Synthesis of Phosphorus-Containing Wofatit Cation Exchangers and Their Affinity toward Selected Cations

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Synopsis

A number of solid Cationits have been prepared derived from Wofatit* gel and canal structures: styrene/DVB, chloromethylated ST/DVB, and acrylic acid/DVB copolymers. To functionalize the copolymers, $PCl_3/AlCl_3$ and dialkyl phosphites or trialkyl phosphites were used. The influence of the polymer matrix structure and the chemical structure of the functional groups of obtained Ionits on their affinity toward 23 metallic cations in acidic media has been investigated using the conductivity method. To obtain comparison data, commercial "Wofatit"–sulfonic and –carboxylic Cationits, have been tested under identical conditions.

INTRODUCTION

The phosphor-containing functional group is able to sorb in selective manner different metallic cations from the solution, which is illustrated by differentiated affinity or selectivity coefficients. The first report about solid phosphororganic cation exchangers was made by Bregman and Murata[1] many contributions were made by Kennedy and co-workers[2,3,5]; the most extensive study has been conducted by Heitner-Wirguin and Kendler.[4] But there is still a distinct lack of information. There are also many other contributions in the synthesis of solid or liquid ion exchangers or molecular sorbents and those containing nitrogen.[6,7]

In contrast, in the solid series of phosphororganic cation exchange resins, there exists little information about the influence of the chemical and physical structure of the polymer matrix as well as of the structure of the functional group phosphonic, phosphinic, and phosphoric ester group, especially partly esterified, nuclear-, or aliphatic-chain bound, etc., especially bound to the same matrix) on selective ion exchange properties of these Cationits. Due to free electron pairs on oxygen atoms within the functional groups, there exists the possibility of their differentiated engagement into a free orbital of a given metallic cation, resulting in the creation of coordination bonding. For example, the following structure may be formed:
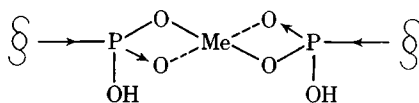
* Trademark, VEB Chemiekombinat Bitterfeld.

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The arrow between the matrix-marking paragraph indicates the differentiated structure-dependent action of the polymer matrix on the complexing ability of the functional group.

Within the micromolecular region, the complexing properties of a given ligand depend as well on the type of complexing agent as on the engaged cation.[8,9] That is why the stability constants of complex compounds differ with various cations. In the macromolecular region, the conditions are still more complicated. The selectivity of complex-forming ion exchange resins depends certainly on the constitution of the functional group, on its location in the macromolecular chain, as well as on the chemical and physical structure of polymer matrix (gel-like or macroporous, degree of crosslinking and peculiar structure defects), expressed by the sieve effect. Since these aspects have not been considered by the cited authors, it was relevant to examine the influence of the matrix structure on the basis of Wofatit copolymers and the constitution of the phosphor-containing functional group, as well as its mode of attachment to the macromolecule, on the selectivity of these cation exchange resins within their first acidic stage.
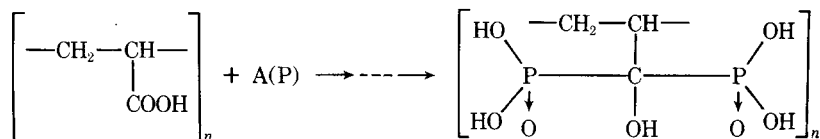
From three pairs of "Wofatit" copolymers (each pair, gel and macroporous), we have synthesized a number of phosphororganic Cationits differentiated by their chemical and physical structure (Table I). For the prepared cation exchange resins, the alkalimetric pH titration curves, pK values of acidic functional groups, and separation factors toward 23 metallic cations in acidic media, as well as the exchange capacities for the same were determined. To increase the usefulness of the obtained results, we compared data by performing the same series of measurements and determinations using commercial "Wofatit"–sulfonic and –carboxylic Cationits, each having gel and canalic structure.

SYNTHESIS OF THE RESINS

The synthesis of phosphororganic ion exchangers may be achieved either by means of polymerization of phosphororganic monomers[10] or by functionalization or ready-made copolymers.[11] We aimed at the synthesis of solid phosphororganic Cationits in which the phosphor atom was connected with aromatic nuclei directly (C_{ar}–P) or indirectly by a methylene group (C_{ar}–CH_2–P) or bound to aliphatic radicals (C_{al}–P, C_{al}–O–P). This was attained by functionalization or modification of "Wofatit" copolymers. The functionalization of styrene/DVB (chloromethylated or not) has been achieved by the Friedel–Crafts reaction with use of phosphor trichloride/$AlCl_3$. Using chloromethylated St/DVB copolymers, we also employed dialkyl phosphites $HOP(OR)_2$ and trialkyl phosphites $P(OR)_3$, where R is methyl or ethyl group. The reaction was conducted by boiling at normal pressure with an excess of phosphites. The use of dialkyl phosphites is not known in this reaction. During the course of the reaction, samples of copolymers were taken to determine the phosphorus content. The samples underwent mineralization by means of Eschka mixture, and the molybdenum–vanadium–phosphoric acid analytical method[12] was applied. In the case of chloromethylated copolymers as starting material, chlorides were also determined by means of an ion-selective electrode.

