



Potentiometric And Thermodynamic Studies Of The Protonation Equilibria And Metal Ions Complexation Of Some Zwitterionic Buffers In NaNO_3 Solutions In Water And In Mixtures Of Water And Dioxane



Corresponding Author

Mohamed Taha
Department of Chemistry, Faculty of Science,
Cairo University, Beni-Suef Branch, Beni-Suef,
(EGYPT)

Received: 1st November, 2006

Accepted: 16th November, 2006

Web Publication Date : 25th February, 2007



Co-Authors

Alaa T.Ahmed¹, Shad A.Saqr², Sawsan A.Mohamed²

¹Geochemistry department, Faculty of Science, Al-Azhar University,
Nasr City, Cairo, (EGYPT)

²Arabian Safety & Industrial security Center, Industrial Estate-Makkah
Al-Mukaramah, Jeddah, (KSA)

ABSTRACT

The protonation equilibria for some selected zwitterionic buffers in solutions have been studied pH-potentiometrically. The second stage dissociation constants (pK_{a2}) of zwitterionic buffers and the thermodynamic quantities (ΔG , ΔH , and ΔS) have been derived at different temperatures in water at ionic strength $I=0.1 \text{ mol}\cdot\text{dm}^{-3} \text{NaNO}_3$ and in the presence of 10%, 30%, and 50%(w/w) dioxane. Titrations were also carried out in water ionic strengths of (0.15, 0.20, and 0.25) $\text{mol}\cdot\text{dm}^{-3} \text{NaNO}_3$. The interactions between the zwitterionic buffers with some metal ions were also studied at different temperatures and in the presence of 10%, 30%, and 50%(w/w) dioxane by using potentiometry. The thermodynamic stability constants were calculated as well as the thermodynamic quantities for the 1:1 binary complexation. © 2007 Trade Science Inc. -

INDIA

KEYWORDS

Binary complexes;
Thermodynamics;
Zwitterionic buffers;
Potentiometric studies;
Stability constant.

INTRODUCTION

Hydrogen ion buffers are required for many different types of in vitro biological and chemical studies.

Over the years a variety of buffers that are suitable for biological systems have been developed.

Some of the criteria used for these buffers have included good solubility in water, low ion effect, low absorbance of light at visible or ultraviolet wave lengths, good stability and high purity^[1]. These characteristics were important in the development of a series of zwitterionic, amino-containing, and sulfonic acid buffers by Good et al. in 1966^[1]. Since then

many new buffers for biological reactions that met most of the criteria described above were developed and tested^[2-4].

Studies involving metal ions in solution, which require pH control, are inevitably subject to the possibility of buffer interferences as a result of complexation. In generating a series of more than 20 buffers for use in biological studies, Good and co-workers¹ listed the prevention of metal complexation as one of their desired goals. Good's buffers (often called 'Good' buffers) are presently used routinely in biochemical and speciation studies under the assumption that they undergo little if any interaction with biologically (or environmentally) important metal ions. However, there has been an increase in reports on buffer interferences when most of Good's buffers were used in the presence of metal ions^[1,5,6]. Many conflicting data and conclusions that were reported by investigators studying identical metal-cation protein systems (at the same pH in carefully executed experiments) might be due in part to the failure to include the presence of metal-buffer complexes. These compounds (Good's buffers) contain hydroxyl groups in addition to a primary nitrogen donor atom. Therefore, one might expect that metal complexes of these buffers would form in biochemical/environmental systems containing metal ions when these compounds are used to control pH.

The complexation of some divalent metal ions with various zwitterionic buffers (2-actamido)-2-aminoethanesulfonic acid (ACES), 3-(N-morpholino) propanesulfonic acid (MOPS), 3-[N-bis (2-hydroxyethyl) amino] 2-hydroxy propane sulfonic acid (DIPSO), 3-(N-tris[hydroxymethyl]methyl amine)-2-hydroxypropanesulfonic acid (TAPSO), N-(2-hydroxyethyl) piperazine-N'-hydroxypropanesulfonic acid (HEPPSO) and 3-[(1,1-dimethyl-2-hydroxyethyl) amino]-2-hydroxy propane sulfonic acid (AMPSO) in aqueous solution at 298.1 K and ionic strength $I=0.1 \text{ mol dm}^{-3} \text{ KNO}_3$ has been studied^[7-12] using the potentiometric technique.

In this work, we report second stage dissociation constants (pK_{a2}) of zwitterionic buffers as well as the stability constants of the binary (1:1) complexes of Cu^{II} , Ni^{II} , Co^{II} , Zn^{II} , Mn^{II} , Mg^{II} , and Ca^{II} metal ions with the zwitterionic buffers described above (ACES,

MOPS, DIPSO, TAPSO, HEPPSO, and AMPSO) in aqueous solution and in the presence of 10 %, 30%, and 50 % (w/w) dioxane at different temperature (298.15 to 328.15) K at ionic strength $I=0.1 \text{ mol} \cdot \text{dm}^{-3} \text{ NaNO}_3$. Also, the second dissociation constants of the zwitterionic buffers has been studied at different ionic strengths (0.15, 0.20, 0.25) $\text{mol} \cdot \text{dm}^{-3} \text{ NaNO}_3$, and at temperature 298.1 K. The present investigation is an extension of our earlier work on solution studies on the biological buffers^[13-18].

