Table IV. Comparison of the Stockmayer Force Constants for Dichloromethane

potential model	N	μ/D	σ/Å	(ϵ/k)/K	b_0/ (cm^3 mol^{-1})	t^*	temp. range/ K	ref
(12-6-3)	7	1.631	2.764	672.6	26.63	0.48	319.4–382.6	*5*
(12-6-3)	5	1.631	3.150	716.6	39.42	0.304	323.16–423.16	*5*
(12-6-3)	10	1.631	2.648	715.29	23.423	0.513	349.53–510	this work
(18-6-3)	7	1.631	3.80	642.62			323.16–423.16	*6*

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Glossary

b_0	second virial coefficient for a rigid sphere of diameter σ, cm^3 mol^{-1}
B	second virial coefficient in eq 1, cm^3 mol^{-1}
B'	second virial coefficient in eq 2, atm^{-1}
C	third virial coefficient in eq 1, cm^6 mol^{-2}
C'	third virial coefficient in eq 2, atm^{-2}
G	Gibbs energy, cal mol^{-1}
H	enthalpy, cal mol^{-1}
k	Boltzmann constant, J K^{-1}
N	number of experimental points
N_A	Avogadro number, mol^{-1}
P	pressure, atm
R	gas constant, cm^3 atm K^{-1} mol^{-1}
S	entropy, cal mol^{-1} K^{-1}
t^*	parameter in the Stockmayer potential
T	temperature, K
T_c	critical temperature, K
U	internal energy, cal mol^{-1}
V	molar volume, cm^3 mol^{-1}
Z	compression factor
ϵ	parameter in the Stockmayer potential, J
μ	dipole moment, D
φ	fugacity coefficient
σ	parameter in the Stockmayer potential, Å

Superscript

$^\circ$	property of the substance in its standard state

Registry No. Dichloromethane, 75-09-2.

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Ion-Exchange Equilibria: Study of the Na^+/Mn^{2+}, Na^+/Ni^{2+}, and Na^+/Cu^{2+} Exchanges on Several Lewatit Cation Exchangers

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Experimental equilibrium data of several Lewatit + Na^+ + B^{2+} ion-exchange binary systems are given under various conditions: (I) with three exchangers of different cross-linking degree (S-100, S-115, and SP-120); (II) with two sizes of particles (SP-120: D1 = 0.74 mm, and D2 = 0.96 mm); (III) at three total ionic concentration levels of the solution phase (1, 0.1, and 0.01 N); and (IV) with three different counterions (B^{2+} = Mn^{2+}, Ni^{2+}, and Cu^{2+}). By means of a previously developed method, where the Wilson equation is employed to evaluate the activity coefficients in the resin phase, the equilibrium constants are determined. The influence of the above variables is studied by using these equilibrium constants.

Introduction

The variables that can influence the equilibrium in a ion-exchange system can be classified in three groups: (1) those that depend on the exchanger such as the type of exchanger, cross-linking degree, and size of the particle; (2) variables that depend on the solution phase such as the kind of solvent, the set of ions involved, both interchangeable and uninterchangeable, and the total ionic concentration; and (3) those that depend on the working conditions such as pressure or temperature.

In order to carry out a systematic study of ion-exchange equilibrium it seems necessary to establish previously a parameter or a set of parameters that characterize in the best possible way such equilibrium. In a previous paper (*1*), the

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most frequently utilized parameters are revised and a method based on the direct adjustment to the equilibrium isotherm is proposed.

The set of systems here studied can be expressed by

$$\overline{2Na^+} + B^{2+} \rightleftarrows 2Na^+ + \overline{B^{2+}} \qquad (1)$$

where the exchanger phase is designated by a bar.

For these systems the equilibrium constant will be then given by

$$k_{B/Na} = \frac{(\bar{x}_B\bar{\gamma}_B)(c_{Na}\gamma_{Na})^2}{(\bar{x}_{Na}\bar{\gamma}_{Na})^2(c_B\gamma_B)} \qquad (2)$$

where $\bar{x}$ is the equivalent fraction of ion in the resin phase, γ and $\bar{\gamma}$ are the activity coefficients of the ions in the solution and resin phase, respectively, and c is the concentration in the solution phase (mol dm^{-3}).

