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Prediction of Multicomponent Ion Exchange Equilibria for the Ternary System SO$_4^{2-}$-NO$_3^-$ -Cl from Data of Binary Systems

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A framework is developed which provides predictions of multicomponent ion exchange equilibria from binary data.

Experimental data are reported for the ion exchange equilibria of the binary systems SO_4^{2-}-Cl^-, SO_4^{2-}-NO_3^-, and Cl^--NO_3^- on a strong base anion exchange resin. These systems exhibit nonideal characteristics in both phases, and the experimental characterization has been based on the reaction equilibrium constants and correlations for the activity coefficients in both phases. The exchanger phase activity coefficients are obtained from the well known Wilson (1964) model

The predictions of the ternary system SO_4^{2-}-NO_3^--Cl^- based solely on the binary data are consistent with the experimental data for this system.

SCOPE

The application of ion exchange in sorption operations is extensive. A major consideration preceding the implementation of this operation is the equilibrium distribution of ionic components between the solid and liquid phases for a particular system.

The aspects of thermodynamic equilibrium of ion exchange have been studied both theoretically and experimentally as reviewed by Helfferich (1962). More recently, Novosad (1973) studied the thermodynamics of ion exchange in the language of solution thermodynamics. Although a number of authors have investigated ternary systems (Klein et al., 1967; Streat and Brignal, 1970; Soldatov and Bychkova, 1971), the majority of published work is concerned with binary systems. This is limiting, since ion exchange is predominant in the fields of hydrometallurgy and water treatment which generally comprise complex multicomponent systems.

This work represents an attempt at the development of a framework from which the general, multicomponent, ion exchange system may be estimated.

The major hypothesis analogous to vapor-liquid equilibria is that the multicomponent system may be predicted from the combination of a number of subsystems that are characterized experimentally.

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CONCLUSIONS AND SIGNIFICANCE

A general scheme for predicting multicomponent ion exchange equilibria from the data for binary systems has been presented.

Each binary has been successfully characterized by means of the thermodynamic equilibrium constant for the reaction and parameters for the calculation of the activity coefficients of species in both phases. Two parameters per ionic component are required in the solution phase and two interaction coefficients per binary in the resin phase. The Wilson (1964) model has been applied to calculate the activity coefficients of species in the exchanger phase.

The prediction of the equilibrium distribution of components in the resin phase for the ternary system SO_4^{2-}-NO_3^--Cl^- based solely on the characteristics of the binaries SO_4^{2-}-NO_3^-, SO_4^{2-}-Cl^-, and Cl^--NO_3^- is consistent with the experimental data over the entire composition range.

The binary equilibria may be calculated at normalities different from those used in the characterization experiments.

For a multicomponent system which may be decomposed into a set of binary systems, it is sufficient experimentally to characterize each binary. If the equilibrium constants and the parameters obtained are applied, one need only solve simultaneously the resulting binary exchange-reaction equations to determine the equilibrium compositions. No further experimental characterization is required.

There is a need to develop a framework from which the general, multicomponent, ion exchange system that exhibits nonideal behavior in both phases can be predicted. Pieroni and Dranoff (1963) report that the ternary system H^+-Na^+-Ca^{2+} may be treated in terms of the binaries, and that, effectively, the third component is ignored in the graphical presentation. This limitation is restrictive.

Klein et al. (1967) consider all the components of a ternary system, but nonideal characteristics are not accounted for in this appoarch.

Soldatov and Bychkova (1970) have described the calculation of the ternary system K^+-NH_4^+-H^+ that is based on the concept that the activity coefficients in the binary mixture may be calculated from the experimental data and may then be applied to find the corresponding quantities for the ternary mixture. For accurate results, the treatment requires that the main binary system be close to ideal.

Danes and Danes (1972) proposed a method for calculation of ion exchange equilibria of polyionic systems, where the molar excess free mixing enthalpy of the resinates is expressed as a polynomial. The predictive power of the method is limited to systems which obey ideal or regular solution rules. If, for example, the equilibria of a ternary system are to be predicted from binary experimental data alone, then it is necessary that all the binary systems exhibit linear relationships between the apparent equilibrium constant and the exchanger composition.

An approach which incorporates nonideal characteristics in all the binary systems without these limitations will obviously have wider applicability.

In the estimation of vapour-liquid equilibria, the liquid and gas phases are separated, and the nonideal characteristics of each phase are individually correlated (Prausnitz et al., 1967). By analogy, in this work the solution and solid phases are separated for the purpose of thermodynamic description. The desirable models are those that correlate the experimental data so that good estimates of multicomponent systems are possible from binary experiments.

With these models, the equilibrium distribution of components in a multiphase, multicomponent system may be determined from the solution of the set of nonlinear, simultaneous equilibrium equations.

The prediction of multicomponent ion exchange equilibria solely from binary data is restricted to those systems which do not form complexes in the resin phase. The presence of complexes in the resin phase implies the characterization of systems of order higher than binary.

THERMODYNAMIC EQUILIBRIUM CONSTANT

If the possibility that simple and complex ions can distribute themselves between the liquid and solid phases according to N different chemical reactions is allowed for, then the multireaction stoichiometry may be represented by

$$\sum_{j=1}^{S} \alpha_{ij}A_j + \sum_{k=1}^{M} \beta_{ik}B_k = 0 \quad i = 1, 2 \text{ - -} R, \text{- - -} N \tag{1}$$
$$R \leqq N$$

The condition of equilibrium for this generalized reaction scheme is given by,

$$\sum_{j=1}^{S} \alpha_{ij}\overline{G}_j' + \sum_{k=1}^{M} \beta_{ik}\overline{G}_k = 0 \tag{2}$$
$$i = 1, 2, \ldots\ldots R$$

Expressions are required for the partial molar free energies which involve selection of standard states.

For the solutes in the aqueous phase, the following convenient reference state is adopted (Denbigh, 1966):

$$\overline{G}_j' = \underline{G}_j'^{o}(T) + RT \ln a_j'$$
$$\overline{G}_j' = \underline{G}_j'^{o}(T) + RT \ln (\gamma_j' C_j')$$

for

$$\gamma_j' \to 1 \quad \text{as} \quad C_j' \to 0 \tag{3}$$

For the solutes in the resin phase, the pure component is selected as the standard state, that is, when the mole fraction of resin form k is unity:

$$\overline{G}_k = \underline{G}_k^{o}(T) + RT \ln a_k$$
$$\overline{G}_k = \underline{G}_k^{o}(T) + RT \ln (\gamma_k x_k)$$

for

$$\gamma_k \to 1 \quad \text{as} \quad x_k \to 1 \tag{4}$$

Introduction of the activities, and rearrangement, causes Equation (2) to become

$$\exp \left[\frac{-\left[\sum_{j=1}^{S} \alpha_{ij}\underline{G}_j'^{o} + \sum_{k=1}^{M} \beta_{ik}\underline{G}_k^{o} \right]}{RT} \right] = K_i(T)$$

$$= \overset{S}{\underset{j=1}{\pi}} (a_j')^{\alpha_{ij}} \overset{M}{\underset{k=1}{\pi}} (a_k)^{\beta_{ik}} \quad i = 1, 2 -- R \qquad (5)$$

Where $K_i(T)$ is the thermodynamic equilibrium constant for reaction i at temperature T.