The results of a detailed investigation in several stages of phsophororganic cation exchange resin synthesis, i.e. on the oxidation of intermediary phosphinic groups and on hydrolysis of transient ester groups, will be published elsewhere.

Derived from acrylic acid/DVB copolymers, we sought a chemical modification of the carboxylic acid group to a phosphonic group by the introduction of phosphonic acid groups in addition to the existing carboxylic groups.

$$\left[\begin{array}{c} -CH_2-CH- \\ | \\ COOH \end{array}\right]_n + A(P) \longrightarrow - - - \longrightarrow \left[\begin{array}{c} HO \quad -CH_2-CH- \qquad OH \\ \diagdown \qquad\qquad | \qquad\qquad \diagup \\ P \text{———} C \text{———} P \\ \diagup \downarrow \qquad | \qquad \downarrow \diagdown \\ HO \quad O \qquad OH \qquad O \quad OH \end{array}\right]_n$$

As the carboxylic macromolecular agent, carboxylate cation exchangers Wofatit CP and Wofatit CA-20 were used. As phosphorylating agents, the following chemical compounds were applied: $A(P) = PO_x$, P_2O_5, H_3PO_3, H_3PO_4, PCl_3, PCl_5, $POCl_3$, $HOP(OCH_3)_2$, $HOP(OC_2H_5)_2$, $P(OCH_3)_3$, and $P(OC_2H_5)_3$.

In many instances, the phosphorylating reaction did not go at all; in other cases, there was only an insignificant amount of phosphorus bound to the polymer matrix (ca. 2%). We therefore converted starting materials to the acid chloride §-COCl, or acid anhydride §(CO)$_2$O or ester §-COOCH$_3$ prior to phosphorylations. Unfortunately, these reactions did not yield the expected results.

The best phosphorylating agent for acrylic acid/DVB copolymers is a mixture of dialkyl phosphite and phosphorus pentoxide. Using this mixture in connection with subsequent multistage hydrolysis, we obtained four new phosphororganic Cationits,[13] although their chemical structure is quite different from that initially predicted.

PROPERTIES OF CATIONITS

The obtained and tested Cationits display a multifunctional medium acidic character, expressed by at least two different dissociation constants. On titrimetric curves (Figs. 1 and 4), one observes more than two inflection points. They contain phosphoric groups connected differently to the matrix, (e.g. see Cationit PP) or their functional groups differ in constitution or structure (see, e.g., Cationit IV). The obtained Wofatit skeleton cation exchange resins react within pH 2.0 and 9.5. In the case of Cationit P or PP, the more acidic hydrogen dissociates in the range of pH 2–6, whereas the weaker acidic hydrogen dissociates between pH 6 and 9.5.

Independently of the determined relative high pK values listed (Table II), in conducting an ion exchange process H$^+$/Me^{n+}, a mineral acid solution is much more acidic than expected from the pK values. The higher acidity is different and depends on the kind of metallic cation used in the process. The metallic cations are held more strongly by the phosphor-containing functional group than the proton is. In column experiments using Cationit P-M and an aqueous solution of NaCl, CaCl$_2$, and FeCl$_3$ effluents were obtained having the following corresponding pH values: 0.64, 0.27, and 0.03. These differences are explained by the stability constants of complexes formed between the individual metallic cation and the functional group of the resin.

Cationits P and P-M show higher acidic power than Cationits PP and PP-M, due to the influence of π electrons of the aromatic system on the functional group. The more complicated run of titrimetric curves of Cationits PP and PP-M is due to functional groups in the side chain and those attached directly to the aromatic nuclei.

TABLE I
Synthesis of Phosphororganic Cationits

Symbol[a]	Structure of functional group	Reagents	
		Copolymer[b] used as starting material (gel and canal structure)	Phosphorylating agent
P, P-M	$-P\overset{O}{\underset{OH}{\overset{\uparrow}{\diagup}}}\diagdown OH$	Styrene/DVB, gel-7% DVB, canal ~20% DVB	$PCl_3/AlCl_3$
PP, PP-M	$-CH_2-P\overset{O}{\underset{OH}{\overset{\uparrow}{\diagup}}}OH$, $\overset{O}{\underset{OH}{\overset{\uparrow}{P}}}\diagdown OH$	Chloromethylated styrene/DVB gel 4% DVB, canal str. ~20% DVB	$PCl_3/AlCl_3$
DM, DM-M	$-CH_2-P\overset{O}{\underset{OH}{\overset{\uparrow}{\diagup}}}OCH_3$, $-CH_2-O-P\diagup^{OCH_3}\diagdown_{OH}$	Chloromethylated styrene/DVB gel 4% DVB, canal str. ~20% DVB	Dimethyl phosphite
TM, TM-M	$-CH_2-P\overset{O}{\underset{OH}{\overset{\uparrow}{\diagup}}}OCH_3$	Chloromethylated styrene/DVB gel 4% DVB, canal str. ~20% DVB	Trimethyl phosphite