If the activity coefficients of resin phase are calculated from the well-known Wilson equation, the adjusting parameters used in the previously mentioned method are the equilibrium constant ($k_{B/Na}$) and the interaction coefficients of wilson equation ($\Lambda_{Na/B}$ and $\Lambda_{B/Na}$).

In order to systematize and reduce the experimental work in the study of the influence of the previously mentioned variables it is necessary to keep some of them invariant. In the case studied here the type of exchanger, the solvent, co-ion, pressure, and temperature were kept invariant.

Exchangers with the same functional structure but with three different cross-linking degrees were chosen and in one of them two fractions of different size were taken.

As a partial and provisional goal of a more ambitious research, the study of several ionic systems in the aqueous phase has been carried out. These systems have the Cl^- ion as a common co-ion, and as counterions the pairs Na^+/Mn^{2+}, Na^+/Ni^{2+} and Na^+/Cu^{2+} at 1, 0.1, and 0.01 N total ionic concentrations.

It has been deliberately intended that the systems studied here are not close to ideality, and because of this, on the one hand, divalent cations are used and on the other, the equilibria at very different total ionic concentrations are studied.

Experimental Section

The ion exchangers used were Lewatit synthetic resins, cation exchangers of sulfonated polystyrene. These resins are cross-linked with 15, 10, and 8.5% of divinylbenzene, which have the commercial names S-115, SP-120, and S-100, respectively. These strongly acidic cation exchangers have high total capacity, great chemical stability, and high mechanical resistance and are stable up to a temperature of 120 °C. The properties of these resins (specially the Lewatit S-115) make them useful to eliminate the cations from the waste waters of electrochemical industry due to their high capacity and great selectivity and also because of their great resistance to oxidizing agents.

All the exchangers used were classified by sieving and later elutriation in order to make the samples utilized homogeneous in size and shape. In their sodic form, the diameter of each of the selected fractions is determined with the aid of microscopy (for the SP-120, two different-sized fractions). The obtained values with their standard deviations within parentheses are shown in Table I.

The humidity was determined in triplicate, using exactly weighed samples between 3 and 4 g of Na^+ ion form drained resin, drying at 110 °C until a constant weight was obtained. The well-centered values for each resin can be seen in Table I.

Table I. Physicochemical Characteristics of Ion Exchangers

	LW SP-120			
	D1	D2	LW S-100	LW S-115
D_p, mm	0.74 (0.05)	0.96 (0.09)	0.76 (0.06)	0.71 (0.05)
moisture, %	53.86	54.14	37.06	28.18
av sat. cap.[a]				
Mn^{2+}	4.35 (0.07)	4.42 (0.04)	4.65 (0.03)	4.11 (0.04)
Ni^{2+}	4.33 (0.04)	4.42 (0.03)	4.58 (0.02)	4.20 (0.10)
Cu^{2+}	4.50 (0.12)	4.59 (0.08)	4.74 (0.03)	4.26 (0.08)

[a] Average saturation capacity in mequiv B^{2+}/dry g of Na^+ ion form.

