STUDY OF SOME BINARY INTERACTIONS IN SOLVENT EXTRACTION SYSTEMS EMPLOYING THE METHOD OF CONTINUOUS VARIATIONS

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A rigorous treatment for studying binary interactions in solvent extraction systems by the method of continuous variations has been developed. Employing this method the systems I_2–KI, I_2–NaOH, HCl–TBP, HNO_3–TBP and $HClO_4$–TBP in water–CCl_4 at $35\pm0.1°C$ have been successfully analysed. In all the above systems, excepting HNO_3–TBP, 1:1 interactions take place.

Job's method of continuous variations[1] for studying binary interactions has been most frequently applied to one-phase systems. Assuming validity of the method to two-phase systems, Specker and his co-workers have absorptiometrically determined the composition of a number of extractable complexes[2] including some which form solvates with TBP (tri-n-butyl phosphate)[3-6] in water–organic solvent systems. Recently, Bukata and Marinsky[7] have successfully used the method for identifying complexes in aqueous solutions in equilibrium with solid ion-exchange resins and we have found this method suitable for studying precipitation reactions as well.[8-10] The following rigorous treatment derived for solvent extraction suggests that binary interactions in such systems can be conveniently studied by using a simple modification of the method. With this method we have successfully analysed the systems I_2–KI, I_2–NaOH, HCl–TBP, HNO_3–TBP and $HClO_4$–TBP, in water–CCl_4 at $35\pm0.1°C$.

Theoretical

Let the system consist of two immiscible liquids 1 and 2 and the principal reaction occurring be represented as:

$$A+nB \rightleftharpoons AB_n \qquad (1)$$

for which the equilibrium constant K is given by

$$K = a_{AB_n} \Big/ a_A \cdot a_B^n$$

In the most general case all the three entities A, B and AB_n may partition between the two liquids. Let us now choose a set of conditions such that the product AB_n (P) and A remain mostly confined to phase 1, and B distributes itself freely between 1 and 2 so that the equilibrium (1) is essentially confined to phase 1. Now if equimolar solutions (molarity M) of the reactants A and B are mixed in the proportion (V_T-x) and x ml, the total volume V_T remaining essentially constant throughout, then at equilibrium,

$$C_{A_1} = M(V_T - x) - C_{P_1} - C_{A_2} \qquad (2)$$

$$C_{B_1} = Mx - nC_{P_1} - C_{B_2} \qquad (3)$$

and $$C_{P_1} = K \cdot C_{A_1} \cdot C_{B_1}^n \qquad (4)$$

where concentrations are in millimoles. The activity corrections have been ignored. Since we have already assumed that the component A almost exclusively remains in phase 1, the last term in equation 2 may be equated to zero and the relation is reduced to:

$$C_{A_1} = M(V_T - x) - C_{P_1} \qquad (5)$$

Equation 3 on the other hand can be expressed as:

$$C_{B_1} = Mx - nC_{P_1} - D_B \cdot C_{B_1} \qquad (6)$$

where $D_B = C_{B_2}/C_{B_1} = $ constant.

On differentiating the concentration terms of equations 5, 6 and 4 with respect to x we get the following relations:

$$dC_A/dx = -M - dC_P/dx \qquad (7)$$

$$dC_B/dx = \{M - ndC_P/dx\}/(1+D_B) \qquad (8)$$

and $$dC_P/dx = K \cdot C_B^{n-1}$$

$$\{nC_A \cdot dC_B/dx + C_B \cdot dC_A/dx\} \qquad (9)$$

where all the concentration terms refer to phase 1.

The condition for a maximum or minimum in the plot of C_P against x is $dC_P/dx = 0$. $\qquad (10)$

Therefore from equations 9 and 10,

$$nC_A \cdot dC_B/dx = -C_B \cdot dC_A/dx$$

or $$n = -C_B \cdot dC_A/dx / C_A \cdot dC_B/dx$$

Now employing equations 7 and 8, the above relation reduces to:

$$n = C_B(1+D_B)/C_A.$$

Finally using equation 5 and 6 it can be shown that,

$$n = (Mx-nC_P)/\{M(V_T-x)-C_P\}$$

or $$n = x/(V_T-x) \qquad (11)$$

In order to construct Job's plots we should now choose a suitable physical property of the system which must be a linear function of the concentration of product P.

