

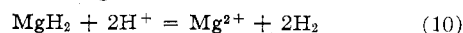
that under some conditions, e.g., 4.7 *M* HCl, the nature of the oxide film is altered by the incorporation of anions and hydride ions to give compounds such as  $U(O)XH$ , which Katzin<sup>20</sup> has suggested is the residue from the dissolution of uranium metal in dilute HCl. Such a barrier layer might be permeable to hydrogen, providing a means for the exchange.

Two points in connection with the observations made with  $O_2$  as oxidizing agent seem worthy of special mention. The oxygen in the oxide layer was found to have been derived from the solvent rather than the  $O_2$ . Although the result is consistent with the hypothesis we have advanced, it does not provide additional support. Exchange of massive  $UO_2$  with solvent is known not to be rapid, but exchange at the surface as  $UO_2$  develops slowly may be rapid enough to ensure the isotopic identity of the  $UO_2$  and solvent oxygen. It appears fairly definite that the reaction of  $UH_3$  in 4.8 *M* HCl with oxygen present is more rapid than when HCl alone is used.

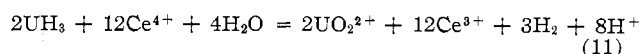
(20) L. I. Katzin, L. Kaplan, and T. Steitz, *Inorg. Chem.*, **1**, 963 (1962).

In the experiment, the average oxidation state of U in solution was found to be 4.3. The enhanced reaction rate may result from the fact that the oxide layer contains oxygen in excess of the stoichiometry  $UO_2$ . The conductivity of  $UO_{2+x}$  increases with increasing oxygen content.<sup>19</sup>

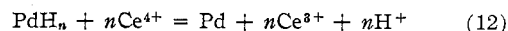
It is interesting to compare the reactions of  $MgH_2$ ,  $UH_3$ , and palladium hydride with solutions of Ce(IV). When  $MgH_2$  is the reactant, Ce(IV) is not at all involved in the net change.



When  $UH_3$  is used, the metal is oxidized, but not the contained hydrogen.



When palladium hydride reacts, the contained hydrogen, but not the metal, is oxidized.



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CONTRIBUTION FROM THE OAK RIDGE NATIONAL LABORATORY,  
OAK RIDGE, TENNESSEE

## The Absorption of Anionic Species by Strong-Acid Cation Exchangers: Identity of the Iron(III) Ion Taken up from Concentrated Aqueous Halide Solutions<sup>1</sup>

By G. E. BOYD, S. LINDENBAUM, AND Q. V. LARSON

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Spectrophotometric examinations and chemical analyses were conducted on a cross-linked polystyrene sulfonate (0.5% DVB Dowex-50) and on a liquid cation exchanger prepared by dissolving dinonylnaphthalenesulfonic acid in toluene in an attempt to find an explanation for the anomalous increase in the absorption of Fe(III) from concentrated aqueous HBr and LiBr solutions by strong-acid cation exchangers. The characteristic ligand field bands of the tetrahedral anion,  $FeBr_4^-$ , were observed in both exchangers when they had been brought to equilibrium with solutions more concentrated than 5 *N* in  $Br^-$  ion. Measurements of the  $Li^+$  (or  $H^+$ ) ion content of the liquid exchanger showed that the amount in excess of the exchange capacity was sufficient to give  $LiFeBr_4$  (or  $HFeBr_4$ ). It was concluded that the absorption of Fe(III) from concentrated HBr and LiBr involved the  $FeBr_4^-$  complex ion, and that the ion pairs,  $H^+FeBr_4^-$  and  $Li^+FeBr_4^-$ , were "salted" into the organic cation-exchange phase. Thus, in special circumstances, ion exchangers may extract salts by essentially a solvent extraction mechanism involving ion association complexes.