Table II. Experimental Equilibrium Data Set: LW + Na^+ + Mn^{2+} Systems

	total ionic concentration, N					
	1		0.1		0.01	
exchanger	$x_{Mn^{2+}}$	$\bar{x}_{Mn^{2+}}$	$x_{Mn^{2+}}$	$\bar{x}_{Mn^{2+}}$	$x_{Mn^{2+}}$	$\bar{x}_{Mn^{2+}}$
SP-120 (D1)	0.061	0.137	0.020	0.151	0.014	0.301
	0.105	0.225	0.069	0.413	0.069	0.648
	0.190	0.325	0.183	0.549	0.116	0.772
	0.276	0.456	0.315	0.743	0.189	0.825
	0.415	0.592	0.427	0.788	0.281	0.868
	0.475	0.624	0.516	0.851	0.374	0.880
	0.587	0.727	0.589	0.870	0.501	0.921
	0.712	0.830	0.696	0.930	0.612	0.930
	0.793	0.862	0.750	0.962	0.705	0.973
	0.906	0.955				
SP-120 (D2)	0.051	0.091	0.015	0.125	0.012	0.202
	0.122	0.225	0.059	0.336	0.050	0.548
	0.236	0.382	0.112	0.500	0.135	0.776
	0.345	0.516	0.291	0.691	0.224	0.848
	0.386	0.571	0.495	0.822	0.414	0.901
	0.489	0.639	0.624	0.900	0.487	0.912
	0.621	0.746	0.701	0.925	0.599	0.940
	0.658	0.777	0.765	0.941	0.694	0.956
	0.798	0.891			0.801	0.971
	0.871	0.942				
S-100	0.035	0.065	0.025	0.165	0.025	0.355
	0.095	0.174	0.086	0.395	0.046	0.512
	0.206	0.345	0.139	0.551	0.093	0.711
	0.285	0.416	0.191	0.614	0.166	0.790
	0.407	0.564	0.295	0.684	0.316	0.873
	0.525	0.656	0.355	0.742	0.391	0.893
	0.611	0.732	0.485	0.811	0.495	0.926
	0.675	0.788	0.614	0.887	0.645	0.948
	0.809	0.898	0.727	0.918	0.726	0.964
	0.863	0.932				
S-115	0.045	0.105	0.033	0.198	0.015	0.296
	0.096	0.193	0.075	0.413	0.056	0.586
	0.193	0.345	0.118	0.544	0.110	0.765
	0.312	0.484	0.267	0.683	0.182	0.821
	0.405	0.584	0.388	0.764	0.353	0.852
	0.514	0.665	0.512	0.850	0.518	0.933
	0.598	0.746	0.605	0.877	0.620	0.938
	0.701	0.825	0.664	0.908	0.715	0.957
	0.792	0.901	0.779	0.951	0.787	0.975
	0.877	0.946				

Resin saturation capacities and equilibrium data were determined by using samples of about 1 g, exactly weighed.

The several solutions used were prepared from the chloride of each cation, using reactants of p.a. Merck analytical grade and deionized water as solvent.

Saturation Capacities. Saturation capacity of the exchangers for each cation B^{2+} was determined by utilizing a column dynamic method: The exchanger is placed in a small column through which 100 cm^3 of a 0.5 N solution of cation B^{2+} at a 0.5 cm^3 min^{-1} flow rate are passed. After it is washed with deionized water the resin is regenerated to the sodic form by passing 100 cm^3 of 1 N NaCl solution through the column at the same flow rate as above. First the effluent is collected in a filtering flask together with the waters of the later washings, and then it is poured into a volumetric flask and the amount of

Table III. Experimental Equilibrium Data Set: LW + Na^+ + Ni^{2+} Systems

	total ionic concentration, N					
	1		0.1		0.01	
exchanger	$x_{Ni^{2+}}$	$\bar{x}_{Ni^{2+}}$	$x_{Ni^{2+}}$	$\bar{x}_{Ni^{2+}}$	$x_{Ni^{2+}}$	$\bar{x}_{Ni^{2+}}$
SP-120 (D1)	0.040	0.105	0.024	0.192	0.017	0.350
	0.085	0.226	0.082	0.453	0.035	0.585
	0.215	0.437	0.130	0.546	0.118	0.771
	0.309	0.525	0.265	0.739	0.234	0.822
	0.416	0.644	0.401	0.817	0.346	0.885
	0.531	0.725	0.502	0.857	0.411	0.916
	0.602	0.791	0.585	0.888	0.508	0.925
	0.697	0.845	0.695	0.921	0.595	0.950
	0.786	0.920	0.772	0.945	0.722	0.968
	0.885	0.946				
SP-120 (D2)	0.045	0.101	0.036	0.224	0.030	0.505
	0.095	0.220	0.082	0.435	0.094	0.753
	0.196	0.358	0.137	0.571	0.161	0.810
	0.281	0.488	0.194	0.672	0.230	0.848
	0.392	0.600	0.301	0.744	0.318	0.891
	0.468	0.706	0.422	0.825	0.425	0.910
	0.574	0.754	0.510	0.896	0.489	0.928
	0.741	0.872	0.626	0.904	0.608	0.966
	0.800	0.924	0.715	0.930	0.690	0.967
	0.895	0.949				
S-100	0.035	0.090	0.030	0.186	0.020	0.253
	0.101	0.242	0.060	0.381	0.055	0.670
	0.222	0.426	0.119	0.555	0.135	0.766
	0.296	0.500	0.248	0.696	0.195	0.825
	0.402	0.605	0.362	0.774	0.405	0.912
	0.505	0.726	0.471	0.843	0.486	0.937
	0.588	0.782	0.602	0.886	0.585	0.944
	0.666	0.827	0.688	0.925	0.705	0.965
	0.775	0.895	0.752	0.948	0.792	0.978
	0.901	0.945				
S-115	0.049	0.132	0.036	0.249	0.019	0.423
	0.098	0.276	0.092	0.524	0.031	0.621
	0.191	0.396	0.144	0.584	0.070	0.704
	0.315	0.537	0.283	0.758	0.145	0.785
	0.392	0.631	0.388	0.824	0.214	0.852
	0.542	0.784	0.488	0.874	0.346	0.905
	0.605	0.801	0.570	0.889	0.525	0.942
	0.709	0.859	0.668	0.905	0.639	0.974
	0.795	0.910	0.701	0.935	0.768	0.984
	0.865	0.935				

