Kinetics of Base Hydrolysis of Low-spin Iron(II)-diimine Complexes in Methanol–Water Mixtures*

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Rate constants are reported for base hydrolysis of several low-spin iron(II)-diimine complexes, mostly of polydentate ligands, in water and in aqueous methanol (up to 40% methanol). Rate constant trends from these and earlier studies of a variety of iron(II)-diimine complexes are compared and discussed in terms of ligand structure, ligand substituents, and solvation properties of the various complexes.

Key words: low-spin iron(II)-diimine complexes, base hydrolysis, kinetics.

INTRODUCTION

Low-spin iron(II) complexes of diimine ligands have been of interest to inorganic kineticists for many years, ever since the first reports on formation and dissociation kinetics of tris(1,10-phenanthroline)iron(II)[1] and of tris(2,2'-bipyridyl)iron(II)[2] in 1948. Since these initial studies kinetic investigations have flourished and expanded, to cover substitution reactions, such as aquation, base hydrolysis, and cyanide attack, and redox reactions such as peroxodisulphate oxidation and various outer-sphere electron trans-

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* Dedicated to Professor Smiljko Ašperger on the occasion of his 80th birthday.
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fer reactions.[3] The range and variety of such complexes have been extended from the original 2,2'-bipyridyl and 1,10-phenanthroline ligands to include their substituted derivatives, bidentate Schiff bases derived from pyridine 2-carboxaldehyde, 2-acetylpyridine and 2-benzoylpyridine plus a host of aliphatic and aromatic primary amines,[4] diazabutadienes,[5] terdentate analogues of many of these bidentate ligands,[6,7] and various hexadentate ligands incorporating two or three diimine moieties, including linear (garland),[8] semi-encapsulating (tripod),[9] and encapsulating (cage) species.[10] The first kinetic investigations were conducted in aqueous solution, but studies in organic solvents, particularly methanol, and in binary aqueous solvent mixtures soon followed.[11] One of the most popular reactions for assessing ligand and medium effects has been that of base hydrolysis,[12] *i.e.* of nucleophilic attack by hydroxide. There has long been controversy as to whether this takes place by initial attack at the metal centre or at the coordinated ligand,[13] but this does not affect the bimolecular nature of the reaction nor, in many situations, discussion of ligand and medium effects. This is particularly true of solvent effects, where the changing solvation of the hydroxide and its consequent change in chemical potential and nucleophilicity play a key role in determining reactivity trends.[14] Of course solvation of the complexes, which can be established in terms of transfer chemical potentials,[15] cannot be ignored; the various contributions of solvation changes to reactivity trends can be assessed by initial state – transition state analyses as detailed elsewhere.[11,16]

Base hydrolysis kinetics of iron(II)-diimine complexes in binary aqueous media, particularly for cosolvents methanol and dmso, have been reported in a large number of papers over the past 40 years and more. The choice of methanol as cosolvent has been connected with the availablity of a wide range of transfer chemical potential data for the interpretation of the observed rate constant trends, the choice of dmso by its great enhancement of the reactivity of hydroxide. Very large rate accelerations are usually observed on going from water to dmso-rich media, reflecting the large increase in chemical potential of the hydroxide, *e.g.* of 14 and 45 kJ mol^{-1} on going from water to 40[17,18] and 80%[17,19] dmso. Previous published discussions have tended to focus on the role of hydroxide, on specific types of complex, or on inter-cosolvent comparisons. In this present paper we report a few further kinetic data for base hydrolysis of various iron(II)-diimine complexes in methanol–water media. We then review, in the light of these and copious data published previously, how the nature and type of ligand affects reactivity trends – a much more extensive review is now possible than could be undertaken in earlier discussions.[8,20]

EXPERIMENTAL

The complexes were all samples prepared previously for earlier kinetic or solubility measurements. Their purity was checked by visible absorption spectra (wavelengths of maximum absorption and extinction coefficients). Kinetic runs were carried out in the thermostatted cell compartment of a Pye-Unicam SP8-100, Hewlett-Packard HP8451A, or Jasco V-530 spectrophotometer.

