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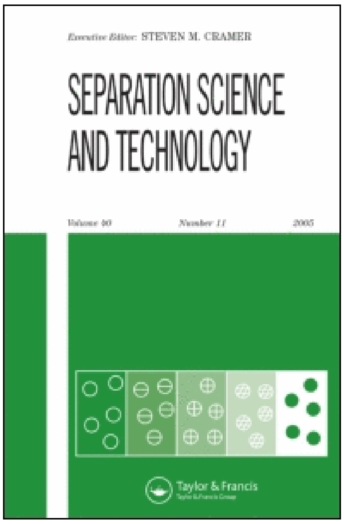

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Isotope Effects in Ion-Exchange Equilibria in Aqueous and Mixed Solvent Systems

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Isotope Effects in Ion-Exchange Equilibria in Aqueous and Mixed Solvent Systems

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Abstract

Isotope effects in ion-exchange equilibria in aqueous and mixed solvents are analyzed in terms of the general features of ion-exchange equilibria and of isotope effects in chemical equilibria. The special role of solvent fractionation effects in ion-exchange equilibria in mixed solvents is pointed out. The various situations arising in isotope fractionation in ion exchange in mixed solvents due to solvent fractionation effects are theoretically discussed. The experimental data on lithium isotope effects in ion-exchange equilibria in mixed solvents are shown to conform to the above situations. The limitations of ion-exchange equilibria in mixed solvents for isotope fractionation are pointed out.

INTRODUCTION

Isotope effects in ion-exchange equilibria in aqueous medium have been studied by a number of investigators (*1–10*). If the ion-exchange system also involves a chemical exchange (*11–15*) (isotopic equilibrium between two different chemical species containing the isotopically substituted atom) or an electron-exchange reaction (*16*), the observed isotope effects are usually much larger than in simple ion-exchange reactions. In such cases the isotope effects in the ion-exchange equilibria are primarily governed by the chemical exchange involved in the system. On the other hand, in simple ion-exchange reactions, the isotope effects are very much smaller than in chemical-exchange reactions and have been attributed to differently solvated species of the ions in the resin and the solution phase (*17*). The underlying idea in all such interpretations is that the ions are partially dehydrated in the resin phase.

A few studies have been reported on isotope effects in simple ion-exchange equilibria in mixed solvents (*6*, *7*, *10*, *18*) (aqueous-nonaqueous) systems, mostly involving lithium isotopes. Kakihana et al. (*6*) have studied lithium isotope effects on various types of cation exchangers in ethanol-water and acetone-water mixtures. An increase in the separation factor $\alpha_7{}^6$ with an increase in the organic solvent is observed. (The mass number of the isotope concentrating in resin phase is given at the top.) This group of workers has also investigated sodium (*19*) and nitrogen (*20*) (as $NH_4{}^+$) isotope effects on various cross-linked exchangers in ethanol-water mixtures. In both cases, $\alpha_{24}{}^{23}$ and $\alpha_{15}{}^{14}$ increased in mixed solvent systems. Davies and Owen (*18*) and Botter (*7*) have also observed an increase in the lithium isotope separation factor, $\alpha_7{}^6$, in a 20%(v/v) acetone-water mixture. All these studies were conducted on polystyrene sulfonic acid-type cation exchangers in dilute solutions (~0.25 *M*). Ciric and Pupezin (*10*), employing lithium nitrate solutions of ~1.0 *M*, found that the separation factor decreases in ethanol-water (0–100%), glycol-water (0–100%), and dioxane-water (0–50%) mixtures. However, these workers reported a very high value for $\alpha_7{}^6$ (1.013) in an aqueous system (1.0 *M* $LiNO_3$ on Amberlite IR-120), which is inconsistent with the generally observed value for $\alpha_7{}^6$ when using ~0.2 *M* lithium hydroxide, chloride, or acetate solutions on similar types of cation exchangers. Recently, lithium isotope effects on Dowex 50WX8 in 76%(w/w) acetone-water, 52.5%(w/w) DMSO-water, and 20.7%(w/w) isopropanol-water mixtures have been reported (*21*). These variations in the isotope effects in simple ion-exchange equilibria when the medium is changed from an aqueous to an aqueous-nonaqueous system have found no satisfactory explanation so far. This is not surprising because until recently even the enhanced ionic selectivity observed in ion-exchange equilibria in mixed solvents was not clearly understood. Recent work in this field, particularly on the thermodynamics of ion-exchange equilibria in mixed solvents (*22–24*), has identified the various important factors governing the enhanced ionic selectivity exhibited by ion exchangers in mixed solvents. In the present communication an attempt is made to explain the observed variations in isotope effects in ion-exchange equilibria in mixed solvents by taking into consideration various factors which influence ionic selectivity in mixed solvent systems and isotope effects in chemical-exchange systems.