	Structure	Matrix	Reagent
TE, TE-M	$-CH_2-P(\!\!\uparrow\!O)(OC_2H_5)(OH)$	Chloromethylated styrene/DVB gel 4% DVB, canal str. ~20% DVB	Triethyl phosphite
I	$-COOC_2H_5,\ -C(=\!O)-O-P(OC_2H_5)(OH)$	Acrylic acid/DVB gel 5% DVB, canal str. ~20% DVB	
II	$-COOH,\ -C(=\!O)-O-P(OC_2H_5)(OH)$	Acrylic acid/DVB gel 5% DVB, canal str. ~20% DVB	$HOP(OC_2H_5)_2 + P_2O_5$
III	$-COOH,\ -C(=\!O)-O-P(OH)(OH)$	Acrylic acid/DVB gel 5% DVB, canal str. ~20% DVB	
IV	$-COOH,\ -C(=\!O)(\!\!\uparrow\!O)-P(OH)(OH)$	Acrylic acid/DVB gel 5% DBV, canal str. ~20% DVB	

a Letter M after dash means canal structure of matrix. Absence of M means gel structure of matrix.
b All copolymers used in this work (practical grade) were produced by VEB Bitterfeld, GDR (0.3–1.2 mm in diameter, spheric particles).
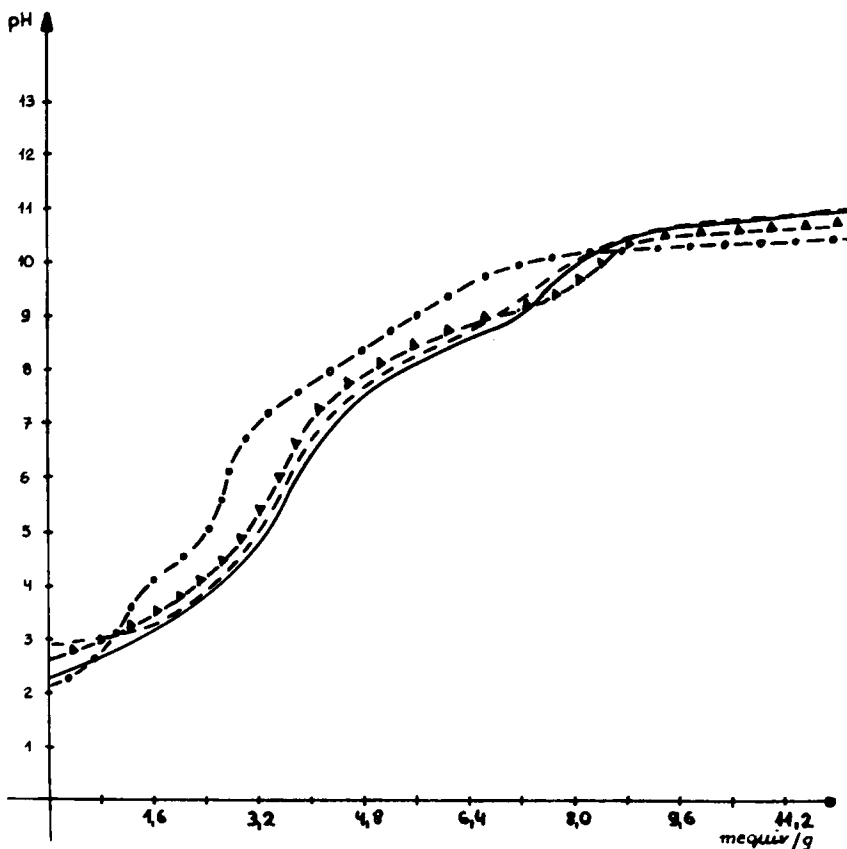
Fig. 1. Titrimetric curves of Cationits mark P and PP: (——) Cationit P; (—o—o—o—) Cationit PP; (------) Cationit P-M; (—Δ—Δ—Δ—) Cationit PP-M.

The obtained titrimetric curves served also to estimate ion exchange capacity (Table II) which, for medial acidic ion exchangers is dependent on the pH of the external solution. On the basis of the Henderson-Hasselbach formula, taking each range separately, $a = 0.5$, the acidity constants and pK values have been derived (Table II).

