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STUDY OF THE Ph_4SbBPh_4 ASSUMPTION FOR SINGLE ION FREE ENERGIES IN SOME ORGANIC SOLVENTS

ESAM A. GOMAA *

Chemistry Department, Faculty of Science, Mansoura University, Mansoura (Egypt)

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ABSTRACT

A critical study has been carried out to verify the Ph_4SbBPh_4 electrolyte assumption, in which the standard free energies of transfer of the electrolyte $\Delta G^{\ominus}$ from one solvent to another are divided equally between the cation and the anion. A discussion is presented on the basis of a model which treats the total solvation energy of an ion as a composite of electrostatic and non-electrostatic contributions. The neutral molecules Ph_4Sn and Ph_4C, are proved to be (from their sizes and structures) neutral analogues of the reference ions Ph_4Sb^+ and Ph_4B^-, respectively. The single free energies of the reference ions Ph_4Sb^+ and Ph_4B^- were also estimated.

On plotting the relationship between the free energies of transfer of Ph_4SbBPh_4 against Gutmann's acceptor and donor numbers, good agreement was obtained, indicating the similarity of the electrostatic charges on the two reference ions.

INTRODUCTION

The estimation of single ion free energies requires extra thermodynamic assumptions, for which a wide variety of methods have been introduced. The existing methods have been continuously discussed by a number of workers [1–6] and most extensively by Parker [2] and Popovych [3]. The methods [7–10] that have been used most extensively for single ion thermodynamic determination are based on the assumption that the thermodynamic values for a large reference cation can be equal to those of a reference anion of molecular similarity. Different pairs of large reference ions have been suggested, i.e. $TABPh_4B$ (TAB, triisoamyl-*n*-butylammonium) [11] and Ph_4AsBPh_4 [12]. It has been proved by Kim [13, 14] that Ph_4AsBPh_4 is an asymmetric model. The aim of this work is to study the plausibility of Ph_4SbBPh_4 electrolyte for single ion thermodynamic determination.

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* Present address: Teachers Training College, Salalah-P.O.19905, Sultanate of Oman.

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EXPERIMENTAL

Tetraphenylantimony tetraphenylborate (Ph_4SbBPh_4) was prepared by adding tetraphenylantimony bromide (Ph_4SbBr; Alfa Inorganic Chemicals) to sodium tetraphenylborate ($NaBPh_4$; Merck) solutions in water, followed by filtration and recrystallization (several times) from acetonitrile. The Ph_4Sn used (Alfa Inorganic Chemicals) was purified by repeated crystallization from chloroform. The solvents acetonitrile (MeCN) and dimethylacetamide (DMA) were obtained from Merck, whereas *N,N*-dimethylformamide (DMF), dimethylsulphoxide (DMSO), dioxane and ethanol (EtOH) were obtained from BDH. The solvents were used without further purification (a dehydrating agent was added for storage). Saturated solutions of Ph_4Sn and Ph_4SbBPh_4 in the organic solvents were prepared by shaking solutions (10 ml) in test tubes in a water thermostat (Assistent) for 1 week, followed by 2 days without shaking [15]. The saturated solutions (3–5 ml) were then evaporated to dryness in a small beaker under an IR lamp. These were dissolved in ethanol and their solubilities were determined spectroscopically (UV) using a Jobin Yvon JY 101 spectrophotometer and a calibration curve. In the case of water, saturated solutions of Ph_4Sn and Ph_4SbBPh_4 were prepared in 1 l of water. Samples (250 ml) were shaken with 10 ml of chloroform in a separating funnel. The choroform layer was extracted, evaporated to dryness, dissolved in ethanol and the solubility of the tetraphenyl derivatives was determined spectrophotometrically.

