Stability Sequences of Cadmium(II) and Zinc(II) Monohalide Complexes in Alcohols and Binary Solvent Mixtures Containing Methanol, Dimethylsulfoxide, Acetonitrile and Water

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Abstract

Classification schemes, such as Ahrland's 'a'–'b' organization of ligand acceptors, are important to the systemization of coordination chemistry. Aside from Ahrland's extensive studies in dimethylsulfoxide, little is known about the effects of solvent choice upon acceptor classification. Furthermore, there is a dearth of information about the behavior of fluoride complexes under non-aqueous conditions due to the lack of a suitable measurement technique for such studies. This renders previous halide studies incomplete, since the hardest ligand has been systematically excluded. We report the results of potentiometric studies of the stabilities of monohalide complexes (F^-, Cl^-, Br^-) of cadmium(II) and zinc(II) in methanol, ethanol and binary solvent mixtures such as methanol/water, dimethylsulfoxide/methanol, dimethylsulfoxide/water and acetonitrile/water. This data provides important new information related to non-aqueous behavior of these d^{10} acceptors, particularly with respect to solvent-related stability sequence changes previously reported for cadmium(II).

Introduction

The Group II-B d^{10} metal ions constitute a particularly interesting set of ligand acceptors from the viewpoint of 'hard—soft' or 'a—b' classification concepts [1]. In aqueous solution, zinc(II) is distinctly 'a' in that it prefers 'hard' ligands and forms predominantly ionic bonds, mercury(II) is distinctly 'b', preferring covalent interactions, and cadmium(II) is borderline, showing 'a' behavior with some ligands and 'b' behavior with others. However, relatively little is known about the general role played by the solvent

in determining acceptor classification. The very hard fluoride ligand occupies a key role in acceptor classification, but virtually nothing is known about the fluoride complex stabilities in non-aqueous media. We report a study of the stability sequences of monohalide, including monofluoride, complexes of cadmium(II) and zinc(II) in several neat and mixed solvents based upon classical and ion-selective electrode potentiometric measurements.

In the most important systematic studies previously done in this area, Ahrland and others have examined the thermodynamic properties of the chloride, bromide and iodide (but not fluoride) complexes of these metal ions in water and in dimethylsulfoxide (DMSO) [2–7]. They have observed the 'b' stability sequence: $CdCl^+ < CdBr^+ < CdI^+$ in aqueous systems, but the reverse 'a' sequence in DMSO. Moreover, they found that the corresponding zinc(II) complexes become more markedly 'a' in DMSO than in water and the stabilities of the corresponding Hg(II) species, which were distinctly 'b' in water showed no distinct stability trend with respect to a halide sequence in DMSO [7]. In summary, in each case, transfer of the complex from water to DMSO results in an apparent decrease in covalent character. Ahrland ascribes this shift in stability trends to the less favorable solvation of hydrogen bonding ligands by DMSO [7]. The difference between the solvation enthalpies of halide ions in DMSO compared to water increases strongly according to the trend: $I^- < Br^- < Cl^-$ as a result of the same trend in hydrogen bonding strength. Thus, if the stability sequence is controlled by these differences in ligand solvation, the trend in complex stabilities should become more 'a', or less 'b', when changing from water to a less hydrogen-bonding solvent, as Ahrland claims is the case for water *versus* DMSO [7].

The goal of this present study was to further test these trends by two means. Firstly, information concerning the stability of monofluoride complexes in

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various solvent systems has been obtained. Unfortunately, Ahrland excluded fluoride complexes from his studies. The fluoride complex is usually either very much more stable or very much less stable than the corresponding chloride species and, thus, is very important in assigning the classification of metal. Recent developments in application of fluoride ion-selective electrode potentiometry to non-aqueous systems have made it possible to extend fluoride complex stability studies to a range of non-aqueous and mixed solvent systems [8, 9]. Secondly, the relative stabilities of halide complexes in methanol, ethanol and a range of binary solvent mixtures have been measured. The hydrogen bonding properties of the solvent systems examined are between the extremes exhibited by water and DMSO. Thus, if ligand solvation is the critical factor in establishing these complex stability trends, the results in these solvent systems should show classification trends intermediate between those for the water and DMSO systems.

