Excess adsorption on hydrophobic and hydrophilic solid-liquid interfaces: Negative adsorption of electrolytes and urea. Part 2

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The extent of hydration of charcoal, cationic and anionic resin powders in the presence and absence of some inorganic salts and urea has been studied using isopiestic vapour pressure technique. The shapes of water vapour adsorption isotherms for different solids agree with type III BET isotherms. At water activity approaching unity, maximum values of water adsorption $\Delta n_w$ in moles per square meter of solid at 30°C are in the order: cationic resin $>$ anionic resin $>$ charcoal. Standard free energies ($AG^0$) of adsorption of water vapour have also been evaluated. The negative and positive excess hydration of these solid powders for different mole fractions of LiCl, NaCl, KCl, NaSO$_4$ and urea in the bulk phase have been estimated using data obtained from the isopiestic experiments. The free energies of excess hydration for all these systems have been evaluated using the integrated forms of the Gibbs adsorption equation. The absolute values of water and salt binding to these solids have been estimated in the bulk phase.

Studies on the adsorption of water and electrolytes on solid surfaces are of great importance to understand molecular interactions occurring in colloidal systems, catalytic processes, adsorption chromatography and in many biosurface phenomena. Adsorption of water on the surface of solids has been extensively studied using various physicochemical techniques. Competitive adsorption of water and electrolytes on the surface of powdered solids such as carbon, alumina and silica has been studied extensively using various physicochemical techniques. However, concentrations of electrolytes are relatively low in most of the systems studied and the role of water in the preferential adsorption of solute or solvent has not been examined quantitatively on thermodynamic grounds. Chatteraj and co-workers have studied extensively preferential adsorption of water vapour in the absence and presence of inorganic salts by powdered proteins, polyamino acids, cationic and anionic surfactants, powdered alumina, silica and barium sulphate using isopiestic vapour pressure method.

We report here the extent of adsorption of water vapour in the presence and absence of urea and inorganic salts on the surfaces of charcoal, cationic and anionic resin using isopiestic vapour pressure technique. An attempt has been made to calculate the standard free energies for adsorption of electrolytes in these systems using integrated forms of the Gibbs adsorption equation, and to clearly identify a suitable standard state of reference for the changes of free energies of negative adsorption of electrolytes of the solid-liquid interface so that relative affinities of these solids for water and salts can be compared.

Materials and Methods

Charcoal was purchased from Sigma Chemicals Co., USA. Amberlite resin (H$^+$ exchange) IR 120 (16-45 mesh) and amberlite resin IR 402 Cl$^-$ exchange (standard grade) were obtained from Fluka, Germany. Before use, charcoal was washed with distilled water for removing trace of impurities from solid and then dried at 850°C for 8 h. The dried materials were then stored in a desiccator containing concentrated sulfuric acid. Resin (Cl$^-$ particles) was washed with distilled water till the washing had a constant pH 7.0. Resin (H$^+$) was washed several times with 2-4 $M$ NaCl solution to make it a Na$^+$ exchange resin. Both the resins were air-dried and the kept in a vacuum desiccator containing conc. sulfuric acid to remove the last trace of water. After drying, these materials were kept in a desiccator containing anhydrous CaCl$_2$. The electrolytes LiCl, NaCl, KCl and NaSO$_4$ (analytical grade) were used without further
purification. Urea was recrystallised twice from warm ethanol. Double distilled water was used throughout the investigations.

The surface area of solid powders of charcoal was determined using adsorption of acetic acid from aqueous solution. Surface area of the resins was determined from palmitic acid adsorption in benzene. These methods are discussed elsewhere\textsuperscript{13}. The surfaces of charcoal, resin (Na\textsuperscript{+}) and resin (Cl\textsuperscript{-}) were found to be 63.4 ± 2.1, 55.0 ± 0.5 and 29.0 ± 1.0 meter square per g of the powder.

