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Combined Ion Exchange–Solvent Extraction of Metal Ions on Ion-Exchange Papers

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Summary

The chromatographic behavior of 14 metal ions with aqueous-organic wash liquids on ion-exchange papers is compared with results in columns and thin layers of the same resin. It is shown that many column separations can be obtained on paper, and that paper chromatography can often be used to preevaluate systems for separations on columns. The mechanism for the chromatographic processes and differences between techniques employed with columns and papers are discussed.

It has been repeatedly demonstrated that the use of mixed aqueous-organic eluents in the column ion-exchange chromatography of inorganic ions leads to greatly increased selectivities (*1*). Korisch has termed this technique combined ion exchange–solvent extraction (CIESE) (*2*). It seemed desirable to study the applicability of this technique to commercially available ion-exchange papers, which are sheets of cellulose loaded with up to 55% by weight of polystyrene ion-exchange resin. Separations of inorganic ions with these papers have been limited, except for one report (*3*), to systems with aqueous solutions of complexing agents as the wash liquid. Extensive studies (for example, *4*,*5*) have shown that the results of column and paper ion-exchange separations are usually (*6*), but not always (*7*,*8*), identical. It is therefore generally possible to reproduce column separations on ion-exchange papers, and conversely to use ion-exchange papers as a rapid medium to test potential solvents for column separations.

Described below are comparisons in selected systems of separations by CIESE on ion-exchange papers, in columns and on thin layers of ion-exchange resin. No such direct comparative study has yet been reported.

EXPERIMENTAL

Amberlite SA-2 and SB-2 ion-exchange papers (H. Reeve Angel Co., Clifton, N.J.) were used. The former contains Amberlite IR-120 sulfonic acid cation-exchange resin. It was changed from the sodium to the hydrogen form by soaking overnight in 4% HCl, equilibrating for eight 30-min periods with distilled water, and air drying (*8*). The SB-2 paper contains Amberlite IRA-400 quaternary ammonium anion-exchange resin. It was used as received in the chloride form.

Initial zones were spotted with micropipettes, 1 inch apart and 1 inch from the bottom, along the long side of sheets 20 by 25 cm. The paper was formed into a cylinder, fastened with tongued clips, and developed by the ascending technique in a Unikit tank (Shandon Co., Sewickley, Pa.) which had been equilibrated for at least 15 min with 50 ml of wash liquid. The solvent front traveled 15 cm past the origin in each case, which required 20 to 150 min, depending on the system. The developed sheets were air-dried and sprayed with appropriate detecting reagents (9).

The migration behavior of 5 to 10 μl of a 0.050 *M* solution of each ion was tested individually in each chromatographic system. The composition of these test solutions has already been reported (*10*). The ions studied were: Ag(I), Al(III), Au(III), Bi(III), Cd(II), Co (II), Cu(II), Fe(III), Mg(II), Ni(II), Pb(II), UO_2(II), V(V), and Zn (II). Five to 10 μl samples of certain mixtures, which were 0.050 *M* in each component, were also tested.

The R_F values reported below are the average of at least duplicate runs and usually more. R_F is defined as the ratio of the distance traveled by the center of the developed zone to the distance traveled by the solvent front. The developed zones were quite compact unless otherwise stated.

RESULTS AND DISCUSSION

Cation-Exchange Systems

Table 1 shows the R_F values obtained for iron, cobalt, and nickel ions with two wash liquids on SA-2 paper, as well as the batch distribution coefficients, *D*, previously reported (2) for the same solvent and resin. As expected, those ions with low *D* values (little affinity for the resin) had high R_F values, and vice versa. The separation of a mixture of these three ions was easily obtained in 10% 6 *N* hydrochloric acid, 90% acetone on SA-2 paper, the iron and cobalt zones being separated by 2.5 cm and the cobalt and nickel zones by 4.5 cm. A change of solvents was not required, as was indicated for the separation of these ions on a column of cation-exchange resin (2). Although the *D* value for iron in this system is not given (2), the R_F value indicates that it must be approximately 1.

The successful separation of 1.3×10^{-4} mm of cobalt or nickel from up to 100 times as much iron was achieved with 10% 6 *N* hydrochloric acid, 10% H_2O, 80% acetone, demonstrating the usefulness of CIESE on paper for separating relatively large amounts of iron from very small amounts of the other two ions. Cobalt and nickel cannot be separated from each other with this solvent.

Table 2 shows similar data for all ions studied as a function of the per cent tetrahydrofuran mixed with 10% 6 *N* nitric acid in the wash liquid. The data of Tables 1 and 2 show that in general, ions with *D* values of 1 to 5 showed considerable movement, and that ions with $D > 20$ were at or near the origin. Many ions with *D* values in the range 20 to 200 had R_F values of about 0.1, whereas most ions with $D > 200$ did not move at all (R_F 0.0). The R_F values thus indicate the relative magnitude of *D* values and can help in the screening of new solvent systems for column ion-exchange

TABLE 1

R_F and *D* Values for Acetone–HCl Solvents with Cation-Exchange Resin

Ion	R_F[a]	D[b]
10% 6 *N* HCl, 10% water, 80% acetone (v/v)		
Fe	0.95	1
Co	0.045	332
Ni	0.00	411
10% 6 *N* HCl, 90% acetone (v/v)		
Fe	0.93	—
Co	0.55	5
Ni	0.00	107

[a] R_F on SA-2 ion-exchange paper.