RESULTS

First-order kinetics (hydroxide was always present in large excess over the iron complex) were followed over at least three half-lives for all runs. The absence of significant deviations at the start or towards the end of runs indicates that there are no significant amounts of minor isomeric forms present in complexes where this is a possibility (*e.g.* for linear hexadentate ligands). Observed first-order rate constants, k_{obs}, for base hydrolysis of the complexes of the multidentate Schiff base ligands N7K and N8K (formulae and abbreviations* for ligands are given in Scheme 1) are reported in Table I.

The general rate law for base hydrolysis of iron(II)-diimine complexes is[12]

$$d[\text{complex}] / dt = \{k_1 + k_2[\text{OH}^-] + k_3[\text{OH}^-]^2\} [\text{complex}]$$

The k_1 term represents a generally minor (bidentate ligands) or negligible (ter- to hexa-dentate ligands) rate-determining dissociative path, the k_2 term corresponds to the major reaction path, nucleophilic attack by hydroxide; the k_3 term is only significant for certain complexes at high hydroxide concentrations. The Table I results conform to the rate law

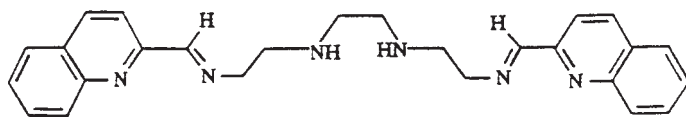$$d[\text{complex}] / dt = k_2 [\text{complex}] [\text{OH}^-]$$

indicating that both the k_1 and k_3 terms of the above general rate law are, as expected, negligible for these hexadentate ligand complexes. Table I includes second-order rate constants, k_2, derived from the experimental k_{obs} values. For other complexes we have determined base hydrolysis rate constants at only one hydroxide concentration (0.33 mol dm^{-3}); these k_{obs} values are reported in Table II. For all the Table II complexes it may be confidently expected that the simple second-order rate law will apply; the k_2 values in this Table are thus simply k_{obs} / [OH$^-$].

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* For some ligands we give earlier abbreviations as well as those used in this paper, for the involvement of different authors, changing practices, and occasionally the efforts of over-zealous editors have led to the use of several different abbreviations for some ligands of this type.
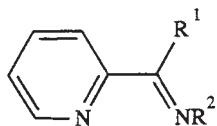
Figure 1 ligands
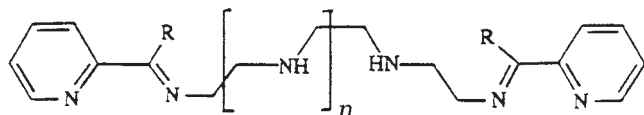
R	n	
H	1	hxsbH
Me	1	hxsbMe
Ph	1	hxsbPh
Ph	2	N7K
Ph	3	N8K

hxsbq

Figure 2 ligands

R^1	R^2	
H	H	api
H	Me	apmi
H	Ph	appi
Ph	Ph	bppi
Ph	$3,4\text{-}Me_2C_6H_3$	bppi-3,4-Me2 (Me_2bsb)

Figure 3 ligands
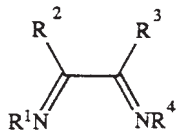
R^1	R^2	R^3	R^4	
Me	H	H	Me	gmi
Me	Me	H	Me	pmi (mmi)
Et	H	H	Et	gei
Ph	Me	Me	Ph	bpi (dab)

(cont.)

Figure 4 ligands
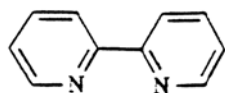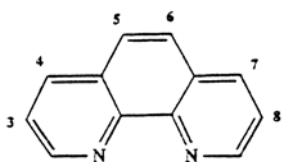
Figure 5: cage complex

bipy (bpy)

phen
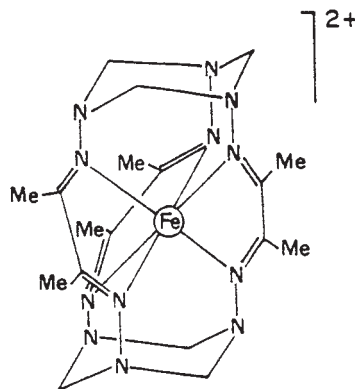
cxcage

Figure 5 ligands
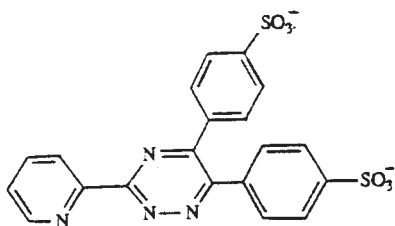
fz (ppsa)
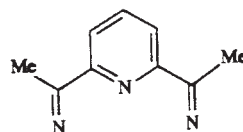
dapi
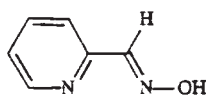
pyox
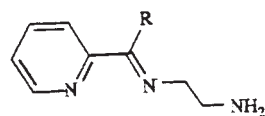
R	
H	tsbh
Me	tsbm
Ph	tsbp

Scheme 1.