Experimental

Chemicals and Solutions

Reagent grade methanol and ethanol were used as received from freshly opened bottles with less than 0.1% nominal water content. Deionized distilled water was used for all aqueous and mixed solvent studies. Reagent grade DMSO was distilled twice, the second time from calcium oxide, keeping the middle 70% fraction from each distillation. HPLC grade acetonitrile (AN) was used as received; alternatively, reagent grade AN was distilled under dry nitrogen from calcium hydride, keeping the middle 70% fraction. Our rationale for not attempting to rigorously exclude water has been discussed previously [8], and all measurements were made in the open laboratory.

All solvents were made 0.05 M in tetraethylammonium perchlorate (TEAP) to control the ionic strength, except for ethanol where 0.05 M tetrabutylammonium perchlorate (TBAP) was used. TEAP was repeatedly recrystallized from distilled deionized water until no halide could be detected in the supernate by silver halide turbidimetry, followed by a single recrystallization from methanol. TBAP was recrystallized twice from ethyl acetate and petroleum ether.

Aldrich tetraethylammonium chloride and bromide, tetrabutylammonium fluoride and chloride, and Eastman tetraethylammonium fluoride were used as received for preparing stock halide solutions. These solutions were standardized potentiometrically by the method of Grans standard additions. Stock solutions of cadmium and zinc perchlorate were prepared from hydrated salts, which were dried in a vacuum

desiccator over phosphorus pentoxide prior to dissolution in non-aqueous solvents. The corresponding aqueous stock cadmium and zinc solutions were prepared directly from the hydrated perchlorate salts. These metal ion solutions were standardized complexometrically against EDTA.

Apparatus

All potentiometric measurements were made in polyethylene beakers which were thermostated to ±0.1 °C. Fluoride measurements were made with an Orion 94-09A fluoride ion-selective electrode. An Orion 94-17A solid-state chloride electrode was used for aqueous measurements, but was unstable in systems containing large fractions of non-aqueous solvent. In these cases, chloride measurements were made with a silver—silver chloride electrode prepared by anodizing a Beckman 39261 silver billet electrode in a dilute chloride solution. A silver—silver bromide electrode for bromide measurements was prepared in a similar fashion. Voltage measurements were made with Corning Model 130 digital pH meters. The reference electrode was either an Orion 90-02 double-junction reference electrode or a non-aqueous silver—silver chloride electrode filled with 1.0 M lithium chloride in methanol. The reference electrode was coupled to the test solution through a porous Vycor salt bridge filled with the same electrolyte and solvent as was in the test solution.

Procedure

Fifty milliliters of solvent which is 0.05 M in TEAP or TBAP was placed in a polyethylene beaker, a measured portion of tetraalkylammonium halide solution was added using a microburet, the electrodes were inserted, the cell was capped and the e.m.f. was recorded at steady-state (less than 0.1 mV drift in 90 s). Several more portions of halide solution were added and the steady-state e.m.f. was measured after each addition. This information permitted calculation of the electrode calibration parameters. Following the final halide addition several successive portions of stock cadmium or zinc solution were added and the steady-state e.m.f. was recorded after each addition. The final total halide concentration prior to the addition of metal ion solution to the cell typically ranged between 2×10^{-5} and 4×10^{-4} M. The metal ion concentration after the addition of the final portion generally did not increase the total ionic strength by more than a few percent; however it was observed that increasing the ionic strength by as much as 20–30% by metal ion additions did not significantly affect or produce an anomalous trend in the observed stability data.

