Role of Mixed Solvents on the Stabilities of Monoethanolamine Complexes

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Acidity and stability constants of cobalt(II), nickel(II), and copper(II) complexes with monoethanolamine (MEA) were determined at 25 °C in mixed aqueous solutions (1 M ionic strength) of methanol, dioxane, acetonitrile, and dimethylformamide. The stability constants of the metal complexes increase with increasing concentration of the cosolvent in the order methanol < acetonitrile < dimethylformamide < dioxane. The role of solvents is discussed.

Mixed solvents have been found to improve the analytical methods for studying complex reactions and the equilibrium and kinetic mechanisms for inorganic reactions (*1-6*). In a sequel to our studies on enthanolamine complexes (*7-12*), the present work is an effort to study the complex equilibria of Co(II), Ni(II), and Cu(II) with monoethanolamine (MEA) in four organic solvents, methanol (MET), dioxane (DOX), acetonitrile (ACN), and dimethylformamide (DMF), with concentrations ranging from 40% to 100% by volume.

Experimental Section

Acidity and stability constants were determined by using acid-base titration technique. A 10^{-2} M stock solution of the ligand was prepared. A 10^{-2} M NaOH solution was prepared by dissolving AnalaR NaOH Pellets in CO_2-free distilled water and was standardized by using the usual chemical methods of analysis. KCl (0.01 M) was used as a supporting electrolyte.

Stock metal salt solutions (0.1 M) were prepared. The exact concentrations were determined by direct complexometric titration with EDTA (*13*). More dilute solutions were prepared by appropriate dilution of the stock.

BDH spectroscopic-quality solvents (methanol, dimethylformamide, dioxane, and acetonitrile) were used. Their purities were checked by the convential methods (*14*).

A Radiometer 28 pH meter was employed for recording the pH with a sensitivity of ±0.01 pH. The instrument was calibrated before and after each titration against two buffers (*15*), one in the acid range of potassium hydrogen phthalate (pH 4.01) and one with a borate buffer in the alkaline range (pH 9.14). When the electrodes were not in use, the bulbs of the electrodes were kept immersed in solvent mixtures with compositions comparable to those used for this study. The electrodes behaved reversibly in the media under study where the pH titration curve of HCl in aqueous medium was nearly identical with the curves obtained in other solvents below pH 9. All measurements were done at 25 ± 0.1 °C.

Results and Discussion

The standard state for hydrogen-ion activity in water is the basis for constructing a scale of acidity in aqueous or mixed solvents (*16*). This has been applied to glycine and ethylenediamine complexes (*17*). The hydrogen-ion activity was measured with a pH meter. The following relation applies:

$$\mathrm{pH}_{\mathrm{cor}} = -\log\,[\mathrm{H}^+] = B + \log U_{\mathrm{H}}$$

where B is the pH meter reading. $\log U_{\mathrm{H}}$ is a correction factor which accounts for the residual liquid junction potential and the medium effects at a given solvent composition and at a fixed temperature and any ionic strength.

All acidity and other equilibrium constants were calculated as concentration functions (*18-22*).

