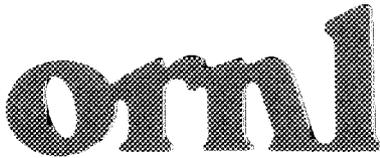




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SXLSQI

A Program for Modelling Solvent Extraction Systems

C. F. Baes, Jr.

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SXLSQI

A PROGRAM FOR MODELLING SOLVENT EXTRACTION SYSTEMS

C. F. Baes, Jr.

Dec. 7, 1998

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1. INTRODUCTION

The program SXLSQI (1998) models solvent extraction systems involving an acidic extractant (HA) and/or a neutral extractant (B). It has evolved from SXLSQA, described briefly by Baes et al. (1990) and SXLSQ (Baes et al. 1987). The most important new feature of SXLSQI is that it permits the formation of ionic species in the nonaqueous phase. Like SXLSQA, it permits the calculation of activity coefficients of species in either phase; permits the extraction of two different cations (M and N) in addition to H^+ , and two different anions (X and Y) in addition to OH^- ; and allows the formation of product species in the aqueous phase.

The following section describes briefly the main program and subroutines of SXLSQI. In subsequent sections, instructions are given for preparing input files containing the data (SXLSQI.DAT) and the model (SXLSQI.PAR) that will be used to fit them. This is followed by a description of the output files produced by the program. Finally, to permit validation of the program, sample input files are listed, followed by the output files they produce.

2. THE PROGRAM

The program, written in FORTRAN 77, consists of a main program whose only function before it calls the first subroutine is to set the size of two arrays to be shared by the subroutines. If, after launching a calculation, one or both of these arrays is found not to be large enough to accommodate the specified model and data set, then the calculation will be terminated with a message indicating the array sizes that are required. It is only necessary to specify larger array sizes in the source code of the main program, recompile, and execute again. The source code for the subroutines contains extensive comment statements describing the various arrays, the entry of the model and data, and the various steps involved in fitting the model to the data. For the purposes of debugging, the source code includes additional print statements that may be invoked by removing the "C" in column 1.

2.1 THE MAIN PROGRAM

The size of two arrays are declared in the program: N of length LGN and S of length LGS, which will contain the arrays that depend on the size of the model and of the data set. It is necessary that the numerical values assigned to dimension N and S in the common statement of this program match the values assigned to LGN and LGS.

2.2 S. ARRAYS

This subroutine is called by the main program. It reads the first line of the file SXLSQI.PAR to determine the size of the model and the first line of the file SXLSQI.DAT to determine the size of the data set. The length of the various arrays that depend on these quantities is determined as is their starting points in the linear arrays N and S. The required lengths of N and S are displayed and the calculation is terminated if the lengths exceed those specified in the main program.

Included in the first line of the file SXLSQI.PAR read by this subroutine is a quantity (SMINS) that sets an upper limit to the residuals of simultaneous nonlinear equations to be solved. If this limit is exceeded because of one or more poor choices for the initial values of the unknown concentrations to be determined by the equation solver (S. HYBRD2), then a slower but surer simplex procedure (S. SMPLX) is employed to improve the estimates of the unknowns and to reduce the residuals to acceptable levels. Also read are the integers MXHCY and NTRY, which place limits on the number of iterations permitted in S. HYBRD2.

2.3 S. WATER

This is a subroutine package called by S. ARRAYS to return needed properties of water at the specified temperature.

2.4 S. READPR

Called by S. ARRAYS, this subroutine reads the remaining lines of the model file SXLSQI.PAR.

2.5 S. READAT

Called by S. ARRAYS, this subroutine reads the remaining lines of the data file SXLSQI.DAT. It determines that various properties specified for each data point are compatible with one another and that charge balance is preserved in the aqueous phase.

2.6 S. CAMWVL

Called by S. ARRAYS, this subroutine calculates molecular weights and molar volumes in the non-aqueous phase of the species specified by the model.

2.7 S. ORGLS

This subroutine, a slightly modified version of the general least-squares program ORGLS written by Busing and Levy (1962), is the final subroutine called by S. ARRAYS. It carries out a specified number of refinement cycles in which selected parameters of the model are adjusted to optimize the fit to the data. When the calculation is finished, control is returned to S. ARRAYS, and then to the main program.

2.8 S. CALC

Called by S. ORGLS, this subroutine returns the calculated value, based on the model, of the observed quantity for a data point. For each refinement cycle performed by S. ORGLS, this subroutine is called first with the model parameters set at their current values, and then once with each adjusted parameter incremented to determine partial derivatives needed in the least-squares calculation.

2.9 S. ORGAC

This subroutine is called by S. CALC to prepare for the calculation of solute-activity coefficients and the solvent activity in the nonaqueous phase, using the treatment of Hildebrand and Scott (1950). Subsequent calls from S. CALC and S. FCN (see Sect. 2.12) are to an entry point E. ENTOAC, which returns activity-coefficient and solvent-activity values for the current composition of the nonaqueous phase.

2.10 S. AQUAC

This subroutine is called by S. CALC to prepare for the calculation of solute activity coefficients and the water activity in the aqueous phase, using the Pitzer (1991) treatment. Subsequent calls from

S. CALC and S. FCN (see Sect. 2.12) are to an entry point E. ENTAAC, which returns activity coefficient and water activity values for the current composition of the aqueous phase.

2.11 S. EST

Called by S. CALC, this subroutine returns initial estimates of the equilibrium concentrations of reactant species (i.e., the extractants and the extractable aqueous ions). If the parameters of the model have changed little from the those of the previous refinement cycle or from the previous call in the present cycle, the concentrations found previously for this point are returned as the initial estimates. Otherwise, estimates for the first data point are based on total reactant concentrations; estimates for subsequent data points are obtained by extrapolation or interpolation from concentrations found for previous data points.

2.12 S. FCN

This subroutine is called by S. CALC to establish the reactant and product species whose concentrations must be determined for the current data point. Subsequent calls from S. CALC or S. HYBRD2 (see Sect. 2.14) are to an entry point E. ENTFCN, which returns for the current values of these concentrations the residuals of an equal number of nonlinear equations based on material balances and equilibrium constants.

2.13 S. SMPLX

This subroutine, written by W. R. Busing (ORNL, ret.), is based on the method of Nelder and Meade (1965). It is called by S. CALC if the initial estimates returned by S. EST are poor ones. It performs a preliminary refinement of the unknown concentrations by a robust iteration procedure.

2.14 S. HYBRD2

This subroutine, a slightly modified version of the IBM Core Library subroutine package HYBRD1, is called by S. CALC and returns the equilibrium concentrations of reactant and product species. It solves the N nonlinear equations in the N unknown concentrations by iteration.

2.15 S. DCALC

This subroutine is called by S. CALC if needed to return the extraction coefficient for a cation or an anion.

2.16 S. TCALC

This subroutine is called by S. CALC if needed to return the total concentration in the nonaqueous phase of an extractable cation or anion.

2.17 S. WCALC

This subroutine is called by S. CALC if needed to return the total concentration of water in the nonaqueous phase.

2.18 S. PCALC

This subroutine is called by S. CALC if needed to return the total concentration of solute species in the nonaqueous phase that would be determined by vapor-pressure osmometry.

2.19 S. HCALC

This subroutine is called by S. CALC if needed to return the heat of mixing of two nonaqueous solutions.

2.20 S. ECALC

This subroutine is called by S. CALC if needed to return the spectral absorbance of the nonaqueous phase at a specified wavelength.

2.21 S. GCALC

This subroutine is called by S. CALC if needed to return the mean activity coefficient of an electrolyte, the osmotic coefficient, or the activity of water in the aqueous phase.

2.22 S. USRCAL

This is a dummy subroutine the user may replace with one or more subroutines to return needed calculated quantities not already provided for. Calls to these subroutines occur in S. CALC when the first two digits on a line of data match a two-digit number assigned by the user to each new subroutine (see Sect. 2.8).

3. INPUT FILE: SXLSQL.DAT

The following is a line-by-line listing of the items to be read from this file. The default (*) format is used in reading input files, and hence it is necessary that the expected number of items appear in each line and any continuation lines that may be needed. If an item is irrelevant, a dummy number must nonetheless be entered for it. Eleven lines precede the listing of the data.

3.1 LINE 1: LTITLE, TC, NO

- Title, containing up to 60 characters enclosed in single quotes.
- Temperature ($^{\circ}\text{C}$).
- The number of data points to be read.

3.2 LINE 2: WS, VS, DS

- The molecular weight of the nonaqueous solvent (g/mol).
- The molar volume of the nonaqueous solvent (cm^3/mol).
- The dielectric constant of the nonaqueous solvent. This value will be needed for the calculation of activity coefficients of any charged species assumed in the nonaqueous phase.

3.3 LINE 3: WR, VR, GOR

- The molecular weight of the reference solute used in vapor-pressure osmometry (VPO), if any (g/mol).
- The molar volume of the reference solute (cm^3/mol).
- The solubility parameter of the reference solute ($\text{cal}^{1/2}\text{cm}^{-3/2}$).

3.4 LINE 4: W(HA), V(HA)

- The molecular weight of the acidic extractant HA (g/mol).
- The molar volume of the acidic extractant HA (cm^3/mol).

3.5 LINE 5: W(B), V(B)

- The molecular weight of the neutral extractant B (g/mol).
- The molar volume of the neutral extractant B (cm^3/mol).

