An Interpretation of Water Sorption Isotherms of Ion Exchange Resins

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The water sorption isotherms of polystyrene-divinylbenzene-sulphonic acid resins (Dowex 50W) of varying DVB contents in Li\textsuperscript{+}, Na\textsuperscript{+} and K\textsuperscript{+} forms have been analysed using D'Arcy-Watt equation. The equation fits the isotherms over the whole range of water activity, i.e., 0 to 1. The values of the five parameters involved in the equation, namely, \(K, K', C, k\) and \(k'\), obtained using a non-linear least square computer programme, are consistent with the physical characteristics of these resin systems. The direct correlations of \(K'\) values with the exchange capacities, of \(K\), with the nature of the cation which determines the strength of ion-water interaction, and of \(k\) and \(k'\) with the multilayer formation in different ionic systems, support the physical basis of this equation. The existence of second hydration shell in Li-resinates on the basis of \(K'\) (computed) ratios, the correlation of \(w\), \(-w_m\), albeit very approximate, with the enthalpy change in water sorption on primary hydration shell water molecules in gas phase, particularly for lithium ions, provide additional insight into ion-water and water-water interactions in these resin systems.

Water sorption isotherms of ion exchangers over the whole water activity range (0 to 1) have so far not been explained by any single equation\textsuperscript{1}. For example, BET equation\textsuperscript{2} has been fitted to the water sorption isotherms in the water activity range of 0 to 0.33. D'Arcy-Watt\textsuperscript{3} equation has been very successful in explaining the water sorption isotherms of many natural and synthetic polymer substances\textsuperscript{4}.

In the present paper, an attempt has been made to apply this equation to the case of synthetic organic ion exchange resins and to get insight, if possible, into the various types of interactions of the water molecules in the resin phase.

Theory

The general form of the D'Arcy-Watt equation is:

\[ W = \sum_{i=0}^{5} K_i K_j (p/p_0) + C(p/p_0) + \frac{k'k(p/p_0)}{I-k(p/p_0)} \]  \hspace{1cm} \ldots(1)

where the first term refers to the Langmuir-type sorption sites, the second term to the sorption sites which have been approximated to linear sorption isotherm (both these terms refer to the formation of unimolecular adsorption layer), and the third term refers to the multilayer formation, i.e., water molecules attached to those already absorbed on primary sites. The various parameters are defined as follows: \(K_i = m\beta_i p_o\) (where \(m\) is the molecular weight of solvent and \(\beta_i\) the number of sites of \(i\)th type); \(l = n - j\), number of different types of sites; \(K_j = 2\beta_j p_o\) \([\text{where } x = \exp(\mu_o/RT), \beta_i = Q, \exp(w_{ij}/RT), Q = \text{molar partition function of the sorbate in the monolayer } (i\text{th site})\text{ and } w_j = \text{heat of sorption of the sorbate on the } i\text{th site}]; \)

\[ C = \frac{mK p_o}{N}; \quad K = \sum_{i=0}^{5} n_i \beta_i \]  \hspace{1cm} \ldots(2)

\([n_i = \text{the number of Langmuir expressions (sites)}\text{ approximated to linear isotherm and } \beta_j = \exp(w/RT)\text{ } w_j\text{ being the heat of sorption of the sorbate on } j\text{-sites}; k' = mD/N (D = \text{the number of sites for multilayer formation}); \text{ and } k = Q_m \exp(w_{m}/RT), \text{ } (Q_m = \text{molar partition function of sorbate molecules in multilayers and } w_m = \text{the heat of sorption of sorbate in multilayer formation}].\]

A computer programme based on non-linear least square\textsuperscript{3} analysis, was used for fitting the equation to water sorption isotherms of variously crosslinked Dowex 50W resins in Li\textsuperscript{+}, Na\textsuperscript{+} and K\textsuperscript{+} forms. The main objectives of these studies were to assess (i) the possibility of reproducing the water sorption isotherms over the whole water activity range, i.e., 0 to 1 and (ii) the physical significance and interpretation of the various parameters of the equation in terms of the various types of water interactions in resin phase.

Results and Discussion

The experimentally observed water sorption isotherms of the various resinates were taken from literature\textsuperscript{5}. The actually observed values of the amount of water sorbed by the various resinates, at different water activities, which were reported as mol of water per equivalent resin, were converted into g water (\(W\))/g resins. For the individual systems, eight or nine experimental points were used to obtain the best values of the five parameters of the equation. The five parameters separately converged to a narrow range of values which reproduced the \(W\)-values at different water activities to better than \(\pm 0.002\) (which is better
than the accuracy of the experimental data). In that sense, a unique set of values for the five parameters was not obtained. On the other hand, the best values of the parameters were consistent with the known physicochemical characteristics of the various systems and their variations with the crosslinking of the resins and the nature of the counterion. While applying this equation to \( \text{Na}^+ \) and \( \text{K}^+ \) resins, \( l = 1 \) was adequate to describe the sorption isotherms. In those cases where \( l = 2 \) was tried, the first term split into two parts with \( k_1' + k_2' = k' \) and \( k_1 = k_2 = k \).

