

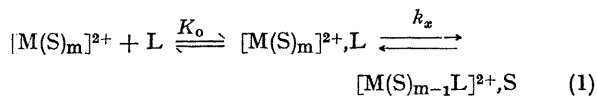
## Solvent Effects and Substitution Mechanisms: Kinetics of the Reaction of Nickel(II) Ion with 2,2'-Bipyridyl

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**Summary** The commonly accepted mechanism for the substitution of a ligand at a solvated metal ion fails to explain solvent effects on the kinetics of reaction of nickel(II) ion with bipyridyl, for which a correlation with fluidity is noted.

In recent years much evidence has accumulated<sup>1</sup> in support of the hypothesis<sup>2</sup> that in the substitution of a ligand (L) into the first hydration sphere of a metal cation ( $M^{2+}$ ) the rate-determining step is the loss of a solvent molecule from that sphere, preceded by the formation of an outer-sphere complex in a fast equilibrium:<sup>3</sup>



If  $k_x$  is the rate constant for the first-order exchange of solvent between the first hydration sphere and the bulk

solvent, the second-order rate constant  $k_f$  for the overall forward reaction should be given in the simplest case by:

$$k_f = K_0 k_x \quad (2)$$

The evidence mainly refers to reactions in aqueous solutions, and the need for more results in solvents other than water is evident.<sup>1</sup> Preliminary results<sup>4</sup> for the reaction of nickel(II) with 2,2'-bipyridyl in methanol-water mixtures have suggested that structural features of the solvent are important.

We have now measured the rate of the same reaction in a series of solvents for which the solvent-exchange rate  $k_x$  is known from n.m.r. work.<sup>5</sup> In order to test the validity of equation 2, a value of  $K_0$  is required. Although values may be available for charged ligands,<sup>6</sup>  $K_0$  has not been experimentally determined for uncharged ligands, but a reasonable value<sup>4,7</sup> is 0.1 l.mole<sup>-1</sup>. Since only weak interactions are involved, this may be supposed to be the same in all solvents. Defining a quantity  $n$  as the chance that a

ligand molecule will enter the primary solvation shell of the nickel ion at a particular site when a solvent molecule leaves it, we have:

$$n = k_f/K_0k_x = k_f/0.1k_x$$

For equation 2 to be correct,  $n$  should be unity or at least constant. Values of  $k_f$ ,  $k_x$ , and  $n$  are given in the Table. From the 200-fold variation in  $n$  it is evident that equation

2 fails the test badly, though the value of  $n$  for water is reasonable. We also find that the difference in enthalpies of activation ( $\Delta H_f^\ddagger - \Delta H_x^\ddagger$ ), which should be near zero<sup>4</sup> if the mechanism applies, varies from  $+4.7 \pm 1$  kcal. mole<sup>-1</sup> in Me<sub>2</sub>SO to  $-5.1 \pm 1$  kcal. mole<sup>-1</sup> in acetonitrile. Clearly if this analysis is valid equation 2 is unsatisfactory, at least for this reaction in these solvents.

The elucidation of substitution mechanisms<sup>1,8</sup> may, however, be aided by taking the structural properties of

TABLE

Solvent	$10^{-3}k_f$ (l.mole <sup>-1</sup> sec. <sup>-1</sup> )	$10^{-3}k_x^a$ (sec. <sup>-1</sup> )	$n = k_f/0.1k_x$
Acetonitrile .. .. .	4.7	2.8	17
Methanol .. .. .	0.14	1.0	1.4
Dimethylformamide ("DMF") .. .. .	0.5 <sub>4</sub>	7.7 <sup>b</sup>	0.7 <sub>0</sub>
H <sub>2</sub> O .. .. .	1.6 <sub>3</sub>	30	0.5 <sub>4</sub>
D <sub>2</sub> O .. .. .	1.0 <sub>8</sub>	30 <sup>c</sup>	0.3 <sub>6</sub>
Dimethyl sulphoxide ("DMSO") .. .. .	0.06 <sub>9</sub>	7.5	0.09 <sub>2</sub>
Ethylene glycol ("EtGl") .. .. .	0.03 <sub>3</sub>	4.4 <sup>d</sup>	0.0 <sub>8</sub>

<sup>a</sup> From ref. 5 unless otherwise stated.

<sup>b</sup> Ref. 11.

<sup>c</sup>  $k_x^{(D_2O)} = k_x^{(H_2O)}$  is assumed on the basis of data for Mn<sup>2+</sup> in ref. 12.

<sup>d</sup> Ref. 13. Approximate value.

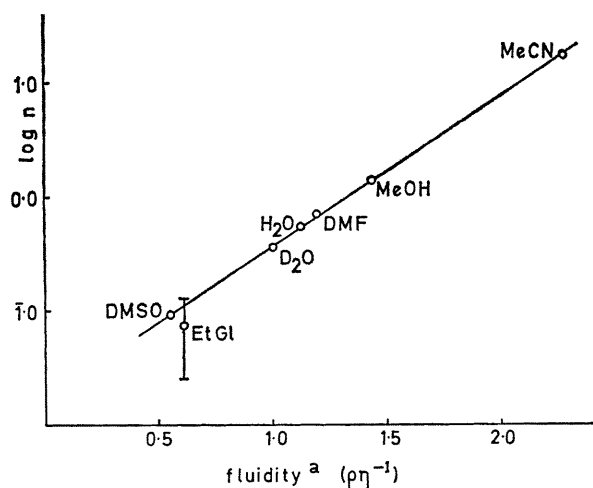


FIGURE. Fluidity correlation for the reaction of nickel(II) ion with 2,2'-bipyridyl.

<sup>a</sup> Fluidity defined as the reciprocal of kinematic viscosity; values of  $\rho$  and  $\eta$  from the literature.

the solvent into account. This is suggested by the correlation (see Figure) which is found for  $\log n$  with the fluidity of the solvent. The relationship, which holds moderately well over the whole range of temperature studied (0 to 55°), is remarkable in view of the variety of the solvents, some of which are hydrogen-bonded while others are dipolar-aprotic. The "degree of structure" of a liquid is still an elusive property, but in general terms it must be reflected in two main characteristics (inevitably related) of the liquid structure, namely its "open-ness" and its "stiffness". These features must ultimately depend on the particular molecular geometry and on the intermolecular forces, but the former may be measured by the free volume ( $V_f$ ) of the liquid, and the latter by the energy ( $\Delta E_h$ ) required to make a hole in it of molecular dimensions; both  $V_f$  and  $\Delta E_h$  appear in working expressions for the viscosity (and fluidity) of a liquid.<sup>9</sup> For instance, there is evidence<sup>10</sup> that solvent effects on  $\Delta H^\ddagger/\Delta S^\ddagger$  relations for reaction rates run parallel with those for solvent fluidity, although the rates themselves are not determined by fluidity.

Detailed results will later be discussed in these terms, and in the light of current mechanistic schemes.<sup>8</sup>

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<sup>1</sup> See A. McAuley and J. Hill, *Quart. Rev.*, 1969, **23**, 18, L. I. Budarin and K. B. Yatsimirskii, *Russ. Chem. Rev.*, 1968, **37**, 209 and refs. therein.

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