ISOTOPE EFFECTS IN CHEMICAL EQUILIBRIA

The isotope effects in chemical equilibria are mainly governed by changes in the force constants of the different chemical species involved in the system and changes in the vibrational frequencies of a molecule on isotopic substitution. Thus, the direction and magnitude of the isotope effects in chemical systems help in understanding the molecular dynamics of the system. The extensive theoretical work carried out by Biegeleisen and his associates (*25*) has amply demonstrated that as a general rule, the heavier isotope concentrates in that species or phase where overall binding of the isotopically substituted atom is greater. Hence the direction and magnitude of isotope effects give information about the strength of the chemical or physical bonds in which the isotopically substituted atom is involved.

ISOTOPE EFFECTS IN ION-EXCHANGE EQUILIBRIA IN AQUEOUS SYSTEMS

Ion-exchange processes are two-phase systems. In the simple ion-exchange systems being considered here, molecules and compounds are fully dissociated into ions and no chemical-exchange equilibria are involved. As no complexation and ion association are involved in simple ion-exchange systems, it is the state of the ions in the resin and solution phases which determines the magnitude and direction of isotope effects in such systems. As most of the work on isotope effects in ion-exchange equilibria in aqueous and mixed solvents has been carried out on polystyrene–divinyl benzene–sulfonic acid-type exchangers, the state of the ions in such exchangers is considered first.

State of the Ions in the Exchanger Phase

In the low and moderately cross-linked resins (up to 8 % DVB content), it is generally believed that counterions in PSS-type exchangers are fully hydrated (*26*). In the past, several attempts have been made to deduce hydration numbers from ion-exchange data. Pepper and Reichenberg (*27*) used the increase in the equivalent volume of the ion exchanger on water sorption as the criterion. Glueckauf and Kitt (*28*) computed hydration numbers from water sorption isotherms at different temperatures and defined the water of hydration as those water molecules whose sorption decreases the free energy of the system. These attempts and the ones (*29*, *30*) based on a comparison of water sorption isotherms of variously cross-linked ion exchangers give information regarding the primary solvation of the ions in the resin phase. On the other hand, in proton magnetic resonance studies of ionic solvation in ion-exchange resins (*31*), the effective solvation numbers, which include primary as well as secondary and higher solvation, are deduced. These studies have shown that the effective hydration number of alkali metal ions decreases with increasing cross-linking of the ion exchangers, i.e., overall solvation of an ion is lesser in a highly cross-linked resin than in a low cross-linked one.

In a more detailed analysis of the swelling equilibria in ion exchangers (*32*), the separate contributions of the primary solvation of the ions, the secondary solvation of the ions, and the extension of the resin network to the free energy of swelling of the resins have been considered. The overall picture which emerges is that the contribution of the primary solvation remains constant except in very highly cross-linked exchangers. The contribution from the secondary solvation decreases and from the extension of the resin network increases with an increase in the cross-linking of the resin.

Isotope Effects

Considering the isotope effects in simple ion-exchange equilibria in the light of the above analysis, it is obvious that no contribution to the isotope effect is to be expected from the resin network. The isotope effect in ion-exchange equilibria then primarily arises because of the lesser solvation of the ions in the resin phase. In general, for the ionic isotopic species, the ion-exchange reaction can be written as

$$M'(H_2O)_n{}^{z+} + \overline{M(H_2O)_{n'}{}^{z+}} \rightleftarrows M(H_2O)_n{}^{z+} + \overline{M'(H_2O)_{n'}{}^{z+}} \qquad (1)$$

where M represents the heavier isotope, and n and n' are the "hydration" numbers for the ion in solution and the resin phase, respectively, with $n > n'$. The bars represent the resin phase and z is the charge on the ion.* It is difficult to assign any specific hydration number for the ions because of contributions from both primary and secondary solvation. Considering the fact that the isotope effects in chemical equilibria arise from differences in vibrational frequencies of isotopically substituted molecules, only the

