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Standard Potentials of the Silver, Silver Bromide Electrode and the Thermodynamic Properties of Hydrobromic Acid in 1,2-Dimethoxyethane and Its Aqueous Mixtures

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The standard potentials of the silver, silver bromide electrode have been determined in 1,2-dimethoxyethane (*DME*) and in nineteen *DME* + water solvents from the e.m.f. measurements of cells of the type

$$Pt \mid H_2\,(g,\ 1\,atm) \mid HBr\,(m), solvent \mid AgBr \mid Ag$$

at intervals of 5 °C from 5 to 45 °C. The molality of HBr covered the range from 0.01 to 0.1 $mol\,kg^{-1}$. In solvents of high *DME* content, where the dielectric constant is small, it was necessary to correct for ion-pair formation. The temperature variation of the standard potential has been used to evaluate the standard thermodynamic functions for the cell reaction, and the standard quantities for the transfer of HBr from water to the respective solvents. The results have been discussed both in relation to the acid-base nature of the solvent mixtures and also their structural effects on the transfer process.

(Keywords: 1,2-Dimethoxyethane + water solvents; Electromotive force measurements; Silver, silver bromide electrode; Standard electrode potentials; Thermodynamics)

Standardpotentiale der Silber, Silberbromid-Elektrode und thermodynamische Eigenschaften von HBr in 1,2-Dimethoxyethan und 1,2-Dimethoxyethan—Wasser-Mischungen

Die Standardpotentiale der Silber, Silberbromid-Elektrode wurden in 1,2-Dimethoxyethan (*DME*) und in 19 verschiedenen *DME*—Wasser-Gemischen aus EMK-Messungen der Zelle

$$Pt \mid H_2\,(g,\ 1\,atm) \mid HBr\,(m), Lsgsm. \mid AgBr \mid Ag$$

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in Temperaturintervallen von 5° zwischen 5 und 45 °C bestimmt. Die Molalität von HBr deckte den Bereich von 0,01 bis 0,1 mol kg^{-1}. Bei Lösungen mit höherem *DME*-Gehalt — und damit niedrigen Dielektrizitätskonstanten — war es nötig, für die Bildung von Ionenpaaren eine Korrektur einzuführen. Über die Temperaturvariation wurden die thermodynamischen Größen für die Zellenreaktion und die Standardgrößen für den Transfer von HBr aus Wasser in das jeweilige Lösungsmittel bestimmt. Die Ergebnisse werden sowohl im Zusammenhang zur Säure-Base-Natur der Lösungsmittelmischungen als auch in bezug auf strukturelle Effekte im Transferprozeß diskutiert.

Introduction

Electromotive force measurements of galvanic cells involving hydrogen, silver, silver halide electrodes have been extensively used[1, 2] in recent years to determine the thermodynamics of hydrogen halides in aqueous and nonaqueous media. Such studies further offer a method of understanding the medium effects associated with the transfer of these electrolytes from water to any solvent and under suitable conditions can also be employed[3] for the estimation of transfer free energies of single ions.

Recently, we have undertaken[4] comprehensive e.m.f. measurements of HCl solutions in pure 1,2-dimethoxyethane (*DME*) and its aqueous mixtures using the silver, silver chloride electrode. The standard potentials of this electrode as well as the thermodynamic properties of hydrochloric acid in these solvents have been reported[4]. The silver, silver bromide electrode is highly reproducible[5] and, because of its low solubility, it performs better than the silver, silver chloride electrode, particularly for the determination of the dissociation constants of the nitrogen bases[6] in such dipolar aprotic solvents. *Roy* et al.[7] studied the thermodynamics of hydrobromic acid in three *DME* + water solvents containing 10, 30 and 50% (*w*/*w*) *DME* at 5-55 °C. However, no e.m.f. data have so far been reported in pure *DME* or its aqueous mixtures, other than these three mixed solvents.