EXPERIMENTAL

Materials and solutions

The complexation of some divalent metal ions with various zwitterionic buffers (2-actamido)-2-aminoethanesulfonic acid (ACES), 3-(N-morpholino) propanesulfonic acid (MOPS), 3-[N-bis (2-hydroxyethyl) amino] 2-hydroxy propane sulfonic acid (DIPSO), 3-(N-tris[hydroxymethyl]methyl amine)-2-hydroxypropanesulfonic acid (TAPSO), N-(2-hydroxyethyl) piperazine-N'-hydroxypropanesulfonic acid (HEPPSO) and 3-[(1,1-dimethyl-2-hydroxyethyl) amino]-2-hydroxy propane sulfonic acid (AMPSO) were sigma products. The metal salts were provided by BDH as nitrates or chlorides. Stock solutions of the metal salts were prepared in deionized water, and the metal concentration was obtained by standard analytical methods^[19]. A carbonate-free sodium hydroxide (titrant, prepared in $0.1 \text{ mol dm}^{-3} \text{ NaNO}_3$ solution) was standardized potentiometrically with KH phthalate (Merck AG). A nitric acid solution ($\approx 0.03 \text{ mol dm}^{-3}$) was prepared and used after standardization. Sodium hydroxide, nitric acid, and sodium nitrate were from Merck p.a.

Apparatus

For the potentiometric pH titrations, an automatic titration set (SM 702 Metrohm) including a 665 dosimat autoburette, an Orin 710 A precision digital pH-meter and IBM-compatible personal computer were used.

Calibration of a glass electrode cell

A computer program (GLEE, glass electrode evaluation)^[24] has been used for the calibration of a glass electrode by means of a strong acid-strong base

Full Paper

titration. This program provides an estimate of the carbonate contamination of the base, the pseudo-Nernstian standard potential and slope of the electrode, and, optionally, the concentration of the base and pK_w .

Procedure for equilibrium titration

The following solutions were prepared (total volume 50 cm^3) and titrated potentiometrically against a standard CO_2 -free NaOH (0.10 mol dm^{-3}): $0.003 \text{ mol dm}^{-3} \text{ HNO}_3 + 0.1 \text{ mol dm}^{-3} \text{ NaNO}_3$ (a), solution a + $0.001 \text{ mol dm}^{-3}$ zwitterionic buffers (b), solution b + $0.0004 \text{ mol dm}^{-3} \text{ M}^{\text{II}}$ (c). Each solution was thermo-stated at the required temperature with accuracy of $(\pm 0.1)^\circ\text{C}$, where the solutions were left to stand for about 15 min before titration. A magnetic stirrer was used during all titrations. The pH-metric titrations were carried out at the desired temperature in a purified nitrogen atmosphere. The titration was repeated at least four times for each buffer and metal ion. At the experimental pH values used in the calculation in this work, the interfering effects of hydroxyl complexes are negligible. The initial estimates of the protonation constants and the stability constants of the binary formed in solution have been determined using the Irving and Rossotti formula^[21,22]. Initial estimates of the protonation constants and the stability constants of the binary complexes formed in solution have been refined with the Clinp 2.1 computer program^[23,24]. Standard deviations were also evaluated for the corresponding equilibrium constants.

The pH-meter readings have been corrected in accordance with the method described by Douheret^[25,26]. This was carried out to account for the difference in acidity, basicity, permittivity, and ion activity in partially aqueous solutions relative to the pure dioxane.

In a typical experiment, a sample volume of 50 cm^3 containing $0.003 \text{ mol dm}^{-3} \text{ HNO}_3$ in the presence of 10, 30, and 50% (w/w) of dioxane (a), $0.003 \text{ mol dm}^{-3} \text{ HNO}_3 + 0.001 \text{ mol dm}^{-3}$ zwitterionic buffers in the presence of 10, 30, and 50% (w/w) of dioxane (b), $0.003 \text{ mol dm}^{-3} \text{ HNO}_3 + 0.001 \text{ mol dm}^{-3}$ zwitterionic buffers + $0.0004 \text{ mol dm}^{-3} \text{ M}^{\text{II}}$ in the presence of 10, 30, and 50% (w/w) of dioxane (c). The ionic strength of the studied solutions was adjusted at 0.10

mol dm^{-3} using a NaNO_3 solution and titrated individually against $0.10 \text{ mol dm}^{-3} \text{ NaOH}$, prepared in the ionic medium used for the test solution.

