Studies on α-Pinene–Furfural-Based Cation Exchange Resins. II. Characterization and Equilibrium Studies

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Synopsis

The cation-exchange resins based on α-pinene and furfural were characterized systematically as to their polyfunctionality, rate of exchange and thermal stability. Equilibrium studies for univalent and bivalent ions were also conducted.

EXPERIMENTAL

Characterization

pH Titration Curve. About 0.5-g lots of the resin [−20 + 40 British Standard Sieve (B.S.S.)] in the H^+ form were weighed accurately and transferred to 100-ml glass-stoppered flasks. Different volumes of $1.0N$ solution of sodium chloride and $0.1N$ solution of sodium hydroxide in $1.0N$ solution of sodium chloride were added keeping the total volume to 50 ml in each. The contents were equilibriated at 28° ± 1°C until the solution attained a constant pH (24 hr). Blank solutions were also kept and analyzed. After the predetermined interval of contact aliquots were withdrawn from each flask and titrated for acidity or alkalinity and from this, the capacity was calculated. The equilibrium pH of the supernatant solution from each flask was also measured. A plot of equilibrium pH versus capacity (meq/g dry resin) was made (Fig. 1).

Rate of Exchange. Accurately weighed quantities of the air-dried resins (−20 + 40 B.S.S.) in the H^+ form were transferred to different 100-ml glass-stoppered flasks; 50 ml $0.1N$ solution of sodium hydroxide was added to each flask and shaken occasionally at room temperature (21° ± 1°C). After a predetermined time interval, 10 ml of the solution was withdrawn and titrated for alkalinity. The same procedure described above was followed using $1.0N$ solution of sodium chloride as the contact solution. The acidity liberated was titrated and capacity realized was calculated at various time intervals. The results are presented in Figures 2 and 3.

Thermal Stability. 0.5-g lots of the hydrogen form of the resins (−20 + 40 B.S.S.) and 50 ml distilled water were taken in different glass ampoules. The ampoules were sealed and heated at the desired temperature for 24 hr

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TABLE I
Thermal Stability of Cation Exchange Resins Prepared from α-Pinene and Furfural[a]

Resin	Temperature, °C	Total capacity, meq/g (dry)		Loss in capacity, %
		Before heating	After heating	
PFS	40	3.36	3.28	2.24
	60	3.36	3.19	5.12
	80	3.36	3.02	9.94
	100	3.36	2.98	11.37
PFP	40	3.13	3.08	1.52
	60	3.13	3.05	2.65
	80	3.13	2.98	17.56
	100	3.13	2.46	21.39
PFAP	40	4.59	4.53	1.35
	60	4.59	4.47	2.51
	80	4.59	3.89	15.12
	100	4.59	3.89	15.12

[a] Period of heating: 24 hr.

