

CONCLUSION

Self Propagating High Temperature (SPHT) method using an internal fuel resulted in the stoichiometrically satisfactory cathode materials (LiNiVO₄ and LiMnVO₄) with better purity and crystallinity. Despite the lowest temperature (573 K) and minimum time adopted for the heat treatment, the products obtained from the fuel based synthesis (SPHT) showed growth controlled sub micronic particles with larger surface area. The electrochemical behavior of both the cathodes was found to be better for the products obtained from SPHT method compared to those of carbonate and acetate precursor methods. Also, higher fuel calorific value fuels in SPHT method yielded products that exhibited enhanced cycle life without much capacity fade.

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Solute-Solvent Interactions in the Acidic Dissociation of Protonated Indicator Bases Containing Nitrogen in Water / 1,2 Dimethoxyethane Binary Mixtures at Different Temperatures from emf Measurements

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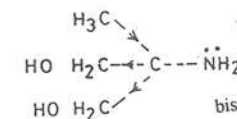
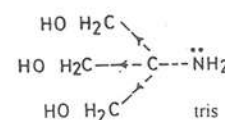
ABSTRACT:

The acidic dissociation constants of the protonated form of 2-amino-(2-hydroxymethyl)propane-1,3-diol (tris) and 2-amino-2-methylpropane-1,3-diol (bis) in a series of water/1,2 dimethoxy ethane mixtures at 5 °C temperature intervals from 25 to 45 °C are determined using a cell without liquid junction potential. The corresponding thermodynamic parameters (ΔG° , ΔH° , and ΔS°) of the protonated form of these buffer indicators in the various solvent mixtures are evaluated. The variation of the standard free energy change of transfer with solvent compositions for both indicators indicates a characteristic minimum which is attributed to selective solvation of the individual species participating in the equilibrium process. Solubility measurements of these indicators at different temperatures are determined in order to evaluate the thermodynamic functions of the transfer of the free bases which may provide a better insight on the nature of the ion-solvent interactions and the relative basicity of the solvent.

Key words: Acidic dissociation, tris, bis, 1,2 dimethoxyethane, solubility, solvent effect, ion-solvent interactions.

INTRODUCTION

As part of extensive studies[1-5] on the dissociation equilibria in different aquo-organic mixtures, we report the results of measurements of the dissociation constants for protonated forms of 2-amino-(2-hydroxymethyl) propane-1,3-diol (tris) and 2-Amino-2-methyl propane-1,3-diol (bis) in a binary 1,2-dimethoxyethane (DME)/water mixtures. Their molecular structures are:



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Studies such as these give important insights into the role of the solvent in dissociation equilibria and ion-solvent interactions, as well as providing information regarding the acid-base properties of this solvent and its structural features. Both tris and bis are solid bases, easily purified, stable and water soluble bases of considerable interest as biological buffers[6-7]. The present work reports on a study of the behaviour of these two closely related indicators in aqueous mixtures in terms of dissociation equilibria and other thermodynamic parameters.

RESULTS AND DISCUSSION

The method used for determining the dissociation constant $(K)_{BH^+}$ of tris.H⁺ and bis.H⁺ was exactly similar to that adopted for 2-methoxyethanol (MCS)/water [4] solvents. The emf values of the cell

Pt/H₂ (g, 1atm)/Tris.HCl or Bis HCl(m₁), Tris or Bis (m₂), H₂O-DME mixture/AgCl/Ag. (A),

where m₁ and m₂ are the molalities of BHCl and B, respectively, were measured at different ionic strengths.

The $p(K)_{BH^+}$ value in each of the solvent mixtures at each temperature was calculated by plotting the function $p(K)_{BH^+}$ defined by equation 1,

$$p(K)_{BH^+} = \frac{(E_m - E_m^0)F}{2.303RT} + \log \frac{m_1^2}{m_2} - \frac{2A\sqrt{I}}{1 + Ba^0\sqrt{I}} = p(K)_{BH^+} - 2\beta I \quad (1)$$

against I and extrapolating to I=0. In equation 1, E_m is the emf of cell (A) corrected to a partial pressure of 1 atm of dry hydrogen, E_m^0 is the standard potential of the AgCl-Ag electrode on the molal scale at the particular solvent composition and temperature, A and B are the Debye-Hückel constants, a⁰ and β are adjustable parameters, the first being the ion-size parameter, and I is the ionic strength. The proper value of a⁰ is considered to be that which gives the minimum standard deviation for linear regression[4]. The emfs of cell (A) in the series of DME-H₂O as a function of temperature are summarized in Tables 1a and 1b.

Table (1a) Electromotive force of the cell (A) for tris H⁺ at different temperatures.

m ₁ /mol Kg ⁻¹	m ₂ /mol Kg ⁻¹	E _{corr} /Volt				
		25 °C	30 °C	35 °C	40 °C	45 °C
Pure aqueous medium						
0.05333	0.04968	0.78496	0.78252	0.78104	0.77892	0.77684
0.04153	0.03869	0.79034	0.78849	0.78689	0.78479	0.78260
0.03136	0.02485	0.79255	0.79021	0.78950	0.78599	0.78515
0.02356	0.01867	0.79878	0.79653	0.79591	0.79218	0.79143
0.01237	0.00980	0.81378	0.81132	0.81062	0.80742	0.80625
10.8 wt. % DME						
0.06061	0.05900	0.77307	0.77097	0.77006	0.76763	0.76897
0.04693	0.04569	0.77940	0.77735	0.77526	0.77311	0.77108
0.03734	0.03053	0.77740	0.77565	0.77483	0.77319	0.77148
0.02426	0.02361	0.79158	0.78876	0.78524	0.78304	0.78180
0.01003	0.00937	0.80351	0.80217	0.80288	0.80012	0.79841
27.5 wt. % DME						
0.05832	0.04769	0.74866	0.74741	0.74639	0.74599	0.74402
0.04795	0.03921	0.74961	0.75121	0.75137	0.74958	0.74784
0.03081	0.02320	0.75267	0.75068	0.74806	0.74578	0.74322
0.02476	0.02024	0.76027	0.75868	0.75578	0.75385	0.75212
0.00973	0.00906	0.77435	0.77361	0.77144	0.77015	0.76834
48.7 wt. % DME						
0.06555	0.04936	0.72018	0.71701	0.71370	0.71061	0.70735
0.04528	0.03410	0.72595	0.72120	0.71784	0.71311	0.70909
0.03761	0.02832	0.72472	0.72217	0.71957	0.71662	0.71414
0.02345	0.01766	0.73278	0.72918	0.72524	0.72145	0.71881
0.01358	0.01022	0.73018	0.72950	0.72560	0.72343	0.72093
74.3 wt. % DME						
0.04938	0.04600	0.69522	0.69040	0.68784	0.68454	0.68103
0.04395	0.03593	0.69481	0.69112	0.68948	0.68915	0.68415
0.03730	0.03050	0.69485	0.68706	0.68409	0.68047	0.67566
0.01967	0.01832	0.69531	0.68578	0.68472	0.68234	0.67728
0.01443	0.01405	0.69800	0.68870	0.68710	0.68222	0.67874