**Isopiestic studies**

Water vapour adsorption by powdered solid materials such as silica, alumina\textsuperscript{12} and barium sulphate\textsuperscript{13} has been quantitatively estimated using isopiestic vapour pressure method using a definite weight of the dried powder in an accurately weighed sample bottle. Lid of the bottle was then removed and the bottle without lid was floated on conc. sulphuric acid solution (using suitably a tripod stand) in a specially designed desiccator. The desiccator was then evacuated and the H\textsubscript{2}SO\textsubscript{4} solution inside was stirred by a magnetic stirrer for a week to attain vapour pressure equilibrium between hydrated powder present in the sample bottle and the H\textsubscript{2}SO\textsubscript{4} solution present in the desiccator (referred as reference solution). The sample bottle was then taken out of the desiccator quickly (with lid on) and was weighed. From the difference in weights, moles (n\textsubscript{1}) of water vapour adsorbed per kg (or per unit area) of the powder were calculated. The [H\textsubscript{2}SO\textsubscript{4}] in the reference solution was determined titrimetrically and the corresponding relative humidity (p/p\textsubscript{r}) at this [acid] was obtained using the standard table. The water activity (a\textsubscript{1}) at this state of isopiestic equilibrium is equal to p/p\textsubscript{r}, according to the Raoult’s law.

For the determination\textsuperscript{12,15} of the extent of excess hydration of the powdered solid in the presence of inorganic salt or an organic solute (sucrose or urea), a definite amount of dry salt was taken in a sample bottle. The bottle was floated on the reference solution containing same solute present in the sample. The sample in the weighing bottle and the reference solution were brought in isopiestic equilibrium as before for a week. After this, the sample bottle was taken out from the desiccator (with lid on) and weighed accurately. From the difference in weights, total weight (W\textsubscript{1}) and total moles (n\textsubscript{1}') of water present per kg of powdered sample were calculated.

Moles (n\textsubscript{1}') of salt per kg of powdered solid was already known. Total molality m\textsubscript{2}' of the salt (or organic solute) in the reference solution was estimated by direct weighing of the definite weight of the solution to complete dryness at 105-110°C. For LiCl and urea, a special method\textsuperscript{16-17} was used in place of drying. Total molality m\textsubscript{2}' of the solute in the sample per kg of the powder is equal to 1000 n\textsubscript{2}/M\textsubscript{2}n\textsubscript{1}' so that its value was calculated from known values of n\textsubscript{1}' and n\textsubscript{1}.' However, after adsorption of the salt and water by one kg of the solid powder, free molality of the solution in contact with one kg of powder, will be m\textsubscript{2}. This free solution was in vapour pressure equilibrium with the reference solution of molality m\textsubscript{2}'. The small contribution of the solid powder to the vapour pressure can be neglected\textsuperscript{15,17} so that we can assume that m\textsubscript{2} = m\textsubscript{2}'.

**Results and Discussion**

Moles of water vapour (n\textsubscript{1}) bound per kg of charcoal, cationic and anionic resins, respectively at 30°C and 40°C were plotted against water activity (a\textsubscript{1}) within the total range zero to unity (not shown). All these isotherms are sigmoidal in shape and similar in form which can be expected from the type 3 BET isotherm\textsuperscript{12,10}. In all these isotherms, the absolute values of n\textsubscript{1} at a given value of a\textsubscript{1} increase with increase in temperature. This indicates that with increase in temperature, more water molecules are bound to the solid surface possibly due to the hydrophobic effect. This also indicates that the adsorption in all these cases is endothermic in nature. These isotherms may qualitatively be divided into three parts\textsuperscript{15}. First part of the isotherm in the range of relative humidity zero to 0.20 is for the formation of primary layer of water of the solid surface. In this region, water molecules are bound strongly to the surface of solid thus forming a monolayer\textsuperscript{10,12}. The second part of the curve for relative humidity 0.30-0.80 is responsible for the formation of new sites or holes on the solid surfaces. The steep third part of the curve is probably due to the condensation of randomly oriented water molecules on the hydrated surface of solids, i.e. the formation of multilayers of adsorbate water molecules\textsuperscript{9,10,17}. For anionic resin, n\textsubscript{1} is independent of temperature up to relative humidity 0.50. The extrapolated values of n\textsubscript{1} at a\textsubscript{1} equal to unity correspond to the maximum and effective amount of
water bound by solids and for each system it is referred to as $\Delta n^0$. The values of $\Delta n^0$ for charcoal, cationic resin and anionic resin at 30 and 40°C are given in Table 1. It may be noted that values of both $n_1$ and $\Delta n^0$ are positive or zero; it cannot be obviously negative. $\Delta n^0$ for all systems increases with the increase of temperature (Table 1). The table shows that in terms of $\Delta n^0$, the adsorbents at 30°C are in the order: cationic resin > anionic resin > charcoal.

