Gamma Irradiation of Individual and Mixed Ion Exchange Resins

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Effects of gamma radiation were investigated for individual and mixed ion exchange resins of the sulfonic acid and quaternary ammonium types. At the maximum dose of 2 × 10^8 rad, fractional loss of exchange sites was independent of mixing: less than 10% for the hydrogen form and about 50% for the hydroxyl form. Water-soluble products were released from irradiated individual resins, but not from mixed H-OH resins, because each resin retained ionic degradation products of the other, thereby depleting usable exchange capacity. Mixed Li-OH resins released water-soluble lithium compounds and anion resin degradation products. The cation exchange resin swelled to 110% of its original wet-packed volume, anion exchange resin shrank to 87%, and the mixed resin shrank even more, to 76%.

RADIATION damage to ion exchange resins causes loss in exchange capacity, volume changes, and production of water-soluble material. Loss of exchange capacity is economically undesirable, shrinkage or swelling of resin may cause process problems, and release of material from the resins may produce undesirable effects downstream of the resin bed.

Much of the early work concerning radiation damage to individual resins was summarized by Marinsky and Giuffrida (*6*). Additional work (*4, 7*) has confirmed that anion exchange resins are generally more susceptible to radiation damage than cation exchange resins. Although it has been recognized that water-soluble materials are produced, quantitative information is limited. The effect of radiation on mixed resins has only been inferred from behavior of individual resins.

The present work describes the water-soluble material produced, the loss of exchange capacity, and volume changes that occurred in cation, anion, and mixed resins exposed to gamma radiation. Of particular interest was loss of exchange capacity in the resin mixture by the following probable reactions:

DEGRADATION

$$[\text{X-SO}_3]^- [\text{H}]^+ \xrightarrow{\text{H}_2\text{O}} [\text{X}] + \text{H}_2\text{SO}_4 \qquad (1)$$

$$[\text{Y-NR}_3]^+ [\text{OH}] \longrightarrow \begin{cases} [\text{YOH}] + \text{NR}_3 & (2a) \\ [\text{Y-NR}_2] + \text{ROH} & (2b) \end{cases}$$

ABSORPTION OF DEGRADATION PRODUCTS IN MIXED BED

$$[\text{X-SO}_3]^- [\text{H}]^+ + \text{NR}_3 \rightarrow [\text{X-SO}_3]^- [\text{HNR}_3[^+ \qquad (3)$$

$$[\text{Y-NR}_3]^- [\text{OH}]^- + \text{H}_2\text{SO}_4 \rightarrow [\text{Y-NR}_3]_2^+ [\text{SO}_4]^{-2} + 2\text{H}_2\text{O} \quad (4)$$

where X and Y represent cation and anion exchange resin matrices, respectively, and R represents an organic group, such as CH_3.

EXPERIMENTAL DETAILS

Resins Examined. The resins were commercial products with a matrix of styrene-divinylbenzene copolymer and crosslinkage equivalent to 8% divinylbenzene. The cation exchange resin had sulfonic acid exchange groups, originally in the hydrogen or lithium form. The anion exchange resin had quaternary ammonium exchange groups of the trimethylamine type and was in the hydroxyl form. The size range of the beads was 16- to 50-mesh (U. S. Standard sieve series).

Column Experiments. Water-soluble nonvolatile material released, volume changes, and exchange capacity losses on irradiation were determined in "column experiments," in which 250 ml. of resin was rinsed, then subjected to a sequence of irradiations. The moist resin was irradiated with a 10,000-curie ^{60}Co source at a dose rate of 10^6 rad per hour. The vented container was designed to minimize exposure to air. The temperature of the resin did not exceed 40°C. during irradiation. After each irradiation the resin was rinsed with water at 40° C. The rinses were evaporated at room temperature and finally dried over a desiccant. Elements of interest were determined when residues were sufficiently large.

Volume changes were determined from measurements of the height of the wet-packed column after each irradiation.