TABLE I

Observed first-order rate constants, $10^6 k_{obs}$ / s^{-1}, and derived second-order rate constants, k_2 / dm^3 mol^{-1} s^{-1}, for base hydrolysis of low-spin iron(II)-diimine complexes of linear and cage multidentate Schiff base diimine ligands in aqueous and methanol–water solution, $I = 0.33$ mol dm^{-3} (NaCl), at 308.2 K

[NaOH]/ mol dm^{-3}:	$10^6 k_{obs}$ / s^{-1}							k_2 / dm^3 mol^{-1} s^{-1}
	0.10	0.13	0.17	0.23	0.27	0.30	0.33	
N7K								
water	7.5	11.7		19.0		24	28	8.4×10^{-5}
20% MeOH	6.8	9.2		16.8	19.1		22	6.6×10^{-5}
40% MeOH	5.3	7.5		14.4		17.9	20	6.0×10^{-5}
N8K								
water	7.0		12.0		16.3	22	24	7.2×10^{-5}
20% MeOH	5.3	7.1		11.8	14.0		17.5	5.2×10^{-5}
40% MeOH	4.2		7.0		12.3		15.5	4.6×10^{-5}
[NaOH]/ mol dm^{-3}:	0.0067	0.013	0.020	0.027	0.033			
cxcage								
water	146	243	310	410	570			1.6×10^{-2}
20% MeOH	174	300	490					2.3×10^{-2}
40% MeOH	193	380	570	760				2.9×10^{-2}

TABLE II

Observed first-order rate constants, k_{obs}, and derived second-order rate constants, k_2, for base hydrolysis of low-spin iron(II)-diimine complexes in aqueous and methanol–water solution, [NaOH] $= I = 0.33$ mol dm^{-3}, at 308.2 K

Complex	in water		in 40% MeOH	
	$\dfrac{k_{obs}}{\text{s}^{-1}}$	$\dfrac{k_2}{\text{dm}^3\,\text{mol}^{-1}\,\text{s}^{-1}}$	$\dfrac{k_{obs}}{\text{s}^{-1}}$	$\dfrac{k_2}{\text{dm}^3\,\text{mol}^{-1}\,\text{s}^{-1}}$
[Fe(bpi)$_3$]$^{2+}$	4.0×10^{-4}	1.2×10^{-3}	1.7×10^{-3}	5.1×10^{-3}
[Fe(hxsbMe)]$^{2+}$	6.0×10^{-6}	1.8×10^{-5}	4.7×10^{-5}	1.4×10^{-4}
[Fe(tripodH)]$^{2+\ a}$	5.3×10^{-6}	1.6×10^{-5}	9.1×10^{-6}	2.7×10^{-5}

[a] The ligand tripodH is the Schiff base derived from N(CH$_2$CH$_2$NH$_2$)$_3$ and three molecules of pyridine 2-carboxaldehyde.