However with increase in temperature from 30°C to 40°C, $\Delta n^0$ for charcoal increases significantly possibly due to hydrophobic interaction and its magnitude becomes same as that for anionic resin. $\Delta n^0$ for cationic resin at both temperatures is significantly large.

The integral free energy change ($\Delta G^0_a$) due to the hydration of powdered solid for the change of $a_1$ from zero to unity has been evaluated using Eq. (1) derived by Bull,17,19 on thermodynamic ground:

$$\Delta G^0_a = -RT \int_{a_1}^{1} n_1 \frac{da_1}{a_i}$$  \hspace{1cm} (1)

From the graphical evaluation of the area under the curve obtained by plotting $\left( \frac{n_1}{a_i} \right)$ as function of $a_1$ between the limit $a_1 = 0$ to $a_1 = 1$, the value of the integral for each system may be calculated. $\Delta G^0_a$ for charcoal, cationic and anionic resins is given in Table 1. $\Delta G^0_a$ according to Eq. (1), is always negative which indicates that the hydration of charcoal, cationic and anionic resin is thermodynamically spontaneous process. Values of $\Delta G^0_a$ at 30°C also are in the order: cationic resin > anionic resin > charcoal. But at 40°C, $-\Delta G^0_a$ for charcoal due to the increase of the hydrophobic interaction exceeds that of anionic resin (Table 1).

<table>
<thead>
<tr>
<th>Solids</th>
<th>Temp. (K)</th>
<th>$\Delta n^0$ (mole/m$^2$ of solid)</th>
<th>$-\left[ \Delta G^0_a \right]$ (kJ/m$^2$ of solid)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Charcoal</td>
<td>303</td>
<td>0.338</td>
<td>4.52</td>
</tr>
<tr>
<td></td>
<td>313</td>
<td>0.730</td>
<td>10.4</td>
</tr>
<tr>
<td>Cationic resin (Cl$^-$)</td>
<td>303</td>
<td>2.00</td>
<td>28.0</td>
</tr>
<tr>
<td>Anionic resin (Na$^+$)</td>
<td>303</td>
<td>4.10</td>
<td>30.0</td>
</tr>
<tr>
<td></td>
<td>313</td>
<td>0.664</td>
<td>5.52</td>
</tr>
<tr>
<td></td>
<td>313</td>
<td>0.736</td>
<td>5.65</td>
</tr>
</tbody>
</table>

Here measured value $m_2$ is related to $n_1$ moles of free solute and $n_2$ moles of free solvent respectively per unit area of the solid powder. $X_1$ and $X_2$ are their respective mole fractions of the free components in the sample bottle at adsorption equilibrium.

We can replace $m_1$, $m_2$, and $W_1$ by $1000 n_1$, $1000 n_2$, $M_1 n_1$, $M_2 n_2$, and $M_1 n_1$, respectively so that inserting these in Eq. (2), we obtain

$$\Gamma^\ast_2 = n_1^1 - n_1^2 \frac{n_2}{n_1}$$

$$= n_2^2 \frac{X_2}{X_1}$$  \hspace{1cm} (4)

Here $n_1^1$ and $n_2^1$ stand for total moles of solute (of molecular weight $M_1$) and solute respectively per unit surface area of the solid powder before adsorption. Equation (4) can be written as\textsuperscript{5} Eq. 5.
\[ \Gamma_1^2 = \eta_1 - \eta_2 \frac{m_1}{n_2} \] ... (5)

\[ = \eta_1 - \eta_2 \frac{X_1}{X_2} \]

so that upon combining Eqs (4) and (5), we get:

\[ \Gamma_1^2 X_2 + \Gamma_2^2 X_1 = 0 \] ... (6)

This equation has been derived earlier by Schay and Kipling for the adsorption of liquid mixtures on various solid powders. Eq. (6), can be written as:

\[ \Gamma_1^2 = - \frac{X_1}{X_2} \Gamma_2^2 \] ... (7)

Eqs (6) and (7) show that \( \Gamma_1^2 \) and \( \Gamma_2^2 \) are not independent quantities and their values are opposite in sign. Also, if \( \Gamma_1^2 \) is calculated from Eq. (2) using experimental values of \( m_1^a \) and \( m_2 \), the value of excess adsorption of solvent \( \Gamma_1^1 \) can be evaluated using Eq. (7).