Table (1b) Electromotive force of the cell (A) for bis H⁺ at different temperatures.

m ₁ /mol Kg ⁻¹	m ₂ /mol Kg ⁻¹	E _{corr} /Volt				
		25 °C	30 °C	35 °C	40 °C	45 °C
Pure aqueous medium						
0.04860	0.03858	0.82352	0.82221	0.82047	0.81886	0.81670
0.04234	0.04689	0.83572	0.83439	0.83228	0.83104	0.82905
0.03016	0.02984	0.84048	0.83941	0.83717	0.83568	0.83400
0.02286	0.01811	0.84058	0.83963	0.83788	0.83615	0.83536
0.01092	0.00950	0.85957	0.85931	0.85817	0.85605	0.85597
12.1 wt. % DME						
0.05122	0.05672	0.82947	0.82635	0.82435	0.82274	0.82183
0.04163	0.04610	0.83718	0.83139	0.83521	0.83371	0.83233
0.03490	0.03865	0.83566	0.83478	0.83151	0.83469	0.83473
0.02119	0.02347	0.84674	0.84668	0.84751	0.84760	0.84713
0.00955	0.00959	0.85677	0.85882	0.85985	0.85906	0.85775
27.2 wt. % DME						
0.04897	0.05423	0.80609	0.80462	0.80481	0.80349	0.80367
0.04073	0.04511	0.81082	0.81081	0.80952	0.80863	0.80726
0.03072	0.03411	0.81402	0.81370	0.81448	0.81132	0.80903
0.01798	0.01991	0.82188	0.82259	0.82145	0.82004	0.81861
0.01183	0.01310	0.83469	0.83531	0.83388	0.83212	0.83073

Cont. table (1b)

m ₁ /mol Kg ⁻¹	m ₂ /mol Kg ⁻¹	E _{corr} /Volt				
		25 °C	30 °C	35 °C	40 °C	45 °C
48.2 wt. % DME						
0.05192	0.05749	0.77354	0.77233	0.77068	0.76805	0.76665
0.03383	0.03746	0.77839	0.77691	0.77546	0.77633	0.77355
0.02174	0.02407	0.77822	0.77639	0.77521	0.77335	0.76997
0.01870	0.02073	0.77889	0.78072	0.77872	0.77821	0.77615
0.01295	0.01371	0.78499	0.78400	0.78242	0.78091	0.78067
79.3 wt. % DME						
0.04810	0.04759	0.72269	0.71700	0.71385	0.70999	0.71603
0.04009	0.04439	0.73111	0.72641	0.72355	0.72005	0.71581
0.02951	0.03268	0.73191	0.72661	0.72428	0.72082	0.71646
0.02216	0.02454	0.73405	0.72947	0.72664	0.72313	0.72060
0.01141	0.01264	0.74235	0.73923	0.73511	0.73178	0.72856

The values of E° for the AgCl/Ag electrode in the solvent mixtures, the values for density, and the Debye-Hückel constants A and B are from previously published data [9].

The observed p_s(K)_{BH}⁺ values (molal) at each solvent composition and temperature are listed in Table 2. The p_s(K)_{BH}⁺ value derived in this way was fitted to equation 2:

$$pK = \frac{A_1}{T} - A_2 + A_3 T \quad (2)$$

where T is the Kelvin temperature. The constants A₁, A₂, and A₃ were evaluated by a computer program based on the method of orthogonal polynomials outlined by Please[10]. The standard thermodynamic quantities for the acidic dissociation of the protonated form of tris and bis in the various water/DME mixtures were calculated by the application of the usual thermodynamic formulae to equation 2. The following expressions for the standard changes of Gibbs energy (ΔG°), entropy (ΔS°), and enthalpy (ΔH°) were derived.

$$(\Delta G^\circ) = -RT \ln K = 2.3026R(A_1 - A_2T + A_3T^2),$$

$$(\Delta S^\circ) = -d\Delta G^\circ/dT = 2.3026R(A_2 - 2A_3T)$$

$$(\Delta H^\circ) = \Delta G^\circ + T\Delta S^\circ = 2.3026R(A_1 - A_3T^2)$$

Values of p_s(K)_{BH}⁺ on the mole fraction scale were computed from the corresponding values of p_s(K)_{BH}⁺ on the molal scale by the usual relation. The resulting values were fitted to equation 2 and the constants A₁, A₂ and A₃ were evaluated and are collected in Table 3, for both indicators.

Table 2. The acidic dissociation constants p_s(K)_{BH}⁺ as a function of composition and temperature (on molal scale).

Wt% DME	pK (obs.) of tris H ⁺				
	25 °C	30 °C	35 °C	40 °C	45 °C
0	8.088	7.937	7.829	7.663	7.566
10.8	7.916	7.799	7.662	7.534	7.431
27.5	7.625	7.500	7.368	7.260	7.151
48.7	7.503	7.409	7.272	7.170	7.094
74.3	7.805	7.705	7.574	7.491	7.429
wt% DME	pK (obs.) of bis H ⁺				
	25 °C	30 °C	35 °C	40 °C	45 °C
0	8.777	8.650	8.512	8.365	8.267
12.1	8.764	8.715	8.896	8.490	8.397
27.2	8.598	8.513	8.383	8.263	8.130
48.2	8.105	8.052	7.909	7.821	7.731
79.3	9.093	8.926	8.839	8.725	8.615

Table (3) Values of the constants (A₁, A₂, A₃) in Equation 2, and the values of p_s(K)_{BH}⁺ for tris H⁺ and bis H⁺ at different temperatures (on mole fraction scale).

wt. % DME	A ₁	A ₂	A ₃	p _s (K) _{BH} ⁺				
				25 °C	30 °C	35 °C	40 °C	45 °C
(a) tris H ⁺								
0.0	3549.7020	5.32672	0.01091	9.831	9.689	9.554	9.424	9.304
10.8	1509.0550	-7.30070	-	9.625	9.496	9.369	9.245	9.127
27.5	2957.8100	2.74734	0.009180	9.262	9.133	9.010	8.891	8.781
48.7	4856.3100	16.12496	0.007004	9.041	8.921	8.810	8.707	8.615
74.3	9910.3720	49.42485	0.02978	9.164	9.041	8.935	8.847	8.777
			0.08502					
(b) bis H ⁺								
0.0	5202.5420	15.56203	0.2898	10.527	10.384	10.251	10.126	10.010
12.1	-6129.3710	-56.01292	-0.08379	10.474	10.394	10.303	10.202	10.090
27.2	-7131.4190	-63.6409	-0.09889	10.240	10.140	10.028	9.903	9.766
48.2	-1443.9380	-24.86867	-0.03480	9.650	9.556	9.459	9.360	9.258
79.3	7143.3350	29.11866	0.05216	10.390	10.256	10.134	10.025	9.927

