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**SXLSQA, A COMPUTER PROGRAM FOR INCLUDING BOTH COMPLEX FORMATION AND ACTIVITY EFFECTS IN THE INTERPRETATION OF SOLVENT EXTRACTION DATA**

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**ABSTRACT**

A previously reported computer program for the interpretation of solvent extraction data in systems that can include two extractants, one acidic and one neutral, has been extended to treat the effects of: (1) variation of activity coefficients of solute species and of water activity in the aqueous phase, calculated by the Pitzer treatment; (2) variation of activity coefficients of solute species in the organic phase, calculated by the Hildebrand-Scott treatment; and (3) product species formed in the aqueous phase. The interaction parameters of the Pitzer treatment and the solubility parameters of the Hildebrand-Scott treatment can be refined along with the formation constants of various assumed product species to fit the data. Like its predecessor, the program is capable of fitting simultaneously a variety of data, including the distribution of an extractable cation, anion, or water, as well as spectra, vapor pressure, or heats of mixing for the organic phase. Use of the program is illustrated by modeling the extraction of water and  $\text{HNO}_3$  from aqueous nitric acid by di(2-ethylhexyl)sulfoxide in dodecane.

**INTRODUCTION**

In a previous publication (1), a computer program (SXLSQ) was described for fitting a variety of data from a solvent extraction system involving an acidic extractant (HA) and/or a neutral extractant (B) by assuming a set of product species in the organic phase

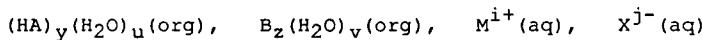
and adjusting their formation constants through an iterative non-linear least-squares procedure to obtain the best fit to the data. Such a modeling process is deemed essential for interpreting observed behavior, for smoothing data, and for predicting behavior of many solvent extraction systems.

There was, however, no provision in SXLSQ for the variation of activity coefficients in either phase. Since it is common in solvent extraction equilibrations to employ reagent concentrations greater than 0.1 M in the organic phase and a variety of aqueous compositions, variation of activity coefficients in either phase can be appreciable. Furthermore, species in the organic phase are often hydrated, and so the activity of water in the aqueous phase can be an important variable if concentrated aqueous solutions are involved.

In SXLSQA, aqueous activity coefficients and the water activity are estimated by the Pitzer treatment (2), as has been described previously (3), and activity coefficients in the organic phase are estimated by the treatment of Hildebrand and Scott (4). The purpose of this paper is to outline the modifications made in SXLSQ to produce this more general program, including the effect of activity coefficients on various observable quantities that are calculated, and the formation of product species in the aqueous phase. Use of the program will be illustrated by modeling the extraction of water and  $\text{HNO}_3$  from aqueous nitric acid by di(2-ethylhexyl)sulfoxide in dodecane. In other publications SXLSQA has been used to aid in the interpretation of the data on the extraction of water alone (5) and of uranium (VI) (6) in this system.

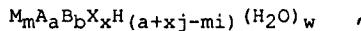
#### DEFINING THE SOLVENT EXTRACTION MODEL

As described previously (1), the organic extractants and the extractable aqueous ions are defined as reactant species by the integers  $y$ ,  $u$ ,  $z$ ,  $v$ ,  $i$  and  $j$  in the following formulae;

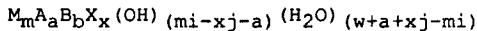


These species, along with  $\text{H}^+$  or  $\text{OH}^-$ , may react to form product species in either phase.

The general formula for product species in the organic phase is



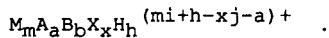
or, if the number of  $\text{H}^+$  ions is negative, the form is



Product species in the organic phase are thus defined by the integers  $m$ ,  $a$ ,  $b$ ,  $x$ , and  $w$ , and, since any of these may be zero,

it is possible to define a wide variety of compositions.

