TABLE IV
DIMENSIONS OF THE OCTAHEDRON AROUND MANGANESE IN $MnCl_2 \cdot 4H_2O$

Atoms	Distance, Å.
Mn–Cl(1)	2.500 ± 0.002 (2.506)[a]
Mn–Cl(2)	2.475 ± 0.002 (2.478)
Mn–O(1)	2.224 ± 0.004 (2.229)
Mn–O(2)	2.209 ± 0.004 (2.215)
Mn–O(3)	2.185 ± 0.006 (2.198)
Mn–O(4)	2.206 ± 0.005 (2.216)

Atoms	Angles	Atoms	Angles
Cl(1)–Mn–Cl(2)	96°	O(1)–Mn–O(2)	177°
Cl(1)–Mn–O(1)	92°	O(1)–Mn–O(3)	87°
Cl(1)–Mn–O(2)	87°	O(1)–Mn–O(4)	92°
Cl(1)–Mn–O(3)	93°	O(2)–Mn–O(3)	92°
Cl(1)–Mn–O(4)	174°	O(2)–Mn–O(4)	90°
Cl(2)–Mn–O(1)	88°	O(3)–Mn–O(4)	82°
Cl(2)–Mn–O(2)	94°		
Cl(2)–Mn–O(3)	169°		
Cl(2)–Mn–O(4)	89°		

[a] Distances in parentheses are values corrected for thermal motion assuming that the O and Cl atoms "ride" on the Mn.

TABLE V
DISTANCES UNDER 4.0 Å. WITH STANDARD DEVIATIONS IN $MnCl_2 \cdot 4H_2O$[a]

Atom	Distance, Å.	Atom	Distance, Å.
Cl(1)–Mn	2.500 ± 0.002	O(2)–Mn	2.209 ± 0.004
Cl(1)–O(2)	3.233 ± 0.005[b]	O(2)–O(4)	3.117 ± 0.007[b]
Cl(1)–O(1)	3.391 ± 0.005[b]	O(2)–O(3)	3.146 ± 0.008[b]
Cl(1)–O(3)	3.414 ± 0.006[b]	O(2)–Cl(1)	3.233 ± 0.005[b]
Cl(1)–Cl(2)	3.708 ± 0.003[b]	O(2)–Cl(2)	3.442 ± 0.005[b]
Cl(1)–O(1)	3.169 ± 0.005[c]	O(2)–O(1)	2.926 ± 0.006[c]
Cl(1)–O(4)	3.292 ± 0.005[c]	O(2)–Cl(2)	3.166 ± 0.005[c]
Cl(1)–O(2)	3.477 ± 0.005	O(2)–Cl(1)	3.477 ± 0.005
Cl(2)–Mn	2.475 ± 0.002	O(3)–Mn	2.185 ± 0.006
Cl(2)–O(1)	3.254 ± 0.005[b]	O(3)–O(4)	2.872 ± 0.008[b]
Cl(2)–O(4)	3.285 ± 0.005[b]	O(3)–O(1)	3.033 ± 0.008[b]
Cl(2)–O(2)	3.442 ± 0.005[b]	O(3)–O(2)	3.146 ± 0.008[b]
Cl(2)–Cl(1)	3.708 ± 0.003[b]	O(3)–Cl(1)	3.414 ± 0.006[b]
Cl(2)–O(2)	3.166 ± 0.005[c]	O(3)–Cl(2)	3.815 ± 0.007
Cl(2)–O(3)	3.815 ± 0.007	O(4)–Mn	2.206 ± 0.005
O(1)–Mn	2.224 ± 0.004	O(4)–O(3)	2.872 ± 0.008[b]
O(1)–O(3)	3.033 ± 0.008[b]	O(4)–O(2)	3.117 ± 0.007[b]
O(1)–O(4)	3.185 ± 0.006[b]	O(4)–O(1)	3.185 ± 0.006[b]
O(1)–Cl(2)	3.254 ± 0.005[b]	O(4)–Cl(2)	3.285 ± 0.005[b]
O(1)–Cl(1)	3.391 ± 0.005[b]	O(4)–Cl(1)	3.292 ± 0.005[c]
O(1)–O(2)	2.926 ± 0.006[c]	O(4)–O(1)	3.339 ± 0.006
O(1)–Cl(1)	3.169 ± 0.005[c]		
O(1)–O(4)	3.339 ± 0.006		

[a] Hydrogen atom distances are not included. [b] Octahedral edge. [c] Hydrogen bond.

bonded hydrogens are indicated in Table V. The four hydrogen bonds are as given below.