From the pH titration experiments for the ligand alone (and by calculating the average number of protons associated with the ligand ($\bar{n}_A$)) and for its metal complexes (and by calculating the average number associated with the metal ($\bar{n}$) and the free-ligand concentration (pL)) (*23*), we calculated the acidity and stability constants, respectively. The interesting results are collected in Table I. The medium plays a major role in controlling the mechanism of dissociation for the systems under investigation (*24*). It has been reported that the dissociation of -COOH in glycine increases nearly linearly with increasing concentration of the cosolvent while the dissociation of the substituted-ammonium hydrogen is nonlinear and, in most cases, passes through a maximum (minimum pK_a) at some solvent composition (*17*). The variation in pK_1 for glycine with solvent composition, as with carboxylic acids in general, can be explained by an electrostatic model based on the Born equation (*25*). The cationic acids of ethylenediamine failed to follow this model, where both the solvent and the dielectric effects control their behavior. The former is assumed to be greater in acids involving $=\!NH^+$ dissociation (*26*). The nonelectrostatic contribution to the change in pK_a has been regarded as representing the sum of medium effects for individual ions (*4*). For the monoethanolamine ligand, as the percentage of the cosolvent increases in the four solvents used (Table I), the pK_a increases. Also, the pK_a values of the ligand at a particular solvent composition follow the order dioxane > dimethylformamide > acetonitrile > methanol. On complexation with any one of the selected transition-metal ions for this study—Co(II), Ni(II), and Cu(II)—a large decrease in pK values is apparent (Table I). This leads one to assume that these solvents help the mechanism of complexation. The profile of polarity order for the complex compounds showed a parallelism to that of the free ligand. The order for the dielectric constants of the solvents, DMF (41) > CH_3CN (37.5) > CH_3OH (32.6) > dioxane (2) does not exactly follow the order for the relative solvent effects as noted above. The relative solvent effect in increasing the stability constants of the "cosolvo" metal complexes follows the order dioxane > dimethylformamide > acetonitrile > methanol. Collected data on empirical solvent parameters from physical and chemical measurements on pure nonaqueous solvents have made it possible to establish the following polarity order: water > methanol > acetonitrile > dimethylformamide > dioxane (*27*, *28*). The autoprotolysis constant, K_s, of the solvent is a measure of the absolute scale of acidity of solvents, where its greater value means the solvent is less ionized with smaller solvent capacity. The magnitudes of K_s follow closely the polarity order with interchange of positions of acetonitrile and dimethylformamide (*29*). The apparent increase in stability of the complex in an aqueous mixed solvent compared to that in water alone could be related to the lower concentration of water in the mixed solvent compared to that in pure water. Thus, the solvation of the reacting species is controlled by water and the cosolvent molecules. The water molecules are preferentially solvated in mixed solvents, and

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Table I. Dissociation Constant of Monoethanolamine and Stability Constants of Metal Complexes in Mixed Aqueous Organic Solvents at 25 °C in the Presence of 0.1 M KCl As a Supporting Electrolyte

	methanol				dioxane				acetonitrile				dimethylformamide			
compd	40%	60%	80%	100%	40%	60%	80%	100%	40%	60%	80%	100%	40%	60%	80%	100%
MEA	10.05	10.4	10.5	10.6	10.7	11.0	11.3	11.5	10.3	10.7	10.9	11.2	10.4	10.8	11.0	11.3
Co(II) complex	4.72	5.01	5.34	5.93	7.3	7.5	7.7	8.1	6.0	6.2	6.35	6.35	6.3	6.5	6.6	8.82
Ni(II) complex	4.65	4.93	5.522	6.05	7.1	7.3	7.3	7.9	6.2	6.4	6.5	6.7	6.5	6.56	6.82	6.9
Cu(II) complex	4.83	5.22	5.82	6.25	7.0	7.2	7.5	7.9	5.8	5.95	6.2	6.5	6.1	6.32	6.4	6.6

Table II. Slopes of pK vs. Solvent Composition (%)

	slope			
system	dioxane	dimethylformamide	acetonitrile	methanol
MEA	1.25	1.50	1.40	
Co-MEA	1.33	1.25	1.25	
Ni-MEA	1.30	0.85	0.80	2.22
Cu-MEA	1.65	0.83	1.20	2.57

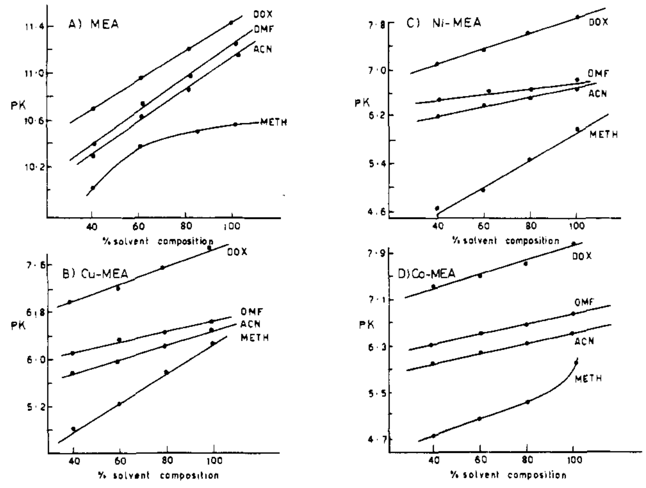

Figure 1. pK vs. solvent composition (%).