The anomalous increase in the absorption of Fe(III) from concentrated electrolyte solutions by sulfonic acid type cation exchangers apparently was first observed in 1950 by Djurfeldt and Samuelson,<sup>2</sup> who found that if too high a concentration of hydrochloric acid were used it became practically impossible to elute Fe(III) quantitatively from the exchanger. Measurements of the equilibrium absorption of iron further showed that for acid concentrations greater than 5.5 *N* the affinity of the exchanger for Fe(III) increased rapidly. Minima have since been observed in the concentration depend-

ence of the uptake of many of the rare earths and several actinides<sup>3</sup> and of calcium, strontium, and sodium<sup>4</sup> from hydrochloric acid solutions by Dowex-50. The absorption of Au(III) and Ga(III) from HCl and LiCl solutions<sup>5</sup> has been found to exhibit a similar concentration dependence, and detailed investigations with In(III)<sup>6</sup> ion have revealed minima with LiI, NaI, KI,  $MgI_2$ , LiBr, NaBr, and  $MgBr_2$  solutions. Cationic species presumably were not involved in the work with Fe(III), Au(III), Ga(III), and In(III), as all of them

(1) Presented before the Division of Inorganic Chemistry, 147th National Meeting of the American Chemical Society, Philadelphia, Pa., April 5-10, 1964.

(2) R. Djurfeldt and O. Samuelson, *Acta Chem. Scand.*, **4**, 165 (1950).

(3) R. M. Diamond, K. Street, Jr., and G. T. Seaborg, *J. Am. Chem. Soc.*, **76**, 1461 (1954).

(4) R. M. Diamond, *ibid.*, **77**, 2978 (1955).

(5) K. A. Kraus, D. C. Michelson, and F. Nelson, *ibid.*, **81**, 3204 (1959).

(6) H. Irving and G. T. Woods, *J. Chem. Soc.*, 939 (1963).

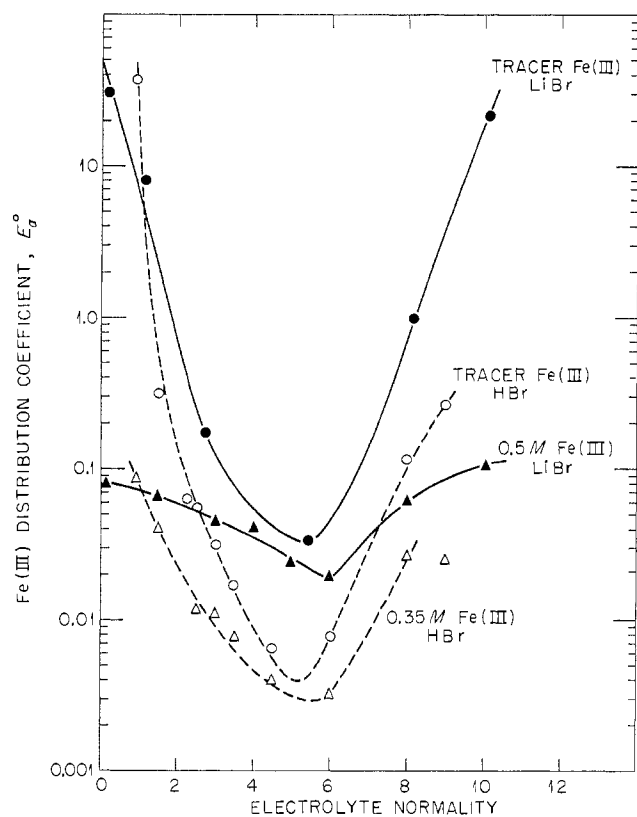


Fig. 1.—Concentration dependence at 25° of the distribution coefficient for the uptake of Fe(III) from aqueous electrolyte solutions by a liquid cation exchanger based on a 0.1 *N* solution of dinonylnaphthalenesulfonic acid in toluene.

form stable negatively-charged complex ions in concentrated halide ion solutions. However, no experimental proof has as yet been presented that the anionic species of these elements were, in fact, the ones absorbed by the cation exchanger. The possibility cannot be excluded that the cations of Fe(III), Au(III), and In(III) were the ionic species involved. The trivalent rare earths are strongly taken up from concentrated HCl and LiCl solutions, and the formation of negatively-charged complexes of these elements is unlikely. If anion complexes of the former elements were indeed absorbed, the possibility that anion-exchange impurities are present in cation exchangers must be considered.