A quantity, $f(C)$ can be calculated from the experimental data obtained at each addition of cadmium or zinc solution [8, 10]:

$$f(C) = \frac{C_X - [X^-]}{(C_M - C_X + [X^-])[X^-]}$$

$$= \frac{\beta_1 + 2\beta_2[X^-] + \dots + n\beta_n[X^-]^{n-1}}{1 - \beta_2[X^-]^2 - \dots - (n-1)\beta_n[X^-]^n} \quad (1)$$

C_X is the total analytical concentration of the halide species, C_M is the total analytical concentration of cadmium or zinc ions and $[X^-]$ is the concentration of uncomplexed halide ions as determined potentiometrically. The value of $f(C)$ is independent of metal ion concentration for mononuclear complexes and is also independent of free halide concentration if only 1:1 complexation occurs, in which case: $f(C) = \beta_1$. This situation is favored by employing high metal-to-ligand concentration ratios (always greater than four), and in most cases, it was possible to study the monohalide species alone, avoiding the uncertainties related to multiple species extrapolations. In studies of zinc chloride in methanol, cadmium bromide in methanol—DMSO mixtures and cadmium fluoride in AN—water mixtures above 80% AN it was not possible to completely avoid formation of some dihalide species. In these cases, β_1 was obtained from a linear least square data treatment of the data based on eqn. (1).

Results and Discussion

Cadmium(II) monohalide species are considered initially and in detail for two reasons. Firstly, Ahrland claims that cadmium, unlike zinc or mercury, shows a reversal in stability sequence when changing from aqueous to DMSO solution [7]. Secondly, the fluoride species can be studied potentiometrically using a fluoride-selective electrode under conditions favoring accurate measurement of low average ligand numbers [8, 10]. Supplementary information is reported for the corresponding zinc(II) species, but the analogous fluoride studies cannot be made with mercury(II) because of intractable solubility problems [11].

Thermodynamic Studies in Alcohol and Alcohol–Water Mixtures

A Born-type plot of the stability constant data for CdF^+ and $CdCl^+$ in water—methanol mixtures over the range 0 to 100% is given in Fig. 1. The dielectric constants for the solvent mixtures were estimated from the mole fractions [8]. Both complexes show Born-like stability constant dependency up to about 80% (v/v) methanol, above which both plots are nonlinear. This suggests that the aqueous solvation terms involved in the equilibrium: $Cd(solv.)^{2+} + X(solv.)^- \rightleftharpoons CdX(solv.)^+$ are not appreciably disrupted by methanol in methanol—water mixtures below 80%
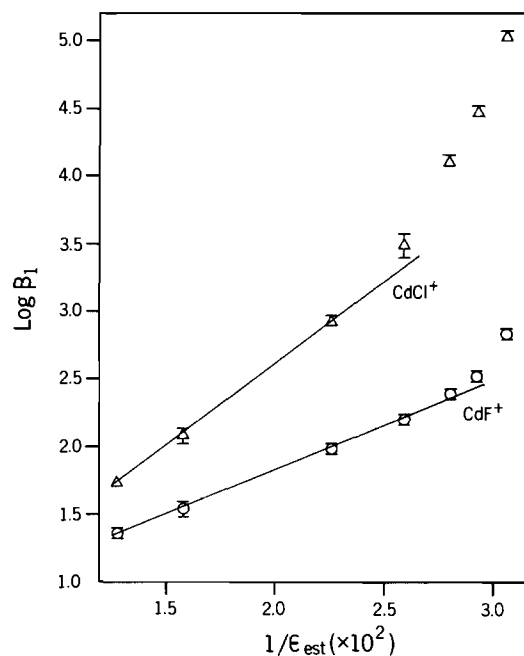

Fig. 1. Plot of Born equation variables for methanol—water mixtures containing 0.05 M TEAP at 25 °C: ($\triangle$) $CdCl^+$, ($\circ$) CdF^+. Error bars indicate ± 2 standard deviations.

methanol. Of particular significance is the observation that the stabilities of the CdF^+ and $CdCl^+$ complexes diverge, rather than converge, as the fraction of methanol in the solvent mixture increases. Thus, the relative stabilities of CdF^+ and $CdCl^+$ become increasingly 'b', rather than less 'b' as the solvent goes from water to methanol. This behavior is contrary to what would be predicted from ligand solvation considerations. Although no corroborating data exists in the literature for methanol or water at a low ionic strength, $\log \beta_1$ values of 2.1 and 4.0 for $CdCl^+$ and $CdBr^+$ respectively at 2 M ionic strength in methanol [12, 13] at least support our observation that a distinctly 'b' sequence is seen in methanol.

