measured in DMF and the value in NE for the second oxidation step of tmen, they also change their signs. The temperature coefficient of a potential measured in a nonisothermal cell may be interpreted as a measure of the redox entropy, if the contribution from the temperature gradient across the liquid junction and of the mercury in the working electrode can be neglected.[17,20] The latter is known[17] to be negligibly small ($\leqslant 16 \times 10^{-6}$ VK^{-1}). The former is unknown, but may be estimated to be smaller than the measurement accuracy as the same solvent was used in working and reference electrode.[21,22]

Complex formation is known to lead to a decrease of the entropy associated with reduction or oxidation of the ligands which may be interpreted as a decrease of the entropy of formation of the ligands with coordination towards Ni^{2+}. The only exception is found for the second oxidation step of tmen in NE. This seems to indicate π-interactions in NE, in agreement with the results mentioned above. Although the reduction and oxidation potentials remain almost unchanged in different solvents, their temperature coefficients (entropies) vary strongly with solvent variation. Increasing donor properties of the solvent yield increasing entropies for the oxidation of free tmen and decreasing entropies of the reduction of free bzac. After complex formaton with Ni^{2+} this behaviour is reversed, *i.e.*, the entropies are decreased for tmen and increased for bzac with increasing donor properties of the solvent. In contrast to the ligand potentials the Ni reduction potentials, which are found to be strongly influenced by a solvent variation, have almost constant temperature coefficients, *i.e.*, isoentropic behaviour in different solvents. Within a homologous series of reactions a common point of intersection found in the Arrhenius or van't Hoff plots indicates both kinetic and thermodynamic compensation effects.[24-29] In Figs. 3-6 the $E_{1/2}$ values are plotted

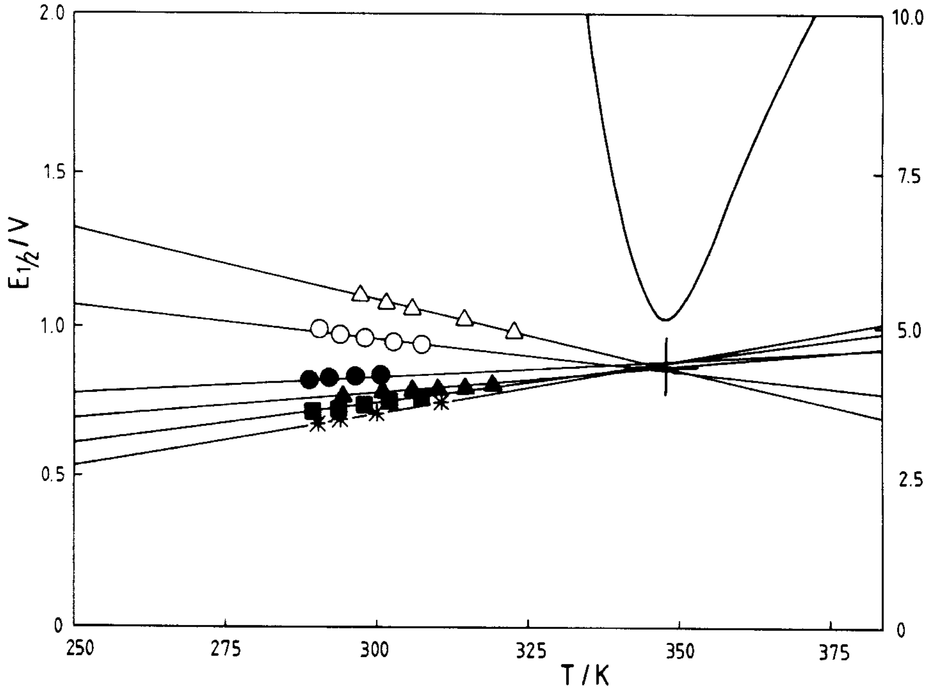

FIGURE 3 Isokinetic relationship of the tmen-ox$_1$ half wave potentials. Curved lines refer to sum of squares of deviations of constrained straight lines from experimental points (●... free ligand in DCE, ○ ... complex in DCE, ▲ ... free ligand in NE, △ ... complex in NE, ■ ... free ligand in DMF, □ ... complex in DMF, * ... free ligand in DMSO, + ... complex in DMSO).

