On the Existence of Ternary Interactions in Ion Exchange

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Davidson and Argersinger (1953), Gaines and Thomas (1953), and Baumann and Argersinger (1956) developed the mass action theory of ion exchange and presented procedures for integrating experimental partitioning data over the range of composition to obtain equilibrium constants and resinate activity coefficients. More recently, Hogfeldt (1984), Soldatov and Bichkova (1980, 1984), and Smith and Woodburn (1978) employed data reduction techniques in which a thermodynamically consistent formulation for the excess Gibbs free energy associated with solid phase nonidealities is used in a parameter fitting process to obtain simultaneously the equilibrium constant and a set of constants characterizing solid phase nonidealities. Either a Margueles expansion (Hogfeldt, 1984; Soldatov and Bichkova, 1984) or the Wilson (1964) equation (Smith and Woodburn, 1978) have been used for this purpose.

Working with Amberlite IRA 400 resin, and the system $SO_4^{-2}/NO_3^-/Cl^-$, Smith and Woodburn fitted data from the three binary systems to the Wilson model for solid phase activity coefficients and obtained consistency among the redundant data. They then tested the predictions on a ternary system containing all three exchanging species. The reader is referred to Table 2 of their paper, which compares observed vs. predicted results. On the basis of this data, they concluded that binary interactions suffice to characterize the ion exchange equilibrium in this system, however no quantitative statistical comparison was made.

Based on their data, the results presented in Table 1 were computed. For the three replicate runs performed by Smith and Woodburn, not considered in the analysis, standard deviations for the solid phase equivalent fractions of sulfate, nitrate, and chloride were respectively 0.004784, 0.008730, and 0.001247. It is clear that there is a statistically significant difference (t test, $P < 0.01$) in the nitrate and chloride solid phase compositions as predicted from the binary and found in the ternary experiments, and that this difference is large when compared with the experimental error.

Table 1. Observed – Predicted Solid-Phase Equivalent Fraction

	Sulfate	Nitrate	Chloride	
Average	−0.00407	0.01007	−0.00600	
Std. dev.	0.00974	0.00941	0.00643	
Paired t test	−1.61710 (NS)	4.145265 ($P < 0.01$)	−3.61448 ($P < 0.01$)	12 points

The deviations further can be seen to be systematic if, for each pair of ions, the quantity in Eq. 1 is computed:

$$K_2^1 = r_1 f_1 (m_2 g_2)^z / (r_2 f_2)^z m_1 g_1 \tag{1}$$

where f_i and g_i are respectively the solid phase and solution phase activity coefficients. The former are tabulated in the original paper, and the latter were computed from the extended

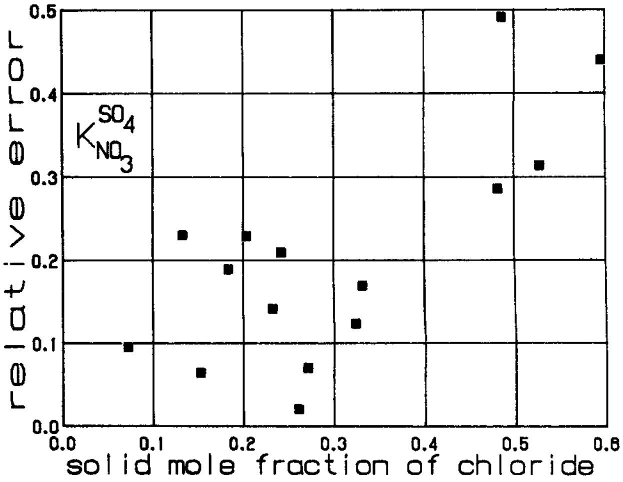

Figure 1. Effect of chloride on sulfate-nitrate equilibrium.

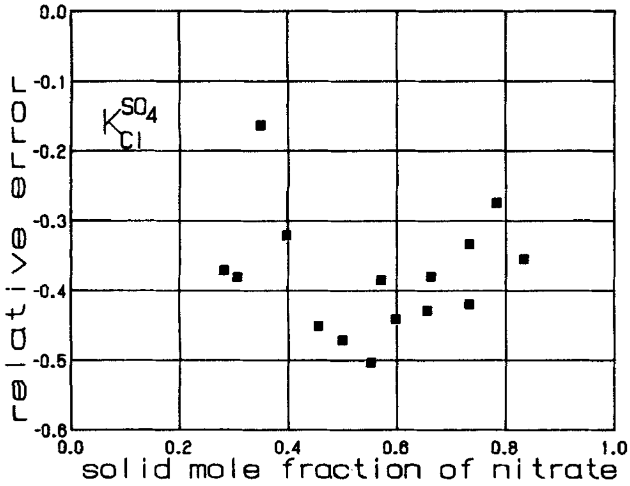

Figure 2. Effect of nitrate on the sulfate-chloride equilibrium.

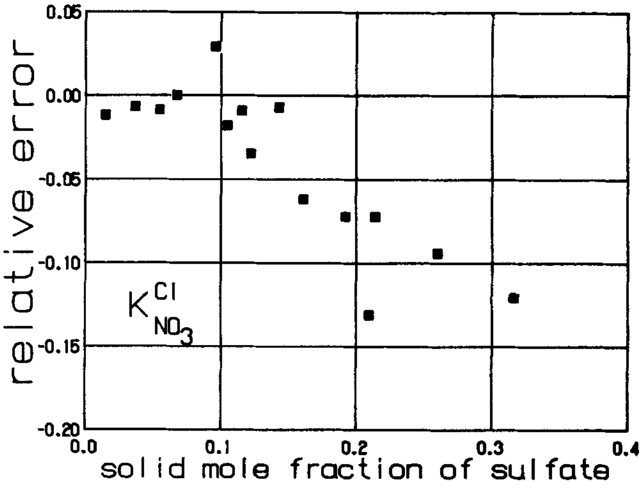

Figure 3. Effect of sulfate on the nitrate-chloride equilibrium.

Debye equation used therein. The quantity m_i is the solution phase (observed) molarity of ion i (computed, in the case of sulfate, after correction for sodium sulfate ion pairing), r_i is the solid phase (observed) mole fraction, and z is the stoichiometry (moles of species 2 exchanged per mole of species 1). In the absence of ternary interactions, the f_i's, which are computed based solely on the basis of binary interactions, should contain all information on the effect of a third component on a binary equilibrium. There are three equations that can be constructed from Eq. 1 based on permuting subscripts. In the absence of ternary interactions, then, for each binary pair a plot of K_2^1 vs. r_3 should show random scatter around the binary equilibrium constant.

Figures 1 through 3 plot the relevant quantities (which, for clarity, are the relative excess values of Eq. 1 with respect to the reported binary equilibrium constants). It is clear that there is a systematic trend in all three equilibria with the presence of the third component. The reported root mean square error in the determination of the equilibrium constants from the binary isotherms is 3–6%. It is clear that the deviations in Figures 1–3 exceed these values.

It is therefore concluded, contrary to the interpretation placed upon it by the original authors, that there are significant ternary interactions in the sulfate-nitrate-chloride-Amberlite IRA 400 system. The existence of such interactions in other exchange systems and whether these can be rectified by the addition of suitable ternary interaction parameters, remain open questions. It is suggested that the quantity in Eq. 1 may provide a suitable test for such interactions.

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