Partitioned Mixture Experiments. Supplementary information regarding exchange capacities in irradiated mixed resins was obtained from "partitioned mixture experiments." Cation and anion resins were maintained physically separate, with water as the connecting phase. Capsules of 100-mesh stainless steel screen, previously described (*1*), contained weighed amounts of anion resin; weighed cation resin was loose in the container, and water covered both the capsule and the loose resin.

These irradiations were conducted in sealed containers in the gamma field produced by mixed fission products from spent reactor fuel, at a dose rate of 2.3 × 10^6 rad per hour.

Analysis of Resins. The quantities defined in Table I were determined by standard techniques on material eluted from the resin. Resins from the partitioned mixture experiments, which were already physically separate, were analyzed by procedures similar to those used for individual resins.

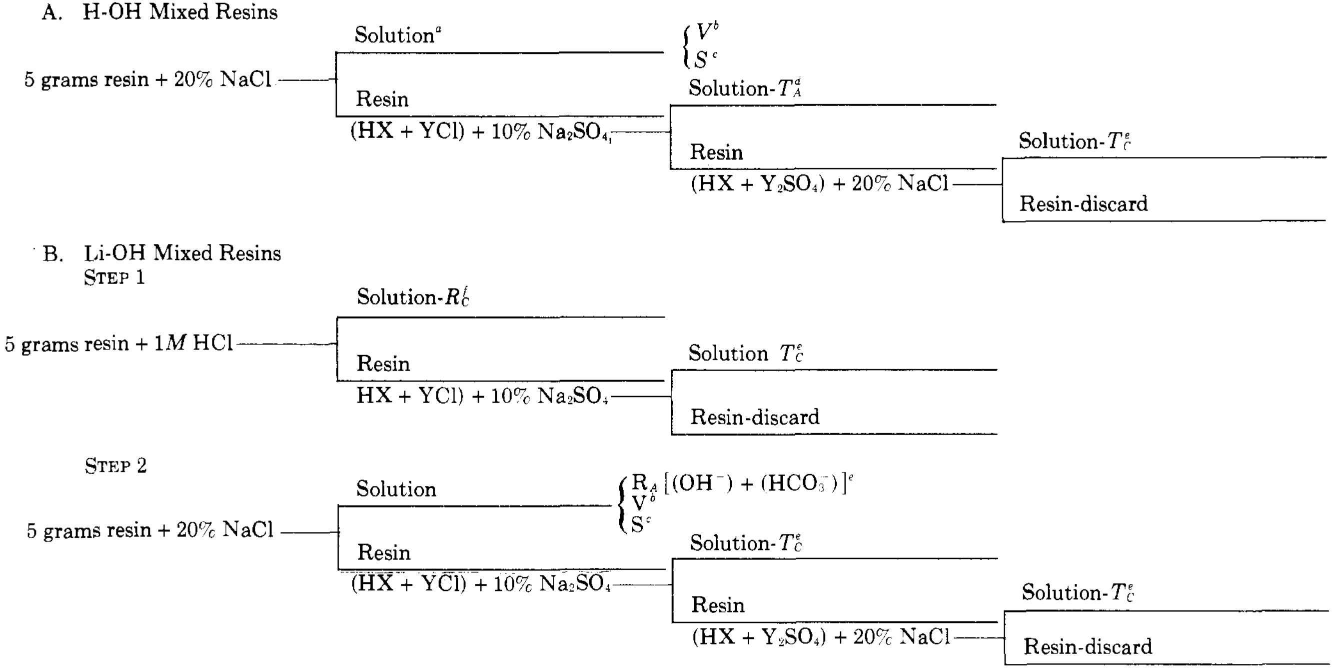
Mixed resins from the column experiments could not be separated into the individual components. Therefore, the mixed resin was analyzed by a scheme involving sequential elutions, as shown in Table I. All quantities were determined on a single sampling of mixed resin and results were calculated in terms of the original exchange capacity of the individual resins. This averted loss in precision due to nonuniformity of the resin mixture in the samples analyzed.