AFFINITY OF CATIONS TOWARD MEDIAL ACIDIC ION EXCHANGERS

Many methods are published leading to the determination of selectivity coefficients of solid ion exchangers toward different ions.[2,4,14,15] This also concerns the solid phosphonic ion exchangers known as Duolite C-63 or Bio-Rex 63. Nevertheless, an insufficiency in this field exists especially if one wants to compare the published data obtained by different authors for different ion exchangers with different functional groups. This state is probably connected, too, with the lack of unequivocal measure of selectivity. There exist selectivity coefficients based on thermodynamic and kinetic constants of ion exchange reactions. Rational, corrected, distribution, separation, and some other coefficients are also applied.

To estimate the selectivity of the prepared Wofatit skeleton phosphororganic
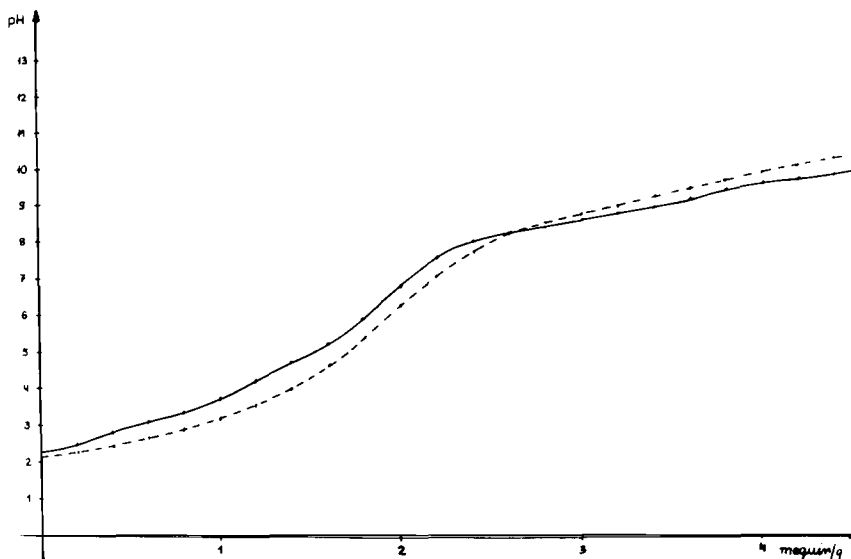
Fig. 2. Titrimetric curves of obtained Cationits mark DM: (——) Cationit DM; (------) Cationit DM-M.

TABLE II
Main Properties of Tested Phosphororganic Cation Exchange Resins

Symbol of Cationit	Phosphor content, %	Cation exchange capacity, m equiv/g of dry resin		Acidic exponent of resin pK	
		Analytic	Derived from pH-metric curve[a]	pK_1	pK_2
P	13.1	8.45	7.2	3.3	8.1
P-M	10.4	6.7	6.8	3.4	8.2
PP	11.0	7.1	5.4	2.4	4.4 $pK_3 = 7.7$
PP-M	11.9	7.7	6.6	3.5	8.5
DM	6.8	2.2–4.4	3.5	3.8	—
DM-M	6.7	2.2–4.4	3.2	3.3	—
DE	1.5 (P^{III})	0.5	—	—	—
DE-M	2.0 (P^{III})	0.6	—	—	—
TM	9.7	3.3–6.6	3.1	3.7	—
TM-M.	8.7	2.9–5.8	3.4	3.2	—
TE	9.9	3.5–7.0	4.0	3.4	—
TE-M	8.9	3.3–6.6	4.7	2.2	4.1
I	13.1	4.2	5.4	3.3	—
II	17.1	11.0	8.5	2.2	7.0
III	18.3	17.7	10.4	2.1	6.3
IV	10.8	10.4	9.8	1.4	2.8
					$pK_3 = 5.9$

[a] The dependence of cation exchange capacity on pH of external solution is shown by titrimetric curves of tested resins.