In continuation of our studies on this subject[8–10], we now have measured the e.m.f. of the cell without liquid junction

$$\mathrm{Pt}\,|\,\mathrm{H_2}\,(g,\ 1\,\mathrm{atm})\,|\,\mathrm{HBr}\,(m),\ \mathrm{solvent}\,|\,\mathrm{AgBr}\,|\,\mathrm{Ag} \qquad \mathrm{(I)}$$

in nineteen *DME* + water solvent mixtures as well as in pure *DME*. The standard e.m.f. of cell (I), which is the standard potential of the silver, silver bromide electrode, has been determined for each solvent at intervals of 5 °C from 5 to 45 °C with a view to a comprehensive understanding of the thermodynamic properties of hydrobromic acid in these media.

Experimental

The preparation and analysis of the hydrobromic acid solutions in the various solvent mixtures were identical with the methods described previously[8,9]. The molality of HBr solutions covered the range from 0.01 to 0.1 mol kg^{-1}. The acid concentration was known to within ± 0.03%. Redistilled de-ionized water was generally used in preparing the solutions. *DME* (Fisher Certified) was purified in the manner described by *Wallace* and *Mathews*[11]. The middle fraction of the second distillate was subsequently used in the preparation of the cell solutions. Dry nitrogen was bubbled through the distillation flask during the distillation process. The purity of the middle fractions was verified by gas chromatography. The mixed solvents were prepared by weight dilution methods by diluting the aqueous stock solution of HBr with a known amount of *DME* and water. The *DME* content of the solutions was accurate to ±0.02 *wt*%. The solutions were all stored in dark bottles under a nitrogen atmosphere. Dissolved air was always removed from all of the cell solutions by bubbling purified hydrogen gas through them for 1-2 h before the cells, which were fitted with triple saturators, were filled. All solutions were freshly prepared before taking measurements.

The electrodes were prepared essentially as described elsewhere[8,9]. The experimental set up and the general procedure used for the e.m.f. measurements were identical with those given previously[8,9]. The measurements were made with three hydrogen electrodes and three silver, silver bromide electrodes for each solution, at intervals of 5 °C from 5 to 45 °C. The cells were thermostated at each temperature with an accuracy of ± 0.01 °C. The silver, silver bromide electrodes were found to be stable over the entire temperature range, and constancy of the cell e.m.f. to ± 0.09 mV over a period of 1 h was considered as an adequate criterion of equilibrium in the e.m.f. measurements. As a precaution, a given cell was never measured over the entire temperature range. Three series of results were made at each acid concentration. The first was from 5 to 25 °C, the second from 20 to 35 °C and the third from 30 to 45 °C. As new solutions were prepared for the measurements in each, the results serve as an excellent means of checking the reproducibility of the procedure. The e.m.f.'s were generally reproducible to ± 0.09 mV for different solutions. The cell measurements were in triplicate, and the mean values of these observations recorded. The triplicates generally agreed within ± 0.15 mV. In order to correct the e.m.f. data to a hydrogen partial pressure of 1 atm, total vapour pressures (p) for the DME + water solvents over the temperature range 5-45 °C were taken from the previous data[4,7,12]. Extrapolation and interpolation procedures were based on the linear plots of log p as a function of $1/T$, where T is the thermodynamic temperature. The dielectric constants (D) of the solvents required to evaluate the *Debye-Hückel* constants were obtained from the data of *Roy* et al.[7] by the method of extrapolation and interpolation, which utilized the straight-line plots of log D versus T.