The solubilities S of tris and bis in pure water and in aqueous mixtures of DME at the five experimental temperatures together with their relative deviations are recorded in Tables 4a and 4b. Variation of the solubility with the temperature for each solvent composition was expressed by fitting log S (mole fraction scale) at different temperatures by the method of least squares according to equation (3):

$$\log S = A_1 + A_2/T + A_3 \ln T \quad (3)$$

Table (4a) Solubilities (mol kg⁻¹) of tris in water/1,2-dimethoxyethane solvent mixtures at different temperatures.

wt. % DME	20 °C			25 °C			30 °C			35 °C			40 °C		
	S	a.d	r.d ^o _s	S	a.d	r.d ^o _s	S	a.d	r.d ^o _s	S	a.d	r.d ^o _s	S	a.d	r.d ^o _s
0.0	5.34	0.01	0.37	5.86 (5.78) ²	0.04	0.68	6.53	0.01	0.15	7.20 (7.26) ²	0.07	0.97	7.76	0.03	0.39
9.4	4.50	0.01	0.22	4.96	0.00	0.00	5.53	0.05	1.81	6.22	0.01	0.16	6.79	0.04	0.59
30.50	2.90	0.02	0.69	3.26	0.02	0.61	3.66	0.00	0.00	4.20	0.03	0.71	4.77	0.02	0.42
48.50	1.77	0.05	0.28	2.02	0.01	0.50	2.26	0.01	0.44	2.69	0.01	0.37	2.89	0.03	1.04
70.9	0.712	0.00	0.28	0.752	0.001	0.13	0.944	0.009	1.69	1.14	0.00	0.00	1.32	0.00	0.00
100.0	0.0199	0.0001	0.50	0.0239	0.000	0.31	0.0277	0.0003	8.30	0.0326	0.0001	0.31	0.0381	0.001	0.52

Table (4b) Solubilities (mol kg⁻¹) of bis in water/1,2-dimethoxyethane solvent mixtures at different temperatures.

wt. % DME	20 °C			25 °C			30 °C			35 °C			40 °C		
	S	a.d	r.d ^o _s	S	a.d	r.d ^o _s	S	a.d	r.d ^o _s	S	a.d	r.d ^o _s	S	a.d	r.d ^o _s
0.00	20.39	0.03	0.15	23.51	0.11	0.47	26.70	0.00	0.00	30.42	0.02	0.07	34.36	0.00	0.00
9.4	16.56	0.08	0.48	19.41	0.02	0.10	22.39	0.08	0.36	26.30	0.01	0.04	30.51	0.05	0.16
30.2	12.27	0.04	0.33	14.75	0.06	0.41	17.78	0.07	0.39	21.39	0.04	0.19	25.55	0.01	0.04
48.2	9.77	0.05	0.51	11.65	0.00	0.00	14.12	0.02	0.14	16.55	0.05	0.30	19.70	0.02	0.10
74.7	6.35	0.02	0.31	7.69	0.03	0.39	9.12	0.02	0.22	10.95	0.05	0.46	12.59	0.06	0.48
100.0	0.393	0.002	0.51	0.426	0.006	1.41	0.465	0.004	0.94	0.529	0.002	0.38	0.533	0.001	0.19

The standard thermodynamic quantities ΔG° , ΔH° , and ΔS° for the dissolution process were derived by application of the following thermodynamic relationships:

$$\Delta G^\circ = -2.303 RT \log S = -2.303R [A_1 T + A_2 + A_3 T \ln T] \quad (4)$$

$$\Delta S^\circ = -d\Delta G^\circ/dT = 2.303R [A_1 + A_3 + A_3 \ln T] \quad (5)$$

$$\Delta H^\circ = \Delta G^\circ + \Delta S^\circ = 2.303R [-A_2 + A_3 T^2] \quad (6)$$

These values at 25 °C are listed in Tables 5a and 5b. The standard free energy change, $\Delta G^\circ_1(B)$, accompanying the transfer of the two indicators from the standard state in water to the standard state in the water/DME mixture, was computed at 25 °C (Table 6) using the following relationship:

$$\Delta G^\circ_1(B) = \Delta_s G^\circ(B) - \Delta_w G^\circ(B) = 2.303RT \log (S_w/S_s) \quad (7)$$

where s and w refer to water and the mixed solvent, respectively.

Table (5a) Thermodynamic functions calculated from the solubilities of tris in water/1,2-dimethoxyethane mixtures (on mole fraction scale).

wt. % DME	S(obs)/mol kg ⁻¹	S(cal)/mol kg ⁻¹	Δ	ΔG° /kJmol ⁻¹	ΔH° /kJmol ⁻¹	ΔG° /Jmol ⁻¹ K ⁻¹
t= 25 °C						
0.0	0.0955	0.0960	0.0005	5.81	12.95	24.0
9.4	0.0881	0.0886	0.0005	6.01	14.41	28.2
30.5	0.0727	0.0724	0.0003	6.51	18.08	38.8
48.5	0.0561	0.0560	0.0001	7.14	18.12	36.8
70.9	0.0304	0.0325	0.0021	8.50	24.24	52.8
100.0	0.00215	0.00213	0.00002	15.25	24.45	30.8

Table (5b) Thermodynamic functions calculated from the solubilities of bis in water/1,2-dimethoxyethane mixtures (on mole fraction scale).

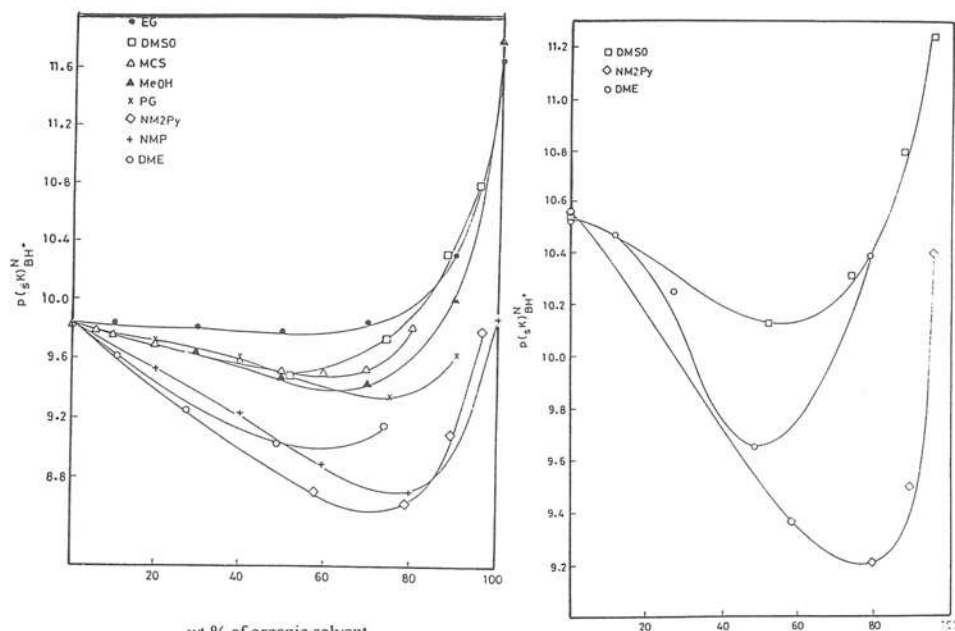
wt. % DME	S(obs)/mol kg ⁻¹	S(cal)/mol kg ⁻¹	Δ	ΔG° /kJmol ⁻¹	ΔH° /kJmol ⁻¹	ΔG° /Jmol ⁻¹ K ⁻¹
t= 25 °C						
0.0	0.298	0.296	0.002	3.02	13.38	34.8
9.4	0.274	0.273	0.001	3.22	16.12	43.3
30.2	0.259	0.259	0.000	3.35	19.65	54.7
48.2	0.255	0.255	0.000	3.39	18.92	52.1
74.7	0.254	0.254	0.000	3.40	19.24	53.1
100.0	0.0370	0.0373	0.0003	8.16	12.04	13.0