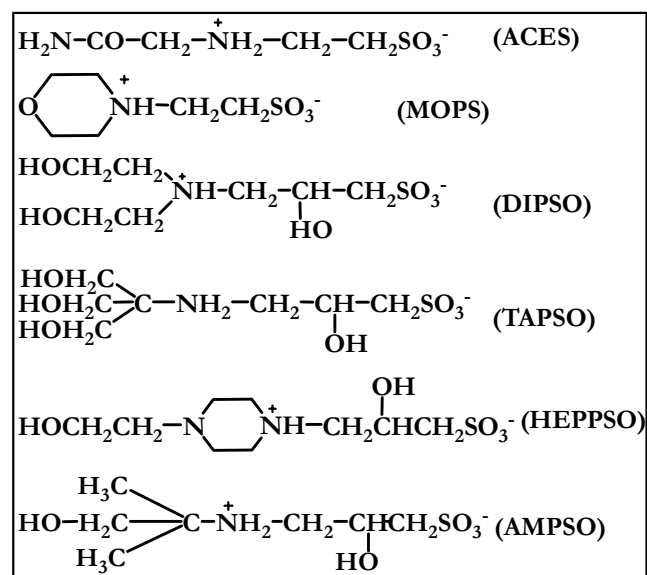
The free energy change ΔG can be calculated from the equation:

$$\Delta G = -RT \ln K \quad (1)$$

Similar to the potentiometric studies, the DH can be determined by using temperature dependence method ($\Delta G = \Delta H - T \Delta S$). In this case, ΔH can be calculated from the straight line slope obtained by plotting $\log K$ against the reciprocal of absolute temperature ($1/T$).

RESULTS AND DISCUSSION

The zwitterionic structures of the ampholytes ACES, MOPS, DIPSO, TAPSO, HEPPSO, and AMPSO are:



The first protonation constant (pK_{a1}) is due to the sulfonic group, the second one is related to a proton on the amino group (pK_{a2}). It was not possible to determine the exact value of pK_{a1} potentiometrically under the present experimental conditions because of the highly acidic nature of the associated proton. The values of the pK_{a2} determined at $(298.15 \pm 0.1) \text{ K}$ and $I = 0.1 \text{ mol dm}^{-3} \text{ NaNO}_3$ for ACES ($pK_{a2} = 6.78 \pm 0.02$), MOPS ($pK_{a2} = 7.20 \pm 0.02$), DIPSO ($pK_{a2} = 7.37 \pm 0.03$), TAPSO ($pK_{a2} = 7.62 \pm 0.02$), HEPPSO ($pK_{a2} = 8.04 \pm 0.06$), and AMPSO ($pK_{a2} = 9.01 \pm 0.02$) were compared with those of other workers in aqueous medium^[2,27,28] and show that the maxi-

imum deviation never exceeds than 0.2 units. Such deviations between the results obtained by different physical methods are not unusual; examples are plentiful in the literature^[28].

To the author's knowledge, no data have been published for dissociation constants of zwitterionic buffers for ACES, MOPS, DIPSO, TAPSO, HEPPSO, and AMPPO in the presence of different ratios of dioxane at different temperatures. The observed increase in pKa2 of the zwitterionic buffer as the medium is enriched in the aprotic nonionizing dioxane solvent may be attributed to the fact that the release of the proton is rendered more difficult in the presence of this co-solvent.

As can be seen from TABLE 1, the slight increase in the value of ΔG (TABLE 1)in going from+10

to+50 wt % dioxane could possibly be explained by the decrease in the dielectric constant of the mixed solvent, which could then cause a resulting increase in the electrostatic free energies of the various ions in solutions produced by the dissociation process. The values of ΔH decrease with the increasing organic content of the solvent mixture, suggesting that the second dissociation process is becoming increasingly exothermic. The similarity between ΔH values of the dissociation processes of zwitterionic buffers in water and(water+dioxane) indicates similar pattern of solvation in this media. The values of ΔS are expected to be negative in these solvents but in(water+ dioxane) they are more negative. This may be due to the fact that the degree of reorientation and partial immobilization of the dioxane and water

TABLE 1: Second dissociation(pKa2) for the dissociation process of zwitterionic buffers in 0.1 mol·dm⁻³ NaNO₃ solution in water and(Water+Dioxane) mixtures at different temperatures and the thermodynamic quantities