Results and Discussion

Standard Electrode Potential

The observed e.m.f. data (E) were corrected in the usual way to 1 atm partial pressure of hydrogen and the extrapolation function E' given[8–10] by

$$E' = E + 2\,k \log m - \frac{2\,k A\,(\mathrm{d}m)^{\frac{1}{2}}}{1 + B\mathring{a}\,(\mathrm{d}m)^{\frac{1}{2}}} - 2\,k \log\,(1 + 0.002\,\mathrm{m}M) + 2\,k\,E_{ext} = E^{\ominus}_{m} - 2\,kbm \qquad (1)$$

was constructed for each solvent at each temperature. In equ. (1), $E^{\ominus}_{m}$ is the standard molal potential of the cell, k equals 2.3026 RT/F, m is the molality of HBr, A and B are the *Debye-Hückel* constants on the molal scale, d is the solvent density, M is the average molecular weight of the solvent, E_{ext} denotes the *Debye-Hückel* extended terms, b is an adjustable parameter and $\mathring{a}$ is the ion-size parameter. The standard e.m.f. was obtained by the usual extrapolation technique and the procedure is essentially the same as that used in our previous determinations[8–10].

In the *DME*-rich solvents, where the dielectric constant is smaller than 25, ion-pair formation occurs and hydrobromic acid behaves as a weak electrolyte. So, corrections for ion-association in these solvents were taken into account. The standard e.m.f. can no longer be obtained by the simple procedure, but the method that involves preliminary knowledge of the ionisation constant of HBr is applicable[13,14]. As in our previous work[8–10], following the procedure reported by *Mussini* et al.[13], the standard e.m.f. in the *DME*-rich solvents have been determined.

The least-squares values of the standard potential $E^{\ominus}_{m}$ (molality scale) of the silver, silver bromide electrode found in this investigation are summarized in Table 1, for each solvent, along with the values for water as the solvent[8,9]. The ion-size parameters that gave a satisfactory linear extrapolation were in the range 0.46 to 0.62 nm depending on both temperature and solvent composition. The standard deviation in $E^{\ominus}_{m}$ is $\pm$ 0.09 and $\pm$ 0.18 mV for solvents containing 5 to 40 and 45 to 100% (*w*/*w*) *DME*, respectively.

The new standard e.m.f. value for the 30% *DME* solvent is in full agreement with that obtained by *Roy* et al.[7] at 25 °C, namely 0.06696 V. On the other hand, the discrepancies between the results for the rest of the solvents might be ascribed either to some unsuspected fault present in the silver, silver bromide electrodes used by *Roy* et al.[7] or to some undetectable malfunctioning of their hydrogen electrodes[15]. Moreover, some comments should be made in regard to the arbitrary choice of the ion-size parameters ($\mathring{a}$) in the determination of $E^{\ominus}_{m}$. *Roy* et al.[7] reported that the suitability of the $\mathring{a}$ value was based on the standard deviation for regression of the experimental E' as a function of m. Their results[7] indicate that $\mathring{a} = 0.6$ nm gives the best linear fit, and consequently $\mathring{a} = 0.6$ nm was used for the 10, 30 and 50% *DME* solvents and at all the eleven temperatures in the range 5–55 °C. However, as they stated[7], it should be mentioned that the standard deviation of regression is not a reliable guide to the best choice of the ion-size parameter.

Table 1. *Standard molal potentials* ($E_m^\ominus$/V) *of the silver, silver bromide electrode in 1,2-dimethoxyethane and its aqueous mixtures at 5-45 °C*