The effect of enriching the aqueous solvent with DME on altering the dissociation of trisH⁺ and bisH⁺ at 25,30, 35, 40, and 45 °C is given in Table 3. It is clear that the solvent effect is similar at all five experimental temperatures. Addition of DME first reduces the value of $p(K)_{BH^+}^N$ until a solvent composition of about (50-60) wt% minimum is reached, after which $p(K)_{BH^+}^N$ rises steeply upon further increasing the solvent composition. Since the reaction $BH^+ + SH = B+SH^+_2$ is isoelectric, the variation of pK may not be much influenced by the dielectric constant of the medium. $p(K)_{BH^+}^N$ decreases, i.e. the basicity of the solvent increases, and the base is poorly solvated at higher percentage composition of DME. Figures 1 and 2 show a comparison of these results with those obtained earlier for both protonated bases in various aqueous organic solvent [3,4,11-14] systems at 25 °C. It is easy to predict that tris has the strongest preference for NM2 Py > NMP > DME > PG > MeOH > MCS > DMSO > EG, while for bis, the order of decreasing basicities is NM2Py > DME > DMSO.

Figure 3 compares the acidic dissociation constants for the protonated forms of bis, tris, 2,2'-bipyridine, and 1,10-phenanthroline[15]. A minimum is observed at nearly about 60-80 wt % of DME. Thus, the trend of changing basicities in water is

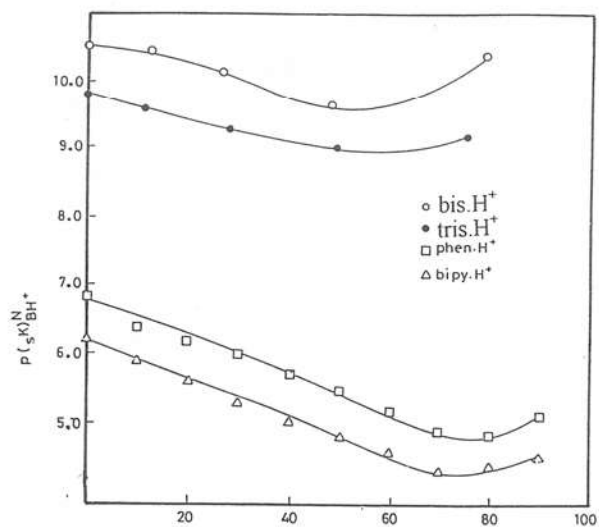


The lower basicity of tris relative to bis may be due to the hydrogen-bonds formed between water and the three hydroxy groups of tris make the solvent interaction with the basic nitrogen atom more difficult. A more likely explanation is that the presence of hydroxy group tempers the inductive effect of the substituent alkyl groups, known to lead to an enhancement of the strength of nitrogen bases. Addition of DME solvent to H₂O up to a composition of 50wt. % lowers the pK_a of bis by 0.9 unit as compared with 0.8 unit for tris. This difference, as well as the lower pK_a of tris, is probably attributed to the enhanced stabilization, through hydrogen-bonding with water, of tris as compared with bis.



wt. % of organic solvent
Fig. (1): Variation of $p(sK)_{BH^+}^N$ of tris H^+ with wt. % of organic solvent mixtures at 25 °C

wt. % of organic solvent
Fig. (2): Variation of $p(sK)_{BH^+}^N$ of bis H^+ with wt. % of organic solvent mixtures at 25 °C



wt. % of 1,2- dimethoxyethane
Fig. (3): Values of $p(sK)_{BH^+}^N$ of different Protonated bases in water/1,2- dimethoxyethane solvent mixtures at 25 °C

The lower basicity of 2,2'-bipyridine than 1,10-phenanthroline may be due to the presence of lone pair of unshared electrons on the two nitrogen atoms in the rings which does not share in the formation of π - cloud of the azine ring. Due to the presence of the steric effect in the isolated system, which causes the two azine rings to be perpendicular to each other, i.e. there will be no conjugation, and accordingly the basicity will be decreased. For 1,10-phenanthroline which contains two lone pairs of electrons on the two nitrogen atoms, may present a rigid planer structure, i.e. it possesses more hybride structure which leads to the increase of basicity.

In order to understand the effect of solvent on the equilibrium, we have calculated the free energy change accompanying the transfer process, ΔG_i^o (diss), of tri H^+ and bis H^+ dissociation from H_2O to the mixed DME- H_2O solvents on the mole fraction scale at 25 °C. This function is given by the equation

$$\Delta G_i^o \text{ (diss)} = 2.3026 RT [p(sK)_{BH^+}^N - p(wK)_{BH^+}^N] \quad (8)$$

$$= \Delta G_i^o(H^+) + \Delta G_i^o(B) - \Delta G_i^o(BH^+) \quad (9)$$

Equation (9) may also be expressed in an equivalent form as:

$$= \Delta G_i^o(HCl) + [\Delta G_i^o(B) - \Delta G_i^o(BHCl)] \quad (10)$$

The different thermodynamic quantities, i.e., ΔG_i^o (diss), $\Delta G_i^o(B)$, $\Delta G_i^o(BHCl)$, and $[\Delta G_i^o(B) - \Delta G_i^o(BHCl)]$ have been evaluated and represented in table (6). Values of $\Delta G_i^o(Cl^-)$ [16] and the total free energy of transfer, $\Delta G_i^o(BH^+)$ in mixtures of H_2O -DME (computed from equation (9) together with the values of $\Delta G_i^o(H^+)$ which is easily obtained from the relation $\Delta G_i^o(H^+) = \Delta G_i^o(HCl) - \Delta G_i^o(Cl^-)$ are also represented in Table 6.