Table IV. Experimental Equilibrium Data Set: LW + Na^+ + Cu^{2+} Systems

	total ionic concentration, N					
	1		0.1		0.01	
exchanger	$x_{Cu^{2+}}$	$\bar{x}_{Cu^{2+}}$	$x_{Cu^{2+}}$	$\bar{x}_{Cu^{2+}}$	$x_{Cu^{2+}}$	$\bar{x}_{Cu^{2+}}$
SP-120 (D1)	0.031	0.110	0.035	0.237	0.027	0.503
	0.086	0.175	0.075	0.401	0.081	0.702
	0.180	0.314	0.118	0.522	0.148	0.808
	0.289	0.432	0.163	0.618	0.234	0.855
	0.423	0.605	0.264	0.700	0.312	0.910
	0.496	0.684	0.416	0.808	0.397	0.915
	0.583	0.755	0.490	0.844	0.582	0.944
	0.688	0.828	0.625	0.914	0.695	0.973
	0.802	0.900	0.717	0.930	0.775	0.974
	0.871	0.957	0.780	0.961		
SP-120 (D2)	0.041	0.100	0.030	0.193	0.044	0.511
	0.089	0.174	0.084	0.411	0.092	0.736
	0.185	0.323	0.146	0.525	0.127	0.820
	0.275	0.402	0.193	0.624	0.188	0.829
	0.391	0.567	0.301	0.726	0.276	0.872
	0.510	0.691	0.427	0.807	0.416	0.885
	0.646	0.795	0.506	0.870	0.502	0.926
	0.693	0.844	0.573	0.869	0.609	0.943
	0.788	0.895	0.702	0.920	0.718	0.965
	0.843	0.922				
S-100	0.061	0.133	0.038	0.248	0.019	0.250
	0.098	0.175	0.090	0.421	0.045	0.566
	0.213	0.351	0.136	0.535	0.163	0.817
	0.294	0.466	0.272	0.712	0.291	0.875
	0.365	0.544	0.387	0.795	0.382	0.901
	0.479	0.675	0.494	0.832	0.506	0.915
	0.595	0.755	0.615	0.880	0.603	0.948
	0.701	0.836	0.695	0.913	0.691	0.976
	0.807	0.885	0.751	0.946	0.748	0.972
	0.887	0.937				
S-115	0.049	0.133	0.031	0.187	0.022	0.398
	0.094	0.200	0.055	0.399	0.051	0.675
	0.196	0.333	0.105	0.502	0.125	0.801
	0.315	0.488	0.140	0.576	0.230	0.846
	0.392	0.605	0.211	0.645	0.363	0.907
	0.497	0.695	0.297	0.751	0.446	0.921
	0.615	0.775	0.445	0.814	0.531	0.946
	0.714	0.855	0.518	0.861	0.656	0.964
	0.802	0.875	0.661	0.899	0.801	0.978
	0.849	0.937	0.793	0.951		

retained B^{2+} is determined. Five determinations are made for each cation and each kind of resin. Once the resin weight and the amount of retained ion in the exchanger are known, its total or saturation capacity is determined. The average saturation capacity values of the determinations for each cation and each kind of resin, given in mequiv B^{2+} per dry gram of Na^+ ion form resin, together with their standard deviations in parentheses are shown in Table I.

Equilibrium Data. The equilibrium data of Lewatit + Na^+ + B^{2+} (B^{2+} = Mn^{2+}, Ni^{2+}, or Cu^{2+}) binary systems were determined.

For each system the total ionic concentration was kept at 1, 0.1, and 0.01 N and the equivalent fraction of each cation over all the range of concentrations was varied.