Relations (2), (4) and (5) do not, however, exhibit explicitly the individual contributions of solute and solvent in the measured values of \( \Gamma_1^2 \) and \( \Gamma_2^1 \). To overcome this difficulty, Chatteraj et al. have recently shown that the surface phase in contact with liquid is inhomogeneous whereas the bulk phase of binary solution is always homogeneous in nature. The inhomogeneous surface phase is composed of \( \Delta n_1 \) and \( \Delta n_2 \) moles of solvent and solute respectively per unit surface area and it is in contact with \( n_1 \) and \( n_2 \) moles of solvent and solute forming homogeneous bulk phase of binary solution. We can, thus, write:

\[ n_1^a = n_1 + \Delta n_1 \] ... (8)

\[ n_2^a = n_2 + \Delta n_2 \] ... (9)

Combining relations (4), (5), (8) and (9), original fundamental relations (10) and (11) are obtained:

\[ \Gamma_1^2 = \Delta n_1 - \Delta n_2 \frac{X_1}{X_2} \] ... (10)

\[ \Gamma_2^2 = \Delta n_2 - \Delta n_1 \frac{X_2}{X_1} \] ... (11)

These relations indicate how \( \Gamma_2^1 \) and \( \Gamma_1^2 \) are related to the actual compositions \( \Delta n_1 \) and \( \Delta n_2 \) of solvent and solute, respectively. Relations (10) and (11) indicate that \( \Delta n_1 \) and \( \Delta n_2 \), moles of solvent and solute respectively actually forming inhomogeneous surface phase per unit area are both related to the excess or relative adsorption quantities \( \Gamma_1^1 \) and \( \Gamma_2^2 \). If \( \Delta n_1 \) is equal to zero, then from relation (10), \( \Gamma_1^1 \) becomes equal to \( \Delta n_2 \). Similarly, if \( \Delta n_2 \) is zero, \( \Gamma_2^2 \) becomes equal to \( \Delta n_1 \). Further, unlike \( \Gamma_1^1 \) or \( \Gamma_2^2 \), \( \Delta n_1 \) and \( \Delta n_2 \) are absolute values which may be positive or zero but never become negative. Also, if under certain circumstances, \( \Gamma_1^1 \) varies linearly with change of \( X_2/X_1 \) (or \( m_2/55.5 \)), then using Eq. (10), values of \( \Delta n_1 \) and \( \Delta n_2 \), respectively can be evaluated from the slope and intercept of the linear plot.

Figures 1-3 show excess adsorption \( \Gamma_1^1 \) for different solutes expressed in moles per kg of solid

![Fig. 1 — Plot of \( \Gamma_1^1 \) vs \( (X_2/X_1) \times 10^4 \) for charcoal in presence of different solutes at - 30°C: (●) LiCl; (△) NaCl; (●) KCl; (■) Na₂SO₄; ( ●) Urea.](image-url)
powder as functions of $\frac{X_\infty}{X_1}$. $\Gamma_2^i$ is negative for higher values of $\frac{X_\infty}{X_1}$ (i.e., $m^i_1 < m^i_0$). But at lower values of the mol ratio composition, $\Gamma_2^i$ becomes positive (i.e., $m^i_1 > m^i_0$). From Eq. (7), we find that excess adsorption of water $\Gamma_2^w$ becomes positive when $\Gamma_2^i$ is negative and vice versa. Further, we note from the figures that $-\Gamma_2^i$ varies linearly with $\frac{X_\infty}{X_1}$ in wide range of concentrations. From the slope and intercept of these straight lines, absolute values of $\Delta \eta_i$ and $\Delta \eta_2$ for different systems have been evaluated using Eq. (10). Values of $\Delta \eta_1$ and $\Delta \eta_2$ for different systems are given in Table 1.

From Table 2, we note that values of $\Delta \eta_1$ at 30°C for different solid powders are in the order: charcoal: Na$_2$SO$_4$ > KCl > LiCl > urea > NaCl; Cationic resin: Na$_2$SO$_4$ > KCl > NaCl > LiCl > urea; Anionic resin: Na$_2$SO$_4$ > LiCl > KCl > NaCl > urea.