Thermodynamic data for cadmium(II) monohalide complexes in various solvents are summarized in Table I. Considering the nominal water content of neat methanol, the water-to-metal molar ratio probably exceeds 100 in the '100% methanol' studies. Thus, the stability constant data in this medium should be taken as minimum values, since the total exclusion of water would undoubtedly enhance the stabilities even more. Inclusion of data for $CdBr^+$ in methanol further confirms the markedly 'b' stability sequence in this solvent: $CdBr^+ > CdCl^+ \gg CdF^+$. Assuming the difference in stability constants, $\Delta(\log \beta_1)$, between $CdCl^+$ and CdF^+ to be a qualitative gage of the level of 'a' or 'b' behavior, it is clear from data in Table I that the 'b' character of cadmium halides is nearly as strong in ethanol as in methanol. Thus, ethanol, like methanol, shows a

TABLE I. Thermodynamic Data for the Equilibria: $M^{2+} + X^- \rightleftharpoons MX^+$ ($M^{2+} = Cd^{2+}, Zn^{2+}; X^- = F^-, Cl^-, Br^-$) at 25.0 ± 0.1 °C

	80% MeOH, 20% H₂O 0.05 M TEAP		100% MeOH 0.05 M TEAP			100% EtOH 0.05 M TBAP	100% MeOH 0.05 M TEAP		
	CdF^+	$CdCl^+$	CdF^+	$CdCl^+$	$CdBr^+$	CdF^+	$CdCl^+$	$ZnF^{+\,a}$	$ZnCl^+$
$\log \beta_1$	1.95 ± 0.02	2.93 ± 0.02	2.82 ± 0.03	4.89 ± 0.02	5.13 ± 0.04	5.60 ± 0.01	7.11 ± 0.07	3.36 ± 0.04	2.81 ± 0.04
ΔG_1 (kJ/mol)	−11.2 ± 0.1	−16.7 ± 0.1	−16.1 ± 0.2	−27.9 ± 0.1	−29.0 ± 0.2	−31.8 ± 0.7	−40.5 ± 0.4	−19.2 ± 0.2	−16.0 ± 0.2
ΔH_1 (kJ/mol)	+10	−7	+30	~0				+40	+20
ΔS_1 (probable sign)	+	+ (?)	+	+				+	+

ᵃRef. 10.

trend which is distinctly different from that reported by Ahrland for DMSO solutions [7].

Some insight into the reasons for the increased 'b' character of these cadmium monohalide complexes in methanol can be obtained from information about the enthalpy changes which accompany complex formation in this medium. The sign and approximate magnitude of ΔH_1 were estimated from the temperature dependence of the stability constant in methanol and in 80% methanol—20% water. The latter mixture was chosen as an 'aqueous-like' reference system to avoid the experimental difficulties and attendant large uncertainties associated with such measurements on the very weak aqueous complexes. The temperature interval used, 15 °C to 25 °C, was fixed by experimental difficulties encountered with the fluoride electrode in methanol; the electrode response was unstable at higher temperatures and gave exceedingly sluggish response at lower temperatures. At least fifteen data points were used to obtain the mean value at each temperature. Sample plots of $\log \beta_1$ for cadmium monofluoride *versus* the reciprocal of Kelvin temperature are shown in Fig. 2. These plots are also representative of the quality of analogous data for the other systems studied. As is seen in Fig. 2, the available temperature range and experimental uncertainty in the stability data severely limits the quality of the enthalpy data obtained by this approach. However, with a single exception, the sign on ΔH_1 for each system studied was unambiguous and the order of magnitude of ΔH_1 could be ascertained. The values of ΔH_1 in Table 1 are reported to one significant digit to indicate the approximate magnitude of the values. In the case of $CdCl^+$ in neat methanol, the apparent stability constant variation over the ten degree temperature range (3%) was half of the experimental uncertainty in the constant itself
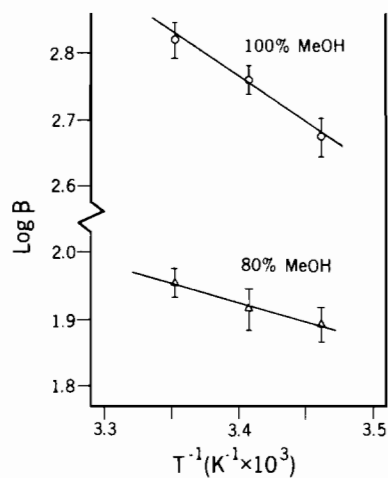