Variation of ΔG_i^o (diss): An examination of ΔG_i^o (diss) values (Table 6) for tri H^+ and bis H^+ shows a decrease initially with the addition of DME. These results suggest that the equilibrium ($BH^+ \leftrightarrow B + H^+$) is favoured for tri H^+ and bis H^+ in the mixed solvent than in pure water and the behaviour is not consistent with simple Born electrostatic equation. On further increasing the organic solvent composition, ΔG_i^o (diss) increases again. Therefore, the solvent basicity plays an important factor on this equilibrium. From equation (10) it is seen that ΔG_i^o (diss) is a composite function of $\Delta G_i^o(HCl)$ and $[\Delta G_i^o(B) - \Delta G_i^o(BHCl)]$, while

Table (6) Thermodynamic parameters of various species involving tris, bis, 2,2-bipyridine and 1,10-phenanthroline in H₂O-DME at 25 °C on the mole fraction scale.

Base	Wt% DME	$\Delta G_1^0(\text{diss})^{(a)}$	$\Delta G_{\text{L,d}}^0(\text{diss})^{(b)}$	$\Delta G_{\text{L,nonel}}^0(\text{diss})^{(c)}$	$\Delta G_{\text{L,cl}}^0(\text{H}^+)$	$\Delta G_{\text{L,cl}}^0(\text{BH}^+)$	$\Delta G_{\text{L,cl}}^0(\text{H}^+)$	$\Delta G_{\text{L,cl}}^0(\text{BH}^+)$	$\Delta G_{\text{L,cl}}^0(\text{BH}^+)$	$\Delta G_{\text{L,cl}}^0(\text{BH}^+)$		
tris	10	-1.18	-0.20	-0.98	0.20	1.68	0.30	2.2	-1.90	-0.52	-0.18	-0.34
	20	-3.25	-0.20	-3.05	0.70	4.81	0.85	6.2	-5.35	-1.40	-1.05	-0.35
	30	-4.52	0.68	-5.20	1.33	7.95	2.10	12.6	-10.50	-4.65	-5.84	+1.2
	40	-3.81	2.51	-6.32	2.69	14.45	7.95	21.8	-13.85	-7.35	-11.96	4.61
	50	-0.31	-0.20	-0.11	0.20	0.83	0.32	2.4	-2.08	-1.57	-1.20	-0.34
	60	-1.65	-0.21	-1.44	0.33	2.69	0.71	6.0	-5.29	-3.32	-2.98	-0.35
bis	10	-5.01	0.64	-5.65	0.37	7.15	1.77	12.0	-10.23	-4.85	-5.94	1.12
	20	-0.78	3.13	-3.91	0.38	11.53	10.37	24.0	-13.63	-12.47	-18.41	5.82
	30	-1.94	-0.17	-1.77	-3.02	-0.77	0.31	2.3	-1.99	-3.09	-2.73	-0.36
	40	-5.08	-0.18	-4.90	-6.44	-0.45	0.91	6.9	-5.99	-7.38	-7.00	-0.38
	50	-8.33	0.62	-8.95	-9.48	1.08	2.23	12.7	-10.47	-11.71	-13.11	1.40
	60	-9.48	1.82	-12.48	-11.46	5.79	6.59	22.0	-15.41	-16.34	-20.53	4.19
2,2-bipyridine	10	-10.67	-0.17	-2.17	-4.01	-1.36	0.31	2.3	-1.99	-3.68	-3.32	-0.36
	20	-3.42	-0.18	-4.56	-7.62	-1.97	0.91	6.9	-5.99	-8.91	-8.53	-0.38
	30	-6.05	0.62	-8.04	-9.21	0.44	2.23	12.7	-10.47	-12.35	-13.75	1.40
	40	-7.42	1.82	-12.77	-12.60	4.94	6.59	22.0	-15.41	-17.19	-21.38	4.19
	50	-9.02	1.82	-14.30	-14.30	15.96	19.07	19.07				
	60	-11.19										
1,10-phenanthroline	10	-2.34	-0.17	-2.17	-4.01	-1.36	0.31	2.3	-1.99	-3.68	-3.32	-0.36
	20	-3.42	-0.18	-4.56	-7.62	-1.97	0.91	6.9	-5.99	-8.91	-8.53	-0.38
	30	-6.05	0.62	-8.04	-9.21	0.44	2.23	12.7	-10.47	-12.35	-13.75	1.40
	40	-7.42	1.82	-12.77	-12.60	4.94	6.59	22.0	-15.41	-17.19	-21.38	4.19
	50	-9.02	1.82	-14.30	-14.30	15.96	19.07	19.07				
	60	-11.19										

(a) $\Delta G_1^0(\text{diss}) = \Delta G_{\text{L,d}}^0(\text{diss}) + \Delta G_{\text{L,nonel}}^0(\text{diss})$ (b) $\Delta G_{\text{L,d}}^0(\text{H}^+) = \Delta G_{\text{L,d}}^0(\text{H}^+) - \Delta G_{\text{L,cl}}^0(\text{BH}^+)$ (c) $\Delta G_{\text{L,nonel}}^0(\text{BHCl}) = \Delta G_{\text{L,cl}}^0(\text{HCl}) + \Delta G_{\text{L,cl}}^0(\text{B}) - \Delta G_{\text{L,cl}}^0(\text{diss})$
 (d) from reference 9) (e) from reference 16) (f) $\Delta G_{\text{L,cl}}^0(\text{BH}^+) = \Delta G_{\text{L,cl}}^0(\text{BH}^+) - \Delta G_{\text{L,cl}}^0(\text{BH}^+)$ (g) Calculated from Hepler (17) using radii of 4A° for BH⁺.

$\Delta G_1^0(\text{HCl})$ increases continuously with the addition of DME; $[\Delta G_{\text{L,cl}}^0(\text{B}) - \Delta G_{\text{L,cl}}^0(\text{BHCl})]$ continuously decreases. Therefore the observed minimum in $\Delta G_1^0(\text{diss})$ in the two cases may thus be due to the opposite variation of the above two factors, the dominant factor being $[\Delta G_{\text{L,cl}}^0(\text{B}) - \Delta G_{\text{L,cl}}^0(\text{BHCl})]$ up to 60% DME. The increasing values of $\Delta G_1^0(\text{diss})$ at higher concentration of DME arises due to the dominance of $\Delta G_1^0(\text{HCl})$ over the other factor.