3.6 LINES 6 TO 11: W(I), V(I), V0(I), SV(I)

These six lines contain the following properties of the ions MZ^{M+} , NZ^{N+} , XZ^{X-} , YZ^{Y-} , H^+ , and OH^- , respectively.

- The molecular weight of the ion (g/mol).
- The molar volume of the ion in the nonaqueous phase (cm^3/mol).
- The coefficients in the Masson Equation (Masson, 1929),

$$\phi(I) = V0(I) + SV(I) * SQRT[C(I)] ,$$

giving the apparent molar volume $\phi(I)$ of the ion in the aqueous phase (cm^3/mol) as a function of its molar concentration $C(I)$. For details on how V0 and SV should be assigned, see the section "Apparent molar volumes" in *Notes for SXLSQI* (Baes 1998).

3.7 LINES 12 TO NO+11: NIDT, YO, SIGYO, X(I)....X(10)

The remainder of the file consists of a line, along with any continuation lines that may be needed, for each data point. Thirteen items will be read sequentially for each point.

3.7.1 NIDT

This is a six-digit integer defining various characteristics of a data point.

- The first two digits define the kind of observed quantity YO:
 - 01 The extraction coefficient of M (naq./aq.).
 - 02 The total concentration of M in the nonaqueous phase.
 - 03 The extraction coefficient of N (naq./aq.).
 - 04 The total concentration of N in the nonaqueous phase.
 - 05 The extraction coefficient of X (naq./aq.).
 - 06 The total concentration of X in the nonaqueous phase.
 - 07 The extraction coefficient of Y (naq./aq.).
 - 08 The total concentration of Y in the nonaqueous phase.
 - 10 The total concentration of water in the nonaqueous phase.
 - 11 The log of the extraction coefficient of M (naq./aq.).
 - 12 The log of the total concentration of M in the nonaqueous phase.
 - 13 The log of the extraction coefficient of N (naq./aq.).
 - 14 The log of the total concentration of N in the nonaqueous phase.
 - 15 The log of the extraction coefficient of X (naq./aq.).
 - 16 The log of the total concentration of X in the nonaqueous phase.
 - 17 The log of the extraction coefficient of Y (naq./aq.).
 - 18 The log of the total concentration of Y in the nonaqueous phase.
 - 20 The particle concentration in the nonaqueous phase (from VPO).
 - 30 The heat of mixing of two nonaqueous solutions.
 - 40 The spectral absorbance of the nonaqueous phase (aqueous phase absent).
 - 41 The spectral absorbance of the nonaqueous phase (aqueous phase present).

- 60 The osmotic coefficient of the aqueous phase.
- 61 The activity of water in the aqueous phase.
- 62 The mean activity coefficient of the electrolyte of M and X in the aqueous phase.
- 63 The mean activity coefficient of the electrolyte of M and Y in the aqueous phase.
- 64 The mean activity coefficient of the electrolyte of N and X in the aqueous phase.
- 65 The mean activity coefficient of the electrolyte of N and Y in the aqueous phase.
- 66 The mean activity coefficient of the electrolyte of H and X in the aqueous phase.
- 67 The mean activity coefficient of the electrolyte of H and Y in the aqueous phase.
- 68 The mean activity coefficient of the electrolyte of M and OH in the aqueous phase.
- 69 The mean activity coefficient of the electrolyte of N and OH in the aqueous phase.

The mean activity coefficients are defined in the usual way, with the formula of the electrolyte containing the minimum whole number of cations and anions required to express its stoichiometry; e.g., MX, MX₂, MX₃, M₂X, M₂X₃.

Another data type may be defined if the user appends a subroutine to calculate YO and adds a calling statement where indicated near the end of subroutine CALC.

- The third digit of NIDT indicates the phases present.
 - 0 Only a nonaqueous phase is present.
 - 1 Both nonaqueous and aqueous phases are present.
 - 2 Only an aqueous phase is present.
- The fourth digit of NIDT indicates initial or equilibrium concentrations of each reactant except H⁺.
 - 0 Initial total aqueous concentrations are specified. This value must be assigned if the third digit is 0 or 2; i.e., if only one phase is present.
 - 1 Equilibrium total aqueous concentrations are specified. There is no provision for an equilibrium total concentration of HA or B in the aqueous phase; hence, this option does not permit assumption of an aqueous product species involving A or B.
- The fifth digit of NIDT indicates initial or equilibrium concentrations of H⁺.
 - 0 The initial total aqueous acid (or base) concentration is specified. This value can be assigned only if the fourth digit is 0.
 - 1 The equilibrium total aqueous acid (or base) concentration is specified.
 - >1 The equilibrium concentration of H⁺ (e.g., from pH measurements) is specified. The value of this integer determines the other aqueous reactant whose concentration will be adjusted to establish charge balance in the aqueous phase:
 - 2 = M adjusted
 - 3 = N adjusted
 - 4 = X adjusted
 - 5 = Y adjusted

As indicated above, certain of these digits are determined by values assigned to others. These required values are shown in parentheses in the following table.

Digit No.:	3	4	5
	0	(0)	(0)
	1	1	(≥1)
	2	(0)	(0 or >1)

- The sixth digit of NIDT indicates the concentration scale used for both the nonaqueous and the aqueous phase.
 - mol/L (molarity).
 - mol/kg of solvent (molality).
 - mol/kg of solution.

The program will check the values of digits 3, 4, and 5 that have been supplied. It will note any unacceptable values and will either change them or halt execution.

Regarding the choice of concentration scale (digit 6), as already noted, it will be applied to both phases if two are present for the current point. In addition, if more than one concentration scale is specified within a data set, the program stores the one specified for the first point as the concentration scale upon which the model being tested is defined. For points with a differing concentration scale, all equilibrium constants will be corrected to the new scale.

3.7.2 YO

This is the observed quantity.

3.7.3 SIGYO

This is the +/- uncertainty in YO (in the same units).

3.7.4 X(1)...X(10)

These are the ten independent variables associated with each observation.

- The first seven are:
 - The concentration of A in the nonaqueous phase.
 - The concentration of B in the nonaqueous phase.
 - The concentration of M in the aqueous (or nonaqueous) phase.
 - The concentration of N in the aqueous (or nonaqueous) phase.
 - The concentration of X in the aqueous (or nonaqueous) phase.
 - The concentration of Y in the aqueous (or nonaqueous) phase.
 - The concentration of H⁺ (or OH⁻ if negative) in the aqueous phase.

Nonzero values less than 10⁻¹⁰ assigned to any of the first six concentrations will be read as zero.

If both phases are present, the only nonaqueous reactants are taken to be HA and B, and the aqueous reactants are taken to be the ions. If the total concentration of H⁺ is specified, the given concentration

of an anion will be adjusted as needed to satisfy the charge balance condition. If present, anion Y will be adjusted first. If needed and present, anion X will be adjusted next, followed, if needed and present, by hydroxide. If a charge balance cannot be established for a data point by adjusting anion concentrations, this condition will be noted and the calculation terminated. Charge balance is preserved during the calculation of specie concentrations by maintaining material balances for each reactant in all its forms.

If there is no aqueous phase, X(1) – X(6) are taken to be the total concentrations of A, B, M, N, X, and Y, respectively, in the nonaqueous phase. The charges are balanced by addition of H⁺ or OH⁻ to the phase as needed. X(7) is irrelevant. It is important that the composition of this phase specified by X(1) to X(6) be compatible with the model to be employed by the user. If, for example, a single product species MA₂ is to be assumed, then it is necessary that the corresponding ratio of X(1) to X(3) exceed 2 by a finite amount; otherwise the program will not be able to satisfy simultaneously the requirements of material balance and of finite concentrations of both HA and MA₂.

If the equilibrium concentration of H⁺ is given for a data point, then charge balance will be established during the calculation of the concentrations of aqueous species. As indicated above, this will be done by adjusting the concentration of an aqueous reactant – M, N, X, or Y – specified by the fifth digit of NIDT.

- The next two independent variables are usually:
 - 8 The water activity.
 - 9 The ratio of the amounts of each phase (naq./aq.) by volume of solution, by weight of solvent, or by weight of solution, depending on the concentration scale specified.

X(8) is irrelevant if an aqueous phase is present and activity coefficients are calculated by the Pitzer treatment (Pitzer 1991), since the water activity will be calculated as well. If X(8) = 0, an aqueous phase is present, and unit activity coefficients are specified, then the water activity will also be calculated by the program. If $0 < X(8) \leq 1$ and either an aqueous phase is present with unit activity coefficients specified or the aqueous phase is absent, then X(8) will be adopted as the water activity.

- For heats of mixing data (type 30 above), which are assumed to be generated by a titration procedure, the last two independent variables are:
 - 9 Amount of initial solution (volume of solution, weight of solvent, or weight of solution, depending on the concentration scale).
 - 10 Amount of titrant solution.

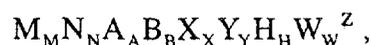
The composition of each solution is indicated on the first two lines of such data, with the absence of the other solution indicated by a 0 entered for X(9) or X(10). Compositions for the remaining heat data are calculated from the amounts and compositions of the solutions being mixed; hence, dummy values of X(1) to X(7) are specified for these points.

