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Coordination Power Series of Solvents
2. The Solvent Effects on Complex Formations, Half-wave Potentials, ^{113}Cd NMR Resonances and Gibbs Free Energy Changes of Transfer

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Abstract

Coordination power (*CP*), a measure of a solvent's donor ability, which is related to the Gibbs free energy change on the solvation of nickel(II) ion, was determined for some solvents. The solvent dependency of complex formations, polarographic half-wave potentials, Gibbs free energy changes of transfer, ^{113}Cd NMR chemical shifts and transfer activity coefficients were investigated for Cu^{2+}, Cd^{2+}, Ag^+, Tl^+ and Li^+ on the basis of the concept of *CP*, indicating that the metal–solvent interaction depends on the hardness–softness of both the metal ion and the solvent. The *CP* series can be satisfactorily used for the metal ions such as Cu^{2+} and Cd^{2+} which resemble Ni^{2+} ion in hardness–softness, and also roughly hold for the soft metal ions such as Ag^+ ion with the exception of soft nitrile and for hard metal ions such as Li^+ and Mg^{2+} ions only in the solvents having the same donor atom. These results are supported by the facts that the stability sequence for nickel(II) complexes is the same as those for copper(II) and cadmium(II) complexes. The *CP* scale was compared with the α, σ, Y and donor number scales.

Introduction

The metal ion–solvent interactions are directly reflected in its solubility, chemical stability, oxidizing or reducing power, complexing ability, and the rates and mechanism of its reactions [1–5]. Therefore, much attention has been devoted to the metal ion–solvent interaction in almost all fields of chemistry, especially coordination chemistry, solution chemistry, electrochemistry and catalytic chemistry [1–5].

Despite the difficulties and complexity involved in the construction of scales of the solvating power of solvents, such scales are based either on an intrinsic property of the solvent (dielectric constant, ionization potential) or on the respective interactions of a series of solvents with a reference solute [5]. Quantitative characterization of a solvent's solvating ability in terms of any of its intrinsic properties was, however, found to be impossible. This led to an attempt to express these abilities in terms of empirical scales based on a variety of manifestations of solvent–solute interactions.

The Y value scale of Grunwald and Winstein [6] was proposed on the basis of the rate of solvolysis of t-butyl chloride. The Z value scale of Kosower [7] was based on charge-transfer frequencies for 1-ethyl-4-carbometoxypyridinium iodide. Kamlet and Taft have proposed a β-scale of solvent hydrogen-bond acceptor ability and an α-scale of solvent hydrogen-bond donor ability [8, 9]. A much more extensive scale of values has been provided by Reichardt's E_T parameter. The E_T values [10] correlate well with Z values, whereas correlation of Y values with E_T and Z is not quite so good. The softness scale, μ, of Marcus was proposed on the basis of the standard Gibbs free energy of the transfer of the soft silver relative to the corresponding quantities for the hard ions, sodium and potassium [11, 12]. Gutmann reported the donor number [13, 14], *DN*, which is related to the enthalpy change on the solvation of pentachloroantimony in 1,2-dichloroethane solution and is widely used as a measure for donor ability of a solvent. Attempts to establish a correlation of donor number and the metal–solvent interactions have been resumed, with some limited success in certain restricted areas.

We have recently proposed a new scale, coordination power, on the basis of the solvation of the nickel(II) ion [15]. The coordination power has been demonstrated to be well correlated with the variation in the stability constants of nickel(II) complexes, the ligand splitting parameter of nickel(II) ion, the half-wave potentials of the Ni^{2+}/Ni^0 couple and the activation enthalpy for the ligand substitution reaction of nickel(II) ion with solvent. Present investigations were undertaken to see if the coordination power series could be applied to other metal ions in addition to the nickel(II) ion.

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Experimental

Chemicals

Nickel(II) perchlorate hexahydrates were crystallized twice from aqueous solvent. $Ni(ClO_4)_2 \cdot 2H_2O$ was obtained by heating the corresponding pure hexahydrates for 4 h at 120 °C under vacuum over P_2O_5. Hexakis(dimethyl sulfoxide)nickel(II) perchlorate, $[Ni(Me_2SO)_6](ClO_4)_2$ [16], and hexakis-(acetonitrile)nickel(II) perchlorate, $[Ni(MeCN)_6](ClO_4)_2$ [17] were prepared by the same procedure as described in the literature. Anhydrous cadmium(II) perchlorate, $Cd(ClO_4)_2$, was obtained on heating the corresponding pure hexahydrates for 1 day at 50 °C. Bis{4,4,4-trifluoro-1-(2-trienyl)-1,3-butanedionate)copper(II) was prepared by modifying the method of Halzelaw *et al.* [18]. Acetonitrile, propionitrile, benzonitrile, acrylonitrile, n-propanol, i-propanol, n-butanol, i-butanol, s-butanol, t-butanol and trimethylphosphate were dried over calcium hydride for 1 day and then distilled. Formamide, *N*-methylformamide, *N*,*N*-dimethylformamide and *N*,*N*-diethylformamide were dried over P_2O_5 and then distilled under reduced pressure. *N*,*N*-dimethylacetoamide was dried over calcium hydride for 1 day and then distilled under reduced pressure. Methanol and ethanol were dried by heating under reflux over magnesium turnings and then distilled. Propylene carbonate was dried over molecular sieves for 1 day and distilled under 1 mm Hg atmosphere. Dimethyl sulfoxide was dried over calcium chloride for 1 day and then distilled under reduced pressure. Acetone was dried by heating under reflux over sodium carbonate for 3 h and then distilled. Nitromethane was dried by heating under reflux over calcium chloride under dried nitrogen and then distilled. The water content of the solvents was estimated by the Karl Fischer titration and found to be less then 0.01% by weight.