with occasional shaking. They were then removed and the contents were analyzed. The percentage losses in capacities were determined and presented in Table I.
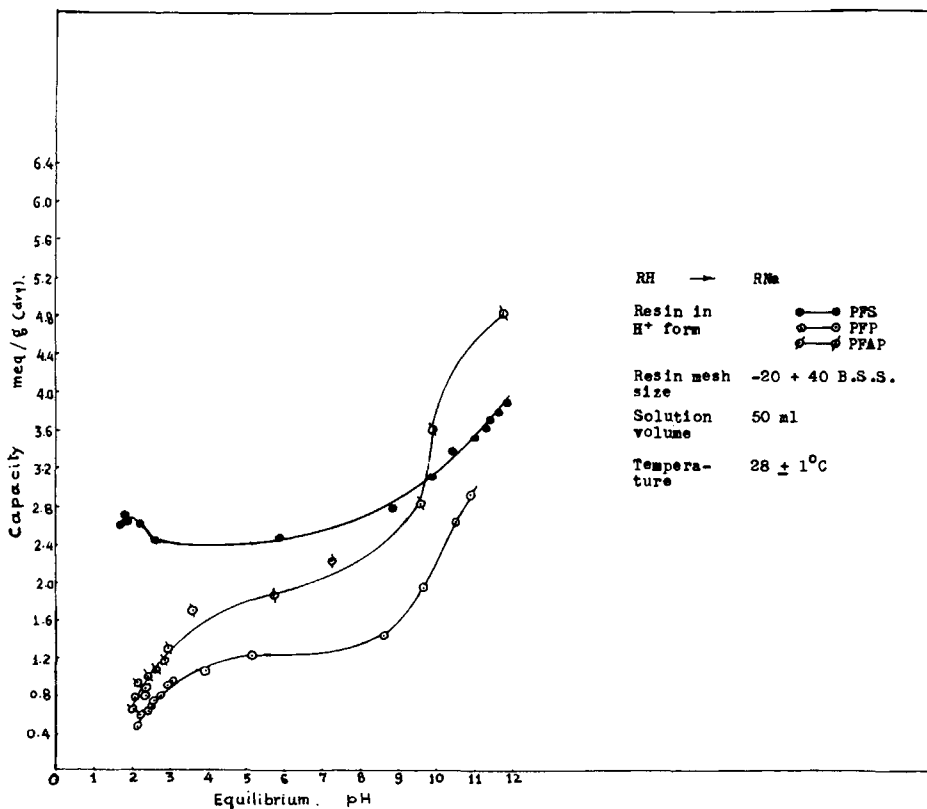

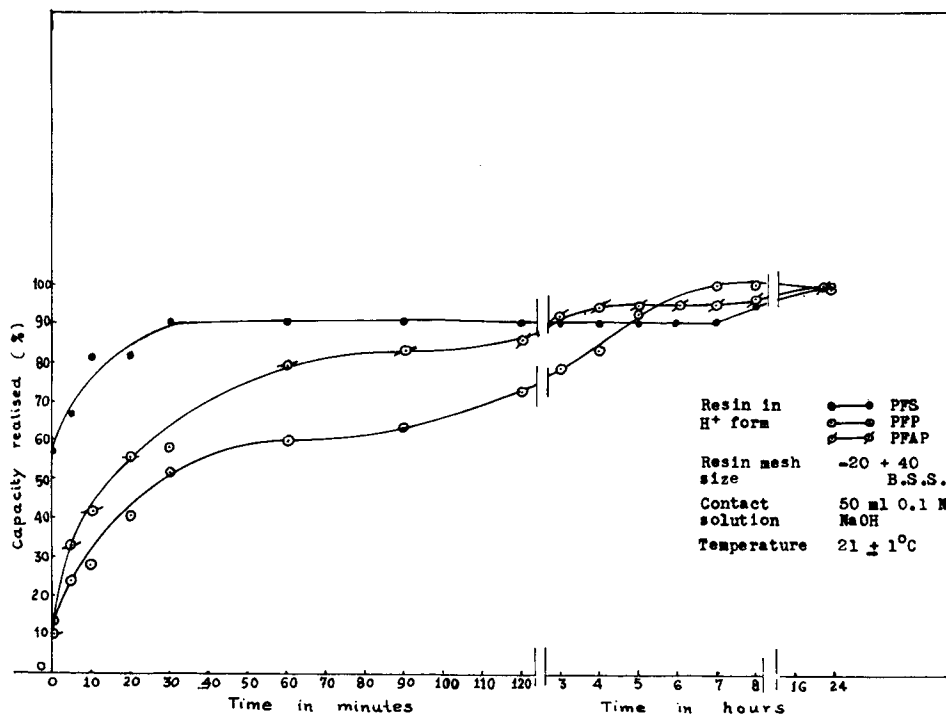Fig. 1. pH Titration curve of resins PFS, PFP, and PFAP.