For the system under discussion,

$$C_{B\ total} = C_{B_1} + C_{B_2} \qquad (12)$$

In absence of any A in the system,

$$C_{B\ total} = C_{B_2}/D_B + C_{B_2} = C_{B_2}(1+1/D_B)$$

Let this particular value of C_{B_2} be termed

$$C_{B_2\ theoretical} = C'_{B_2} \qquad (13)$$

In presence of the component A in the system the actual relation is as follows:

$$C_{B\ total} = nC_{P_1} + C_{B_1\ free} + C_{B_2} = nC_{P_1} + C_{B_2}$$
$$(1+1/D_B) \qquad (14)$$

For the same value of $C_{B\ total}$,

$$C'_{B_2}(1+1/D_B) = nC_{P_1} + C_{B_2}(1+1/D_B)$$

or $$C'_{B_2} - C_{B_2} = nC_{P_1}.D_B/(1+D_B) = Y' \qquad (15)$$

Thus Y', the difference between the calculated and the actual amount of B in phase 2 is directly proportional to the concentration of product P. A plot of $-Y'$ against x should therefore give a Job's type of curve showing a minimum.

By using similar considerations we find that,

$$C_B = C_{B_{total}}.(1+D_B) = C'_{B_1\ theoretical}(1+D_B) \qquad (16)$$

With the help of foregoing relations it can be shown that,

$$C_{B_1} - C'_{B_1} = nC_{P_1}.D_B/(1+D_B) = Y'' \qquad (17)$$

Therefore, a plot of Y'' against x should give a Job's curve showing a maximum from the position of which n may be evaluated in the usual way.

If subscript 1 refers to the aqueous phase and subscript 2 to CCl$_4$ then the systems I$_2$–KI and I$_2$–NaOH, would fulfil the conditions. In the case of mineral acid—TBP systems too the equations will be valid provided subscript 1 refers to the organic and 2 to the aqueous phase.

Experimental

Stock solutions were prepared from B.D.H. Analar solid reagents and acids. Tributyl phosphate (B.D.H. Technical) was purified.[11] Solutions of iodine and TBP were prepared in E. Merck grade (S-free) CCl$_4$.

Distribution coefficients for iodine and mineral acids were first determined in the absence of KI,NaOH or TBP over a range of concentration selected for subsequent experiments and the maximum variation was around $\pm 1.5\%$. Subsequently, equilibration of mixtures containing known amounts of reactants were carried out in the usual way and after phase separation aliquots of aqueous and organic phases were titrated for either I$_2$ with thiosulphate or for acid with alkali solutions standardised previously. In all experiments the aqueous/organic phase volume ratio was 1:1 and all experiments were performed at $35 \pm 0.1°$C.

Results and Discussion

The Systems: I$_2$–KI and I$_2$–NaOH in H$_2$O–CCl$_4$.— In order to examine the reaction between iodine and KI (i.e. I$_2$ and I$^-$) by the proposed method three series of experiments were performed employing 0.115 M solutions and varying the total reactant input from 10 to 20 ml while keeping the total phase volume (organic+aqueous) 50 ml throughout.

The results are given in Fig. 1. In complete agreement with our expectations Job's type of plots could be obtained showing maximum and minimum from the position of which it can be at once concluded that only one 1:1 compound is formed as is well known.[12] The curves for the aqueous phase are better defined and this may be due to the greater certainty in determining iodine titrimetrically in the aqueous phase. The difference between Y' and Y'', which should normally have been zero, may also be ascribed to this
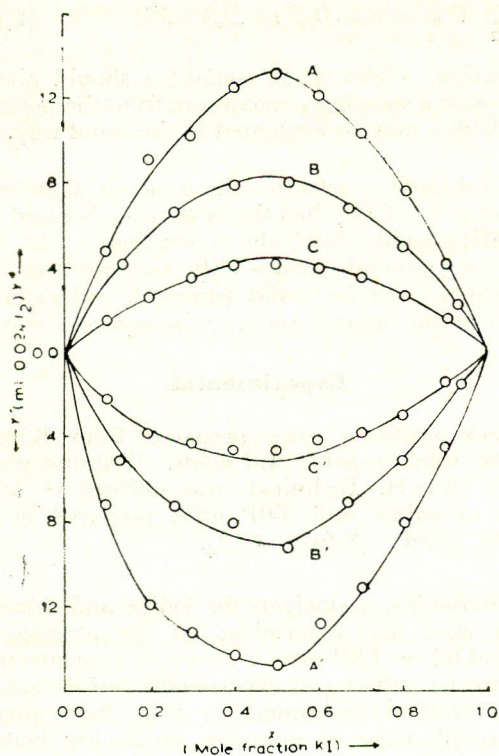
Fig. 1.—Method of continuous variations for the system I$_2$–KI in H$_2$O–CCl$_4$. A–A': Total concentration of I$_2$+KI solution 20 ml of 0.115m. B–B': Total concentration of I$_2$+KI solution 15 ml of 0.115m.C–C': Total concentration of I$_2$+KI solution 10 ml of 0.115m.