Measurements

The solutions of nickel(II) ion were prepared by the direct addition of weighed amounts of $Ni(ClO_4)_2 \cdot 2H_2O$, $[Ni(MeCN)_6](ClO_4)_2$ or $[Ni(Me_2SO)_6](ClO_4)_2$ to pure or mixed solvents in a glove box. The solutions were sealed in absorption cells, and the electronic spectra were measured from 250 to 1800 nm on a Hitachi 340 spectrophotometer. ^{113}Cd NMR spectra were measured at 44.27 kHz using a JEOL FX 200 NMR spectrometer equipped with a multinuclear broad-band probe. Tubes of 10 and 15 mm diameter were used. Standard acquisition parameters were as follows: spectral width, 40 kHz; pulse delay, 0.1 ms; acquisition time, 0.136 s; data points, 16 304; collected number of scans, 1000–5000. ^{113}Cd chemical shifts are referenced to an aqueous (D_2O) solution of 0.1 M $Cd(ClO_4)_2$ at 23 °C.

Results and Discussion

Definition of CP

Consider the equilibrium between the nickel(II) ion and two donor solvents, A and B,

$$\begin{aligned} &NiA_6 + 6B \rightleftharpoons NiA_5B + A + 5B \rightleftharpoons \\ &\quad NiA_4B_2 + 2A + 4B \rightleftharpoons NiA_3B_3 + 3A + 3B \rightleftharpoons \\ &\quad\quad NiA_2B_4 + 4A + 2B \rightleftharpoons NiAB_5 + 5A + B \rightleftharpoons \\ &\quad\quad\quad NiB_6 + 6A \end{aligned} \tag{1}$$

$$K_n = \frac{[NiA_{6-n}B_n][A]}{[NiA_{7-n}B_{n-1}][B]} \quad (n = 1\text{–}6) \tag{2}$$

When the nickel solution exhibits 10 *Dq* of $[NiA_3B_3]^{2+}$ [15], it is assumed that the mole ratio of A to B is proportional to the reciprocal of the ratio of the coordination ability of A (CA_A) to that of B (CA_B)*, and eqn. (3) is obtained.

$$[A]^6/[B]^6 = K_1 X K_2 X \cdots X K_6 = \beta_6{}^B/\beta_6{}^A \tag{3}$$

where

$$\beta_6{}^A = [NiA_6{}^{2+}]/[Ni^{2+}][A]^6 \tag{4}$$

$$\beta_6{}^B = [NiB_6{}^{2+}]/[Ni^{2+}][B]^6 \tag{5}$$

From eqns. (6) and (7)

$$\log(CA_B/CA_A = \tfrac{1}{6}(\log \beta_6{}^B/\beta_6{}^A) \tag{6}$$

The logarithmic values of the coordination ability of a given solvent (=S) on the basis of that of MeCN (i.e. $CA_A = CA_{MeCN} = 1$) is defined as the coordination power of the solvent, *CP*, (eqn. (7)).

$$CP = \log(CA_S/CA_{MeCN}) \tag{7}$$

$$= \tfrac{1}{6}(\log \beta_6{}^S/\beta_6{}^{MeCN}) \tag{8}$$

where

$$\beta_6{}^S = [NiS_6{}^{2+}]/[Ni^{2+}][S]^6 \tag{9}$$

$$\beta_6{}^{MeCN} = [Ni(MeCN)_6{}^{2+}]/[Ni^{2+}][MeCN]^6 \tag{10}$$

Coordination power for a solvent is the difference in the stability constant between hexa(solvento)-nickel(II) ion and hexa(acetonitrile)nickel(II) ion (eqn. (8)) and is subsequently related to the relative Gibbs free energy change for solvation of the nickel(II) ion (eqn. (11)).

$$CP = \frac{1}{2.3RT}(-\Delta G_B + \Delta G_{MeCN}) \tag{11}$$

where

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*It was here assumed that the steric effect of A and B on the formation of solvated ions is almost the same. Strictly speaking, the activity coefficient of the solvents should be considered.

$$\Delta G_{\mathrm{MeCN}} = -RT \ln \beta_6^{\mathrm{MeCN}} \qquad (12)$$

$$\Delta G_{\mathrm{S}} = -RT \ln \beta_6^{\mathrm{B}} \qquad (13)$$

Measurement of CP

The *CP* values of nitromethane ($MeNO_2$), dimethylacetoamide (dma), *N*-methylformamide (mfa) and formamide (fa) were determined. Figure 1 shows a plot of the observed 10 *Dq* value versus the mole fraction of Me_2SO in Me_2SO–mfa mixed solvents. The mole fraction is 0.44 at the 10 *Dq* value, 8.17 k cm^{-1}, of $[Ni(mfa)_3(Me_2SO)_3]^{2+}$ calculated from the rule of average environment* [19, 20]. The coordination power of mfa on the basis of Me_2SO is therefore −0.10. It can be converted to the *CP* value of 1.14 (1.24–0.10) on the basis of MeCN, since the *CP* value of Me_2SO is 1.24 [15]. The *CP* value, −0.10, of mfa is larger than that of dmf.

Similarly, the *CP* values for $MeNO_2$, dma and fa were measured to be −1.60, 0.50 and 1.34, respectively (Table 1). The value, −1.60, of $MeNO_2$ is very small compared with those of the other solvents but is a little larger than the value for t-BuOH. The value, 0.50, of dma is smaller than that of dmf. The 10 *Dq* and *CP* values were reexamined using $Ni(H_2O)_2(ClO_4)_2$ which was obtained on heating $[Ni(H_2O)_6](ClO_4)_2$ for 4 h at 120 °C over P_2O_5 under vacuum, since $Ni(H_2O)_2(ClO_4)_2$** obtained on heating for 24 h at 120 °C in previous studies did not always give the clear solution upon dissolution in the solvents. The obtained *CP* values did not differ relatively from the previous values as shown in Table 2. The values of 10 *Dq* for the hexakis(alcohol)nickel(II) ion and the hexakis(formamide)nickel(II) ion increased with the increase in the coordination power of the alcohols and the formamides, respectively (Fig. 2). The same trend has been found for the nitrile series [15]. This demonstrates that the coordination power reflects well the splitting energy of ligand field of the nickel(II) ion in the series of solvents having the same functional groups.