O(1)—H(1)1············Cl(1)	3.17 Å.
O(2)—H(2)1············Cl(2)	3.17 Å.
O(2)—H(2)2············O(1)	2.93 Å.
O(4)—H(4)1············Cl(1)	3.29 Å.

All of the distances above represent hydrogen bonding between atoms in different octahedra.

The distances calculated for the O–H distances in water from the parameters listed in Table I are 0.8 and 1.0 Å. for O(1); 0.8 and 0.9 Å. for O(2); 0.5 and 0.6 Å. for O(3); and 0.9 and 1.0 Å. for O(4). It is because of the limited accuracy of our hydrogen parameters that we have not presented a detailed list of distances to the hydrogen atoms.

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Ion Exchange in Mixed Solvents. I. Monovalent Cations on a Strong Acid Exchanger[1]

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The ion-exchange behavior of Li^+, Na^+, and K^+ on Amberlite CG-120 Type 1 (strong acid exchanger) in H^+ and NH_4^+ forms was studied in the presence of water-miscible alcohols: methanol, ethanol, 1-propanol, and 2-propanol. The effects of these organic solvents observed in the exchange behavior have been explained on the basis of increased ion association in the resin phase. The anomalous behavior of NH_4^+ in the presence of organic solvents is also explained.

Introduction

It has generally been observed that addition of organic solvents to the solution phase enhances the affinities of monovalent cations toward the exchanger.[2–10] A few probable explanations in terms of the dielectric constant of the solution phase,[9,10] ion association,[6,11,12] solvation of ions,[2b–7] etc., have been put forward to account for the phenomenon, based on limited experimental data. There are some experimental results, which are not adequately explained; for example, reversal of affinities of Li^+ and H^+[9] or NH_4^+ and Na^+[2b,6] with increase of organic solvent in the solution phase.

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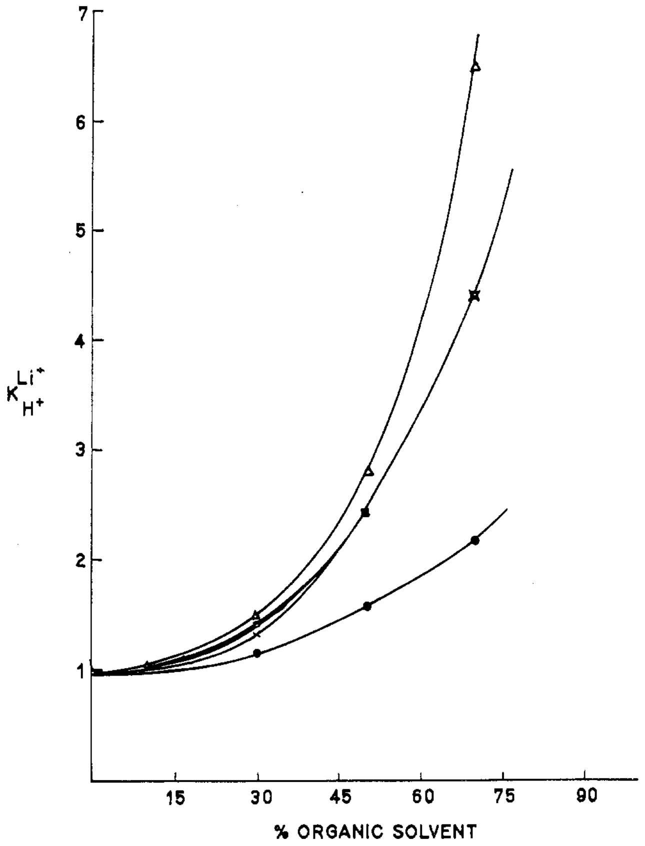

Fig. 1.—Variation of $K_{H^+}^{Li^+}$ with per cent organic solvent: ●, methanol; ×, ethanol; □, 1-propanol; △, 2-propanol; ○, acetone.