RESULTS AND DISCUSSION

To determine the partial molar volume of Ph_4SbBPh_4, the density was measured with a digital oscillator densimeter (Heraeous-Paar DMA-50) in dimethylformamide (DMF). The molar volume of a solute in solution is evaluated by the relation [16]

$$\phi_v = \frac{M}{d} + \frac{(d_0 - d) \times 10^3}{mdd_0} \tag{1}$$

where M is the molecular weight of the solute, m is its concentration and d and d_0 are the densities of water and the solution, respectively. The volume of Ph_4Sb^+ was estimated by subtraction of the volume of Ph_4B^- [17] from the volume of the salt electrolyte. The van der Waals' volume of the cation (V_w, Ph_4Sb^+) was estimated by subtracting the Ph_4B^- value given in ref. 17 from the van der Waals' volume of Ph_4SbBPh_4 calculated using the Bondi model [18]. From the experimental data and the calculated van der Waals' volumes, the packing density P_d of each molecule is calculated by

$$P_d = \frac{V_w}{\phi_v} \tag{2}$$

TABLE 1

Van der Waals' volume V_w, molar volume ϕ_v, packing density P_d and volume quotient f for tetraphenyl molecules

	Ph_4C [a]	Ph_4B^- [a]	Ph_4Sn	Ph_4Sb^+
$V_w(cm^3\ mol^{-1})$	186.7	188.2	204.32	205.84
$r_w(cm)$	4.2×10^{-8}	4.21×10^{-8}	4.59×10^{-8}	4.61×10^{-8}
$\phi_v(cm^3\ mol^{-1})$	278.1	280.6	304.36	307.38
P_d	0.671	0.671	0.671	0.669
$f_1^0 = V_w Ph_4Sn/V_w Ph_4C = 1.0943$				
$f_2^0 = V_w Ph_4Sb^+/V_w Ph_4B^- = 1.0937$				
$f_1 = \phi_v Ph_4Sn/\phi_v Ph_4C = 1.0944$				
$f_2 = \phi_v Ph_4Sb^+/\phi_v Ph_4B^- = 1.0954$				

[a] Ref. 17.

The calculated P_d values are given in Table 1; the average value is found to be 0.671 ± 0.02, which agrees well with the data of King [19] for large molecules. The van der Waals' volumes and the partial molar volumes provide evidence for the similarity in molecular size of Ph_4Sn and Ph_4Sb^+ and Ph_4C and Ph_4B^-. The data given in Table 1 indicate that the reference cation (Ph_4Sb^+) and the reference anion (Ph_4B^-) do not have equal molecular volumes, although the difference is small. From the molal solubility values of Ph_4SbBPh_4 in the solvents under consideration, the pK_{sp} values and the free energies of transfer $\Delta_w^sG^\ominus$ from water to the organic solvents were calculated following eqns. (3) and (4) [15] and their values are listed in Table 2.

$$pK_{sp} = -2\log C + 2\log\gamma_\pm \quad (3)$$

$$\Delta_w^sG^\ominus = 2.303RT\left[pK_{sp(s)} - pK_{sp(w)}\right] \quad (4)$$

C is the molal solubility, $\gamma_\pm$ is the activity coefficient [15], s denotes organic solvent and w denotes water molecules. By subtracting $\Delta_w^sG^\ominus$ values for

TABLE 2

Free energies of transfer of Ph_4SbBPh_4 from water to organic solvent (kcal mol^{-1}) (molal scale at 25 °C)

Solvents	Molar solubility	Molal solubility	$\log\gamma_\pm$	Ph_4SbBPh_4		Ph_4AsBPh_4
				$\Delta G^\ominus$	$\Delta_w^sG^\ominus$	$\Delta_w^sG^\ominus$ [a]
MeCN	3.5761×10^{-3}	4.6031×10^{-3}	−0.0966	6.6387	−16.655	−16.09
DMF	0.08146	0.0863	−0.2840	3.6772	−19.615	−18.52
DMSO	0.03705	0.03381	−0.1497	4.4211	−18.871	−17.86
DMA	0.04756	0.05077	−0.2300	4.1585	−19.134	−18.53
Dioxane	1.6012×10^{-3}	1.5593×10^{-3}	−0.0314	7.7434	−15.549	–
EtOH	4.877×10^{-5}	6.2116×10^{-5}	−0.1307	11.460	−11.830	−10.59
H_2O	2.9446×10^{-9}	2.9530×10^{-9}	−0.0103	23.297	0	0

[a] Mean values in ref. 17.