Fig. 2. Temperature dependence of β_1, for CdF^+ in methanol (○) and 80% methanol—20% water (△). Error bars indicate ± 1 standard deviation.

(±5%). Thus we conclude that ΔH_1 is close to zero for this system.

The enthalpy change was endothermic or nearly zero for three of the four CdX^+ systems for which ΔH_1 was estimated. Hence the entropy change for these three systems is probably positive. The formation of $CdCl^+$ in 80% methanol–20% water is slightly exothermic, but it appears that complex formation is most likely entropy-controlled in all four cases. This is consistent with the entropy-controlled stability of CdF^+, $CdBr^+$ and CdI^+ in water [7, 14] and of the latter two species in DMSO [7]. It is clear that the 'b' stability sequences for CdX^+ in methanol and methanol–water are also enthalpy-controlled like the corresponding aqueous sequences [7, 14]. It also seems likely that the increasing 'b' character of cadmium(II) when going from 80% methanol to neat methanol is attributable to ΔH differences, *i.e.*, it is a 'heat effect'.

Since zinc(II) is distinctly 'a' in water and apparently even more strongly 'a' in DMSO [7], it was of interest to learn if zinc(II) monohalide complexes behave similarly to cadmium(II) complexes in methanol. The variation of the stability of ZnF^+ and $ZnCl^+$ with methanol–water composition is shown in Fig. 3. These plots suggest that zinc(II) becomes marginally more 'a' in character when going from water to methanol, which is contrary to what was observed for cadmium(II) species in methanol. This is consistent with the stability trend reported by Doe and coworkers, who found the concentration stability constants for $ZnCl^+$, $ZnBr^+$ and ZnI^+ to be 757, 218 and 62.9 respectively in methanol at an ionic strength of 0.05 [15, 16]. They have corrected their stability constants for Zn^{2+}–ClO_4^- ion-pairing. Their stability constant for $ZnCl^+$ is in reasonable agreement with our value of 646 ± 49, considering that application of their ion pairing correction would increase our value by about 5%.
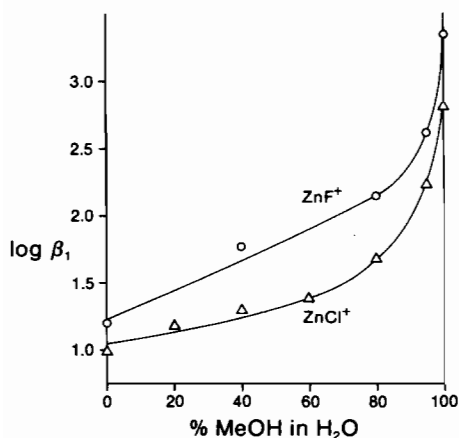
Thermodynamic data for ZnF^+ and $ZnCl^+$ in methanol are included in Table I. The sign and approximate magnitude of ΔH_1 were determined from the temperature variation of β_1. The formation of both complexes are strongly endothermic in methanol, as is the case in DMSO [7]. Thus, the formation of these zinc species in methanol is entropy-controlled. The 'a' stability sequence for these species is entropy-controlled in methanol, as is also the case in water [7, 17]. This is in contrast to the enthalpy-controlled 'a' sequence reported for zinc monohalide species in DMSO [7] and also for the corresponding cadmium species 'b' sequence in methanol (see Table I). A more detailed analysis of the thermodynamic properties of these species must await the availability of accurate calorimetric data.