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*The underlying assumption in this formulation is that the isotopic ions, M and M′, have the same hydration numbers, i.e., the solvation process is independent of the mass of the ion. This is true to a very high degree of approximation as the solvation of the ions depends upon their charge and size, and isotopic ions have the same charge and (to a very high degree of approximation) the same size.

primary solvation shell of the hydrated ions would make significant contributions to the isotope effects. Though many different values have been quoted for lithium ions, a value of four has generally been accepted. The effect of changes in the secondary solvation then can be visualized as departure from the integral value of four for the hydration number. Thus n' in the resin phase can be considered as a fractional number, not necessarily an integral number. For this reason it is not possible to carry out quantitative model calculation for the isotope effect in these systems. All the same, one can still discuss qualitatively the effect of many variables of the system on the isotope effects.

Effect of Resin Cross-Linking

The effect of increasing the resin cross-linking on the solvation of the ions in the resin phases is primarily to reduce the secondary solvation whose contribution to isotope effect is not significant. Large isotope effects can therefore be expected only in highly cross-linked exchangers where the primary solvation shell of the ions is affected. The effect of cross-linking on the lithium isotope separation factor on Dowex 50 resins has been studied by Lee and Begun (*4*, *33*) and Kakihana et al. (*6*) (Table 1). It is clear from the data that on resins of lower cross-linkings ($<16\%$ DVB resin), $\alpha_7{}^6$ is small and increases slightly as cross-linking increases. As discussed earlier, in this range of resin cross-linking only the secondary

TABLE 1

Effect of Cross-Linking on the Lithium Isotope Separation Factor, $\alpha_7{}^6$, on PSS-Type Cation Exchangers

	Lee and Begun (*4*)	Kakihana et al. (*6*)		
	Elution,	Breakthrough		
Resin	0.1–0.3 *M* HCl	0.1 *M* LiCl	0.1 *M* LiOH	State of lithium ions in the resin phase
Dowex 50WX4	1.001_0	1.001		Reduction in secondary solvation
Dowex 50X8	1.001_6	1.001		″
Dowex 50X12	1.002_7		1.002 (*9*)	″
Dowex 50X16	1.003_7	1.004		Primary solvation shell affected
Dowex 50X24	1.003_8	1.004	1.005 (*6*)	″
Dowex 50X35		1.005	1.008 (*6*)	″

solvation shell of the ions in the resin phase is affected. In resins of $>16\%$ DVB content, the primary solvation shell is affected and the magnitude of $\alpha_7{}^6$ as well as its variations with resin cross-linking are appreciable. Lee and Begun (*4*, *33*) also interpreted the observed isotope effect on Dowex 50X24 on the basis of an assumed partial dehydration of lithium ions. Though the effects of resin cross-linking on sodium (*19*) and nitrogen isotope effects (*20*) have been reported, no definite conclusion can be drawn from the data because the isotope effects are small and the experimental uncertainties are large.

Effect of Anions

Anions tend to be excluded from the resin phase (cation exchangers), and therefore their effect on the state of metal ions in the resin phase is negligible. As moderate or low concentrations of electrolytes are generally employed in the solution phase, any significant effect because of direct interactions between anions and cations is ruled out. The effect of anions on isotope effects in ion-exchange systems can then best be analyzed in terms of the effect of various anions on the water structure in these solutions. The available data on the lithium isotope effects on PSS-type cation exchangers in the presence of different anions are summarized in Table 2.

Halide ions are considered to be "structure breakers," except for fluoride ion which is a "structure maker" (*34–36*). Jancso, Bopp, and Heinzinger (*36*) have pointed out that the structure-breaking property of the anion enhances the solvation of the cations. Consequently, the solvation number of lithium ions increases in aqueous solution as one goes from chloride to iodide (*36*). As the partial dehydration of the lithium ions in the resin phase remains the same, this overall increase in the solvation of the lithium ions in the solution in the presence of the "structure-breaker" anions increases the difference $n - n'$ and hence the isotope effect. The nitrate ion has a special position because it produces a very much broken down water structure which should produce a greater increase in the solvation of lithium ions as compared to chloride. Ceric et al.'s data on $\alpha_7{}^6$ on Amberlite IR 120 using $LiNO_3$ solutions are consistent with this. (The value for LiCl solutions reported by them is too high. The expected value for $\alpha_7{}^6$ for this electrolyte, based on data on Dowex 50X8 and X12 resins, is 1.001 to 1.002, as shown in Table 2.) On similar arguments, slightly lower solvation of lithium ions is expected in the presence of "structure-making" anions, leading to smaller values of $\alpha_7{}^6$ in these systems. The slightly lower values of $\alpha_7{}^6$ observed in the presence of "structure-making" anions like sulfate