DISCUSSION

The complexes in Table II are of known structure, but before considering reactivity trends and comparisons we should comment briefly on the nature of the complexes in Table I. The ligands N7K and N8K are potentially hepta- and octa-dentate, but the properties of their iron(II) complexes all indicate that they behave as hexadentate, octahedrally-coordinating, ligands. The Table I complexes react at very similar rates to the complex of the parent linear hexadentate ligand hxsbPh, indicating that the additional –NHCH$_2$CH$_2$NH– groups of the N7K and N8K ligands have only a very minor effect on mechanism and reactivity. The hexadentate ligand hxsbH has been shown, by X-ray crystal structure analysis of its thiocyanate salt,[21] to bond effectively at all six nitrogen donor sites to the metal (Fe–N bond distances are 1.868 Å to the imine-nitrogens, 1.969 to the pyridine-nitrogens, and 1.999 to the nitrogens of the –NHCH$_2$CH$_2$NH– unit). Presumably hxsbPh bonds similarly – the reactivity of [Fe(hxsbPh)]$^{2+}$ is considerably less than that of [Fe(hxsbH)]$^{2+}$ so its Fe–N bonding must also be strong. It seems likely that the ligands N7K and N8K bond through their two diimine groups and two of the NH groups, leaving one or two NH units uncoordinated, and thus readily accessible to hydrating water. This may well be the reason why their base hydrolysis reactivity trends in water–methanol mixtures, themselves extremely similar, are distinctly different from the other hexadentate Schiff base ligand complexes. As can be seen in Figure 1, the N7K and N8K complexes react somewhat more slowly as the proportion of methanol increases, whereas the hxsbH, hxsbMe, and hxsbq complexes all react markedly more rapidly. That base hydrolysis rate constant trends may be deter-
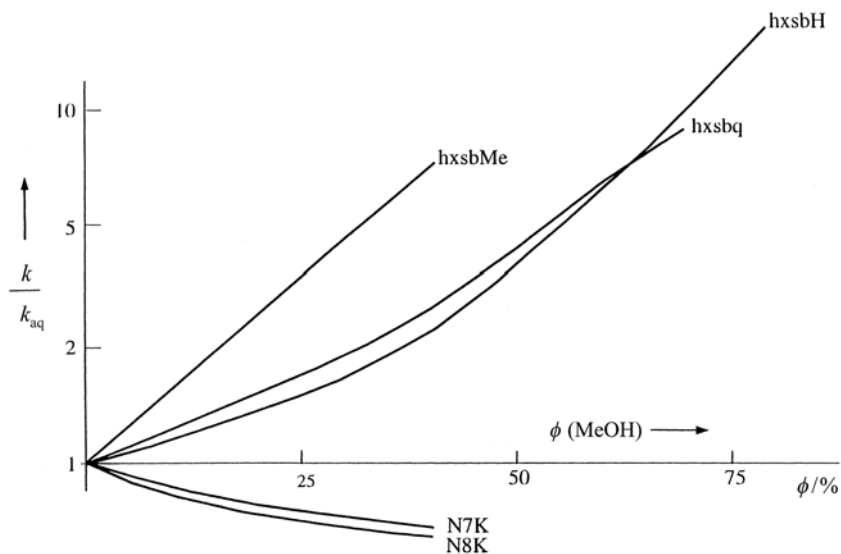
Figure 1. Dependence of rate constants on solvent composition for base hydrolysis of iron(II) complexes of hexadentate diimine ligands. Rate constants are from Tables I (for $[Fe(N7K)]^{2+}$ and $[Fe(N8K)]^{2+}$) and II ($[Fe(hxsbMe)]^{2+}$), Refs. 23 ($[Fe(hxsbq)]^{2+}$) and 24 ($[Fe(hxsbH)]^{2+}$).
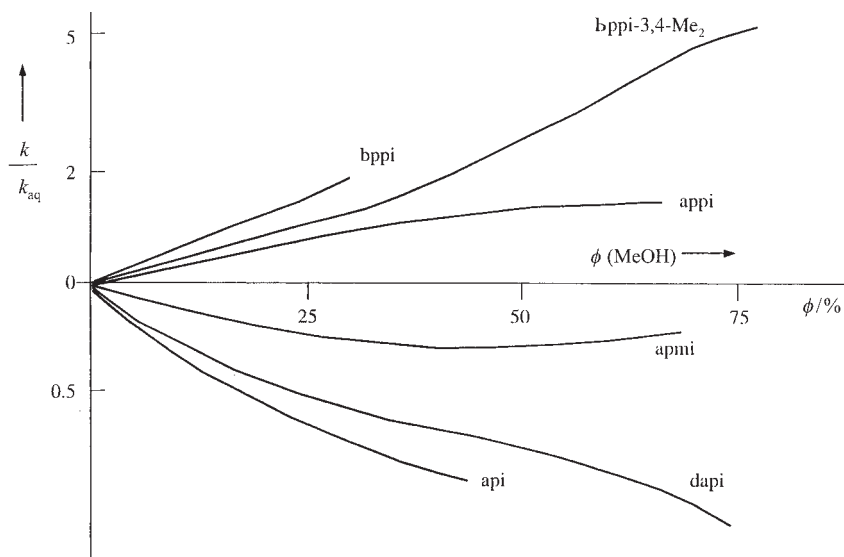