Stability Studies in Dimethylsulfoxide–Water Mixtures

Ideally, Ahrland's stability sequence in DMSO [7] would be completed by measuring the stability constant of CdF^+ in this solvent. Unfortunately, the response of the fluoride ion-selective electrode in neat DMSO is not sufficiently stable and is distinctly non-Nernstian. Thus it is necessary to resort to mixed solvent studies to obtain useful information. The fluoride ion-selective electrode responds acceptably in DMSO–water mixtures containing up to 75%(v/v) DMSO. Therefore, the stabilities of CdF^+, $CdCl^+$ and $CdBr^+$ have been measured in various DMSO–water mixtures up to 75% DMSO. The results of these studies are shown in Fig. 4. The stabilities of $CdCl^+$ and $CdBr^+$ cross at about 50% DMSO, above which

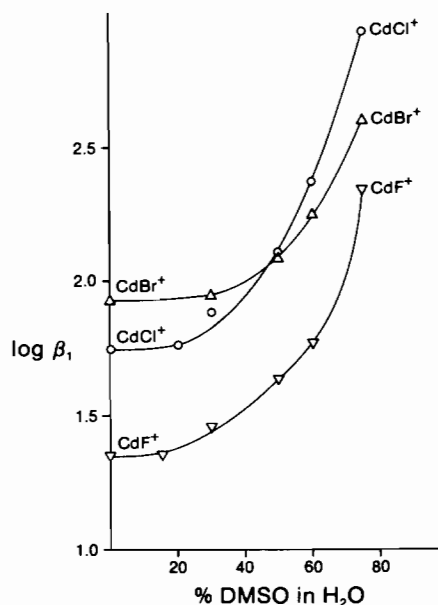Fig. 3. Effect of methanol–water solvent composition upon complex stability at 25 °C: (△) $ZnCl^+$, (○) ZnF^+.

Fig. 4. Effect of DMSO–water solvent composition upon complex stability at 25 °C: (△) $CdBr^+$, (○) $CdCl^+$, (▽) CdF^+.

the $CdCl^+ > CdBr^+$ trend is the same 'a' sequence reported by Ahrland in neat DMSO. It should be noted that the stability of CdF^+ remains distinctly below that for the other two species, giving the anomalous $CdCl^+ > CdBr^+ > CdF^+$ stability sequence in the range between 50 and 75% DMSO. While it is conceivable that the CdF^+ stability constant data could cross both of the other lines at some higher DMSO percentage, no logical extrapolation relating to the curve shapes in Fig. 4 would warrant this assumption. Analogous experiments in DMSO—methanol mixtures gave similar results; the fluoride electrode functioned acceptably up to about 50% DMSO and the $CdBr^+$–$CdCl^+$ stability cross-over occurred at approximately 30% DMSO. The stability constant for CdF^+ seems to be independent of solvent composition from about 30% DMSO up to the 50% DMSO limit and is more than two orders of magnitude below those of the $CdBr^+$ or $CdCl^+$ in these mixtures. These trends strongly suggest the anomalous stability sequence: $CdCl^+ > CdBr^+ > CdF^+$ might persist at much higher fractions of DMSO.

Although the stability sequence cannot be determined in pure DMSO, it is possible that unique solvent effects result in a stability sequence other than the classical 'a' or 'b' sequence described by Ahrland. This is not unreasonable, since the use of the extremely 'hard' fluoride ligand could certainly lead to specific and distinct solvent effects upon complex stability.