[b] *D* on Dowex 50, from (2).

TABLE 2

Variation of R_F and D Values with Cation-Exchange Resin for Metal Ions as a Function of Percentage of Tetrahydrofuran Mixed with 10% 6 N HNO_3 (v/v)

	Percentage of tetrahydrofuran					
	90		60		20	
Ion	R_F[a]	D[b]	R_F[a]	D[b]	R_F[a]	D[b]
Ag	0.00	—	0.00	—	0.13	—
Al	0.00	$>10^3$	0.00	479	0.00	137
Au	0.91	—	0.97	—	0.10	—
Bi	c	47	c	592	0.10	280
Cd	0.00	$>10^4$	0.00	10^3	0.067	49
Co	0.00	$>10^3$	0.00	306	0.067	42
Cu	0.00	—	0.00	—	0.067	—
Fe	0.00	$>10^3$	0.00	550	0.067	200
Mg	0.00	$>10^3$	0.00	72	0.13	21
Ni	0.00	$>10^3$	0.00	316	0.067	40
Pb	0.00	$>10^3$	0.00	934	0.067	185
U	0.13	40	0.00	243	0.080	96
V	0.070	—	0.00	—	0.10	—
Zn	0.00	$>10^4$	0.00	704	0.075	58

[a] R_F on SA-2 ion-exchange paper.
[b] D on Dowex 50, from (2).
[c] Cometed zone.

separations. For example, silver probably has a very high D value in the 90% and 60% solvents but a much lower value in 20%. One would predict that silver could be easily separated from uranium in a column with the 90% solvent but not with the 20% solvent.

It was possible to perform the following separations on SA-2 paper: Uranium was separated from all ions except vanadium and bismuth, and gold from all ions except bismuth with 90% tetrahydrofuran. These results for uranium are the same as in columns; column results for vanadium and gold were not reported in this system (2). Gold was separated from every other ion in 60% tetrahydrofuran. Bismuth formed a long streaking zone out to R_F 0.88 and 0.70, respectively, in these solvents.

Anion-Exchange Systems

Table 3 is a comparison of R_F and log D values with 10% 6 N hydrochloric acid, 90% methanol, and anion-exchange resin. Again it is generally true that a given ion exhibits either high or low affinity for both the resin and the resin paper. Anomalous behavior was exhibited by cobalt, which cometed from the origin to R_F 0.58, and by vanadium, which formed a double zone. On anion-exchange paper, nickel, magnesium, or aluminum was separated from every other ion except vanadium. Relatively large amounts of these three ions could again be separated from very small amounts of those ions that remained at the origin.

When a mixture of iron, cobalt, and nickel was developed on SB-2 paper in the usual way with 10% 6 *N* hydrochloric acid, 90% acetone (v/v), the R_F values were 0.43, 0.00, and 0.00, respectively. In this system the wash liquid was altered as it passed over the paper, so that the hydrogen-ion front did not coincide with the bulk wash-liquid front. It was determined by spraying the developed paper with universal indicator solution that the acid front was at R_F 0.47 and that the leading edge of the iron zone was at this front. Frontal analysis of the wash liquid is often encountered in paper

TABLE 3

R_F and Log *D* Values for 10% 6 *N* HCl, 90% Methanol (v/v) with Anion-Exchange Resin

Ion	R_F[a]	log D[b]	R_F[c]
Ag	0.00	—	0.00
Al	0.93	−1.0	—
Au	0.00	—	0.00
Bi	0.00	—	0.00
Cd	0.00	2.5	0.00
Co	[d]	1.7	0.00[e]
Cu	0.00	2.2	0.00
Fe	0.00	1.5	0.00
Mg	0.93	−1.0	—
Ni	0.90	−1.0	0.75
Pb	0.00	—	—
U	0.00	3.0	0.00
V	0.00; 0.70[f]	—	0.00
Zn	0.00	2.8	—

[a] R_F on SB-2 ion-exchange paper.

[b] *D* on Dowex 1, from (*11*).

[c] R_F by thin-layer chromatography on Dowex 1, from (*12*).

[d] Cometed zone.

[e] Faint forward comet.

[f] Double zone.

chromatography and can lead to differences in results between ion-exchange papers and columns which are due to the difference in technique and not in principle (7). In column chromatography the column is first washed with eluent and the sample is applied to the wet, conditioned resin. In paper chromatography the sample is applied to dry paper and the wash liquid is passed over it. If the paper retains some of the components of the wash liquid more than others, front effects will be noted, and some of the ions of the sample may not be in contact with the bulk was liquid. To overcome this one can allow the solvent to irrigate over the paper and then place the initial zone on the origin behind the front (7).