DME /*wt*%	temperature/°C 5	10	15	20	25	30	35	40	45
0	0.07962	0.07773	0.07567	0.07342	0.07105	0.06852	0.06585	0.06302	0.06003
5	0.07928	0.07736	0.07524	0.07290	0.07049	0.06784	0.06509	0.06211	0.05898
10	0.07889	0.07685	0.07481	0.07252	0.06994	0.06728	0.06437	0.06114	0.05796
15	0.07847	0.07657	0.07438	0.07188	0.06936	0.06649	0.06358	0.06033	0.05687
20	0.07796	0.07604	0.07385	0.07142	0.06870	0.06583	0.06267	0.05929	0.05562
25	0.07743	0.07549	0.07321	0.07069	0.06791	0.06486	0.06164	0.05813	0.05428
30	0.07676	0.07478	0.07245	0.06988	0.06696	0.06387	0.06038	0.05672	0.05267
35	0.07597	0.07392	0.07153	0.06885	0.06583	0.06257	0.05899	0.05510	0.05089
40	0.07495	0.07273	0.07036	0.06760	0.06441	0.06103	0.05725	0.05314	0.04872
45	0.07378	0.07152	0.06897	0.06607	0.06275	0.05919	0.05521	0.05083	0.04625
50	0.07224	0.06996	0.06722	0.06419	0.06069	0.05685	0.05273	0.04821	0.04324
55	0.07073	0.06825	0.06539	0.06206	0.05848	0.05442	0.05006	0.04518	0.04012
60	0.06871	0.06602	0.06306	0.05950	0.05572	0.05136	0.04682	0.04167	0.03623
65	0.06637	0.06350	0.06034	0.05662	0.05255	0.04800	0.04307	0.03752	0.03176
70	0.06333	0.06031	0.05698	0.05293	0.04858	0.04372	0.03844	0.03263	0.02621
75	0.05952	0.05642	0.05255	0.04846	0.04362	0.03845	0.03262	0.02634	0.01963
80	0.05467	0.05119	0.04713	0.04239	0.03735	0.03163	0.02556	0.01871	0.01158
85	0.04745	0.04357	0.03918	0.03403	0.02854	0.02236	0.01578	0.00833	0.00062
90	0.03720	0.03281	0.02805	0.02252	0.01647	0.00973	0.00255	—0.00532	—0.01384
95	0.02195	0.01713	0.01188	0.00574	—0.00082	—0.00804	—0.01607	—0.02463	—0.03370
100	0.00196	—0.00328	—0.00912	—0.01571	—0.02303	—0.03093	—0.03968	—0.04897	—0.05881

The values of $E^{\ominus}_m$ obtained for each solvent were fitted by the method of least-squares to

$$E^{\ominus}_m = a - b\,(t - 25) - c\,(t - 25)^2 \qquad (2)$$

where t is the temperature in °C. The parameters a, b and c are given in Table 2, for each solvent, along with the values for water as the solvent[8,9]. Values of $E^{\ominus}_m$ calculated by equ. (2) and the experimental values (given in Table 1) agree generally within $\pm$ 0.11 mV.

Table 2. *Values of the parameters a, b and c of Equ. (2) for evaluation of* $E^{\ominus}_m$ *in 1,2-dimethoxyethane + water solvents at 5-45 °C and the standard potentials of the silver, silver bromide electrode on the molar concentration* ($E^{\ominus}_c$/V) *and mole fraction* ($E^{\ominus}_N$/V) *scales calculated at 25 °C*

DME /*wt*%	$a/10^{-2}$ V	$b/10^{-4}$ V °C^{-1}	$c/10^{-6}$ V °C^{-2}	$E^{\ominus}_c$/V	$-E^{\ominus}_N$/V
0	7.105	4.903	3.027	0.07090	0.13535
5	7.049	5.073	3.413	0.07023	0.13380
10	6.992	5.232	3.800	0.06954	0.13218
15	6.935	5.401	4.207	0.06885	0.13047
20	6.869	5.587	4.613	0.06806	0.12874
25	6.791	5.797	5.033	0.06714	0.12701
30	6.696	6.022	5.447	0.06603	0.12533
35	6.582	6.273	5.880	0.06472	0.12369
40	6.441	6.553	6.333	0.06313	0.12216
45	6.274	6.885	6.787	0.06125	0.12071
50	6.068	7.271	7.253	0.05897	0.11946
55	5.848	7.662	7.753	0.05650	0.11811
60	5.571	8.124	8.260	0.05342	0.11707
65	5.254	8.642	8.813	0.04990	0.11612
70	4.857	9.247	9.393	0.04551	0.11562
75	4.362	9.994	9.980	0.04008	0.11567
80	3.734	10.786	10.627	0.03324	0.11655
85	2.853	11.706	11.333	0.02378	0.11930
90	1.646	12.753	12.040	0.01098	0.12451
95	—0.082	13.897	12.787	—0.00714	0.13386
100	—2.302	15.231	13.533	—0.03083	0.14669

The standard potentials $E^{\ominus}_c$ on the concentration and $E^{\ominus}_N$ on the mole-fraction scales were computed at 25 °C with the help of the usual relations[8], and are also included in Table 2.