Recently Titze and Samuelson<sup>7</sup> have investigated further the anomalous absorption of Fe(III) from HCl solutions by variously cross-linked and desulfonated Dowex-50 type cation exchangers. An increased absorption with decreasing cross linking and with decreasing exchange capacity was observed, and it was concluded that the aromatic structures in the exchanger must act as effective extracting agents for ferric chloride complexes. No experimental evidence for the uptake of anionic Fe(III) species was presented, however.

It has seemed, therefore, that an identification of the Fe(III) species extracted by cation exchangers was to be desired and that the question of whether anion-exchange impurities are present in Dowex-50 also deserved further investigation. In our recent work with

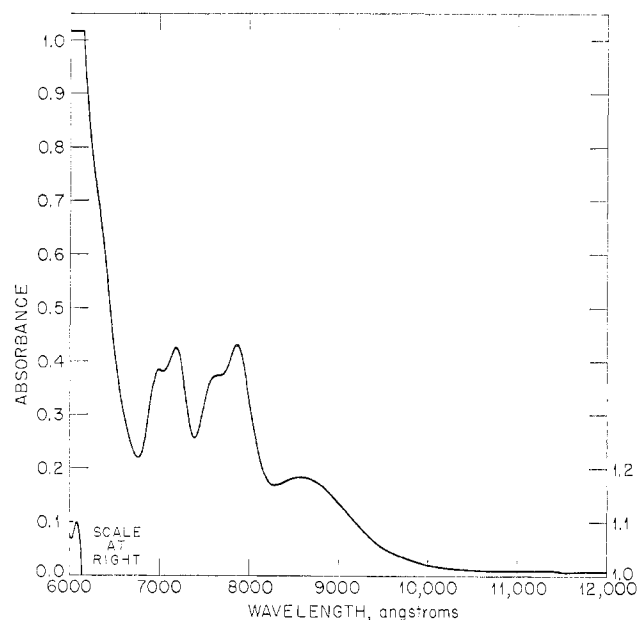


Fig. 2.—Absorption spectrum at 25° of a liquid cation exchanger in equilibrium with aqueous 9 *N* HBr containing *ca.* 1 *M* FeBr<sub>3</sub> (0.1 *N* DNNS in toluene; 1-cm. quartz cells).

liquid anion exchangers<sup>8a,b</sup> we were able to utilize the characteristic ligand field bands in the electronic absorption spectra of the halo complex ions of the 3d transition metals to identify the ionic species in the equilibrium exchanger phase. Therefore, spectrophotometric measurements on cation exchangers which had been brought to equilibrium with Fe(III)-containing aqueous halide solutions were undertaken in an attempt to resolve the questions of identity and impurity mentioned above. Two types of exchangers were examined: (a) a strong-acid liquid exchanger prepared by dissolving dinonylnaphthalenesulfonic acid (HDNNS) in toluene and (b) a weakly cross-linked (nominal 0.5% DVB) polystyrenesulfonate (Dowex-50). Aqueous HBr and LiBr rather than HCl and LiCl solutions were employed because the ligand field bands of the FeBr<sub>4</sub><sup>-</sup> ion possessed much larger molar absorbancy indices than did the FeCl<sub>4</sub><sup>-</sup> ion. In addition to the optical measurements, the equilibrium distributions of Fe(III) and H<sup>+</sup> and Li<sup>+</sup> ions between the aqueous and organic phases were determined.