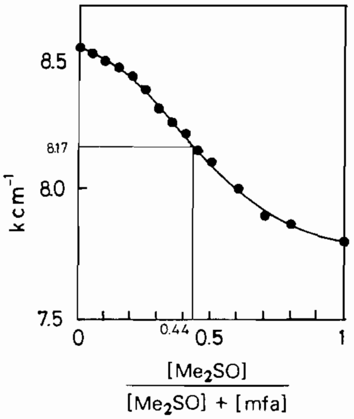

Fig. 1. The relationship between 10 *Dq* values of nickel(II) solvate ions and the mole fraction of Me_2SO in Me_2SO–mfa (*N*-methylformamide) mixed solvent. $Ni(ClO_4)_2$, 0.1 M; temperature, 25 °C.

TABLE 1. Relative coordination ability and *CP* values of solvents

	$CA_{\mathrm{Me_2SO}}$[b]	CA_{MeCN}[b]	*CP*
fa	1.26		1.34
Me_2SO	1.00		1.24
mfa	0.79		1.14
dma	0.18		0.50
$MeNO_2$		0.025	−1.60
H_2O[c]	0.35	6.1	0.79
MeOH[c]	0.075	1.3	0.11

[a]At 25 °C. [b]$CA_{\mathrm{Me_2SO}}$ and CA_{MeCN} are relative coordination abilities on the basis of acetonitrile and Me_2SO, respectively. [c]Ref. 15.

Application of CP to Other Metal Ions

Copper and silver cannot be classified in Group I, since this group has little in common with the alkalis except formal stoichiometries in the +1 oxidation state. From a purely chemical point of view it is appropriate to consider copper and silver as transition elements because their chemical behavior is, on the whole, quite similar to other transition elements [21]. Copper(II) ion and silver(I) ion are classified as a borderline acid and soft acid, respectively [22, 23]. Gibbs free energies, ΔG_{tr}, of the transfer of a cation from water to other solvents, give a better indication of the relative solvating abilities than the free energies of solvation. The free energies of solvation are relatively insensitive to the solvent because they are dominated by gas phase free energies, but this overshadowing effect is absent from the ΔG_{tr} values [5]. However, the ΔG_{tr} values are sensitive to small variations in the e.m.f. measurements from which they are normally obtained [5]. Mention has already been made of a good correlation between *CP* and Gibbs free energies [24] of transfer for copper ion from water to other solvents (Fig. 3(a)) [15].

Metal complex formation from the solvated ions involves the replacement of the solvent by the ligand. The stability constant of the metal complex should be inversely proportional to the coordination power

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*This rule applies to the *fac*-$[MA_3B_3]$ systems and would not seem to apply to *mer*-$[MA_3B_3]$. Thus, the *mer*/*fac* ratio must be taken into account. The purpose, however, is to obtain experimentally 'relative' coordination ability, but not 'absolute' coordination ability.

**The weight of $Ni(ClO_4)_2 \cdot 2H_2O$ was slightly decreased for 4 to 24 h under the given conditions, suggesting the formation of the hydroxide rather than $Ni(ClO_4)_2 \cdot H_2O$.

TABLE 2. Ligand field splitting energies of nickel(II) solvate ions, Ni(solvent)$_6^{2+}$ and coordination power of solvents[a]

Solvent	$10Dq^b$ (k cm^{-1})	*CP*
Formamide (fa), 1	8.60	1.34
N-Methylformamide (mfa), 2	8.55	1.14
N,*N*-Dimethylformamide (dmf), 3	8.42	0.95(0.72)^c
N,*N*-Dimethylacetamide (dma), 4	7.56	0.50
Methanol (MeOH), 5	8.55	0.11(0.11)
Ethanol (EtOH), 6	8.44	−0.11(−0.12)
n-Propanol (n-PrOH), 7	8.26	−0.29(−0.14)
n-Butanol (n-BuOH), 8	8.30	−0.52(−0.12)
i-Butanol (i-BuOH), 9	8.26	−0.68(−0.46)
i-Propanol (i-PrOH), 10	8.09	−0.96(−0.54)
s-Butanol (s-BuOH), 11	8.00	−1.13(−0.68)
t-Butanol (t-BuOH), 12	7.86	−173(−0.92)
Acetonitrile (MeCN), 13	10.31^d	0(0)
Propionitrile (PrCN), 14	10.18^d	−0.15(−0.15)
Benzonitile (PhCN), 15	10.03^d	−0.37(−0.37)
Acrylonitrile (AN), 16	9.98^d	−0.46(−0.46)
Pyridine (py), 17	10.26^d	2.26(2.24)
Dimethyl sulfoxide (Me_2SO), 18	7.81	1.24(1.24)
Water (H_2O), 19	8.58	0.79(0.79)
Trimethyl phosphate (tmp), 20	7.31	0.30(0.08)
Acetone (Me_2CO), 21	8.20	−0.57(−0.48)
Propylene carbonate (pc), 22	8.13	−0.78(−0.77)
Nitromethane ($MeNO_2$), 23	8.47	−1.60
N,*N*-Diethylformamide (def), 24	8.45	0.96(0.85)

[a] 25 °C. [b] This work. [c] The values in parentheses are *CP* values from ref. 15. [d] Ref. 15.