Cationits and to compare them with commercial stronger or weaker acidic Wofatit-Cationits (i.e., having the group —SO_3H or —COOH), we took as its measure the "affinity factor," expressed as percent to which an ion exchange reaction occurred in reference to a given amount of active ion exchange capacity. To
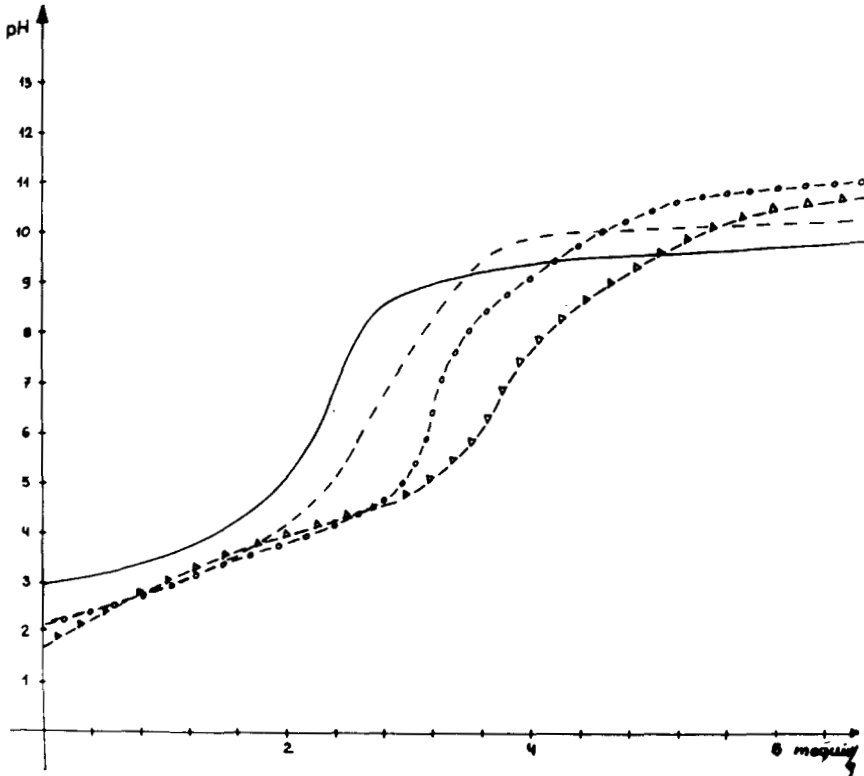
Fig. 3. Titrimetric curves of obtained Cationits mark TM and TE: (—) Cationit TM; (—O—O—O—O) Cationit TE; (------) Cationit TM-M; (—△—△—△—△) Cationit TE-M.

determine the degree of ion exchange process, the conductivity method has been applied.   This method was formerly described by Gürtler and co-workers[16,17] in application to strong basic anion exchange resins.

The "separation factor" has been calculated according to the formula
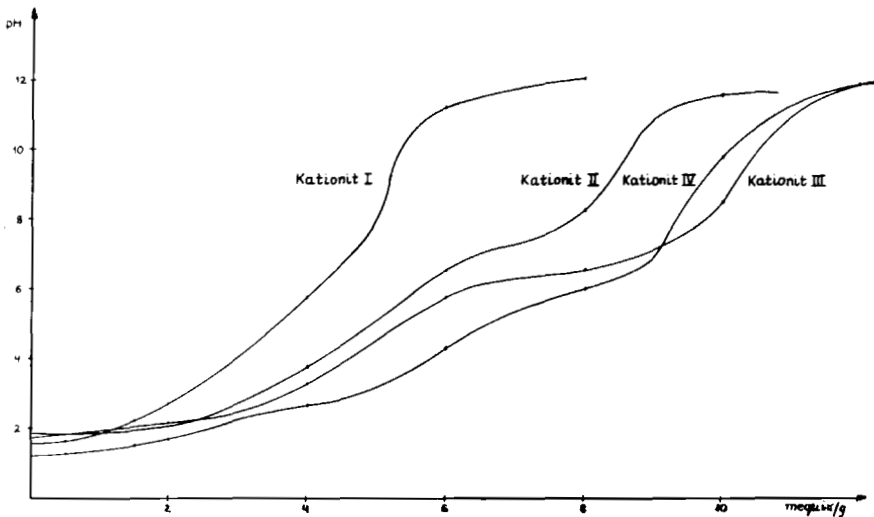
Fig. 4. Titrimetric curves of obtained Cationits mark I–IV.

$$\alpha_{Me/H} = \frac{\bar{X}_{Me} X_H}{\bar{X}_H X_{Me}}$$

where $X, \bar{X}$ means the equivalent fraction of exchanged ions corresponding to the solution phase or resin phase (relative to the unity of active ion exchange capacity taking into account the pH-value of the solution, read from titrimetric curves).

The measurements consisted of carrying through the following cation exchange reaction:

$$\S{-}H_n + Me^{n+} \rightleftharpoons \S{-}Me + nH^+$$

where Me^{n+} equals the cation by which affinity and separation factors of the resin are measured.

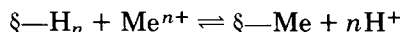The given cation exchange resin in the hydrogen form was mixed with the aqueous solution of a metallic cation until the equilibrium state was attained. Then, the concentration of hydrogen ions was measured by means of a thermostated conductivity cell and calculated using the following formula:

$$X_{H^+} = \frac{\left(\dfrac{1}{R}\right)_{postreaction} - \left(\dfrac{1}{R}\right)_{0.1N\ Me^{n+}}}{\left(\dfrac{1}{R}\right)_{0.1N\ HCl} - \left(\dfrac{1}{R}\right)_{0.1N\ Me^{n+}}}$$

The remaining three values, which are necessary for calculation of the affinity and separation factors, were attained using the difference method. The achieved formula for affinity factor is

$$P_{Me} = 100 \times X_{H^+}$$

while the separation factor formula is

$$\alpha_{Me/H} = \left(\frac{P}{100 - P}\right)^2$$

In the case of the phosphororganic cation exchangers, obtaining comparable results depends on taking into consideration the natural acidity of the solution of different cations and the active capacity of the resin. To give all cations equal chances to undergo completely the ion exchange reaction, the amount of the resin should be different each time, whereas the amount of cation solution should remain the same.