For the aqueous phase, the general formula for product species is



Since an aqueous species may be charged, the number of  $H^+$  (or  $OH^-$  ions if  $h$  is negative) it contains must be specified rather than calculated by charge balance. No waters of hydration are included in the aqueous species. Thus each of the aqueous product species is defined by a set of integers similar to those defining product species in the organic phase except that  $h$  is specified rather than  $w$ . Since any of the integers may be zero, aqueous product species may include complexes of the metal ion with the aqueous anion, complexed or uncomplexed extractant molecules, or unionized aqueous acid.

As described previously (1), a preliminary value must be supplied for the formation constant defined by the balanced chemical reaction producing each product species from the reactants. These constants are among the parameters that may be adjusted to fit the experimental data.

#### ACTIVITY EFFECTS

##### Aqueous Phase

In its present form, SXLSQA accepts the following parameters for estimating aqueous activity coefficients by the Pitzer treatment (2, 3):  $\beta^{(0)}_{CA}$ ,  $\beta^{(1)}_{CA}$ , and  $C\phi_{CA}$  for all pairwise combinations of cations with anions;  $\theta_{CC'}$  and  $\theta_{AA'}$  for all pairwise  $\geq 2$  combinations involving differing cations and anions;  $\psi_{CC'A}$  and  $\psi_{CAA'}$  for all triple combinations involving differing cations and anions with counter ions;  $D_N$  for each neutral species;  $\rho_{NC'}$  and  $\rho_{NA'}$  for pairwise combinations of neutral species with ions other than those defining  $D_N$ ; and  $\lambda_{NN}$  parameters for each pairwise combination of neutral species. Extensive tabulations of the  $\beta$ ,  $C\phi$ ,  $\theta$ , and  $\psi$  parameters have been compiled for many electrolytes and their mixtures by Pitzer (2) and by Harvie et al. (7). All these parameters can be adjusted by the program if desired.

Solvent extraction measurements usually employ the molarity ( $c$ ) scale rather than the molality ( $m$ ) scale used in the Pitzer treatment. The present program will accept data on the  $c$ ,  $m$ , or the mole/kg solution scale, but concentrations other than molality are converted to the  $m$  scale for the calculation of all aqueous activity coefficients and the water activity; the activity coefficients are then converted back to the given concentration scale.

If the  $c$  scale is used, the density of the aqueous solution is required and is estimated by the program. This is done using a method described by Harned and Owen (8) for electrolyte mixtures.

It involves the apparent molar volumes  $v_i$  for each electrolyte, estimated from the Masson Equation,

$$V_i = V_i^0 + S_i C_{i,I}^{1/2} \quad (1)$$

Here  $V_i^0$  and  $S_i$  are user-supplied constants characteristic of the electrolyte;  $C_{i,I}$  denotes the molarity it would have if it were the only solute present at the ionic strength of the aqueous solution. For any nonelectrolytes (neutral species) present in the aqueous phase,  $S_i$  is assumed to be zero. In calculating the density of the solution from these  $V_i$  values, it is assumed that there is zero volume change on mixing solutions of equal ionic strength.

In addition to the extractable ions  $M^{i+}$ ,  $H^+$ ,  $X^{j-}$ , and  $OH^-$ , SXLSQA also assumes the presence of a nonextractable univalent cation  $N^+$ . The components needed for the definition of  $V_i^0$  and  $S_i$  are defined as follows:



and the parameters in the Masson Equation ( $V^0$  and  $S$ ) for these components must be supplied. A good source of values is Millero (9), or they may be readily calculated from density data for solutions of the separate components. If the contribution of aqueous product species to the density of the aqueous phase is likely to be appreciable, then  $V^0$  and  $S$  parameters may be estimated for components defined by them. If the product species is a cation, the component is formed by combination with the anion  $X^{j-}$ ; if it is an anion, the component is formed by combination with the cation  $N^+$ .