Zwitterionic buffers	% w/w Dioxane	T/K				ΔG	ΔH	$-\Delta S$
		298.1	310.1	318.1	328.1	kJ· mol ⁻¹	kJ· mol ⁻¹	J· mol ⁻¹ · K ⁻¹
ACES	0	6.78 ± 0.02	6.74 ± 0.04	6.71 ± 0.06	6.67 ± 0.03	38.70 ± 0.02	6.49 ± 0.11	108.04 ± 0.09
	10	6.82 ± 0.06	6.78 ± 0.03	6.76 ± 0.04	6.72 ± 0.06	38.93 ± 0.03	6.01 ± 0.08	110.41 ± 0.08
	30	6.90 ± 0.02	6.85 ± 0.02	6.83 ± 0.03	6.80 ± 0.02	39.38 ± 0.04	5.93 ± 0.12	112.12 ± 0.07
	50	6.96 ± 0.02	6.92 ± 0.04	6.90 ± 0.04	6.86 ± 0.03	39.73 ± 0.04	5.64 ± 0.10	114.29 ± 0.13
MOPS	0	7.20 ± 0.02	7.17 ± 0.02	7.13 ± 0.04	6.98 ± 0.04	41.10 ± 0.02	14.28 ± 0.11	90.08 ± 0.08
	10	7.29 ± 0.03	7.26 ± 0.02	7.22 ± 0.02	7.07 ± 0.03	41.61 ± 0.04	13.42 ± 0.09	94.73 ± 0.11
	30	7.35 ± 0.02	7.32 ± 0.04	7.28 ± 0.04	7.13 ± 0.02	41.95 ± 0.03	13.36 ± 0.08	96.22 ± 0.09
	50	7.43 ± 0.03	7.40 ± 0.02	7.36 ± 0.03	7.21 ± 0.02	42.41 ± 0.04	13.17 ± 0.12	98.31 ± 0.09
DIPSO	0	7.37 ± 0.03	7.34 ± 0.02	7.27 ± 0.02	7.23 ± 0.02	42.07 ± 0.02	9.42 ± 0.11	109.63 ± 0.07
	10	7.46 ± 0.02	7.40 ± 0.03	7.36 ± 0.03	7.31 ± 0.03	42.56 ± 0.03	9.26 ± 0.08	110.69 ± 0.09
	30	7.52 ± 0.02	7.47 ± 0.02	7.40 ± 0.02	7.38 ± 0.05	42.91 ± 0.03	9.14 ± 0.09	113.25 ± 0.07
	50	7.57 ± 0.03	7.52 ± 0.06	7.47 ± 0.03	7.45 ± 0.02	43.18 ± 0.02	7.63 ± 0.07	119.19 ± 0.11
TAPSO	0	7.62 ± 0.02	7.57 ± 0.03	7.53 ± 0.03	7.39 ± 0.04	43.49 ± 0.02	11.37 ± 0.11	107.72 ± 0.13
	10	7.71 ± 0.03	7.66 ± 0.04	7.63 ± 0.04	7.54 ± 0.03	44.01 ± 0.02	10.52 ± 0.09	112.47 ± 0.09
	30	7.84 ± 0.03	7.79 ± 0.03	7.76 ± 0.02	7.68 ± 0.04	44.75 ± 0.03	10.15 ± 0.09	116.18 ± 0.07
	50	7.95 ± 0.02	7.90 ± 0.04	7.86 ± 0.02	7.78 ± 0.02	45.38 ± 0.03	10.02 ± 0.12	118.57 ± 0.08
HEPPSO	0	8.04 ± 0.06	8.00 ± 0.03	7.93 ± 0.02	7.83 ± 0.02	45.89 ± 0.03	13.11 ± 0.09	110.25 ± 0.09
	10	8.12 ± 0.03	8.08 ± 0.04	8.01 ± 0.04	7.91 ± 0.04	46.35 ± 0.02	12.95 ± 0.13	112.32 ± 0.07
	30	8.26 ± 0.04	8.22 ± 0.02	8.15 ± 0.03	8.05 ± 0.03	47.15 ± 0.02	12.62 ± 0.09	116.00 ± 0.09
	50	8.41 ± 0.02	8.37 ± 0.03	8.30 ± 0.02	8.20 ± 0.04	48.00 ± 0.04	12.31 ± 0.11	119.88 ± 0.10
AMPPO	0	9.01 ± 0.02	8.93 ± 0.03	8.88 ± 0.02	8.83 ± 0.05	51.43 ± 0.03	11.27 ± 0.09	134.59 ± 0.08
	10	9.08 ± 0.03	8.98 ± 0.03	8.95 ± 0.05	8.90 ± 0.03	51.83 ± 0.04	10.97 ± 0.13	136.79 ± 0.09
	30	9.13 ± 0.05	9.05 ± 0.02	9.00 ± 0.03	8.97 ± 0.04	52.11 ± 0.02	10.18 ± 0.09	140.49 ± 0.08
	50	9.21 ± 0.02	9.14 ± 0.03	9.10 ± 0.03	9.05 ± 0.02	52.57 ± 0.03	10.00 ± 0.09	142.72 ± 0.12

Full Paper

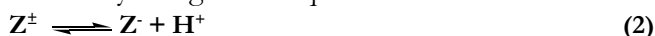
TABLE 2: Second dissociation constants(pKa2) for the dissociation process of zwitterionic buffers at different ionic strength(NaNO₃) and (298.1 ± 0.1) K

Zwitterionic buffers	Ionic strengths/mol.dm ⁻³			
	0.10	0.15	0.20	0.25
ACES	6.78 ± 0.02	6.74 ± 0.02	6.69 ± 0.02	6.64 ± 0.02
MOPS	7.20 ± 0.02	7.17 ± 0.03	7.13 ± 0.04	7.01 ± 0.03
DIPSO	7.37 ± 0.03	7.35 ± 0.02	7.31 ± 0.03	7.27 ± 0.04
TAPSO	7.62 ± 0.02	7.58 ± 0.02	7.56 ± 0.04	7.51 ± 0.03
HEPPSO	8.04 ± 0.06	8.01 ± 0.04	7.97 ± 0.02	7.92 ± 0.04
AMPSO	9.01 ± 0.02	8.94 ± 0.03	8.91 ± 0.02	7.86 ± 0.03

TABLE 3: The stability constant of binary systems(log K₁) at different temperatures and 0.1 mol.dm⁻³ NaNO₃