Fig. 2.—Method of continuous variations for the system I$_2$–NaOH in H$_2$O–CCl$_4$. A–A': Total concentration of I$_2$+NaOH solution 15 ml of 0.102M B–B': Total concentration of I$_2$+NaOH solution 10 ml of 0.102M.

behaviour. With variation in reactant concentrations the steepness of the curves varies, showing the influence of dilution on the dissociation of the product.

The reaction between I$_2$ and NaOH (i.e. I$_2$ and OH$^-$) was studied employing 0.102M solutions and the total reactant input was varied between 10 and 15 ml only. Results are given in Fig. 2. In this system as well, satisfactory Job's type plots could be obtained showing formation of a 1:1 compound (NaOI) as expected. Therefore, there can be no significant formation of iodate and iodine due to disproportionation of hypoiodite, under the experimental conditions. The first portion of the curves (for the CCl$_4$ phase) especially for higher concentrations is rather ill defined. This may be due to partition of free HI formed (NaOH/I$_2$ < 1) disturbing the overall equilibrium, and also due to the influence of higher reactant concentrations on activity coefficients. There is again a difference between Y' and Y'' which should have been equal in magnitude. Nevertheless, maximum and minimum occur at
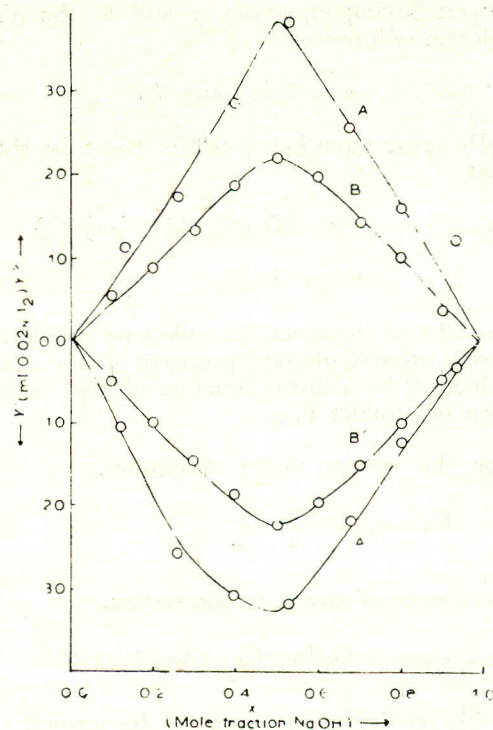
the expected points. The influence of dilution of dissociation of the product is again perceptible.

The System: HCl–TBP, HNO$_3$–TBP and HClO$_4$–TBP in H$_2$O–CCl$_4$.—So far as we know, solvation of mineral acids by TBP during extraction has been studied mainly by the method of dilution.[13] Encouraging results obtained by us during analysis of the foregoing two well-known systems by the proposed method prompted us to examine the solvation of mineral acids by TBP using the same technique.

To study the solvation of HCl by TBP, 1.0M reactant solutions were employed because at lower concentrations extraction of the acid was poor and at higher concentrations it was difficult to prepare stable solutions of the acid; moreover TBP solutions stronger than 3.6M in CCl$_4$ could not be prepared. Even for 1.0M solutions KCl (2.5 ml, 4M aq. in each experiment) had to be used to enhance the extraction of the acid into the organic phase. The total reactant input was varied between 20 and 25 ml and all other conditions were similar to those for the foregoing set of experiments.
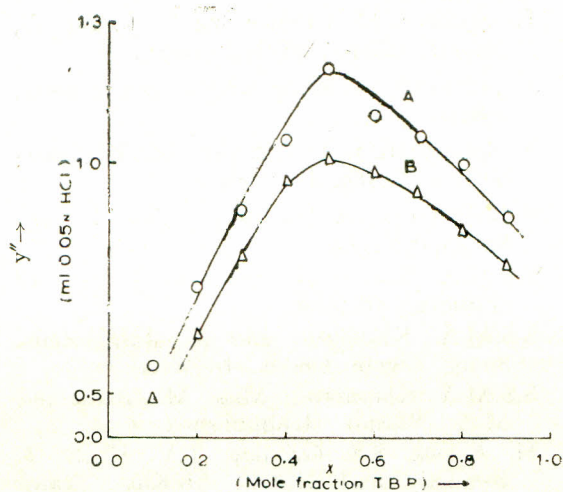
Fig. 3.—Method of continuous variations for the system HCl—TBP in H_2O—CCl_4. A:Total concentration of HCl+TBP solution 25 ml of 1.0M B: Total concentration of HCl+TBP solution 20 ml of 1.0M.