### Experimental

The dinonylnaphthalenesulfonic acid employed in the preparation of the liquid cation exchanger was received from King Organic Chemical, Inc., as a 42.5% solution in low-boiling naphtha. Purifications were made following published procedures.<sup>9</sup> The concentrate was treated with an equal volume of methanol, and the less dense phase was discarded. The more dense phase containing most of the HDNNS was evaporated under vacuum at room temperature to remove the naphtha and methanol. The residue was dissolved in Spectrograde toluene to give a stock solution which was analyzed by diluting measured volumes with methanol and titrating with 0.1000 *N* sodium hydroxide to the phenolphthalein end point. Toluene solutions

(8) (a) S. Lindenbaum and G. E. Boyd, *J. Phys. Chem.*, **66**, 1383 (1962), (b) *ibid.*, **67**, 1238 (1963).

(9) S. Kaufman and C. R. Singleterry, *J. Colloid Sci.*, **10**, 139 (1955); *ibid.*, **12**, 465 (1957).

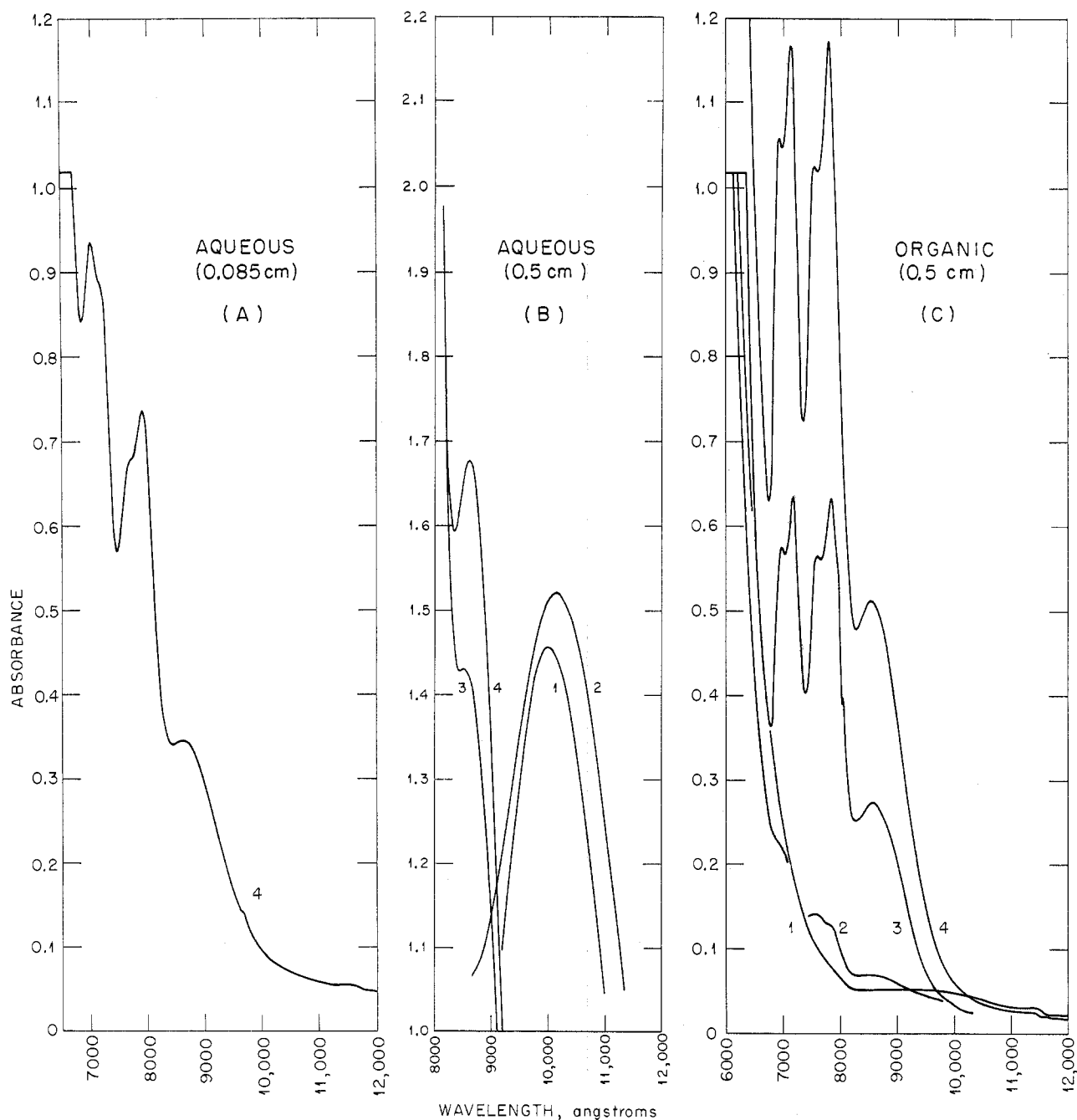


Fig. 3.—Absorption spectra at 25° of liquid cation-exchange phases in equilibrium with aqueous LiBr solutions containing 0.5 *M* FeBr<sub>3</sub>. Aqueous LiBr concentrations: (1) 5.0 *N*, (2) 6.0 *N*, (3) 8.0 *N*, and (4) 10.44 *N*.

0.1 *N* in HDNNS or LiDNNS were employed in the distribution and spectrophotometric measurements. Concentrated aqueous solutions of HBr and LiBr were made up with reagent grade chemicals and diluted to the desired molarities. Ferric bromide was prepared by adding concentrated HBr to Fe(NO<sub>3</sub>)<sub>3</sub> and evaporating to remove all HNO<sub>3</sub>.