Zwitterionic buffers	T/K	Metal ions						
		Cu ^{II}	Ni ^{II}	Co ^{II}	Zn ^{II}	Mn ^{II}	Mg ^{II}	Ca ^{II}
ACES	298.1	4.72 ± 0.03	3.61 ± 0.02	3.49 ± 0.03	3.78 ± 0.06	3.71 ± 0.02	3.31 ± 0.02	3.25 ± 0.03
	310.1	4.67 ± 0.02	3.60 ± 0.02	3.44 ± 0.05	3.73 ± 0.06	3.66 ± 0.03	3.26 ± 0.03	3.20 ± 0.03
	318.1	4.63 ± 0.02	3.53 ± 0.04	3.40 ± 0.03	3.64 ± 0.03	3.58 ± 0.05	3.22 ± 0.02	3.16
	328.1	4.49 ± 0.05	3.44 ± 0.02	3.33 ± 0.02	3.59 ± 0.03	3.54 ± 0.06	3.16 ± 0.03	3.10
MOPS	298.1	4.01 ± 0.02	3.31 ± 0.03	3.27 ± 0.04	3.38 ± 0.04	--	3.42 ± 0.02	--
	310.1	3.94 ± 0.05	3.26 ± 0.04	3.21 ± 0.04	3.30 ± 0.03	--	3.36 ± 0.02	--
	318.1	3.87 ± 0.02	3.20 ± 0.04	3.12 ± 0.03	3.27 ± 0.02	--	3.29 ± 0.02	--
	328.1	3.78 ± 0.03	3.09 ± 0.03	3.06 ± 0.02	3.15 ± 0.02	--	3.19 ± 0.02	--
DIPSO	298.1	4.92 ± 0.03	3.71 ± 0.02	3.54 ± 0.06	3.76 ± 0.06	3.48 ± 0.03	3.32 ± 0.03	3.26 ± 0.02
	310.1	4.89 ± 0.04	3.62 ± 0.05	3.49 ± 0.03	3.73 ± 0.06	3.43 ± 0.04	3.29 ± 0.04	3.23 ± 0.02
	318.1	4.79 ± 0.03	3.57 ± 0.02	3.43 ± 0.06	3.65 ± 0.04	3.37 ± 0.02	3.22 ± 0.03	3.14 ± 0.03
	328.1	4.64 ± 0.02	3.44 ± 0.04	3.28 ± 0.03	3.49 ± 0.04	3.23 ± 0.03	3.11 ± 0.04	3.06 ± 0.04
TAPSO	298.1	4.47 ± 0.05	3.65 ± 0.02	3.38 ± 0.04	3.52 ± 0.04	3.68 ± 0.04	3.24 ± 0.03	3.41 ± 0.02
	310.1	4.42 ± 0.02	3.57 ± 0.02	3.33 ± 0.04	3.47 ± 0.03	3.60 ± 0.02	3.19 ± 0.03	3.36 ± 0.03
	318.1	4.35 ± 0.03	3.52 ± 0.04	3.27 ± 0.02	3.41 ± 0.03	3.57 ± 0.03	3.15 ± 0.04	3.30 ± 0.02
	328.1	4.24 ± 0.02	3.42 ± 0.02	3.18 ± 0.02	3.31 ± 0.03	3.44 ± 0.03	3.04 ± 0.02	3.20 ± 0.03
HEPPSO	298.1	5.04 ± 0.05	3.47 ± 0.02	3.38 ± 0.04	4.01 ± 0.03	--	3.52 ± 0.03	--
	310.1	5.00 ± 0.02	3.38 ± 0.04	3.34 ± 0.02	3.91 ± 0.02	--	3.46 ± 0.04	--
	318.1	4.87 ± 0.05	3.35 ± 0.03	3.23 ± 0.03	3.87 ± 0.03	--	3.40 ± 0.02	--
	328.1	4.80 ± 0.03	3.23 ± 0.04	3.17 ± 0.04	3.76 ± 0.03	--	3.29 ± 0.02	--
AMPSO	298.1	5.30 ± 0.04	3.58 ± 0.03	3.42 ± 0.02	4.30 ± 0.04	--	--	--
	310.1	5.20 ± 0.02	3.44 ± 0.02	3.38 ± 0.03	4.26 ± 0.04	--	--	--
	318.1	5.19 ± 0.06	3.47 ± 0.04	3.26 ± 0.06	4.19 ± 0.03	--	--	--
	328.1	5.03 ± 0.03	3.33 ± 0.03	3.22 ± 0.05	4.05 ± 0.02	--	--	--

molecules by Z[±], Z⁻ and H⁺ ions are greater in (water + dioxane) than in pure water, the (acid+base) equilibrium of the zwitter ions form buffer can be represented by the general equation:



The dissociation constant of zwitterionic buffers studied were determined at different ionic

strengths of I=(0.1, 0.15, 0.20, and 0.25) mol.dm⁻³ NaNO₃ and are listed in TABLE 2. The linear square-root dependence is observed according to the Debye-Huckel or Davies equations.

