Kinetics of Complexation of Nickel(II) in Nonaqueous Solvents with Some Azo-Dyes

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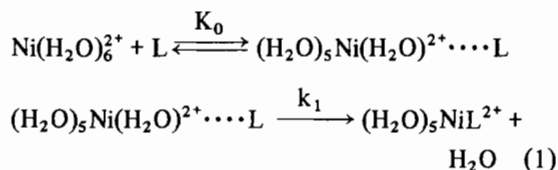
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The kinetics of reactions of nickel(II) with 2-(4-dimethylaminophenilazo)pyridine (DPAP) in methanol, dimethylformamide and dimethylsulphoxide and with 4-(2-pyridylazo)resorcinol (PAR) and 1-(2-pyridylazo)2-naphthol (PAN) in dimethylsulphoxide have been investigated. The rate constants k_f (25 °C) for Ni^{II}–DPAP reaction in the solvents used are 3.6 × 10^3 M^{-1} sec^{-1}, 4.4 × 10^3 M^{-1} sec^{-1} and 7.9 × 10^2 M^{-1} sec^{-1} respectively. The rate constants k_f (25 °C) for Ni^{II}–PAR and Ni^{II}–PAN reactions are 8.0 × 10^2 M^{-1} sec^{-1} and 0.6 × 10^2 M^{-1} sec^{-1} respectively. The low value of k_f for Ni^{II}–PAN and Ni^{II}–PAR reactions in dimethylsulphoxide is interpreted assuming that the process is governed by a sterically controlled mechanism. The values of activation parameters $\Delta H^{\neq}$ and $\Delta S^{\neq}$ for the reactions investigated are correlated through an isokinetic relationship.

Introduction

The kinetics of complexation of nickel(II) in water have been widely studied [1, 2]. The mechanism generally accepted for these reactions involves rapid formation of an outer-sphere complex between the two reacting species, followed by the rate-limiting replacement of a water molecule in the inner coordination sphere by the ligand, as illustrated below

$$Ni(H_2O)_6^{2+} + L \xrightleftharpoons{K_0} (H_2O)_5 Ni(H_2O)^{2+} \cdots L$$

$$(H_2O)_5 Ni(H_2O)^{2+} \cdots L \xrightarrow{k_1} (H_2O)_5 NiL^{2+} + H_2O \quad (1)$$

Reaction (1) has been written for a special case of a neutral monodentate ligand; when the incoming ligand is multidentate, additional steps leading to ring closure must be considered. Usually, however, the release of a first water molecule remains the rate limiting step of the complexation reaction [2]. If the concentration of the outer-sphere complex is small the rate constant for the complex formation k_f is given by the expression:

$$k_f = K_0 \times k_1 \quad (2)$$

where k_1 is equal to the rate constant for the solvent exchange k_{ex} and K_0 can be estimated through the following theoretical equation derived independently by Fuoss [3] and Eigen [4]:

$$K_0 = \frac{4\pi N a^3}{3000} e^{-U(a)/kT}$$

$$U(a) = \frac{z_1 z_2 e^2}{Da} - \frac{z_1 z_2 e^2}{D(1 + Ka)} \quad (3)$$

a represents the minimum approach distance between the two particles and all the other symbols have their usual meaning. Although values of observed rate constants k_f for substitution reactions in water are usually in good agreement with those evaluated by the product $K_0 \times k_1$, equation (2) is often inadequate to predict the values of rate constants in nonaqueous solvents [5–8]. This is particularly relevant for multidentate ligands which can produce steric retardation [7, 9] in one of the two steps of ring formation or (and) can enhance their reactivity through an extra-electron interaction [10, 11] during the formation of the outer-sphere complex.

In the present work I report the results of a kinetic investigation of the reaction of nickel(II) with 2-(4-dimethylaminophenylazo)pyridine (DPAP) in methanol, dimethylformamide and dimethylsulphoxide and with 4-(2-pyridylazo)resorcinol (PAR) and 1-(2-pyridylazo)-2-naphthol (PAN) in dimethylsulphoxide at various temperatures. The ligands used are all capable to exert either steric or electronic effects upon coordination with the solvated nickel(II) ion. They are all potentially bidentate [12, 13] and probably coordinate through one of the nitrogens in the azo-linkage and the pyridine nitrogen; no acid–base equilibrium associated with the ligands should be involved in the kinetics and spectral changes on complexation reaction are large.