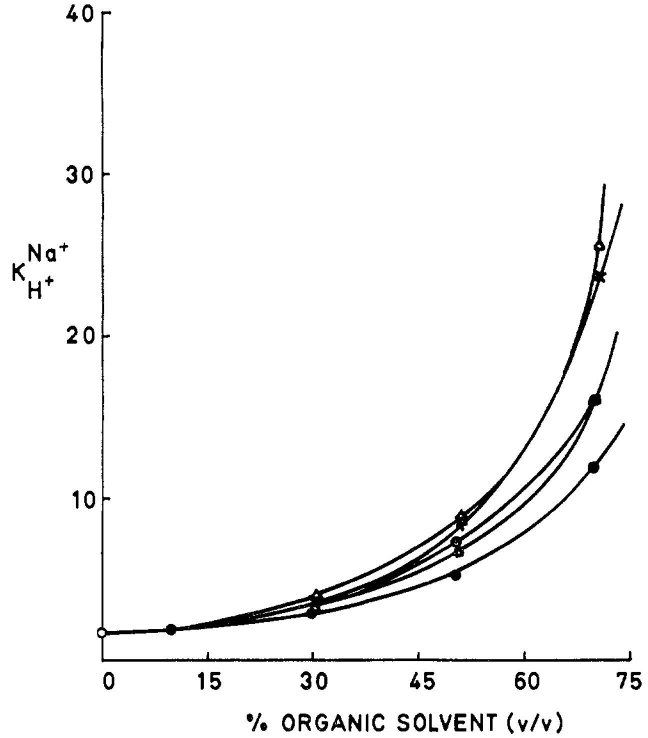

Fig. 2.—Variation of $K_{H^+}^{Na^+}$ with per cent organic solvent: ●, methanol; ×, ethanol; □, 1-propanol; △, 2-propanol; ○, acetone.

Hence, the exchange behavior of Li^+, Na^+, and K^+ against H^+ as well as NH_4^+ was investigated in the presence of water-miscible alcohols: methanol, ethanol, 1-propanol, and 2-propanol.

Experimental

Materials.—Amberlite CG-120 Type 1 exchanger was taken in a column of conventional design. The H^+ form of the exchanger was prepared by passing sufficient 3 N hydrochloric acid through it and washing with de-ionized water till free of acid. Then it was removed from the column, dried over a hot water bath, and stored in a Pyrex bottle.

The NH_4^+ form of the exchanger was prepared by passing a sufficient amount of 10% ammonium hydroxide through the H^+ form of the exchanger and washing with de-ionized water until free of the base.

The moisture content, estimated by heating at 110 ± 2° to constant weight, is 18.0 and 27.8% for the H^+ and NH_4^+ forms of the exchanger, respectively. The capacity of the H^+ form of the exchanger was determined to be 3.90 mequiv./g. by treating it with a known amount of alkali and back titrating the excess alkali. The capacity of the NH_4^+ form of the exchanger was determined to be 3.42 mequiv./g. by converting it into the H^+ form and then following the same procedure as before. The alkali chlorides, 1-propanol, 2-propanol, and acetone were BDH Analar reagents. The methanol and ethanol were distilled in the laboratory.

Procedure.—To 50-ml. Quickfit Pyrex flasks, each containing 1.0 g. of the exchanger, various volumes of water, solvent, and 1.00 mequiv. of alkali chloride solution were added (total volume 50 ml.). The temperature was maintained at 25 ± 2°. After equilibrating for 24 hr., an aliquot of the solution was analyzed for alkali ion content flame photometrically using a Beckman spectrophotometer, Model DU, with flame attachment and oxy-hydrogen flame.

The exchange coefficient $K_{D^+}^{C^+}$ $(=([D^+][CR])/([C^+][DR]))$ of the exchange reaction $C^+ + DR \rightleftharpoons CR + D^+$ ($C^+ = Li^+$, Na^+, or K^+ and $D = NH_4^+$ or H^+) was calculated. [CR] and [DR] are the mole fractions of the two cations in the resin phase. The other terms denote the molar concentrations of the cations in solution. In view of the large volume of the solution phase, no allowance was made for the uptake of solvent by the resin phase.

Results

The variation of $K_{H^+}^{C^+}$ as a function of the organic solvent content in the solution phase is shown in Fig. 1–3. The exchange coefficients of Li^+, Na^+, and K^+ increase continuously with increase of the organic solvent, the relative increases depending on both metal ion and the solvent. During this general behavior a reversal of the affinities of Li^+ and H^+ to the exchanger is shown by $K_{H^+}^{Li^+}$ varying from <1 to >1.