In the binary systems metal-zwitterionic buffers(1:1) have been titrated. It has been observed that when an equivalent amount of metal to chelating

agent is titrated, 1:1 chelate is formed with Cu^{II} , Ni^{II} , Co^{II} , Zn^{II} , Mn^{II} , Mg^{II} , and Ca^{II} metal ions by displacement of one proton from the amino group of the chelating agent. In all cases no calculations have been performed beyond the precipitation point; hence, the hydroxy species likely to be formed at this point could not be studied. Generally, it is observed that the binary metal complexes of zwitterionic buffers begin to form in the pH range of 3.2-6.8.

It was noted that values of the stability constants decrease with increasing temperature of the medium in accord with the results of Pitzer^[29]. The $\log K_1$ values at different temperatures ($I=0.1 \text{ mol dm}^{-3} \text{ NaNO}_3$) are given in TABLE 3.

The overall free energy change is reported in TABLE 4. The negative free energy change (ΔG) in each case indicates that the chelation is spontaneous; furthermore, ΔG becomes more negative with decrease in temperature indicating an increase in the extent of complex formation at lower temperatures. The enthalpy changes are exothermic. The change in entropy upon complexation is related both to changes in the number of particles in the system and to changes in the mode of vibration of particles in the system.

Considering that it is by now well established that the 'effective' or 'equivalent solution' dielectric constants in proteins or active site cavities of enzymes are reduced compared to that in bulk water, i.e., that activity of water is decreased due to the presence of aliphatic and aromatic amino acid side chains at the protein-water interface, one has to ask: to what extent are metal ion complex equilibria affected by these effects? Estimates for the effective dielectric constants in such locations range from about 30 to 70^[30] compared with the approximately 80 of bulk water; hence, by employing aqueous solutions that contain about 20 to 50 dioxane, one may expect to simulate to some degree the situation in active site cavities. The dielectric constants of the two indicated mixed solvents are about 60 and 35, respectively. Consequently, the investigation of stability constant of metal ions-zwitterionic buffers complexes in water-dioxane mixture is of biological significance.

The dielectric constant^[31], hydrogen bonding, solvent basicity, dispersion forces, and proton-solvent interaction effects are commonly recognized as influencing factors in the ionization constant of ligands in partial aqueous medium^[32] and consequently the

TABLE 4: Thermodynamic quantities of the binary system ($\log K_1$) at $0.1 \text{ mol} \cdot \text{dm}^{-3} \text{ NaNO}_3$

Zwitterionic buffers	Thermo dynamic quantities	Metal ions						
		Cu^{II}	Ni^{II}	Co^{II}	Zn^{II}	Mn^{II}	Mg^{II}	Ca^{II}
ACES	$-\Delta G$	26.94 ± 0.03	20.61 ± 0.03	19.92 ± 0.04	21.58 ± 0.02	21.18 ± 0.02	18.89 ± 0.03	31.37 ± 0.02
	$-\Delta H$	14.11 ± 0.09	11.12 ± 0.07	10.77 ± 0.08	12.23 ± 0.08	10.13 ± 0.09	9.57 ± 0.13	9.34 ± 0.08
	ΔS	43.46 ± 0.09	33.78 ± 0.09	33.41 ± 0.07	31.42 ± 0.13	32.97 ± 0.09	31.37 ± 0.08	30.97 ± 0.08
MOPS	$-\Delta G$	22.89 ± 0.02	18.89 ± 0.03	18.66 ± 0.02	19.29 ± 0.03	--	19.52 ± 0.02	--
	$-\Delta H$	14.70 ± 0.08	13.60 ± 0.08	13.36 ± 0.09	13.90 ± 0.07	--	14.09 ± 0.09	--
	ΔS	27.63 ± 0.13	18.08 ± 0.08	17.90 ± 0.07	18.21 ± 0.07	--	18.43 ± 0.08	--
DIPSO	$-\Delta G$	28.08 ± 0.03	21.18 ± 0.03	20.19 ± 0.02	21.46 ± 0.04	19.86 ± 0.02	18.95 ± 0.02	18.61 ± 0.02
	$-\Delta H$	36.05 ± 0.06	16.59 ± 0.08	15.51 ± 0.07	16.94 ± 0.09	15.30 ± 0.13	13.07 ± 0.11	12.92 ± 0.11
	ΔS	17.51 ± 0.07	15.53 ± 0.07	16.14 ± 0.06	15.80 ± 0.13	15.69 ± 0.08	20.12 ± 0.09	19.42
TAPSO	$-\Delta G$	25.51 ± 0.02	20.83 ± 0.03	19.29 ± 0.02	20.09 ± 0.03	21.00 ± 0.02	18.49 ± 0.02	19.46 ± 0.04
	$-\Delta H$	13.91 ± 0.12	13.59 ± 0.08	12.48 ± 0.01	13.11 ± 0.09	13.66 ± 0.07	11.84 ± 0.09	12.60 ± 0.12
	ΔS	39.25 ± 0.08	24.33 ± 0.08	23.09 ± 0.09	23.68 ± 0.07	24.74 ± 0.06	22.58 ± 0.06	23.29 ± 0.09
HEPPSO	$-\Delta G$	28.77 ± 0.03	19.81 ± 0.02	19.29 ± 0.03	22.89 ± 0.02	--	20.09 ± 0.02	--
	$-\Delta H$	15.79 ± 0.12	14.12 ± 0.08	13.69 ± 0.01	15.13 ± 0.08	--	14.21 ± 0.11	--
	ΔS	43.85 ± 0.13	19.11 ± 0.07	19.04 ± 0.08	26.06 ± 0.07	--	19.97 ± 0.1	--
AMPSO	$-\Delta G$	30.25 ± 0.03	20.43 ± 0.04	19.52 ± 0.02	24.54 ± 0.03	--	--	--
	$-\Delta H$	15.60 ± 0.07	13.99 ± 0.13	13.42 ± 0.12	15.22 ± 0.13	--	--	--
	ΔS	49.30 ± 0.11	21.40 ± 0.13	20.62 ± 0.08	31.73 ± 0.09	--	--	--