Experimental

Solvents

Dimethylsulphoxide was distilled from calcium hydride under reduced pressure. Methanol was dis-

tilled from magnesium methoxide. Dimethylfor-
mamide was dried over anhydrous calcium sulphate
and then distilled under reduced pressure. The sol-
vents were kept over molecular sieves. Their water
content, as determined by Karl Fischer titration, was
ca. 0.01%.

Reagents and Solutions

Solutions of nickel(II) were prepared in glove bags
filled with dry nitrogen by dissolving the anhydrous
$NiClO_4$ in the appropriate solvent. The anhydrous
nickel perchlorate was obtained on heating the corre-
sponding hexahydrate salt for 24 h *in vacuo* over
P_2O_5. In order to avoid decomposition [14] and
possible formation of basic salts the temperature of
heating did not exceed 90 °C. All nickel solutions
were standardized by EDTA titration. The water
content of the solutions (Karl Fischer titration) was
similar to that of the pure solvents.

The ligands DPAP (Sigma), PAR and PAN (Fluka)
were reagent grade and were used without further
purification.

Instruments and Experimental Procedure

Visible and ultraviolet spectra were recorded with
an Optica CF 4 recording spectrophotometer
equipped with a thermostatted cell compartment
(±0.05°). The equilibrium constant for the formation
of the 1:1 complex between Ni^{2+} and DPAP in DMSO
at 25 °C was determined spectrophotometrically by
recording the absorbance of a solution of DPAP and
that of a series of solutions containing a fixed amount
of DPAP and a variable amount of Ni^{2+} in the range
520–560 mμ. The concentration of Ni^{2+} was in all
cases much larger than that of the ligand. By plotting
the optical density OD of the Ni–DPAP mixtures
against $(OD - OD_0)/[Ni^{2+}]$, where OD_0 represents
the absorbance of the ligand alone, a straight line was
obtained from the slope of which $(-1/K)$ the
equilibrium constant was evaluated.

Kinetic measurements were made with a Durrum–
Gibson Model 110 stopped-flow spectrophotometer
equipped with a Kel-F flow system. All kinetic runs
were performed under pseudo-first-order conditions

with respect to the ligand; the total ligand concentra-
tion was varied through at least six values.

The observed pseudo-first-order rate constants
were obtained with the standard procedure from the
analysis of Polaroid photographs of the oscilloscope
traces; their values were in all cases independent of
wavelength and of ligand concentration. The observed
rate constants k_{obsd}, were reproducible within 5% (a
Table of them is available from the Editor on
request).

Results and Discussion

DPAP

Reaction of Ni^{2+} with DPAP proceeds according
to the scheme (4)

$$NiS_6^{2+} + DPAP \underset{k_d}{\overset{k_f}{\rightleftharpoons}} NiS_4DPAP^{2+} + 2S \qquad (4)$$
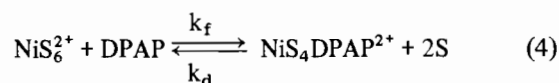
The complex absorbs at 560 mμ whereas the free
ligand has a maximum of absorption at 430 mμ.
Complexation reactions were studied by recording
variations of absorbance as a function of time in the
range 520–560 mμ. Ionic strength was maintained
constant by adding $NaNO_3$; its value was 0.3 for the
kinetic runs performed in DMSO and DMF and 0.1
for the kinetic runs performed in MeOH; this lower
limit was imposed by the limited solubility of $NaNO_3$
in MeOH. Kinetic data are in agreement with the rate
law:

$$\frac{d[NiS_4DPAP^{2+}]}{dt} = k_f[NiS_6^{2+}][DPAP] -$$

$$k_d[NiS_4DPAP^{2+}] \qquad (5)$$

When the nickel concentration is much larger than
that of DPAP

$$k_{obsd} = k_f[NiS_6^{2+}] + k_d \qquad (6)$$

The term k_d is negligible when the solvent is meth-
anol or dimethylformamide.