When data on \( \text{Li}^+ \)-form of resins were analysed with \( l = 2 \), the contribution of the second term decreased (i.e. \( C \) decreased) and an almost equal contribution came from the second Langmuir isotherm with small value of \( \text{K}_2 \) (\( \leq 0.4 \)). However, there was no significant improvement in the fit (i.e. error sum square remained nearly the same). This only emphasizes that the linear term adequately describes the Langmuir isotherms with \( K_2 \leq 0.5 \). However, it overestimates Langmuir isotherm at higher water activities which means an underestimation of the third term. This points to the correlation between the various parameters in D'Arcy-Watt equation and the existence of correlation errors.

The extent of agreement between the observed and computed isotherms is illustrated in Figs 1 and 2 where observed and computed water sorption isotherms of some representative systems have been plotted. In general, the agreement between the computed and observed \( W \)-values for all systems is very good, indicating that D'Arcy-Watt equation is applicable to the water sorption isotherms of the strong acid cation exchange resins over the whole range of water activity, i.e. 0 to 1.

The best values for the five parameters for all the systems are summarised in Table 1, along with the square root of the error sum square. The last quantity is a measure of the fit of the computed values to the observed values.

Discussion of first term involving \( k' \) and \( k \)

This term (Langmuir sorption isotherm) describes the monolayer formation on sorption sites. The constant \( K' \) has a direct relationship with the exchange

![Fig. 1 — Water sorption isotherms of Dowex 50W × 2 resins in Li⁺, Na⁺ and K⁺ forms [Experimental (points): computed from D'Arcy-Watt equation using values of parameters listed in Table 1 (solid curve)].](image-url)
capacity of the ion exchangers, as in these materials the counterions and the inogenic groups (i.e. the sulphonic acid groups in the present case) act as the sorption sites for water molecules. The constant $K$ is a measure of the binding strength of the water molecules to the sorption sites. The values of $K'$, expected on the basis of the ionexchange capacities of the resins are: LiR (0.086-0.09); NaR (0.081-0.084); and KR (0.076-0.079). The derived values of $K'$ (Table I) are LiR (0.059-0.062); NaR (0.13-0.17); and KR (0.074-0.082). The values of $K'$ for KR are in very good agreement with the expected values, for LiR are in reasonable agreement but for NaR, $K'$ values are nearly twice the expected values. This implies that the first water molecule absorbed by Li$^+$ or K$^+$ resin is more strongly attached than the others, whereas in Na$^+$ resin the first two water molecules are bound with nearly equal strength. The relative enthalpies of hydration for the three cations follow the order: Li$^+ >$ Na$^+ >$ K$^+$. However, the values of $K$-parameter which is a measure of the strength of the binding of water molecules to sorption sites, follow the order: LiR > KR > NaR.

In this connection Zundel’s observations, based on IR studies of the membranes of similar resins, that the strength of hydrogen bond bridges made by water molecules with sulphonic acid groups decreases as the cation-water interaction increases, is relevant. This would suggest that the sulphonate-water bond strength would be greatest in KR and least in LiR. However, a recent study of hydrogen isotope effects in the dehydration of these resins has shown that the first few water molecules (~2) form hydrogen bonds in LiR, NaR or KR which are much weaker than water-water hydrogen bonds, indicating that sulphonate groups are not hydrated. Thus the low values of $K$ in NaR must arise because of the coupling of $K$ and $K'$ in first term and their further correlation with $C$ in the second term, as the monolayer formation (1st hydration shell) includes contribution form $C$ term also. $K$ varies with the addition of each water molecule in the first hydration shell. Because $K'$ in NaR is very much larger than expected on the basis of one water molecule per cation, $K$ is averaged over and a lower value is obtained. A comparison of $K$ values would be valid only when it refers to the first water molecule entering the hydration shell as in LiR or KR.