The equilibrium partition at room temperature of Fe(III) between HBr and LiBr solutions of various concentrations and 0.1 *M* DNNS in toluene was measured at tracer level concentrations with 45.1-day Fe<sup>69</sup> and at an initial concentration of 0.5 *M* Fe(III) by mixing equal volumes of aqueous and organic solutions together. Ten ml. of each phase (with the Fe(III) initially in the aqueous layer) was added to a separatory funnel and shaken together for 15–30 min. Phase separation was effected by centrifugation under conditions in which the temperature remained close to 25°. The two immiscible phases were sampled and assayed for their  $\gamma$ -ray activity with an argon gas-filled (40 atm.) ionization chamber. Chemical analyses for iron, also were made

on the initial aqueous phases. In a portion of this investigation the organic solution was analyzed for its H<sup>+</sup> ion by acidimetric titration or for Li<sup>+</sup> ion content by flame photometry. Radioactivity or mass balances were obtained in all experiments.

Spectrophotometric measurements on the equilibrium phase were performed at 25° with a Cary Model 14P recording spectrophotometer. Matched quartz optical cells of 0.5 and 1.0 cm. path length were used; variable path length cells also were employed in several of the measurements. An aliquot of a solution identical except for the presence of Fe(III) was placed in the reference cell. The optical absorption of Dowex-50 (nominal 0.5% DVB) beads was determined by compressing the exchanger between two optically flat glass plates mounted in a rigid frame which could be placed in the spectrophotometer. Because of the difficulty in matching the path length in the ion exchanger between the working and reference frames it was not possible to eliminate entirely the absorption by the exchanger.