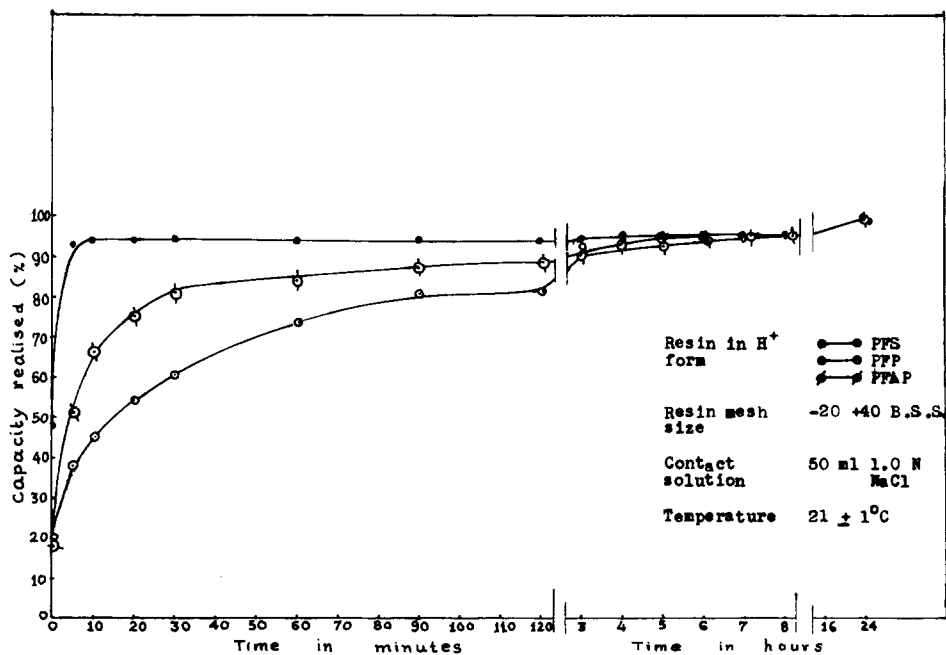Fig. 2. Rate of exchange (H → Na) in sodium hydroxide solution.

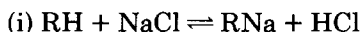Fig. 3. Rate of exchange (H → Na) in sodium chloride solution.

Equilibrium Studies

(i) $RH + NaCl \rightleftharpoons RNa + HCl$

Weighed quantities of the air-dried resins ($-20 + 40$ B.S.S.) in the hydrogen form were transferred to dry 250-ml iodine value flasks. 100 ml of a solution containing a mixture of known amounts of sodium chloride and hydrochloric acid was added to flask 1. Similarly, the other flasks were filled with different proportions of acid and sodium chloride solution, keeping the total volume the same. The flasks were allowed to attain equilibrium by keeping them for 24 hr at 28° ± 1°C. Then, the contents were filtered, washed, and diluted to a known volume. Chloride and acid contents were estimated by adopting a standard procedure.[1]

(ii) $2RH + CaCl_2 \rightleftharpoons R_2Ca + 2HCl$
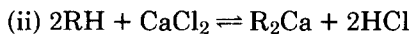
The above exchange was followed by using solutions containing a mixture of calcium chloride and hydrochloric acid by the same procedure described under (i). Calcium was estimated by titrations against EDTA.[1]

(iii) $2RH + FeCl_2 \rightleftharpoons R_2Fe + 2HCl$
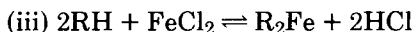
Ferrous chloride and hydrochloric acid mixture was contacted with the hydrogen form of the resin. The ferrous content was estimated by following a standard procedure.[1]