The data in Table I show that in all the three cases $K$ increases slightly as the resin crosslinking increases. This trend is consistent with decrease in the water content of the resins with increase in crosslinking. As the number of water molecules available for sorption on various ionic sites decrease, their interaction

Fig. 2—Water sorption isotherms of Dowex 50W x 12 resins in Li$^+$, Na$^+$ and K$^+$ forms [Experimental (points); computed from D’Arcy-Watt equation using values of parameters listed in Table I (solid curve)]
Table 1 — Parameters of D'Arcy-Watt Equation for Various Dowex-50 W-resin Systems

<table>
<thead>
<tr>
<th>Sl No</th>
<th>System ion crosslinking</th>
<th>K'</th>
<th>K</th>
<th>C</th>
<th>k'</th>
<th>k x 10^{-3}</th>
<th>Square root* of error sum square</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Li × 1</td>
<td>0.0610</td>
<td>23.02</td>
<td>0.2288</td>
<td>0.08957</td>
<td>980.28</td>
<td>0.009</td>
</tr>
<tr>
<td>2</td>
<td>Li × 2</td>
<td>0.0588</td>
<td>25.45</td>
<td>0.2283</td>
<td>0.0944</td>
<td>966.99</td>
<td>0.009</td>
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<tr>
<td>3</td>
<td>Li × 4</td>
<td>0.0614</td>
<td>25.51</td>
<td>0.208</td>
<td>0.1077</td>
<td>939.21</td>
<td>0.008</td>
</tr>
<tr>
<td>4</td>
<td>Li × 12</td>
<td>0.0608</td>
<td>28.34</td>
<td>0.2277</td>
<td>0.1066</td>
<td>836.93</td>
<td>0.005</td>
</tr>
<tr>
<td>5</td>
<td>Na × 1</td>
<td>0.1704</td>
<td>3.174</td>
<td>0.067</td>
<td>0.0708</td>
<td>982.88</td>
<td>0.006</td>
</tr>
<tr>
<td>6</td>
<td>Na × 2</td>
<td>0.1602</td>
<td>3.538</td>
<td>0.0709</td>
<td>0.0707</td>
<td>973.18</td>
<td>0.009</td>
</tr>
<tr>
<td>7</td>
<td>Na × 4</td>
<td>0.163</td>
<td>3.856</td>
<td>0.0536</td>
<td>0.072</td>
<td>951.68</td>
<td>0.002</td>
</tr>
<tr>
<td>8</td>
<td>Na × 8</td>
<td>0.1675</td>
<td>3.904</td>
<td>0.00585</td>
<td>0.1133</td>
<td>855.14</td>
<td>0.002</td>
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<tr>
<td>9</td>
<td>Na × 12</td>
<td>0.1386</td>
<td>4.281</td>
<td>0.0843</td>
<td>0.0841</td>
<td>859.07</td>
<td>0.002</td>
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<tr>
<td>10</td>
<td>K × 1</td>
<td>0.0865</td>
<td>12.203</td>
<td>0.0285</td>
<td>0.0534</td>
<td>985.97</td>
<td>0.006</td>
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<tr>
<td>11</td>
<td>K × 2</td>
<td>0.0819</td>
<td>12.465</td>
<td>0.0474</td>
<td>0.0494</td>
<td>977.20</td>
<td>0.007</td>
</tr>
<tr>
<td>12</td>
<td>K × 4</td>
<td>0.0771</td>
<td>13.036</td>
<td>0.068</td>
<td>0.0440</td>
<td>964.23</td>
<td>0.005</td>
</tr>
<tr>
<td>13</td>
<td>K × 8</td>
<td>0.0772</td>
<td>13.631</td>
<td>0.0578</td>
<td>0.0526</td>
<td>910.25</td>
<td>0.004</td>
</tr>
<tr>
<td>14</td>
<td>K × 12</td>
<td>0.0745</td>
<td>14.382</td>
<td>0.0649</td>
<td>0.0520</td>
<td>898.28</td>
<td>0.003</td>
</tr>
</tbody>
</table>

*Error sum square = ∑(W'(obs) - W'(calc))^2

energies with the binding sites also increase. The hydrophobic interaction of the resin network, which would increase with resin crosslinking, could also contribute to this increase in the ionic sites—water interactions with resin crosslinking.

Discussion of second term involving C-parameter

This term describes the water sorption on those primary sorption sites which could be approximated by a linear sorption isotherm, i.e., those sites which have \( K_{1} (p/p_{w}) < 1 \). As \( p/p_{w} \) changes from 0 to 1, \( K_{1} \) value of 0.1 or 0.2 gives a Langmuir isotherm which is approximately linear. Even with \( K_{1} \) value as high as unity, Langmuir isotherm can be approximated to a linear isotherm at low water activities, though at higher activities linear isotherm overestimates, i.e., the contribution from Langmuir-type isotherm with \( K_{1} = 1 \) would be less. We are assuming here that Langmuir terms with \( K_{1} \leq 1 \) are approximated by a linear isotherm and are included in the second term. This assumption would lead to an underestimation of the contribution from third term at higher activities. This splitting of the primary sorption sites into Langmuir or linear sorption sites is to some extent arbitrary and a result of curve fitting process. Together they should represent the monolayer formation on all sorption sites. The contribution of these two terms, at any specific water activity, is independent of resin crosslinking up to \( a_{w} \sim 0.6 \), for all ionic forms. This is consistent with the observations made earlier that water sorption isotherms, of any ionic form of resin, are independent of resin crosslinking up to \( a_{w} \sim 0.6 \) and the water sorption in the region \( (a_{w} = 0 \) to 0.6) is due to the formation of primary hydration shell of the ions. In other words, the total contribution from first and second terms describes the formation of primary hydration of the cations in these systems. The primary hydration numbers can be estimated from these terms.

