Ion Exchange Equilibria in Mixed Solvents: Part I—Na\(^+\)/H\(^+\), Cu\(^{2+}\)/H\(^+\), Cu\(^{2+}\)/Na\(^+\), Ni\(^{2+}\)/H\(^+\), Ni\(^{2+}\)/Na\(^+\) & Cu\(^{2+}\)/Ni\(^{2+}\) Exchanges on Dowex 50 WX8 in 25\% (v/v) Acetone-Water Mixture

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Six binary exchanges, namely Na\(^+\)/H\(^+\), Cu\(^{2+}\)/H\(^+\), Cu\(^{2+}\)/Na\(^+\), Ni\(^{2+}\)/Na\(^+\) and Ni\(^{2+}\)/Cu\(^{2+}\), have been investigated in 25\% (v/v) acetone-water mixture on Dowex 50 WX8. Selectivity coefficients (K\(_D\)) have been obtained over the whole range of resin composition. In the absence of solution phase activity coefficient data for electrolytes in this solvent, apparent equilibrium constants (K\(_D\)) have been obtained. As compared to the selectivity of the resin in aqueous medium, the resin selectivity for divalent ions increases in relation to H\(^+\) but decreases in relation to Na\(^+\), in this medium. The rule of the triangle stated in terms of K\(_D\) has been verified using the equilibrium data for these exchanges in aqueous medium reported earlier and its validity in mixed solvent systems has been established.

The use of mixed or non-aqueous solvents in ion exchange reactions is of considerable interest as the ion exchangers exhibit enhanced selectivities for certain ions in such systems. A large amount of data on the enhanced selectivity of ion exchangers in uni-univalent exchanges in a variety of mixed solvents have been reported in the literature\(^1\)-\(^11\). A rigorous thermodynamic treatment which explains this enhanced selectivity of ion exchangers in mixed and non-aqueous media has been developed and experimentally verified\(^12\)-\(^18\).

Though a large amount of data are available on the distribution coefficients of multivalent metal ions in ion-exchange equilibria in mixed solvents\(^3\)-\(^8\), very few studies on such systems have reported selectivity coefficients or equilibrium constants\(^9\)-\(^14\).

Kressman and Kitchner’s work on phenol-sulphonate resin in calcium form indicated that univalent alkali metal ions were preferentially sorbed by the exchanger with increasing ethanol content in the mixed solvent. Selectivity coefficients, K\(_M\), increased with increase in the equivalent fraction of the organic solvent \(X_S\), when \(M\) was alkali metal ion but decreased when \(M\) was ammonium ion. Materova et al.\(^19\) also reported a decrease in log K\(_M\) from its value of 1-12 in water to 0-62 in mixed solvent at \(X_S = 0\) on carboxylate resins. Elovich and coworkers\(^20\) in their studies on sulphonate exchanger KU-2 observed decreasing preference for the divalent metal cations over sodium ion as the ethanol content of the solution was increased. Because of the lack of sufficient data on ion exchange equilibria in mixed solvents, even the rule of the triangle in mixed solvents has not been verified so far. The present study was, therefore, undertaken. Six binary exchange systems, namely Na\(^+\)/H\(^+\), Cu\(^{2+}\)/H\(^+\), Cu\(^{2+}\)/Na\(^+\), Ni\(^{2+}\)/H\(^+\), Ni\(^{2+}\)/Na\(^+\) and Ni\(^{2+}\)/Cu\(^{2+}\) have been studied on Dowex 50 WX8 in 25\% (v/v) acetone-water mixture. The selectivity coefficients, K\(_D\), have been determined over the entire range of resin compositions. As the solution phase activity coefficient data for these electrolytes, involved in the exchanges, are not available in acetone-water mixture, only apparent equilibrium constants, K\(_D\), have been obtained by integrating log K\(_D\) over the entire range of resin compositions.

An attempt has been made to verify the rule of the triangle in mixed solvents, by assuming that the solution phase activity coefficient ratios in mixed solvents are governed by Robinson’s\(^21\) equations for these ratios in aqueous medium.

**Materials and Methods**

All the chemicals were E. Merck (G.R.) reagents and were used as such without further purification. Acetone used for these studies was B.D.H. reagent of L.R. grade. The strong acid cation exchanger Dowex 50 WX8 (50-100 BSS mesh) was supplied by J. T. Baker & Co. (Pennsylvania, USA). The equilibrium experiments for the binary and ternary exchanges were carried out using the batch technique at 30\(\pm\)\(^\circ\) K. Titrimetric methods were used for the estimation of hydrogen ions (acid-base), copper ions (iodometric) and nickel ions (EDTA back titration). Sodium ions, wherever present, were estimated as the difference. Other details of the experimental procedure and analytical methods have been given in an earlier publication\(^22\).
Theoretical

(i) Equilibrium constants — Equilibrium in a general ion exchange reaction can be described by Eq. 1

\[ Z_B A^+ + Z_A + Z_A B R_G \Rightarrow Z_A B^+ + Z_B + Z_B A R Z_A \ldots (1) \]

