Gibbs Transfer Energies of Single Ions from Solubilities of Reference Electrolyte Salts in Water-Propylene Glycol Mixtures

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The Gibbs transfer energies of the ions, such as H⁺, halide ions, K⁺, Ag⁺, PiC⁻ and AsPh₄⁻ in water-propylene glycol mixtures have been determined at 25°C from solubility measurements employing tetraphenylarsoniumtetraphenylborate reference electrolyte method. The solubilities of various salts have been determined potentiometrically and spectrophotometrically. The results have been interpreted in terms of various types of ion-solvent interactions like acid-base interactions, dispersion effects, Born-type and HSAB-type interactions.

The knowledge of ion-solvent interactions in non-aqueous or mixed aqueous amphiprotic media is of considerable fundamental and technological importance. An important parameter towards understanding of these interactions is the Gibbs transfer free energy of an ion from the reference solvent to the solvent in question, as it reflects the differences in the interaction of the ion with the solvent molecules.

As a part of our programme towards understanding the ion-solvent interactions in water-propylene glycol (PG) mixtures, the Gibbs transfer energies of several ions such as H⁺, halide ions, Ag⁺ etc., have been determined using the extra-thermodynamic assumption based on the reference electrolyte (R.E.) method¹⁻³. Tetraphenylarsoniumtetraphenylborate (TATB)²⁻³ has been chosen as the reference electrolyte. Studies using TATB assumption in amphiprotic media are only few⁴⁻⁹, and no report on the use of TATB assumption in the evaluation of single ion transfer energies in water-PG-mixtures is available.

Materials and Methods
Propylene glycol (BDH, LR) was purified following the procedure reported earlier¹⁰. Conductivity water was used in the preparation of all solutions. Sodium tetraphenylborate (AR, Merck) was dried before use. Pure and dry samples of potassium picrate (KPi), tetraphenylarsoniumpicrate [Ph₄AsPi] and potassium tetraphenylborate [KBPh₄] were prepared as described previously¹¹. Silver tetraphenylborate¹² [AgBPh₄] and silver perchlorate¹³ [AgClO₄] were prepared according to literature methods. Other reagents used were of AR grade. The silver electrodes were prepared on a platinum base according to the procedure given by Carmody¹⁴. All solvent mixtures used in the experiments were prepared by weight.

An H-type cell, connected through an inverted U-type salt bridge was used for e.m.f. measurements. The ends of salt bridge were closed with G-4 frits to reduce diffusion of bridge electrolyte into the experimental solutions. A Keithley solid state electrometer (model 602) with an input impedance > 10¹⁴Ω was used for e.m.f. measurement. Absorbances required for the determination of solubilities of reference electrolyte salts were measured on a PMQ II Carl-Zeiss spectrophotometer. The solubility measurements of tetraphenylborate salts were carried out in thoroughly deaerated solutions by flushing them with nitrogen at every stage of the experiment. All measurements were carried out at 25±0.1°C.

The solubilities of KPi, Ph₄AsPi and KBPh₄ in different solvent mixtures were determined spectrophotometrically as described previously. All solubility measurements, accurate to within ±1%, were made in duplicate to check reproducibility. The solubility products of AgBPh₄ and AgCl in different solvent mixtures were determined potentiometrically following the method of Kolthoff and Chantooni¹⁵. The silver ion activity of the saturated solutions was determined using the cell (A).

\[
\text{Ag} | \text{Saturated soln. of AgBPh₄} | \text{NEt₄Pi} | \text{AgClO₄} \\
\text{containing NaBPh₄} | \text{bridge in} | (0.005 \text{ m}) \text{ in} | \text{solvent} \\
\text{solvent} | \text{solvent} | \text{Ag} (A)
\]

A similar procedure was followed for AgCl, except that KCl was used in place of NaBPh₄. The results are given in Table 1.

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Table I—Solubility Product (Ksp) of Different Electrolytes in Water-PG Mixtures at 25°C

<table>
<thead>
<tr>
<th>Wt %</th>
<th>Kpi</th>
<th>Ph4AsPi</th>
<th>KBPh4</th>
<th>AgBPh4</th>
<th>AgCl</th>
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<tbody>
<tr>
<td>0</td>
<td>8.90 × 10^{-4}</td>
<td>2.03 × 10^{-9}</td>
<td>2.95 × 10^{-8}</td>
<td>6.31 × 10^{-15}</td>
<td>1.69 × 10^{-10}</td>
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<tr>
<td>20</td>
<td>2.59 × 10^{-4}</td>
<td>6.24 × 10^{-9}</td>
<td>3.01 × 10^{-8}</td>
<td>3.87 × 10^{-14}</td>
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<td>1.44 × 10^{-12}</td>
<td>9.96 × 10^{-12}</td>
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Results and Discussion

From the e.m.f. of the cell (A), the activity of silver ion was computed using the expression

\[ E = \frac{RT}{F} \ln \frac{a_{Ag^+} (ref.)}{a_{Ag^+} (soln.)} \]  

where \( a_{Ag^+} \) (ref.) refers to the activity of silver ion in the silver perchlorate solution and \( a_{Ag^+} \) (soln.) refers to the activity of silver ion in the saturated solution of silver tetraphenylborate. The solubility product was then computed by calculating the activity of \( BPh_4^- \) ion from the known molal concentration of \( BPh_4^- \) and the activity coefficient from the extended Debye-Hückel limiting equation with \( a = 5 \text{ Å} \) (ref. 4).

