Thermochimica Acta, 55 (1982) 315–326
Elsevier Scientific Publishing Company, Amsterdam—Printed in The Netherlands

STANDARD POTENTIALS OF THE SILVER–SILVER TUNGSTATE, SILVER–SILVER PHOSPHATE, AND SILVER–SILVER ARSENATE ELECTRODES IN WATER–DIOXANE AND WATER–UREA MIXTURES AND RELATED THERMODYNAMIC FUNCTIONS

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(Received 25 November 1981)

ABSTRACT

The standard potentials of the silver–silver tungstate, silver–silver phosphate and silver–silver arsenate electrodes in four different compositions of water–dioxane and water–urea mixtures at seven different temperatures from 5 to 35°C have been determined from EMF measurements of cells of the type Ag(s), AgCl(s), NaCl(c)//$Na_xZ(c/x)$, $Ag_xZ(s)$, Ag(s), where x is 2 or 3, and Z is WO_4, PO_4 or AsO_4. These values have been used to evaluate the transfer thermodynamic quantities accompanying the transfer of 1 g ion of WO_4^{2-}, PO_4^{3-} or AsO_4^{3-} ion from the standard state in water to the standard state in water–dioxane or water–urea mixtures.

INTRODUCTION

In a previous communication [1], we reported the standard potentials of the silver–silver tungstate, silver–silver phosphate and silver–silver arsenate electrodes in aqueous medium at different temperatures. With a view to elucidating the ion–solvent interactions in binary solvent systems [2], the present work was undertaken to determine the standard potentials of these electrodes in various compositions of water–dioxane and water–urea mixtures over the temperature range 5–35°C.

EXPERIMENTAL

The sodium chloride, sodium tungstate, sodium phosphate and sodium arsenate were the same samples used in the previous study [1]. Dioxane was

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purified as described earlier [3]. Urea (BDH, Analar) was used without further purification. The solvent mixtures of various mass percentages were prepared as described previously [2,3]. Stock solutions of various sodium salts were prepared by dissolving the appropriate weighed amounts of the sodium salts in known volumes of water–dioxane and water–urea mixtures of various compositions. Solutions for EMF measurements were prepared from stock solutions by double dilution method.

Preparation of the silver–silver chloride, silver–silver tungstate, silver–silver phosphate and silver–silver arsenate electrodes, preparation of the cell solutions, setting up of the cells, the EMF and conductance measurements were essentially similar to the procedures described earlier [1,2].

RESULTS AND DISCUSSION

As usual [1], the standard molar potentials, E_c^0 were obtained by the method of extrapolating [1–3] the auxiliary functions, E_c^0, given by

$$E_c^{0\prime} = E - \frac{1}{2}k\log(2c) - \frac{1}{2}k\left[\frac{4A\sqrt{3c/2}}{1+\sqrt{3c/2}} - \frac{2A\sqrt{c}}{1+\sqrt{c}}\right] + E^0_{\mathrm{Ag,AgCl}} - E_{\mathrm{j}}$$

$$= E^0_{\mathrm{Ag,Ag_2WO_4}} + bc \tag{1}$$

for the silver–silver tungstate electrode, and

$$E_c^{0\prime} = E - \frac{1}{3}k\log(3c) - k\left[\frac{3A\sqrt{2c}}{1+\sqrt{2c}} - \frac{A\sqrt{c}}{1+\sqrt{c}}\right] + E^0_{\mathrm{Ag,AgCl}} - E_j$$

$$= E^0_{\mathrm{Ag,Ag_3Z}} + bc \tag{2}$$

where Z is PO_4 or AsO_4, for the silver–silver phosphate and silver–silver arsenate electrodes, to the molarity, $c = 0$. In the foregoing equations $E^0_{\mathrm{Ag,AgCl}}$ is the standard potential of the silver–silver chloride electrode, A is the Debye–Huckel constant, and is known over the temperature range under investigation for various water–dioxane [4] and water–urea [5] mixtures, E is the observed EMF of the cell, Ag(s), AgCl(s), NaCl(c)//$\mathrm{Na}_x\mathrm{Z}(c/x)$, $\mathrm{Ag}_x\mathrm{Z}$(s), Ag(s), k is 2.3026 RT/F, E_{j} is the liquid junction potential, and b is $1/2k\{2\beta_{\mathrm{Cl^-}} - (3/2)\beta_{\mathrm{WO_4^{2-}}}\}$ in eqn. (1), or $k\{\beta_{\mathrm{Cl^-}} - (2/3)\beta_{\mathrm{Z^{3-}}}\}$ in eqn. (2), where β is the usual constant in the Debye–Huckel expression for the activity coefficient, i.e.