For evaluating the equilibrium constant of the above reaction in any mixed solvent, the thermodynamic treatment of Gaines and Thomas\textsuperscript{20} can be used if the standard states of the resinsates and electrolytes are referred to the mixed solvent used, i.e. the mono ionic form of the resin in equilibrium with the mixed solvent for the resinate and the hypothetical one molar solution of the electrolyte in the mixed solvent for the ions. The contribution of the solvent activity terms in this treatment is small for moderately crosslinked resin and at low ionic strengths (~0-1M)\textsuperscript{31}, conditions prevailing in the present study, no such data are available. Therefore, only the dynamic equilibrium constant, therefore, involves the solvent and electrolytes in the mixed solvent used in the present study, and can be neglected. Hence the equilibrium constant evaluated on this basis refers to the reaction exchange: \(2A+ + B^+ + B^+ = B_R + 2A^+\), where \(Z_A = 1, Z_B = 2, 2AR\) is in equilibrium with infinitely dilute solution of \(AX\) in mixed solvent, \(B^+\) is in the usual molal scale but in the mixed solvent, \(BR_G\) is in equilibrium with infinitely dilute solution of \(BX\) in mixed solvent and \(2A^+\) is in molal scale in the mixed solvent. The equilibrium constant can be represented by Eq. 2.

\[ \ln K_D^D = \int_0^1 \frac{Z_B (Z_B + 1)}{(Z_A + 1)} dX_A \ldots (2) \]

where \(K_D = \frac{(N_B)}{(N_A)} \frac{Z_B}{Z_A} \frac{Z_A}{Z_B} \frac{(m_B)}{(m_A)} \frac{(m_A)}{(m_B)} \)

\(N's\) are the mole fractions of the ions in the resin, \(m's\) are the molalities of the ions in the mixed solvent and \(X_A\) is the equivalent fraction of the resinate \(AR\). The computation of the thermodynamic equilibrium constant, therefore, involves the activity coefficient terms in the solution. For the electrolytes in the mixed solvent used in the present study, no such data are available. Therefore, only \(K_D\) terms have been evaluated for various resin compositions and integrated to obtain the function \(K_D\), the apparent equilibrium constant (Eq. 3):

\[ \ln K_D^D \left( \frac{A}{B} \right) = \int_0^1 \ln K_D dX_A \ldots (3) \]

(ii) Rule of the triangle — The rule of the triangle states (Eq. 4):

\[ Z_c \quad Z_a \quad Z_b \quad (K_a^D) \quad (K_b^C) \ldots (K_c^A) = 1 \ldots (4) \]

where \(K's\) are equilibrium constants (given by Eq. 2) and \(Z_i\) is the valency of the ion \(i\). Within the approximation that activity coefficient ratio in Eq. 2 remains constant and can be taken outside the integral, Eq. 4 can be rewritten (for the specific case \(Z_A = Z_C = 1, Z_B = 2\)) as Eq. 5.

\[ \left[ K_D (\gamma_A^D) K_D (\gamma_B^C) K_D (\gamma_C^A) \right] \left( \frac{\gamma_A^D}{\gamma_B^C} \frac{\gamma_B^C}{\gamma_C^A} \right) = 1 \ldots (5) \]

It should be emphasized here that the values of activity coefficient of an electrolyte occurring in different ratios (in brackets) are not identical because they pertain to different electrolyte mixtures. For example, \(\gamma_A^D \cdot BX\) in the first bracket is the activity coefficient of \(BX\) in a solution of \(BX+AX\) whereas \(\gamma_B^C \cdot BX\) in the second term is the activity coefficient of \(BX\) in a solution containing \(BX+CX\).

In principle, Robinson's Equations for the activity coefficient ratios, which are based on the equations of Guggenheim\textsuperscript{24-26}, Scatchard\textsuperscript{27} and Bronsted's principle of specific ion-interaction, should be applicable to mixed solvent systems also — the values of interaction coefficients being different for different solvent systems. Using this approach, the product of the activity coefficient ratios in Eq. 5 can be written in the logarithmic form as:

\[ \log P = -\log \gamma_A^D + \log \gamma_B^C + \log \gamma_C^A \]

\[ = -1\cdot0214\sqrt{\gamma} - B m_{AX} - B m_{BX} + \frac{1\cdot0214\sqrt{\gamma}}{1 + 1\cdot5 V^2} \]

where \(B_1 = 2B_{AX} - 2B_{BX}, B_2 = 2B_{CX} - B_{BX} + B_{A+}\) and \(B_3 = B_{AX} - B_{AX}, B_{BX}, B_{CX} \) and \(B_{AX}\) being the interionic coefficients. Therefore,

\[ \log P = -(m_{AX} + 2m_{BX}) B_1 + (m_{CX} + 2m_{BX}) B_2 + 2 (m_{CX} + m_{AX}) B_3 \ldots (6) \]

Under the experimental conditions used in the present study, the sum of the molalities in the brackets is kept constant (= 0-1m) in all the experiments. With this simplification and putting the values of \(B_1, B_2\) and \(B_3\), Eq. 7 becomes:

\[ \log P = 0.1 (-B_1 + B_2 - 2B_3) \]

\[ = 0.1 (-2B_{AX} + 2B_{BX} - 2B_{CX} - 2B_{AX} + 2B_{AX}) \]

Therefore, the product over the activity coefficient ratios in Eq. 5 is unity. The rule of the triangle, then, can be stated in terms of \(K_D\) (Eq. 3), which includes the activity coefficient ratios of the ions in the resin phase but not the solution phase activity coefficients.