The Gibbs transfer energies of different electrolytes were calculated using the expression

\[ \Delta G_i^0 = 2.303 \frac{Ksp(W)}{Ksp(S)} \]  

where \( Ksp(W) \) and \( Ksp(S) \) represent the thermodynamic solubility products of the electrolyte in water and water-PG mixtures respectively in which

\[ Ksp = m_1 \cdot m_2 \cdot \gamma^+_1 \cdot \gamma^-_2 = S^+ \cdot \gamma_2 \]  

In Eq. (3) \( M^+ \) and \( X^- \) stand for cation and anion, \( S \) and \( \gamma_2 \) represent the molal solubility and mean molal activity coefficient of the electrolyte respectively in saturated solution. The activity coefficient \( \gamma_2 \) was evaluated from the extended Debye-Hückel equation. The values of \( \Delta G_i^0 \) of KPi, Ph4AsPi and KBPh4 have been obtained on mol fraction scale using the procedure reported earlier\(^5\) and from these results, the \( \Delta G_i^0 \) of R.E., i.e., Ph4AsBPh4, in different solvent mixtures was obtained using Eq. (4).

\[ \Delta G_i^0(Ph_4AsBPh_4) = \Delta G_i^0(Ph_4AsPi) + \Delta G_i^0(KBPh4) - \Delta G_i^0(KPi) \]  

The transfer energies of tetraphenylarsonium \( [\Delta G_i^0(Ph_4As^+)] \) and tetraphenyloborate \( [\Delta G_i^0(BPh_4^-)] \) ions and subsequently \( \Delta G_i^0 \) of other ions were obtained using Eqs (5-12).

\[ \Delta G_i^0(Ph_4As^+) = \Delta G_i^0(BPh_4) = \frac{1}{2} \Delta G_i^0(Ph_4AsBPh_4) \]  

The Gibbs energies of transfer of hydrogen halides necessary for the evaluation of \( \Delta G_i^0(H^+) \) and \( \Delta G_i^0(\text{halide ions}) \) were taken from literature\(^1\). The transfer energies of electrolytes and ions obtained on mol fraction scale in different solvents are given in Tables 2 and 3.

Variation of transfer free energies of salts

While the transfer energies of Ph4AsPi, KBPh4 and AgBPh4 continually decrease with the addition of PG (Table 2), the \( \Delta G_i^0 \) (KPi) initially increases up to 20 wt% PG and then decreases continuously. The \( \Delta G_i^0 \) (AgCl) decreases initially with the addition of PG, reaches a minimum around 20 wt% PG and then increases.

Variation of \( \Delta G_i^0 \) of ions

These \( \Delta G_i^0 \) values decrease almost continuously with the addition of PG (Table 3), the values being negative throughout. Further, \( \Delta G_i^0 \) (PiC^-) values are larger in magnitude (i.e., less negative) than \( \Delta G_i^0 \) (Ph4As^+) in all the solvent compositions. The negative values of \( \Delta G_i^0 \) of these ions suggest that they are in a lower free energy state in the mixed solvents than in water. Similar results were reported by Kundu et al., for these ions in water-ethylene glycol\(^5\) and water-glycerol\(^6\) mixtures. Thus, tetraphenyl-arsonium and borate ions are highly stabilized in water-PG mixtures. This is presumably due to the dispersive\(^4\) interactions of these large ions which is controlled by the polarizability of the solvent molecules. The negative \( \Delta G_i^0 \) values may also be due to the cavity-
Table 2—Gibbs Energies of Transfer of Various Electrolytes from Water to Water-PG Mixtures at 25°C on Mol Fraction Scale

<table>
<thead>
<tr>
<th>Wt % PG</th>
<th>KPi</th>
<th>Ph₄AsPi</th>
<th>KBPh₄</th>
<th>Ph₄AsBPh₄</th>
<th>AgBPh₄</th>
<th>AgCl</th>
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*Values are accurate to within ±50 J mol⁻¹.

Table 3—Gibbs Energies of Transfer of Various Ions from Water to Water-PG Mixtures at 25°C on Mol Fraction Scale

<table>
<thead>
<tr>
<th>Wt % PG</th>
<th>K⁺</th>
<th>Ag⁺</th>
<th>H⁺</th>
<th>Cl⁻</th>
<th>Br⁻</th>
<th>I⁻</th>
<th>Pi⁻</th>
<th>AsPh₄⁺/BPh₄⁻</th>
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*Values are accurate to within ±50 J mol⁻¹.

forming effect generally associated with large sized ions. However, in the case of picrate ion, its stabilization in the mixed solvents may be ascribed to dispersion interaction of the ion with the solvent because of its flat shape.