$$-\log y_{\mathrm{i}} = \frac{AZ_{\mathrm{i}}^2\sqrt{\mu}}{1+\sqrt{\mu}} - \beta_{\mathrm{i}}\mu$$

where i is Cl^-, WO_4^{2-}, PO_4^{3-} or AsO_4^{3-}.

As previously [1–3], the values of the liquid junction potentials, E_{j}, were calculated and found to vary in the range 0.001–0.009 V in all solvents for all

TABLE 1

Standard molar potentials (E_c^0 in abs. volts) for the Ag(s)–Ag_2WO_4(s), WO_4^{2-}, Ag(s)–Ag_3PO_4(s), PO_4^{3-} and Ag(s)–Ag_3AsO_4(s), AsO_4^{3-} electrodes in water–dioxane and water–urea mixtures from 5 to 35°C

Wt.% organic solvent	t(°C)						
	5	10	15	20	25	30	35
Ag(s)–Ag_2WO_4(s), WO_4^{2-} electrode							
0	0.4692	0.4598	0.4528	0.4435	0.4351	0.4282	0.4200
10% Dioxane	0.5101	0.4997	0.4933	0.4806	0.4708	0.4625	0.4529
20% Dioxane	0.4923	0.4831	0.4769	0.4721	0.4617	0.4518	0.4416
30% Dioxane	0.4739	0.4646	0.4616	0.4510	0.4422	0.4345	0.4231
40% Dioxane	0.3935	0.3873	0.3769	0.3682	0.3619	0.3557	0.3460
11.52% Urea	0.4831	0.4741	0.4684	0.4637	0.4555	0.4502	0.4439
20.31% Urea	0.4852	0.4784	0.4709	0.4673	0.4598	0.4551	0.4501
29.64% Urea	0.5117	0.5077	0.5040	0.4974	0.4901	0.4861	0.4817
36.83% Urea	0.5175	0.5128	0.5079	0.5016	0.4969	0.4933	0.4883
Ag(s)–Ag_3PO_4(s), PO_4^{3-} electrode							
0	0.4917	0.4797	0.4675	0.4605	0.4523	0.4456	0.4370
10% Dioxane	0.4618	0.4511	0.4433	0.4320	0.4219	0.4108	0.4014
20% Dioxane	0.4432	0.4258	0.4124	0.4013	0.3920	0.3816	0.3708
30% Dioxane	0.4339	0.4222	0.4103	0.3977	0.3860	0.3743	0.3622
40% Dioxane	0.4305	0.4145	0.3995	0.3888	0.3764	0.3629	0.3509
11.52% Urea	0.4872	0.4807	0.4740	0.4687	0.4603	0.4526	0.4454
20.31% Urea	0.5019	0.4930	0.4854	0.4782	0.4704	0.4633	0.4559
29.64% Urea	0.5318	0.5238	0.5160	0.5066	0.5008	0.4945	0.4861
36.83% Urea	0.5440	0.5369	0.5292	0.5227	0.5156	0.5097	0.5024
Ag(s)–Ag_3AsO_4(s), AsO_4^{3-} electrode							
0	0.4391	0.4288	0.4173	0.4114	0.4008	0.3938	0.3849
10% Dioxane	0.4238	0.4170	0.4079	0.3973	0.3889	0.3780	0.3685
20% Dioxane	0.4158	0.4020	0.3878	0.3753	0.3634	0.3505	0.3386
30% Dioxane	0.3822	0.3710	0.3604	0.3519	0.3425	0.3321	0.3241
40% Dioxane	0.3744	0.3602	0.3441	0.3316	0.3210	0.3077	0.2957
11.52% Urea	0.4807	0.4718	0.4622	0.4551	0.4424	0.4337	0.4226
20.31% Urea	0.4839	0.4757	0.4656	0.4576	0.4486	0.4411	0.4304
29.64% Urea	0.4997	0.4889	0.4819	0.4728	0.4634	0.4551	0.4468
36.83% Urea	0.5034	0.4968	0.4886	0.4800	0.4717	0.4631	0.4557