To obtain the equilibrium activities a_j' and a_k, this set of R independent equations has to be solved.

SOLUTION OF THE SET OF SIMULTANEOUS REACTION EQUATIONS

That set of equilibrium concentrations which simultaneously satisfy the R equilibrium conditions is required.

To solve these equations, the equilibrium constants at temperature T and pressure P are required together with the relationships between C_j' and γ_j' and between x_k and γ_k. The equations for the solution phase are well known. The experimental section of this work is concerned with the obtaining of the equilibrium constants for the combined reactions of the resin and solution phase and the relationship between γ_k and x_k.

With this information available, it is possible to solve these reaction systems. A method or technique of solving the equations is required.

The calculation of complex chemical equilibria has been reviewed by Zeleznik and Gordon (1968). More recently, Van Zeggeren and Storey (1970) published a critical survey of the analytical techniques that have been developed for the computation of chemical equilibria.

Aris (1965) describes the calculation of equilibrium compositions from simultaneous heterogeneous reactions using the concept of extent of reaction.

Expressed in terms of extents Equation (5) becomes

$$K_i = \overset{S}{\underset{j=1}{\pi}} \left\{ \gamma_j' \left[C_j'^o + \frac{1}{V} \sum_{i=1}^{R} \alpha_{ij} X_i \right] \right\}^{\alpha_{ij}}$$

$$\overset{M}{\underset{k=1}{\pi}} \left\{ \gamma_k \frac{n_k^o + \sum_{i=1}^{R} \beta_{ik} X_i}{\sum_{k=1}^{M} \left[n_k^o + \sum_{i=1}^{R} \beta_{ik} X_i \right]} \right\}^{\beta_{ik}} \quad i = 1, --- R \qquad (6)$$

where

$$\gamma_j' = \gamma_j'(\underline{X}) \quad \text{and} \quad \gamma_k = \gamma_k(\underline{X})$$

At a specified temperature T, the R equations can be solved implicitly for the R extents if the equilibrium constants and the activities in both phases are known.

In general, however, knowledge of activities and the equilibrium constants is incomplete. It is therefore necessary to use regression procedures to infer the best set of the unknown parameters which are consistent with the experimental data.

The choice of a procedure based on thermodynamic concepts should minimize experimental effort by its ability to use existing parameters to predict behavior outside the range of the experiments.

In the system chosen for investigation, it is possible to infer solution phase ionic activities from the extended Debye-Hückel treatment. This leaves the equilibrium constants and activity coefficients of the resin phase to be determined from the experimental data.

The successful application of this general framework depends on the availability of models for calculation of the activity coefficients in both phases for multicomponent systems.

In the following sections consideration will be given to these aspects.

ACTIVITY COEFFICIENTS IN THE SOLUTION PHASE

In the multicomponent solutions of industrial interest, electrolyte concentrations are relatively high and make the activity coefficients difficult to obtain either theoretically or from experimental data.

Equations for the accurate estimation of the activity-coefficient ratios in ion exchange problems have been reported by Pal et al. (1974).

Kusik and Meissner (1975) have reviewed the calculation of activity coefficients in hydrometallurgy. Examples of some multicomponent systems have given estimates of the activity coefficients with errors within 20% of the measured quantities.

Recently, Sengupta et al. (1975) have applied the concept of ionic interaction coefficients to activity calculations in mixed electrolyte solutions of ion exchange systems.

A somewhat simplified approach applicable to multicomponent systems has been applied by Truesdell and Jones (1973) in the development of a computer programme for the calculation of the chemical equilibria of natural waters.

The availability of the parameters required in this treatment when applied to the system under consideration has justified its use in this work.

The extended Debye and Hückel equation (Robinson and Stokes, 1959) with two parameters per ionic component has been selected to calculate the single ion-activity coefficients

$$\ln \gamma_j' = \frac{-Az_j^2\sqrt{I}}{1 + Ba_j\sqrt{I}} + b_jI \qquad (7)$$

Truesdell and Jones (1973) have calculated the parameters a_j and b_j from experimental mean salt activity coefficients.

Thus, with the two parameters per ionic species and the ionic strength of the solution, it is possible to estimate the activity coefficient and hence the activity of each species in a multicomponent system.

ACTIVITY COEFFICIENTS IN THE RESIN PHASE

Davidson and Argensinger (1953), Hogfeldt (1953), and Gaines and Thomas (1953) in principle have solved the problem of the calculation of the equilibrium constant and activity coefficients of the resin phase components from experimental ion exchange data. For a binary system, the Gibbs-Duhem equation and the equation for the thermodynamic ion exchange equilibrium constant are solved.

More recently, Soldatov and Bychkova (1971) have extended the method to multicomponent systems. The method is used to calculate the activity coefficients from multicomponent data.

Freeman (1961) has derived expressions for the dependence of the logarithms of the activity coefficients of a binary system upon the equivalent fraction of the counterion in the exchanger. These expressions are based on the excess free energy of the resinates expressed as a polynomial. The coefficients are derived from experimental measurements of activities of the solution species at different exchanger compositions.

The principle of this method has been extended to multicomponent systems that incorporate models for the excess free energy that are applicable to multicomponent systems.

The properties of excess mixture are useful for the description of nonideal characteristics of solid phases. The activity coefficients are generated from the functional relationship between the excess property and composition.

The Wilson (1964) model has been selected to correlate the excess Gibbs free energy. This equation is a semiempirical generalization of the Flory (1941, 1942) and Huggins (1942) equations and has been successfully applied to vapor-liquid equilibria (Prausnitz et al., 1967).

The Wilson equation with two adjustable parameters per binary is

$$\frac{\Delta \underline{G}^E}{RT} = - \sum_{i=1}^{M} x_i \ln \left[\sum_{j=1}^{M} \Lambda_{ij} x_j \right] \tag{8}$$

Differentiation of this expression with respect to n_i gives

$$\ln \gamma_i = 1 - \ln \left[\sum_{j=1}^{M} x_j \Lambda_{ij} \right] - \sum_{k=1}^{M} \left[\frac{x_k \Lambda_{ki}}{\sum_{j=1}^{M} x_j \Lambda_{kj}} \right] \tag{9}$$

Only binary interaction parameters Λ_{kj} and Λ_{ki} appear, and the parameters Λ_{ii}, Λ_{jj}, Λ_{kk}, etc., are equal to unity.