$\Delta G_1^0(\text{diss})$ consists of an electrostatic and a non-electrostatic part. A comparison of the results of $\Delta G_{\text{L,nonel}}^0$ for the acidic dissociation processes of protonated tris and bis in water-DME with those obtained for both protonated bases in other organic solvent mixtures[3,4,11-14] is represented in figures (4a-4b). Inspection of these figures indicates that DME is almost more basic solvent than any of the other solvents. Bates and Popovych[18,19] studied the basicity effect ($\Delta G_{\text{L,nonel}}^0$) for tris H⁺ and NH₄⁺ ion in H₂O-MeOH solvent mixtures. They assumed that it displays considerable uniformity and consistency for all charge types and it could be regarded as a solvent parameter and is best characterized as a measure of the increase in basicity of the medium. Since the values of $\Delta G_{\text{L,nonel}}^0(\text{diss})$ are found to be inconsistent for all these charge types indicators which invalidate the assumption of Bates and Popovych and lend support to the view[20] that the overall behaviour of protonated amines with different chemical nature and also with different solvophilism is largely dictated by solute-solvent interactions besides the effect of the relative solvent basicities.

Variation of $\Delta G_{\text{L,cl}}^0(\text{B})$: It is noticed that, for tris and bis compounds, values of $\Delta G_{\text{L,cl}}^0(\text{B})$ (Table 6) increase positively and slowly with increasing organic solvent. This indicates that, they are more strongly stabilized by water than by the organic solvent. The higher values of $\Delta G_{\text{L,cl}}^0(\text{B})$ obtained for tris than for bis may be interpreted as due to: water stabilizes tris compound (3-OH group) more effectively than bis (2-OH group) through solute-solvent interactions.

For the case of 2,2'-bipyridine and 1,10-phenanthroline bases, values of $\Delta G_{\text{L,cl}}^0(\text{B})$ are always negative. The presence of the azine and aromatic rings which are hydrophobic in nature, showed a greater affinity towards the organic solvents, resulting in increasing negative contributions to $\Delta G_{\text{L,cl}}^0(\text{B})$ values. Accordingly solvation through hydrogen-bonding has a small effect as compared to the dispersion interaction with the aromatic nuclei, and the hydrophobism

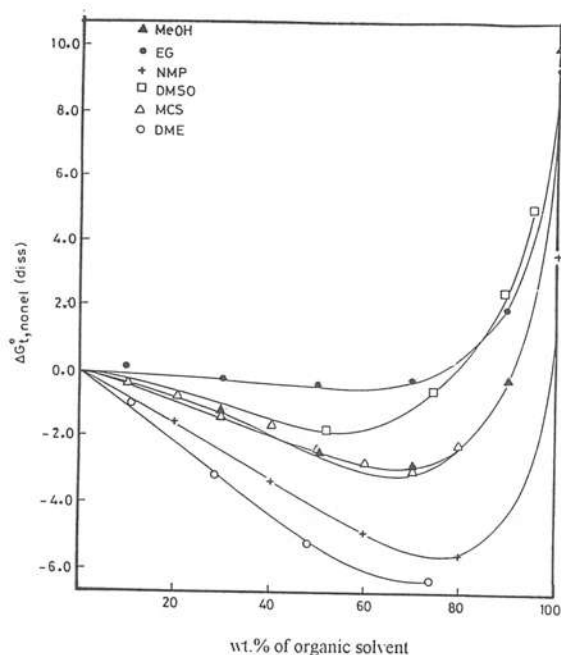


Fig. (4a) values of $\Delta G_{L1,nonel}^{\circ}(\text{diss})$ for the dissociation of tris. H^+ in different organic-solvent mixtures at 25 °C

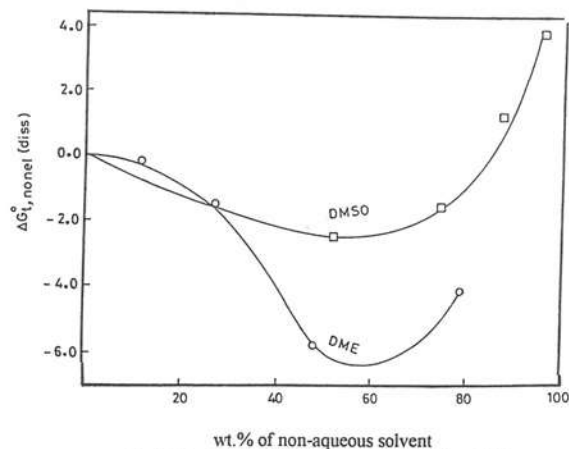
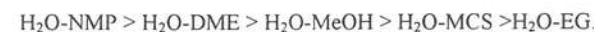


Fig. (4b) values of $\Delta G_{L1,nonel}^{\circ}(\text{diss})$ for the dissociation of bis. H^+ in H_2O -DMSO and H_2O -DME at 25 °C

of the base is presumably the largest single factor causing an increased affinity of the base towards the organic solvent. The presence of resonance between the lone pair of electrons on the two nitrogen atoms and the azine rings for 1,10-phenanthroline may lead to a difference in the extent of the interaction of the two bases with the solvent dipoles. Fig (5) represents a comparison between $\Delta G_t^{\circ}(B)$ with the corresponding values obtained in other aqueous organic solvent[3,4,11-14] mixtures. It is clear that the order of non-spontaneity is:

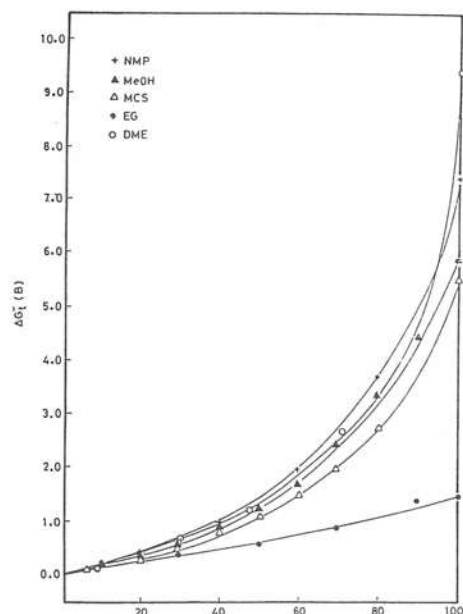


This behaviour is in accordance with the previous comment that tris is essentially hydrophilic in nature[11], which is possibly due to the participation of the three terminal hydroxy groups and the amino group in the hydrogen-bonded structure of water, which naturally becomes less important with the decrease in the proportion of water in the mixed medium.

