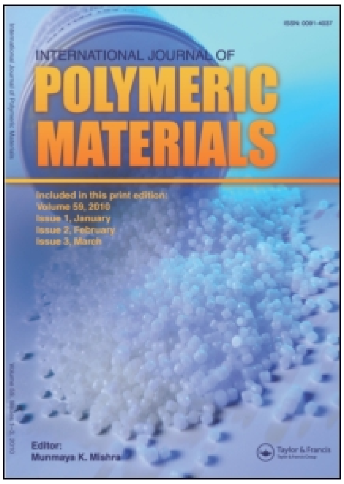

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Lewis Acid-Base Properties of a Gel-type Cation Exchange Resin

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Lewis Acid-Base Properties of a Gel-type Cation Exchange Resin

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Gel-type cation exchange resins like SK-1B are based on DVB-crosslinked polystyrene with sulfonic acid functional groups. The behavior of some conjugate acid-base pairs was studied and explained in terms of Lewis and Pearson Acid-Base Theories. The application of these resins as a no contaminant medium for pH regulation has special interest in biological systems and is not limited to water conditioning like deionization or dealkalization.

Keywords: Cation exchange; gel type resin; acid hardness; Pearson rules

1. INTRODUCTION

The crosslinked gel type resins are solid state acids with an apparent porosity no greater than 40 Angstrom units and the ions to be exchanged must diffuse through the gel structure to the exchange sites. The size of the ion that can migrate is limited by the inter-molecular distances. There are little information about the resin performance outside standard conditions related with familiar ions, normal range of concentrations or purity of regenerant, and it is necessary simulate some process in the laboratory.

2. EXPERIMENTAL PROCEDURE

2.1. Sample Preparation

Because of the ionic form of an ion-exchange material affects both its equivalent mass and its equilibrium water content, the cation resin was pretreatment to obtain a representative sample in accordance with ASTM Practices [1]. The selected gel type resin have very high whole-bead count, low uniformity coefficient, good resistance to mechanical attrition, and excellent chemical and physical stability. The resin is recommended for the removal of all cations from water and non-aqueous systems as well as water softening. The typical characteristics of the resin are shown in Table I.

The samples were in contact with the cation solutions with different residential time to select the minimum necessary to obtain repetitive data.

2.2. Measurements

The pH was measured with an Altronix digital instrument and the cation concentrations were verify using a Perkin Elmer Atomic Absorption Spectrometer. The resin structure alterations because of the cation retention were studied with a Shimadzu Fourier Transform Infrared Spectrophotometer-8100 with Attenuad Total Reflection and Diffuse Reflectance Attachment.

RESULTS

3.1. Contact time

The effect of the contact time on the pH measurements of selected five stirred systems is shown in Table II. It was adopted an average contact time of one hour to obtain repetitive results.

TABLE I Typical characteristics of selected cation exchange resin

Type	*SK-1B*
Polymer Structure	Gel
Functional Groups	Sulfonic
Ionic Form Shipped	Na/H
Total Capacity (meq/ml)	1.9
Water Retention (%)	45–50
Effective Size (mm)	0.53
Uniformity Coefficient	1.5
Reversible Swelling (%) (Na to H form)	5
Temp. Stability H form (°C)	120
Specific Gravity	1.28

TABLE II Contact time effects on pH measurements

System	*I*	*II*	*III*	*IV*	*V*
Resin, g	5.5213	5.5497	5.5535	5.4939	5.5143
Water, ml	25	25	25	25	25
Acetic acid 0.0419M, ml	10	50	65	68	95
Temperature °C	29.0	29.0	28.5	30.5	29.5
Initial pH	10.77	10.15	5.20	4.03	3.33
pH, 1 hr	10.80	10.18	5.22	4.05	3.35
pH, 14 hs	12.77	10.57	5.98	4.58	3.43
pH, 23 hs	12.35	10.67	5.80	4.73	3.49

3.2. Resin Pretreatment Effect on pH Measurements

The ionic form of an ion-exchange material affects both its equivalent mass and its equilibrium water content. To provide a uniform basis for comparison, a cation exchange material should be converted to the sodium form before analysis [1].

The pretreatment effect on pH measurements, in the case of neutralization of water, pretreatment resin and non-pretreatment resin with NaOH, are shown in Table III.

The behavior of the pretreatment resin is more close to water than to non-pretreatment resin.

3.3. Characterization of Metals Bonded to Resin

The relation between the adsorption capacity for metal ions and the Lewis acid-base conduct of resin studied using Cu(II), Ni(II) and Zn(II) salts which were in contact with resin in similar conditions of concentration and residential time.

The presence of metals bonded to resin was characterized by Fourier Transform Infrared Spectroscopy. The observed frequencies and band assignments are shown in Table IV. Some vibrational data corresponding to functional group and pure resin are included to allow comparisons.