Full Paper

TABLE 5: Stability constant of binary system($\log K_1$) in water and(Water+Dioxane) mixtures at $T=298.1$ K and $I=0.1$ mol·dm⁻³ NaNO₃

Zwitterionic buffers	w/w % Dioxane	Metal ions						
		Cu ^{II}	Ni ^{II}	Co ^{II}	Zn ^{II}	Mn ^{II}	Mg ^{II}	Ca ^{II}
ACES	0	4.72 ± 0.03	3.61 ± 0.02	3.49 ± 0.03	3.78 ± 0.06	3.71 ± 0.02	3.31 ± 0.02	3.25 ± 0.03
	10	4.79 ± 0.02	3.68 ± 0.06	3.56 ± 0.04	3.83 ± 0.05	3.78 ± 0.04	3.43 ± 0.03	3.40 ± 0.03
	30	4.85 ± 0.02	3.72 ± 0.04	3.63 ± 0.04	3.92 ± 0.04	3.85 ± 0.02	3.48 ± 0.02	3.51 ± 0.03
	50	4.97 ± 0.04	3.86 ± 0.02	3.71 ± 0.05	4.11 ± 0.05	3.97 ± 0.04	3.59 ± 0.03	3.58 ± 0.04
MOPS	0	4.01 ± 0.02	3.31 ± 0.03	3.27 ± 0.04	3.38 ± 0.04	--	3.42 ± 0.02	--
	10	4.11 ± 0.04	3.43 ± 0.03	3.36 ± 0.03	3.45 ± 0.03	--	3.53 ± 0.03	--
	30	4.18 ± 0.02	3.48 ± 0.02	3.46 ± 0.02	3.53 ± 0.02	--	3.59 ± 0.02	--
	50	4.26 ± 0.03	3.55 ± 0.03	3.53 ± 0.02	3.64 ± 0.03	--	3.64 ± 0.04	--
DIPSO	0	4.92 ± 0.03	3.71 ± 0.02	3.54 ± 0.06	3.76 ± 0.06	3.48 ± 0.03	3.32 ± 0.03	3.26 ± 0.02
	10	5.01 ± 0.02	3.80 ± 0.02	3.63 ± 0.05	3.85 ± 0.03	3.57 ± 0.06	3.41 ± 0.03	3.35 ± 0.03
	30	5.11 ± 0.03	3.86 ± 0.04	3.74 ± 0.03	3.90 ± 0.05	3.63 ± 0.05	3.49 ± 0.02	3.43 ± 0.03
	50	5.18 ± 0.05	3.97 ± 0.03	3.89 ± 0.04	4.12 ± 0.03	3.74 ± 0.03	3.58 ± 0.02	3.52 ± 0.04
TAPSO	0	4.47 ± 0.05	3.65 ± 0.02	3.38 ± 0.04	3.52 ± 0.04	3.68 ± 0.04	3.24 ± 0.03	3.41 ± 0.02
	10	4.53 ± 0.03	3.71 ± 0.03	3.47 ± 0.03	3.58 ± 0.02	3.72 ± 0.02	3.32 ± 0.02	3.46 ± 0.02
	30	4.61 ± 0.02	3.79 ± 0.03	3.52 ± 0.02	3.66 ± 0.03	3.82 ± 0.02	3.38 ± 0.03	3.55 ± 0.03
	50	4.68 ± 0.04	3.88 ± 0.02	3.63 ± 0.03	3.79 ± 0.02	3.91 ± 0.02	3.46 ± 0.02	3.63 ± 0.02
HEPPSO	0	5.04 ± 0.05	3.47 ± 0.02	3.38 ± 0.04	4.01 ± 0.03	--	3.52 ± 0.03	--
	10	5.17 ± 0.02	3.60 ± 0.03	3.53 ± 0.03	4.12 ± 0.03	--	3.65 ± 0.02	--
	30	5.24 ± 0.03	3.68 ± 0.02	3.58 ± 0.03	4.26 ± 0.02	--	3.71 ± 0.02	--
	50	5.30 ± 0.03	3.73 ± 0.03	3.65 ± 0.03	4.32 ± 0.02	--	3.78 ± 0.02	--
AMPSO	0	5.30 ± 0.04	3.58 ± 0.03	3.42 ± 0.02	4.30 ± 0.04	--	--	5.30 ± 0.04
	10	5.37 ± 0.02	3.65 ± 0.02	3.46 ± 0.05	4.35 ± 0.05	--	--	5.36 ± 0.03
	30	5.43 ± 0.03	3.71 ± 0.06	3.55 ± 0.02	4.46 ± 0.02	--	--	5.47 ± 0.03
	50	5.60 ± 0.06	3.78 ± 0.03	3.62 ± 0.02	4.52 ± 0.06	--	--	5.58 ± 0.02

stability of a metal-ligand complex. This investigation shows that the $\log K_1$ values increase as the amount of dioxane increase (i.e., the dielectric constant values decrease) (TABLE 5); thus, the dielectric constant plays an important role in the determination of these values.