- For absorbency data (types 40 and 41), the ninth and tenth independent variables are:
 - 9 A wavelength index (1, 2, 3...) corresponding to the sequence of absorbency parameters specified in the model (see Sect. 4.1).
 - 10 The phase ratio (naq./aq.), by volume of solution, by weight of solvent, or by weight of solution, depending on the concentration scale specified (needed for type 41 data only).

4. INPUT FILE: SXLSQLPAR

4.1 THE MODEL

This file defines the model to be used in fitting the data. A model consists of sets of product species that form in the aqueous phase and in the nonaqueous phase. These species are defined by the subscript integers M, N, A, B, X, Y, H, and w in the formula



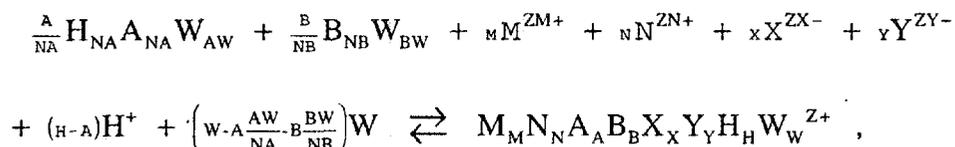
where W is a molecule of water and z is the charge on the species. For aqueous species, w is 0 by definition. Any of the other integers may be assigned a value of 0 and any number of species can be specified in either phase. If H is negative, then OH⁻ ion replaces H⁺ ion in that formula.

Unlike previous versions of this program, in SXLSQI the charge z on a product species in the nonaqueous phase need not be zero. If, however, charged species are assumed, at least one of positive charge and one of negative charge must be included in the model to permit charge neutrality in the nonaqueous phase.

All product species in either phase are formed from reactant species defined by the subscript integers NA, AW, NB, and BW, and the ion charges ZM, ZN, ZX, and ZY in the formulae



The formation constant (K) for each product species in the aqueous phase and for each uncharged product species in the nonaqueous phase is defined by a chemical reaction that produces one molecule of that species from the reactant species defined by these integers, and from H⁺ and H₂O. Thus the formation reaction for an aqueous or a neutral nonaqueous product species is of the form



and the expression for K assumed by the program is

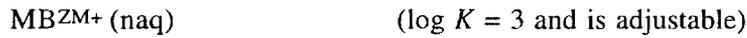
$$K = \frac{[M_M N_N A_A B_B X_X Y_Y H_H W_W^{Z+}]}{[H_{NA} A_{NA} W_{AW}]^{\frac{A}{NA}} [B_{NB} W_{BW}]^{\frac{B}{NB}} [M^{ZM+}]^M [N^{ZN+}]^N [X^{ZX-}]^X [Y^{ZY-}]^Y [H^+]^{(H-A)}} \times \frac{Q_g}{a_w^{\left(W-A \frac{AW}{NA} - B \frac{BW}{NB} \right)}}.$$

The reactants HA and B are assumed to be in the nonaqueous phase, and the reactant ions M^{ZM+}, N^{ZN+}, X^{ZX-}, Y^{ZY-}, and H⁺ are assumed to be in the aqueous phase. The quotient Q_g contains the activity coefficient of each solute species raised to the appropriate power. If the integer H is negative, then

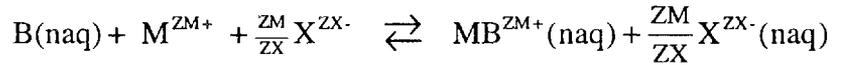
“(OH)_{-H}” replaces “H_H” in the formula of the product species, -H molecules of water are added to the left side of the reaction, and -H is added to the exponent of the water activity (a_w) in the expression for *K*.

For charged product species in the nonaqueous phase, the formation reaction is written in analogous fashion but includes, in addition to *one* ionic product species on the right side, an *equivalent* amount of a second product ion that has been designated as the *reference* ion by assigning it a *fixed* log *K* value of zero. If the reference ion is of opposite charge, it is placed on the right side of the formation reaction to balance the charges in the nonaqueous phase; if it is of the same charge type, it is placed on the left side of the formation reaction to balance the charges in the nonaqueous phase. The following example illustrates this formalism.

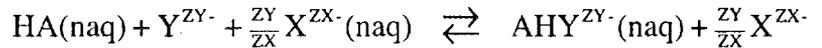
If one assumes the following charged nonaqueous product species,



and if the reactants HA and B in the nonaqueous phase are present as unhydrated monomers, then the resulting formation reaction for which log *K* = 3 is



and the formation reaction for which log *k* is 5 is



Thus, if *n* charged species are assumed in the nonaqueous phase (*n* must be ≥ 2), then there will be *n*-1 independent reactions defining their formation. The user may choose any one such species by assigning to it a fixed log *K* of zero, to define the formation reactions for the others.

4.2 ACTIVITY COEFFICIENTS

The file includes solubility parameters for the solvent and solute species in the nonaqueous phase needed for the calculation of activity coefficients by the treatment of Hildebrand and Scott (1950). It also includes the following parameters for calculating aqueous activity coefficients by the Pitzer (1991) treatment:

$$\begin{array}{l}
B^{(0)}_{CA}; \quad B^{(1)}_{CA}; \quad B^{(2)}_{CA}; \quad C^{\Phi}_{CA}; \quad \alpha^{(1)}_{CA}; \quad \alpha^{(2)}_{CA}; \\
\Theta_{CC'}; \quad \Theta_{AA'}; \quad \Psi_{CC'A}; \quad \Psi_{CAA'}; \\
D_N; \quad \rho_{NC'}; \quad \rho_{NA'}; \quad \lambda_{NN}.
\end{array}$$

Where the subscripts CA denote binary interactions between cations and anions; CC' and AA' denote binary interactions between different kinds of cations and between different kinds of anions, respectively; CC'A and CAA' denote the corresponding ternary interactions involving a counterion; N denotes binary interactions of a neutral species with a selected cation and a selected anion; NC' and NA' denote other binary interactions of a neutral species with ions; NN denote binary interactions involving only neutral species. (The quantities D and ρ were defined in Baes and Moyer 1988).

4.3 LINE 1: MODEL PARAMETERS

This is the first of a line-by-line listing of the quantities to be entered. Continuation lines may again be inserted wherever needed to provide space for all the items specified in a line of the file.

Fifteen quantities, all but one being integers, are entered on the first line of the file. Among other things, they determine the size of the model and the sequence of quantities to be read:

- **NSO.** The number of product species formed in the nonaqueous phase.
- **NPH.** A flag indicating a heat parameter is (1) or is not (0) to be read for each product species and for HA and B.
- **NPA.** The number of absorbency parameters to be supplied with each product species.
- **NSA.** The number of product species formed in the aqueous phase.
- **NIO.** A flag indicating that solute activity coefficients in the nonaqueous phase are to be calculated (0) or set to unity (1).
- **NIA.** A flag indicating that solute activity coefficients in the aqueous phase are to be calculated (0) or set to unity (1).
- **NUM.** A flag indicating that effects of unsymmetrical mixing of aqueous ions will be (1) or will not be (0) included in the calculation of activity coefficients.
- **NCA.** The number of aqueous cations present, including any aqueous product species formed.
- **NAN.** The number of aqueous anions present, including any aqueous product species formed.
- **NNU.** The number of neutral product species formed in the aqueous phase.
- **NUP.** The number of user-defined adjustable parameters.
- **SMINS.** A positive value that establishes the procedure to be used in solving sets of nonlinear simultaneous equations. When the residuals of these equations exceed a limit derived from the value of SMINS, a simplex procedure (S.SMPLX) is used to reduce the residuals below this limit. Thereafter, a more efficient, but less robust, equation solver (S.HYBRD2) is employed. A value of SMINS = 2 is recommended. If problems are encountered with convergence in S.HYBRD2 that cannot be overcome any other way, the value of SMINS can be reduced, although this will increase the computation time.
- **MXHCY.** In S.HYBRD2, the maximum number of iterations permitted before a calculation is terminated. The recommended value is 1000.

- **NTRY.** In S.HYBRD2, the number of iterations after which a calculation is terminated if the residual of the set of equations to be satisfied is not reduced by at least one per cent. The value of this quantity depends on the number and properties of the equations being solved. It can be as small as 20 or as large as necessary.
- **NC.** The maximum number of refinement cycles to be performed in fitting the data.

4.4 LINE 2: THE NONAQUEOUS REACTANT SPECIES

Four integers define the reactant species of HA and B:

- **NA.** The degree of association of HA.
- **NB.** The degree of association of B.
- **AW.** The number of water molecules in the species of HA.
- **BW.** The number of water molecules in the species of B.

4.5 LINE 3: THE AQUEOUS REACTANT SPECIES

A total of 6+NSA integers specify the charge on the aqueous solutes:

- **ZM.** Charge on cation M.
- **ZN.** Charge on cation N.
- **ZH.** Charge on H⁺ (1).
- **ZX.** Charge on anion X (without sign).
- **ZY.** Charge on anion Y (without sign).
- **ZOH.** Charge on OH⁻ (0 OR 1).
- **ZP(I).** Charge on each of the NSA aqueous product species I (with sign).