Figure 2. Dependence of rate constants on solvent composition for base hydrolysis of iron(II) complexes of bi- and ter-dentate pyridine-based Schiff base ligands. Rate constants are from Refs. 24 ($[Fe(bppi-3,4-Me_2)_3]^{2+}$) and 20 (all other complexes). The formula for the terdentate ligand dapi can be found with the Figure 5 ligands in Scheme 1.
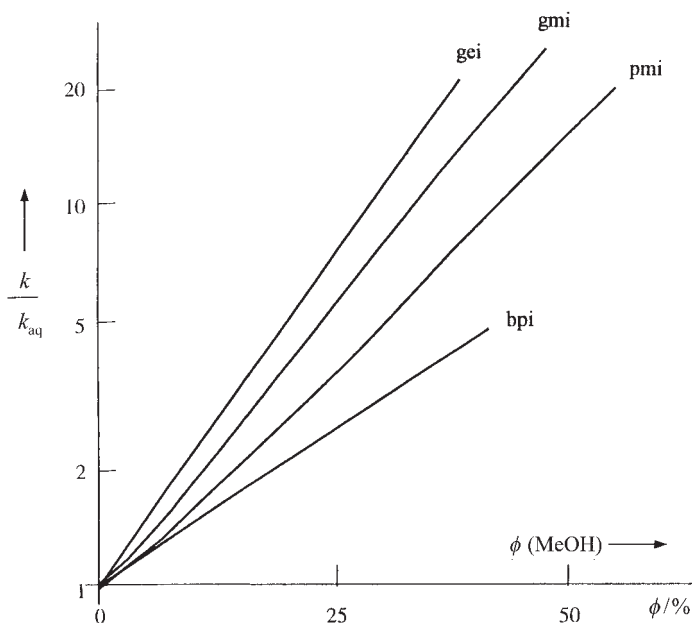
Figure 3. Dependence of rate constants on solvent composition for base hydrolysis of iron(II) complexes of diazabutadiene ligands. Rate constants are from Refs. 23 ($[Fe(gmi)_3]^{2+}$), 25 ($[Fe(gei)_3]^{2+}$), and Table II ($[Fe(bpi)_3]^{2+}$).

mined by the relative hydrophilic/hydrophobic properties of the complexes is also suggested by the sequence of plots in Figure 2 for bidentate Schiff base complexes. The trends appear to represent a balance between hydrophilic =NH groups and hydrophobic methyl and phenyl groups.

If one examines trends for groups of complexes of similar solvation properties, then close similarity is seen, as is shown for the group of diazabutadiene complexes (no =NH groups) in Figure 3 and the phen and bipy complexes in Figure 4. The 5-bromo substituent has a negligible effect; presumably its hydrophilicity is too weak to significantly counteract the hydrophobic character of the rest of the periphery of this complex.