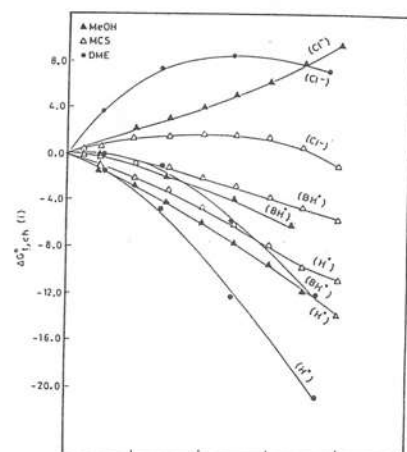
Since, the acidity of the hydroxyl group in (MeOH), (MCS), and (EG) is weaker than that in pure H_2O due to the inductive effect of (- CH_3) group in MeOH and the intermolecular hydrogen-bonding present in the two other organic solvents. Therefore, H_2O will be less basic than any of these solvent mixtures. The methoxy groups, (- OCH_3), which attached to the two flexible etherial oxygen atoms, make DME more hydrophilic and more basic than the above organic solvents by inductive effect. These differences in solvent basicities will in turn affect the interactions between the lone pair of electrons on the NH_2 group of tris and the hydrogen atom of the solvent mixtures. The resulting values of $\Delta G_t^{\circ}(B)$ should thus be expected to increase continuously as has been found experimentally. As far as aqueous NMP mixtures are concerned, the non-aqueous component being protophilic in nature, this means that they are more likely to be weaker solvating media for tris as compared to other solvents.

Variation of $\Delta G_t^{\circ}(BHCl)$: From Table (6) it is seen that, $\Delta G_t^{\circ}(BHCl)$ for tris and bis-hydrochlorides increases with increasing organic solvent composition, which suggests that they are more strongly solvated by water than by the mixed solvent. The higher values of $\Delta G_t^{\circ}(BHCl)$ obtained for tris HCl than bis HCl may be explained as due to structural effects as discussed before. On the other hand, values of $\Delta G_t^{\circ}(BHCl)$ for 2,2-bipyridine and 1,10-phenanthroline are found to be negative and decrease initially and thereafter increase with increasing addition of DME. This indicates that, with the first addition of the solvent the hydrochloride of these bases are better solvated by the organic solvent than by water. Fruitful

discussion on the transfer energies for neutral ion combination is possible with knowledge of the transfer free energies of individual ions in this solvent system.



wt.% of organic solvent
Fig. (5) values of $\Delta G^{\circ}_1(B)$ for transfer of tris from water to water- non- aqueous organic solvents at 25 °C



wt.% of non-aqueous solvent
Fig. (6) values of $\Delta G^{\circ}_{1,chl}(i)$ for Cl^- , tris. H^+ , and H^+ ions from water to water/1,2 -dimethoxyethane at 25 °C

Variation of $\Delta G^{\circ}_1(BH^+)$: Table (6), shows that a general trend of increasing negative values of $\Delta G^{\circ}_{1,chl}(BH^+)$ with increasing the organic solvent content in the medium. Tris. H^+ and bis. H^+ ions are likely to be solvated in the mixed solvents through the partially protonated hydrogen atoms attached to the nitrogen atom and the negatively charged oxygen center of the solvent dipoles[16], where the negative charge densities on the two oxygen atoms in DME is greater than in H_2O and since the ions have terminal hydroxyl groups and the overall species is positively charged, solvation may also occur through these terminal hydroxy groups, imparting an increasing negative contribution to $\Delta G^{\circ}_{1,chl}(BH^+)$. Apparently, the number of solvation centers of tris. H^+ is six, while for bis. H^+ is five leading to more negative values in $\Delta G^{\circ}_{1,chl}(BH^+)$ for bis. H^+ .

For the case of 2,2-bipyridinium and 1,10-phenanthroline ions, the presence of $2(NH)^+$ groups, may also be taking part in the solvation with the solvent dipoles. Thus, the nature of interaction of the groups in both protonated bases would be similar, since they can not show resonating structure. This effect causes values of $\Delta G^{\circ}_{1,chl}(BH^+)$ to be approximately the same. Therefore, the difference in the solvent effect on the dissociation of both cationic acids reflected in $\Delta G^{\circ}_1(diss)$ values is primarily due to the difference in $\Delta G^{\circ}_1(B)$ values for the two bases.

Although $\Delta G^{\circ}_{1,chl}(BH^+)$ for all these studied bases is positive in the region of (50-90) wt.% DME due to the higher dielectric constant of water than any of the mixed solvents, the observed overall values of $\Delta G^{\circ}_{1,chl}(BH^+)$ are negative, which indicates that the solvation of BH^+ ions arising from specific ion-dipole interactions outweighs the electrostatic or the secondary solvation effect[21].

Fig. (6) compares values of $\Delta G^{\circ}_{1,chl}(tris.H^+)$, $\Delta G^{\circ}_{1,chl}(Cl^-)$ and $\Delta G^{\circ}_{1,chl}(H^+)$ in H_2O -DME with those obtained in aqueous mixtures of MeOH and MCS. It is observed that, values of $\Delta G^{\circ}_{1,chl}(BH^+)$ usually decrease with increasing the wt.% of the studied solvents and the most stabilization of tris. H^+ takes place in H_2O -DME which confirms the higher basicity of DME than the other solvents as already explained before. $\Delta G^{\circ}_{1,chl}(Cl^-)$ increases monotonically in H_2O -MeOH mixtures, whereas the values in H_2O -DME or H_2O -MCS become increasingly positive up to about 40 wt. % of the solvent beyond which the values assume less positive values resulting in a distinguished maximum. Since, the positive charge on the hydroxyl hydrogen atom in water is greater than in DME, MeOH, or MCS due to inductive effect, it is expected that the transfer of chloride ion from water to aqueous mixtures of these solvents would be increasing positive with increasing the solvent content as experimentally found in H_2O -MeOH mixtures. The observed maximum in either H_2O -DME or H_2O -MCS is however, difficult to be explained. $\Delta G^{\circ}_{1,chl}(H^+)$ increases negatively with increasing the solvent composition for all studied systems. This indicates that despite the positive contribution to $\Delta G^{\circ}_{1,chl}(H^+)$ in these aquo-solvents, the stronger protophilism of the organic solvent plays the important role in controlling this behaviour than the electrostatic effect.

Now, from the trend of changing $\Delta G^{\circ}_{1,chl}(BH^+)$ as well as $\Delta G^{\circ}_{1,chl}(H^+)$ with solvent composition, the trend of changing basicities of the organic solvents decreases in the order DME

> MeOH > MCS. This result has been earlier suggested during the interpretation of the thermodynamic transfer parameters of tris and bis in these mixed solvents.

Variation of ΔH and ΔS of transfer for various species:

It is evident from ΔS_i° (diss) (Table7), that the values are generally negative. This observation is found consistent with the result obtained for glycine in DME-H₂O[22] and in 1,2-propanediol mixture[22]. These results have been explained as follows[5]: The mixed aqueous solvents are less structured than pure, H₂O, therefore they can be regarded as offering less resistance than pure H₂O to solvent reorientation. For this reason, ions or centers of charges, will orient solvent molecules more readily in these mixed media than in water, which results in negative ΔS_i° (diss).

From Table 7 the observed increase in values of ΔS_i° (tris) or ΔS_i° (bis) indicates decreasing order of the mixed solvents around the hydrophilic groups (-CH₂OH) in the two molecules through the reinforcement of the hydrogen – bonded three dimensional structure "bulky iceberge" of liquid water induced by hydrocarbon moieties of the solvent. On further addition of DME, however, the "Supernormal" structure is rapidly broken up with the commencement of formation of the DME-H₂O hydrogen-bonded associates, the so-called two-dimensional structure[1].