TABLE I. Rate Constants and Activation Parameters for Reaction of Nickel(II) with PAR and PAN in Dimethylsulphoxide.
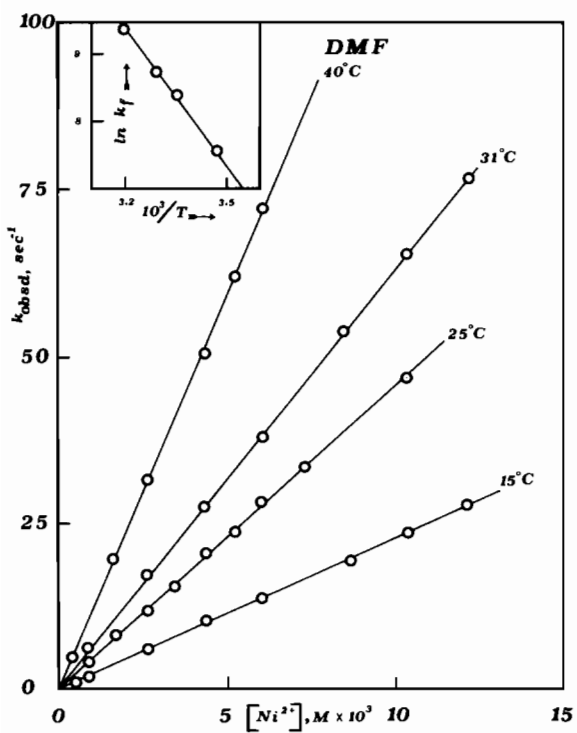
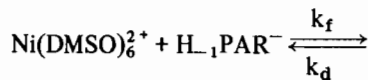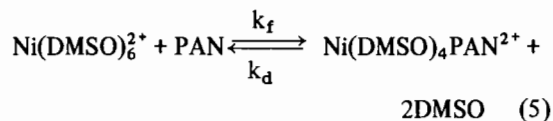| Ligand	Temp, °C	$10^3[Ni^{2+}]M$	k_{obsd}, sec^{-1}	$10^{-2}k_f$, M^{-1} sec^{-1}	$10^{-2}k_f(25°)$, M^{-1} sec^{-1}	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu
PAR	25	1.09–10.90	0.70–10.20	7.85 ± 0.61			
	35	1.09–13.08	1.90–21.00	15.8 ± 0.91	7.99	10.8 ± 1.6	−9 ± 4
	47	1.09–13.08	3.10–39.00	29.5 ± 0.91			
PAN	25	1.09–10.90	0.05–0.62	0.58 ± 0.02			
	36	2.18–13.08	0.28–1.64	1.24 ± 0.08	0.56	13.0 ± 0.8	−7 ± 3
	44	1.09–13.08	0.29–3.05	2.29 ± 0.20			

(a)