The C-parameter is a product of two terms of \( K'_{1} \) and \( K_{1} \) type, i.e., \( C = K_{1}K'_{2} \), where \( K_{2} < K_{1} \). When the upper limit for \( K_{2} \) is one, i.e., \( C = K'_{2} \), the sum \( C + K'_{1} \) gives the total number of water molecules sorbed on all sorption sites. As the counterions are the water sorption sites in the resin, dividing this sum by the value of \( K'_{1} \) expected for various ionic forms on the basis of their exchange capacities, one gets the number of water molecules primarily absorbed per ion, i.e., the primary hydration number of ions in the resin phase. These numbers for various resinates are: LiR, 3.2; NaR, 2.80; and KR, 1.8, which compare very favourably with the hydration numbers of these ions in the resin phase derived earlier.

Discussion of third term describing multilayer formation—Parameters \( k' \) and \( k \)

This term takes into account the multilayers formed by further adsorption of water molecules on primarily adsorbed water molecules. The parameter \( k' \) is related to the number of sites available for multilayer formation. In the discussion of the first term it has been shown that one water molecule per sorption site is strongly adsorbed. Therefore the ratio \( k'/K' \) should give the number of water molecules adsorbed on each strongly adsorbed water molecule. These ratios averaged over all resin crosslinking are LiR \( \sim 1.7 \); NaR \( \sim 1.0 \); KR \( \sim 0.6 \). For the formation of a second

Since two water molecules per sorption site are involved in \( K'_{1} \) in this system, for computing this ratio, 0.5 \( K'_{1} \) has been used.
hydration shell round an ion, each water molecule should attach two water molecules through two hydrogens. These ratios clearly indicate that the second hydration shell of the lithium ions in LiR is fairly well formed and there seems to be no secondary hydration shell round Na⁺ or K⁺ ions.

The parameter $k$ reflects the amount of heat adsorbed per water molecule in the multilayer formation. It is also a measure of the extent of multilayer formation. Hence, $k$-parameter should decrease with increase in a crosslinking. This expectation is fully realised in the data presented in Table 1. The parameter $k = Q_m e^{w_m/RT}$ and $K = Q_i e^{w_i/RT}$ where $Q_m$ and $Q_i$ are the molar partition functions of water molecules in the multilayer and primary hydration shells and $w_m$ and $w_i$ the heats of adsorption in the multilayer and primary hydration shell. The ratio $K/k$ is then given by Eq. (3).

$$\ln K/k = \ln \frac{Q_i}{Q_m} + \frac{w_i - w_m}{RT} \quad \ldots (3)$$

As the maximum contribution to $Q/Q_m$ comes from the vibration partition function, $Q/Q_m$ can be approximated to the ratio of vibrational partition functions.

For computing this the vibrational frequencies of water in crystal hydrates and liquid water have been taken into consideration. The maximum shift of nearly 300 cm⁻¹ is observed in the $v_{as}$OH; the other two vibrational modes show only marginal shifts and can be taken as identical. On this basis $\ln(Q/Q_m)$ is estimated to be $-0.766$. Using observed $K/k$ ratios and estimated $Q/Q_m$, $w_i - w_m$ values have been computed for the various resin systems.

The values are: LiR, 2.3-2.5 kcal; NaR, 1.2-1.3 kcal; and KR, 1.9-2.1 kcal. The first number refers to resin of 1% DVB content and the second number to the resin with 12% DVB content. An idea about the difference between the heat of adsorption of water molecules in the primary hydration shell and in the multilayer formation can be obtained from the work of Kebarle on gas phase hydration of these ions. Assuming that the fifth water molecule belongs to the second hydration shell (multilayer), the difference in $\Delta H$ between the adsorption of fourth and fifth molecules should give a measure of $w_i - w_m$. These numbers for the various ions are: Li⁺, 2.5 kcal; Na⁺, 1.5 kcal; and K⁺, 1.1 kcal. The agreement between Li and Na data from Kebarle's work and the present study is too good to be true, considering the approximations involved. However, it does indicate that the present approach gives a meaningful estimate of $w_i - w_m$. The disagreement between the two sets of numbers for K⁺, indicates either that the hydration and multilayer formation in KR, most probably, does not involve potassium ions or the assumption of 4 water molecules in the first hydration shell of K⁺ is grossly in error.

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