RESULTS

Water-Soluble Material. The preliminary rinse of each unirradiated cation resin was light yellow; rinses after irradiation were light yellow to brown and murky as though suspended polymers were present. Water from anion resin was yellow; the irradiated resin, which had turned dark brown on irradiation, had a strong ammonia-like odor.

Table I. Analysis of Mixed Resins

I. Analysis Scheme



X and Y are respective cation and anion resin matrices with exchange groups.

II. Calculations

$$\begin{aligned} T_c^0 &= T_c + S \\ R_c &= T_c - V \\ T_A^0 &= T_A + V \\ R_A &= T_A - S \end{aligned}$$

Unirradiated mixed resins contained small amounts of S and V, so that $T_c \neq T_c^0$ and $T_A \neq T_A^0$. Ratios for Figures 3 and 4 were normalized as follows:

$$(T/T^0) = \frac{(T/T^0) \text{ irradiated}}{(T/T^0) \text{ unirradiated}}$$

$$(R/R^0) = \frac{(R/T^0) \text{ irradiated}}{(R/T^0) \text{ unirradiated}}$$

[a] Volume of solution 200 ml. throughout. [b] Volatile base distilled from caustic solution. [c] SO_4^{-2} by turbidimetry (5). [d] Cl^- by Mohr titration. [e] Acid-base titration. [f] Li^+ by flame photometry.

Rinses from irradiated H-OH and Li-OH mixed resins were colorless.

After evaporation, the residues were considered fairly representative of the total material washed from the resins; however, certain volatile constituents such as amines of low molecular weight and other light organic compounds were undoubtedly lost during evaporation. For this reason the nitrogen content of the anion residue is not reported. The residue from the cation exchange resin never completely solidified, presumably because sulfuric acid was part of the degradation product.

The total amount of water-soluble residue is given in Figure 1. Carbon and sulfur releases are shown in Figure 2. The weights of residue and the carbon content for only the unirradiated anion resin are included because of the uncertain validity of other values. The mixed H-OH resin released substantially less material than the individual resins. More residue was produced from the Li-OH mixture than from the H-OH mixture: it was white and contained 5 to 10% Li.

Exchange Capacity. Figures 3 and 4 show exchange capacities of cation and anion resins, when irradiated individually and in a mixture, expressed as the fraction of original residual or total exchange capacity. Loss of total exchange capacity (destruction of exchange sites) was independent of whether the resin was irradiated alone or in a mixture. On the other hand, residual capacity (titratable acidity or alkalinity) was reduced in the mixtures by absorption of ionic degradation products from the other component.

The residual capacity of the cation resin was reduced more in the H-OH mixture than in the Li-OH mixture. Removal of amine degradation products by the hydrogen form of the resin is favored by the neutralization reaction; removal by the lithium form involves only simple exchange. Reduction of residual capacity of the anion resin was similar for the two mixtures.

Production of Carbon Dioxide. The irradiated anion resin was partially converted to the carbonate form, presumably from CO_2 formed by radiolysis of organic material in the