For each data point involving an aqueous phase, the user supplies the concentrations of  $M^{i+}$ ,  $X^{j-}$ , and usually  $H^+$  or  $OH^-$ , either before contact with the organic phase or at equilibrium. Since, even in basic solutions,  $H^+$  is employed as a reacting species, its aqueous concentration is established either by input or by calculation. The  $OH^-$  ion concentration is included in the aqueous phase at pH values above 4, and the ion product of water is of course satisfied. The concentration of the remaining aqueous cation  $N^+$  is determined by charge balance. Data for which  $OH^-$  is the only aqueous anion may be included by defining the concentration of  $X^{j-}$  as zero, or data for which there is no inert cation  $N^+$  may be included by equating the equivalents of  $M^{i+}$  with the sum of the equivalents of  $X^{j-}$  and  $OH^-$ .

#### Organic Phase

For the organic phase, regular solutions (4) are assumed with the activity coefficient of the solvent and each neutral solute species given on the mole fraction scale by

$$\ln \gamma_i = \frac{\Delta \bar{H}_i}{RT} = \frac{V_i}{RT} (\delta_i - \bar{\delta})^2 \quad (2)$$

Here  $\Delta H_i$  is the partial molal heat of mixing,  $V_i$  is the molar volume, and  $\delta_i$  is the solubility parameter of a component  $i$ . The quantity  $\bar{\delta}$  is the average solubility parameter for the mixture, weighted by the volume fractions  $\phi$ :

$$\bar{\delta} = \sum_i \phi_i \delta_i \quad (2a)$$

The solubility parameters of the solvent (not adjustable) and all solute species (adjustable), along with their molar volumes must be supplied by the user. A good source of solubility parameters is the handbook by Barton (10). The molar volumes of the product species formed in the organic phase are calculated from their formulae, assuming additivity of the volumes of the reactants involved. In converting from one concentration scale to another, volume additivity is assumed for all components of the solution.

The standard state for each activity coefficient given by Eq. 2 is the (often hypothetical) pure liquid. The activity coefficient of a solute component on the concentration scale of the data,  $g_i$ , is then calculated; e.g., for the molarity scale

$$\ln g_i = \ln \gamma_i + \ln \left( \frac{1000 x_i}{c_i V_s} \right) - \frac{V_i}{RT} (\delta_i - \delta_s)^2 \quad . \quad (3)$$

Here  $x$  and  $c$  denote mole fraction and molarity, respectively, and the subscript  $s$  refers to the solvent. If the scale is molality or moles/kg soln.,  $c$  in this equation is replaced by the appropriate concentration value and  $V_s$  is replaced by the molecular weight of the solvent. As the concentration of all solute species approaches zero,  $g_i$  for each approaches unity.

#### THE PROGRAM

SXLSQA has much the same structure as SXLSQ (1), the main program being a slightly modified version of the general least squares program ORGLS (11). The major changes arise from the need to calculate activities and activity coefficients.

#### Calculation Procedure

In order to calculate the concentrations of all species in both phases for each data point,  $n$  non-linear equations in  $n$  unknowns must be solved. With unit activity coefficients assumed in SXLSQ

(1), just one material balance equation and an unknown concentration was needed for each reactant required by the product species assumed, hence  $n$  was no greater than five, the number of reactants defined by the program -  $M_i^+$ (aq),  $X_j^-$ (aq),  $(HA)_y$ (org),  $B_z$ (org), and  $H^+$ (aq). In the present case, with activity coefficients that depend upon the concentrations of all species present in each phase, it is necessary to include in the set of simultaneous non-linear equations an additional relationship of the form

$$Q = K / G , \quad (4)$$

for each product species assumed;  $Q$  is the equilibrium quotient of concentrations, replacing the equilibrium constant  $K$  in Eq. 2 of ref. (1), and  $G$  is the corresponding quotient of activity coefficients. The number  $n$  of simultaneous equations now equals the number of reactants needed plus the number of product species. In other respects, the calculation procedure is similar to that described previously for SXLSQ (1).

In the material balance condition that must be satisfied for each reactant [Eqs. 12a-c in ref (1)], a transfer of material between the two liquid phases involves a ratio  $R$  related to the concentration scale being used,  $c$ ,  $m$ , or mol/kg soln.,  $R$  is the ratio of the volumes, the solvent weights, or the gross weights of the two phases. Since the transfer of material can produce a change in the volume and the gross weight of both phases, the effect on  $R$  when the  $c$  or mol/kg soln. concentration scales are used has been included in the present program. The resulting correction is trivial unless a large amount of material is transferred between phases.