The results are given in Fig. 3. Satisfactory curves could be obtained for only the CCl_4 phase, the data for the aqueous phase being much less accurate because of the small magnitude of -Y'. The same behaviour was also noticed for the other two systems containing HNO_3 and $HClO_4$.

It will be seen that the curves show reasonably good maximum in the region where HCl/TBP ratio is 1, providing evidence for formation of only a monosolvate HCl. TBP. This is in good agreement with previous work on this system employing other techniques.[13,14] The curves obtained by us are better defined in the low TBP concentration regions while for higher concentrations non-ideal extraction behaviour is indicated.

For experiments with HNO_3 solutions, again 1.0M concentrations were used but because of good extraction no 'salting out agent' had to be used. Other conditions were similar to the HCl-TBP system.

The results are given in Fig. 4. Interestingly well-defined curves for the entire concentration region were obtained which show maxima suggesting association of about 1.5 molecules of the acid with each TBP. Kinney and Smutz[15] have recently found that in such systems when HNO_3/ TBP mole ratio in the organic phase is greater than 1, the additional HNO_3 may be present in a solution of the monosolvate (HNO_3. TBP). Alternately, we may consider this behaviour to be arising out of the presence of more than one HNO_3. TBP solvate in the organic phase. The curves in this system are better defined, possibly because of more ideal extraction behaviour.
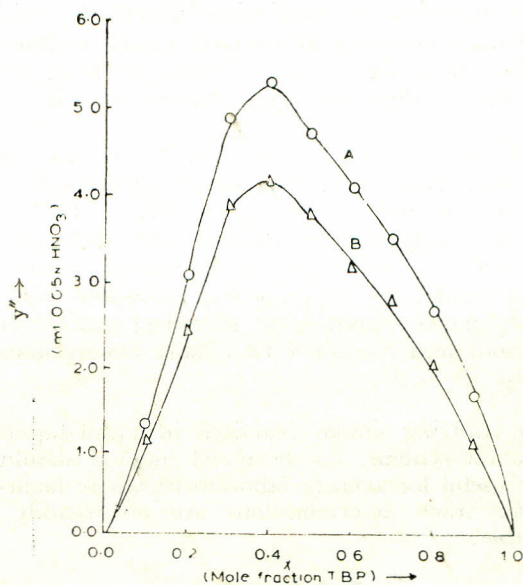
Fig. 4.—Method of continuous variations for the system HNO_3—TBP in H_2O—CCl_4. A:Total concentration of HNO_3 + TBP solution 25 ml of 1.0M. B. Total concentration of HNO_3 +TBP solution 20 ml of 1.0M.
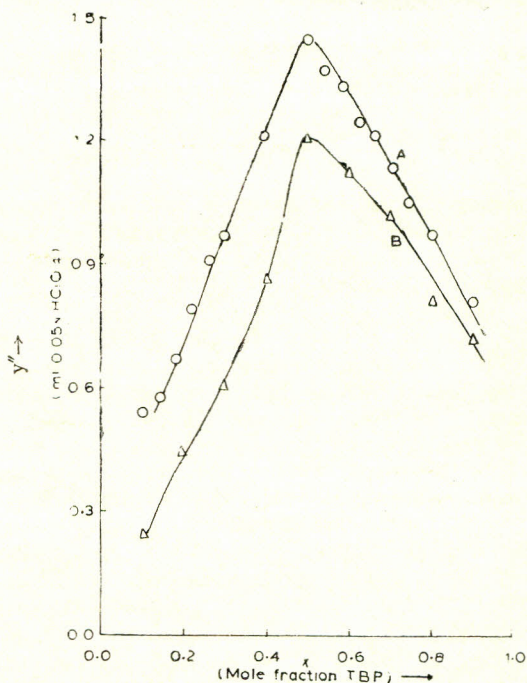
Fig. 5.—Method of continuous variations for the system $HClO_4$—TBP in H_2O—CCl_4. A:Total concentration of $HClO_4$ +TBP solution 25 ml of 1.0MB:Total concentration of $HClO_4$ +TBP solution 20 ml of 1.0M.

For experiments employing perchloric acid solutions, general conditions were similar to those for the other two systems; because of good extraction no 'salting out agent' had to be used.

The results are given in Fig. 5. It will be seen that maxima in the curves correspond to formation of only one solvate i.e. $HClO_4$. TBP as previously suggested by Hesford and McKay,[13] but there is no indication for formation of other solvates under the experimental conditions used. $HClO_4$ shows considerable non-ideal extraction behaviour and resembles HCl more closely than HNO_3.

For studying similar reactions in liquid–liquid extraction systems, the proposed method should prove useful for average laboratories where facilities for trace determinations are not readily available.

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