The Wilson model for a multicomponent system requires parameters that can be obtained from binary mixture data. This feature reduces significantly the experimental program required to characterize a multicomponent system.

The model has its theoretical origin as an athermal solution theory. This makes it particularly applicable to ion exchange resin systems, since generally heats of mixing are small (Helfferich, 1962).

PARAMETER ESTIMATION

The expression for the thermodynamic equilibrium constant Equation (5) is rearranged in terms of the experimentally accessible equilibrium quotient λ_i.

From Equation (12) and with introduction of the equilibrium quotient λ_i

$$\lambda_i = K_i \mathop{\pi}_{k=1}^{M} \gamma_k - \beta ik \quad i = 1, \ldots . R \tag{10}$$

where

$$\lambda_i = \mathop{\pi}_{j=1}^{S} (a_j')^{\alpha_{ij}} \mathop{\pi}_{k=1}^{M} (x_k)^{\beta_{ik}} \quad i = 1, - - R \tag{11}$$

Provided the activity coefficient in the solution phase can be calculated, λ_i may be determined from the ion exchange experiments.

Substitution of Equation (9) into (10) yields

$$\ln \lambda_i = \ln K_i - \sum_{k=1}^{M} \beta_{ik} \left\{ 1 - \ln \left[\sum_{l=1}^{M} x_l \Lambda_{kl} \right] - \sum_{n=1}^{M} \left[\frac{x_n \Lambda_{nk}}{\sum_{l=1}^{M} x_l \Lambda_{nl}} \right] \right\} i = 1, - - R \tag{12}$$

Therefore, λ_i should be uniquely determined by x_1, $x_2 - - x_k$.

Since λ_i and x_k are experimental values, and β_{ik} are known stoichiometric coefficients, the parameters to be estimated are K_i and the binary interaction coefficients Λ_{kj}.

The objective function F to be minimized is the square of the normalized error of the fitted and experimental equilibrium quotients:

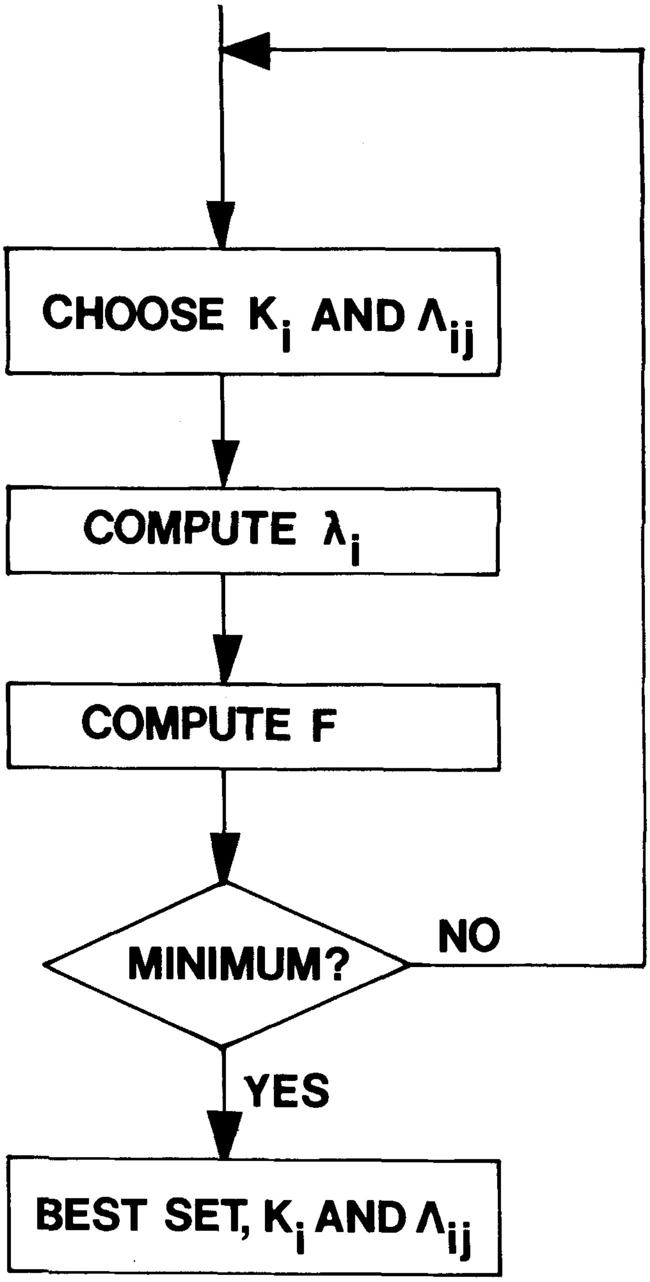


Fig. 1. Computation scheme.

$$F = \sum_{i=1}^{R} \left(\frac{\lambda_i^{\text{exp}} - \lambda_i^{\text{fitted}}}{\lambda_i^{\text{exp}}} \right)^2 \tag{13}$$

The fitted equilibrium quotients are given by Equation (12). A search is made for the K_i and set of interaction parameters Λ_{kj} which minimize the function F.

The procedure is outlined in Figure 1.

Data processing has two aspects.

1. Selection of the best set of parameters. Values determined from these parameters for resin composition are referred to in the experimental section as fitted values which, when compared to the experimental values from which they were derived, provide a basis for estimating the effectiveness of the regression procedures.
2. It is possible, by use of lower-order systems, to infer all the interaction parameters required to specify a higher-order system. The values predicted in this way are referred to as predicted values which, when compared with experimental values obtained for the higher-order system, provide a severe test of the linearized procedure employed.

TABLE 1. SYSTEMS INVESTIGATED

	Equilibrium solution		Elution solution		
System	Chemicals	Concentration	Chemicals	Concentration	Chemical analysis
Capacity	NaCl	1N	$NaNO_3$	1N	Chloride
NO_3-Cl	NaCl $NaNO_3$	0.2 and 0.4N	$NaNO_3$	1N	Chloride
SO_4-Cl	NaCl Na_2SO_4	0.2 and 0.4N	$NaNO_3$	1N	Chloride
NO_3-SO_4	$NaNO_3$ Na_2SO_4	0.2, 0.4, and 0.6N	NaCl	1N	Sulfate
SO_4-NO_3-Cl	Na_2SO_4 $NaNO_3$ NaCl	0.2N	Na_2CO_3 $HClO_4$	0.1M 0.1M	Sulfate and chloride

EXPERIMENTAL

The ion-exchange equilibria were determined according to the column technique described by Klamer et al. (1958). The major advantage of the method is that the solution composition at equilibrium may be specified beforehand.