EXPERIMENTAL

In a thermostated glass beaker a determined amount of well-swollen cation exchange resin was placed and 100 cm^3 of $0.1N$ solution of the given cation (see Table III) such as a metal chloride. The required amount of the resin was determined according to the shape and exact run of the titration curve of the investigated Cationit, as well as its swelling degree. For example, to provide 10 miliequivalents active ion exchange capacity of Cationit PP destined to react with aluminum (Al^{3+}) or sodium (Na^+) chloride with corresponding pH 4.25 and 6.5, 5.55 g (12.2 cm^3) and 3.33 g (7.3 cm^3) of water-swollen resins were used. The suspension in the beaker was mixed by an electromagnetic stirrer, while the temperature of $20 \pm 0.5°$ was observed until the equilibrium was reached. After

careful separation of the resin from the solution, its conductivity was determined at the said temperature, using a conductometer of the type OK-102, Radelkis, Hungary.

RESULTS AND DISCUSSION

To evaluate the separating ability of a resin, one has to consider not so much the absolute value of the affinity or separation factors but their difference, their relation, or the scatter of these values of different ions. The more extended the range of these factors is, the better the separating properties of a resin.

The experimental results obtained by conductivity measurements show very distinctly that the distance between affinity or separation factors of the alkali metals, alkali earth metals, and transition and multivalent metals in acidic media in the Wofatit skeleton series is much more extensive in phosphor-containing Cationits than sulfonic cation exchangers. Carboxylic resins occupy, however, a middle place, due to differing complexing ability of their functional groups. The most distinct ability is shown by the phosphonic group; weaker complexing properties are exhibited by the carboxylic group; whereas the sulfonic group does not possess any complexing properties.

As the affinity of the sodium ion is, as a rule, the smallest within the investigated cation series (neglecting Hg^{2+} and some resins), we have divided the affinity factors in each column of Table III by the sodium value in that column. The obtained range of numbers illustrates how well the individual Cationit differentiates various cations:

Cationit P	5.7 (UO_2^{2+})	Cationit TM	4.4 (Ag^+)
Cationit P-M	7.9 (UO_2^{2+})	Cationit TM-M	8.3 (UO_2^{2+})
Cationit PP	9.2 (UO_2^{2+})	Cationit TE	2.1 (NH_4^+)
Cationit PP-M	9.9 (UO_2^{2+})	Cationit TE-M	10.2 (UO_2^{2+})
Cationit DM	3.1 (NH_4^+)	Wofatit KPS	1.7 (Cr^{3+})
Cationit DM	9.3 (Th^{4+})	Wofatit KS-10	1.6 (Fe^{3+}, Th^{4+})
Cationit IV	5.6 (Fe^{3+})	Wofatit CP	3.6 (Pb^{2+})
Cationit IV-M	17.2 (UO_2^{2+})	Wofatit CA-20	2.9 (Pb^{2+})

Nevertheless, detailed statistical calculations have shown that within the same physical structure of the resin (say, macroporous), the nuclei-bound phosphonic group (P-M) exhibits the best separation factor differences among various cations, better than does the methylene-bound phosphonic group (PP-M). The aliphatic chain-bound phosphonic group (Cationit IV) succoured by a carboxylic group, has still weaker distinguishing properties. Methylene-bound phosphonic groups containing one active proton [e.g., ester (DM, TM, TE)] show weaker separating abilities (smaller separation factor differences) than diprotonic groups. The presence of an oxygen-bound phosphonic group (DM) seems to diminish the separating ability of the resin.

For the Wofatit skeleton cation exchangers (phosphonic or sulfonic), the macroporous (canalic) structure promotes affinity scattering (range extension), compared with the gel structure. When a carboxylic group is present in the resin, the influence of the physical structure of the resin is inverted (Cationit IV and IV-M, Wofatit CP and CA-20). The positive influence of the macroporous structure over the gel structure on affinity is much more distinctive when an ester group is present (DM-M, TM-M, TE-M).

TABLE III

Affinity of Synthesized Phosphoric Cationits as Well as Sulfonic and Carboxylic Ones Towards Selected Cations in the Wofatit Series