4. DISCUSSION

The principal contributions to Lewis acid and base strengths are the dependence of the strength of the acid-base bond, the rearrangement of the substituents, the steric interaction between substituents and the

TABLE III Pretreatment effect on pH measurements

ml NaoH added (0.009142 N)	*pH sample 1 (30 ml water + NaoH)*	*pH sample 2 (30 ml water + 5.1439 g resin without pre-treatment + NaOH)*	*pH sample 3 (30 ml water + 5.1439 g resin with pre-treatment + NaOH)*
0	6.00	4.00	7.40
1	10.15	4.04	7.78
2	11.20	4.10	9.22
3	11.43	4.18	10.26
4	11.55	4.25	10.66
5	11.69	4.34	10.95
6	11.77	4.42	11.17
7	11.87	4.54	11.30
8	11.95	4.68	11.43
9	11.98	4.88	11.53
10	12.03	5.20	11.63
11	12.07	5.62	11.69
12	12.12	6.34	11.73
13	12.15	6.99	11.77
14	12.19	7.74	11.80
15	12.21	8.36	11.85
16	12.24	8.97	11.88
17	12.26	9.58	11.91
18	12.28	10.09	11.94
19	12.29	10.47	11.95

TABLE IV Vibrational frequencies of SO_3 group

Compound	$\nu_3(E)$	$\nu_1(A_1)$	$\nu_4(E)$	$\nu_2(A_1)$
SO_3^{2-}, free(2)	933	967	469	620
Na_2SO_3, ref(3)	983R	974R		
Na_2SO_3, ref(4)			633	498
NH_4CuSO_3,(4)	963		669	497
$TI_2[Cu(SO_3)_2]$,(4)	989–902	862	673–602	506–460
SO_3 in SK1B without pretreatment	1182.5	1128–1040	677–621	583
SO_3 in SK1B with pretreatment	1184.4	1128–1040	677–623	584
SO_3 in CuSK1B	1182.5	1128–1040	675–623	584
SO_3 in NiSK1B	1186.4	1128–1040	677–623	581
SO_3 in ZnSK1B	1192.5	1128–1040	677–621	583

solvatation [5]. Electronic considerations were into account by Pearson [6] to define hard and soft acids and bases and he proposed the simple rule that hard acids prefer to bind hard bases and soft acids prefer soft bases, therefore solvents can be classified as hard or soft by virtue of their basic properties as well, and this will influence their interactions with cations.

TABLE V The classification of Lewis acids and bases

	Hard	*Borderline*	*Soft*
Acids	$\mathrm{H^+, Li^+, Na^+, K^+, Be^{2+}, Mg^{2+}, Ca^{2+}, Cr^{3+}, SO_3, BF_3}$	$\mathrm{Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Pb^{2+}, SO_2, BBr_3}$	$\mathrm{Cu^+, Ag^+, Au^+, TI^+, Hg^+, Pd^{2+}, Cd^{2+}, Pt^{2+}, Hg^{2+}, BH_3}$
Bases	$\mathrm{F^-, OH^-, H_2O, NH_3, OH^-}$	$\mathrm{Br^-, N_2,}$ $\mathrm{SC}N^-$	$\mathrm{H^-, R^-, CN^-, CO, I^-,}$ SCN^-, $\mathrm{R_2S}$

When the substances are analyzed with the mentioned rules in mind, the classification included in Table V is possible.

Klopman's description[6] suggests that the soft-soft interactions are essentially covalent bonding between an empty and a filled orbital of comparable energy, where as the hard-hard interactions are essentially determined by the Madelung potential. Therefore it will be expected that soft-soft interactions between cations and resin cause a greater effect on the vibrational frequencies of the main group and the soft-hard interactions cause a smaller cation retention by resin.

The frequency data of Table IV confirm that the resin can be defined as a Lewis borderline base. The interaction between borderline acids like Cu(II), Ni(II) or Zn(II) and resin caused a little effect on the characteristic frequencies of RSO_3 group.

The atomic polarizabilities: Cu(II): 1.6, Ni(II): 1.0, Zn(II): 0.8 and the relation between the low polarizability and the hardness were reported by Jorgensen[8] and they confirm the obtained results.

5. CONCLUSIONS

The Lewis viewpoint systematizes many reactions in solids and molten salt solutions.

The main conclusion of this work is that Lewis and Pearson correlation between the type of bond and the hardness can be evaluated using vibrational frequencies data and allow us to select resins and to explain the cation retention reported by different authors [9], [10].

The application of these resins as a no contaminant medium for pH regulation has special interest in biological systems and is not limited to classical water conditioning, chromatographic applications [11] or desiccants for drying organic liquids [12].

6. RECOGNITION

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