Results and Discussion

Plots of \(\log K_D\) versus \(X_{AR}\) for various binary mixtures are given in Fig. 1. The values of \(\log K_D\) (Eq. 3) computed from plots by graphical integration have been given in Table 1. The same exchange systems in aqueous medium have been studied earlier\textsuperscript{28}. Values of \(\log K_D\) have been computed from data and included in Table 1 for comparison. These data clearly show the following trends:

(i) In the exchagenes involving hydrogen ions, i.e. \(Na^+ / H^+, Cu^{2+} / H^+\) and Ni\(^{3+} / H^+\), metal ions are the...
preferred ions in aqueous medium. This preference for the metal ions by the resin is increased in the mixed solvent (25% v/v, acetone-water) system.

(ii) In exchanges involving uni-divalent metal ions, i.e. Cu\(^{2+}/Na^+\) and Ni\(^{2+}/Na^+\), divalent metal ion is the preferred cation in the aqueous medium. This preference for the divalent metal cation decreases in 25% (v/v) acetone-water mixture. Such a decrease in the selectivity of ion-exchangers in divalent metal cation-alkali metal ion exchanges in mixed solvent systems has been observed by earlier workers also\(^{26,27}\).

(iii) In di-divalent exchange, i.e. Ni\(^{2+}/Cu^{2+}\), there is no significant increase in the selectivity of the exchanger for nickel ions in mixed solvent as compared to aqueous system.

The selectivity behaviour of PSS type resins in acetone-water mixtures will be discussed in greater detail in a subsequent publication.

**Verification of the rule of the triangle in terms of** \(K_D\) **in aqueous and mixed solvent systems** — The rule of the triangle should hold for log \(K_D\) values if the solution phase activity coefficients can be expressed in terms of Robinson's equations. In

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**Table 1 — Log \(K_D\) Values Observed Experimentally and Obtained by Rule of Triangle in Aqueous Medium and in 25% (v/v) Acetone-Water Solution**

<table>
<thead>
<tr>
<th>SI No.</th>
<th>System</th>
<th>Log (K_D) in aqueous medium</th>
<th>Log (K_D) in 25% (v/v) acetone-water solution</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Observed</td>
<td>Computed by rule of triangle*</td>
</tr>
<tr>
<td>1</td>
<td>Na(^+)/H(^+)</td>
<td>0.176</td>
<td>0.182</td>
</tr>
<tr>
<td>2</td>
<td>Cu(^{2+})/H(^+)</td>
<td>0.800 (2, 3)</td>
<td>0.801 (4, 5)</td>
</tr>
<tr>
<td>3</td>
<td>Cu(^{2+})/Na(^+)</td>
<td>0.435 (1, 3)</td>
<td>0.448 (4, 6)</td>
</tr>
<tr>
<td>4</td>
<td>Ni(^{2+})/H(^+)</td>
<td>0.844 (1, 2)</td>
<td>0.843 (5, 6)</td>
</tr>
<tr>
<td>5</td>
<td>Ni(^{2+})/Na(^+)</td>
<td>0.480 (1, 5)</td>
<td>0.492 (2, 6)</td>
</tr>
<tr>
<td>6</td>
<td>Ni(^{2+})/Cu(^{2+})</td>
<td>0.043 (2, 4)</td>
<td>0.044 (3, 5)</td>
</tr>
</tbody>
</table>

*The systems from which the values have been derived are given in parentheses.
order to verify this, log $K_D$ data for the six binary exchange systems in aqueous medium (where Robinson’s equations are known to be valid) reported in an earlier publication and listed in Table 1, have been used. Application of the rule of triangle yielded additional 12 values for the six exchange systems. The observed and computed (rule of triangle) values for log $K_D$ have been given in Table 1. The agreement between the observed and computed values of log $K_D$ is as good as observed earlier when log $K$ values were used for this purpose. Hence, validity of the rule of the triangle, formulated in terms of Robinson’s equations for the solution phase activity coefficient ratios are valid in mixed solvent (Table 1) in various combinations, additional values of log $K_D$ for the six exchanges in the mixed solvent have been obtained and these are given in Table 1. Again the agreement between the observed and computed (rule of the triangle) values of log $K_D$ for all the six exchanges in mixed solvent is quite good. On the basis of the above mentioned data the following conclusions can be drawn:

(i) The rule of the triangle holds for log $K_D$ values, provided Robinson’s equations for the solution phase activity coefficient ratios are valid.

(ii) The rule of the triangle holds for mixed solvent systems.

(iii) Robinson’s equations for the solution phase activity coefficient ratios are valid in mixed solvent systems.

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References