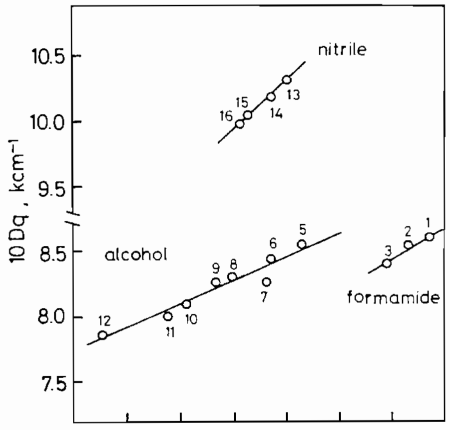

Fig. 2. The relationship between 10*Dq* values of nickel(II) ions in nitriles, alcohols and formamides and the *CP* values of solvents (for explanation of numbers, see Table 2).

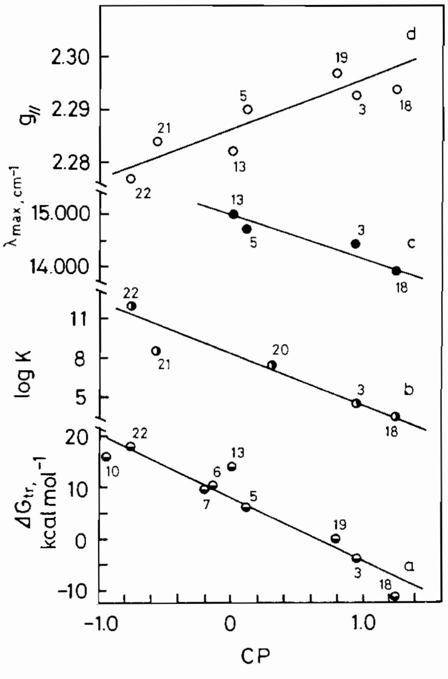

Fig. 3. The dependence of the Gibbs free energy values (ΔG_{tr}) [24] of transfer for the Cu^{2+} ion from water to other solvents (a), the stability constants (*K*) [25] of the chloro-copper(II) complex (b), the visible absorption peaks of solvent adducts of $Cu(tta)_2$ (c) and ESR parameter ($g_{\|}$) of $Cu(bidm)_2$ (d) [27] (see Table 2).

of the solvent because of the competition between ligand and solvent, if the metal–solvent interaction is much more sensitive to the solvent than that of the ligand–solvent interaction. The stability sequence for chloro copper(II) complexes [25] increases in the order Me_2SO < dmf < tmp < Me_2CO < pc, and is in accord with the inverse order of the CP series for the respective solvents (Fig. 3(b)). The chloride–solvent interaction should be considered as well as the copper–solvent interaction in the solvent effect on the complex formation. The result shown in Fig. 3(b) shows that the latter is more sensitive to the solvents used than the former. The stability constants with bicyclic cryptands (211, 221 and 222) also increase in the inverse order of the *CP* series [26]. Furthermore, the visible absorption of bis(2-thenoyltrifluoroacetonato)copper(II) (Cu-(tta)$_2$) shifts to a lower wavenumber in the order CH_3CN (15.100 cm^{-1}) > MeOH (14.700 cm^{-1}) > dmf (14.400 cm^{-1}) > Me_2SO (13.900 cm^{-1}) which has an increasing order of *CP* because of the formation of solvent adducts (Fig. 3(c)).

$$\mathrm{Cu(tta)_2} + n\mathrm{S} \rightleftharpoons \mathrm{Cu(tta)_2S}_n \qquad (14)$$

S = solvent, n = 1 and 2

The reported ESR parameter [27], $g_{\parallel}$, of bis(2,6-dimethyl-3,5-heptanedionato)copper(II), in various solvents can be successfully correlated with *CP* as well as donor number (Fig. 3(d)). Thus, these findings demonstrate that *CP* satisfactorily serves as a measure of the copper(II)–solvent interaction.

Since the cadmium(II) ion forms no compound in which the d shell is other than full, they are regarded as non-transition elements. Indeed, the cadmium(II) ion somewhat resembles Mg^{2+} in its tendency to form no complexes such as carbonyl and olefin complexes and two coordination complexes as well as four- and six-coordination complexes [21]. However, there is also some resemblance to the d-group elements in their ability to form complexes, particularly with amines, halide ions and cyanide, although the cadmium(II) ion is classified as a soft acid.

The e.m.f. of a cell, E°, is related to the Gibbs free energy change, ΔG°, for the cell reaction (eqn. (15)).

$$\Delta G^\circ = -nFE^\circ \qquad (15)$$

It has been demonstrated that polarographic half-wave potentials ($E_{1/2}$) parallel E° in a solvent. Figure 4(a) shows a plot of $E_{1/2}$ of Cd^{2+}/Cd couple [28–31] in a variety of solvents against their *CP*, where $E_{1/2}$ was measured by using the Cr(biphenyl)$_2^+$/Cr-(biphenyl)$_2$ couple as a reference potential. There is quite a good correlation between the two terms: the $E_{1/2}$ sequence shifts to more negative potentials in the order pc < MeCN < tmp < dmf $\leqslant$ H_2O < Me_2SO, which is the increasing order of their *CP*.

The dependence of the Gibbs free energy values (ΔG_{tr}) [32] of transfer for Cd^{2+} ion from water to other solvents on the *CP* of the solvents is illustrated in Fig. 4(b). The negative value of ΔG_{tr} increased as the cation–solvent interaction became stronger than the cation–water interaction, while the positive value increased as the interaction became weaker. This is, the ΔG_{tr} values became more negative with increasing *CP* of the solvents.

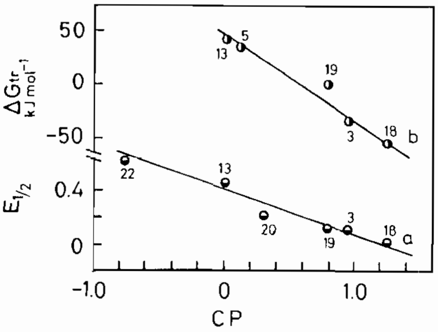

Fig. 4. The dependence of half-wave potentials ($E_{1/2}$) [28–31] of the Cd^{2+}/Cd couple (a) and the Gibbs free energy values (ΔG_{tr}) [32] of transfer for the Cd^{2+} ion from water to other solvents (b) upon *CP* values of solvents (see Table 2).