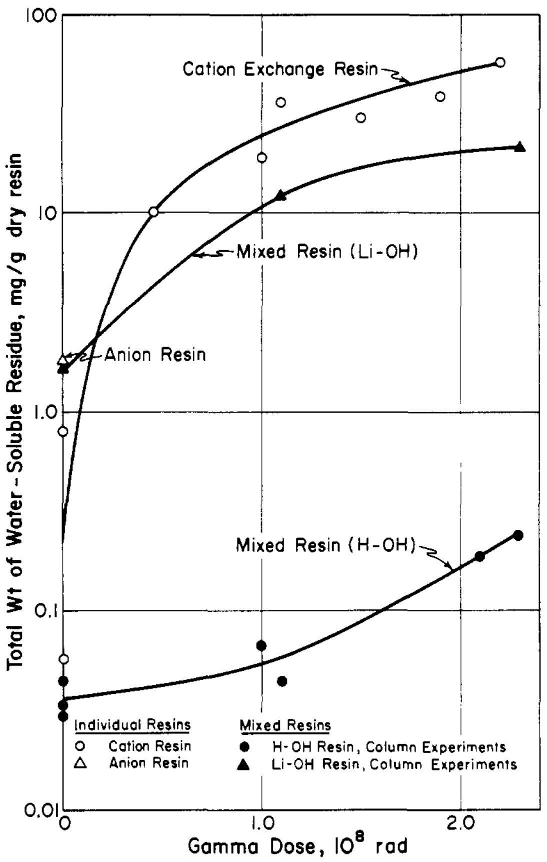


Figure 1. Weight of water-soluble material from irradiated resins

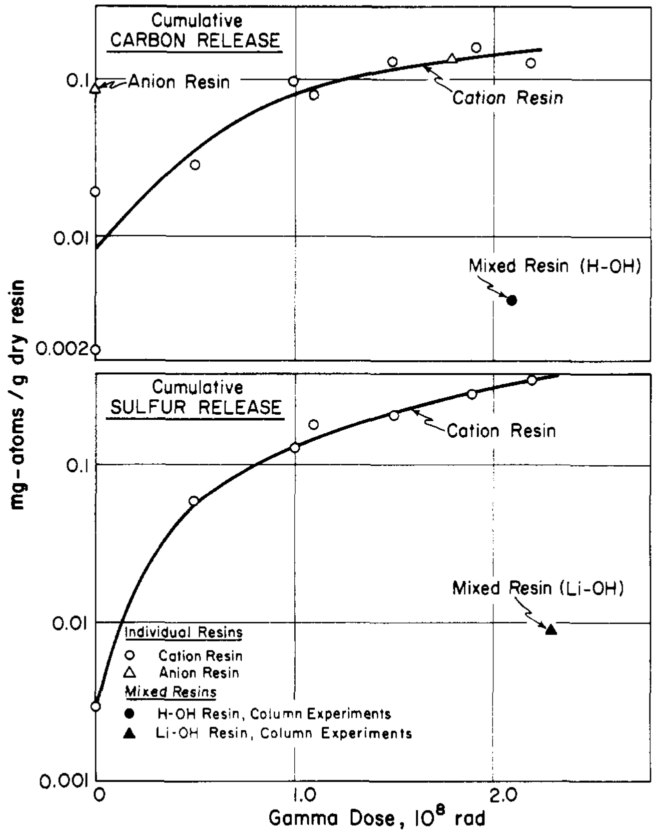


Figure 2. Carbon and sulfur released in water-soluble products

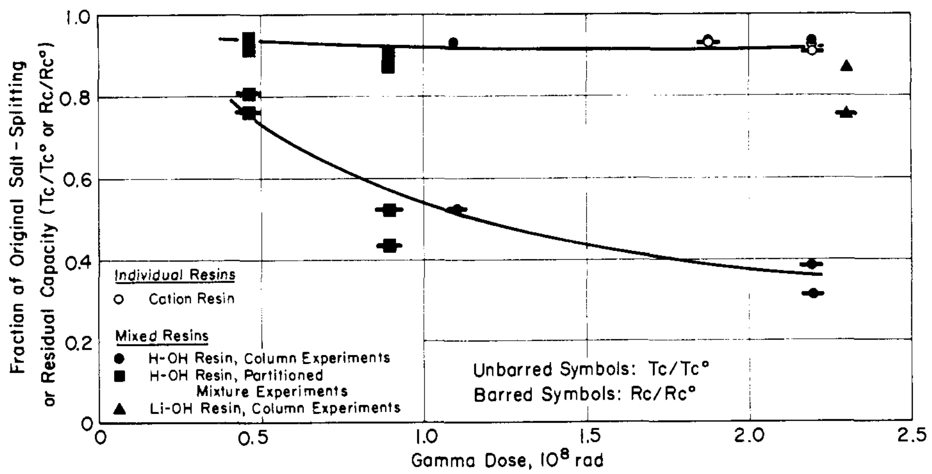


Figure 3. Effect of gamma radiation on exchange capacities of cation exchange resin alone and mixed with anion exchange resin