The ion exchange resin used in these tests was a strong base polystyrene resin, Amberlite IRA 400, supplied by Rohm and Haas. The anion exchange capacity of the resin was determined as 1.4 eq/l of free settled resin in the sulfate form.

The feed solutions were prepared from reagent grade chemicals and distilled water. The solutions used to elute the ions of interest, after equilibrium was obtained were prepared from analytical grade reagents and distilled water.

Solid-liquid separation at equilibrium was achieved by centrifuge as described by Helfferich (1962).

Five liters of the solution at the desired equilibrium composition were passed through each of six 10 ml resin samples in glass columns for a period of 48 hr. Details of apparatus and procedure are given by Smith (1976). At equilibrium, these columns of resin were rotated by centrifuge and eluted with 2l of the desired eluant for 24 hr. The systems analyzed in this way are summarized in Table 1.

The ions on the resin exchanger were eluted with a known volume of a strong eluant, and their concentration was determined. The chloride ion concentration was determined by automatic potentiometric titration with standard silver nitrate solution with a solid silver electrode and a saturated potassium sulfate reference electrode. The precision obtained was better than 1%. The total sulfate ion concentration was determined gravimetrically with a precision of better than 2%. The nitrate ion concentration was determined by difference because spectrographic analysis of the nitrate ion did not provide good mass balances. The temperature of the system was held at 295 ± 3°K.

RESULTS AND DISCUSSION

Characterization of Binary Systems

The experimental equilibrium composition of the resin and solution phases at the solution normalities specified are summarized in Table 2 for the three binary systems SO_4^{2-}-NO_3^-, SO_4^{2-}-Cl^-, and Cl^--NO_3^-.

From the basic equilibrium data, the equilibrium quotients are determined for each equilibrium condition. The variation of the experimental equilibrium quotients with composition in the resin phase for the binary systems is illustrated in Figures 2, 3, and 4. It can be seen that the data for the SO_4^{2-}-Cl^- system falls within the range of the published data of Wheaton and Bauman (1951) and O'Connor (1954). The data of O'Connor (1954) for the SO_4^{2-}-Cl^- and of Korngold (1973), for the system NO_3^--Cl^- are reported for samples of Amberlite 400 with 8% DVB. It can be seen that in both cases

TABLE 2. EQUILIBRIUM COMPOSITION OF BOTH PHASES OF BINARY SYSTEMS, AMBERLITE 400, SODIUM SULFATE, SODIUM NITRATE; SODIUM SULFATE, SODIUM CHLORIDE AND SODIUM NITRATE SODIUM CHLORIDE FOR VARIOUS TOTAL NORMALITIES OF THE SOLUTIONS AT 298°K

	SO_4^{2-}-NO_3^-				SO_4^{2-}-Cl^-				Cl^--NO_3^-			
Solution normality	Solution equivalent fraction		Resin mole fraction		Solution equivalent fraction		Resin mole fraction		Solution equivalent fraction		Resin mole fraction	
N	ΣSO_4	NO_3	SO_4	NO_3*	ΣSO_4	Cl	SO_4*	Cl	Cl	NO_3	Cl	NO_3*
0.2	0.90	0.10	0.401	0.599	0.90	0.10	0.721	0.279	0.95	0.05	0.794	0.206
	0.80	0.20	0.259	0.741	0.80	0.20	0.553	0.447	0.90	0.10	0.689	0.311
	0.60	0.40	0.119	0.881	0.60	0.40	0.343	0.657	0.80	0.20	0.527	0.473
	0.40	0.60	0.059	0.941	0.40	0.60	0.205	0.792	0.70	0.30	0.412	0.588
	0.20	0.80	0.021	0.979	0.20	0.80	0.109	0.891	0.50	0.50	0.244	0.756
	0.10	0.90	0.011	0.989					0.30	0.70	0.129	0.871
0.4	0.90	0.10	0.305	0.695	0.90	0.10	0.622	0.378	0.95	0.05	0.806	0.194
	0.80	0.20	0.177	0.823	0.80	0.20	0.434	0.566	0.90	0.10	0.703	0.297
	0.60	0.40	0.071	0.929	0.60	0.40	0.236	0.764	0.80	0.20	0.539	0.461
	0.40	0.60	0.029	0.971	0.40	0.60	0.127	0.873	0.70	0.30	0.422	0.578
									0.50	0.50	0.251	0.749
									0.30	0.70	0.133	0.867
0.6	0.90	0.10	0.247	0.753								
	0.80	0.20	0.133	0.867								
	0.60	0.40	0.049	0.951								
	0.40	0.60	0.019	0.981								
	0.20	0.80	0.006	0.994								