temperatures. The values of E_c^0 obtained on extrapolating $E_c^{0\prime}$ to $c = 0$ for the silver–silver tungstate, silver–silver phosphate and silver–silver arsenate electrodes are presented in Table 1. The average standard deviation in the values of E_c^0 is ±0.3 mV.

Standard potentials on the molal (E_m^0), mole fraction (E_N^0) and molar (E_c^0) scales (correlated by the usual equation [6]) at various temperatures for any solvent were fitted by the method of least-squares, to an equation of the form [7]

$$E_{\mathrm{p}}^{0} = A + BT + CT \ln T + DT^{2}/2 \tag{3}$$

TABLE 2

Constants for eqn. (3) for molar (c). molar (m) and mole fraction (N) scales in water–dioxane and water–urea mixtures

Wt.% organic solvent	p	A	$-10^2 B$	$10^3 C$	$10^5 D$
Ag(s)–Ag$_2$WO$_4$(s), WO$_4^{2-}$ electrode					
0	c	1.1760	0.062505	−0.58581	0.99182
	m	1.1378	0.14016	−0.96556	1.1700
	N	1.2016	0.14236	−0.60278	1.0705
10% Dioxane	c	0.99955	−0.020407	−0.38951	0.16379
	m	1.0230	−0.076414	−0.54856	0.34233
	N	1.0401	0.010231	−0.53386	0.37390
20% Dioxane	c	−0.16130	0.38087	2.0855	−4.0150
	m	−0.22804	0.20841	1.8069	−3.9589
	N	−0.22848	0.31432	1.8922	−4.0178
30% Dioxane	c	−0.08285	0.17914	1.5161	−3.4107
	m	−0.065312	0.35828	1.8637	−3.5792
	N	−0.09576	0.33217	1.7141	−3.5472
40% Dioxane	c	1.1011	0.12141	−0.47074	0.94957
	m	1.1056	0.32672	−0.048407	0.69938
	N	1.0739	0.30488	−0.18249	0.71625
11.52% Urea	c	1.1273	0.15105	−0.37504	0.93591
	m	1.1874	0.28539	-0.18047	0.95495
	N	1.1287	0.11318	−0.60770	1.1098
20.31% Urea	c	1.3035	0.056652	−0.85175	1.7378
	m	1.4223	0.34502	−0.41475	1.7289
	N	1.3174	0.040914	−1.0537	1.9204
29.64% Urea	c	0.5132	−0.39598	−0.64489	−0.23984
	m	0.5466	−0.21423	−0.31283	−0.37367
	N	0.5875	−0.077751	−0.22040	−0.34114
36.83% Urea	c	1.005	−0.13898	−0.82024	1.0602
	m	1.0842	0.17055	−0.28346	0.89584
	N	1.0708	0.22598	−0.29146	0.89799
Ag(s)–Ag$_3$PO$_4$(s), PO$_4^{3-}$ electrode					
0	c	2.4068	0.22377	−1.9833	4.6821
	m	2.4550	0.35939	−1.7661	4.6532
	N	2.3890	0.17280	−2.2164	4.8065
10% Dioxane	c	0.74017	0.087957	0.17084	−0.77968
	m	0.70801	−0.053774	−0.090115	−0.66140
	N	0.76537	0.11336	0.037562	−0.61218
20% Dioxane	c	2.7920	0.12576	−2.7201	5.8359
	m	2.8280	0.27548	−2.4605	5.7652
	N	2.8274	0.34305	−2.4574	5.7636

TABLE 2 (continued)