If zero is assigned to ZM, ZN, ZX, ZY, or ZOH, the corresponding ion will be assumed absent from the system. A value of 1 should be assigned to ZH since it is assumed by the program always to be present. The values assigned each aqueous product species ZP(I) should correspond to the order and formulae specified in subsequent lines. The total number of cations, anions, and neutral species present in the aqueous phase should correspond to the previously specified values of NCA, NAN, and NNU. (The program will check these values for the required consistency.)

4.6 NSO LINES: THE NONAQUEOUS PRODUCT SPECIES

These lines specify the formula, Log *K*, and any heat and absorbency parameters for each product species formed in the nonaqueous phase.

The first nine entries are integers, any of which may be 0:

- **M.** The number of cations M.
- **N.** The number of cations N.
- **A.** The number of anions of HA.

- **B.** The number of molecules of B.
- **X.** The number of anions X.
- **Y.** The number of anions Y.
- **H.** The number of H⁺ (or, if negative, OH⁻) ions.
- **W.** The number of molecules of water.
- **Z.** The charge. This number will be checked by the program for consistency with the specified formula. If charged species are specified, at least one must have a positive charge and at least one must have a negative charge. In addition, as noted below, one charged species must be assigned a formation constant fixed at $\text{Log } K = 0$.

There are $2 * (1 + \text{NPH} + \text{NPA})$ items remaining on each line and any continuation lines needed to contain them. They are entered as consecutive pairs, the first of each pair being a floating-point number for the array P and the second an integer for the array KI.

The array P is used by the subroutine ORGLS to store parameters that may be refined. The array KI is used to store integers indicating whether or not the corresponding parameter of array P is to be fixed ($\text{KI} = 0$) or refined ($\text{KI} = 1$ to 9). If greater than 1, the value of KI determines the damping factor to be used in the refinement; i.e., the factor by which each change calculated by the least-squares procedure will be reduced. The highest value of KI selected will be assigned by the program to all nonzero KIs before the calculation begins.

The order of P(I) values, each followed by a KI(I) value, on a line is:

- **P(I).** $\text{Log}_{10} K$ for the formation of this product species.
- **P(I+NPH).** The heat parameter assigned to this species if NPH is 1.
- **P(I+NPH+1)...P(I+NPH+NPA).** The NPA absorbency parameters assigned to each species if NPA is greater than 0, ordered to correspond to the indices of wavelength specified by X(9) for data of type 40.

If any charged species are specified in the nonaqueous phase, the program will require that $\text{P(I)} = 0$ and $\text{KI(I)} = 0$ for one of them. This species will be used to define the formation reactions and equilibrium constants for the remaining nonaqueous charged species, as described previously.

4.7 TWO LINES: HEAT AND ABSORBENCY PARAMETERS OF HA AND B

These lines are required only if NPH and/or NPA is greater than 0. They each contain NPH+NPA pairs of P and KI values.

- **P(I).** If NPH is 1, a heat parameter assigned to HA on the first line and to B on the second.
- **P(I+NPH)...P(I+NPH+NPA-1).** If NPA is greater than 0, NPA absorbency parameters assigned to HA on the first line and to B on the second, ordered to correspond to the indices of wavelength specified by X(9) for type 40 data.

4.8 NSA LINES: THE AQUEOUS PRODUCT SPECIES

These lines specify the formula, Log K , and parameters in the Masson Equation for each product species formed in the aqueous phase.

The first eight entries are integers, any of which may be 0:

- **M.** The number of cations M.
- **N.** The number of cations N.
- **A.** The number of anions of HA.
- **B.** The number of molecules of B.
- **X.** The number of anions X.
- **Y.** The number of anions Y.
- **H.** The number of H⁺ (or, if negative, OH⁻) ions.
- **Z.** The charge.

The value of Z has already been specified in the series ZP(I) on line 3 above, and the value read here is not actually used.

- **P(I).** Log K for the formation of this aqueous product species.
- **KI(I).** Flag (0 to 9) indicating whether or not K is to be refined (see above).
- **V0.** Coefficient in the Masson Equation (Sect. 3.6).
- **SV.** Coefficient in the Masson Equation. If the charge on this species is zero, SV is not used.

4.9 THE SOLUBILITY PARAMETERS

These parameters (in the units $\text{cal}^{1/2}\text{cm}^{-3/2}$) are needed to calculate the activity coefficients of species in the nonaqueous phase and the activity of the solvent. If unit activity coefficients have been specified for the nonaqueous phase (NIO = 1), these parameters will not be used, but these lines will still be read.

4.9.1 One Line: The Nonaqueous Solvent

- **GOS.** This quantity is not adjusted.

4.9.2 2+NSO Lines: The Nonaqueous Species

- **P(I), KI(I).** Solubility parameters of the species of HA and B, and then of the NSO product species in the nonaqueous phase. These are entered in the same order as they have been specified on lines above. Each solubility parameter on each of these lines is followed by a refinement integer KI in the range 0 to 9 (see Sect. 4.8).

4.10 ENTERING THE PITZER PARAMETERS

The next lines contain the Pitzer parameters (Pitzer 1991) needed to calculate the activity coefficients of aqueous species and the water activity. If unit activity coefficients have been specified for the aqueous phase (NIA = 1), these parameters will not be used, but the lines will still be read. The number of entries required is determined by the number of cations (NCA), anions (NAN), and neutral species (NNU) present. The order in which they are read is determined from the following sequences:

Cation: MZM+, NZN+, H+, CS1, CS2...

Anions: XZX-, YZY-, OH-, AS1, AS2...

Neutral: NS1, NS2...

Here, CSn, ASn, and NSn denote aqueous product species. Their order in each sequence is assigned according to the order in which they were defined on previous lines. If a reactant ion has been specified to be absent, it is deleted from the sequence. The total number of species in each sequence must correspond to the integers NCA, NAN, and NNU entered on the first line of this file.

4.10.1 NCA*NAN Lines: Cation-Anion Interactions

Each line contains the four adjustable quantities $\beta^{(0)}(I,J)$, $\beta^{(1)}(I,J)$, $\beta^{(2)}(I,J)$, and $C^\phi(I,J)$, each followed by a refinement integer KI:

- P(L),KI(L)...P(L+3),KI(L+3)

There are two additional parameters, $\alpha_1(I,J)$ and $\alpha_2(I,J)$, that are not adjustable:

- ALP(1), ALP(2).

These six parameters correspond to an interaction between a cation I and an anion J. The sequence of the cation-anion indices for successive lines is: I, J = 1,1; 1,2; ... 1,NAN; 2,1; 2,2; ... 2,NAN; ... NCA,1; NCA,2; ... NCA,NAN.

4.10.2 NCA*(NCA-1)*NAN Lines: Cation-Cation-Anion Interactions

If NCA is greater than 1, these lines are arranged in NCA*(NCA-1) groups, each group containing NAN lines. The first line in each group contains the two adjustable quantities $\theta(I,I')$ and $\psi(I,I',J)$, for interactions involving cation I and cation I', each followed by a refinement integer.

- P(L), KI(L), P(L+1), KI(L+1)

The subsequent lines, if any, contain one adjustable quantity, $\psi(I,I',J)$, and its refinement integer:

- P(L+2), KI(L+2)

- $P(L+NAN), KI(L+NAN)$.

The sequence of the cation indices for successive line groups is: $I, I' = 1, 2; 1, 3; \dots 1, NCA; 2, 3; 2, 4; \dots 2, NCA; \dots NCA-1, NCA$. On successive lines within each group, J runs from 1 to NAN .

4.10.3 $NCA * NAN * (NAN-1)$ Lines: Cation-Anion-Anion Interactions

If NAN is greater than 1, the next lines are arranged in $NAN * (NAN-1)$ groups, each group containing NCA lines. The first line in each group contains the two adjustable quantities $\theta(J, J')$ and $\psi(I, J', J)$, for interactions involving anion J and anion J' , each followed by a refinement integer.

- $P(L), KI(L), P(L+1), KI(L+1)$.

The subsequent lines, if any, contain one adjustable quantity, $\psi(I', J, J')$, and its refinement integer.

- $P(L+2), KI(L+2)$
- \vdots
- $P(L+NCA), KI(L+NCA)$

The sequence of the anion indices for successive line groups is: $J, J' = 1, 2; 1, 3; \dots 1, NAN; 2, 3; 2, 4; \dots 2, NAN; \dots NAN-1, NAN$. On successive lines within each group, I runs from 1 to NCA .

4.10.4 $NNU * (NCA + NAN)$ Lines: Neutral-Cation,-Anion Interactions

If NNU is greater than 0, the next lines are arranged in NNU groups, each group containing $NCA + NAN$ lines. The first line in each group contains two adjustable quantities, $D(K)$ and $\rho(K, I)$, and the next $NCA-1$ lines contain single values of $\rho(K, I)$, followed by NAN lines containing single values of $\rho(K, J)$. Each of these adjustable parameters is followed by a refinement integer.

- $P(L), KI(L), P(L+1), KI(L+1)$.
- $P(L+2), KI(L+2)$.
- \vdots
- $P(L+NCA+NAN), KI(L+NCA+NAN)$.

The sequence of the neutral species for successive line groups is: $K = 1, 2, \dots NNU$. Within each group $I = 1, 2, \dots NCA$ followed by $J = 1, 2; \dots NAN$. The parameter $D(K)$ actually represents the binary interaction of a neutral species with a selected cation and a selected anion. These selections are implied by assigning a value of 0 to the corresponding $\rho(K, I)$ and $\rho(K, J)$.