When this was done iron had $R_F = 0.95$ (after subtracting the distance the solvent migrated before the sample was applied). This was in line with the value of log $D = -1.0$ for iron on Dowex 1 resin (*11*). Another method which was tried to overcome the front effects was to presoak the paper in the wash liquid and partially dry it prior to spotting and development. This left a reserve of wash liquid in the paper during the migration. When this was done with the present system, iron migrated with $R_F = 0.65$. With both these methods the cobalt and nickel remained near the origin ($R_F < 0.10$), so that it was impossible to reproduce the separation of these three ions reported with the same solution in a 10-cm column (2). This column separation is surprisingly good considering that the reported (*11*) log D values of 2.3 for cobalt and 2.0 for nickel in this system are so similar.

These front phenomena were noted on SB-2 paper when other organic solvents were mixed with 10% 6 *N* hydrochloric acid; for example: 90% ethanol, R_F H^+ front = 0.83; 90% isopropanol, $R_F =$ 0.73; 90% *n*-butanol, $R_F = 0.50$; and 90% tetrahydrofuran, $R_F =$ 0.33. To get paper results which are comparable to columns with these solvents, the front effects would have to be overcome as suggested above. This is illustrated by 10% 6 *N* hydrochloric acid, 90% 2-methoxyethanol (methyl glycol). This solvent gave an acid front with $R_F = 0.77$ on SB-2 paper, and ions such as nickel and aluminum migrated exactly with this front. When the solvent was allowed to run 5 cm past the origin before the initial zones were placed at the origin, very good correlation between (corrected) R_F and log D values resulted (Table 4). In this system we could separate nickel, vanadium, aluminum, or magnesium from any other ion but not from each other.

TABLE 4

R_F and Log D Values for 10% 6 N HCl, 90% 2-Methoxyethanol (v/v) with Anion-Exchange Resin

Ion	R_F[a]	log D[b]
Ag	0.00	—
Al	0.86	−1.0
Au	0.17	—
Bi	0.00	—
Cd	0.00	2.6
Co	0.00	3.5
Cu	0.00	2.4
Fe	0.27	−1.0
Mg	0.78	−1.0
Ni	0.89	−1.0
Pb	0.00	—
U	0.00	4.3
V	0.68	—
Zn	0.00	2.7

[a] R_F on SB-2 ion-exchange paper, corrected for front effect.

[b] D on Dowex 1, from *(11)*.

Tables 3 and 4 show that, in general, ions with log D values of −1.0 showed significant migration, and that ions with log D values of 1.3 or more had R_F values <0.10 on anion-exchange paper.

Front effects were never noted on SA-2 paper or with methanol-containing solvents on SB-2 paper.

Comparisons between Paper and Thin-Layer CIESE

CIESE has been recently performed on thin layers of starch-bound ion-exchange resins *(12)*. The results for Dowex 1-X8, chloride form, with 10% 6 M hydrochloric acid, 90% methanol, are shown in Table 3. In most cases the results compare favorably with paper chromatography for those ions studied by both procedures. R_F values for cobalt, nickel, and iron on Dowex 50 layers with 10% 5 M hydrochloric acid, 74% acetone *(12)*, are virtually identical to those shown for a similar solvent in Table 1. Similar results should be expected because the techniques for development are identical. However, there are differences in the nature of the stationary phases involved. CIESE on paper is more convenient because the paper is commercially available, and time need not be taken to prepare thin layers.

Qualitative Mechanism of CIESE

Korkisch has pointed out (2) that increased selectivities in CIESE are due to a bidimensional ion-exchange competition between a liquid exchanger in the outside phase and a solid phase, the resin itself. Two points should be emphasized in addition to this. Even in pure aqueous systems, solid resins can sorb solutes not only by actual ion exchange but by other mechanisms, such as sorption on the organic network and complex formation with the functional groups (*13*). Factors of this type have led to the strong affinity of solid ion exchangers for ions of both charges, neutral salts and organic molecules (*13–15*). Second, another important reason for increased sorption and selectivity with aqueous-organic solvent mixtures must be the nonuniform distribution of solvent components between the resin and external phases. The resin prefers the water from a mixed solvent, so that the relative amount of water is higher in the resin phase than in the external solution; i.e., the resin salts out the organic component (*16*). [This is more or less balanced by the attraction of the resin network for long-chain organic compounds (*17*), which in most cases have not been used in CIESE.] Because the resin phase is more aqueous, the inorganic complexing agent will prefer to go inside. Complex formation inside the resin is therefore favored relative to the external phase, resulting in increased *D* values. *D* values often decrease again at very high concentrations of organic constituent because there is so little water present that the concentration of complexing agent inside the resin is not very much different from that outside. This picture can apply equally well for an anion or cation exchanger. CIESE on ion-exchange paper is further complicated by the possible interactions of the solutes and the solvent components with the binder chemicals (if any are present) and cellulose.

It is shown above that results obtained in column and paper ion-exchange experiments with aqueous-organic solvents are quite similar and can often be used to compliment each other. Most column separations can be obtained on comparable ion-exchange paper, and such paper can be used to predict column separations. Differences are to be expected, however, because of the differences between the two techniques, and because there are actual differences in the composition of the stationary phases involved in each case.

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