Further in all cases, comparison of values of $\Delta \eta_i$ in the presence of salt increases significantly from their respective values of $\Delta \eta_i^0$ (Table 1). Thus, addition of salts increases the absolute hydration of the solid powder. It has some similarly with salting-in phenomena observed for increase in solubility of biocolloids in the presence of salt. The order of electrolytes observed probably depends upon the activity coefficients of electrolytes in the wide range of high electrolyte concentrations besides amount of electrolyte binding $\Delta \eta_i$ which are different for different surfaces (Table 2).

Deviation of the plots of $\Gamma_2^i$ against $X_\infty/X_1$ in Figs 1-3 from linearity in certain regions of $\frac{X_\infty}{X_1}$ is an indication that $\Delta \eta_1$ or $\Delta \eta_2$ are not always
Table 2—Hydration parameters of different solid surfaces in presence of different solutes at 30°C

<table>
<thead>
<tr>
<th>Solid surfaces</th>
<th>Solute</th>
<th>$\Delta h \times 10^9$ (mol H$_2$O/hr$^2$ solid)</th>
<th>$\Delta \mu_2 \times 10^9$ (mol solute/m$^2$ solid)</th>
<th>$m_2^{\text{act}}$</th>
<th>$\Delta G^\circ (\Delta G_2^\circ)$ (kJ/m$^2$ × 10$^5$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Charcoal</td>
<td>LiCl</td>
<td>3.28</td>
<td>8.50</td>
<td>1.44</td>
<td>18.8</td>
</tr>
<tr>
<td></td>
<td>NaCl</td>
<td>0.71</td>
<td>2.33</td>
<td>1.82</td>
<td>67.8</td>
</tr>
<tr>
<td></td>
<td>KCl</td>
<td>3.63</td>
<td>10.1</td>
<td>1.54</td>
<td>69.4</td>
</tr>
<tr>
<td></td>
<td>Na$_2$SO$_4$</td>
<td>3.68</td>
<td>7.71</td>
<td>1.16</td>
<td>59.9</td>
</tr>
<tr>
<td></td>
<td>Urea</td>
<td>1.49</td>
<td>4.4</td>
<td>1.64</td>
<td>17.7</td>
</tr>
<tr>
<td>Cationic resin</td>
<td>LiCl</td>
<td>6.7</td>
<td>17.4</td>
<td>1.43</td>
<td>2.41</td>
</tr>
<tr>
<td></td>
<td>NaCl</td>
<td>7.27</td>
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<td>1.15</td>
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<td>KCl</td>
<td>7.34</td>
<td>19.2</td>
<td>1.45</td>
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<td>Na$_2$SO$_4$</td>
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<td>0.647</td>
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<td>Anionic resin</td>
<td>LiCl</td>
<td>3.82</td>
<td>9.11</td>
<td>0.264</td>
<td>18.2</td>
</tr>
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<td></td>
<td>NaCl</td>
<td>3.30</td>
<td>12.5</td>
<td>2.09</td>
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<td>Na$_2$SO$_4$</td>
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<td>5.9</td>
<td>0.86</td>
<td>41.8</td>
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<tr>
<td></td>
<td>Urea</td>
<td>2.10</td>
<td>3.31</td>
<td>0.875</td>
<td>34.2</td>
</tr>
</tbody>
</table>

For a given solute, it is observed that $\Gamma_2^n$ becomes positive or negative depending on the value of $X_2/X_1$. For each solute, there exists a definite value of $X_2/X_1$ when $\Gamma_2^n$ becomes zero (Figs 1-3). This is the azeotropic state for adsorption of solvent and solute onto solid surfaces. In this state, $\Delta n_2/\Delta n_1$ becomes equal to $X_2/X_1$. Values of $m_2^{\text{act}}$ for various solutes of the azeotropic states are given in Table 2.

Gibbs defined the surface excess quantities $\Gamma_1$ and $\Gamma_2$ as the difference of total moles of solvent and solute components, respectively present in the whole system and those present in the bulk separated from imaginary surface phase (σ) due to the arbitrary placement of the dividing plane. By changing the position of the dividing plane arbitrarily inside the inhomogeneous σ-phase in a suitable position, $\Gamma_1$ may become zero so that Eq. (12) becomes:

$$-d\gamma = \Gamma_2^n d\mu_2 + \Gamma_1^n d\mu_1$$  \hspace{1cm} (12)

Here, $\gamma$ stands for the surface tension per unit length (or surface free energy per unit area) of the interface. Also $d\mu_1$ and $d\mu_2$ in Eq. (12) represent chemical potentials of solvent and solute in the bulk phase which may be taken to be equal to $RT \ln a_1$ and $RT \ln a_2$, respectively. Here $a_1$ and $a_2$ stand for the activities of the solvent and solute in the bulk phase.