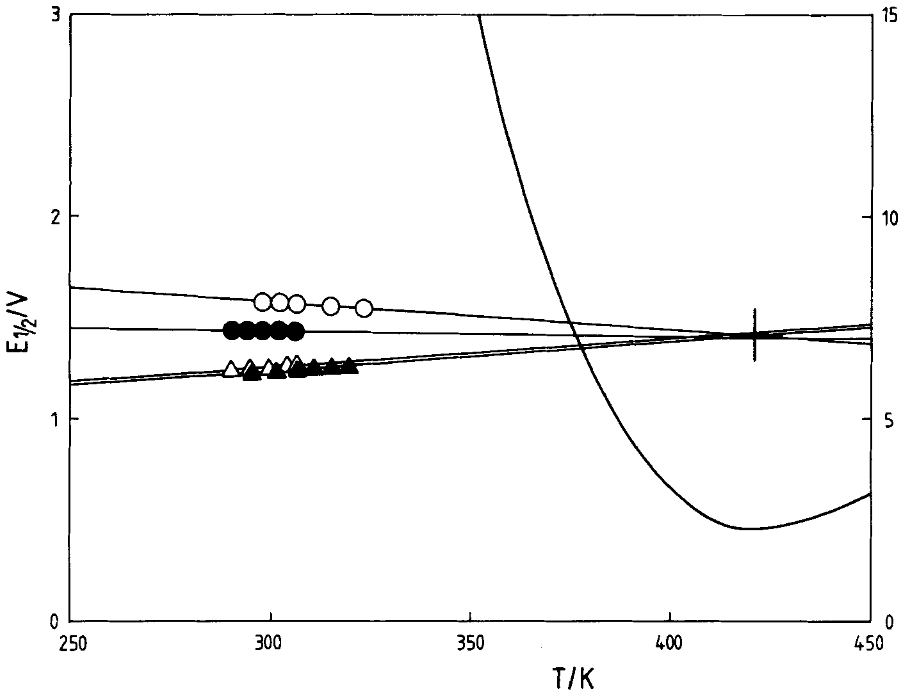

FIGURE 4 Isokinetic relationship of the tmen-ox_2 half wave potentials (for symbols see Fig. 3).

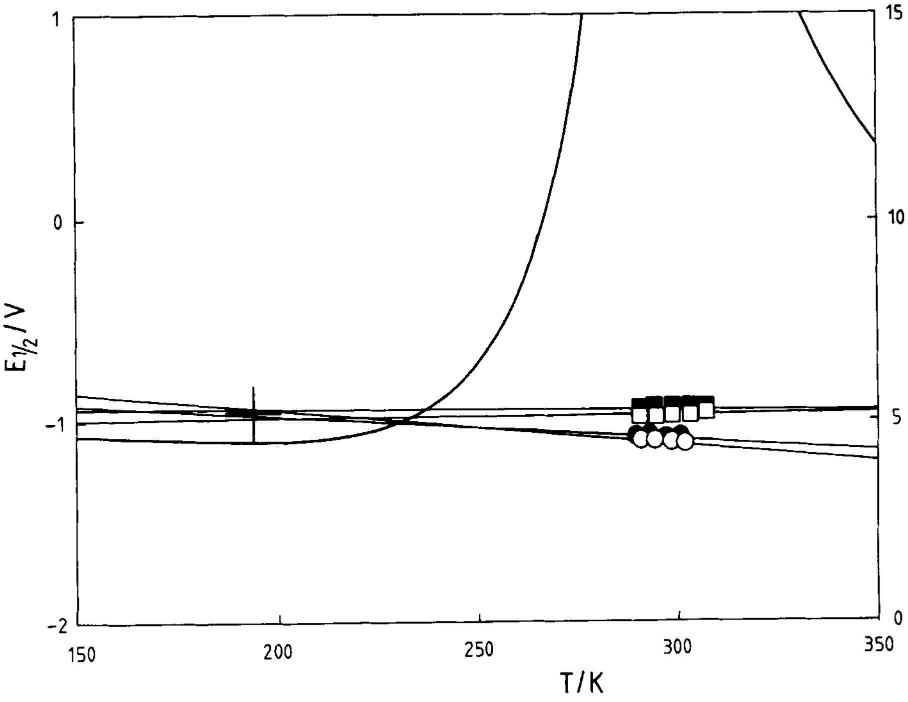

FIGURE 5 Isokinetic relationship of the bzac-red half wave potentials (for symbols see Fig. 3).