TABLE 2

Effect of Anions on Lithium Isotope Effects, $\alpha_7{}^6$, on PSS-Type Cation Exchangers

Resin	Salt concentration (*M*)	Anion	$\alpha_7{}^6$	Refs.
Amberlite IR120	0.25	Cl^-	1.012(1.001–1.002)[a]	*10*
	0.25	$NO_3{}^-$	1.0043	*10*
	0.25	$SO_4{}^{2-}$	1.0016	*10*
Dowex 50WX8	0.25	OH^-	1.0037	*33*
	0.5	Cl^-	1.0029	*33*
	0.5	$SO_4{}^{2-}$	1.0027	*33*
	0.1	OH^-	1.0013	*44*
	0.1	Cl^-	1.001	*6*
Dowex 50WX12	0.1	OH^-	1.0021	*9*
	0.1	Cl^-	1.002	*9*
	0.1	Acetate	1.003	*9*
Dowex 50WX24	0.1	OH^-	1.005	*6*
	0.1	Cl^-	1.004	*6*
	(0.30 *M*)	Cl^-	1.0038	*6*

[a] Expected value on the basis of data in Ref. *4*.

are consistent with this analysis. However, the higher value of $\alpha_7{}^6$ in the presence of hydroxide anions, a known "structure maker," is inconsistent with this. Lee (*37*) has attributed this increase in $\alpha_7{}^6$ in lithium hydroxide solutions to the localized hydrolysis of hydrated lithium ions, leading to the $Li(H_2O)_x{}^+ \ldots OH^-$ species. Kakihana et al. (*6*) have also attributed higher values with LiOH solutions to ion association between hydrated lithium ions and hydroxide ions. As isotope effects in ion-exchange equilibria are small and the effects of anions on these are still smaller, reliable data on these anion effects are scarce. As such, it is not possible to discuss these anion effects in greater detail.

Effect of Resin Functional Group

The effect of a resin functional group on lithium isotope separation factors in ion-exchange equilibria has been investigated by Lee (*38*). The general conclusions were consistent with the model that the isotope effects arise because of dehydration of lithium ions in the exchanger phase and large separation factors result only when lithium ions are dehydrated in the primary hydration shell.

ISOTOPE EFFECTS IN ION-EXCHANGE EQUILIBRIA IN MIXED SOLVENTS

Before discussing the variations in the isotope effects on changing the solvent system, one very important aspect of ion-exchange equilibria in mixed solvents, namely the solvent fractionation effects, should be considered first.

Solvent Fractionation Effects

When an ion exchanger is equilibrated with a mixed solvent, the solvent composition inside the exchanger phase is different from that of the outside solution (*39*). In aqueous–nonaqueous systems, the anionic groups in the resin phase prefer water for their solvation. This is necessary to overcome the electrostatic interaction between the counterions and the ionogenic group. Thus the solvation of the cations in the resin phase is indirectly governed by the solvation of the ionogenic (e.g., sulfonic acid group) group. It is for this reason that the resin phase generally shows a preference for water, i.e., the organic solvent is excluded to some extent from the resin phase even when the metal cation has a stronger interaction with the organic solvent than with water. The solvent composition in the resin phase is strongly influenced by the counterion in the resin and the resin structure, besides the nature of the organic solvent. These differences in the solvent composition in the resin and solution phase can contribute to the difference in the solvation of the metal ion in the two phases and thence to the isotopic equilibrium in simple ion-exchange systems.