(c)
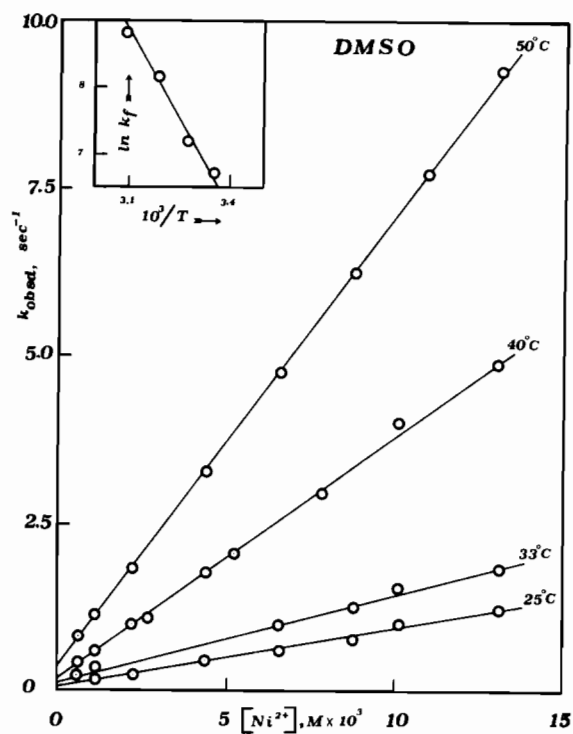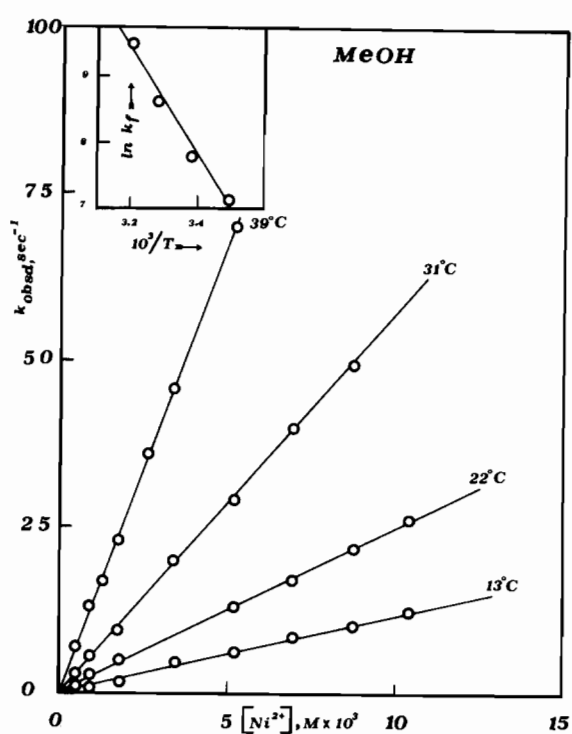
Figure 1. Observed pseudo-first-order rate constants plotted against nickel ion concentration for reactions of Ni^{2+} with DPAP in the solvents DMSO, DMF, and MeOH at various temperatures.

The equilibrium constant K_1 for reaction (4) in DMSO at 25 °C was evaluated from the ratio gradient–intercept of the plot of k_{obsd} against $[Ni^{2+}]$ (Fig. 1). This value (1.36×10^3 M^{-1}) was compared with that obtained independently by spectrophotometry (1.43×10^3 M^{-1}). The satisfactory agreement between the two values is evidence that the process monitored is that of reaction (4). The values of k_d and k_f obtained by least-squares analysis from intercepts and gradients of plots of Fig. 1 are presented in Table I together with those of the activation parameters $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ associated with the reactions.

PAR and PAN

Ni^{2+} reacts with PAN according to scheme (5) and with PAR according to scheme (6)

$$Ni(DMSO)_6^{2+} + PAN \underset{k_d}{\overset{k_f}{\rightleftharpoons}} Ni(DMSO)_4PAN^{2+} +$$

$$2DMSO \quad (5)$$

$$Ni(DMSO)_6^{2+} + H_{-1}PAR^- \underset{k_d}{\overset{k_f}{\rightleftharpoons}}$$

$$Ni(DMSO)_4H_{-1}PAR^+ + 2DMSO \quad (6)$$

(b)

In equation (6) $H_{-1}PAR^-$ represents the ligand which has lost the *o*-phenolic proton*. The complex with PAN absorbs at 560 mμ whereas the free ligand has a maximum of absorption at 465 mμ; the complex with PAR absorbs at 525 mμ and the uncomplexed ligand absorbs at 390 mμ. The kinetics of complexation in the solvent DMSO were studied by recording the change of absorbance at 525 mμ for $NiH_{-1}PAR^+$ and at 560 mμ for $NiPAN^{2+}$ as a function of time. All the kinetic runs were performed at a constant ionic strength of 0.3 M.

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*The statement that PAR is present in solution as the monoanion is based on both conductometric and spectral
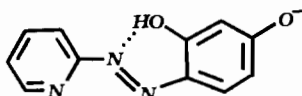
evidence. Conductivity measurements indicate large 1:1 dissociation in DMSO solutions of PAR; furthermore no spectral change associated with proton removal is observed on addition of a large amount of piperidine to the ligand in DMSO. The absence of a significant *ortho*-phenolic dissociation has been attributed to the presence of a strong hydrogen bond between this group and the nitrogen of the azo-linkage [13].

Kinetic data are consistent with the rate law

$$\frac{d[Ni(DMSO)_4L]}{dt} = k_f [Ni(DMSO)_6] [L] \qquad (7)$$

where charges are omitted for simplicity and L represents either $H_{-1}PAR$ or PAN.