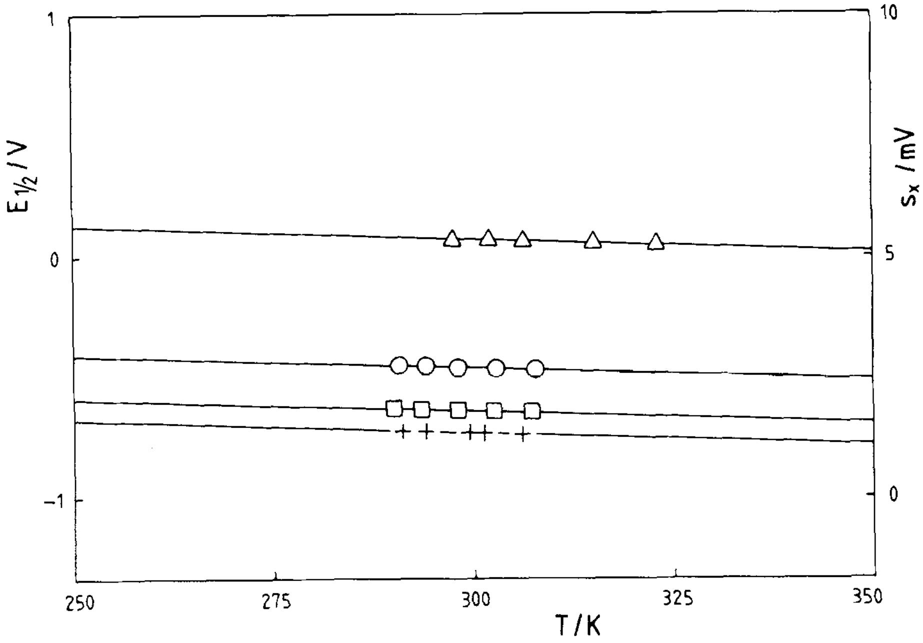

FIGURE 6 Isoentropic relationship of the Ni-reduction half wave potentials (for symbols see Fig. 3).

TABLE III
Results of the statistical analysis of the $E_{1/2}$ *vs* T data of the ligands for isoequilibrium behaviour (for details see ref[27,29])

reaction	$T_{iso}/^{K}$	$y_{iso}/^{mV}$	F	f_1	f_2
tmen-ox$_1$	348	854	2.21	4	15
tmen-ox$_2$	421	1415	2.16	3	13
bzac-red	194	−960	1.79	3	9

versus T to show such isokinetic relationships (IKR). Using proper statistical analysis[23,26,29] IKR's are found with high statistical significances in the $E_{1/2}$ *versus* T scale for all ligands varying both solvent and complexation, (see Table III).

The isokinetic temperatures for the tmen oxidation steps were found above the measurement temperature range in agreement with the so called selectivity-reactivity principle.[30] On the other hand, the bzac-reduction potentials yielded a T_{iso} value below the experimental temperature range. As pointed out above, the Ni reduction potentials are isoentropic (although strongly solvent dependent, see Fig 5). We suggest the interpretation of the isoentropic Ni potentials as due to compensation of the temperature dependencies of the ligands. The isokinetic temperature of the Ni potentials $T_{iso,Ni}$ are related[31,31] to the isokinetic temperatures of the ligands by

$$\frac{1}{T_{iso,Ni}} = \frac{1}{T_{iso,tmen-ox_1}} + \frac{1}{T_{iso,tmen-ox_2}} - \frac{1}{T_{iso,bzac-red}} \tag{7}$$

By using the values in Table III a $\frac{1}{T_{iso,Ni}}$ value of $9.4 \times 10^{-5}\,K^{-1}$ ($T_{iso,Ni} = 1.06 \times 10^4$ K) is obtained in agreement with the observed isoentropic behaviour. The fact that the coordination centre remains entropically unchanged is paralleled by the behaviour of $Fe(phen)_3{}^{2+}$ and $Fe(phen)_3{}^{3+}$ complexes. The electron distribution around the central ion seems merely independent from its surrounding[33] as any change in electron density is redistributed over the whole molecule. This has been assigned to a well-developed molecular system organisation.[34]

In the course of the reaction, energy redistribution is expected to occur over the whole system so that the reaction medium (*i.e.* solution and working electrode) either provides or absorbs energy and hence is acting as a "heat-bath system.". It has been shown that the isokinetic relatonship may be interpreted as a resonance phenomenon connected with the energy exchange between heat-bath and reactants[31,32]. Because of the continuous vibrational spectrum of amorphous mercury the frequency of resonance should be found in the vibrational spectra of the reactants.[35] According to the relation $1/RT_{iso} = 1/\hbar\nu$, infrared or Raman spectra should show bands at $241.1\,cm^{-1}$ and $293.1\,cm^{-1}$ for tmen and at $134\,cm^{-1}$ for bzac, respectively. The Raman spectrum for tmen exhibits bands at $257\,cm^{-1}$ and $287\,cm^{-1}$. Unfortunately bzac shows fluorescence and could not be measured by Raman spectroscopy. However, these reactions may contribute to our knowledge of molecular system organization[34] and therefore they will be subject to further investigations.

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