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Short Communications

New Types of Input in DISTR. Application of LETAGROP for Analysis of Liquid-liquid Distribution Equilibria Data

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The Letagrop version DISTR [1] has succesfully been used for the analysis of liquid-liquid distribution data.[2-8] The program can be used for data analysis of a four components system $A_pB_qC_rL_t$ in which B represents the component for which the distribution between the two phases, the organic phase and the aqueous phase, is studied and A, C, L are ligands. Usually B represents metal ions and ligand A hydrogen ions. In the DISTR program 4 different types of data input are previously available, namely by specifying *Typ*=1, 2, 3 or 4. We now report the following additional new types of data input for analysis of liquid-liquid distribution equilibria data.

Typ=*5 or 6*. These types of data input may be used for liquid-liquid distribution data for which the volume ratio *V*=(volume phase 1)/(volume phase 0) is given as one of the *ap* values, *i.e.* *V* is given for each experimental point. In the program we denote phase 1 as the organic and phase 0 as the aqueous phase.

As can be seen from the input data of *Typ*=5 or 6 (see Table 1) and *Typ*=1 or 2 (*cf.* Table 2 in Ref. 1), these types treat the same sort of distribution data. However, for *Typ*=1 or 2 the volume ratio *V* is given a constant value for each group of data.

Input data of *Typ*=5 or 6 are thus of more general application since they also can be used for distribution data with constant *V* values. These new types of input data are especially suitable for treating distribution data collected by the AKUFVE technique.[7,8]

Typ= *7 or 8*. These new types of input data may be used for analysis of two-phase potentiometric titration data from a three or four components system. *Typ*=7 is used for the three components system $(H^+)_pB_qC_r$ and *Typ*=8 for the four components system $(H^+)_pB_qC_rL_t$.

A two-phase system of aqueous and organic phase is considered to contain a set of species $(H^+)_pB_qC_rL_t$(org) and $(H^+)_kB_lC_mL_n$(aq) with the reacting components H^+, B, C and L; *e.g.* B= quaternary amine, C=HX an organic acid. In the potentiometric titration either acid solution or alkaline solution is added to the two-phase system and the value of $-\log[H^+]$ in the aqueous phase is measured for each point. Given the values of the total concentration C_B, C_C and C_L and that of the added acid or base with respect to the aqueous phase, $C_i=N_i/V_{aq}$ where N_i is the total moles of component *i*, we can calculate the proton excess over a chosen zero level (I_{exp}). In the titration of a quaternary amine (B) with an acid HX, the proton excess may, *e.g.*, be taken over B(org), HX(aq) and

Table 1. Input for DISTR=LETAGROP version of liquid-liquid distribution equilibria, *Typ*=5, 6, 7, and 8 (*cf.* Ref. 1).

Typ=5 or 6

Data: 14(*Rurik*), text, 9(*Rurik*), *Typ*(5 or 6), 6(*Rurik*), *Ns*, 2(*Nag*), 0(*Nas*), (6 or 7[a] (*Nap*), λ) or (7 or 8[a] (*Nap*), −1, if λ is given as *ap*), τ, $(Np, (\log a, Btot, Ctot, Ltot,^a V, I_0, I_1, (\lambda, \text{if given as } ap))_{Np})_{Ns}$

Day order follows: (see below)

Typ=7 or 8

Data: 14(*Rurik*), text, 9(*Rurik*), *Typ*(7 or 8), 6(*Rurik*), *Ns*, 0(*Nag*), 0(*Nas*), 5 or 6[b](*Nap*), $(Np, (\log a, Btot, Ctot, Ltot,^b V, I_{exp})_{Np})_{Ns}$

Day order follows:

7(*Rurik*), *Nk*, *Nk*, *Nak*(5 or 6[a,b]), $(k, pot, p, q, r, t,^{a,b} fas)_N$, 0, 0, 0, 8(*Rurik*), 2 or 3[a,b] (*Nok*), *stegbyt*, *start*(ln*b*), *tol*(*B*/*Btot*), *start*(ln*c*), *tol*(*C*/*Ctot*), *start*(ln*l*),[c,d] *tol*(*L*/*Ltot*)[a,b] *etc.*

[a] Additional data for *Typ*=6. [b] Additional data for *Typ*=8.

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H_2O. The following mass-balance apply for B, C and L:

$$C_B = b + \sum q[(H^+)_p B_q C_r L_t]_{org} V + \sum l\,[(H^+)_k B_l C_m L_n]_{aq}$$

$$C_C = c + \sum r[(H^+)_p B_q C_r L_t]_{org} V + \sum m[(H^+)_k B_l C_m L_n]_{aq}$$

$$C_L = l + \sum t\,[(H^+)_p B_q C_r L_t]_{org} V + \sum n\,[(H^+)_k B_l C_m L_n]_{aq}$$

Given the values of the equilibrium constants for the formation of the species, $[H^+]$, b, c, l and V(= volume ratio 0/A), we can calculate for each point a calculated proton excess:

$$I_{calc} = h + \sum p[(H^+]_p B_q C_r L_t]_{org} V + \sum k[(H^+)_k B_l C_m L_n]$$

The OH^- ions must be included as a separate complex with the equilibrium constant K_w(= ionization constant of water) and denoted as the species (−1,0,0,0) in *Typ*=7 and as (−1,0,0,0,0) in *Typ*=8. In the program I_{calc} is denoted by I_{Ber}.

We have in the program the choice to minimize the following error-square sums:

Val	*U*, minimized error-square sum
1	$\sum_1^{Np} (\log I_{Ber} - \log I_{Exp})^2$
2	$\sum_1^{Np} (I_{Exp}/I_{Ber} - 1)^2$
3	$\sum_1^{Np} (I_{Exp} - I_{Ber})^2$

Np represents the number of experimental points used for the analysis. The DISTR program with *Typ*=7 or 8 has been tested for the analysis of several two-phase potentiometric titration data.[9] The complete list of the DISTR program is available on request.

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