TABLE 3. Chemical shifts[a] of ^{113}Cd NMR of $Cd(ClO_4)_2$ in various solvents[b]

Solvent	Chemical shift (ppm)	Solvent	Chemical shift (ppm)
py	78.0	i-BuOH	−0.40.5
MeCN	25.0	i-PrOH	−42.0
PrCN	22.3	s-BuOH	−46.4
PhCN	10.3	t-BuOH	−51.1
AN	14.0	fa	−44.7
H_2O	0.0	mfa	−49.4
Me_2SO	−24.2	dmf	−50.6
MeOH	−29.4	dma	−78.2
EtOH	−36.3	Me_2CO	−59.0
n-PrOH	−36.9	pc	−73.0
n-BuOH	−36.3	$MeNO_2$	−109.3

[a]ppm relative to 0.1 M $Cd(ClO_4)_2$ in D_2O, at 23 °C. [b]Abbreviations: see Table 2.

The chemical shifts of metal cation NMR are generally very sensitive to solvents [33, 34]. However, their chemical shifts correlate to neither donor numbers, *Z* values [35], nor dielectric constant, although the ^{23}Na [36], ^{27}Al [33] and ^{133}Cs [33, 37] chemical shifts in solvents have been reported to correlate with the donor numbers; large deviations of H_2O, MeOH, MeCN and Me_2SO for ^{133}Cs, and those of H_2O and MeOH for ^{23}Na and ^{27}Al are observed. Thus, it is difficult to avoid the pessimistic conclusion that there are no wide range correlations between metal cation chemical shifts and the solvent properties [5].

The ^{113}Cd chemical shifts of Cd(II) ion in a variety of solvents were measured and are listed in Table 3. Neither of the donor numbers and physicochemical properties of the solvents correlate with the ^{113}Cd chemical shifts of Cd^{2+} ion in these solvents. Figure 5 shows the plot of ^{113}Cd chemical shift versus *CP* of alcohols, formamides and nitriles. It should be noted that the ^{113}Cd resonances shift

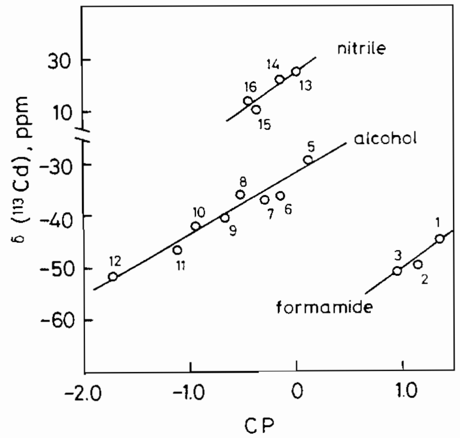

Fig. 5. The dependence of ^{113}Cd NMR chemical shifts of 0.1–1 M $Cd(ClO_4)_2$ in nitriles, alcohols and formamides upon the *CP* values of solvents (see Table 2).

downfield with increasing *CP* in the series of alcohols. Such good correlations are seen in both the nitrile and formamide series. The ^{113}Cd chemical shift has been demonstrated to be remarkably sensitive to coordination number, geometry and donor atoms (i.e. nature of Cd-donor atom bonding) [38, 39]. In fact it has been found that the ^{113}Cd resonances of cadmium complexes with 4-position-substituted pyridines, of which the coordination number, geometry and donor atoms are the same, shift downfield with increasing pK_a values of the ligand, i.e. the strength of the Cd(II)–ligand interaction [40]. The good correlations shown in Fig. 5 suggest that in the series of solvents with the same functional group (i) the coordination numbers of the cadmium solvate ions are the same, (ii) the metal ion–the solvent bond nature is similar and (iii) the *CP* clearly reflects the bond strength. Thus, *CP* is a useful guide for elucidating the solvent effect on the chemical shift of the ^{113}Cd NMR. In conclusion, the results in Figs. 4 and 5 demonstrate that *CP* is applicable to the Cd^{2+} ion.

Specific interactions between Ag^+ and acetonitrile have also been reported to be reflected in the half-wave potential ($E_{1/2}$) [41], the Gibbs free energy of transfer (ΔG_{tr}) [42–44], the transfer activity coefficient ($^{MeCN}\gamma^S$) [45] and the stability constants (*K*) [15] because of their strong π bonding character. In fact, the nitrile complex, $[Ag(MeCN)_4]^+$, is especially stable and MeCN cannot be displaced, e.g. by alkenes.

Figure 6 illustrates that $E_{1/2}$ [41] of the Ag^+/Ag couple, log $^{MeCN}\gamma^S$ [45], ΔG_{tr} of Ag^+ ion from MeCN to other solvents [42], and log *K* [46] for the Ag(I) complex with bicyclic cryptand (221) roughly correlate with the *CP* values of solvents with the exception of acetonitrile. The *CP* values of acetonitrile are estimated from the extrapolation to the linear correlations to be 9.0 (Fig. 6(a)), 0.88 (Fig. 6(b)), 0.90 (Fig. 6(c)) and 1.0 (Fig. 6(c)), respectively. It should be noted that these values fall only within the range 0.86–1.00. The average value, 0.92, seems to be a reliable *CP* value of acetonitrile for the Ag^+ ion, and suggests that the so called specific interaction between Ag^+ and acetonitrile is nearly equal to the Ag^+–dmf interaction.