For the experimental determination of the equilibrium compositions in the solution phase and resin phase, the discontinuous method proposed by Gregor and Bregman (*2*) and later developed by others was employed. In this method the exchanger is kept in contact with the solution that contains the ions until equilibrium is reached and then the composition of both phases is determined.

Drained resin samples are put together in a flask containing the solution of the known composition for 4 days, and shaken periodically. The two phases are later separated and analyzed; the resin phase is obtained by extracting the cation and analyzing as was done for the capacity determination.

In order to analyze the B^{2+} cations, complexometric and atomic absorption spectrophotometry methods were employed, whereas Na^+ ion was obtained by material balance.

The experiments were carried out at room temperature (18 ± 2 °C) and atmospheric pressure. The obtained results are shown in Tables II–IV.

Data Treatment, Results and Discussion

Saturation Capacities. Exchanger saturation capacity is a parameter usually considered as a characteristic constant and independent from the involved ions. The dispersion of the obtained values for each resin (Table I) is small in all cases, which seems to be in agreement with the idea above. Nevertheless, the fact that Cu^{2+} ion always presents values slightly higher leads us to think that the capacity is not a parameter strictly constant but that its value slightly depends on the counterion. This is in agreement with previous results (*3*) and it is necessary to keep it in mind as a possible source of error when the equilibrium data are determined.

It was observed that the SP-120 resin has a slightly smaller capacity when the particle size decreases. Likewise, it has been found that, for each cation, the saturation capacity increases when cross-linking decreases.

Equilibrium Constant. To evaluate the equilibrium constant indicated in eq 2 it is necessary to know the activity coefficients for both phases.

The individual activity coefficients of the solution phase for the exchangeable ions are evaluated from both the activity coefficients of the salts in the literature (*4*, *5*) and from ion Cl^-

Table V. Equilibrium Constant, Parameters of Wilson Equation, and Average Deviations of Adjusted Data

		$k_{B/Na}$			$\Lambda_{Na/B}$			$\Lambda_{B/Na}$			av deviation[b]		
ion B	exchanger	1 N[a]	0.1 N[a]	0.01 N[a]	1 N	0.1 N	0.01 N	1 N	0.1 N	0.01 N	1 N	0.1 N	0.01 N
Mn^{2+}	SP-120 D1	11.539	4.206	0.797	0.481	0.122	1.580	1.625	2.317	0.122	0.009	0.018	0.012
	SP-120 D2	10.115	3.777	0.722	1.572	1.216	0.973	0.413	0.651	0.459	0.009	0.011	0.011
	S-100	10.296	3.206	0.622	0.228	1.798	1.114	2.012	0.249	0.302	0.007	0.012	0.007
	S-115	11.937	2.810	0.814	0.249	1.977	1.330	1.941	0.011	0.302	0.005	0.011	0.015
Ni^{2+}	SP-120 D1	14.478	4.314	0.772	0.284	1.115	1.554	1.883	0.600	0.052	0.008	0.005	0.013
	SP-120 D2	12.241	3.672	0.722	0.535	1.258	1.423	1.254	0.344	0.051	0.011	0.008	0.007
	S-100	13.123	2.966	0.531	0.424	1.861	1.053	1.538	0.004	0.044	0.009	0.008	0.017
	S-115	15.113	3.216	0.881	0.411	1.719	1.550	1.561	0.010	0.010	0.011	0.010	0.016
Cu^{2+}	SP-120 D1	15.411	3.835	1.415	0.259	1.296	0.417	1.734	0.435	1.470	0.012	0.008	0.007
	SP-120 D2	14.493	3.561	0.417	0.323	0.789	0.961	1.579	0.884	0.024	0.010	0.009	0.019
	S-100	14.018	3.654	0.479	0.873	1.063	1.215	0.834	0.660	0.006	0.008	0.008	0.008
	S-115	15.843	2.186	0.672	0.552	1.104	1.067	1.265	0.426	0.045	0.014	0.019	0.020

[a] Total ionic concentration. [b] Average deviation = $\sum_{i=1}^{n}|\bar{x}_B - \bar{x}_B^*|_i/n$.