4.10.5 $(NNU * (NNU+1))/2$ lines: Neutral-Neutral Interactions

If NNU is greater than 0, then the next lines each contain the adjustable quantity $\lambda(K, K')$, for a binary interaction involving neutral species.

- $P(L), KI(L)$.

The sequence of indices for successive lines is: $K, K' = 1, 1; 1, 2; \dots 1, NNU; 2, 2; 2, 3; \dots 2, NNU; \dots NNU, NNU$.

4.11 NUP LINES: USER-DEFINED PARAMETERS

Finally, if there are any user-defined parameters ($NUP > 0$), then each NUP line contains one user-defined adjustable parameter $P(I)$, its refinement integer $KI(I)$, and a user-specified increment $DP(I)$, which will be used in any refinement of $P(I)$ by the program.

- **NUP lines: $P(I), KI(I), DP(I)$.**

5. OUTPUT FILES

5.1 SXLSQLLSQ

This file summarizes the course of the calculation. The initial values of the parameters to be refined are listed first, followed by two agreement factors indicating the quality of the fit to the data that they produce. The first, designated $\text{SUM}(W*(O-C)**2)$, is the sum of the squares of the weighted deviations of calculated values from the observed data values. The second, designated $\text{SQRTF}(\text{SUM}(W*(O-C)**2)/(\text{NO}-\text{NV}))$, is the square root of this sum divided by the number of observations less the number of parameters adjusted. Ideally, if the proper uncertainties have been assigned to the observed quantities, a perfect fit should yield a value of unity for this latter quantity.

For each refinement cycle, the adjustment in each parameter is listed along with its estimated uncertainty. If one or more of the adjustments is too large (e.g., if a Log K value is to be changed by more than one log unit), this is noted and all the adjustments are reduced by an appropriate factor. The predicted agreement factors are listed next, followed by the values actually obtained. If changes in the parameters being refined become small enough before the specified number of refinement cycles have been performed, the calculation is terminated. The calculation can also be terminated if a parameter is found to have no detectable effect on the fit to the data (this is reported during the calculation of adjustments in the parameters) or if it has been assigned an unrealistic value, either initially or during a refinement cycle (this usually produces a failure during the calculations for a data point).

After the last refinement cycle has been completed, a matrix is listed that shows the covariance among the parameters that have been adjusted.

5.2 SXLSQLFIT

This file summarizes the fit to the data that has been obtained. Two lines are printed for each data point. The first line contains:

- **I.** Point No.
- **YO.** The observed quantity.
- **YC.** The corresponding calculated value.
- **YO-YC.** The deviation.
- **SIGYO.** The uncertainty in YO.
- **(YO-YC)/SIGYO.** The deviation in multiples of the uncertainty.
- **X(1).** Values of the first independent variables.
- **X(2).** Values of the second independent variable.

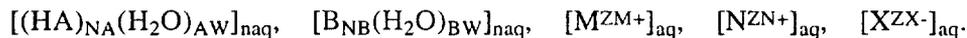
The second line contains:

- **X(3)...X(8).** Values of the third to eighth independent variable.

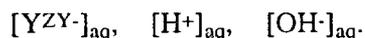
5.3 SXLSQL.SPC

This file reports the equilibrium concentration (in the units specified by the data) of all species present in the two phases for each data point.

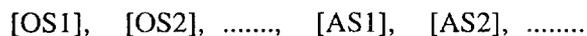
The first line for a data point begins with the point number, followed by the five reactant concentrations:



The second line contains the remaining reactant concentrations:



The remaining lines printed for each point contain the NSO + NSA concentrations of the product species in the nonaqueous phase and in the aqueous phase. Five concentrations are printed per line, in the order used to define the species within each group:



5.4 SXLSQL.GMA

This file reports for each data point: (1) the activity coefficient of all species present in the two phases (on the concentration scale specified by the data); (2) the activity in the nonaqueous phase of the species of the reactants HA and B, and of the NSO product species (excluding any ones with charges), with the pure liquid as the standard state for each; and (3) the activity of water and of the nonaqueous solvent, again with the pure liquid as the standard state for each. The activities of neutral species in the nonaqueous phase relative to their (often hypothetical) pure liquid form are of interest because they may exceed unity if the corresponding solubility parameters have been assigned values that are too large.

The first line for a data point begins with the point number, followed by activity coefficients of the eight reactant species in the same order ($H_{NA}A_{NA}$, B_{NB} , M, N, X, Y, H^+ , and OH^-) as specified for the concentrations of these species in the first two lines of each data point in the file SXLSQL.SPC.

The next line(s) for each point contain the activity coefficients of the NSO + NSA product species. Eight activity coefficients are printed per line, in the same order used for the concentration of product species in SXLSQL.SPC. The last item in this series is the electrostatic factor included in the activity coefficient of a singly charged ion in the nonaqueous phase.

The next line(s) for each point contain activities of the species $(HA)_{NA}(H_2O)_{AW}$, of the species $B_{NB}(H_2O)_{BW}$, and of the NSO product species in the nonaqueous phase. (The activities of any such species that are ions are assigned a dummy value of zero.) Eight activities are printed per line. The order of product species is the same as for the previous line(s).

The last line for each data point contains three quantities; the activity of water, the activity of the nonaqueous solvent, and the electrostatic factor included in the activity of the nonaqueous solvent.

5.5 SXLSQI.MBL

When two phases are present, this file reports calculated quantities related to volume changes and/or weight changes that accompany the transfer of material between phases.

The first line contains:

- **IPT.** The point number.
- **ICN.** The concentration scale (1 = molarity, 2 = molality, 3 = mol/kg soln.)
- **DEN.** Calculated density of the aqueous phase at equilibrium (g/cm^3), printed only if the molarity scale is used.
- **TSAL.** Initial apparent volume or weight of solute in the aqueous phase ($\text{cm}^3/\text{L soln.}$, g/kg water , or g/kg soln.).
- **TVWSA.** Equilibrium apparent volume of solute in the aqueous phase ($\text{cm}^3/\text{L soln.}$), if the molarity scale is used; otherwise, an analogous quantity (g/kg water , or g/kg soln.) is listed.
- **VWPA.** Amount of water produced by formation of aqueous product species ($\text{cm}^3/\text{L soln.}$, g/kg water , or g/kg soln.).
- **RMBA.** Ratio of the amount (volume, weight of contained water, or weight) of the aqueous phase after extraction to that before extraction.

The second line contains:

- **TSOI.** Initial solute content of the nonaqueous phase ($\text{cm}^3/\text{L soln.}$, g/kg solvent , or g/kg soln.).
- **TVWSO.** Volume of solute in the nonaqueous phase at equilibrium ($\text{cm}^3/\text{L soln.}$), if the molarity scale is used; otherwise, an analogous quantity (g/kg water , or g/kg soln.) is listed.
- **VWPO.** Amount of water produced by formation of nonaqueous product species ($\text{cm}^3/\text{L aq.soln.}$, g/kg water , or g/kg aq.soln.).
- **RMBO.** Ratio of the amount (volume, weight of contained solvent, or weight) of the nonaqueous phase after extraction to that before extraction.

5.6 SXLSQI.ITR

This file summarizes iterative calculations carried out to determine species concentrations.

The first line for a data point begins with the point number. This is followed by the value of NCAL, which indicates that the calculation of species concentrations is for two phases (NCAL = 1), for the nonaqueous phase alone (NCAL = 2), or for the aqueous phase alone (NCAL = 3). Next is listed the maximum value permitted for the initial residual of the set of simultaneous nonlinear equations that must be satisfied by S. HYBRD2 to determine specie concentrations. This is followed by the actual value of the initial residual. If it is larger than the permitted value, indicating one or more poor initial estimates of the species concentrations, the initial refinement is carried out using S. SMPLX, which is

slower but more robust. When the residual has been reduced sufficiently, further refinement is carried out by S. HYBRD2.

If S. SMPLX is needed, the next line(s) summarize the course of the S. SMPLX refinement, each line containing the number of refinement cycles carried out and the current value of the residual.

The final line for a data point indicates the number of refinement cycles used by S. HYBRD2.

5.7 SXLSQLREF

This file lists for the convenience of the user final values of parameters that have been adjusted in the calculation. On each line is the number of the parameter in the array P, followed by its value.

6. SAMPLE INPUT/OUTPUT

The following pages contain a set of input files and most of the resulting output files. These serve to illustrate the formats described above and also may be used to validate SXLSQL.

The data set in **SXLSQL.DAT** simulates the extraction of NaNO_3 (MX) from aqueous mixtures of NaNO_3 and HNO_3 by an acidic (HA) and a neutral (B) extractant, both separately and in mixtures in a polar diluent that produces some ionization.

- The first four data points give the logs of the total concentration of nitrate in 0.1 M B after contact with aqueous 0.01 M NaNO_3 containing widely varying concentrations of HNO_3 .
- The next four data points give the logs of the extraction coefficient of Na given by mixtures of 0.1 M HA and 0.1 M B from the same four aqueous mixtures.
- The next four data points give the logs of the extraction coefficient of Na given by 0.2 M HA from the four aqueous mixtures.
- The last four data points give the concentration of water in 0.1 M B after contact with the four aqueous mixtures.