Willard Gibbs$^{24}$ derived his elegant adsorption equation by arbitrary placement of an imaginary dividing plane near the interface between two fluid phases containing multi-component mixtures. For two component solute and solvent system in bulk in contact with an air-water interface, this equation will be:

$$-d\gamma = \Gamma_2^n d\mu_2 + \Gamma_1^n d\mu_1$$  \hspace{1cm} (12)

Here, $\gamma$ stands for the surface tension per unit length (or surface free energy per unit area) of the interface. Also $d\mu_1$ and $d\mu_2$ in Eq. (12) represent chemical potentials of solvent and solute in the bulk phase which may be taken to be equal to $RT \ln a_1$ and $RT \ln a_2$, respectively. Here $a_1$ and $a_2$ stand for the activities of the solvent and solute in the bulk phase.

Superscript of $\Gamma_2^n$ indicates that the surface excess of component I has been put to zero in Eq. (12). $\Gamma_2^n$ has been shown$^{17,25}$ to be invariant with respect to the position of the dividing plane. Defay and Prigogine$^{26}$ have shown from thermodynamic analysis that:

$$\Gamma_1 = n_1^a - n_1^* \frac{n_2^*}{n_2}$$  \hspace{1cm} (14)

Chattoraj and co-workers$^{22}$ have shown that Eq. (13) will remain valid if air-water interface is replaced by solid-water interface. The similarity in forms between relations (4) and (14) indicates that directly measured value of $\Gamma_2^n$ based on relation (2) is same as the Gibbs surface excess based on arbitrary placement of dividing plane near the interfacial region.
Gibbs equation indicates that by the addition of surface active substances in solution, $\gamma$ is lowered since $\Gamma_{2}^{i}$ becomes positive whereas on addition of inorganic salt $\gamma$ increases since surface excess of salt in the system becomes negative. It can be shown that all equations related to $\Gamma_{2}^{i}$ and $\Gamma_{1}^{i}$ discussed here are consistent with positive and negative surface excess quantities introduced by Gibbs for the adsorption of solute and solvent components at a fluid interface.

The chemical potential $\mu_2$ of an electrolyte $P_e$, $Q_e$ in the bulk phase may be written as:

$$\mu_2 = \mu_c + \mu_{\text{sol}} \mu_1$$  \hspace{1cm} (15)

Here $\mu_c$ and $\mu_{\text{sol}}$ are chemical potentials of cations and anions in the bulk phase, respectively. Also, $\mu_c$ and $\mu_{\text{sol}}$ are number of cations and anions when one molecule of salt is completely dissociated in the bulk phase.

Putting this value of $\mu_2$ in Eq. (13), Chattoraj has shown that:

$$d\gamma = RT \left(\mu_c + \mu_{\text{sol}}\right) d\ln f_i X_i$$  \hspace{1cm} (16)

The mean mole fraction $X_2$ of the electrolyte in bulk can be calculated using:

$$X_2 = (X_c X_a)^{\mu_c + \mu_{\text{sol}}}$$  \hspace{1cm} (17)

Here $X_c$ and $X_a$ stand for mole fractions of cations and anions, respectively, which can be calculated from measured value of $m_2$. The mean activity coefficients $f_i$ of the electrolytes for given values of $x_i$ have been calculated using the procedures followed earlier.

One can fix the equation for the apparent standard free energy change $\Delta G_{ap}$ for the excess adsorption of an electrolyte by integration of Eq. (16) between limits $X_2$ equal to zero and unity so that relation (18) will be obtained:

$$\Delta G_{ap}^{\text{ex}} = \int_{X_2}^{0} d\gamma$$

$$= -RT \left(\mu_c + \mu_{\text{sol}}\right) \int_{0}^{X_2} \frac{1}{f_i X_i} df_i X_i - \Gamma_{2}^{i} \ln(f_i X_i)$$  \hspace{1cm} (18)

The integral part of the right side of Eq. (18) stands for free energy of adsorption when $f_i X_i$ is altered from zero to a particular value of $X_2$ and the second part represents the free energy change due to hypothetical dilution from this value of $X_2$ to unity at constant value of $\Gamma_{2}^{i}$.