Table VI. Adjusted Equilibrium Data: LW S-100 + Na^+ + Mn^{2+} Systems

total ionic concentration, N					
1		0.1		0.01	
$\bar{x}_{Mn^{2+}}$	$\bar{x}_{Mn^{2+}}^*$	$\bar{x}_{Mn^{2+}}$	$\bar{x}_{Mn^{2+}}^*$	$\bar{x}_{Mn^{2+}}$	$\bar{x}_{Mn^{2+}}^*$
0.065	0.076	0.165	0.163	0.355	0.352
0.174	0.180	0.395	0.415	0.512	0.526
0.345	0.333	0.551	0.527	0.711	0.689
0.416	0.425	0.614	0.600	0.790	0.790
0.564	0.550	0.684	0.703	0.873	0.877
0.656	0.660	0.742	0.746	0.893	0.903
0.732	0.737	0.811	0.819	0.926	0.929
0.788	0.791	0.887	0.876	0.948	0.956
0.898	0.894	0.918	0.917	0.964	0.968
0.932	0.930				

individual coefficients obtained by means of the generalized Debye–Hückel equation with the parameters given by Truesdall and Jones (*6*).

The resin-phase activity coefficients are evaluated from the Wilson equation, and it is necessary to know the interaction parameters $\Lambda_{Na/B}$ and $\Lambda_{B/Na}$ of that equation previously. To do this, a calculation program, based on the direct fitting to the equilibrium isotherm, was used. This program, described in detail in a previous paper (*1*), allows one to obtain, at the same time, the best set of $k_{B/Na}$, $\Lambda_{Na/B}$, and $\Lambda_{B/Na}$ parameters that minimize the objective function

$$\psi = \sum_{i=1}^{n} (\bar{x}_B^* - \bar{x}_B)_i^2 \qquad (3)$$

where $\bar{x}_B$ is the experimental datum and $\bar{x}_B^*$ the calculated one.

The optimum parameters resulting from this calculation for the studied systems are shown in Table V, together with the average deviations of the data calculated with such parameters.

Since the information given for such average deviations is not too intuitive to analyze the goodness of the fitting, the experimental and calculated equivalent fractions of the resin phase for the system LW S-100 + Na^+ + Mn^{2+} are given in Table VI, just as an example. This information for the LW S-115 + Na^+ + Ni^{2+} systems is compared in Figure 1.

Both the results in Tables IV and V and those in Figure 1 show that the utilized fitting method allow one to reproduce the experimental data with the minimum deviation.

A major criticism that can be made against this method is not the goodness of the fitting, but the fact that, as is shown in ref *7*, it is not possible to calculate independently the activity coefficients (and consequently Wilson equation parameters) and $k_{B/Na}$. This makes the constant really a pseudoconstant on becoming another fitting parameter although, by its definition (2) it should be the same for each system, independent of the total ionic concentration.

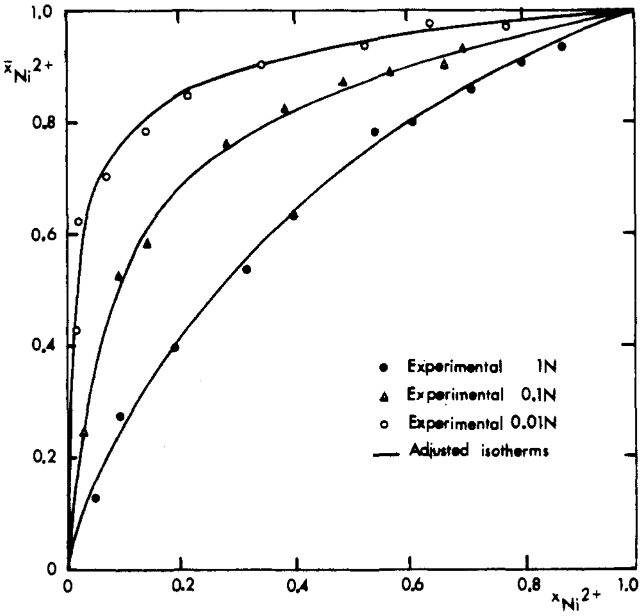

Figure 1. Experimental data and fitted isotherms for the LW S-115 + Na^+ + Ni^{2+} systems.

In this way, experimental data for other systems are now being obtained to contrast them with the results given in this paper and to make a critical analysis of the optimization process itself.

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Registry No. Lewatit S 100, 11138-38-8; Lewatit S 115, 37267-78-0; Lewatit SP 120, 53025-10-8; Na, 7440-23-5; Mn, 7439-96-5; Cu, 7440-50-8; Ni, 7440-02-0.

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