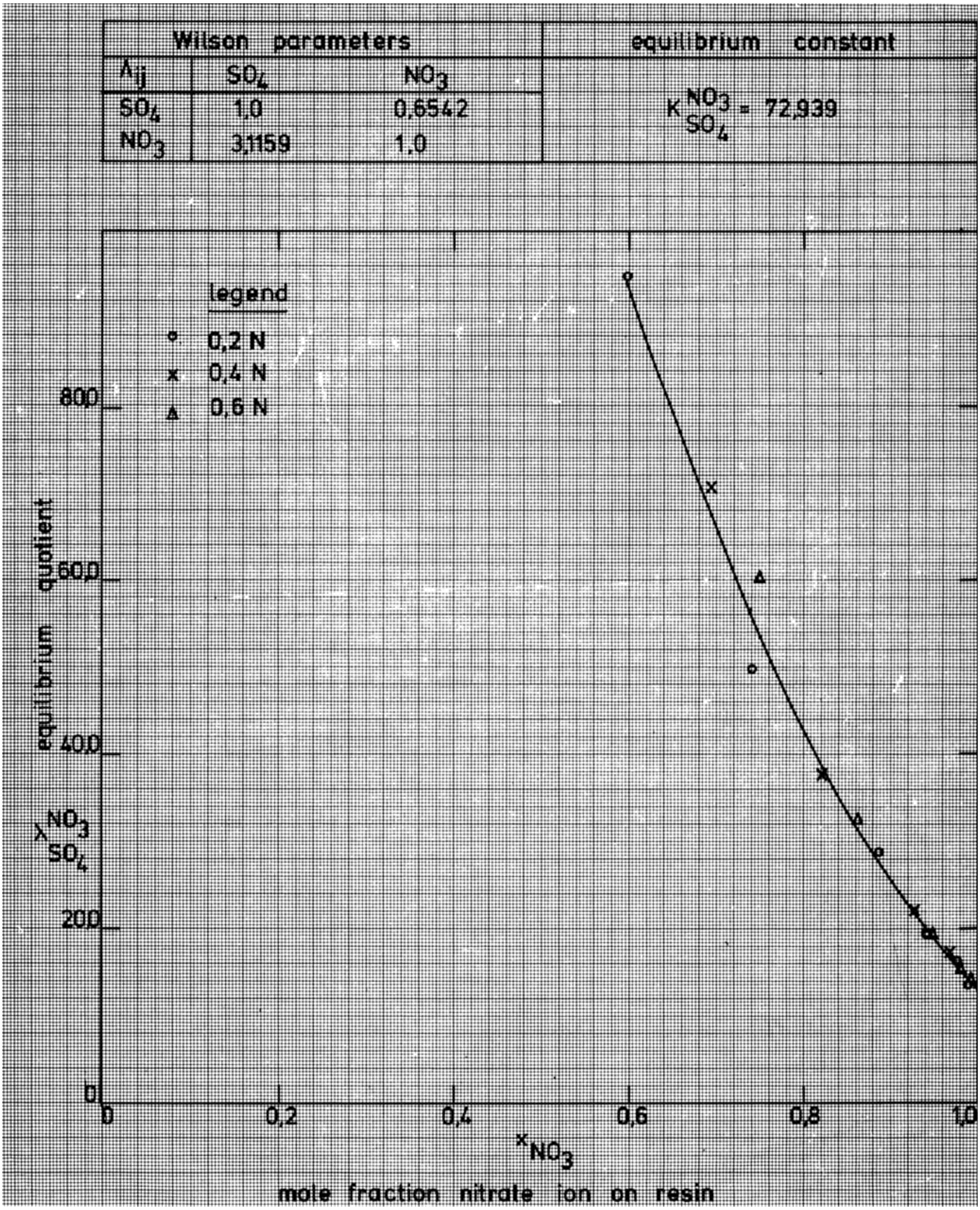
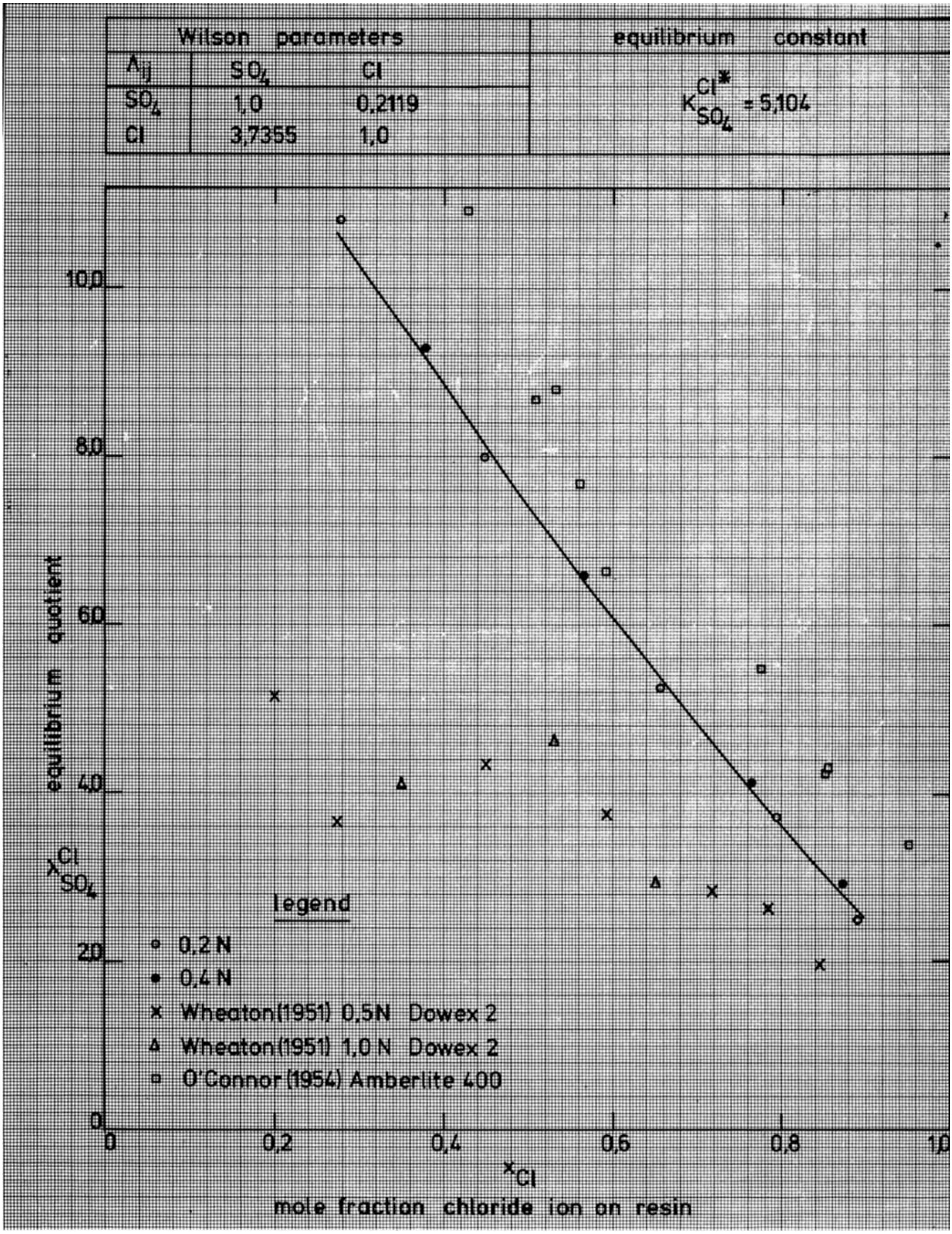


Fig. 2. Variation of equilibrium quotient with nitrate ion mole fraction for binary system Amberlite 400, 0.2 N, 0.4 N, 0.6 N mixture of sodium nitrate, sodium sulfate at 298°K. The solid line represents the least-squares fit of the experimental data with the Wilson parameters and equilibrium constant reported.

the experimental data reported for this work, which employs the same resin, are consistent with those of these two investigators.

The difference between this work and that of Wheaton and Bauman (1951) and Gregor et al. (1955) is acceptable because although Amberlite 400 is also a polystyrene strong base anion resin with the same cross linkage, the functional group of Dowex 2 is $-N(\text{alkylol})(\text{alkyl})_2^+$, as compared to $-N(\text{alkyl})_3^+$ for Amberlite 400.