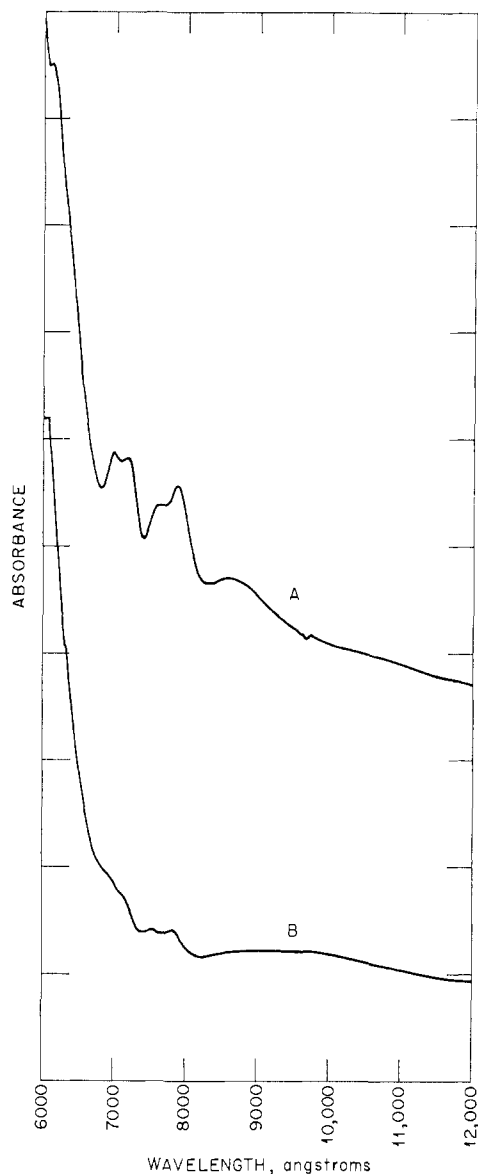


Fig. 4.—Absorption spectra at 25° of 0.5% DVB Dowex-50 in equilibrium with: A, 9 *N* HBr; B, 4.5 *N* HBr solutions containing 0.25 *M* FeBr<sub>3</sub> (absorbance units are relative; each division equals 0.1 unit).

### Results and Discussion

Equilibrium distribution coefficients,  $E_a^\circ$ , for the partition of tracer and macro concentrations of Fe(III) between the liquid cation exchanger and various electrolyte solutions are presented in Fig. 1. The uptake of Fe<sup>59</sup> from the HBr and LiBr solutions shows a minimum at a concentration of about 5 *M*; the absorption from the salt solution is significantly larger than from HBr. This behavior is quite similar to the changes in the distribution coefficient with concentration previously observed<sup>2,5</sup> in the absorption of Fe(III) from HCl and LiCl by sulfonic acid cation-exchange resins. The pronounced increase in absorption (Fig. 1) when the bromide ion concentration exceeded *ca.* 5 *N* is in apparent violation of the mass law prediction for an ion-exchange reaction involving a trivalent cation. The decrease with increasing concentration below 5 *N*, however, is in qualitative agreement with the mass law.

Other measurements<sup>10</sup> made with HClO<sub>4</sub> solutions more dilute than 0.5 *N* have given a slope of  $-3.1$  when  $\log E_a^\circ$  is plotted against  $\log a_{\text{HClO}_4}$ , in accord with expectations for the exchange reaction of Fe(III) ion. The extraction of macro concentrations of Fe(III) when present in LiBr and HBr was found (Fig. 1) to parallel the extraction of micro concentrations, although  $E_a^\circ$  was smaller because of the near saturation the liquid cation-exchange phase.

Spectrophotometric observations were made on an aliquot of liquid cation exchanger brought to equilibrium with a 9 *N* HBr solution initially approximately 1 *M* in FeBr<sub>3</sub>. The spectrum (Fig. 2) may be assigned entirely to the tetrahedral species, FeBr<sub>4</sub><sup>-</sup>. The ligand field bands reported<sup>11</sup> at 844, 779, 752, 713, 688, and 608 *mμ* for this ion in dimethylformamide were all present although they were shifted *ca.* 5–10 *mμ* to the red; their relative intensities are in excellent agreement with the published values. The band reported at 688 *mμ*, in fact, is somewhat better resolved than in the previously published spectrum where it was described as a "shoulder" on the 713 *mμ* band.<sup>12</sup>

Spectrophotometric measurements on liquid cation-exchange phases brought to equilibrium with 0.5 *M* Fe(III) in 5.0, 6.0, 8.0, and 10.44 *N* LiBr solutions, respectively, are shown in Fig. 3C. The characteristic ligand field bands of FeBr<sub>4</sub><sup>-</sup> again were observed.<sup>13</sup> Interestingly, however, little or no FeBr<sub>4</sub><sup>-</sup> appears in the organic phase in equilibrium with 5.0 *M* LiBr solution. It has seemed logical, therefore, to associate the increase in the distribution coefficient for Fe(III) above a concentration of 5.0 *M* shown in Fig. 1 with the absorption of iron as FeBr<sub>4</sub><sup>-</sup> by the liquid cation exchanger.