As was the case for SXLSQ, subroutines are included in SXLSQA for six different kinds of data; 1) the extraction coefficient of the metal ion  $M_i^+$ , 2) the concentration of extracted aqueous anion  $X_j^-$  (previously, the concentration of extracted acid), 3) the total concentration of species in the organic phase, 4) the water content of the organic phase, 5) the heat of mixing of two organic solutions, and 6) the spectral absorbance of the organic phase. The introduction of activity effects produces changes in the way two of these quantities are calculated.

#### Total Concentration of Solute Species

Determined with the vapor pressure osmometer, this quantity now must include the effect of the non-ideal behavior of the reference solute used in such measurements. The quantity derived from measurements with this device is the concentration of the reference solution that produces the same solvent activity as the sample solution, and this is usually taken to be the total concentration of solute species in the sample solution. The activity of solvent in the reference solution is given by

$$a_s = x_s \exp \left[ \frac{V_s}{RT} \phi_r^2 (\delta_s - \delta_r)^2 \right] \quad (5)$$

(the subscript  $r$  denotes the reference solute) and is assumed to equal the activity of solvent calculated by Eq. 2 for the sample solution. The mole fraction of solvent giving the required activity in the reference solution ( $x_s$  in Eq. 5) is determined by iteration. This in turn gives the calculated concentration of reference solute to be compared with the "observed" value.

#### Heat of Mixing of Two Organic Solutions

This quantity is calculated by an expression

$$\Delta H = Y_m - Y_0 - Y_t, \quad (6)$$

in which the subscripts  $m$ ,  $0$ , and  $t$  refer to the mixture, the initial, and the titrant solutions, respectively, and each of the three terms  $Y$  are of the same form. For the molarity concentration scale, this is

$$Y = V/10^3 \left[ \sum_i c_i H_i + RT \sum_j c_j \ln g_j + \phi_s (\delta_s - \bar{\delta})^2 + RT \sum_j c_j \ln (c_j V_s / 10^3 x_j) \right] \quad (6a)$$

As in SXLSQ (1),  $H_i$  is an adjustable parameter representing the heat of the reaction forming a product species. The subscript  $i$  indicates that the summation is over all the product species assumed in the organic solutions. This first term in the brackets in the expression for  $Y$  is the only one included previously; the remaining three terms arise from activity effects. The first of these reflects the effect of solute species activity coefficients, with the index  $j$  indicating that all solute species (reactants as well as products) are included. The next term is the non-ideal contribution of the solvent, and the last is the effect of the concentration scale used. If the molality (or moles/kg soln.) scale is chosen to express each solute concentration  $c$  in Eq. 6a, the volume of solution  $V$  is replaced by the grams of solvent (or of solution), and the molar volume of the solvent ( $V_s$ ) in the last term is replaced by the molecular weight of the solvent.

#### Other Kinds of Data

With the model and its associated parameters defined, SXLSQA calculates for any specified composition of the phases involved, the equilibrium concentration of all species in each phase, their activity coefficients, and the activity of the water and of the organic diluent. These are available through common statements to

user-defined subroutines that can return calculated values of whatever observed quantity is contained in each data point.

#### Recommendations for the Use of SXLSQA

In view of the freedom gained in modeling equilibrium data with adjustable activity parameters, we suggest the following strategies and precautions. The data set should include more than one data type (e.g., distribution and spectral) reflecting both phase composition and speciation. A preliminary analysis can be performed, with unit activity coefficients assumed in the organic phase, to select the major product species and to estimate their formation constants, either with SXLSQA or by graphical methods.

The data may then be modeled in more detail, with activity parameters estimated from published sources for each reactant and postulated product species. Solubility parameters should be viewed with suspicion if they are assigned values high enough to produce activities on the mole fraction scale greater than unity since this would imply that a new phase should appear with the composition of the corresponding species. Minor species identified in the preliminary analysis but eliminated by the inclusion of activity effects should be considered indeterminate from the given data. If more than one set of species remain that can account for the data, then clearly more data are needed. Care should be taken to minimize the number of species included in models being tested. Otherwise, at worst, the calculation may fail because of covariance of the many parameters being adjusted, or, at best, the conclusions drawn will be questionable.