It is noted that the relationships of equilibrium quotient and composition at different normalities for this work, and that of O'Connor (1954) and Wheaton and Bauman (1951), generate single curves within experimental error. This indicates that the activity coefficient calculations in



Wilson parameters			equilibrium constant
Λ_{ij}	SO_4	Cl	$K_{SO_4}^{Cl*} = 5{,}104$
SO_4	1,0	0,2119	
Cl	3,7355	1,0	

Fig. 3. Variation of equilibrium quotient with chloride ion mole fraction for binary system Amberlite 400, 0.2 N, 0.4 N mixture of sodium chloride and sodium sulfate at 298°K. Comparison of this work with published data. The solid line represents the least-squares fit of the experimental data with the Wilson parameters and equilibrium constant reported.

the solution phase are sufficiently accurate (Davidson and Argensinger, 1953).

Equilibrium data in the form of equilibrium quotients are applied to estimate the interaction coefficients of the Wilson equation and the thermodynamic equilibrium constants of the exchange reactions.

No multiple roots were encountered for the systems investigated.

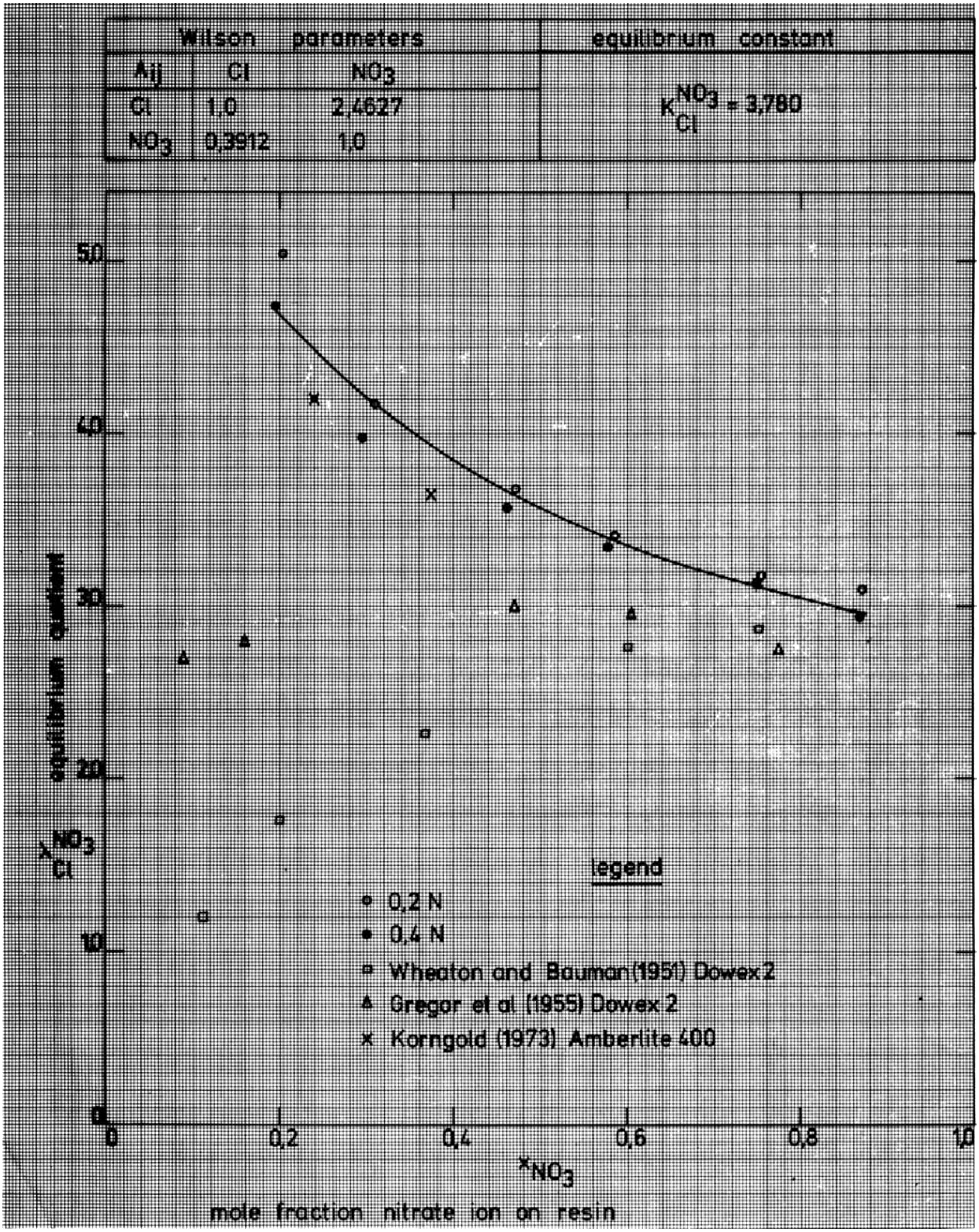


Fig. 4. Variation of equilibrium quotient with nitrate ion mole fraction for binary system Amberlite 400, 0.2 N, 0.4 N mixture of sodium chloride and sodium nitrate at 298°K. Comparison of this work with published data. The solid line represents the least-squares fit of the experimental data with the Wilson parameters and equilibrium constant reported.

The estimates of the binary interaction parameters and ($K_{SO_4}^{Cl} = K_{SO_4}^{NO_3}/(K_{Cl}^{NO_3})^2$) the thermodynamic equilibrium constants are listed for each exchange reaction in Table 3. The three binary constants are related, and hence we may infer for example $K_{SO_4}^{Cl}$ from $K_{SO_4}^{NO_3}$ and $K_{Cl}^{NO_3}$. In this case $K_{SO_4}^{Cl} = K_{SO_4}^{NO_3}/(K_{Cl}^{NO_3})^2 = 5.104$, which agrees within the error ascribed to the estimate of 5.094. This is evidence of the consistency of the experimental data employed.

With the inferred value of $K_{SO_4}^{Cl}$, the Wilson parameters

TABLE 3. ESTIMATES OF PARAMETERS, EQUILIBRIUM CONSTANT AND WILSON PARAMETERS FOR BINARY SYSTEMS. ROOT-MEAN-SQUARE ERROR OF THE EXPERIMENTAL AND LEAST-SQUARES FIT OF EQUILIBRIUM QUOTIENTS. INFERRED EQUILIBRIUM CONSTANT FOR SO_4^{2-}-Cl^- BINARY SYSTEM AT 298°K