Observations (Fig. 3B) also were made on the aqueous phases mentioned above. In the 5.0 and 6.0 *N* LiBr solutions there was no indication of any of the FeBr<sub>4</sub><sup>-</sup> bands; however, possibly with the 8.0 *N* and certainly in the 10.44 *N* LiBr solution (*cf.* Fig. 3A) these bands were present, although their relative intensities were altered by an underlying strong absorption extending from the ultraviolet. It will be noted that as the LiBr concentration increases above 5.0 *N* the band at 1000 *mμ* (FeBr<sub>3</sub>?) increases and then disappears when the concentration exceeds 8.0 *N*.

Lastly, spectra were determined (Fig. 4) on nominal 0.5% DVB Dowex-50 cation exchanger previously brought to equilibrium with 0.25 *M* Fe(III) in aqueous 4.5 and 9.0 *N* HBr solutions. The ligand field bands of the FeBr<sub>4</sub><sup>-</sup> ion also were observed in this cation-exchange phase, although they were superimposed on a broad, strong band, possibly from the exchanger, which extended out to the longest wave lengths measured.

(10) J. M. White, P. Tang, and N. C. Li, *J. Inorg. Nucl. Chem.*, **14**, 255 (1960).

(11) N. S. Gill, *J. Chem. Soc.*, 3512 (1961).

(12) The same electronic absorption spectrum as in Fig. 2 has been observed with liquid anion exchangers brought to equilibrium with 9 *M* HBr containing 0.05 *M* FeBr<sub>3</sub>.<sup>8b</sup>

(13) Molar absorptivity indices,  $\epsilon$ , for the band in the organic phase at 779 *mμ* were measured as a function of the aqueous LiBr concentration. When  $N_{\text{LiBr}} = 10.44$  a value of  $\epsilon = 24.1$  was obtained which agrees with  $\epsilon = 24.0$  from ref. 11.

TABLE I

COMPOSITIONS OF LIQUID CATION EXCHANGER<sup>a</sup> BROUGHT TO EQUILIBRIUM WITH AQUEOUS LiBr SOLUTIONS CONTAINING FeBr<sub>3</sub>

Aqueous phase concn.		Organic phase concn.				
$M_{Li^+}$	$M_{Fe(III)}$	$M_{Fe(III)}^o$	$M_{Li^+}^o$	$N_{Fe(III)}^o + N_{Li^+}^o$	$M_{Li^+}^o - M_{Fe(III)}^o$	$M_{Br^-}^o / M_{Fe(III)}^o$
0.15	0.500	0.0376	0.0030	0.1158	...	...
1.5	0.500	0.0310	0.0209	0.1139	...	...
3.0	0.500	0.0223	0.0396	0.1065	0.0173	...
4.0	0.500	0.0187	0.0497	0.1058	0.0310	...
5.0	0.500	0.0118	0.0703	0.1057	0.0585	...
6.0	0.500	0.0095	0.0919	0.1204	0.0824	...
8.0	0.500	0.0287	0.1081	0.1942	0.0794	3.3
10.44	0.500	0.0437	0.1450	0.2762	0.1013	4.0 <sup>b</sup>
10.44	1.00	0.0543	0.1388	0.3017	0.0845	3.7
10.44	2.00	0.0662	0.1643	0.3629	0.0981	4.0

<sup>a</sup> 0.1 *N* LiDNNS in toluene. <sup>b</sup> Direct measurement of  $M_{Br^-}^o$  gave ratio of 3.7.