Wt.% organic solvent	p	A	$-10^2\,B$	$10^3\,C$	$10^5\,D$
30% Dioxane	c	1.1514	0.3397	0.13862	0.026195
	m	1.0704	0.1519	−0.15319	0.061485
	N	1.0249	0.10628	−0.32256	0.072304
40% Dioxane	c	2.0058	0.40741	−0.92729	2.6066
	m	1.9916	0.58013	−0.54725	2.3414
	N	1.8904	0.22188	−1.2993	2.6204
11.52% Urea	c	0.37039	0.09462	0.64213	−1.6170
	m	0.4334	0.30972	1.0044	−1.7042
	N	0.39185	0.20351	0.69326	−1.5884
20.31% Urea	c	1.226	0.18289	−0.37617	0.96399
	m	1.3372	0.33838	−0.21281	1.1264
	N	1.2176	0.080098	−0.73208	1.2007
29.64% Urea	c	1.3217	−0.062351	−0.99831	1.5490
	m	1.3219	−0.14269	−1.1778	1.6870
	N	1.3950	0.24777	−0.58983	1.4570
36.83% Urea	c	1.0939	−0.099964	−0.75257	0.90454
	m	1.1550	0.18231	−0.24774	0.72021
	N	1.1662	0.33291	−0.087946	0.66412
Ag(s)–Ag_3AsO_4(s), AsO_4^{3-} electrode					
0	c	1.6254	0.24932	−0.85987	2.204
	m	1.5930	0.069794	−1.1986	2.3677
	N	1.6217	0.24959	−1.0038	2.3003
10% Dioxane	c	0.2845	−0.023584	0.51663	−1.8992
	m	0.29443	−0.071772	0.39458	−1.7791
	N	0.35867	0.13679	0.60025	−1.7655
20% Dioxane	c	1.6834	0.1720	−0.99228	1.9741
	m	1.7061	0.29206	−0.77594	1.8998
	N	1.6712	0.27878	−0.89554	1.9019
30% Dioxane	c	1.4783	0.39319	−0.39153	1.5763
	m	1.4201	0.32420	−0.46334	1.5166
	N	1.3821	0.14842	−0.92133	1.7401
40% Dioxane	c	2.0984	0.39954	−1.1664	3.1351
	m	2.0875	0.25519	−1.3956	3.1766
	N	2.002	0.18045	−1.6374	3.2587
11.52% Urea	c	0.36645	−0.02632	0.48319	−1.8503
	m	0.47083	0.30664	1.0367	−1.9720
	N	0.40517	0.21162	0.78538	−1.9544
20.31% Urea	c	0.9407	0.24471	0.19482	−0.21035
	m	0.87292	0.21851	0.086157	−0.04938
	N	0.97764	0.24359	−0.01002	0.02902
29.64% Urea	c	1.1171	−0.016659	−0.60225	0.71938
	m	1.1429	0.13539	−0.32292	0.46492
	N	1.1239	0.10217	−0.50519	0.68475
36.83% Urea	c	0.75602	0.09039	0.13784	−0.5601
	m	0.7788	0.11338	0.14482	−0.49486
	N	0.76727	0.17819	0.15444	−0.50135

where p is c, m, or N, and T is any temperature in Kelvin. The constants A, B, C, and D of eqn. (3) for different solvent mixtures are shown in Table 2.

As before [1,2], the standard thermodynamic quantities (ΔG^0, ΔH^0, and ΔS^0) for the electrode reaction

$$\mathrm{Ag}_x\mathrm{Z(s)} + xe \rightleftharpoons x\,\mathrm{Ag(s)} + \mathrm{Z}^{x-}\,\mathrm{(solvated)}$$

and the standard transfer thermodynamic quantities (ΔG_t^0, ΔH_t^0 and ΔS_t^0) for the process

$$\mathrm{Z}^{x-}\,\mathrm{(in\ water)} \rightarrow \mathrm{Z}^{x-}\,\mathrm{(in\ mixed\ solvent)}$$

have been evaluated at different temperatures for various solvents. These transfer thermodynamic quantities on the mole fraction basis [6] at 25°C are summarized in Table 3, which also includes the changes in electrostatic(el) and chemical(ch) contributions [2,6] to these transfer thermodynamic quantities.