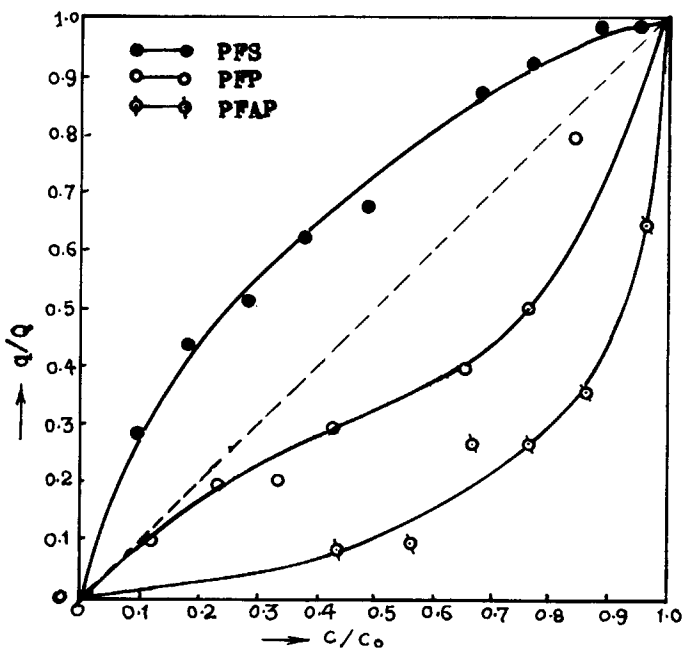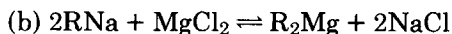The equilibrium data for all the three systems are presented in Figures 4, 5, and 6.

(iv) (a) $2RNa + CaCl_2 \rightleftharpoons R_2Ca + 2NaCl$

(b) $2RNa + MgCl_2 \rightleftharpoons R_2Mg + 2NaCl$

Fig. 4. Equilibrium data for resins in H^+ form with mixture of NaCl and HCl.
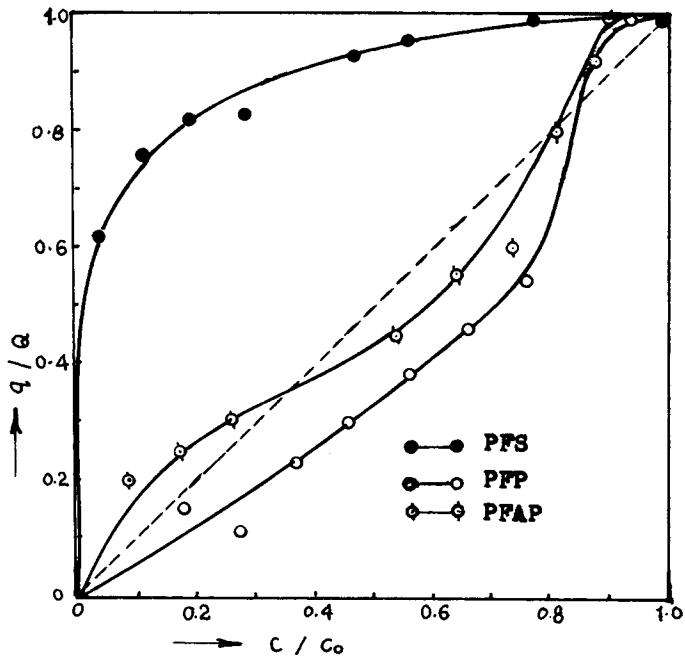
Fig. 5. Equilibrium data for the resins in H$^+$ form with mixture of CaCl$_2$ and HCl.