Stability Studies in Acetonitrile—Water Mixtures

Based on data obtained in other solvents, it is important to examine classification changes occurring in aprotic solvents other than DMSO. Acetonitrile (AN) represents an important prospective choice, since it is both aprotic and anoxic, but has virtually the same dielectric constant value as methanol. The fluoride ion-selective electrode gives near-Nernstian response in AN—water mixtures up to 92% (v/v) AN which also contain 0.05 M TEAP. Coetzee and Martin similarly report obtaining acceptable fluoride electrode response in AN containing at least 10 mol% water [9].

Stability constants for CdF^+ in AN—water mixtures are given in Table II. Born-like behavior is found up to 80% AN, and in this context these data obey similar trends to that in Fig. 1 for methanol—water mixtures. However, the comparative stability of CdF^+ is much greater in AN—water than in corresponding methanol—water mixtures.

Attempts to obtain corresponding stability information for $CdCl^+$ and $CdBr^+$ in AN—water mixtures have been only marginally successful. It has not been possible to discriminate against the formation of two or more higher complexes, even at the highest metal-to-ligand concentration ratio permitted under our experimental conditions. The experimental repro-

TABLE II. Stability Constants for CdF^+ in Acetonitrile–Water Mixtures Containing 0.05 M TEAP at $25.0 \pm 0.1\,^\circ C$

v/v (%) AN	$\log \beta_1$
0	1.36 ± 0.04
40	1.83 ± 0.03
60	2.23 ± 0.03
80	3.04 ± 0.03
85	3.60 ± 0.09
90	4.77 ± 0.08
92	5.26 ± 0.10

ducibility is not sufficient in these media to permit extraction of β_1 from data obtained in mixtures of more than two complex species. At high cadmium concentrations, visual evidence of surface changes at the silver halide sensor has been observed, leading to electrode failure in extreme cases. Nonetheless, it is clear that maximum values of $f(C)$, and hence for β_1, for $CdCl^+$ and $CdBr^+$ in 92% AN are both significantly lower than β_1 for CdF^+ [18]. Misumi and Aihara have studied the stabilities of cadmium halide (excluding fluoride) complexes in AN having coordination numbers of three and four by polarographic and cadmium amalgam potentiometric methods [19, 20]. They report log stability constants of 29.2, 25.3 and 22.4 for $CdCl_3^-$, $CdBr_3^-$ and CdI_3^- respectively, as well as 34.0, 29.8 and 26.5 for $CdCl_4^{2-}$, $CdBr_4^{2-}$ and CdI_4^{2-} respectively [20]. Unfortunately, solubility limitations preclude the corresponding studies with fluoride. However, these trends, taken together with our observations, strongly suggest that the stability sequence in AN is 'a', in contrast to the questionable sequence seen for systems which contain appreciable DMSO.

Conclusions

The data we have obtained in two protic solvents, methanol and ethanol, clearly show that the stability sequence for Group II-B d^{10} halide complexes are not necessarily less 'b' in solvents less hydrogen bonding than water. Thus, ligand solvation is not the controlling factor in every case. Although zinc(II) seems more 'a' (less 'b') in methanol than in water, cadmium(II) is clearly more 'b' in methanol or ethanol than in water. This difference between zinc-(II) and cadmium(II) is not surprising, considering that their stability sequences are governed by different thermodynamic parameters.

Although current evidence all points to 'a' classification for cadmium(II) halide species in AN, the $CdCl^+ > CdBr^+ > CdF^+$ stability sequence established in DMSO—water and DMSO—methanol raises a question concerning whether a strictly 'a' stability

sequence is, in fact, established by cadmium(II) halide complexes in DMSO. Although experimental limitations preclude a direct answer in the case of DMSO, it is interesting to speculate if there is a fundamental difference in the 'a–b' classification properties for cadmium(II) halide species in protic and aprotic solvents. Corresponding studies with other aprotic solvents are under way in our laboratories.

Acknowledgements

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