Isotope Effects in Mixed Solvents (Theoretical Considerations)

In the mixed solvent system, the isotope exchange reaction can be written as:

$$[{}^{6}\mathrm{Li}(\mathrm{H_2O})_n(\mathrm{organic})_m]^+ + \overline{[{}^{7}\mathrm{Li}(\mathrm{H_2O})_{n'}(\mathrm{organic})_{m'}]^+}$$

$$\rightleftarrows [{}^{7}\mathrm{Li}(\mathrm{H_2O})_n(\mathrm{organic})]^+ + \overline{[{}^{6}\mathrm{Li}(\mathrm{H_2O})_{n'}(\mathrm{organic})_{m'}]^+} \qquad (2)$$

where n and m represent the number of water and organic solvent molecules in the solvation sphere of lithium ions in the solution phase, respectively, and n' and m' refer to the resin phase. The solvent fractionation effects should also be taken into consideration. If the solution phase has the composition N_w, N_s $(= 1 - N_w)$ and the resin phase N'_w, N'_s (where N'_w and N'_s are the mole fractions of water and organic solvent in the resin), the following three possibilities arise:

Case I: $N'_w = N_w$, $N'_s = N_s$ (no solvent fractionation)
Case II: $N'_w > N_w$, $N'_s < N_s$ (resin prefers water)
Case III: $N'_w < N_w$, $N'_s > N_s$ (resin prefers organic solvent)

In the first case, where there is no solvent fractionation, the situation is very similar to an aqueous system. Because of high ionic concentration in the resin phase, $n' < n$ and $m' < m$. The difference in the solvation of the lithium ions in the resin and solution phase would be similar to that in an aqueous medium. This implies that the magnitude and direction of the isotope effect in the mixed solvent system would be more or less the same as observed in an aqueous medium.

In the second and third cases, where the resin exhibits preference for one of the solvents, the situation is more complicated. The relative strength of the interaction between the metal ion and the two solvent molecules and the solvent composition in the two phases determine the difference in the overall solvation of the metal ion in the two phases. A qualitative idea of the relative overall solvation of the metal ion in the two solvent compositions in the resin and solution phases can be obtained from considerations of free energy of transfer of metal ion from one solvent composition to another. However, the effect of high ionic concentration in the resin phase would diminish the metal ion solvation in that phase. This decrease in the metal ion solvation can either be enhanced or compensated for by the difference in the solvent composition in the two phases.

In Case II, where $N'_w > N_w$, $N'_s < N_s$, the difference $n - n'$ would be reduced and $m - m'$ would increase. The two possibilities for $\Delta G_t^\circ(\text{Li}^+)$ from composition N_w, N_s to N'_w, N'_s are: (a) $\Delta G_t^\circ(\text{Li}^+)$ is negative and (b) $\Delta G_t^\circ(\text{Li}^+)$ is positive. Situation (a) implies that lithium ions are solvated to a greater extent in water-rich media, i.e., lithium ion–water interactions are stronger than lithium ion–organic solvent interactions. Therefore, the decrease in $n - n'$ would be the dominant influence and a decrease in α should be observed. In Situation (b), lithium ions interact more strongly with the organic solvent; consequently, the increase in $m - m'$ would be the determining factor and an increase in α should be observed.

In Case III, where $N'_w < N_w$ and $N'_s > N_s$, the difference $n - n'$ would increase and $m - m'$ decrease. Using the same convention for defining $\Delta G_t^\circ(\text{Li}^+)$, i.e., from low water content mixture to high water content mixture (in Case III this corresponds to transfer of lithium ions from N_w, N_s to N'_w, N'_s), the two possibilities are (a) ΔG_t° is negative and (b)

ΔG_t° is positive. In Situation III(a), ion–water interactions dominate. Therefore, the increase in $n - n'$ makes the major contribution to isotope effect and an increase in α should be observed. In Situation III(b), the the larger ion–organic solvent interaction makes the decrease in $m - m'$ the major factor and a decrease in α should be observed.

Another general effect of adding an organic solvent of low dielectric constant to the system is that the resinates swell to a lesser extent in the mixed solvents. The effect of this decreased swelling on isotope effects would correspond to the effect of increasing the resin cross-linking. Therefore, in general, the decreased swelling of the resin would increase the isotope effect.

Isotope Effects in Mixed Solvents (Experimental Data)

The available data on the lithium isotope effects in ion-exchange equilibria in mixed solvents on various resins are tabulated in Table 3. The corresponding solvent fractionation effects and $\Delta G_t^\circ(\mathrm{Li}^+)_{\mathrm{HW}\leftarrow\mathrm{LW}}$* values in different solvent mixtures, wherever available, are also given in Table 3. On the basis of solvent fractionation effects, various systems have been categorized according to the three classifications given above.