The sodium forms of the resins were taken, and the above experimental procedure was repeated using a mixture of calcium chloride and sodium chloride for system (a) and a mixture of magnesium chloride and sodium chloride
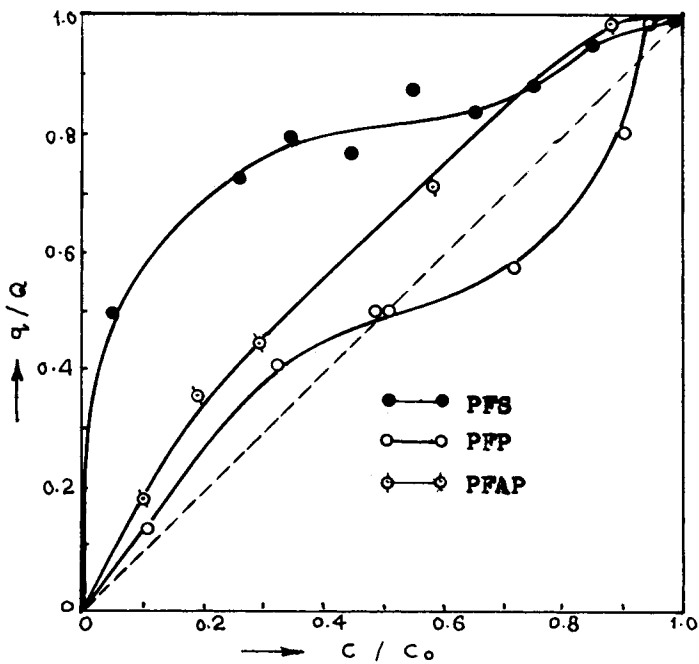

Fig. 6. Equilibrium data for the resins in H$^+$ form with mixture of FeCl$_2$ and HCl.

for system (b), as equilibrating solutions. The Ca/Mg contents in each system were determined by the EDTA titration method.[1]

DISCUSSION

Data on the preparation of polymeric compositions and resins have been reported.[2]

pH Titration Curve

Strong acid and strong base groups are by definition practically completely dissociated under any pH conditon. The exchange capacities of the resins with such groups remain constant and are independent of the pH of the external solution. In contrast, weak acid and weak base groups in contact with the external solution are predominantly undissociated at low and high pH, respectively. Hence, exchange capacities of resins with such groups depend entirely on the pH of the medium. A perusal of the pH titration curves of the three resins (PFS, PFP, and PFAP) shown in Figure 1 indicates their polyfunctionality and the pH dependence of their capacities. Further approximate calculations of the apparent pK_1 and pK_2 values of the phosphorus-containing resins PFP and PFAP were found to be as follows: PFP: $pK_1 = 2.62$, $pK_2 = 8.7$; PFAP: $pK_1 = 2.32$, $pK_2 = 7.62$.

This reveals that the resins are moderately acidic with two dissociable hydrogen ions, the first being stronger than the carboxyl group and the second, weaker. Similar values have been reported in the literature for phosphorus-containing resins based on styrene and furfural.[3]

Rate of Exchange

The rates of exchange of the resins are shown in Figures 2 and 3. It is observed that within 5 min, 90% of the capacity of PFS with sodium hydroxide is realized (Fig. 2). In the case of PFP and PFAP, the rate is slower, while the former takes 7 hr, the latter, 24 hr for complete realization of capacity. PFS resin equilibrated with $1.0N$ sodium chloride solution showed 95% exchange within 5 min, and then it remained constant up to 8 hr (Fig. 3). A preswollen resin sample realized 95% of its capacity within 1 min. This shows that swelling has a marked effect in increasing the rate of exchange of PFS.

Being weak acid resins, PFAP and PFP show very slow rates of exchange with sodium chloride solution. It is interesting to note that the initial rate of exchange with PFAP is higher, and compared to PFP, the overall rate is faster. Hence, this resin can be used with advantage for comparatively fast exchange reactions.

Thermal Stability

The resins prepared by addition polymerization have been reported to be thermally more stable than those prepared by condensation polymerization.[4] The three resins studied here for thermal stability (Table 1) are observed to follow the sequence PFS > PFAP > PFP.

Pore Volume

The pore volumes determined by the method of Benesi et al.[5] were found to be in the ratio of 1.82:1.15:1 for PFS:PFAP:PFP, respectively. It is felt that this variation may be due to the rigorous reaction conditions employed for the chemical processing of the polymer. Sulfonation being a drastic reaction, it rendered PFS the most porous of the three resins, possibly by dissolving the weak links of the basic polymer matrix. Acetylation and phosphorylation have similarly made PFAP more porous than PFP. The sequence PFS > PFAP> PFP is similar to the trend observed in thermal stability.