REFERENCE

- [1] N.E.Good, G.D.Winget, W.Winter, T.N.Connolly, S.Izawa, R.M.M.Singh; *Biochemistry*, **5**, 467-477 (1966).
- [2] W.F.Ferguson, K.I.Braunschweiger, W.R.Braunschweiger, J.R.Smith, J.J.Mc Cormick, C.C.Wasmann, N.P.Jarvis, D.H.Bell, N.E.Good; *Anal.Biochem.*, **140**, 300 (1980).
- [3] M.A.Jermyn; *Aust.J.Chem.*, **20**, 1370 (1987).
- [4] K.Nagira, M.Shiga, K.Sasamoto, K.Kina, M.Hayashida, T.Sugdhard, H.MuraKami; *Biosci.Biotech, Biochem.*, **58**, 67 (1994).
- [5] J.S.Blanchard; *Buffers for Enzymes, Methods Enzymol.*, **104**, 404 (1984).
- [6] R.J.Beynon, J.S.Easterby; 'Buffer Solutions', New York, IRL Press, (1996).
- [7] H.A.Azab, F.S.Deghaidy, A.S.Qrabi, N.Y.Farid; *J. Chem.Eng.Data*, **45**, 709 (2000).
- [8] H.A.Azab, A.S.Qrabi, E.T.Abd El-Salam; *J.Chem. Eng.Data*, **46**, 346 (2001).
- [9] Z.M.Anwar, H.A.Azab; *J.Chem.Eng.Data*, **44**, 1151-1157 (1999).
- [10] Z.M.Anwar, H.A.Azab; *J.Chem.Eng.Data*, **46**, 34-40 (2001).
- [11] Z.M.Anwar, H.A.Azab; *J.Chem.Eng.Data*, **46**, 613-618 (2001).
- [12] C.M.M.Machado, I.Cukrowski, P.Gameiro, H.M.V.M.Soares; *Analytica Chimica Acta*, **493**, 105-119 (2003).
- [13] M.Taha, M.M.Khalil; *J.Chem.Eng.Data*, **50**, 157-163 (2005).

Full Paper

- [14] M.Taha, M.M.Khalil, A.M.Sawsan; *J.Chem.Eng.Data*, **50**, 882 (2005).
- [15] M.Taha, A.E.Fazary; *J.Chem.Thermodynamics*, **37**, 43-48 (2005).
- [16] M.Taha; *Ann.Chim.(Rome)*, **95**, 105-109 (2005).
- [17] M.Taha; *Ann.Chim.(Rome)*, **94**, 971-978 (2004).
- [18] M.M.Khalil, M.Taha; *Mont.Chem.*, **135**, 385-395 (2004).
- [19] F.J.Welcher; 'The Analytical Uses of Ethylenediamine-tetraacetic acid', Von Nostrand, Princeton, (1965).
- [20] P.Gans, B.O'Sullivan; *Talanta*, **51**, 33-37 (2000).
- [21] H.M.Irving, H.S.Rossotti; *J.Chem.Soc.*, 3397-3405 (1953).
- [22] H.M.Irving, H.S.Rossotti; *J.Chem.Soc.*, 2904 (1954).
- [23] S.A.Merny, D.S.Konyaev, Yu.V.Kholin; *Kharkov University Bulletin, Chemical Series*, **420**, 112-120 (1998).
- [24] Yu.V.Kholin, D.S.Konyaev, S.A.Merny; *Kharkov University Bulletin, Chemical Series*, **437**, 17-35 (1999).
- [25] G.Douheret; *Bull.Soc.Chim.Fr.*, 1412-1419 (1967).
- [26] G.Douheret; *Bull.Soc.Chim.Fr.*, 3122-3131 (1968).
- [27] R.N.Roy, J.A.Carlsten, J.A.Nieder Schmidt, W.S.Good, J.M.Rook, C.Brene, A.J.Kilker, L.N.Roy, K.M.Kuhler; *J.Solution Chem.*, **26**, 309 (1997).
- [28] L.G.Sillen, A.E.Maetell; 'Stability Constants Metal Complexes', 2nd Ed., The Chemical Society, London, (1964).
- [29] K.S.Pitzer; *J.Am.Chem.Soc.*, **59**, 2365 (1937).
- [30] H.Sigel, R.B.Martin; *Chem.Soc.Rev.*, **22**, 255-267 (1993).
- [31] G.Charlot, B.Trimillon; 'Chemical Reactions in Solvents and Melts', Pergamon, New York, (1969).
- [32] C.D.Ritchie; In 'Solute-Solvent Interactions', J.F.Coetzee, C.D.Ritchie, Eds., Marcel Dekker, New York, (1969).