methanol molecules are capable of appreciable solvation from aqueous methanol solutions (*30*). The relationship between pK and the solvent composition (Figure 1) was tested in all of the systems; linear plots were obtained for all of the metal complexes, but poorer linearity was noticed in the presence of methanol for the MEA (Figure 1A) and cobalt-MEA (Figure 1D) systems. The values for the slopes of the best-fit lines for the metal-complex systems could be arranged in the following order: methanol > dioxane > acetonitrile > dimethylformamide (Table II). This trend was not valid for the free MEA ligand, where the order proceeds in the following order: dimethylformamide > acetonitrile > dioxane. The maximum slopes in the foregoing correlation were found to be 2.57 and 2.22 in Cu-MEA and Ni-MEA, respectively, in the presence of aqueous methanol. Thus, the transfer of the cosolvent plays a major part in such a mechanism. Assume that the J factor representing a solvent transfer number characteristic of the tested chemical reaction or part of it can be attributed to the transfer of the cosolvent. The following relation was tested in our systems (*17*):

$$(J \log [S] + \log K) = -\Delta G/(2.3RT) - W \log ([H_2O]_s/[S] + J \log [H_2O])$$

where [S] represents the concentration of the solvent. This equation possesses two unknown parameters, J and W. Trial values of J = 2, 3, and 4 are used to find the values of W. Let (J log [S] + log K) = Y and log $[H_2O]_s/[S]$ = X. On plotting Y vs. X for the systems under investigation (Figures 2–5), one may make some valuable conclusions. The values of W are assigned to the gradients of Y vs. X. This relationship was

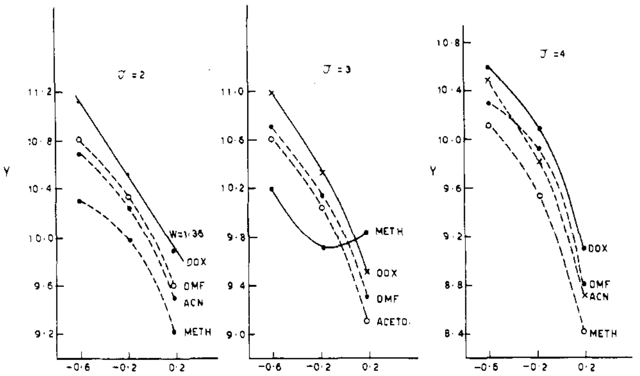

Figure 2. X–Y relationship for monoethanolamine ligand.

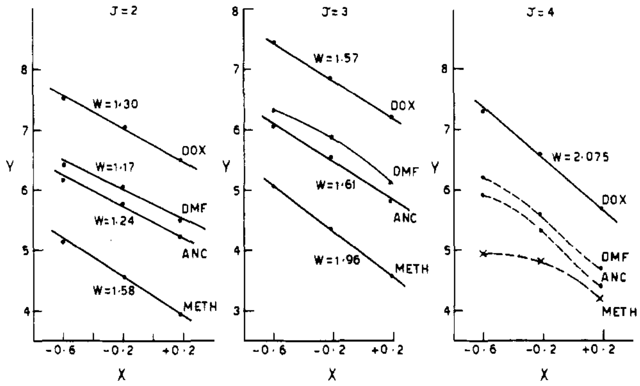

Figure 3. X–Y relationship for cobalt-monoethanolamine complex.

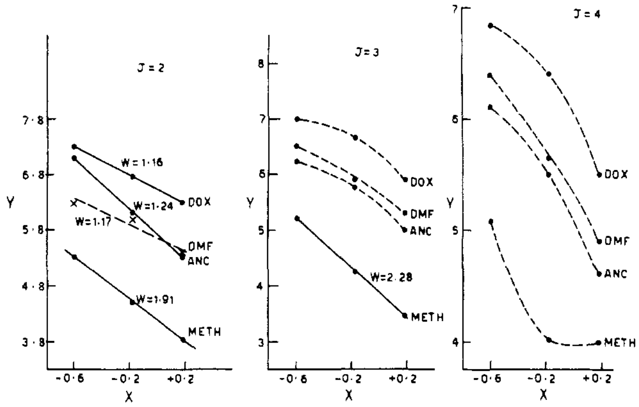

Figure 4. X–Y relationship for nickel-monoethanolamine complex.