Equilibrium Studies

A mass action equilibrium constant for uniunivalent exchange reaction between a cation exchange resin and a dissolved electrolyte in terms of activity can be written as follows:

$$K = \frac{(a\mathrm{H^+})(a_{\mathrm{RM}})}{(^a\mathrm{M^+})(a\mathrm{RH})}. \tag{1}$$

Incorporating concentrations in place of activities, the equilibrium constant K' can be derived[6] as follows:

$$K' = \frac{(q/Q)(1 - C/C_0)}{(1 - q/Q)(C/C_0)} \tag{2}$$

where q = concentration in resin phase, Q = concentration of active sites in resin, C = concentration in liquid phase, and C_0 = initial concentration of liquid phase.

In the exchange of ions of different valencies, the equilibrium parameter K'' can be similarly written as

$$K'' = \frac{(q/Q)(1 - C/C_0)^2}{(1 - q/Q)^2(C/C_0)} \tag{3}$$

TABLE II
Equilibrium Constants [equations (2) and (3)][a]

Resin	A[b]	B[b]	C[b]
	K' Values for the System $\mathrm{H^+} \rightleftharpoons \mathrm{Na^+}$(i)		
PFS	2.85	2.71	3.14
PFP	0.48	0.52	0.57
PFAP	0.07	0.11	0.12
	K'' Values for the Systems $\mathrm{H^+} \rightleftharpoons \mathrm{Ca^{2+}}$(ii)		
PFS	85.26	13.05	
PFP	4.70	0.66	
PFAP	1.13	0.35	
	K'' Values for the System $\mathrm{H^+} \rightleftharpoons \mathrm{Fe^{2+}}$(iii)		
PFS	12.66		
PFP	1.00		
PFAP	2.65		

[a] Temperature: 28° ± 1°C.

[b] A: K' or K'', as the case may be, at C/C_0 = 0.3; B: K' or K'', as the case may be, at C/C_0 = 0.5; C: K' or K'', as the case may be, at C/C_0 = 0.7.
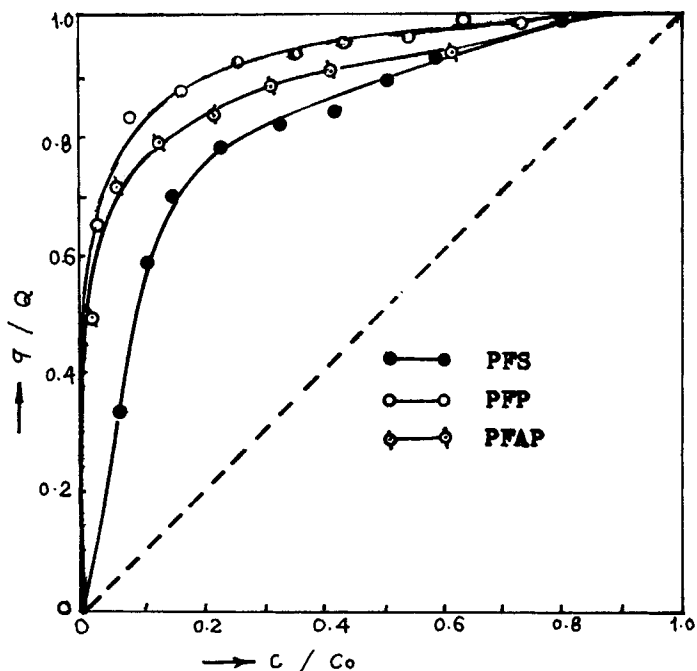
Fig. 7. Equilibrium data for resins in Na$^+$ form with mixture of CaCl$_2$ and NaCl.

where $K'' = K\rho_a Q/C_0$ and ρ_a is the apparent density of the H$^+$ form of the exchanger. Since the literature survey indicated that a systematic study of mono–bivalent equilibrium measurements for phosphorus containing resins have not been carried out, the affinity of PFP and PFAP was determined and results were discussed in the light of the above equations.