As usual [1,2], the values of the changes in electrostatic Gibbs energy ($\Delta G^0_{t,el}$) and the electrostatic entropy ($\Delta S^0_{t,el}$) of transfer have been estimated by the well-known Born equations

$$\Delta G^0_{t,el} = (Ne^2/2)(\epsilon_s^{-1} - \epsilon_w^{-1})(r_+^{-1} + r_-^{-1}) \tag{4}$$

and

$$\Delta S^0_{t,el} = (-Ne^2/2)(\epsilon_s^{-1}\theta_s^{-1} - \epsilon_w^{-1}\theta_w^{-1})(r_+^{-1} + r_-^{-1}) \tag{5}$$

where the symbols have their usual significance. The values of ϵ and θ for water and different mixed solvents are taken from the literature [4b,5]. The radius of the silver ion (r_+) may be taken as 1.26 Å [6] and those of the $\mathrm{WO_4^{2-}}$, $\mathrm{PO_4^{3-}}$ and $\mathrm{AsO_4^{3-}}$ ions (r_-) as 2.57, 2.38, and 2.48 Å, respectively [8].

The values of $\Delta H^0_{t,el}$ were obtained from a knowledge of $\Delta G^0_{t,el}$ and $\Delta S^0_{t,el}$. The chemical parts of these quantities were evaluated from the relation [2]

$$\Delta R^0_t = \Delta R^0_{t,el} + \Delta R^0_{t,ch} \tag{6}$$

where R is any thermodynamic quantity, e.g., G, H, or S.

An inspection of Table 1 shows that the values of the standard potential of the silver–silver tungstate electrode are less in water than in water–dioxane mixtures (except in water + 40 mass % dioxane), whereas the $E°$ values for the silver–silver phosphate and silver–silver arsenate electrodes are higher in water than in water–dioxane mixtures. The observed decrease in the $E°$ values with increase in dioxane content of the solvent mixtures suggests that the standard electrode potential decreases with the decrease in dielectric constant of the water–dioxane mixtures. This is consistent with the conclusions based on purely electrostatic considerations by Feakins and French [9] using the Born equation. However, the higher E^0 values of the silver–silver tungstate electrode in water–dioxane mixtures up to 30 mass %

composition of dioxane than in water, despite their lower dielectric constants, may be explained by the fact that WO_4^{2-} ions are more solvated in these solvents than in water.

The E^0 values of these electrodes in various compositions of water–urea mixtures are found to be more than that in water and increase with the increase in urea content in water, lending support to the linear correlation between the E^0 and reciprocal of dielectric constant of the solvent concerned. The observed increase in the E^0 values of these electrodes with the increase in dielectric constant of the water–urea mixtures as the proportion of urea increases, is in agreement with the electrostatic charging (Born) effect of the media. The higher values of E^0 in various compositions of water–urea mixtures than in water may also be explained by the higher basicity of the water–urea mixtures which decreases the Gibbs free energy of the electrode reaction, by decreasing the free energy of Z^{x-} (solvated), where Z is WO_4 and x is 2, or Z is PO_4 or AsO_4 and x is 3, in these solvents.

It is known that the Gibbs energy of transfer is an important index of the differences in interactions of the ions and solvent molecules in the two different media. As can be seen from Table 3, the values of ΔG_t^0 for the WO_4^{2-} ion appear to be negative, and become decreasingly negative up to 30 mass % composition of water–dioxane mixtures, whereas in water + 40 mass % dioxane, the values are positive. The ΔG_t^0 values for the transfer of PO_4^{3-} and AsO_4^{3-} ions from water to water–dioxane mixtures are positive and become more and more positive with increase of mole fraction of dioxane in the water–dioxane mixtures. But the values of ΔG_t^0 for the transfer of WO_4^{2-}, PO_4^{3-} and AsO_4^{3-} ions from water to water–urea mixtures appear to be negative and become increasingly negative with increase of urea content in the water–urea mixtures. The negative values of ΔG_t^0 (except in 40 mass % dioxane for WO_4^{2-} ion and in water–dioxane mixtures for PO_4^{3-} and AsO_4^{3-} ions) indicate that the transfer of WO_4^{2-}, PO_4^{3-} and AsO_4^{3-} ions from water to water–dioxane or water–urea mixtures is favourable. Thus, WO_4^{2-}, PO_4^{3-} and AsO_4^{3-} ions appear to be in a lower Gibbs energy state and hence, more strongly stabilized in water–dioxane or water–urea mixtures. However, the observed increase in ΔG_t^0 values in the case of WO_4^{2-} ion with increase in dioxane content in water suggests that the transfer of WO_4^{2-} ion from water to water–dioxane mixtures becomes decreasingly favourable up to 30 mass % dioxane and finally, becomes unfavourable in water + 40 mass % dioxane mixture. The increased positive values of ΔG_t^0 for PO_4^{3-} and AsO_4^{3-} ions with the increased proportion of dioxane in water suggest that the transfer of these ions from water to the mixed solvents is increasingly unfavourable. Thus, PO_4^{3-} and AsO_4^{3-} ions appear to be in a higher Gibbs energy state and, therefore, less stabilized in water–dioxane mixtures than in water.