Failure can occur during the calculation of equilibrium concentrations for a data point because one or more of the parameters being adjusted is assigned a value beyond plausible limits. This can be avoided by adjusting parameters a few at a time in the early stages of model testing, and/or by damping the adjustments made by the program in each refinement cycle. In general, the better the fit to the data and the lower the covariance of the parameters being adjusted, the greater the number of parameters that may be refined simultaneously.

#### MODELING EXTRACTION DATA WITH SXLSQA

Some of these points will now be illustrated by modeling the extraction of  $\text{HNO}_3$  and water from aqueous solution by di(2-ethylhexyl)sulfoxide (DEHSO, B) in dodecane at 25°C (Figs. 1 and 2). Previous application of the program to spectral data on the extraction of water (W) alone by DEHSO in dodecane (5) confirmed the formation of the two species BW and  $\text{B}_2\text{W}$ . These were included in all schemes used to test the present nitric acid and water extraction data. The solubility parameter originally reported (5) for the BW species ( $11.0 \text{ cal}^{1/2}, \text{ cm}^{3/2}$ ) produced activities of BW that exceeded unity. This was avoided without appreciably affecting the goodness of fit to the water-extraction data (5) by

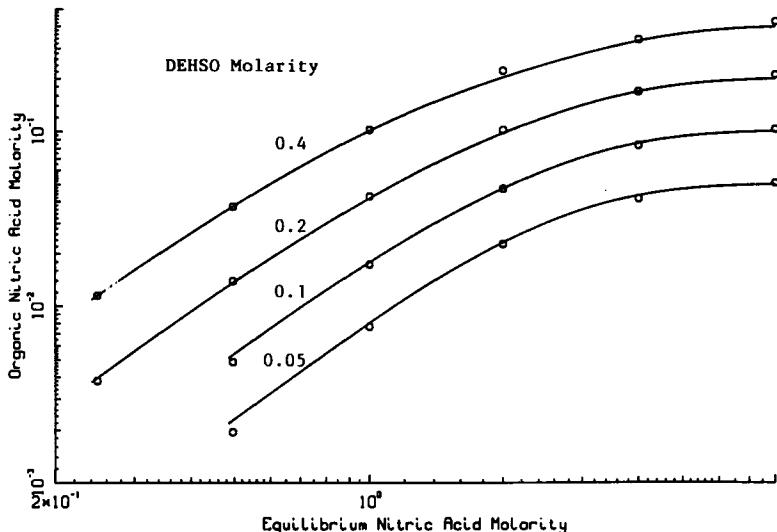


Fig. 1. Equilibrium Organic Phase  $\text{HNO}_3$  Molarity vs. Equilibrium Aqueous  $\text{HNO}_3$  Molarity for Various DEHSO Concentrations. The data were collected by non-aqueous acid-base titrimetry.

reducing this parameter a bit (to  $10.8 \text{ cal}^{1/2} \text{ cm}^{-3/2}$ ) and readjusting the other parameters in the organic phase (Table I). The parameters used to calculate water activities and ion activity coefficients in the aqueous  $\text{HNO}_3$  solutions (Table I) have been reported previously (3). In testing the present data, the parameters in Table I were not varied.

The amount of  $\text{HNO}_3$  ( $\text{HX}$ ) extracted at a given low aqueous concentration of  $\text{HX}$  is roughly proportional to the concentration of  $\text{B}$  (Fig. 1), and it is possible to account for the acid extraction data within 20% assuming the single product species  $\text{BHX}$ . But further inspection of the data indicates one or more additional species must also be formed. At the highest acid concentrations, the ratio of extracted  $\text{HX}$  to DEHSO is somewhat greater than unity suggesting a species containing more  $\text{HX}$  than  $\text{B}$ . At lower acid concentrations, the dependence of  $\text{HNO}_3$  extraction on the DEHSO concentration is in excess of first power, suggesting a species of  $\text{HX}$  containing more than one  $\text{B}$ . Finally, while the amount of water extracted falls at first, it then rises with further increases in the  $\text{HX}$  concentrations (Fig. 2), suggesting a species containing  $\text{B}, \text{HX}$  and  $\text{W}$ .