system. Depletion of anion resin by CO_2, which in general amounted to less than 10%, is shown in Figure 5. For resins from the column experiments, the amount of CO_2 per equivalent of anion resin was apparently not affected by the presence of cation resin. This implies that the precursor of the CO_2 may come from the anion resin.

Mixed resins that were irradiated in the sealed tubes of the partitioned mixture experiments showed a much higher CO_2 content than the others. Different experimental conditions—namely, the closed system in which the irradiations were made and the fact that these resins were not rinsed prior to irradiation—may account for the larger amounts of CO_2 obtained.

Volume Changes. Figure 6 shows that shrinkage of the mixed resins on irradiation was significantly greater than that of either individual component. Similar shrinkage was observed for both H-OH and Li-OH mixed resins. The abnormal shrinkage of the mixed resin may be attributed in part to reduction by irradiation of the clumping tendency of mixed resins. Other factors may have caused the resin beads themselves to shrink more than when irradiated individually. The anion resin not only lost hydrophilic

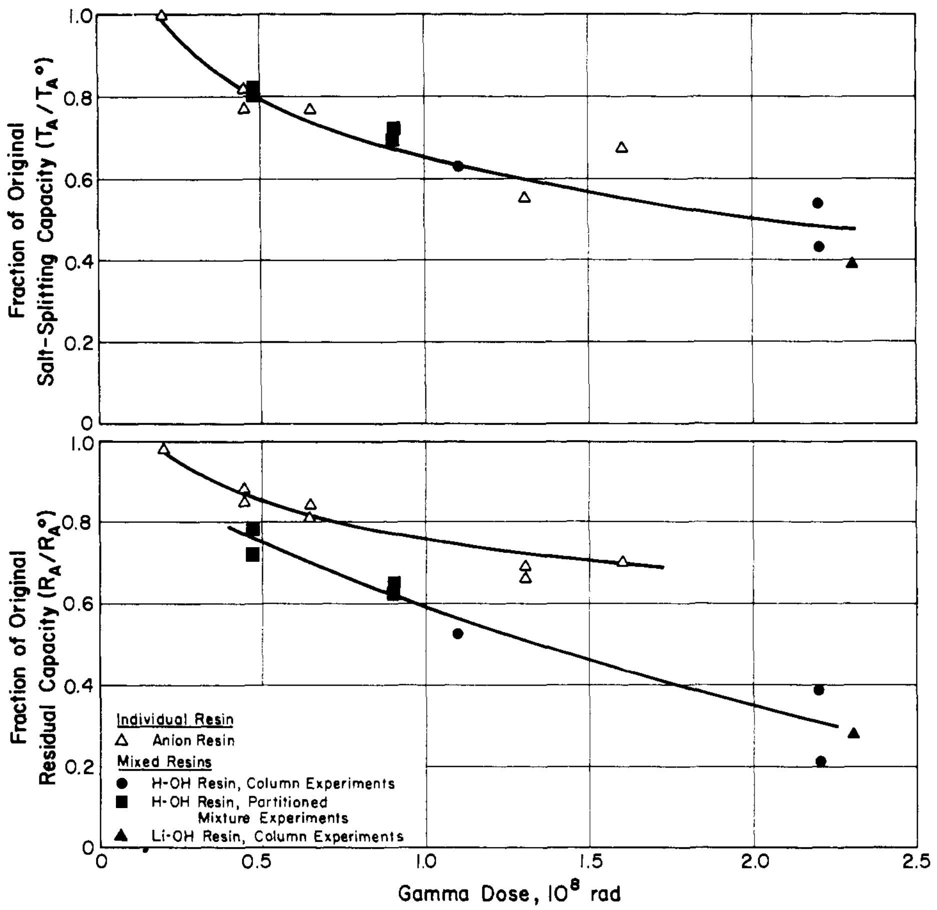


Figure 4. Effect of gamma radiation on exchange capacities of anion exchange resin alone and mixed with cation exchange resin