TABLE 3

Free energies of transfer from water to the organic solvents of the reference cations (Ph_4Sb^+, Ph_4As^+) and reference anion Ph_4B^- at 25 °C (kcal mol^{-1} in molal scale)

Solvents	$\Delta^s_w G^\ominus(Ph_4B^-)$	$\Delta^s_w G^\ominus(Ph_4Sb^+)$	$\Delta^s_w G^\ominus(Ph_4As^+)$
MeCN	−7.96	−8.13	−8.33
DMF	−8.98	−9.54	−9.48
DMSO	−8.44	−9.42	−9.09
DMA	−9.14	−9.39	−9.65
EtOH	−5.02	−5.57	−5.36
H_2O	0	0	0

tetraphenylantimony tetraphenylborate from those of tetraphenylborate given in ref. 13, the corresponding values for Ph_4Sb^+ were evaluated. $\Delta^s_w G^\ominus$ values for the ions Ph_4B^-, Ph_4Sb^+ and Ph_4As^+ are shown in Table 3. The coefficient of $\Delta^s_w G^\ominus(Ph_4Sb^+)/\Delta^s_w G^\ominus(Ph_4As^+)$ has a mean value of 1.006 and $\Delta^s_w G^\ominus(Ph_4Sb^+)/\Delta^s_w G^\ominus(Ph_4B^-)$ has a mean value of 1.0671, indicating the plausibility of the Ph_4SbBPh_4 assumption for the determination of single ion thermodynamics.

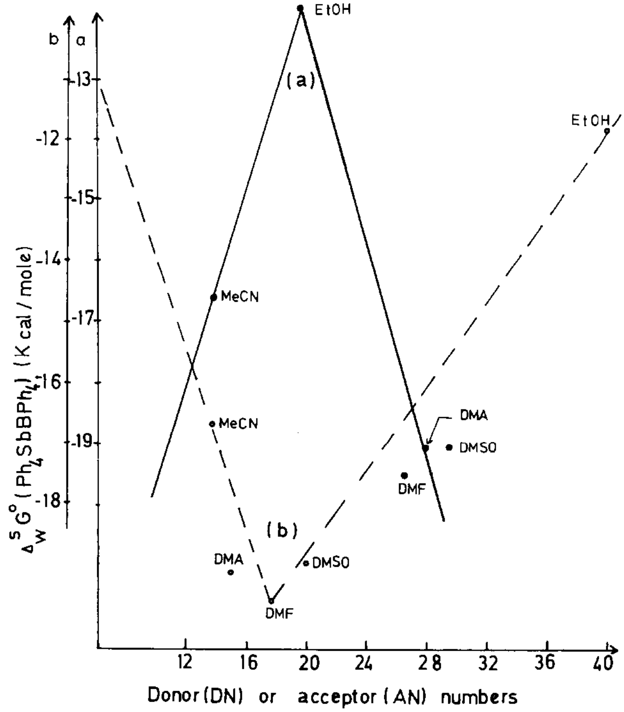

Fig. 1. Plots of free energies of transfer of Ph_4SbBPh_4 from water to organic solvents against the donor (a) and acceptor (b) numbers of solvents.

On plotting the relationship between the free energies of transfer of Ph_4SbBPh_4 against Gutmann's acceptor (AN) and donor numbers (DN) [20,21] volcanic ($\wedge$) and antivolcanic ($\vee$) relations were obtained (see Fig. 1). The lines (a) and (b) in Fig. 1 are symmetric, indicating that opposite relations proceed on the reference electrolyte, i.e. oxidation and reduction for DN and reduction and oxidation for AN at the sites of reference cation (Ph_4Sb^+) and reference anion (Ph_4B^-). That is to say there is a symmetry between the electrostatic free energies of the reference cation and anion.

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