No.	Cation tested	pH of solut.	Symbols of tested phosphoric resins												Symbols of common Cationits (Wofatit trademark)			
			P	P-M	PP	PP-M	DM	DM-M	TM	TM-M	TE	TE-M	IV	IV-M	KPS	KS-40	CP	CA-20
1.	Na$^+$	6.54	13.2	10.1	8.4	7.2	4.2	5.6	2.2	10.1	7.6	6.8	11.8	4.5	60.0	61.7	4.2	4.6
2.	K$^+$	6.38	15.3	11.0	10.1	7.7	5.2	11.7	2.1	10.7	8.0	7.7	12.3	5.7	63.2	65.0	4.3	4.6
3.	NH$_4^+$	6.25	19.0	16.9	15.2	13.7	13.2	17.8	8.0	17.8	15.8	13.7	18.1	9.7	64.4	69.6	9.4	9.1
4.	Mg^{2+}	6.99	22.2	15.7	16.8	14.0	1.6	15.7	0.8	17.3	0.3	14.6	20.1	7.7	84.1	79.7	2.7	3.3
5.	Ca^{2+}	6.15	23.8	23.8	24.0	15.7	1.1	18.5	1.4	20.2	0.6	17.4	26.3	10.4	89.3	94.7	3.9	3.6
6.	Sr^{2+}	6.06	23.0	18.3	18.3	15.5	2.5	16.9	2.7	17.2	1.1	12.7	27.1	11.9	91.1	92.8	5.3	5.0
7.	Ba^{2+}	6.72	21.5	17.1	16.9	14.4	3.1	15.2	2.3	17.8	0.8	13.3	21.5	9.6	93.5	88.7	4.8	3.9
8.	Al^{3+}	4.25	42.3	52.0	55.1	63.5	5.5	42.3	3.9	39.4	2.1	35.2	47.1	47.2	94.0	75.3	11.8	11.5
9.	Pb^{2+}	4.83	42.3	34.3	40.6	39.6	3.7	37.2	3.4	36.7	2.1	37.2	55.7	35.1	89.4	87.1	15.3	13.2
10.	Cu^{2+}	4.86	31.9	25.1	26.8	24.2	4.1	23.7	1.9	25.3	1.1	18.8	44.7	25.9	88.8	76.6	8.4	7.1
11.	Ag$^+$	5.68	40.8	21.1	26.8	26.5	10.1	35.5	9.6	28.7	5.6	23.7	33.6	18.9	77.3	83.9	11.0	10.0
12.	Zn^{2+}	5.59	40.3	22.0	23.7	22.6	4.0	25.8	0.0	26.6	1.9	26.1	34.7	18.3	86.1	75.8	7.3	5.6
13.	Cd^{2+}	6.48	31.3	19.5	20.2	18.2	2.7	18.7	0.4	19.2	0.0	16.5	28.2	12.4	78.6	69.3	5.0	2.7
14.	Hg^{2+}	4.45	1.4	1.3	1.6	1.6	0.5	1.8	0.2	1.6	0.2	1.4	5.0	5.0	1.9	2.1	1.5	2.0
15.	Cr^{3+}	3.19	67.8	42.8	51.0	40.6	3.5	33.2	0.0	44.4	2.4	43.9	59.4	33.2	100.0	83.1	14.2	10.3
16.	Mn^{2+}	5.82	38.7	21.0	22.6	21.4	4.6	23.7	1.1	24.2	1.6	20.7	33.8	14.2	88.1	77.9	7.4	4.6
17.	Fe^{2+}	4.44	26.7	21.1	24.5	20.7	8.2	20.9	1.5	24.2	0.5	20.7	39.2	25.1	85.0	80.1	7.6	5.7
18.	Fe^{3+}	2.41	54.6	67.4	51.7	69.7	9.3	39.1	2.7	37.7	0.9	39.9	65.7	32.8	95.5	100.0	5.7	5.3
19.	Co^{2+}	6.35	24.2	17.4	18.7	16.3	2.6	19.0	0.0	17.9	1.2	14.4	23.9	10.5	88.2	80.8	6.4	4.5
20.	Ni^{2+}	6.07	23.1	17.8	18.2	15.9	2.5	15.9	0.0	17.5	1.4	14.8	25.2	11.2	85.5	72.6	5.7	4.9
21.	Ce^{3+}	5.17	45.8	35.0	36.8	34.4	0.0	31.7	0.0	43.3	0.0	49.7	54.4	30.3	89.2	98.9	6.1	5.3
22.	Th^{4+}	3.46	20.0	69.8	19.0	71.1	0.0	51.9	0.0	41.5	0.0	57.1	25.0	66.2	90.4	100.0	7.7	7.1
23.	UO$_2^{2+}$	2.82	75.0	80.4	77.3	71.7	2.1	42.2	2.4	82.5	1.1	69.2	39.2	77.3	88.4	89.2	7.9	7.1

TABLE IV

Selectivity Factors ($1 \propto \times 10^2$) of the tested cation exchange resins towards metallic cations.