	Parameters estimated				
Ion exchange reaction	Equilibrium constant	Wilson parameters			R.M.S. error
$R_2SO_4 + 2NO_3 \rightleftarrows 2RNO_3 + SO_4$	$K_{SO_4}^{NO_3} = 72.939$	Λ_{ij} SO_4 NO_3	SO_4 1.0 3.1159	NO_3 0.65419 1.0	± 5.8
$R_2SO_4 + 2Cl \rightleftarrows 2RCl + SO_4$	$K_{SO_4}^{Cl} = 5.094$	Λ_{ij} SO_4 Cl	SO_4 1.0 3.674	Cl 0.2280 1.0	± 2.7
$RCl + NO_3 \rightleftarrows RNO_3 + Cl$	$K_{Cl}^{NO_3} = 3.780$	Λ_{ij} Cl NO_3	Cl 1.0 0.39121	NO_3 2.4627 1.0	± 3.5
$R_2SO_4 + 2Cl \rightleftarrows 2RCl + SO_4$	$\overset{*}{K}{}_{SO_4}^{Cl} = 5.104$	Λ_{ij} SO_4 Cl	SO_4 1.0 3.7355	Cl 0.21192 1.0	± 2.7
	$\overset{*}{K}{}_{SO_4}^{Cl} = K_{SO_4}^{NO_3}/(K_{Cl}^{NO_3})^2$				

TABLE 4. PARAMETERS FOR EXTENDED DEBYE-HUCKEL EQUATION (TRUESDELL AND JONES, 1973)

Species	a_j	b_j	z_j
SO_4^{2-}	5.0	−0.04	−2
NO_3^-	3.0	0.0	−1
Cl^-	3.5	0.015	−1
Na^+	4.0	0.075	+1
$NaSO_4^-$	5.4	0.0	−1

$A = 5\ 085$
$B = 0.3281 \times 10^{10}$

have been reestimated. These parameters are subsequently used in calculations.

The root-mean-square error between fitted and experimental equilibrium quotients is less than ±6% for all binary systems considered as reported in Table 3. The variation of the equilibrium quotient with resin composition is shown as the best fit curve through the experimental points in Figures 2, 3, and 4.

From the results presented, it may be concluded that the nonideal characteristics in the resin phase are well described by the Wilson model. The predictive power of this model is tested in the following section.

PREDICTION OF THE TERNARY SYSTEM SO_4^{2-}-NO_3^--Cl^-

The interaction parameters and the equilibrium constants for the three binary systems alone are combined through the Wilson equation to predict the equilibrium activity coefficients and composition in the resin phase for specified initial and solute conditions. The solution phase activities are first determined for the ions SO_4^{2-}, NO_3^-, Cl^-, Na^+, and $NaSO_4^-$ in the test solutions, using the values of the parameters for the Debye-Hückel equation given in Table 4.

The relevant solution phase activities and a specified volume of resin of known capacity and composition, in

TABLE 5. COMPARISON OF EXPERIMENTAL AND PREDICTED EQUILIBRIUM COMPOSITION OF THE TERNARY SYSTEM AMBERLITE 400, 0.2 N MIXTURE OF SODIUM SULFATE, SODIUM NITRATE, AND SODIUM CHLORIDE AT 298°K PREDICTED ACTIVITY COEFFICIENTS OF RESIN SPECIES. CAPACITY IS 1.4 EQ/1 RESIN. THIS DATA IS PRESENTED GRAPHICALLY IN FIGURE 5

	Equivalent fraction in solution			Equivalent fraction in resin predicted			Equivalent fraction in resin experimental			Activity coefficient in resin predicted		
Test No.	ΣSO_4	NO_3	Cl	SO_4	NO_3	Cl	SO_4	NO_3*	Cl	SO_4	NO_3	Cl
1	0.20	0.10	0.70	0.128	0.318	0.554	0.104	0.332	0.564	0.387	0.849	0.926
2	0.40	0.10	0.50	0.234	0.336	0.430	0.218	0.353	0.429	0.495	0.840	0.892
17	0.50	0.05	0.45	0.332	0.218	0.450	0.322	0.235	0.443	0.621	0.751	0.890
4	0.60	0.10	0.30	0.347	0.363	0.290	0.352	0.375	0.273	0.600	0.823	0.842
5	0.70	0.10	0.20	0.413	0.380	0.207	0.412	0.396	0.192	0.653	0.810	0.810
6	0.80	0.10	0.10	0.487	0.401	0.112	0.480	0.419	0.101	0.705	0.790	0.771
7	0.10	0.50	0.40	0.033	0.764	0.203	0.029	0.771	0.200	0.228	0.989	0.806
8	0.20	0.40	0.40	0.073	0.700	0.227	0.070	0.706	0.224	0.268	0.978	0.819
9	0.30	0.30	0.40	0.123	0.619	0.258	0.126	0.620	0.254	0.325	0.958	0.834
10	0.40	0.20	0.40	0.190	0.511	0.299	0.190	0.517	0.293	0.410	0.918	0.851
18	0.60	0.20	0.20	0.284	0.549	0.167	0.278	0.564	0.159	0.487	0.903	0.809
12	0.55	0.05	0.40	0.365	0.222	0.413	0.346	0.253	0.401	0.652	0.746	0.875
13	0.50	0.40	0.10	0.174	0.761	0.064	0.175	0.760	0.065	0.342	0.968	0.779
14	0.50	0.30	0.20	0.201	0.658	0.141	0.207	0.656	0.137	0.386	0.949	0.803
15	0.50	0.20	0.30	0.236	0.528	0.236	0.250	0.522	0.228	0.449	0.912	0.832
16	0.50	0.10	0.40	0.289	0.348	0.363	0.289	0.357	0.354	0.548	0.833	0.869
3	0.50	0.10	0.40	0.289	0.348	0.363	0.280	0.368	0.352	0.548	0.833	0.869
11	0.50	0.10	0.40	0.289	0.348	0.363	0.291	0.354	0.355	0.548	0.833	0.869