The variation of $K_{NH_4^+}^{C^+}$ under similar conditions is presented in Fig. 4–6. The exchange coefficients of the alkali ions against NH_4^+ increased with increase of organic solvent except in the case of Li^+ and that, too, in methanol and ethanol only. The rate of change of $K_{NH_4^+}^{C^+}$ is rather slow up to about 70% of the organic solvent and is considerably high thereafter. The affinities of NH_4^+ and Na^+ to the exchanger are reversed as in the case of Li^+ and H^+. In the case of Li^+ exchange, the organic solvents exhibited only a little effect compared to that of Na^+ and K^+. In this connection, it may be mentioned that Kitchener, *et al.*,[2b] have reported no change in $K_{NH_4^+}^{Li^+}$ in ethanol–water medium. This slight discrepancy in the results may be

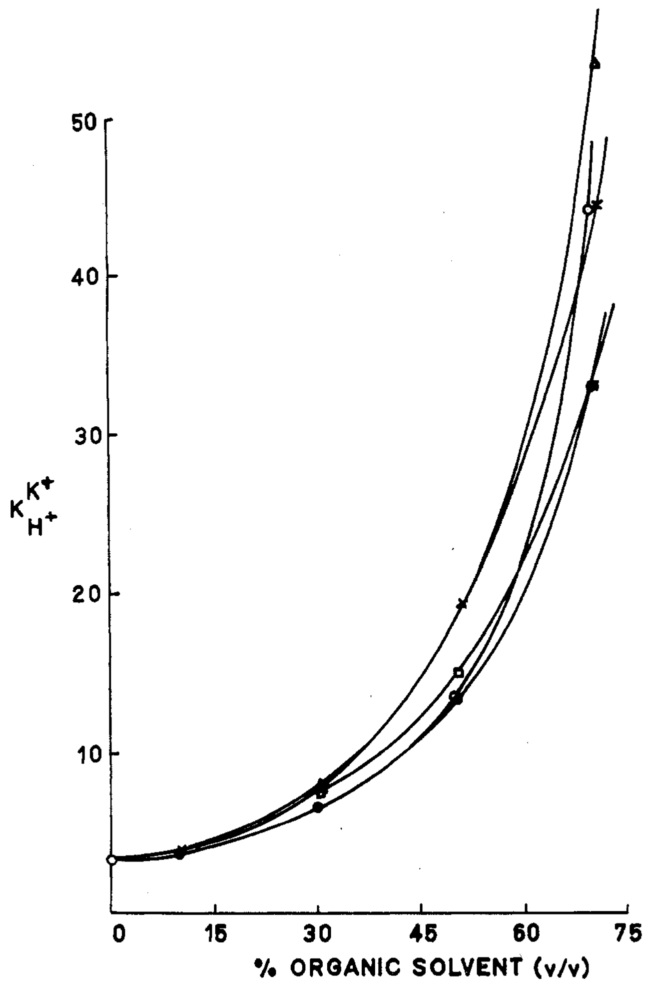

Fig. 3.—Variation of $K_{H^+}^{K^+}$ with per cent organic solvent: ●, methanol; ×, ethanol; □, 1-propanol; △, 2-propanol; ○, acetone.

attributed to the difference in the exchangers employed by Kitchener, *et al.* (phenol–sulfonic acid type) and by the present authors (sulfonic acid type).