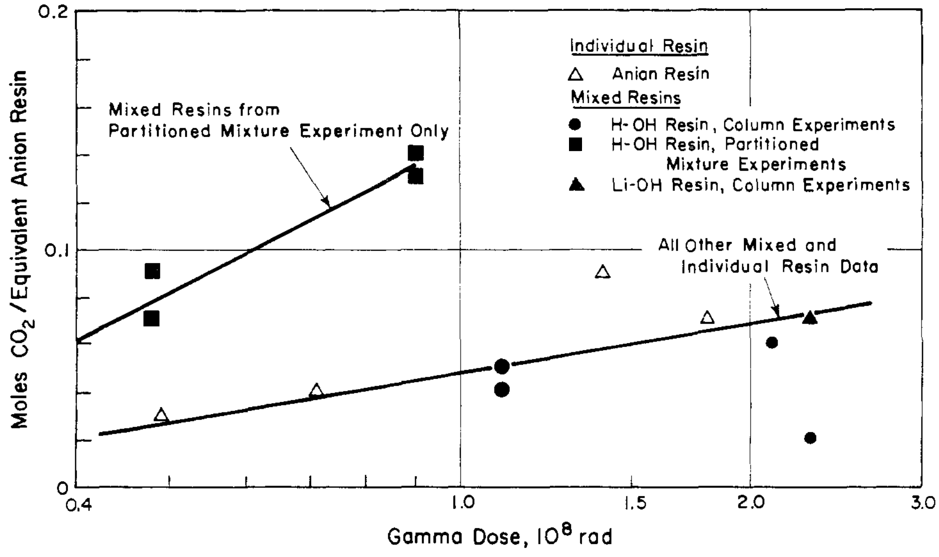


Figure 5. Production of carbon dioxide during gamma irradiation of resins

exchange groups, but also was partially converted from the highly swollen hydroxyl form to the less highly swollen sulfate and carbonate forms. The cation resin was likewise partially converted to a less swollen form by absorption of volatile base.

DISCUSSION

The results from this work have particular application to ion exchange purification of water used in nuclear reactors (*2, 3*), in which case the resins are in service for months as they remove impurities from dilute, highly radioactive solutions. The major radiation dose comes from short-lived radioactivity collected during service, but the radiation dose continues to accumulate from longer-lived radioactivity while resin is out of service. When the dose exceeds 10^7 rad, perceptible damage to the resin is to be expected.

When individual resins are used, release of degradation products to the system can result in formation of activation products in the neutron flux of the reactor. The most objectionable element in this respect is sulfur, from the cation resin. Sulfur is the precursor of the radionuclides ^{35}S and ^{32}P, which have half lives long enough to merit concern from the standpoint of radiological protection of personnel and the environment. Carbonaceous material that is released will probably be converted to CO_2 through radiolysis.