$\Delta G_{ap}$ varies linearly with $1/\sqrt{X_2}$ (Fig. 4), so that extrapolated values of $\Delta G_{ap}$ equal to the standard free energy change for adsorption at $X_2$ equal to unity have been calculated. $\Delta G_{ap}$ for electrolyte adsorption are found from Table 2 to be all positive. This indicates that the excess adsorption of electrolytes and urea on the surfaces of charcoal, cationic and anionic resins, respectively are non-spontaneous processes.

In an alternative approach of the Gibbs treatment for adsorption at fluid interface, one can place arbitrarily the dividing plane in the surface phase $\sigma$ in such a manner so that $\Gamma_{2}^{i}$ becomes zero. In this condition, using Eq. (12) we get:

$$-d\gamma = \Gamma_{2}^{i} d\mu_i$$  \hspace{1cm} (19)

Thus, we find from Eqs (13) and (18), $\Gamma_{2}^{i} d\mu_i = \Gamma_{1}^{i} d\mu_i$. The excess standard free energy change $\Delta G_{ap}^{\text{ex}}$ for the solvent adsorption (hydration) per unit surface area can also be obtained by integration of Eqs (13) and (19).

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**Fig. 4** — Plot of $\Delta G_{ap}^{\text{ex}} - \frac{1}{\sqrt{X_2}}$ for cationic resin in presence of different solutes at $30^\circ\text{C}$: (○) LiCl (■) NaCl (△) KCl (■) Na$_2$SO$_4$ (■) Urea.
\[
\Delta G_{b}^{0} = \int_{0}^{1} \frac{d\gamma}{d\mu} = \int_{x_{2}=0}^{x_{2}=1} \Gamma_{2}^{0} d\mu_{2}
\]
\[
= -\int_{0}^{x_{2}=1} \Gamma_{2}^{0} d\mu_{2} - \int_{x_{2}=1}^{x_{2}=0} \Gamma_{2}^{0} d\mu_{2} = -\Delta G^{\circ}
\]
\[
= + \int_{0}^{x_{2}=1} \Gamma_{2}^{0} d\mu_{2} = -\Delta G^{\circ}
\]

We note that by multiplying values of \(\Delta G^{\circ}\) by -1, one can estimate \(\Delta G_{b}^{0}\) and signs for these quantities (Table 2) will all be negative. We have already mentioned that form of the Gibbs adsorption equation will remain same for fluid as well as solid-liquid interface\(^{27}\). This indicates that surface excess hydration presented in Table 2 for different electrolytes and urea, respectively on the surfaces of charcoal, cationic and anionic resins is spontaneous in nature. Magnitudes of \(\Delta G^{\circ}\) (and \(\Delta G_{b}^{0}\)) for different solutes are comparable since all these quantities refer to standard state \(d_{2}\) (or \(f_{2}X_{2}\)) equal to unity.

From Table 2, we can compare the excess hydration \((-\Delta G_{b}^{0})\) for the solid powder in the presence of various salts and urea. For different solids, \(\Delta G_{b}^{0}\) is in the order (for electrolytes and salts); charcoal: KCl > NaCl > Na\(_{2}\)SO\(_{4}\) > LiCl > urea, cationic resin: urea > Na\(_{2}\)SO\(_{4}\) > KCl > NaCl > LiCl, anionic resin: KCl > Na\(_{2}\)SO\(_{4}\) > Urea > LiCl > NaCl.

Earlier using isopiestic data\(^{28}\), we calculated \(\Delta G^{\circ}\) for alumina, silica and barium sulphate particles. Here, \((-\Delta G_{b}^{0})\) is in the order: alumina: Na\(_{2}\)SO\(_{4}\) > KCl > NaCl > LiCl, silica: Na\(_{2}\)SO\(_{4}\) > KCl > LiCl > NaCl, barium sulphate: Na\(_{2}\)SO\(_{4}\) > LiCl > NaCl > KCl.

This order of electrolytes for all six types of particles is observed to be different from each other. The order of the salts does not strictly follow any regular lyotropic series of electrolytes valid for biocolloid precipitation. Possibly, the observed series of electrolytes for each solid particles depend on its hydrophilic and hydrophobic nature of different solid surfaces having different extents of surface heterogeneities and porosities, surface charge and surface hydration, different orientations of surface water, etc.

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