| Cation tested | Symbols of the tested phosphororganic cation exchange resins Wofatit skeleton | | | | | | | | | | | | Symbols of common Cationits (Wofatit trademark) | | | |
	P	P-M	PP	PP-M	DM	DM-M	TM	TM-M	TE	TE-M	IV	IV-M	KPS	KS-10	CP	CA-20
Na^+	2.31	1.26	0.84	0.60	0.19	0.35	0.05	1.26	0.68	0.53	1.79	0.22	225	259	0.19	0.23
K^+	3.26	1.53	1.26	0.69	0.30	1.75	0.04	1.43	0.76	0.69	1.97	0.36	295	345	0.20	0.23
NH_4^+	5.50	4.13	3.21	2.52	2.31	4.69	0.75	4.69	3.52	2.52	4.88	1.15	327	524	1.08	1.00
Mg^{2+}	8.14	3.47	4.08	2.65	0.03	3.47	0.00	4.38	0.00	2.92	6.33	0.69	2798	1540	0.08	0.12
Ca^{2+}	9.75	9.75	9.97	3.47	0.01	5.15	0.02	6.41	0.00	4.44	12.7	1.35	6965	31926	0.16	0.14
Sr^{2+}	8.92	5.02	5.02	3.36	0.06	4.13	0.08	4.31	0.01	2.12	13.8	1.82	10477	16612	0.31	0.28
Ba^{2+}	7.50	4.25	4.13	2.83	0.10	3.21	0.05	4.69	0.01	2.35	7.50	1.13	20692	6161	0.25	0.16
Al^{3+}	53.7	117	150	302	0.34	53.7	0.16	38.4	0.05	11.4	79.3	79.9	24544	929	1.79	1.69
Pb^{2+}	53.7	2.72	46.7	4.29	0.15	35.1	0.12	33.6	0.05	35.1	158.0	29.2	7113	4559	3.26	2.31
Cu^{2+}	21.9	11.2	13.4	10.2	0.18	9.64	0.04	11.5	0.01	5.36	65.3	12.2	6286	1072	0.84	0.58
Ag^+	46.7	7.15	13.4	13.0	1.26	30.3	1.13	16.2	0.35	9.65	25.6	5.43	1159	2715	1.53	1.23
Zn^{2+}	45.6	7.95	9.65	8.52	0.17	12.1	0.00	13.1	1.94	12.5	28.2	5.02	3836	981	0.62	0.35
Cd^{2+}	20.8	5.87	6.41	4.95	0.08	5.29	0.00	5.65	0.00	3.90	15.4	2.00	1349	509	0.28	0.08
Hg^{2+}	0.02	0.02	0.03	0.03	0.00	0.03	0.00	0.03	0.00	0.02	0.28	0.28	0.04	0.05	0.02	0.04
Cr^{3+}	443	56.0	108	46.7	0.13	24.7	0.00	63.8	0.06	61.2	204	24.7	>10^6	2418	2.74	1.32
Mn^{2+}	39.9	7.07	8.52	7.41	0.23	9.65	0.01	102	0.03	6.81	26.7	2.74	5481	1242	0.64	0.23
Fe^{2+}	13.3	7.15	10.5	6.81	0.80	6.98	0.02	102	0.00	6.81	41.5	11.2	3211	1620	3.63	0.36
Fe^{3+}	144	427	114	529	1.05	41.2	0.08	36.6	0.00	44.1	367	23.8	45038	>10^6	0.36	0.31
Co^{2+}	10.2	4.44	5.29	3.79	0.07	5.50	0.00	4.75	0.01	2.83	9.86	1.38	5587	1771	0.47	0.22
Ni^{2+}	9.02	4.69	4.95	3.57	0.06	3.57	0.00	4.50	0.02	3.02	11.3	1.59	3477	702	0.36	0.26
Ce^{3+}	71.4	29.0	33.9	27.5	0.00	21.5	0.00	58.3	0.00	97.6	142	18.9	6822	80×10^4	0.42	0.31
Th^{4+}	6.25	534	5.50	605	0.00	116	0.00	50.3	0.00	177	11.1	384	8867	>10^6	0.69	0.58
UO_2^{2+}	900	1683	116	642	0.04	53.3	0.06	2220	0.01	505	41.5	115	5807	6821	0.73	0.58

The alkali metal ions and NH_4^+ have the smallest affinity for phosphor-containing Cationits, except for gel resins containing ester bonding, for which the affinity factors of univalent cations are high, even higher than for multivalent cations.

The highest affinity toward the investigated phosphonic resins is generally shown by trivalent cations, above all by Fe^{3+} and Cr^{3+}, as well as by bivalent transition cations such as UO_2^{2+}, with the exception of Co^{2+} and Ni^{2+}, which are similar to alkali earth metals (e.g., Ba^{2+}).

The affinity and separation factors are sometimes larger for gel resins than for macroporous and are probably due to differentiated crosslinking. In contrast, the low affinity of gel-like ester-bonding resins is probably caused by their small wettability. In all these cases the sieve effect plays an important role.

Hg^{2+} in $HgCl_2$ behaves in a peculiar way, showing very little affinity to any resin examined, except to aliphatic phosphonic–carboxylic resin (Cationit IV and IV-M). The reason lies perhaps in the complexed structure of the $HgCl_2$ molecule.

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