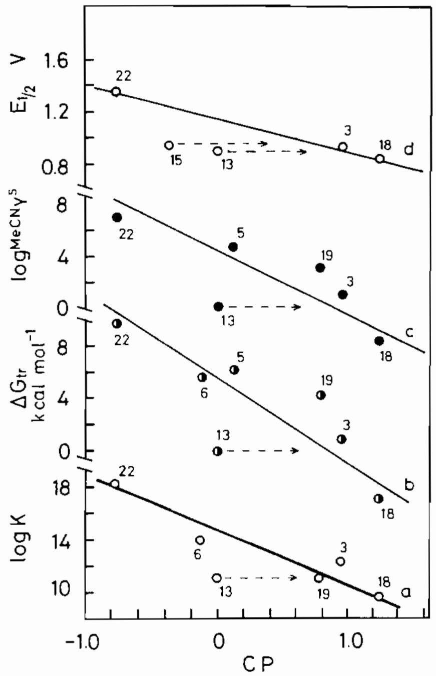

Fig. 6. The dependence of the stability constants (*K*) [46] of the Ag(I)–bicyclic cryptand(221) complex (a), the Gibbs free energy values (ΔG_{tr}) [42] of transfer for Ag^+ ion from MeCN to other solvents (b), the transfer activity coefficients ($^{MeCN}\gamma^S$) [45] (c) and the half-wave potentials ($E_{1/2}$) [41] of Ag^+/Ag couple (d) upon the *CP* values of solvents (see Table 2).

In contrast to acetonitrile, the *CP* value of H_2O obtained for Ni^{2+} is overestimated for Ag^+ as shown in Fig. 6(b) and (c). Reports supporting the small *CP* value of H_2O for Ag^+ have been issued. The ΔG_{tr} of Ag^+ ion from water to other solvents [44], transfer activity coefficients [45] of Ag^+ ion from MeCN to other solvents, log $^{MeCN}\gamma^S$, and log *K* [15] for the Ag(I) complex with 2,9-dimethyl-1,10-phenanthroline decrease with increasing *CP* values of the solvents, respectively, whereas these values for H_2O are all larger than that expected from the *CP* value of 0.79.

Thallium(I) ion has a radius of 1.54 Å which can be compared with those of K^+, Rb^+ and Ag^+ (1.44, 1.58 and 1.27 Å). In its chemistry this ion resembles either the alkali or silver ions [21]. Figure 7 shows the plots of *CP* against transfer activity coefficients ($^{MeOH}\gamma^S$) [47] of the thallium(I) ion between methanol and other solvents, the Gibbs free energy

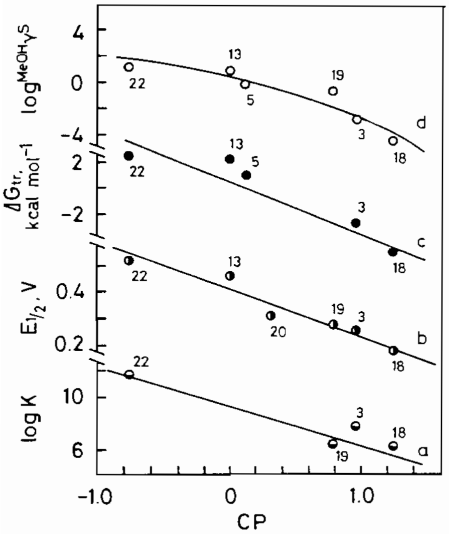

Fig. 7. The dependence of the stability constants (K) [49] of the Tl(I)–bicyclic cryptand(222) complex (a), the half-wave potentials ($E_{1/2}$) [28–31] of the Tl^+/Tl couple (b), the Gibbs free energy values (ΔG_{tr}) [48] of transfer for Tl^+ ion from water to other solvents (c) and the transfer activity coefficients ($^{MeOH}\gamma_S$) [47] (d) upon the *CP* values of solvents (see Table 2).

values (ΔG_{tr}) [48] of transfer for the Tl^+ ion from water to other solvents, half-wave potentials ($E_{1/2}$) [28–31] of the Tl^+/Tl couple and the stability constant (K) [49] of the Tl(I)–bicyclic cryptand(222) complex. All of the plots are found to be approximately linear. No specific interaction between Tl^+ and MeCN was observed, although Tl^+ ion is classified as a soft acid like the Ag^+ ion. The results in Fig. 7 shows the *CP* series roughly holds for the Tl^+ ion.

Figure 8 shows the solvent dependence of the Gibbs free energy values (ΔG_{tr}) [48] of transfer of the Li^+ ion from water to non-aqueous solvents, the half-wave potentials ($E_{1/2}$) [50, 51] of Li^+ ion and the stability constants (K) [46] of the Li(I)–bicyclic cryptand(221) complex. The variations in these values with the solvent are roughly correlated to *CP*, although acetonitrile and benzonitrile exhibit large deviations from the linear correlations. These correlations probably result from the fact that the hardness of the solvents used does not differ greatly except for the nitriles. In contrast to the Ag^+ ion *CP* for MeCN is overestimated and found to be −1.3, −0.7 and −1.2, respectively, with an average value of −1.1 from the correlations (Fig. 8).

Comparison of Stability Constants

The values of *CP* are the relative values of stability constants of hexa(solvento)nickel(II) ions as previously described. The application of the *CP* series to other metal ions, therefore, means that

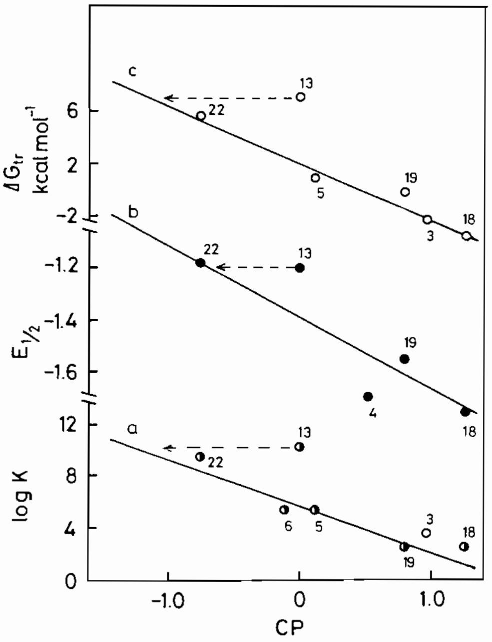

Fig. 8. The dependence of the stability constant (K) [45] of the Li(I)–bicyclic cryptands(221) complex (a), the half-wave potentials ($E_{1/2}$) [50, 51] of the Li^+/Li couple (b) and the Gibbs free energy values (ΔG_{tr}) [48] of transfer for Li^+ ion from water to non-aqueous solvents (c) upon the *CP* values of solvents (see Table 2).

the order of stability constants of hexa(solvento)nickel(II) ions is relatively consistent with that of the stability constants of the solvated metal ions. In this way, a detailed comparison of the stability constants of complexes between nickel(II) and the other metal complexes is expected to give useful information of the metal–solvent interaction.