In the following summary of the numerous schemes of species tested against the data, we will designate each species  $\text{B}_b(\text{HX})_x\text{W}_w$  by a set of concatenated integers  $bwx$ ; thus the three species

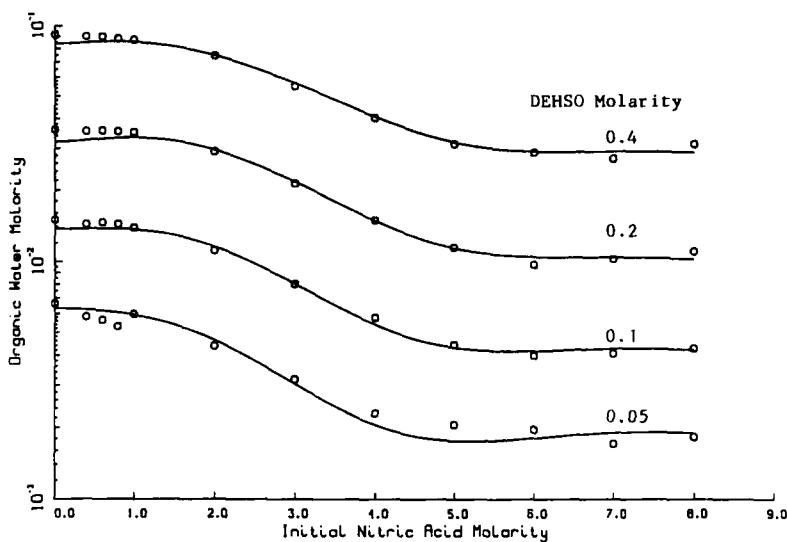


Fig. 2. Equilibrium Organic Phase Excess Water Molarity vs. Initial Aqueous  $\text{HNO}_3$  Molarity for for Various DEHSO Concentrations. Data were collected by Karl-Fischer titrations. The water content of pure dodecane equilibrated at the same  $\text{HNO}_3$  molarity was subtracted from each data point. This blank varied in proportion to the water activity in accordance with Henry's Law (organic water conc. = 0.00264 M at unit water activity).

present in all schemes tested, BW,  $\text{B}_2\text{W}$ , and BHX, are denoted 101, 201, and 110, respectively. As usual, the standard error of fit  $\sigma$  is expressed in terms of the estimated uncertainty in the measurements; i.e., an ideal fit would correspond to  $\sigma = 1$ .

#### Four-Specie Schemes: 101-201-110-bxw

The best schemes of this type included the following as the fourth species (with  $\sigma$  in parentheses): 111 (5.97); 112 (6.12); 221 (6.69); 222 (6.62); 223 (6.96). But the best fit obtainable ( $\sigma = 5.97$  for 111) was not very good. This is not surprising since none of these candidates contains more HX than B. A likely extraction product,  $\text{B}(\text{HX})_2\text{W}_w$  (12w), that could account for both the increasing water content and the excess of HX over B in the organic phase with increasing HX content, gave an even poorer fit; the value of  $\sigma$  decreased from 10.5 to 7.6 as  $w$  was increased from 1 to 8. The parameters given by the best four-specie scheme are listed in Table 2. These tests were sufficient to show that species containing more than two B or two HX groups were not likely to be

Table 1. Parameters Not Varied in Modeling the Extraction of Water and  $\text{HNO}_3$  by DEHSO in Dodecane<sup>a</sup>