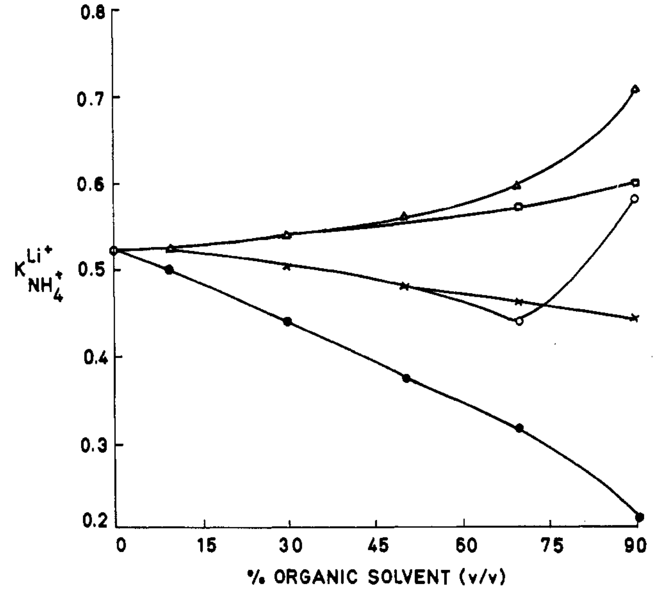

Fig. 4.—Variation of $K_{NH_4^+}^{Li^+}$ with per cent organic solvent: ●, methanol; ×, ethanol; □, 1-propanol; △, 2-propanol; ○, acetone.

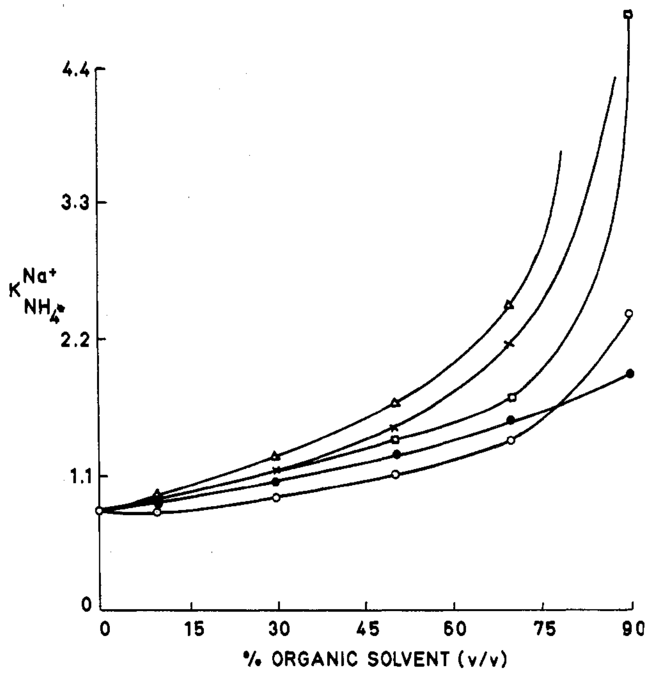

Fig. 5.—Variation of $K_{NH_4^+}^{Na^+}$ with per cent organic solvent: ●, methanol; ×, ethanol; □, 1-propanol; △, 2-propanol; ○, acetone.

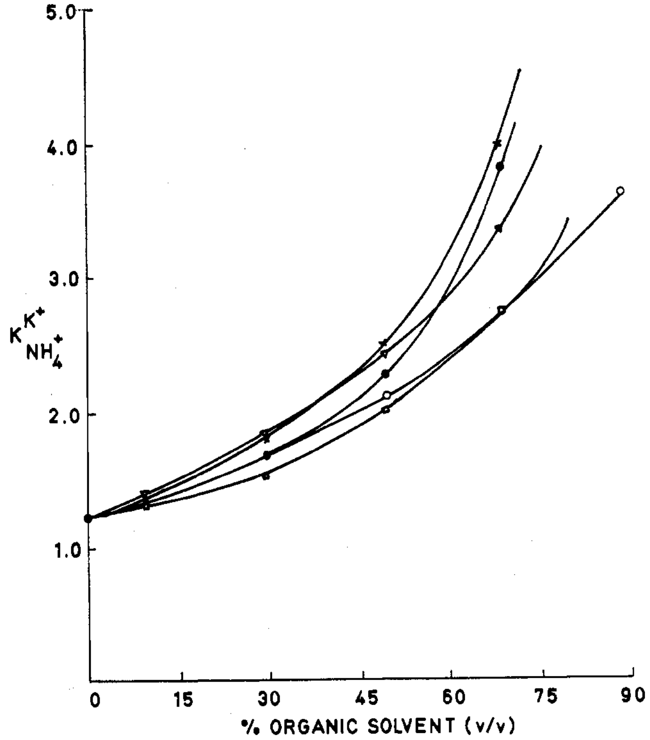

Fig. 6.—Variation of $K_{NH_4^+}^{K^+}$ with per cent organic solvent: ●, methanol; ×, ethanol; □, 1-propanol; △, 2-propanol; ○, acetone.