As the chemical contribution to the Gibbs energy of transfer of an ion in solution is attributed to the solvation of ions, $\Delta G_{t,ch}^0$ of the WO_4^{2-}, PO_4^{3-} and AsO_4^{3-} ions should reflect the solvating capacities of the solvent concerned

TABLE 3

Transfer thermodynamic quantities[a] (mole fraction scale) in different water–dioxane and water–urea mixtures at 25°C

	Wt.% organic solvent							
	Wt.% dioxane				Wt.% urea			
	10	20	30	40	11.52	20.31	29.64	36.83
Ag(s)–Ag_2WO_4(s), WO_4^{2-} electrode								
$-\Delta G_t^0$	7.72	6.55	3.88	−10.76	4.46	5.75	12.38	13.88
$\Delta G_{t,el}^0$	1.34	3.05	5.37	8.65	−0.67	−1.11	−1.51	−1.76
$-\Delta G_{t,ch}^0$	9.06	9.60	9.25	−2.11	3.80	4.63	10.88	12.12
$-\Delta S_t^0$	57	34	28	−26	−73	−102	−107	−142
$-\Delta S_{t,el}^0$	11	22	38	58	−4	−7	−10	−12
$\Delta S_{t,ch}^0$	−46	−12	10	34	69	95	97	130
ΔH_t^0	−24.6	−16.5	−12.1	18.5	17.2	24.6	19.6	28.4
$-\Delta H_{t,el}^0$	1.8	3.5	5.8	8.8	−0.5	−0.9	−1.5	−1.6
$\Delta H_{t,ch}^0$	−22.7	−13.1	−6.3	27.2	16.6	23.7	18.1	26.8
Ag(s)–Ag_3PO_4(s), PO_4^{3-} electrode								
ΔG_t^0	7.52	15.44	15.29	17.01	−3.34	−6.88	−16.42	−21.49

$\Delta G^0_{t,el}$	1.38	3.13	5.51	8.88	−0.69	−1.15	−1.54	−1.80
$\Delta G^0_{t,ch}$	6.14	12.30	9.78	8.13	−2.66	−5.73	−14.88	−19.68
ΔS^0_t	−133	−135	−220	−250	35	36	47	89
$\Delta S^0_{t,el}$	−11	−23	−38	−60	4	7	10	12
$\Delta S^0_{t,ch}$	−122	−112	−182	−190	31	29	37	78
ΔH^0_t	−32.0	−24.7	−50.3	−57.5	7.2	3.7	−2.4	5.2
$\Delta H^0_{t,el}$	−1.9	−3.6	−5.9	−9.0	0.6	0.9	1.5	1.7
$\Delta H^0_{t,ch}$	−30.1	−21.1	−44.3	−48.6	6.6	2.8	−3.9	3.5
Ag(s)–Ag_3AsO_4(s), AsO_4^{3-} electrode								
ΔG^0_t	2.57	8.83	13.52	18.44	−13.05	−15.21	−20.37	−23.39
$\Delta G^0_{t,el}$	1.36	3.09	5.43	8.75	−0.68	−1.13	−1.52	−1.78
$\Delta G^0_{t,ch}$	1.21	5.74	8.09	9.68	−12.37	−14.08	−11.84	−21.61
$-\Delta S^0_t$	71	218	30	201	92	15	0.2	−35
$\Delta S^0_{t,el}$	−11	−22	−38	−59	4	7	10	11
$-\Delta S^0_{t,ch}$	60	196	−7	142	96	22	10	−24
$-\Delta H^0_t$	18.6	56.2	−4.4	41.6	40.4	19.8	20.4	12.9
$\Delta H^0_{t,el}$	−1.9	−3.5	−5.8	−8.9	0.5	0.9	1.5	1.6
$-\Delta H^0_{t,ch}$	16.8	52.7	−10.3	32.8	40.9	20.7	21.9	14.5