Under pseudo-first-order conditions, with $[Ni^{2+}]$ $\gg$ [L], observed rate constants were in each case equal to $k_f[Ni^{2+}]$. Linearity of the plots of k_{obsd}, against nickel(II) concentration (Fig. 2) confirms that the reactions are first-order with respect to the ligands. Spectroscopic measurements on the reaction product indicate that it is a 1:1 bidentate complex. The values of k_f and those of the activation parameters for the reactions were obtained as above and are listed in Table II.

The rate constants for complexation are strongly dependent on the nature of the solvent. This is a quite obvious result because the dependence on the nature of the solvent is the main requirement for the validity of the mechanism [1] proposed to describe complexation reactions and it is in agreement with the results of other investigations [5, 6, 15–17]. One test of the Eigen–Wilkins mechanism is to compare the values of the observed rate constants k_f with those calculated from equation (2). Table III
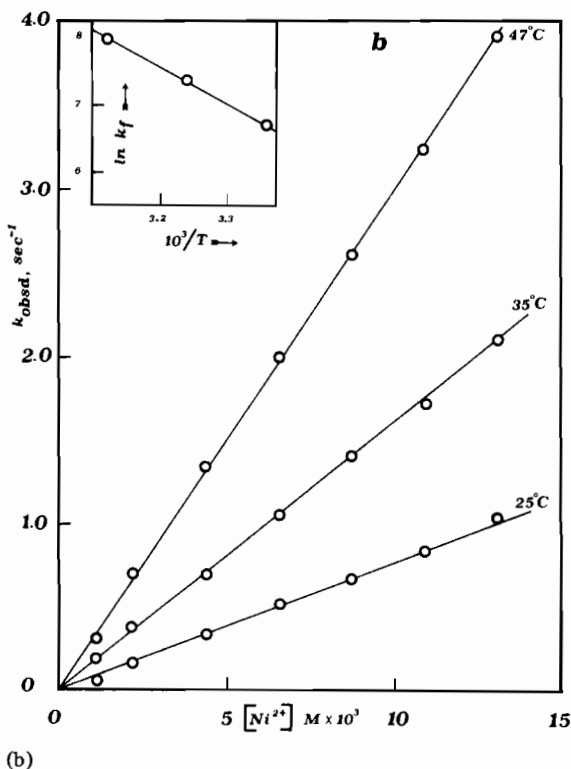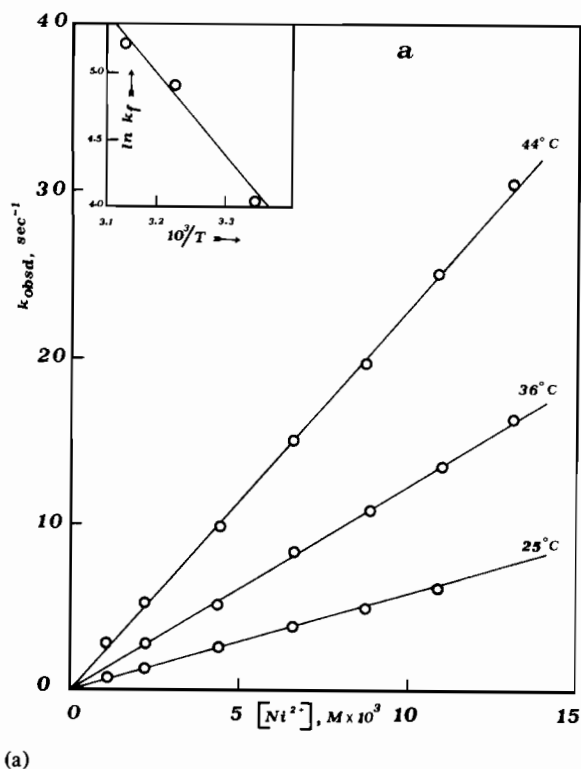

(a)

(b)

Figure 2. Observed pseudo-first-order rate constants plotted against nickel ion concentration for the reactions a) Ni^{2+} + PAR, b) Ni^{2+} + PAN in DMSO at various temperatures.