From Table 7 it is clear that higher observed negative values of ΔS_i° (HCl) as compared with (tris HCl) or ΔS_i° (bis HCl) in all solvent mixtures suggest that HCl is more effective in orienting solvent molecules i.e. the net amount of order created by HCl in H₂O-DME solvents is more than in H₂O and accordingly, it may be responsible for the general increase in the negative values of the transfer entropy for the composite process ΔS_i° (diss).

Table (7) Values of the enthalpies and entropies of transfer for various species involving protonated base, base, base hydrochloride and HCl in H₂O-DME solvent at 25 °C.

wt. % DME	tris.H ⁺		tris		tris HCl		HCl	
	ΔH_i° (diss)/ K Jmol ⁻¹	ΔS_i° (diss)/ Jmol ⁻¹ K ⁻¹	ΔH_i° (B)/ K Jmol ⁻¹	ΔS_i° (B)/ K Jmol ⁻¹	ΔH_i° (BHCl)/ K Jmol ⁻¹	ΔS_i° (BHCl)/ Jmol ⁻¹ K ⁻¹	ΔH_i° (HCl)/ K Jmol ⁻¹	ΔS_i° (HCl)/ Jmol ⁻¹ K ⁻¹
10.8	-4.89	-12.5	1.46	-4.2	6.34	15.6	0.02	-1.1
27.5	-4.69	-4.9	5.13	14.8	8.01	11.2	-1.81	-8.5
48.7	-7.10	-8.7	5.17	12.8	4.97	-10.5	-7.30	-32.0
74.3	-4.36	-1.9	11.29	28.8	-2.15	-53.3	-17.80	-84.0
100			11.5	6.8				
	bis. H ⁺		Bis		bis HCL		HCl	
12.1	-25.04	-82.9	8.5	2.74	27.76	89.9	0.02	-1.5
27.2	-18.52	-56.6	19.9	6.27	23.09	68.0	-1.70	-8.5
48.2	-18.71	-45.9	17.3	5.54	17.25	42.2	-7.0	-30.0
79.3	-2.29	-5.0	16.4	5.29	-11.62	-78.6	-19.2	-100.0
100			-11.2	1.86				

ΔH_i° (BHCl) = ΔH_i° (HCl) + ΔH_i° (B) - ΔH_i° (diss), ΔS_i° (BHCl) = ΔS_i° (HCl) + ΔS_i° (B) - ΔS_i° (diss), ΔH_i° (B) = ΔH_i° (B) - ΔH_i° (B), ΔS_i° (B) = ΔS_i° (B) - ΔS_i° (B), * These data are taken from reference (9).

Experimental

Tris and bis (B.D.H., A.R.) were recrystallized from a water methanol mixture and pure methanol (MeOH), respectively, followed by drying at 105 °C and 55 °C and stored over anhydrous calcium chloride (m.p. of tris. = 171 °C) (m.p. of bis=110 °C). DME (Aldrich grade type) was first purified by refluxing with lithium aluminium hydride overnight, then distilled. The middle fraction was then used (b.p. 84.5 °C).

High purity water (specific conductivity less than 0.7x10⁻⁶ Ω⁻¹ cm⁻¹) was obtained by double distillation of deionized water. Standard aqueous stock solutions of hydrochloric acid were prepared from constant-boiling acid and standardized by gravimetric determination of chloride as silver chloride.

Hydrogen electrodes used were of platinum foil freshly covered with platinum black from Beckmann Instruments platinizing solution. Silver chloride electrodes were the electrolytic type prepared according to Brown.[8] In this work, the all glass cell without liquid junction has been described previously.[4]

Buffered stock solutions were prepared by dissolving an accurately weighed quantity of tris or bis in a known weight of standard hydrochloric acid in a measuring flask. Buffer solutions of five different ionic strengths between 0.01 to 0.05 mol kg⁻¹, were prepared for each respective solvent composition by mixing accurately known quantities of the buffered stock solutions, of DME, and of conductivity water in 50 mL measuring flasks.

The emf values were measured using a precision Decade Pye potentiometer (model 7600) of resolution 0.1 mV. A moving coil galvanometer (type Nok 104) which has a sensitivity of 73 mm/μA was used as a null detector.

The cell was kept at constant temperature in a Colora K-5 type Ultra thermostat of resolution 0.01 °C. The emf measurements were made at intervals of 5 °C from 25 ° to 45 °C. Readings were taken at periods of 10-15 min until 2 or 3 successive readings were constant within ± 0.1 mV. About 2-3 h were required for the attainment of the equilibrium at 25 °C and an additional 1-1.5 h for each higher temperature.

The solubilities of tris and bis were determined according to a previously reported procedure[4]. Three aliquots from each of the filtered saturated solution were analyzed.

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Influence de la Déformation Plastique sur les Propriétés des Films de Passivation Formés sur les Aciers Inoxydables. Relations avec la Corrosion Sous Contrainte

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Résumé

La recherche concerne la corrosion sous contrainte de l'acier inoxydable du type AISI 304 dans les solutions concentrées de H₃BO₃ additionnées de NaCl et portées à l'ébullition. La caractérisation des films passifs est conduite sur des éprouvettes soumises à l'action des milieux corrosifs soit dans l'état recuit soit dans l'état écroui. L'étude montre que la déformation plastique du substrat métallique réduit très fortement la résistance de polarisation, la stabilité vis-à-vis de la réduction cathodique et modifie la réponse obtenue par mesures d'impédance. Par ailleurs, les mesures de capacité et l'application de la méthode de Mott-Schottky montrent que l'effet de l'écrouissage est plus marqué quand la semi-conductivité des films est de type p. L'étude associe aux deux types de structure électronique (type n et type p) deux formes de distribution de charges électriques (de signe opposé) entre la zone de charges d'espace et celle des dislocations présentes dans les couches superficielles du substrat métallique.

Mots clés: corrosion sous contrainte, déformation plastique, propriétés des films passifs.

Abstract

This investigation deals with the stress corrosion cracking of AISI 304 stainless steel in concentrated boiling H₃BO₃ solution with NaCl additions. The characterisation of the passive film was carried out using samples submitted to the corrosive environment, in both the annealed and cold worked states. The study shows that plastic deformation of the metallic material reduces polarisation resistance and film stability (in terms of cathodic reduction). Furthermore, from the capacitance measurements, using the Mott-Schottky approach, it can be concluded that the influence of plastic deformation is higher when the passive film reveals p-type conductivity. Based on the electronic band structure of n-type and p-type semiconductors, a representation for a possible correlation of charges of opposite sign between space charges and near surface dislocation is given.

Key words: stress corrosion, plastic deformation, passive film properties.

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