Case I. In 50%(v/v) DMSO–water and various MEA–water solvent systems in which the lithium form of the resin does not show any or very little solvent fractionation, the direction and magnitude of the separation factor remain the same as in the aqueous system.

Case II. In 80%(v/v) methanol–water and various ethanol–water systems, the lithium form of the resin shows a preference for water. In the 80%(v/v) MeOH–water system, the Li^+-resin phase has a solvent composition of 50%(v/v) MeOH–water (*39*). $G_t^\circ(\mathrm{Li}^+)$ is more negative for water 80%(v/v) methanol–water mixture than for water→50%(v/v) methanol–water (*40*), i.e., $\Delta G_t^\circ(\mathrm{Li}^+)$ 50%(v/v) MeOH–water←80%(v/v) MeOH–water is a positive quantity. In ethanol–water mixtures, the available data on solvent fractionation effects and $\Delta G_t^\circ(\mathrm{Li}^+)$ values show similar trends. In other words, these systems belong to Category II(b). The observed increase in α is consistent with this analysis. Furthermore, the implication of the heavier isotope enriching in the solution phase is that the lithium ions are more strongly bound in the methanol-rich solution

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*The symbol means free energy of transfer of Li^+ from low water content mixed solvent to high water content mixed solvent.

phase as compared to methanol-deficient resin phase. This is consistent with $\Delta G_t^\circ(\mathrm{Li}^+)$ values. This has an interesting implication in the selectivity behavior of these resins in alcohol–water mixtures. The general belief that the enhanced preference of the resin for Li^+ ions in these media is due to the preference for Li^+ ions for the water-rich resin phase is incorrect. The enhanced selectivity of the resins for Li^+ vis à vis H^+ ions (*41*) is due to the more negative $\Delta G_t^\circ(\mathrm{H}^+)$ than $\Delta G_t^\circ(\mathrm{Li}^+)$ in these solvent mixtures (*40*).

Solvent fractionation effects for the solvent systems acetone–water, dioxane–water, and glycol–water clearly show that resin has a preference for water. However, $\Delta G_t^\circ(\mathrm{Li}^+)$ values in these media are not available. All the same, these solvents are known to be poor solvents for electrolytes. As such, one would expect $\Delta G_t^\circ(\mathrm{Li}^+)_{\mathrm{HW}\leftarrow\mathrm{LW}}$ to be negative, i.e., these systems fall in Category II(a) and α should decrease. The observed lower values of α in dioxane–water and glycol–water are consistent with this. The slight increase observed in acetone–water mixtures can be attributed to the great deswelling of the ion exchangers which might more than compensate for the $\Delta G_t^\circ(\mathrm{Li}^+)$ effects. For this reason the effect of acetone addition on the separation factor is very large in resins of high cross-linking (16, 24, and 35% DVB content) where the deswelling and fractionation effects due to acetone addition would be most prominent.

For the 25%(v/v) isopropanol–water system, no data are available either for solvent fractionation effects or for $\Delta G_t^\circ(\mathrm{Li}^+)$. However, data reported on butanol–water and ethanol–water (*43*) at low alcohol content show that the resin has a preference for the organic solvent. On this basis one could expect a similar behavior for the Li^+-resin in an isopropanol–water mixture. Thus this system would belong to Category III. As $\Delta G_t^\circ(\mathrm{Li}^+)_{\mathrm{HW}\leftarrow\mathrm{LW}}$ for most alcohol–water mixtures is positive, this system would correspond to III(b). The observed decrease in α is consistent with this. All the same, this case might also fall under Category II(a). In the absence of definite information on $\Delta G_t^\circ(\mathrm{Li}^+)$ and solvent fractionation data, it is not possible to decide between the two possibilities.