Standard Thermodynamic Functions for the Cell Reaction

The standard thermodynamic functions for the cell reaction

$$\tfrac{1}{2}\mathrm{H_2}\,(g, 1\,\mathrm{atm}) + \mathrm{AgBr}\,(s) = \mathrm{Ag}\,(s) + \mathrm{HBr}\,(\mathrm{solvated}) \qquad (3)$$

were computed at 5-45 °C, by the usual relations[8], from the temperature variation of the standard molal e.m.f. in *DME* + water solvents. The standard free energy changes for the cell reaction increase while the standard entropy changes, which are all negative, decrease with an increase in either the *DME* content in the solvent mixture or the temperature of the solvent system, i.e. with a decrease in the dielectric constant of the solvent. The standard enthalpy changes, $\Delta H^{\ominus}$, are all negative. At 15-45 °C, the values of $\Delta H^{\ominus}$ decrease with increasing temperature or *DME* content. On the other hand, the values of $\Delta H^{\ominus}$ at 5 °C increase to a maximum at around 20% *DME* and thereafter decrease, with increasing concentration of *DME*.

Standard Thermodynamic Quantities for the Transfer Process

The standard thermodynamic quantities for the transfer of one mole of HBr from the standard state in water to the standard states of the respective solvents,

$$\mathrm{HBr}\ (\text{in water}) = \mathrm{HBr}\ (\text{in respective } DME + \text{water solvents}), \qquad (4)$$

were obtained from the temperature variation of standard e.m.f. of the cell ($E_N^{\ominus}$) on the mole-fraction scale to eliminate the *Gibbs* energy change as a result of concentration changes in the transfer process[16]. The standard changes of *Gibbs* free energy ($\Delta G_t^{\ominus}$) can be represented as a function of temperature (in K) by

$$F\,({}^{w}E_N^{\ominus} - {}^{s}E_N^{\ominus}) = \Delta G_t^{\ominus} = A - BT + CT^2 \qquad (5)$$

where ${}^{w}E_N^{\ominus}$ is the standard e.m.f. of the cell in water, and ${}^{s}E_N^{\ominus}$ in each solvent. The least-squares values of A, B and C of equ. (5) are given in Table 3. The standard changes of enthalpy ($\Delta H_t^{\ominus}$), entropy ($\Delta S_t^{\ominus}$) and heat capacity ($\Delta C_p^{\ominus}$) for the transfer process of HBr from water to the respective solvents were obtained by applying the usual thermodynamic relations[8] to equ. (5).

The standard *Gibbs* free energy of transfer is an important index of the differences in interactions of the ions (for example, $\mathrm{H^+}$ and $\mathrm{Br^-}$) and the solvent molecules in the two different media. The values of $\Delta G_t^{\ominus}$ decrease negatively, pass through minima (at around 80, 70 and 60% *DME* at 5, 25 and 45 °C, respectively), thereafter increase with increasing *DME* content in the solvent and become positive in pure *DME* at 5 to 35 °C and in 90 to 100% *DME* solvents at 45 °C. The

Table 3. *Values of the parameters A, B and C of Equ. (5) for evaluation of thermodynamic quantities for transfer of HBr from water to 1,2-dimethoxyethane + water media at 5-45 °C, and difference between the standard free energies of transfer of the chloride and bromide ions,* $\Delta G_t^{\ominus\prime}$, *at 25 °C*