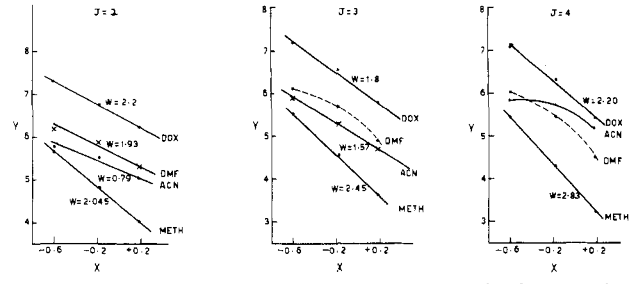

Figure 5. X–Y relationship for copper-monoethanolamine complex.

verified for the free MEA ligand in the presence of dioxane only with the $j = 2$ and with a slope of 1.36 (Figure 2). Best-fit straight lines were obtained for the Co–MEA (Figure 3), Ni–MEA (Figure 3), Ni–MEA (Figure 4), and Cu–MEA (Figure 5) systems in the four solvents used in this study for $j = 2$, with slopes ranging from 0.79 to 2.20. The trial with $j = 3$ gave straight lines for Co–MEA and Cu–MEA in the presence of methanol, dioxane and acetonitrile solvents, but with slopes approaching 2. This confirms that the best results were obtained in most of these systems for $j = 2$. Therefore, solvation by the cosolvent can be assumed to be of major importance. This is readily apparent when the variation between W and j is large. However, it is obvious that, when $W \approx j$, solvation by the cosolvent is of minor importance. The W values obtained are calculated and written on the linear plots in the figures. In summary, the ΔG values for these systems were found to be dependent on the solvent composition (except for Ni–MEA in the presence of methanol, where the ΔG value amounts to 0.929 ± 0.005 kcal/mol). In general, these values decreased with increasing solvent concentration.

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Osmotic and Activity Coefficients of Methyl-Substituted Ammonium Perchlorates at 298.15 K

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Osmotic and activity coefficient data are reported for three methyl-substituted ammonium perchlorates. New data to replace the literature values of the coefficients of ammonium perchlorate are also included. A comparison of the coefficients of the various members of the family illustrates the effect of successive methyl substitution on ion–solvent and ion–ion interactions.

Osmotic and activity coefficient data have been reported for ammonium perchlorate (*1*). Tetramethylammonium perchlorate is soluble to the extent of less than 0.1 *m*, and there have been no colligative property data reported for the other methyl-substituted members of the family. I have recently reported (*2*, *3*) activity coefficients of the methyl-substituted ammonium chlorides and nitrates, and these data should be useful for comparisons of the contributions of the anions to the various ion–ion and ion–solvent interactions.

Method

Aqueous solutions of the free amine bases, as received from Aldrich Chemical Co. or Eastman Kodak Co., were almost neutralized with aqueous perchloric acid. The water and the excess base from each of the solutions were removed by drying in a vacuum desiccator over concentrated sulfuric acid. The dried salts were recrystallized several times from methanol–ether solution and were again dried in the same manner. They were then stored, under vacuum, over P_2O_5. The salts were found to contain no water of hydration, and the molecular weights as determined by ion exchange (*3*) agreed with those calculated for the anhydrous salts within 0.1–0.2%. Certified ammonium perchlorate was used as received from Fisher Scientific Co.

The isopiestic equilibration of solutions, using sodium chloride as the reference solution, was carried out in the usual manner. Complete details of the experimental procedure have been previously reported (*4*).

Results and Discussion

The isopiestic solutions of sodium chloride and the perchlorate salts are listed in Table I. The osmotic and activity coefficients ar rounded concentrations are given in Table II. The osmotic coefficients were calculated from the molality ratios by the relation

$$\phi = (m_{\text{ref}}/m)\phi_{\text{ref}}$$

Activity coefficients were calculated from the equation (*5*)

$$\ln \gamma = \ln \gamma_{\text{ref}} + \ln R + 2\int_0^{m_{\text{ref}}} (R - 1)\, d \ln (m_{\text{ref}}\gamma_{\text{ref}})^{1/2}$$

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