

to have a square-planar configuration, with the plane formed by one edge from each of the two periodate octahedra, and with one water molecule at a distance of about 2.7 Å. from the copper atom.¹⁵ By analogy, the silver(III) compound can be pictured as shown in Fig. 1. It is thought that the periodate acts as a bidentate ligand and contributes to the stabilization of the Ag-(III).

Conclusion

In the reaction between AgO and KIO₃, the iodate is oxidized to periodate, which then forms a complex compound with Ag(III). This compound is identical with one formed by oxidation of Ag(I) with K₂S₂O₈ in the

presence of iodate. Previously, definite proof has been presented for the existence of a soluble species of silver with a valence greater than one arising from AgO in acid solution only. In these cases, only silver(II) species have been found.⁵ In this work we have shown that in basic solution, when nothing is present that could oxidize the AgO, a silver(III) species results. This is consistent with physical evidence for the presence of Ag(III) in AgO.

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Ion Exchange in Mixed Solvents. II. Monovalent Cations on a Weak Acid Exchanger¹

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Ion-exchange behavior of Li⁺, Na⁺, and K⁺ against NH₄⁺ on a carboxylic acid type of exchanger has been studied in mixed solvents. From the various reversals of affinities observed, it has been postulated that, in weak-acid exchanger in aqueous medium, ion-pair formation of the solvent-shared type predominates and that the contact type of ion pairs increases with increase of organic solvent in the solution phase.

Introduction

In a previous communication,² it was postulated that addition of water-miscible organic solvents to the solution phase enhances the contact type of ion-pair formation in the resin phase of a strong-acid exchanger in the inverse order of hydrated ionic radii of Li⁺, Na⁺, and K⁺. Even though various thermodynamic properties of methacrylic acid exchanger have been studied,³ little work has been reported on the exchange behavior of alkali ions except by Bregman⁴ and Gregor, *et al.*,⁵ in aqueous medium. This paper deals with the exchange equilibria of Li⁺, Na⁺, and K⁺ against NH₄⁺ on a carboxylic acid exchanger in aqueous and mixed-solvent media.

Experimental

Materials.—The weak acid exchanger Merck IV, supplied by E. Merck AG., Darmstadt, Germany, is a polyacrylic acid derivative capable of swelling. About 200 g. of this exchanger of 100 to 200 mesh size was taken in a column of conventional

design and then converted several times into NH₄⁺ and H⁺ forms alternatively with ~2 *N* ammonium hydroxide and hydrochloric acid. Finally the exchanger in NH₄⁺ form was prepared by passing a sufficient amount of a mixture of ammonium chloride and hydroxide and then washing with de-ionized water until free of chloride.⁸ The exchanger was then dried over a hot water bath and stored in a stoppered Pyrex bottle.

The moisture content of the exchanger, estimated by heating a known quantity at 110 ± 2° for 4 hr.,⁹ was 17.2%. The exchange capacity of this wet resin was found to be 5.15 mequiv./g. by treating a known quantity of it in a column with excess standard acid and titrating the excess acid.¹⁰

Alkali chlorides, 1-propanol, 2-propanol, and acetone were of B.D.H. AnalaR grade, while methanol and ethanol were distilled in the laboratory.

Procedure.—Various volumes of water, organic solvent, and 1.0 mequiv. of alkali chloride were added into Pyrex quick-fit flasks, each containing 1.0 g. of the exchanger, to maintain a total volume of 50 ml. at 25 ± 2°. After equilibrating for 24 hr.,¹¹ an aliquot of the solution phase was analyzed for the alkali content flame photometrically using a Beckman Model DU spectrophotometer with flame attachment and oxy-hydrogen flame.

The equilibrium exchange coefficient $K^{C^+}_{NH_4^+}$ ($= [NH_4^+][RC]/[C^+][RNH_4]$) of the exchange reaction $C^+ + RNH_4 \rightleftharpoons RC + NH_4^+$ (C^+ represents Li⁺, Na⁺, or K⁺) was calculated using mole

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(4) J. I. Bregman, *Ann. N.Y. Acad. Sci.*, **57**, 125 (1953).

(5) H. P. Gregor, M. J. Hamilton, R. J. Oza, and F. Bernstein, *J. Phys. Chem.*, **60**, 263 (1956).

(6) There was practically no exchange of alkali ions with the H⁺ form of the exchanger.⁷

(7) R. Kunin and R. E. Barry, *Ind. Eng. Chem.*, **41**, 1269 (1949).

(8) Excessive washing results in the hydrolysis of the exchanger.

(9) The exchanger was losing weight continuously but very slowly on heating further.

(10) R. Turse and W. Rieman III, *J. Phys. Chem.*, **65**, 1821 (1961).

(11) Kunin and Barry⁷ have observed that equilibrium is attained rapidly with carboxylic acid exchanger in the salt form, although not in H⁺ form. During the present studies, it has been observed that equilibrium is attained within about 3 hr. in the presence of mixed solvents.

fractions of the two cations in the resin phase and molar concentrations for $[C^+]$ and $[NH_4^+]$.