Parameter	Interaction or Species	Value
<u>Aqueous Phase</u>		
$\beta(0)$	$\text{H}^+ - \text{NO}_3^-$	0.1119
$\beta(1)$	$\text{H}^+ - \text{NO}_3^-$	0.3686
$C\phi$	$\text{H}^+ - \text{NO}_3^-$	0.00247
D	$\text{HNO}_3 - \text{H}^+$ , $\text{HNO}_3 - \text{NO}_3^-$	0.1796
$\lambda$	$\text{HNO}_3 - \text{HNO}_3$	0.0871
Log K	$\text{HNO}_3$ (Assoc. Const.)	-1.3
<u>Organic Phase</u>		
$\delta$	Dodecane	7.84
$\delta$	B	8.7
Log K	BW	-0.8805
$\delta$	BW	10.8
Log K	$\text{B}_2\text{W}$	-0.6806
$\delta$	$\text{B}_2\text{W}$	10.0

<sup>a</sup> The Pitzer parameters ( $\beta(0)$ ,  $\beta(1)$ ,  $C\phi$ ,  $\theta$ , and  $\lambda$ ) and the parameters D and Log K for undissociated  $\text{HNO}_3$  in the aqueous phase are from ref. (3). The Log K and solubility parameter values ( $\delta$ ,  $\text{cal}^{1/2}\text{cm}^{-3/2}$ ) for the organic phase are slightly changed from ref. (5), as described in the text.

important and that at least one more species was needed to account for the data.

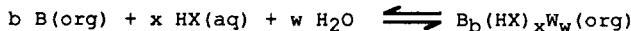
#### Five-Specie Schemes: 101-201-110-b'x'w'-b"x"w"

All possible species containing one or two molecules of B and HX were systematically tested as fourth and fifth members of these schemes. Fits with  $\sigma$  values less than 4 were obtained only when one of these was 211 ( $\text{B}_2\text{HXW}$ ) and the other was 111, 12w, or 221. The best fit ( $\sigma = 2.25$ , Table 2), was found with 211 and 125 as the final two species.

#### Six-Specie Schemes: 101-201-110-211-b'x'w'-b"x"w"

Even with the restriction that b and x be 1 or 2, a thorough search for all possible combinations of three species to be included with 101, 201, and 110 is not practical. Instead, the 211 species found in the best five-specie schemes was included in all

Table 2. Models of Water (W) and  $\text{HNO}_3$  (HX) Extraction by DEHSO (B) in Dodecane<sup>a</sup>



HX-Contg. Species	Log K ( $\sigma_{\text{Log K}}$ )	$\delta$ ( $\sigma_{\delta}$ ) ( $\text{cal}^{1/2}/\text{cm}^{3/2}$ )	$\sigma$
<b>Four Species</b>			
BHX	-0.404 (0.032)	10.80 (0.39)	
BHXW	-1.638 (0.059)	12.19 (0.38)	5.97
<b>Five Species</b>			
BHX	-0.472 (0.013)	10.82 (0.14)	
$\text{B}(\text{HX})_2\text{W}_5$	-3.911 (0.033)	11.39 (0.17)	
$\text{B}_2\text{HXW}$	0.161 (0.039)	9.59 (0.23)	2.25
<b>Six Species</b>			
BHX	-0.481 (0.010)	(10.1)	
$\text{B}(\text{HX})_2\text{W}_5$	-3.913 (0.027)	11.08 (0.17)	
$\text{B}_2\text{HX}$	-0.258 (0.054)	(10.0)	
$\text{B}_2\text{HXW}$	0.128 (0.034)	9.43 (0.20)	1.79

<sup>a</sup>All schemes include the species BW and  $\text{B}_2\text{W}$ . Solubility parameter values in parentheses were not refined. The parameters of the six-specie scheme in this table and those in Table 1 were used to calculate the curves shown in Figs. 1 and 2.

six-specie schemes tested. Fits with  $\sigma$  values less than 2 were obtained when the final three species were 210, 211, and 12w ( $w = 4 - 6$ ); i.e., when the species 210 ( $\text{B}_2\text{HX}$ ) was added to one of the best five-specie schemes. Again the best fit ( $\sigma = 1.64$ ) was found with  $w = 5$ . In both schemes, the freely adjusted solubility parameters of BHX and  $\text{B}(\text{HX})_2\text{W}_5$  were a bit too large and were constrained for the six-member scheme in Table 2 to prevent the corresponding activities on the mole fraction scale from exceeding unity. This increased the value of  $\sigma$  in this case from 1.64 to 1.79. The curves shown in Figs. 1 and 2 were calculated from this scheme with the parameters summarized in Tables 1 and 2.