The model defined in **SXLSQL.PAR** specifies that:

- The extractant HA is dimeric and B is monomeric.
- Four product species (BXW_6^- , MBW_6^+ , NBX, and MA_2H) are formed in the nonaqueous phase. (The two charged species, in this hypothetical case, are assumed to be the only hydrated species in order that their presence may be deduced from the water extraction data.)
- One product species, undissociated HNO_3 , is formed in the aqueous phase.
- Three formation constants of the product species in the nonaqueous phase are to be refined. The remaining one for the ion serving as the reference ion is fixed at $\log K = 0$. No other adjustable parameters are to be refined.
- The Pitzer parameters in the aqueous phase are assigned from the literature (Pitzer 1991). Since the concentration scale specified for the data is molarity, the equilibrium constants of the model are defined on that scale. The Pitzer parameters are always defined on the molality scale.

The output file **SXLSQL.LSQ** indicates that the initial values of the formation constants produced an agreement factor $\sigma = 39.1$, signifying a standard deviation nearly forty times the estimated uncertainty of the data. Just two refinement cycles reduced this to 1.19. The value of σ was not reduced significantly by the additional refinement cycles. The changes in the three parameters being adjusted are given after each refinement along with an estimate of the value of σ to be obtained. The agreement between this estimate and that actually obtained improves as convergence is approached. Finally, a covariance matrix is given for the adjusted parameters.

The output file **SXLSQL.FIT** indicates that the largest deviation of a calculated quantity from an observed quantity is 1.7 times the estimated experimental error.

The output file **SXLSQL.SPC** indicates that the concentration of ions in the nonaqueous phase never exceeds a few percent of the total concentration of product species.

The output file **SXLSQL.GMA** lists activity coefficient values for all solute species. It includes, as the last item on the second line for each data point, the electrostatic factor included in the activity coefficient of a singly charged ion in the nonaqueous phase. If any of these items are irrelevant because ions are absent, they are assigned values of unity. The first two items on the third line for each data point are the activities of HA and B, and the next four denote activities of the four nonaqueous product species. These activities refer to the pure liquid phases, which are hypothetical for the product species. Since not even a hypothetical pure liquid is envisioned for ions, two of the activities on this line are listed as zero. The last line for each data point lists the activities of water and of the nonaqueous solvent. The last item on this line indicates that the electrostatic contribution to the latter activity is negligible.

Output file **SXLSQL.MBA** indicates that the volume changes accompanying extraction are negligible, the largest changes amounting to an increase of about 0.03% for the aqueous phase and a decrease of about 0.03% for the nonaqueous phase.

6.1 INPUT FILE: SXLSQI.DAT

```

'MX extn. by HA and B' 25 16
98.96      79.42      10.37
100.0      100.0      10.000
300        330
270        300
22.9898    10        -1.57  1.873
100.0      100.0      0        0
62.0043    20        29.33  0.543
100.0      100.0      0        0
1.0079     0.0        0        0
17.0073    -4.0      -4.04  2.32
161001    -2.34    0.01  0.0  0.1  0.01  0.0  0.015  0.0  0.005  1.0  1.0  0.0
161001    -2.12    0.01  0.0  0.1  0.01  0.0  0.06  0.0  0.05  1.0  1.0  0.0
161001    -2.01    0.01  0.0  0.1  0.01  0.0  0.51  0.0  0.5  1.0  1.0  0.0
161001    -2.01    0.01  0.0  0.1  0.01  0.0  5.01  0.0  5.0  1.0  1.0  0.0
111001     4.43    0.01  0.1  0.1  0.01  0.0  0.015  0.0  0.005  1.0  1.0  0.0
111001     3.80    0.01  0.1  0.1  0.01  0.0  0.06  0.0  0.05  1.0  1.0  0.0
111001     2.83    0.01  0.1  0.1  0.01  0.0  0.51  0.0  0.5  1.0  1.0  0.0
111001     2.38    0.01  0.1  0.1  0.01  0.0  5.01  0.0  5.0  1.0  1.0  0.0
111001     4.78    0.01  0.2  0.0  0.01  0.0  0.015  0.0  0.005  1.0  1.0  0.0
111001     4.16    0.01  0.2  0.0  0.01  0.0  0.06  0.0  0.05  1.0  1.0  0.0
111001     3.15    0.01  0.2  0.0  0.01  0.0  0.51  0.0  0.5  1.0  1.0  0.0
111001     1.66    0.01  0.2  0.0  0.01  0.0  5.01  0.0  5.0  1.0  1.0  0.0
101001    0.00093  0.00001  0.0  0.1  0.01  0.0  0.015  0.0  0.005  1.0  1.0  0.0
101001    0.00123  0.00001  0.0  0.1  0.01  0.0  0.06  0.0  0.05  1.0  1.0  0.0
101001    0.00122  0.00001  0.0  0.1  0.01  0.0  0.51  0.0  0.5  1.0  1.0  0.0
101001    0.000248  0.00001  0.0  0.1  0.01  0.0  5.01  0.0  5.0  1.0  1.0  0.0
*
```

6.2 INPUT FILE: SXLSQI.PAR

```
4 0 0 1 0 0 0 2 1 1 0 2 500 50 5
2 1 0 0
1 0 1 1 0 0 0
0 0 0 1 1 0 0 6 -1 0.0000 0
1 0 0 1 0 0 0 6 1 -1.5000 1
1 0 0 1 1 0 0 0 0 3.5000 1
1 0 2 0 0 0 1 0 0 3.5000 1
0 0 0 0 1 0 1 0 -1.3000 0 34.000 0.0
9.000
10.000 0
9.500 0
10.000 0
9.500 0
9.500 0
10.000 0
0.00479 0 0.20241 0 0.0 0 -0.00027 0 2.0 0.0
0.1119 0 0.3686 0 0.0000 0 0.00247 0 2.0 0.0
-0.03200 0 0.00000 0
0.1796 0 0.00000 0
0.00000 0
0.00000 0
0.0871 0
```

6.3 OUTPUT FILE: SXLSQILLSQ

MX extn. by HA and B

PRINCIPAL COMPONENT ANALYSIS IN CASE OF ERROR

NUMBER OF OBSERVATIONS READ IS 16

NUMBER OF PARAMETERS TO BE VARIED IS 3

STARTING VALUES

I	P(I)	KI(I)	DP(I)
2	-1.50000E+00	1	1.000E-03
3	3.50000E+00	1	1.000E-03
4	3.50000E+00	1	1.000E-03

AGREEMENT FACTORS BASED ON PARAMETERS BEFORE CYCLE 1

SUM(W*(O-C)**2) IS 1.987E+04

SQRTF(SUM(W*(O-C)**2)/(NO-NV)) IS 3.9091E+01

PARAMETERS AFTER LEAST SQUARES CYCLE 1

	OLD	CHANGE	NEW	ERROR
2	-1.50000E+00	-5.06930E-01	-2.00693E+00	3.74127E-02
3	3.50000E+00	-4.85338E-01	3.01466E+00	3.81761E-02
4	3.50000E+00	5.19717E-01	4.01972E+00	1.63103E-02

ESTIMATED AGREEMENT FACTORS BASED ON PARAMETERS CYCLE 1

SUM(W*(O-C)**2) IS 2.234E+02

SQRTF(SUM(W*(O-C)**2)/(NO-NV)) IS 4.1455E+00

AGREEMENT FACTORS BASED ON PARAMETERS BEFORE CYCLE 2

SUM(W*(O-C)**2) IS 7.025E+01

SQRTF(SUM(W*(O-C)**2)/(NO-NV)) IS 2.3246E+00

PARAMETERS AFTER LEAST SQUARES CYCLE 2

	OLD	CHANGE	NEW	ERROR
2	-2.00693E+00	-1.16017E-02	-2.01853E+00	1.01120E-02
3	3.01466E+00	-3.55681E-02	2.97909E+00	1.09175E-02
4	4.01972E+00	-1.64024E-02	4.00331E+00	4.48929E-03

ESTIMATED AGREEMENT FACTORS BASED ON PARAMETERS CYCLE 2

SUM(W*(O-C)**2) IS 1.809E+01
SQRTF(SUM(W*(O-C)**2)/(NO-NV)) IS 1.1798E+00

AGREEMENT FACTORS BASED ON PARAMETERS BEFORE CYCLE 3

SUM(W*(O-C)**2) IS 1.829E+01
SQRTF(SUM(W*(O-C)**2)/(NO-NV)) IS 1.1861E+00

PARAMETERS AFTER LEAST SQUARES CYCLE 3

	OLD	CHANGE	NEW	ERROR
2	-2.01853E+00	4.83245E-04	-2.01805E+00	9.96089E-03
3	2.97909E+00	6.85101E-04	2.97978E+00	1.08593E-02
4	4.00331E+00	-2.18987E-05	4.00329E+00	4.51143E-03

ESTIMATED AGREEMENT FACTORS BASED ON PARAMETERS CYCLE 3

SUM(W*(O-C)**2) IS 1.828E+01
SQRTF(SUM(W*(O-C)**2)/(NO-NV)) IS 1.1859E+00

AGREEMENT FACTORS BASED ON PARAMETERS BEFORE CYCLE 4

SUM(W*(O-C)**2) IS 1.828E+01
SQRTF(SUM(W*(O-C)**2)/(NO-NV)) IS 1.1859E+00

PARAMETERS AFTER LEAST SQUARES CYCLE 4

	OLD	CHANGE	NEW	ERROR
2	-2.01805E+00	-6.13286E-06	-2.01805E+00	9.96338E-03
3	2.97978E+00	-8.64175E-06	2.97977E+00	1.08606E-02
4	4.00329E+00	3.76857E-07	4.00329E+00	4.51147E-03

