Isotope Effects in Chemical Exchange Systems. Isotope Effects for Sodium between a Cation Exchange Resin and a Methanolic Solution

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Summary A separation factor of 0·94 ± 0·02% for ^{22}Na and ^{24}Na has been obtained in a system consisting of a Li^+-loaded cation exchange resin and a methanolic solution.

ISOTOPE effects for cations of groups 1A and 2A on ion exchange resins have been studied extensively,[1–5] and the effects do not usually exceed about 1·005. We now report a much larger effect for a system involving pure methanol solution. A full description of the experimental procedure is given in ref. 6. The cation exchange resin was Dowex HCR-W (50—100 mesh) loaded with Li^+ or Cs^+. ^{22}Na was obtained in a form containing minimal carrier; ^{24}Na was produced by the irradiation of Na_2CO_3 with neutrons.

LiCl or CsCl was added to an aqueous solution of a mixture of equal activities of both sodium radionuclides in

TABLE. Isotope effects for the sodium isotopes.

Loading of the resin Dowex-HCR-W	Solvent	$\frac{[Na^+].g_{exch.}{}^{-n}}{[Na^+].g_{solv.}{}^{-n}}$	Separation factor $\frac{(^{24}Na/^{22}Na)_{sol.}}{(^{24}Na/^{22}Na)_{exch.}}$	No. of experiments
Cs^+	H_2O	40	1·00 ± 0·002	7
Li^+	H_2O	336	1·004 ± 0·009	14
Cs^+	MeOH	56	1·013 ± 0·014	7
Li^+	MeOH	1479	0·94 ± 0·02	14

the reaction vessel. The amounts of LiCl or CsCl corresponded to the capacity of the resin applied. After acidification the whole mixture was evaporated to dryness and the resulting chlorides were dissolved in 30 ml of water or methanol. The initial isotopic ratio was determined by first measuring the total activity of aliquots and then the residual activity after the decay of the short lived ^{24}Na.

From the stock solution aliquots were taken and transferred to vessels each containing 50 mg of the ion exchange resin. Equilibrium was reached within 3 h, when the activity ratio of the solution was determined as before and used to calculate the separation factor. The results are given in the Table. As expected there are no significant isotope effects for the aqueous solutions and the Cs^+-loaded ion exchange resin with methanol. However, the Li^+-loaded exchange resin with methanol yields, at equilibrium, a surprisingly high effect, the heavier isotope ^{24}Na being significantly enriched in the resin.

The effect can be explained by the theories of Bigeleisen,[7] and Wolfsberg,[8] since the vibrational states of the sodium in the vicinity of the ion exchange resin differ enormously from those of the sodium solvated with methanol. The $^{24}Na^+$ ion, compared with the $^{22}Na^+$ ion, forms a stronger bond with the ion exchange resin, which is substantiated by the different vibrational partition functions of the different isotopes.

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