TABLE II. Rate Constants and Activation Parameters for Reaction of Nickel(II) with DPAP in the Solvents Dimethylsulphoxide, Dimethylformamide and Methanol.

Solvent	Temp, °C	$10^3[Ni^{2+}] M$	k_{obsd}, sec^{-1}	$10^{-2}k_f$, M^{-1} sec^{-1}	k_d, sec^{-1}	$10^{-2}k_f (25°) M^{-1}$ sec^{-1}	$\Delta H^\ddagger$, kcal/mol	$\Delta S^\ddagger$, eu
DMSO	25	1.09–13.08	1.50–11.75	8.45 ± 0.61	0.62 ± 0.03	7.89	16.1 ± 0.9	+9 ± 2
	33	0.54–13.08	1.80–18.20	13.1 ± 0.08	1.03 ± 0.10	(7.40)[a]		
	40	0.54–13.08	4.00–48.80	35.3 ± 0.08	2.03 ± 0.02			
	50	0.54–13.08	8.10–92.50	67.4 ± 0.08	3.79 ± 0.04			
DMF	15	0.43–12.15	2.60 ± 25.50	20.1 ± 0.86		44.2	12.0 ± 0.6	−2 ± 1
	25	0.87–10.40	4.00–46.70	44.6 ± 0.29		(11.50)[a]		
	31	0.87–12.15	6.00–76.60	62.5 ± 0.98				
	40	0.43–6.05	4.70–72.00	118.0 ± 2.05				
MeOH	13	0.87–10.40	1.30–14.50	12.8 ± 1.00		36.2	15.3 ± 1.2	+9 ± 3
	22	0.45–10.40	1.50–26.40	24.5 ± 0.92		(18.60)[a]		
	31	0.45–8.72	2.70–49.20	55.9 ± 1.28				
	39	0.45–5.20	7.10–70.20	132.0 ± 0.24				

[a] Values from reference 16.

lists the observed values of $k_{f(obsd)}$, and those derived by the product $K_0 \times k_{ex}$. The comparison of the two series of values indicates that the trend is not regular; in fact, there is a close similarity between $k_{f(obsd)}$ and $k_{f(calcd)}$ for reaction of Ni^{2+} with DPAP in DMSO, while the two sets of values differ considerably for all the other reactions, the largest difference being observable in the case of reaction of Ni^{2+} with PAR in DMSO. The lack of correspondence of kinetic data to equation (2) is not surprising; the relationship $k_f = K_0 \times k_1$, in fact, holds as long as first-bond formation is rate determining and steric effects are absent [2]. The bidentate ligands used in this study contain large pyridine and phenolic rings and may well exert steric effects in the complexation process; the limit situation may also occur where the ring-closure step, rather than a solvent molecule release, is rate determining. This situation was firstly observed in the reactions of Ni(II) and Co(II) with β-alanine in water [21] and it is fairly common in nonaqueous solvents [7]. The abnormally low values of k_f for reaction of Ni(II) with PAR and PAN can be interpreted assuming that these reactions are sterically controlled; this assumption is supported by the fact that ring-closure for both reactions implies the breaking of the strong hydrogen bond [13] between the *ortho*-phenolic proton and the azo-nitrogen. It is of interest that the value of k_f for reaction of Ni(II) with PAN is comparable with that observed for reaction of Ni(II) with 2,2′-bipyridine for which a S.C.S. mechanism has been recognized [7, 9].

Coetzee *et al.* [10, 11] on discussing values of reactivity larger than predicted on the basis of equation (2) showed that the Fuoss relationship used to calculate the value of K_0 does not lead to correct results if specific interactions occur between the inner and the outer coordination sphere; in particular, multidentate ligands containing pyridine rings form outer-sphere complexes of higher stability than predicted by equation (3). Such an explanation can be applied to the reactions of DPAP with Ni(II) in MeOH and DMF, where the observed rate constants k_f are higher than expected. This assumption is not in contrast with the finding that the values of k_f for reactions of Ni(II) with PAR and PAN are abnormally low, even if these ligands are capable, as well as DPAP, of extra interaction with the metal ion. In fact, the net value of k_f reflects the effect of two opposing factors [11]: steric inhibition of complexation and enhanced stabilization of outer-sphere complex. For PAR and PAN the steric inhibition of reaction, reflected in the low value of k_f, is the dominant factor in the rate of complexation. For the more flexible ligand DPAP [16], steric factors play* proba-

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*The absence of steric factors in the kinetics of Ni(II) with DPAP has recently been shown by Bennetto and Imani [16] who studied this reaction in a series of solvents.