ESTIMATED AGREEMENT FACTORS BASED ON PARAMETERS CYCLE 4

SUM(W*(O-C)**2) IS 1.828E+01
SQRTF(SUM(W*(O-C)**2)/(NO-NV)) IS 1.1859E+00

AGREEMENT FACTORS BASED ON PARAMETERS BEFORE CYCLE 5

SUM(W*(O-C)**2) IS 1.828E+01
SQRTF(SUM(W*(O-C)**2)/(NO-NV)) IS 1.1859E+00

PARAMETERS AFTER LEAST SQUARES CYCLE 5

	OLD	CHANGE	NEW	ERROR
2	-2.01805E+00	7.85651E-08	-2.01805E+00	9.96335E-03
3	2.97977E+00	1.09680E-07	2.97977E+00	1.08606E-02
4	4.00329E+00	-4.83634E-09	4.00329E+00	4.51147E-03

ESTIMATED AGREEMENT FACTORS BASED ON PARAMETERS CYCLE 5

SUM(W*(O-C)**2) IS 1.828E+01

SQRTF(SUM(W*(O-C)**2)/(NO-NV)) IS 1.1859E+00

AGREEMENT FACTORS BASED ON PARAMETERS BEFORE CYCLE 6

SUM(W*(O-C)**2) IS 1.828E+01

SQRTF(SUM(W*(O-C)**2)/(NO-NV)) IS 1.1859E+00

CORRELATION MATRIX

2	1.0000	.8753	-.0406
3	.0000	1.0000	-.0462
4	.0000	.0000	1.0000

@

6.4 OUTPUT FILE: SXLSQL.FIT

MX extn. by HA and B

PT	YO	YC X(3)	YO-YC X(4)	Sigma X(5)	(YO-YC)/Sg X(6)	X(1) X(7)	X(2) X(8)
1	-2.340E+00	-2.356E+00	1.594E-02	1.000E-02	1.594E+00	0.000E-01	1.000E-01
		1.000E-02	0.000E-01	1.500E-02	0.000E-01	5.000E-03	1.000E+00
2	-2.120E+00	-2.122E+00	1.781E-03	1.000E-02	1.781E-01	0.000E-01	1.000E-01
		1.000E-02	0.000E-01	6.000E-02	0.000E-01	5.000E-02	1.000E+00
3	-2.010E+00	-2.022E+00	1.240E-02	1.000E-02	1.240E+00	0.000E-01	1.000E-01
		1.000E-02	0.000E-01	5.100E-01	0.000E-01	5.000E-01	1.000E+00
4	-2.010E+00	-2.002E+00	-7.918E-03	1.000E-02	-7.918E-01	0.000E-01	1.000E-01
		1.000E-02	0.000E-01	5.010E+00	0.000E-01	5.000E+00	1.000E+00
5	4.430E+00	4.424E+00	6.188E-03	1.000E-02	6.188E-01	1.000E-01	1.000E-01
		1.000E-02	0.000E-01	1.500E-02	0.000E-01	5.000E-03	1.000E+00
6	3.800E+00	3.813E+00	-1.287E-02	1.000E-02	-1.287E+00	1.000E-01	1.000E-01
		1.000E-02	0.000E-01	6.000E-02	0.000E-01	5.000E-02	1.000E+00
7	2.830E+00	2.827E+00	3.066E-03	1.000E-02	3.066E-01	1.000E-01	1.000E-01
		1.000E-02	0.000E-01	5.100E-01	0.000E-01	5.000E-01	1.000E+00
8	2.380E+00	2.391E+00	-1.122E-02	1.000E-02	-1.122E+00	1.000E-01	1.000E-01
		1.000E-02	0.000E-01	5.010E+00	0.000E-01	5.000E+00	1.000E+00
9	4.780E+00	4.776E+00	4.238E-03	1.000E-02	4.238E-01	2.000E-01	0.000E-01
		1.000E-02	0.000E-01	1.500E-02	0.000E-01	5.000E-03	1.000E+00
10	4.160E+00	4.164E+00	-4.399E-03	1.000E-02	-4.399E-01	2.000E-01	0.000E-01
		1.000E-02	0.000E-01	6.000E-02	0.000E-01	5.000E-02	1.000E+00
11	3.150E+00	3.161E+00	-1.051E-02	1.000E-02	-1.051E+00	2.000E-01	0.000E-01
		1.000E-02	0.000E-01	5.100E-01	0.000E-01	5.000E-01	1.000E+00
12	1.660E+00	1.644E+00	1.561E-02	1.000E-02	1.561E+00	2.000E-01	0.000E-01
		1.000E-02	0.000E-01	5.010E+00	0.000E-01	5.000E+00	1.000E+00
13	9.300E-04	9.327E-04	-2.670E-06	1.000E-05	-2.670E-01	0.000E-01	1.000E-01
		1.000E-02	0.000E-01	1.500E-02	0.000E-01	5.000E-03	1.000E+00
14	1.230E-03	1.218E-03	1.220E-05	1.000E-05	1.220E+00	0.000E-01	1.000E-01
		1.000E-02	0.000E-01	6.000E-02	0.000E-01	5.000E-02	1.000E+00
15	1.220E-03	1.233E-03	-1.318E-05	1.000E-05	-1.318E+00	0.000E-01	1.000E-01
		1.000E-02	0.000E-01	5.100E-01	0.000E-01	5.000E-01	1.000E+00
16	2.480E-04	2.308E-04	1.716E-05	1.000E-05	1.716E+00	0.000E-01	1.000E-01
		1.000E-02	0.000E-01	5.010E+00	0.000E-01	5.000E+00	1.000E+00

6.5 OUTPUT FILE: SXLSQL.SPC

MX extn. by HA and B

Pt.	C(HA/NA) C(Y) C(aq.sp) ...	C(B/NB) C(H) C(aq.sp)	C(M) C(OH)	C(N)	C(x)
1	0.0000000E-01	9.5503229E-02	5.5940651E-03	0.0000000E-01	1.0592662E-02
	0.0000000E-01	4.9985965E-03	0.0000000E-01		
	7.7722539E-05	7.7722539E-05	4.3284807E-03	0.0000000E-01	2.1494636E-06
2	0.0000000E-01	9.2321609E-02	2.4441991E-03	0.0000000E-01	5.2367905E-02
	0.0000000E-01	4.9923706E-02	0.0000000E-01		
	1.0148369E-04	1.0148369E-04	7.4532469E-03	0.0000000E-01	8.8683016E-05
3	0.0000000E-01	9.0371871E-02	5.0013302E-04	0.0000000E-01	4.9462963E-01
	0.0000000E-01	4.9412950E-01	0.0000000E-01		
	1.0276507E-04	1.0276507E-04	9.3945998E-03	0.0000000E-01	6.0282769E-03
4	0.0000000E-01	8.9998831E-02	4.4883641E-05	0.0000000E-01	4.1527710E+00
	0.0000000E-01	4.1527261E+00	0.0000000E-01		
	1.9236448E-05	1.9236448E-05	9.9329321E-03	0.0000000E-01	8.4896823E-01
5	3.9997466E-02	9.9988241E-02	3.7681538E-07	0.0000000E-01	1.4989858E-02
	0.0000000E-01	1.4989481E-02	0.0000000E-01		
	6.7367182E-07	6.7367182E-07	4.1457444E-07	9.9975352E-03	8.8558423E-06
6	4.0005685E-02	9.9979343E-02	1.5382206E-06	0.0000000E-01	5.9871746E-02
	0.0000000E-01	5.9870208E-02	0.0000000E-01		
	2.5072040E-06	2.5072040E-06	5.6408088E-06	9.9893137E-03	1.1949615E-04
7	4.0338140E-02	9.9644067E-02	1.4872159E-05	0.0000000E-01	5.0343901E-01
	0.0000000E-01	5.0342414E-01	0.0000000E-01		
	1.7888845E-05	1.7888845E-05	3.0960240E-04	9.6565830E-03	6.2399045E-03
8	4.9013995E-02	9.0968795E-02	4.0447786E-05	0.0000000E-01	4.1532071E+00
	0.0000000E-01	4.1531667E+00	0.0000000E-01		
	1.8662033E-05	1.8662033E-05	8.9660440E-03	9.7208624E-04	8.4934371E-01
9	8.9991169E-02	0.0000000E-01	1.6756667E-07	0.0000000E-01	1.4990941E-02
	0.0000000E-01	1.4990774E-02	0.0000000E-01		
	0.0000000E-01	0.0000000E-01	0.0000000E-01	9.9988326E-03	8.8571832E-06
10	8.9991686E-02	0.0000000E-01	6.8474339E-07	0.0000000E-01	5.9879800E-02
	0.0000000E-01	5.9879115E-02	0.0000000E-01		
	0.0000000E-01	0.0000000E-01	0.0000000E-01	9.9983155E-03	1.1952780E-04
11	8.9997911E-02	0.0000000E-01	6.9047788E-06	0.0000000E-01	5.0375114E-01
	0.0000000E-01	5.0374424E-01	0.0000000E-01		
	0.0000000E-01	0.0000000E-01	0.0000000E-01	9.9920967E-03	6.2473336E-03
12	9.0212908E-02	0.0000000E-01	2.2173176E-04	0.0000000E-01	4.1573113E+00
	0.0000000E-01	4.1570895E+00	0.0000000E-01		
	0.0000000E-01	0.0000000E-01	0.0000000E-01	9.7773149E-03	8.5274959E-01
13	0.0000000E-01	9.5503229E-02	5.5940651E-03	0.0000000E-01	1.0592662E-02
	0.0000000E-01	4.9985965E-03	0.0000000E-01		
	7.7722539E-05	7.7722539E-05	4.3284807E-03	0.0000000E-01	2.1494636E-06