In view of the large volume of the solution phase, no allowance was made for the uptake of solvent by the resin phase. The hydrolysis of the exchanger in the Li^+ , Na^+ , K^+ , and NH_4^+ forms in aqueous as well as mixed solvent media was determined¹² and found to be <2% of the total exchange capacity, and hence this factor was ignored in the calculation of exchange coefficients. The error in the values reported is expected to be within 5%.

Results

Table I presents the variation of $K^{C^+}_{NH_4^+}$ values for Li^+ , Na^+ , and K^+ at different percentages of organic solvent contents of the solution phase. $K^{Li^+}_{NH_4^+}$ decreases continuously with increase of methanol and ethanol, but with 1-propanol, 2-propanol, and acetone, it first decreases and then increases. $K^{Na^+}_{NH_4^+}$ increases from <1 to >1 with increase of organic solvent with the exception of methanol, in which case it remains unaffected up to 50% and then decreases. The exchange behavior of K^+ is similar to that of Na^+ in the presence of ethanol, 1-propanol, and 2-propanol, the coefficient increasing from <1 to >1 with increase of organic solvent content. In the case of methanol and acetone it changes very little in the beginning and then increases slightly, but never exceeds 1.0.

TABLE I
EXCHANGE EQUILIBRIUM COEFFICIENTS^a OF Li , Na^+ , AND K^+
AGAINST NH_4^+

$$K^{C^+}_{NH_4^+} = \frac{[NH_4^+][RC]}{[C^+][RNH_4^+]}$$

Solvent	Mole % org. solv.	% org. sol. (v./v.)	$K^{Li^+}_{NH_4^+}$	$K^{Na^+}_{NH_4^+}$	$K^{K^+}_{NH_4^+}$
H_2O-CH_3OH	0	0	0.66	0.57	0.50
	4.72	10	0.62	0.57	0.50
	16.03	30	0.52	0.57	0.50
	30.83	50	0.41	0.57	0.50
	50.98	70	0.29	0.44	0.54
	80.05	90	0.18	0.30	0.54
$H_2O-C_2H_5OH$	3.32	10	0.64	0.59	0.50
	11.68	30	0.59	0.69	0.59
	23.59	50	0.55	0.83	0.70
	41.88	70	0.50	1.00	0.88
$H_2O-n-C_3H_7OH$	73.52	90	0.40	1.29	1.49
	2.61	10	0.61	0.60	0.51
	9.37	30	0.59	0.71	0.61
	19.43	50	0.61	0.85	0.72
	35.99	70	0.66	1.05	0.92
$H_2O-i-C_3H_7OH$	68.45	90	0.68	2.44	1.85
	2.55	10	0.61	0.60	0.53
	8.81	30	0.59	0.74	0.61
	19.05	50	0.63	0.97	0.75
	35.46	70	0.66	1.36	1.01
$H_2O-CH_3COCH_3$	67.97	90	0.95	3.18	2.14
	2.66	10	0.63	0.57	0.50
	9.52	30	0.59	0.58	0.50
	19.71	50	0.51	0.62	0.53
	36.43	70	0.51	0.66	0.56
	68.85	90	0.80	1.13	0.82

^a Temperature 25°; $[C^+] + [NH_4^+] = 0.020 M$.

The order of affinities of alkali ions in aqueous medium ($Li^+ > Na^+ > K^+$) is, in general, reversed

in the presence of sufficient organic solvent in the solution phase. The affinities of Na^+ and K^+ , however, are not reversed in the presence of 1-propanol, 2-propanol, and acetone.

Discussion

A reversal of the order of affinities of Li^+ , Na^+ , and K^+ toward weak-acid exchanger in aqueous medium compared to that toward a strong-acid exchanger, as reported by Bregman⁴ and Gregor, *et al.*,⁵ has been observed in the present studies also. Holm¹³ explained this on the basis of the localized hydrolysis theory of Harned, *et al.*,^{14,15} as well as Gurney's theory¹⁶ of the order-producing and order-destroying nature of ions in solution, both of these theories having been put forward to explain the reversal of activity coefficients of alkali chlorides (nitrates) and acetates (hydroxides). The same can also be independently explained from a consideration of ion-pair formation, in view of the high electrolyte concentration and comparatively low dielectric constant of the resin phase. Two major types of ion pairs in solution are known,^{17,18} *viz.*: (1) contact ion pairs, A^+B^- , and (2) solvent-shared (or separated) ion pairs, A^+ (solvent) B^- . From the proton affinities of RSO_3^- and $RCOO^-$, it can be said that the former favors the formation of contact-type ion pairs while the latter the second type. It, therefore, follows that the higher the hydrated radius of a cation in a series, the lower its affinity to RSO_3^- and the higher to $RCOO^-$.

In the absence of activity coefficient data of alkali salts in mixed solvents, the localized hydrolysis theory and Gurney's theory cannot be extended to explain the reversal of affinities of alkali ions in mixed solvents.