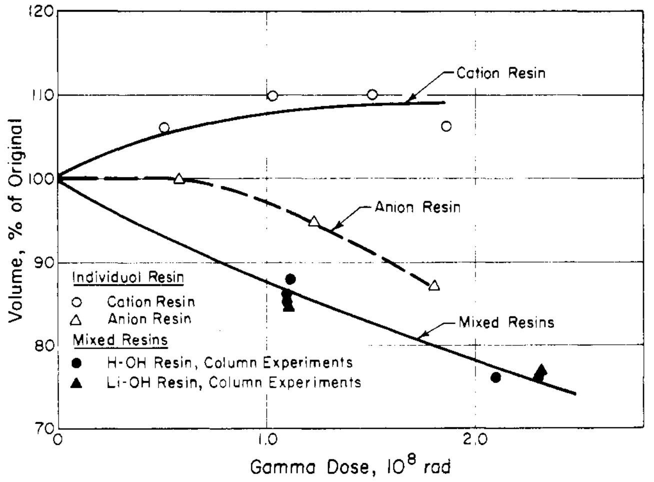


Figure 6. Volume changes on irradiation

Mixed resins provide greater protection against pollution of water by degradation products, although at some sacrifice in usable exchange capacity. Since reactor purification resins are commonly discarded rather than re-used because of radiation and regeneration problems, reduction of ion exchange capacity is costly. When H-OH mixed beds are used, pollution of water is minimal. When Li-OH mixed beds are used, nitrogenous material and lithium may be released.

NOMENCLATURE

R_A = residual anion exchange capacity
Total titratable alkalinity (to pH 4.0) eluted from a resin by a neutral salt solution. There are generally two well-defined inflection points in the titration curve, so that R_A is defined as the sum of (OH^-) and HCO_3^-).
(OH^-), determined by titration to ph 7.2
(HCO_3^-), determined by titration from pH 7.2 to Ph 4.0
Assignment of (OH^-) and (HCO_3^-) as ionic species was made for simplicity.

R_C = residual cation capacity
For H^+ resins, titratable acidity eluted from a resin by a neutral salt solution; for new resins R_C assumed to be same as T_C.
For Li^+ resins, lithium content of resin.

T_C = total cation exchange (salt-splitting) capacity. Titratable acidity eluted by a neutral salt solution from a resin after exhaustive regeneration with acid

T_A = total anion exchange (salt-splitting) capacity
Strong-base exchange groups on resin, determined by converting the resin to the desired anionic form by a salt solution, then eluting this anion from the resin by another salt solution, and determining the concentration of the eluted anion.

S = sulfate content of anion resin in mixed resin (Equation 4)

V = volatile base (NR_3) content of cation resin in mixed resin (Equation 3)

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Solubility Measurements in Lithium-Potassium Nitrate Eutectic

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The solubilities of 10 simple alkali metal salts and seven transition metal salts have been measured in lithium-potassium nitrate eutectic at 160° C. These values were compared to the theoretical values calculated from the random mixture nearest neighbor approximation and ideal solution equations and to values in aqueous solutions. Hydrated transition metal salts, when dissolved in nitrate eutectic, were shown to be dehydrated under vacuum without hydrolysis. A new complex ion was obtained in a precipitate from nickel(II) and chloride solutions.

ALTHOUGH fused alkali metal nitrates are being used increasingly as solvent media for chemical reactions, data on solubility values are still very sparse, as the published values are almost confined to those of sparingly soluble halides of silver and thallium (*7, 10*). However, two correlations have been postulated from these values. Tien and Harrington (*10*) pointed out that the solubilities of silver chloride, bromide, and iodide in fused nitrates were almost equal to those in aqueous solution when extrapolated to the melt temperature, and Seward and Field (*7*) showed that experimental solubilities of silver chloride and thallous bromide could be calculated with a very good degree of agreement from an equation developed from the random mixture nearest neighbor approximation of ion environment.

A series of measurements at constant temperature has now been carried out on 17 solutes dissolved in lithium-potassium nitrate eutectic to extend the amount of data available and to test the general applicability of these two correlations. The temperature selected for measurement (160° C.) was kept near the melting point of the solvent (132° C.) to avoid any complication due to chemical reactions which occur with several of the solutes at temperatures above 200° C.

EXPERIMENTAL

Solvent. Analytical reagent grade potassium nitrate and reagent grade lithium nitrate were dried at 150° C. for 24 hours, mixed in the eutectic proportion (38 mole % $LiNO_3$), melted, and filtered under vacuum through a No. 3 sinter.