The absorption of Fe(III) as the species  $FeBr_4^-$  from concentrated, aqueous HBr or LiBr solutions must be accompanied by the transfer of equivalent amounts of cation into the exchanger. Accordingly, chemical analyses were made for lithium in the liquid cation exchanger (Table I); these analyses (column 4) were performed directly on the organic phase.<sup>14</sup> The amounts of iron present (column 3) were computed from the measured equilibrium extraction coefficients with Fe<sup>59</sup> tracer and the known initial Fe(III) concentration in the aqueous LiBr solutions. The sum (column 5) of the lithium and ferric ion normalities in the organic phase remained constant and virtually equal to the normality of cation-exchange groups (DNNS) present up to a concentration of 5 *N* LiBr in the aqueous phase. At higher aqueous salt concentrations, however, the Fe(III) concentration in the liquid cation exchanger increased rapidly and the amount of lithium taken up corresponded approximately with the iron absorption. Column 6, Table I, shows that the excess of lithium over iron in the organic phase increased and approached the normality of the DNNS. The data listed in the last row of Table I reveal that when the aqueous phase was 2.0 *M* in FeBr<sub>3</sub> and 10.44 *N* in LiBr the organic phase has 0.098 *N* in LiDNNS and 0.0662 *M* in LiFeBr<sub>4</sub>. The data of Table I also permit an estimation of the ratio of the amounts of Br<sup>-</sup> ion to Fe(III) in the organic phase. These ratios (column 7) suggest that iron-containing species other than  $FeBr_4^-$  were present except for the aqueous concentrations listed in the last row.

(14) The absorption of LiBr by the liquid cation exchanger in the absence of Fe(III) was measured over the same concentration range of aqueous LiBr as in Table I. The excess of lithium over 0.1 *N* LiDNNS was negligible except when  $N_{LiBr} = 11.0$ ; then,  $N_{Li^+}^o = 0.126$ , indicating a slight Donnan invasion of the cation-exchange phase. With nominal 0.5% DVB Dowex-50 extensive invasion occurs and  $N_{Li^+}^o = 11.0$ .

### Conclusions

The foregoing spectrophotometric observations and chemical analyses are believed to support the view that the anomalous absorption of Fe(III) present in concentrated aqueous HBr and LiBr solutions by strong-acid cation exchangers is a consequence of the formation of the complex ion,  $FeBr_4^-$ , in these solutions, and that the ion pair,  $Li^+FeBr_4^-$  or  $H^+FeBr_4^-$ , is "salted" into the organic cation-exchange phase. The similarity between the absorptions of Fe(III) by liquid cation-exchange solutions and cross-linked strong-acid cation exchangers (*e.g.*, Dowex-50) supports the interpretation that the increased uptake from concentrated electrolyte was not caused by anion-exchange impurities, as it is unlikely that such impurities would occur in both systems. The possibility that anion-exchange groups are produced in strong-acid cation exchangers by protonation reactions (*i.e.*,  $RSO_3H_2^+$ ) so that  $FeBr_4^-$  can be selectively absorbed appears to be excluded by the fact that this same complex ion is even more strongly taken up from concentrated LiBr than from concentrated HBr solutions. The rapid decrease in Fe(III) absorption with increasing concentration below 5 *N* HBr or LiBr is consistent with the assumption that cationic iron species are participating in an ion-exchange reaction. The ligand field bands for the tetrahedral  $FeBr_4^-$  complex ion were not seen in either the organic liquid cation exchanger or in the cross-linked resin until the concentration of HBr or LiBr exceeded 6 *N*. An increased absorption of Fe(III) also was observed above this latter concentration. Chemical analyses of the liquid cation exchanger show that when the concentration of bromide ion in the aqueous phase exceeds 13 *N* the amount of Li<sup>+</sup> ion absorbed in excess of the exchange capacity is just sufficient to give the ion pair  $Li^+FeBr_4^-$ .