We have attempted to present a more wide-ranging picture in Figure 5. This includes representative complexes from the groups of Figures 1 to 4 plus a range of other complexes of various natures. Again it seems that the overall pattern reflects the hydrophilic/hydrophobic properties of the complexes. Thus at the other extreme from the hydrophobic complexes of Figures 3 and 4 we find $[Fe(fz)_3]^{4-}$, (fz^{2-} = $ppsa^{2-}$ = 3-(2-pyridyl)-5,6-bis(4-phenylsulphonato)-1,2,4-triazine) where the sulphonate substituents confer such high hydrophilicity that it is almost impossible to precipitate this anionic com-
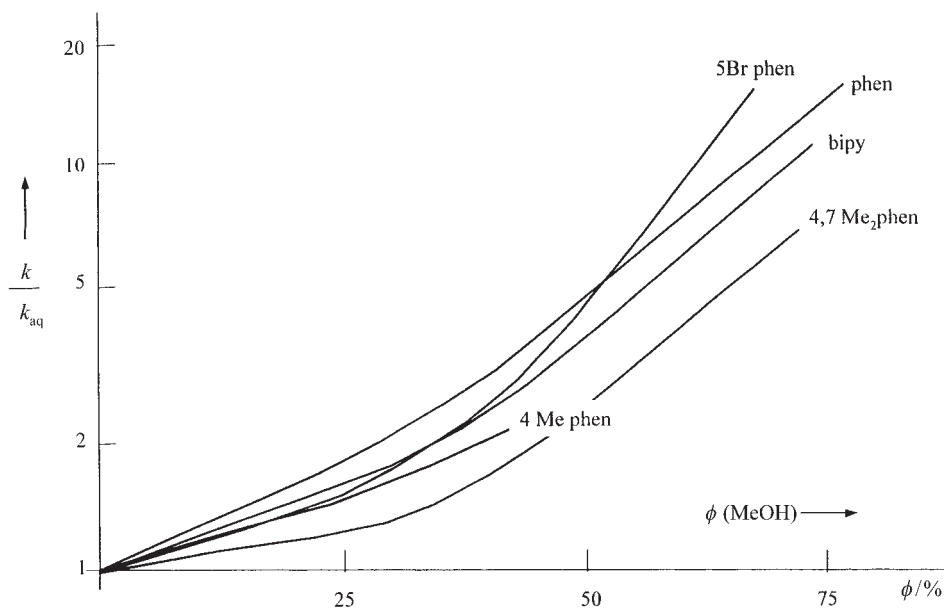
Figure 4. Dependence of rate constants on solvent composition for base hydrolysis of iron(II) complexes of 2,2'-bipyridyl and (substituted) 1,10-phenanthroline ligands. Rate constants are from Refs. 8 ([Fe(bipy)$_3$]$^{2+}$, [Fe(5Brphen)$_3$]$^{2+}$ and [Fe(4,7-Me$_2$phen)$_3$]$^{2+}$) and 26 ([Fe(4Mephen)$_3$]$^{2+}$); rate constants for [Fe(phen)$_3$]$^{2+}$ are from Refs. 16 and 27.

plex from aqueous solution. The aldoxime complex, with its three hydrophilic =NOH groups, along with the complexes containing several =NH groups, come next, followed by the N7K and N8K complexes discussed above. Continuing anticlockwise, the complexes of the terdentate ligands tsbh, tsbm, and tsbp have fairly hydrophilic –NH$_2$ groups but otherwise predominantly hydrophobic exteriors. The cxcage complex, with its two hydrophobic cyclohexyl caps and six peripheral methyl groups behaves similarly to the fully hydrophobic complexes – the nitrogen atoms are presumably quite well shielded and interact only weakly with solvent molecules. It is interesting to compare Figure 5 with its analogue for dmso–water.[22] In the latter system there is a sharp divide between a group of hydrophobic complexes, where rates of base hydrolysis increase rapidly as the proportion of dmso increases, thanks mainly to the increasing chemical potential of the hydroxide, and a very small number of hydrophilic complexes where the opposite trend obtains. The difference is due to the different selection of complexes for which data are available, with the methanol–water systems providing many examples of intermediate hydrophilic/hydrophobic characteristics.
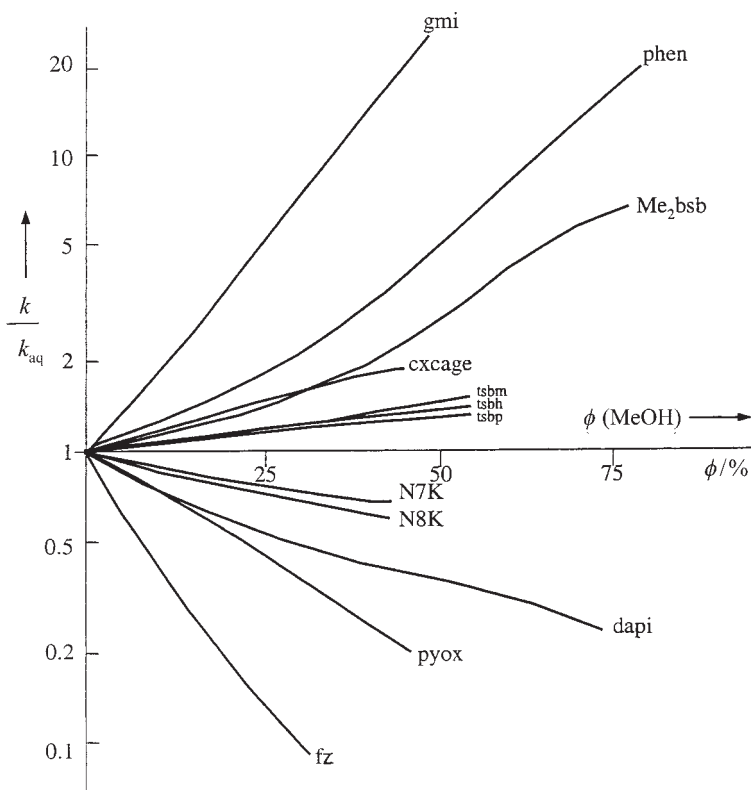
Figure 5. Overview of dependences of rate constants on solvent composition for base hydrolysis of iron(II) complexes of diimine ligands. Several of these plots are taken from Figures 1 to 4; other rate constants are from Refs. 28 ([Fe(fz)$_3$]$^{4-}$), 29 ([FeL$_3$]$^{2+}$, L = tsbh, tsbm, tsbp), and 30 ([Fe(pyox)$_3$]$^{2+}$).