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[a] ΔG^0 in kJ mole^{-1}; ΔH^0 in kJ mole^{-1}, and ΔS^0 in J mole^{-1} K^{-1}

TABLE 4

Primary medium effect, $\lim_{N \to 0}(\log {}^{s}\gamma_{w})$ (on the mole fraction scale), of the WO_4^{2-}, PO_4^{3-} and AsO_4^{3-} ions in various water–dioxane and water–urea mixtures at 25°C

Ion	Wt.% organic solvent							
	Dioxane				Urea			
	10	20	30	40	11.52	20.31	29.64	36.83
WO_4^{2-}	−1.3388	−1.1731	−0.6728	1.8629	−0.7843	−1.0108	−2.1299	−2.4410
PO_4^{3-}	1.3489	2.6522	2.7131	2.9311	−0.5426	−1.1765	−2.8601	−3.7324
AsO_4^{3-}	0.1369	0.4970	0.7708	1.0447	−2.2465	−2.6776	−3.5752	−4.1178

and water towards theses ions. The negative values of $\Delta G^0_{t,ch}$ (Table 3) thus suggest that mixed solvents possess a larger solvating capacity towards the ion concerned and are more basic than water. The increasingly negative values of $\Delta G^0_{t,ch}$ with increasing addition of urea to water amply support this view. The positive values of $\Delta G^0_{t,ch}$ in water–dioxane mixtures indicate that the mixed solvents possess smaller solvating capacities towards PO_4^{3-} and AsO_4^{3-} ions than water, and the solvating capacity decreases as the dioxane content in water increases. However, the decreasingly negative values of $\Delta G^0_{t,ch}$ with increase in dioxane content up to 30 mass % and finally positive value in water + 40 mass % dioxane suggest an increasingly stronger affinity of WO_4^{2-} ions towards water than towards dioxane in the solution.

However, it is interesting to check whether the chemical effects on the entropy and enthalpy of transfer of the WO_4^{2-}, PO_4^{3-} and AsO_4^{3-} ions should influence the solvation of ions. It is known that all structure-forming processes, including solvation of ions, are exothermic and accompanied by a decrease in entropy, and the structure-breaking processes, including desolvation of ions, are endothermic and accompanied by entropy gain. The positive and negative values of entropy of transfer and enthalpy of transfer of the WO_4^{2-}, PO_4^{3-} and AsO_4^{3-} ions from water to the mixed solvents substantiate this view.

The primary medium effect which results from a difference of the ion–solvent interactions at infinite dilution in each solvent can be represented by

$$\lim_{N \to 0} (\log {}^{s}y_{w}) = x\left[(E_N^0)_w - (E_N^0)_s\right]/2.3026(RT/F)$$

where the limit term indicates the primary medium effect and x is 2 for WO_4^{2-} ion, or 3 for PO_4^{3-} or AsO_4^{3-} ion. As the magnitude of this effect indicates the stabilization of the ion in the solvent concerned, the resulting negative magnitudes of this quantity for the WO_4^{2-}, PO_4^{3-} and AsO_4^{3-} ions in water–urea mixtures (Table 4) suggest that the escaping tendency of the ions is less in water–urea mixtures than in pure water. This is consistent with the conclusions based on the fact that the WO_4^{2-}, PO_4^{3-} and AsO_4^{3-} ions are more strongly stabilized in water–urea mixtures than in aqueous medium. But the reverse is the case with the PO_4^{3-} and AsO_4^{3-} ions in water–dioxane mixtures where the primary medium effect values appear to be positive. However, the decreasingly negative values of this quantity for the WO_4^{2-} ion with increase of dioxane content in water point to the fact that the escaping tendency of the WO_4^{2-} ion gradually increases.

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