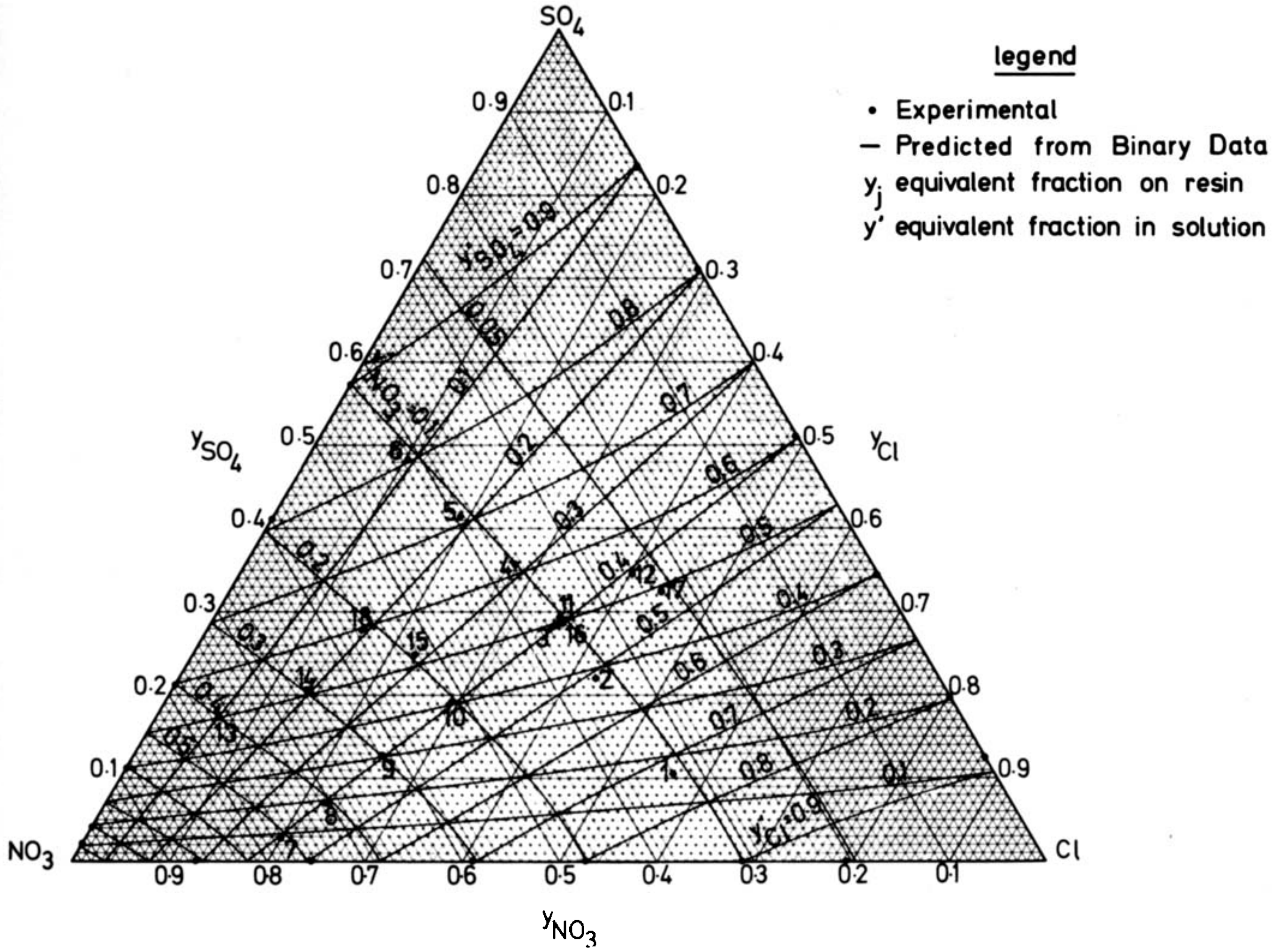


Fig. 5. Comparison of predicted and experimental equivalent fraction of the resin phase and the predicted contour lines for the ternary system Amberlite 400, 0.2 N mixture of sodium chloride, sodium nitrate, and sodium sulfate at 298°K based on experimental data for binary systems. Capacity is 1.4 eq/l resin. The numbered points refer to the test numbers in Table 5.

this case $x_{SO_4} = 1.0$, are used to determine the equilibrium extents and hence the resin composition.

The independent heterogeneous equations required to solve this system are

$$R_2SO_4 + 2NO_3^- = 2RNO_3 + SO_4^{2-}$$
$$R_2SO_4 + 2Cl^- = 2RCl + SO_4^{2-} \qquad (14)$$

A single solution phase complex is considered in this system

$$Na^+ + SO_4^{2-} = NaSO_4^- \qquad (15)$$

with the equilibrium constant for the reaction defined as

$$K' = \frac{a'_{NaSO_4^-}}{(a'_{Na^+})(a'_{SO_4^{2-}})}$$

with a value of 5.248 (Sillen and Martell, 1964).

In the predictions, a capacity of 1.4 eq/l of free setted resin is assumed.

For the solution conditions specified in Table 5, the predicted and experimental resin compositions are consistent over a large composition range. The predicted activity coefficients of the resinates for the corresponding ternary points are included in Table 5. The final three results in Table 5 for solution conditions $y'_{SO_4} = 0.5$, $y'_{NO_3} = 0.1$, and $y'_{Cl} = 0.4$ have been performed in triplicate. The experimental results show a high degree of reproducibility.

Predictions have been made of the resin phase composition expressed in equivalent fractions for the entire solution composition range at 0.2N and presented graphically together with the ternary and binary experimental points on a ternary diagram according to Streat and Brignal (1970) as shown in Figure 5. The equidistant axes refer to the equivalent fractions of species in the resin phase. Superimposed on these axes are contour lines which refer to the equivalent fraction of species in the solution phase.

The results justified the extension of this approach to more complex systems, particularly to the system involved in the recovery of uranium.

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NOTATION

a_j = ion size parameter in Debye-Hückel equation
a_j' = activity of species j in solution mixture
a_k = activity of species k in resin phase
A = parameter for Debye-Hückel equation
A_j = chemical species j in solution phase

B = parameter for Debye-Hückel equation
B_k = chemical species k in resin phase
C' = molar concentration in solution phase
G = Gibbs free energy
$\underline{G}$ = specific Gibbs free energy
$\overline{G}_i$ = partial molar Gibbs free energy
G^E = excess Gibbs free energy
I = ionic strength $\equiv \frac{1}{2} \sum_i Z_i^2 C_i'$
K_i = equilibrium constant for reaction i
K' = stability constant for complex formation
M = number of species in resin phase
n = total number of moles
n_j' = number of moles of species j in solution
n_k = number of moles of species k in resin
N = total number of reactions
P = pressure
R = ideal gas constant, rank of matrix of stoichiometric coefficients
S = number of species in solution phase
T = temperature
x_k = mole fraction of species k in resin phase
x_j' = mole fraction of species j in solution phase
X_i = extent of reaction i
X = vector of extents
Y_k = equivalent fraction of species k in resin phase
Y_j' = equivalent fraction of species j in solution phase
Z_i = charge of species j

Greek Letters

α_{ij} = stoichiometric coefficient for j^{th} species in solution of i^{th} competing reaction
β_{ik} = stoichiometric coefficient for k^{th} species in resin of i^{th} competing reaction
γ_k = activity coefficient in resin phase
γ_j' = activity coefficient in solution phase
Λ_{ij} = Wilson interaction parameters
λ_i = equilibrium quotient for i^{th} reaction

Operators

Δ = finite change in state property
π = cumulative product operator
Σ = cumulative summation operator

Superscripts

E = with operator Δ denotes excess change in property upon mixing
$'$ = solution phase
o = reference state
$*$ = inferred from mass balance or other equation
exp = experimental value of variable
pred = predicted value of variable

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