It is well known that hard acids prefer to bind to hard bases and soft acid prefer to bind to soft bases. The term hard and soft are relative and there is no sharp dividing line between them. The importance of this hard–soft factor, i.e. special stability of hard–hard and soft–soft interactions, is shown in the five ring chelating ligands. The softer nickel(II) favors the sets of donor atoms in the order ox (O, O) < ala (O, N) < en (N, N) < ame (S, N) which is an increasing order of softness, while the harder Mg^{2+} preferentially binds in the reverse order, ame (S, N) < en (N, N) < ala (O, N) < ox (O, O) [52].

Looking more closely at the correlation between the stability constants of the metal complexes and hardness–softness of the metal ions, Fig. 9(a) shows a plot of stability constants [53] of the copper(II) complexes against those [53] of the corresponding nickel(II) complexes and gives a good linear correlation. This clearly indicates the good similarity between both metal ions in softness–hardness and supports the experimental results shown in Fig. 3.

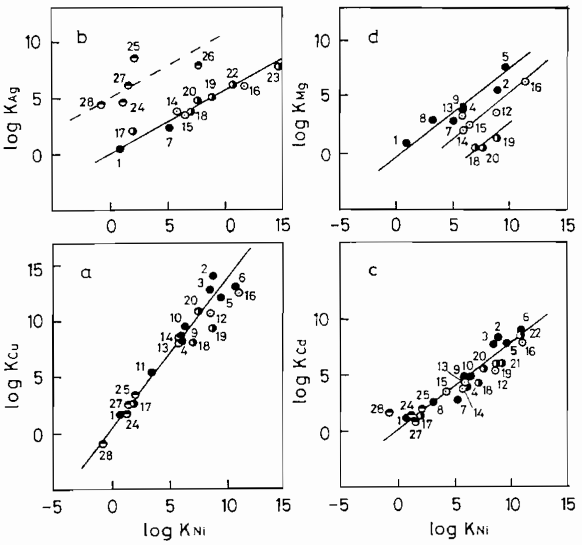

Fig. 9. The comparisons of the stability constants [53] of nickel(II) complexes with those [53] of copper(II) (a), silver(I) (b), cadmium(II) (c) and magnesium(II) complexes (d). 1, acetic acid; 2, 1,2-dihydroxybenzene; 3, 4,5-dihydroxy-1,3-benzenedisulfonic acid; 4, 2,4-pentanedione; 5, 1,3-diphenyl-1,3-butanedione; 6, 1,3-diphenyl-1,3-propanedione; 7, oxalic acid; 8, malonic acid; 9, tropolone; 10, 5-sulfosalicylic acid; 11, salicylaldehyde; 12, iminodiacetic acid; 13, glycine; 14, alanine; 15, 2-pyridinecarboxylic acid; 16, 8-hydroxyquinoline; 17, pyridine; 18, 2,2'-bipyridine; 19, 1,10-phenanthroline; 20, ethylenediamine; 21, *trans*-1,2-diaminocyclohexane; 22, diethylenetriamine; 23, triethylenetetramine; 24, thiocyanate; 25, thiosemicarbazide; 26, mercaptosuccinic acid; 27, bis(carboxymethyl)-phenylarsine; 28, bromide.

Generally, ligands with P, As, S and Se give many silver(I) complexes. The greater stability of these complexes than those of the complexes with O and N analogues has been attributed to the polarizing power of Ag^+ and the high polarizability of the 'soft' donor atom. Comparison of the stability constants [53] between soft silver(I) and nickel(II) gives a linear correlation for non-soft ligand, but exhibits a large deviation from the linear correlation for only the soft ligands such as SCN^-, thiosemicarbazide, mercaptosuccinic acid and phenylarsinodiacetic acid. The result in Fig. 9(b) clearly demonstrates that softness of the Ag(I) ion is very large compared with that of the Ni(II) ion. Cadmium(II) is classified as a soft acid. The plot of the stability constants [53] of Cd(II) against those of Ni(II) complexes, nevertheless, gives a good linear correlation for even soft ligands such as SCN^- and thiosemicarbazide, indicating that the softness of Cd^{2+} is close to that of Ni^{2+} rather than Ag^+ (Fig. 9(c)). This is also consistent with the results shown in Figs. 4 and 5.

TABLE 4. α, σ and *Y* values of metal ions

	α^a	σ^b	Y^c
Hg^{2+}	5.83	1.01	4.25
Cu^+	3.92	0.96	3.45
Ag^+	3.60	1.03	3.99
Cd^{2+}	1.66	0.96	3.04
Cu^{2+}	1.64	0.89	2.89
Ni^{2+}	1.41	0.94	2.82
Co^{2+}	1.39	0.92	2.96
Tl^{2+}	1.24	0.98	3.77
Zn^{2+}	1.25	0.91	2.34
Fe^{2+}	1.13	0.84	3.09
Fe^{3+}	1.62	0.78	2.37
UO_2^{2+}	0.95	0.62	
Alkali and alkali earth metal ions	~0		0.87(Mg^{2+}) 0.36(Li^+)

[a]Ref. 54. [b]Ref. 55. [c]Ref. 6.