Variation of $\Delta G_i^0(H^+)$

The $\Delta G_i^0(H^+)$ values initially decrease sharply with the addition of PG (Table 3) and then increase (i.e., less negative) with further addition of PG, the values, however, becoming positive in pure PG. Similar observations were made by Kundu et al. in water-ethylene glycol mixtures using the same TATB method except that the minimum in $\Delta G_i^0$ was observed at about 50 wt% EG. The negative values of $\Delta G_i^0(H^+)$ in all water-PG mixtures indicate that the proton is in a lower free energy state in mixed solvents than in water. This is suggestive of the fact that all water-PG mixtures are more basic than either water or pure PG. The positive $\Delta G_i^0(H^+)$ in pure PG is ascribed to the lower basicity of this solvent as compared to water i.e., PG like EG is a weaker Brønsted base than water. Kundu et al. on the basis of their studies of autoprotolysis of PG, considered that it is less basic than water. This arises due to the strong intramolecular and intermolecular hydrogen bonding present in this solvent. The initial decrease and subsequent increase of (being less negative) $\Delta G_i^0(H^+)$ beyond 20 wt% PG solvent mixture is possibly due to (i) disruption of H-bonded structure in mixed solvents (in lower compositions of PG) and (ii) the formation of H-bonded clusters between water and PG (in higher composition of PG). The higher basicity of the mixed solvents also derives support from the conclusions of Popovych based on his studies using TATB method in water-ethanol mixtures.

Variation of $\Delta G_i^0(i)$ of halide ions

The $\Delta G_i^0(i)$ values of halide ions are all positive at all solvent compositions and decrease in the order $\text{Cl}^- > \text{Br}^- > \text{I}^-$ (except in 20 wt % PG for iodide). It appears that the variations in $\Delta G_i^0(i)$ arise due to the effect of (i) increasing positive acid-base type interactions, (ii) Born-type electrostatic interaction between the ions and solvent molecules, and (iii) soft-soft interactions superimposed on the above and acting in the opposite direction. The observed large positive values of $\Delta G_i^0$ of halide ions indicate generally the dominant contribution of factors (i) and (ii). The relatively greater stabilisation of bromide and iodide ions over chloride may be attributed to their larger radii which render them softer as compared to chloride ion. The larger $\Delta G_i^0(I^-)$ at 20 wt % PG compared to $\Delta G_i^0(\text{Cl}^-)$ and $\Delta G_i^0(\text{Br}^-)$ seems to be somewhat involved and possibly includes all the three above effects, in addition to structural effects of the solvents in this region.
Variation of $\Delta G^0_1(K^+)$ and $\Delta G^0_1(Ag^+)$

The $\Delta G^0_1(K^+)$ values show only a small variation with the addition of PG to water. The values are all positive throughout the composition range and are similar to those observed in water-ethanol mixtures for $K^+$ ion obtained by Popovych and Dill$^{19}$ and by Kundu et al.$^6$ in water-glycerol mixtures. The positive values are presumably due to the opposing effects of Born-type electrostatic interactions and increasingly negative acid-base type interactions. The considerably small positive $\Delta G^0_1(K^+)$ values seem to arise largely due to a compensation of the latter interactions and the Born-type electrostatic interactions. According to Pearson’s$^{20}$ theory of hard-soft acids and bases, the interaction of a hard acid like $K^+$ would be expected to be difficult with the softer bases, i.e., mixed solvents$^21$ and this is in agreement with the positive $\Delta G^0_1(K^+)$ values. The $\Delta G^0_1(Ag^+)$ values decrease with the addition of PG, reaching a minimum around 20 wt % PG and then increase (i.e. become less negative) with the values showing relatively small changes subsequently.

These results agree with those reported by Feakins and Voice$^{21}$ for silver ion in water-methanol mixtures. The large negative $\Delta G^0_1(Ag^+)$ values may be ascribed to the strong Lewis acid-base type interactions between $Ag^+$ ion and the mixed solvents. Further, there may arise specific interactions of this $d^{10}$-cation with the basic centres of the solvent components in the mixed solvents. Feakins and Voice$^{21}$ suggested that the electron pairs on the solvent molecules in mixed solvents are under stronger electrostatic field from the silver ion than that from an alkali metal ion, because the screening of the nuclear field by $d^{10}$ group is poorer than that by the alkali metal ion. On the basis of Pearson’s theory of HSAB, also, it would be expected that the interaction between a softer acid like $Ag^+$ and softer bases like the mixed solvents is favoured, leading to a decrease in $\Delta G^0_1(Ag^+)$ values on the addition of PG.

References
13 Hill D, J Am chem Soc, 43 (1921) 254.
18 Kundu K K & Das M N, J chem Engng Data, 9 (1964) 82.