TABLE III. Comparison of the Values of the Observed Rate Constants $k_{f(obsd)}$ with Those Calculated from Equation (2).*

Reaction	$10^2 k_{f(obsd)}$, M^{-1} sec^{-1}	$10^2 (K_0^a \times k_{ex})$, M^{-1} sec^{-1}
$Ni(DMSO)_6^{2+}$ + PAN	0.5	7.5[b]
$Ni(DMSO)_6^{2+}$ + PAR	8.0	345.0[b]
$Ni(DMSO)_6^{2+}$ + DPAP	7.9	7.5[b]
$Ni(DMF)_6^{2+}$ + DPAP	44.2	7.7[c]
$Ni(MeOH)_6^{2+}$ + DPAP	36.3	1.0[d]

* the minimum distance of approach between the nickel(II) and the ligand has been chosen in each case equal to 6 Å.
[a] Value of k_{ex} from ref. 18. [b] Value of k_{ex} from ref. 19. [c] Value of k_{ex} from ref. 20.

bly a minor role and the enhanced stability of the outer-sphere complex leads to values of k_f in MeOH and DMF larger than expected. Again a compensation effect can be invoked to explain the agreement between the observed and the calculated value of k_f for DPAP in DMSO. Owing to the bulkiness of the solvent molecules the complexation process is sterically hindered more extensively than in MeOH and DMF.

Activation parameter $\Delta H^{\ddagger}$ range from 12 to 16 kcal/mol; the variation of the activation enthalpy throughout the series of reactions is largely compensated by corresponding variations of the activation entropy $\Delta S^{\ddagger}$. The values of $\Delta H^{\ddagger}$ and those of $\Delta S^{\ddagger}$
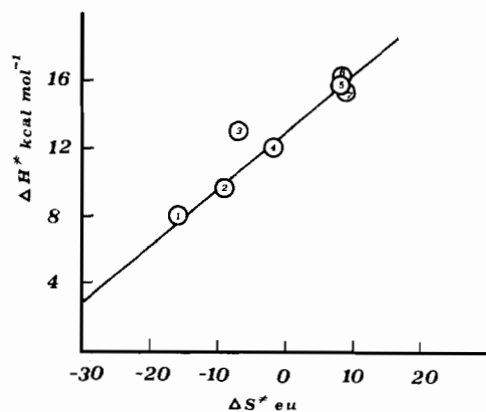

Figure 3. Plot of enthalpy of activation against entropy of activation for solvent exchange and PAN and DPAP substitution at nickel ion in various solvents.

	Reaction	Ref.
1	$Ni(DMSO)_6^{2+}$ + DMSO	18
2	$Ni(DMF)_6^{2+}$ + DMF	19
3	$Ni(DMSO)_6^{2+}$ + PAN	this work
4	$Ni(DMF)_6^{2+}$ + DPAP	this work
5	$Ni(MeOH)_6^{2+}$ + MeOH	20
6	$Ni(DMSO)_6^{2+}$ + DPAP	this work
7	$Ni(MeOH)_6^{2+}$ + DPAP	this work

are roughly correlated through an isokinetic relationship (Fig. 3). This is a fairly typical manifestation of the "compensation law [22]" and has been frequently observed in processes dominated by solvation changes. In the case of metal ion complexation it has been interpreted in terms of a concerted mechanism [5c] (the so-called *solvent modified dissociative process*) where the changes in the activation parameters are related to the transfer of solvent and ligand molecules between the strongly ordered region adjacent to the metal ion, the highly disordered region outside and the relatively ordered region of the "bulk solvent". However the investigations of Coetzee *et al.* [10, 11] on the presence of steric and electronic effects in the complexation process suggest that besides the solvent structure other effects need to be considered to describe the coordination reactions of Ni(II).

Acknowledgments

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