CONCLUSIONS

The above analysis of lithium isotope effect data in various solvent systems (Table 3) leads to some general conclusions about the enhancement of isotope effects in ion-exchange equilibria in mixed solvent systems. The possibility of a system belonging to III(a), i.e., the resin prefers organic solvent and the ion is more solvated by water-rich solution, is rather remote. Solvent fractionation or the exclusion of the low dielectric

TABLE 3

Solvent Fractionation and Isotope Separation Factors for Lithium Isotopes in Ion-Exchange Equilibria in Mixed Solvents

No.	Resin	Medium	$\alpha_7{}^6$	Solvent fractionation (preference of Li–resin)	Refs.
Case I					
1	Dowex 50WX8	50% (v/v) DMSO–water, 0.2 *M* LiAc	1.0015	No fractionation	*21*
2	"	20% (v/v) MEA–water, 0.3 *M* Li(OH)	1.0012	Slight preference for water	*44*
3	"	40% (v/v) MEA–water, 0.3 *M* Li(OH)	1.0014	"	*44*
4	"	60% (v/v) MEA–water, 0.3 *M* Li(OH)	1.0018	"	*44*
Case II(a)					
1	Amberlite IR 120	10% (v/v) dioxane–water, 1.0 *M* Li(NO_3)	1.0063	Prefers water	*10*
2	"	50% (v/v) dioxane–water, 1.0 *M* Li(NO_3)	1.0009	"	*10*
3	"	10% (v/v) glycol–water, 1.0 *M* Li(NO_3)	1.0081	"	*10*
4	"	50% (v/v) glycol–water, 1.0 *M* Li(NO_3)	1.0026	"	*10*
	Aqueous Amberlite IR 120	Aqueous	1.013 (?) (see Table 1)		*10*
5	Dowex 50WX12	20% acetone–water, 0.3 *M* LiOH, aqueous	1.002 1.0017	Prefers water	6

6	Dowex 50X24	20% acetone–water,	1.012	′	*6*
		0.1 *M* LiOH, aqueous	1.005		
7	Dowex 50X35	20% acetone–water,	1.011	″	*6*
		0.1 *M* LiOH, aqueous	1.008		
8	Ionite C (zirconium phosphate)	20% acetone–water,	1.022	″	*6*
		0.1 *M* LiOH, aqueous	1.016		
Case II(b)					
1	Dowex 50WX8	30% ethanol–water, 0.1 *M* LiCl	1.003	″	*6*
2	″	60% ethanol–water,	1.004	″	*6*
		0.1 *M* LiCl, aqueous	1.001		
3	Dowex 50WX16	30% ethanol–water, 0.1 *M* LiCl	1.005	″	*6*
4	″	60% ethanol–water,	1.006	″	*6*
		0.1 *M* LiCl, aqueous	1.004		
5	Dowex 50WX24	60% ethanol–water,	1.006	″	*6*
		0.1 *M* LiCl, aqueous	1.004		
6	Dowex 50WX35	60% ethanol–water,	1.006	″	*6*
		0.1 *M* LiCl, aqueous	1.005		
7	Dowex 50WX8	80% methanol–water, 0.22 *M* LiCl	1.0034	″	*21*
8	″	80% methanol–water,	1.0026	″	*21*
		0.1 *M* LiAc, aqueous	1.0013		*21*
Case III(a) (?)					
1	Dowex 50WX8	25% isopropanol–water,	1.000	?	*21*
		0.22 *M* LiAc, aqueous	1.0013		*21*

constant solvent from the resin phase arises because of considerations of high ionic concentration in the resin and the larger anionic (ionogenic group)–water interactions. If the cation–water interaction is also larger than the cation–organic solvent interaction, then the resin would not prefer the organic solvent. The other case where α is enhanced is II(b), where the cation is more solvated in the organic solvent-rich mixture and the resin prefers water. If the first part is increased, it tends to reduce the solvent fractionation. Consequently, the isotope effects in ion-exchange equilibria cannot be enhanced very much by using a mixed solvent system—not to the extent that such systems can be considered for isotope separation purposes. The very large effects reported by Kakihana in acetone–water mixtures on highly cross-linked exchangers suffer from the drawback that in highly cross-linked exchangers the exchange kinetics are very unfavorable in aqueous systems and the situation becomes worse in acetone–water mixtures where further deswelling takes place. Therefore, the general conclusion is that the simple ion-exchange equilibria in mixed solvent systems do not hold promise as a possible isotope separation process. On the other hand, the study of such systems can provide very valuable information about ion–solvent interactions because the magnitude and direction of isotope effects depend upon the differences in force constants of the solvated ion species in the exchanger and solution phases.

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