DME /*wt*%	$A/10^2$ J mol^{-1}	B/J K^{-1} mol^{-1}	$C/10^{-2}$ J K^{-2} mol^{-1}	$\Delta G_t^{\ominus\prime}$/ J mol^{-1}
10	57.9250	42.6891	7.4583	618
20	118.6292	87.5513	15.3025	1 246
30	179.3157	132.9991	23.3493	1 877
40	242.4917	180.7039	31.8978	2 665
50	304.3429	228.7865	40.7744	3 768
60	370.9688	280.8744	50.4904	5 576
70	442.7283	338.0047	61.4221	8 498
80	515.1295	397.4874	73.3283	13 202
90	599.8818	463.9852	86.9615	20 120
100	694.7419	531.5721	101.3667	29 525

observed negative decrease in $\Delta G_t^{\ominus}$ values suggests that the transfer of HBr from water to the *DME* + water solvents is increasingly favourable. The negative values of $\Delta G_t^{\ominus}$ support the view that water is less basic than the mixed solvent, whereas the positive $\Delta G_t^{\ominus}$ values indicate that HBr is in a higher free energy state in pure *DME* than in water, and therefore the transfer process is not spontaneous.

The standard transfer enthalpy and entropy show similar trends. At 5 °C, the values of $\Delta H_t^{\ominus}$ and $\Delta S_t^{\ominus}$ increase positively, pass over maxima at 20 and 40% *DME*, respectively, and thereafter decrease negatively, with increasing *DME* content in the solvent. At 15-45 °C, the values of $\Delta H_t^{\ominus}$ and $\Delta S_t^{\ominus}$ decrease negatively with an increase in either the temperature or the *DME* content in the solvent mixture. The values of $\Delta H_t^{\ominus}$ and $\Delta S_t^{\ominus}$ could give us an insight into the solvent structure. The transfer process of ions from water to mixed solvent includes a number of changes connected with building up and breaking down the structure[17]. Further, the structure-forming processes are exothermic and accompanied by entropy decrease and the structure-breaking processes are endothermic and leading to the entropy increase. At 15-45 °C, the negative and decreasing values of $\Delta H_t^{\ominus}$ and $\Delta S_t^{\ominus}$ assume that ions are more effectively breaking the water structure than in the mixed solvent. The water is therefore a more structured solvent than the *DME* + water solvents. On the other hand, the positive entropy and enthalpy of transfer of HBr from water to water-rich solvents at 5 °C can be attributed to a greater structure breaking by HBr in these solvents than in water. The values of the heat capacity $\Delta C_p^{\ominus}$ are all negative and decrease with increasing temperature or *DME* content in the solvent.

The $\Delta G_t^{\ominus}$ values by themselves do not provide a clear picture of ion-solvent interactions[18,19]. Single-ion values would be more useful but these will have to wait until standard potential data for the silver, silver iodide electrode become available. Meanwhile, consider the function $\Delta G_t^{\ominus\prime}$ given[18,19] by

$$\Delta G_t^{\ominus\prime} = \Delta G_t^{\ominus}(\mathrm{HCl}) - \Delta G_t^{\ominus}(\mathrm{HBr}) = \Delta G_t^{\ominus}(\mathrm{Cl}^-) - \Delta G_t^{\ominus}(\mathrm{Br}^-) \quad (6)$$

The difference between the free energies of transfer of hydrochloric[4] and hydrobromic acids gives the difference between the free energies of transfer of the chloride and bromide ions. The values of $\Delta G_t^{\ominus\prime}$ so calculated at 25 °C are given in Table 3. The values of $\Delta G_t^{\ominus\prime}$ are positive for all the solvents and increase with increasing *DME* content in the solvent. This is qualitatively in agreement with the *Born* theory which predicts that the bromide ion should be in a lower free-energy state than the chloride ion in mixed solvents of lower dielectric constant than water[19]. The same observations were previously made[8,19].

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