The alkali metal ions form only weak complexes with simple anions and very few with monodentate ligands. Chelation is a necessary condition for significant complexation. Since little data on their stability constants are available, a comparison was made between Ni^{2+} and Mg^{2+}, which is a hard acid. Figure 9 shows that the stability constants [53] of Mg(II) complexes decrease in the order, only O > O and N > only N donor set, i.e. with increasing the softness of the donor atoms, and a linear relationships exist between Ni^{2+} and Mg^{2+} in the series of ligands containing the same donor atom.

Thus, the stability constants of metal complexes strongly depend on the hardness and softness of the metal ions as well as the ligand. These facts demonstrate that the stability sequence for metal complexes is the same among the metal ions which resemble each other in the softness–hardness and in the series of the ligands containing the same donor atom set. This correctly and systematically explains the results obtained concerning the application of the *CP* series to other metal ions.

Correlation of CP with Other Parameters

A few measures of hardness–softness; α [54], β [55] and *Y* values [6], have been reported (Table 4). As previously described, softness of Cd^{2+} and Tl^+ has been found to be close to that of Ni^{2+}, a borderline acid rather than of the Ag^+ ion a soft acid. In other words, it is considered to be a gap between the softness of Ag^+ and Cd^{2+}. Misono *et al.* have proposed a *Y* parameter which is considered to be a measure of the softness of a metal ion. Hard ions have *Y* values below 2.8, soft ions have value greater than 3.2 and borderline species are 2.8–3.2. The *Y* values decrease in the order $Ag^+ > Tl^+ > Cd^{2+} > Cu^{2+} > Ni^{2+} > Li^+$. Softness of Ag^+ is very close to that of Tl^+, indicating no large gap between Ag^+ and Tl^+. Although the α values decrease in the order $Ag^+ > Tl^+ > Cd^{2+} > Ni^{2+} > Cu^{2+}$, there is a large gap between Ag^+ and Tl^+. The α values for Tl^+, Cd^{2+},

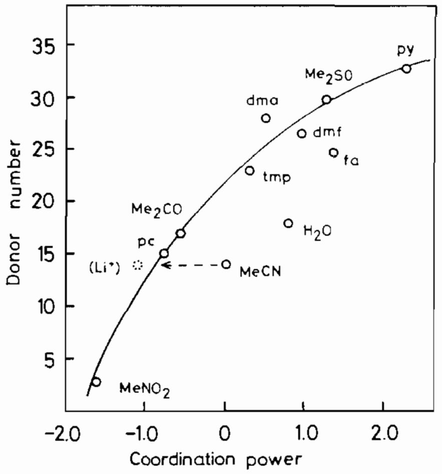

Fig. 10. The comparison of donor numbers [13, 14] with *CP* values (for abbreviations, see Table 2).

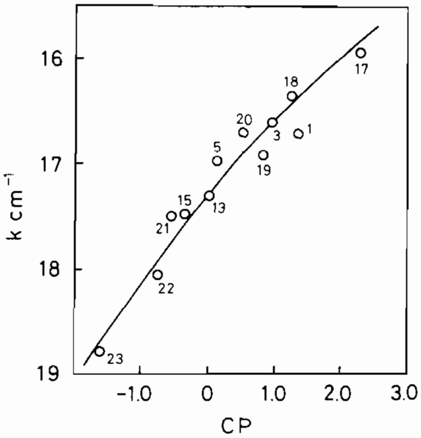

Fig. 11. The comparison of the wavenumber of the maximum absorption band of [Cu(tmen)(acac)]ClO$_4$ [59–61] with *CP* values (for abbreviations, see Table 2).

Ni^{2+} and Cu^{2+} are similar and there is a large gap between Ag$^+$ and Tl$^+$. There is, of course, a remarkable gap between Ni^{2+} and Li$^+$. Thus, the α value seems to be a good indication for application of *CP* to other metal ions. The *CP* series hold for metal ions of which the values are close to that of nickel(II) ion, whereas the CP of MeCN does not hold for metal ions having significantly different values. Such sensitive dependence of the *CP* value of MeCN on the metal ion results from the variation of the covalency and back donation in the metal–MeCN bonding, compared with the other solvents.

Donor number [13, 14] being the negative enthalpy change on the solvation of pentachloroantimony, has been used as a measure for donor ability of a solvent. A plot of donor number against *CP* in Fig. 10 gives a correlation with the exception of fa, H$_2$O and MeCN, although donor number and *CP* are related to enthalpy and Gibbs free energy, respectively. The good correlation shown in Fig. 10 is not surprising, because donor number is often correlated to Gibbs free energy [55–58]. The deviation of MeCN from the correlation was not exhibited when the modified *CP* value for Li was used, indicating that donor number is applicable to hard acids rather than borderline and soft acids.

Sone and Fukuda [59–61], have shown that in the case of [Cu(tmen)(acac)]ClO$_4$, where tmen = *N,N,N′,N′*-tetramethylethylenediamine and acac = acetylacetone, the color of the solution follows the donor ability of the solvent as is revealed by the linear relationship between the wavenumber of the maximum absorption band in the visible and the solvent donor number [62–64]. A good relationship between the wavenumber and *CP* is also obtained as shown in Fig. 11.

Solvent–solute interactions are highly complex in nature even to the extent of making each situation a special case and a number of empirical solvent parameters have been introduced and still are being introduced [63]. Thus any chemical compound used as a standard has its advantages and disadvantages. Strictly speaking, each metal ion should have its inherent solvent donor scale which cannot quantitatively hold for other metal ions. The results obtained in this work, however, indicate that the experimental solvent donor scale obtained for a certain metal can qualitatively hold for other metal ions which resemble the metal ion in the hardness–softness and one approach to the elucidation of solvent–metal ion interactions is to study this in a series of solvents having the same functional group.

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