We have suggested earlier² that addition of organic solvents to the solution phase enhances the contact-type of ion-pair formation in the case of a strong-acid exchanger. The reversals of affinities of alkali ions observed in the present studies suggest that, in the case of weak-acid exchanger also, contact-type ion-pair formation is more favored in mixed solvents and not solvent-shared type by just replacing water molecules in the $A^+OH_2B^-$ type of ion pairs. It may therefore be summarized that in a weak-acid exchanger, the order of affinities in aqueous medium is governed by the capacity of the ions to form solvent-shared type ion pairs while in mixed solvents the order is determined by the contact type of ion-pair formation. A similar change in the nature of ion pairs, formed between Mg^{+2} (or Ba^{+2}) and acetate with increase of concentration, has been suggested by Stokes.¹⁹ Reichenberg's discussion²⁰ on the basic interactions underlying ion-

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exchange selectivities of alkali ions as due to "a balance between (1) Coulomb interactions between the mobile counterions (in various states of hydration) and the fixed groups of the exchanger, and (2) ion-dipole and ion-induced dipole interactions between the counterions and water molecules (ionic hydration)," also lends support to our postulate discussed above regarding the ion-exchange equilibria on both types of exchangers in aqueous and mixed solvents.

As observed in the case of a strong-acid exchanger,² the contact type of ion-pair formation becomes more significant from about 70% (v./v.) and above of the organic solvent content in the solution phase. Also

$K_{\text{NH}_4^+}^{\text{C}}$ in the presence of acetone is lower than in 2-propanol, even though the dielectric constants and the number of carbon atoms in both solvents are nearly the same.

From Table I it can be seen that the position of NH_4^+ among Li^+ , Na^+ , and K^+ in the presence and absence of various organic solvents is changing. This anomalous behavior may be due to its nonspherical nature as stated earlier.²

Similar reversal of affinities of alkaline earths as well as rare earth cations toward the two types of exchangers has been observed. The effect of organic solvents on these systems is under investigation.

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Reactions of Xenon Hexafluoride with Antimony Pentafluoride, Hydrogen Chloride, Ammonia, and Perfluorocyclopentene

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By varying the proportions of the reactants antimony pentafluoride and xenon hexafluoride, it is possible to prepare each of the crystalline solids: $\text{XeF}_6 \cdot 2\text{SbF}_5$, $\text{XeF}_6 \cdot \text{SbF}_5$, $\text{SbF}_5 \cdot 2\text{XeF}_6$. Hydrogen chloride, ammonia, and perfluorocyclopentene react readily with xenon hexafluoride but the products have not been found to include substances in which xenon is in combination with chlorine, nitrogen, and carbon, respectively.

Since xenon hexafluoride reacts with water to give hydrogen fluoride and one or more compounds in which oxygen is bound to xenon,^{1,2} it seems possible that reactions with certain hydrogen compounds other than water should yield hydrogen fluoride and compounds of xenon. For example, hydrogen chloride might give a chloride of xenon, or ammonia might give an amide or nitride. These two reactants have been tested but no new compounds containing xenon have been found. In each case gaseous xenon was formed. In one case, chlorine was also formed and in the other case nitrogen was a product.

An attempt was made to form an addition compound from xenon hexafluoride and an unsaturated fluorocarbon (perfluorocyclopentene). The reaction produced perfluorocyclopentane but no evidence was found for a compound containing both xenon and carbon.

Knowing that xenon hexafluoride dissolves in hydrogen fluoride to give an electrically conducting solution,³ it was thought that the strong fluoride acceptor, antimony pentafluoride, might combine with XeF_6 . It was found that the two substances combine readily, but without the evolution of much heat, and

that at least three different compounds may be formed.

As the work was in progress, Edwards, Holloway, and Peacock⁴ reported that either the difluoride or tetrafluoride of xenon combines with antimony pentafluoride to give $\text{XeF}_2 \cdot 2\text{SbF}_5$. It has also been learned by the authors that results similar to theirs for XeF_6 and SbF_5 have been obtained at the Argonne National Laboratory by Selig, who has already reported the formation of $\text{XeF}_6 \cdot \text{BF}_3$ and $\text{XeF}_6 \cdot \text{AsF}_5$.⁵ Details of Selig's work on SbF_5 are not known to the authors.

When an excess of antimony pentafluoride reacts with xenon hexafluoride, a white solid having the composition $\text{XeF}_6 \cdot 2\text{SbF}_5$ is formed. This is soluble in liquid antimony pentafluoride, but the excess may be easily distilled away leaving the crystalline solid. When an excess of xenon hexafluoride is used, the white crystalline product remaining after vacuum distillation of the excess reagent at room temperature is $\text{SbF}_5 \cdot 2\text{XeF}_6$. If this solid is held at 50°, more xenon hexafluoride may be removed by vacuum distillation until the composition $\text{XeF}_6 \cdot \text{SbF}_5$ is reached.

X-Ray powder spectra of the three products are clearly different and are of such a nature that the $\text{XeF}_6 \cdot \text{SbF}_5$ cannot be a mixture of the other two solids. The compound $\text{XeF}_6 \cdot 2\text{SbF}_5$ melts at $108 \pm 1^\circ$ while neither of the other two has been observed to melt even at con-

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