14 0.0000000E-01 9.2321609E-02 2.4441991E-03 0.0000000E-01 5.2367905E-02
0.0000000E-01 4.9923706E-02 0.0000000E-01
1.0148369E-04 1.0148369E-04 7.4532469E-03 0.0000000E-01 8.8683016E-05
15 0.0000000E-01 9.0371871E-02 5.0013302E-04 0.0000000E-01 4.9462963E-01
0.0000000E-01 4.9412950E-01 0.0000000E-01
1.0276507E-04 1.0276507E-04 9.3945998E-03 0.0000000E-01 6.0282769E-03
16 0.0000000E-01 8.9998831E-02 4.4883641E-05 0.0000000E-01 4.1527710E+00
0.0000000E-01 4.1527261E+00 0.0000000E-01
1.9236448E-05 1.9236448E-05 9.9329321E-03 0.0000000E-01 8.4896823E-01

6.6 OUTPUT FILE: SXLSQL.GMA

MX extn. by HA and B

Pt.	g(HA/NA) g(masp)...	g(B/NB) g(asp)....	g(M) g(el)	g(N)	g(X)	g(Y)	g(H)	g(OH)
	a(HA/NA) a(H2O)	a(B/NB) a(slv)	a(nasp)...	(These activities refer to the pure liquid standard state)				
			a(slv,el)					
1	1.16302 .89424 0.00E-01 .999630	1.07926 .89871 2.18E-03 .991662	.89731 1.08753 0.00E-01 1.000001	1.00000 1.16569 0.00E-01 0.00E-01	.89988 1.00221 7.61E-05 0.00E-01	1.00000 .83568 0.00E-01 0.00E-01	.90210	1.00000
2	1.16378 .87635 0.00E-01 .998205	1.07961 .88074 2.11E-03 .991660	.80535 1.08791 0.00E-01 1.000001	1.00000 1.16646 0.00E-01 0.00E-01	.82682 1.01106 1.31E-04 0.00E-01	1.00000 .81872 0.00E-01 0.00E-01	.82763	1.00000
3	1.16426 .87563 0.00E-01 .982761	1.07983 .88002 2.07E-03 .991659	.59982 1.08815 0.00E-01 1.000001	1.00000 1.16694 0.00E-01 0.00E-01	.73964 1.11181 1.65E-04 0.00E-01	1.00000 .81789 0.00E-01 0.00E-01	.73975	1.00000
4	1.16443 .97055 0.00E-01 .752902	1.07990 .97542 2.06E-03 .991658	.35636 1.08823 0.00E-01 1.000000	1.00000 1.16712 0.00E-01 0.00E-01	1.75427 3.13312 1.75E-04 0.00E-01	1.00000 .90649 0.00E-01 0.00E-01	1.75429	1.00000
5	1.37817 1.13151 7.41E-05 .999477	1.18549 1.15247 2.51E-03 .986413	.88073 1.20583 0.00E-01 1.000000	1.00000 1.38489 0.00E-01 0.00E-01	.88819 1.00315 8.08E-09 1.69E-05	1.00000 .97990 0.00E-01 0.00E-01	.88819	1.00000
6	1.37817 1.11117 7.41E-05 .997949	1.18549 1.13175 2.51E-03 .986413	.79546 1.20583 0.00E-01 1.000000	1.00000 1.38489 0.00E-01 0.00E-01	.82072 1.01266 1.10E-07 1.69E-05	1.00000 .96229 0.00E-01 0.00E-01	.82072	1.00000
7	1.37822 1.04852 7.47E-05 .982438	1.18551 1.06795 2.50E-03 .986413	.59782 1.20585 0.00E-01 1.000000	1.00000 1.38494 0.00E-01 0.00E-01	.73975 1.11396 6.04E-06 1.64E-05	1.00000 .90802 0.00E-01 0.00E-01	.73975	1.00000
8	1.38000 1.04717 9.09E-05 .752851	1.18622 1.06657 2.29E-03 .986405	.35636 1.20665 0.00E-01 1.000000	1.00000 1.38675 0.00E-01 0.00E-01	1.75464 3.13372 1.75E-04 1.65E-06	1.00000 .90632 0.00E-01 0.00E-01	1.75466	1.00000
9	1.40618 1.05603 1.70E-04 .999477	1.20733 1.08465 0.00E-01 .990405	.88072 1.23029 0.00E-01 1.000000	1.00000 1.41346 0.00E-01 0.00E-01	.88819 1.00315 0.00E-01 0.00E-01	1.00000 1.00000 1.73E-05 0.00E-01	.88819	1.00000
10	1.40618 1.05603	1.20733 1.08465	.79545 1.23029	1.00000 1.41346	.82071 1.01266	1.00000 1.00000	.82071	1.00000

	1.70E-04	0.00E-01	0.00E-01	0.00E-01	0.00E-01	1.73E-05		
	.997949	.990405	1.000000					
11	1.40618	1.20733	.59775	1.00000	.73975	1.00000	.73975	1.00000
	1.05603	1.08465	1.23029	1.41346	1.11404	1.00000		
	1.70E-04	0.00E-01	0.00E-01	0.00E-01	0.00E-01	1.73E-05		
	.982427	.990405	1.000000					
12	1.40616	1.20732	.35637	1.00000	1.75800	1.00000	1.75809	1.00000
	1.05603	1.08464	1.23028	1.41344	3.13936	1.00000		
	1.71E-04	0.00E-01	0.00E-01	0.00E-01	0.00E-01	1.69E-05		
	.752375	.990405	1.000000					
13	1.16302	1.07926	.89731	1.00000	.89988	1.00000	.90210	1.00000
	.89424	.89871	1.08753	1.16569	1.00221	.83568		
	0.00E-01	2.18E-03	0.00E-01	0.00E-01	7.61E-05	0.00E-01		
	.999630	.991662	1.000001					
14	1.16378	1.07961	.80535	1.00000	.82682	1.00000	.82763	1.00000
	.87635	.88074	1.08791	1.16646	1.01106	.81872		
	0.00E-01	2.11E-03	0.00E-01	0.00E-01	1.31E-04	0.00E-01		
	.998205	.991660	1.000001					
15	1.16426	1.07983	.59982	1.00000	.73964	1.00000	.73975	1.00000
	.87563	.88002	1.08815	1.16694	1.11181	.81789		
	0.00E-01	2.07E-03	0.00E-01	0.00E-01	1.65E-04	0.00E-01		
	.982761	.991659	1.000001					
16	1.16443	1.07990	.35636	1.00000	1.75427	1.00000	1.75429	1.00000
	.97055	.97542	1.08823	1.16712	3.13312	.90649		
	0.00E-01	2.06E-03	0.00E-01	0.00E-01	1.75E-04	0.00E-01		
	.752902	.991658	1.000000					

6.7 OUTPUT FILE: SXLSQIMBL

MX extn. by HA and B

IPT	ICN	Den (aq)	TSAI TSOI	TVWSA TVWSO	VWPA VWPO	RMBA RMBO
1	1	.997566	.428 30.000	.304 30.125	.000 -.025	.999851 1.000128
2	1	.998900	1.757 30.000	1.543 30.215	.000 -.033	.999752 1.000222
3	1	1.013780	15.179 30.000	14.901 30.272	.000 -.033	.999685 1.000280
4	1	1.157443	155.541 30.000	155.261 30.289	.000 -.006	.999661 1.000298
5	1	.997584	.428 63.000	.441 63.094	.000 0.000	1.000013 1.000100
6	1	.999096	1.757 63.000	1.768 63.094	.000 -.001	1.000010 1.000100
7	1	1.014067	15.179 63.000	15.172 63.099	.000 -.006	.999987 1.000106
8	1	1.157468	155.541 63.000	155.287 63.261	.000 -.006	.999693 1.000278
9	1	.997584	.428 66.000	.441 66.093	.000 .000	1.000013 1.000100
10	1	.999096	1.757 66.000	1.768 66.093	.000 .000	1.000011 1.000100
11	1	1.014078	15.179 66.000	15.182 66.093	.000 .000	1.000003 1.000100
12	1	1.157702	155.541 66.000	155.531 66.091	.000 .000	.999988 1.000098
13	1	.997566	.428 30.000	.304 30.125	.000 -.025	.999851 1.000128
14	1	.998900	1.757 30.000	1.543 30.215	.000 -.033	.999752 1.000222
15	1	1.013780	15.179 30.000	14.901 30.272	.000 -.033	.999685 1.000280
16	1	1.157443	155.541 30.000	155.261 30.289	.000 -.006	.999661 1.000298

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