Considering the schemes in Table II, the species BHX is best established by the data. Though BHGX gives the best four-specie scheme, it yields a poor fit with a solubility parameter so large that the activity of a hypothetical pure phase of this composition would be exceeded over much of the range of the data. The two species  $\text{B}_2\text{HXW}$  and  $\text{B}(\text{HX})_2\text{W}_5$ , both members of the best five- and six-

specie schemes and consistent with our preliminary inspection of the data, seem much more likely as the most important extraction products after BHX. The large number of water molecules associated with  $B(HX)_2W_5$  is surprising, however, and the actual number should be considered uncertain. The five- and six-member schemes differ only in the species  $B_2HX$ , whose relatively uncertain formation constant suggests it to be the most doubtful.

### CONCLUSIONS

The FORTRAN program SXLSQA extends the earlier modeling program SXLSQ for the interpretation of solvent extraction equilibrium data by allowing the estimation of activity effects in both phases and by including complexation in the aqueous phase. Activity coefficients in the aqueous phase are estimated by the Pitzer treatment (2), and activity coefficients in the organic phase are estimated by use of the regular solution model of Hildebrand and Scott (4). This program provides for the first time a tool both for (a) analyzing extraction data over a broad range of conditions not normally subject to detailed interpretation and (b) disentangling the effect of specie formation from that of activity coefficient variation.

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### REFERENCES

1. Baes, Jr., C. F., W. J. McDowell, and S. A. Bryan, *Solv. Extr. Ion Exch.*, **5**, 1 (1987).
2. Pitzer, K. S., *Activity Coefficients in Electrolyte Solutions*, R. M. Pytkowicz, Ed., Vol. 1, CRC Press, Boca Raton, Fl, pp.157-208 (1979).
3. Baes, Jr., C. F., and B. A. Moyer, *Solv. Extr. Ion Exch.*, **6**, 675 (1988).
4. Hildebrand, J. H., and R. L. Scott, *The Solubility of Nonelectrolytes*, 3rd ed., Reinhold Publishing Corp., New York, p. 202 (1950).
5. Moyer, B. A., C. E. Caley, and C. F. Baes, Jr., *Solv. Extr. Ion Exch.*, **6**, 785 (1988).
6. Moyer, B. A., C. F. Baes, Jr., W. J. McDowell, C. E. Caley, and G. N. Case, *Proc. 2nd. Int. Conf. on Sep. Sci. and Technol.*, Oct. 1-4, Hamilton, Ontario, Vol. 1, M. H. I. Baird and S. Vijayan, Eds., Can. Soc. Chem. Eng., Ottawa, Ont., Canada, pp.

173-180, 1989.

7. Harvie, C. E., N. Møller, and J. H. Weare, *Geochem. et Cosmochim. Acta*, **48**, 723 (1984).
8. Harned, H. S., and B. B. Owen, *The Physical Chemistry of Electrolyte Solutions*, Reinhold Publishing Corp., New York, p. 396 (1958).
9. Millero, F. J., *Water and Aqueous Solutions*, R. A. Horne, Ed., Wiley - Interscience, New. York, pp. 519-595 (1972).
10. Barton, A. F. M., *Handbook of Solubility Parameters and Other Cohesion Parameters*, CRC Press, Boca Raton, Fl, (1983).
11. Busing, W. R., and H. A. Levy, "ORGLS, a general FORTRAN Least Squares Program," Oak Ridge National Laboratory Report, ORNL-TM-271, 1962.
12. Nelder, J. A., and R. Mead, *Computer J.*, **7**, 308 (1965).
13. The subroutine SMPLX used in SXLSQA was written by W. R. Busing.