It would be satisfying to put the qualitative trend suggested by the Figure 5 pattern into quantitative form. To this end we have plotted solvent effects on reactivity, in the form of logarithms of quotients of rate constants for base hydrolysis in 40% methanol over those in water, against solvation properties, in the form of transfer chemical potentials of the respective iron complexes,[15] in Figure 6. Although a general trend is apparent, the spread of the points is disappointing, and suggests that, as so often, it is not possible to rationalise the reactivity trends under consideration here in a simple model. It is necessary to carry out and consider full initial state-transition state analyses of rate constant trends to obtain a full picture, but at least the present discussion shows a qualitative underlying pattern for what is a very wide range of complexes.
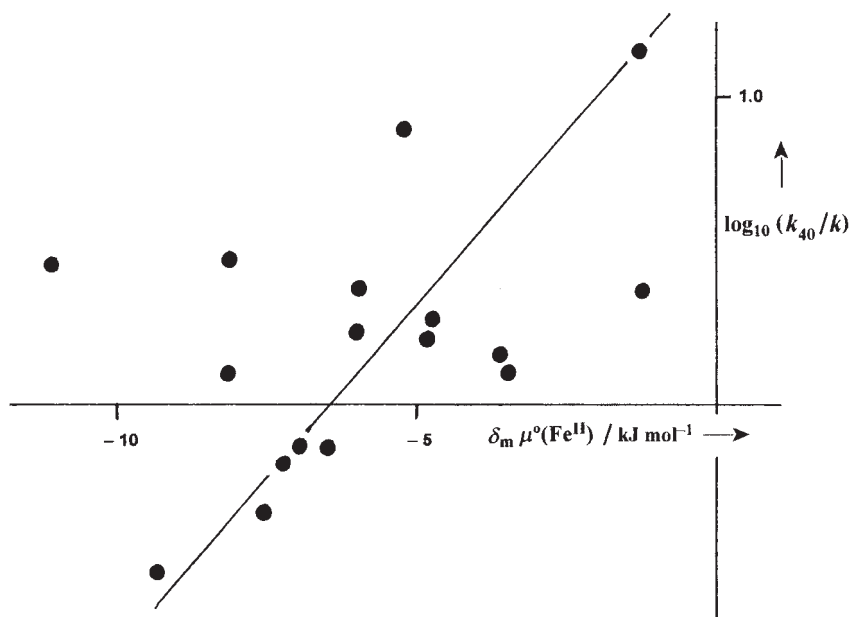
Figure 6. Relation between ratios of rate constants for base hydrolysis of iron(II)-diimine complexes in 40% methanol (k_{40}) to those in water (k) and transfer chemical potentials, $\delta_m \mu°(Fe^{II})$, for the respective complexes from water into 40% methanol. Transfer chemical potentials for the iron(II) complexes are from Refs. 15, 20, 31, and 23.

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SAŽETAK

Kinetika bazne hidrolize niskospinskih željezovih(II) diiminskih kompleksa u smjesama metanol–voda

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Dane su konstante brzine reakcije za baznu hidrolizu niza niskospinskih željezovih(II) diiminskih kompleksa, uglavnom s polidentatnim ligandima u vodi i vodenom metanolu (najviše do 40% metanola). Trendovi konstanata iz ovih i ranijih studija raznih željezovih(II) diiminskih kompleksa uspoređeni su i razmotreni s obzirom na strukturu liganda, supstituente liganda i solvatacijska svojstva tih kompleksa.