Discussion

The resin phase is a system of high electrolyte concentration with low effective dielectric constant compared to the aqueous phase.[13] Diamond, *et al.*,[14] have

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pointed out that water in this phase has a less cooperative structure. These factors favor ion association of the type $A^+ \cdot OH_2 \cdot B^-$ or $A^+ \cdot B^-$ in the resin phase.[15] In strong acid exchanger, $A^+ \cdot B^-$ type[16] ion association may predominate due to the distribution of the electron in RSO_3^- by resonance. Addition of organic solvent to the system further decreases the dielectric constant of the resin phase and enhances the penetrating power of anion into the hydration sheath of cations.

Choppin, *et al.*,[18] stated that ion association in the solution phase is not an important factor in the exchange phenomenon. Mobility experiments by Kitchener, *et al.*,[2b] indicate little change in ion association in solution with addition of organic solvent up to 50%.

In view of the above facts, the present authors feel that $A^+ \cdot B^-$ type ion associations increase in the resin phase with per cent organic solvent in the solution phase. On this basis, observed variations of selectivity coefficients of alkali ions against H^+ and NH_4^+ on a strong acid exchanger with per cent organic solvent are explained below.

In the present studies in the mixed solvents, increase in $K_{D^+}{}^{C^+}$ is maximum for K^+ and minimum for Li^+ n all solvents studied. This order is the same as the one expected by Rosseinsky[19] for the $A^+ \cdot B^-$ type of ion association as a function of hydrated ionic radius. The ion association constants of alkali ions with halides[20] as well as other anions[20,21] in mixed solvents are also in this order. The osmotic and activity coefficients of polysulfonates[22] also indicate the same order of ion association.

In the order of selectivities of monovalent cations, it has often been observed that H^+ behaves anomalously.[23-25] In the presence of organic solvents, as observed in the present studies, selectivities of H^+ and other alkali ions follow the order as expected for the ion association as a function of hydrated ionic radius. Therefore, the rate of increase of ion association in the resin phase is greater for Li^+ than H^+ in mixed solvents, resulting in the reversal of affinities of Li^+ and H^+. The greater swelling of the exchanger in the H^+ form, observed by Gable and Strobel,[6] may be attributed to this factor.

The rate of increase of $K_{D^+}{}^{C^+}$ with per cent organic solvent is faster above $\backsim$70.[26] Probably, the organic solvent up to 70% is entering only the third region (outermost) of water surrounding the cation[28] and the other two above 70%.

Sakaki[9] and Panchenkov, *et al.*,[10] correlated the exchange coefficients with dielectric constant of the medium. The rate of variation of $K_{NH_4^+}{}^{Li^+}$ in acetone and 2-propanol (nearly equal dielectric constants and same number of carbon atoms) clearly shows that this is not the only governing factor.

Davies and Owen[11] attributed the preferential elution of Li^+ to greater formation of Li^+Cl^- ion pairs in the solution phase than Na^+ and K^+ with Cl^-. The increase in elution volume required with acetone content of the eluent (as observed by us) cannot be explained on this basis. In fact, the preferential elution of Li^+ follows from the order of ion association in the resin phase. The larger elution volume required is due to increase in the ion association of cations in the resin phase with increase of per cent organic solvent.

The order of affinities, $Li^+ < Na^+ < NH_4^+ < K^+$, in aqueous medium has been found to change to $Li^+ < NH_4^+ < Na^+ < K^+$ in mixed solvents. This shift of NH_4^+ toward Li^+ does not follow the order of ion association expected. Similar anomalous behavior of NH_4^+ also was observed on weak acid exchanger in aqueous and mixed solvents.[17]

It appears from the above that ion association of NH_4^+ is less than what is expected from its hydrated ionic radius. In agreement with this, the swollen volume of the NH_4^+ form of the exchanger has been reported to be higher than that of the Na^+ form in methanol.[6] The nonspherical nature of NH_4^+ may be responsible for its anomalous behavior. It may be mentioned here that no ion association constants of NH_4^+ have been reported so far.

To confirm the above, the ion-exchange behavior of other monovalent nonspherical cations like substituted ammonium salts as well as anions like CNS^-, CN^-, and NO_3^- in mixed solvents is under investigation.

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