A perusal of equilibrium curves (Figs. 4, 5, and 6) indicates that in acid medium the affinity of the resins toward Na$^+$ and Ca^{2+} follows the sequence PFAP < PFP < PFS, while with Fe^{2+}, the sequence changes slightly, showing the trend PFP < PFAP < PFS. This trend is confirmed from the data of the equilibrium constant tabulated in Table II.

Since only the salt-splitting capacity of the resins is utilized in acid medium, the equilibrium characteristics in Na$^+$ form in neutral medium were determined and are presented in Figures 7 and 8. Here, the selectivity trend followed the sequence PFP > PFAP > PFS for Ca^{2+} and PFAP > PFP > PFS for Mg^{2+}.

The integrated values of equilibrium constants K were evaluated by the usual graphic method.[7] For the 2 Na$^+ \rightleftharpoons$ Ca^{2+} system, the equilibrium constants are found to be 1.48, 4.48, and 9.8 for PFS, PFAP, and PFP, respectively. For the 2 Na$^+ \rightleftharpoons$ Mg^{2+} system, the values are 1.15, 2.66, and 3.27 for PFS, PFP, and PFAP, respectively. These values are in accordance with the pattern of equilibrium curves and also the selectivity sequence indicated above. It is further clearly seen that both PFP and PFAP prefer Ca^{2+} to Mg^{2+}. Hence, it is felt that these resins in sodium form can be used with advantage for the separations of Ca^{2+} and Mg^{2+} in a mixture. In acid medium (as seen from the Figs. 4, 5, and 6), the phosphorus-containing resins show a
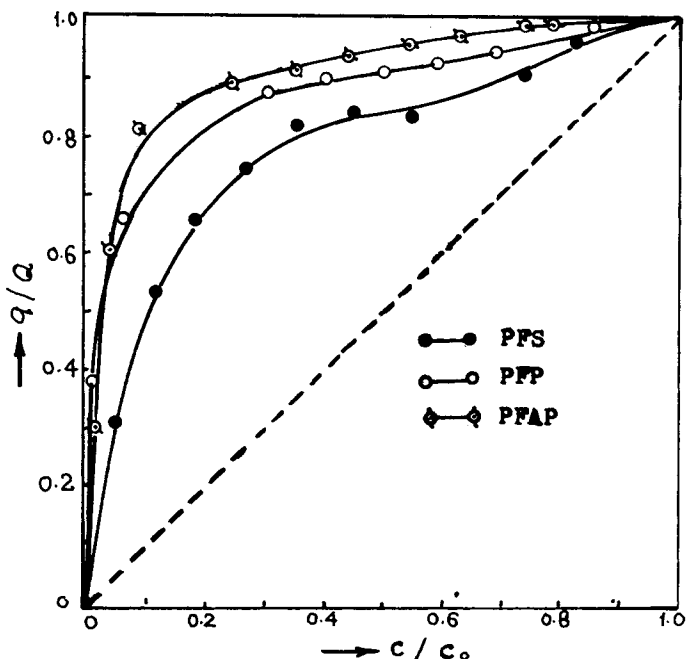
Fig. 8. Equilibrium data for resins in Na^+ form with mixture of $MgCl_2$ and $NaCl$.

higher affinity for Fe^{2+} than Na^+ and Ca^{2+}. This property can be used with advantage for the removal of ferrous iron impurities.

CONCLUSIONS

The results indicate that the performance of resins PFS, PFP, and PFAP shows a reasonable degree of agreement with the characteristics (reported in the literature) of commercially available resins. Equilibrium data for phosphorus-containing resins are presented. Results tend to suggest that these resins can be used for the separation of alkaline earth metals from neutral solutions and iron from acidic solutions.

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