

An Algebraic Approach to Calculating the Solvent Extraction of Complex Mixtures

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In the usual method of calculating the solvent extraction of complex mixtures it is assumed that the complex mixture behaves like a binary mixture. However, the hypothetical binary composition of the mixture is never explicitly used; rather, an additive property of the mixture is used as an indication of its composition. The calculation must be done graphically on a triangular diagram or its equivalent.

On the assumption that the complex mixture consists of only two hypothetical components, empirical equations have been arrived at relating the distribution coefficients of these two components and of the solvent to the phase compositions. These equations contain three arbitrary constants. By use of the data from a minimum of three simple laboratory batch extractions of a given complex mixture, the three constants, plus the hypothetical binary composition of the original complex mixture, can be determined.

With the equations for the distribution coefficients, the equilibrium curve and tie lines for the system can be calculated. Properties of the raffinates and extracts can be measured and related to the hypothetical binary compositions of these mixtures.

The use of the method is demonstrated by comparing calculated results with laboratory yields and properties. The calculated results show good agreement with the experimental results. Calculations can be carried out not only on the triangular diagram, but by any of the other graphical methods that have been developed for the solvent extraction of binary mixtures. Equally important, calculations can be done analytically, and therefore the use of automatic computers is feasible.

In the calculation of the solvent extraction of complex mixtures from laboratory equilibrium data, it is usually assumed that the complex mixture behaves like a binary mixture. The calculations are performed on a triangular diagram, on which the hypothetical binary composition of the complex mixture is represented by some property of the mixture, usually a property that varies linearly with composition. No attempt is made, however, to express the hypothetical binary composition of the mixture explicitly.

On the contrary, in the algebraic method which is presented here, the hypothetical binary composition of the complex mixture is explicitly derived from laboratory equilibrium data and is used in calculating the solvent extraction of the mixture just as though a true binary were being handled.

This algebraic method of approach has three advantages. First, having explicitly derived a value for the hypothetical binary composition of a complex mixture, one can use whichever of the methods of calculation developed for binary mixtures that may be convenient for the problem at hand. Second, since every relationship in this method can be expressed algebraically, the calculations can be made as precise as desired, for comparative studies. And third, the laboratory data

on a system can be reduced to compact algebraic form.

THEORY

Table 1 shows the nomenclature used in considering a one-stage batch extraction of a complex mixture with a pure solvent. The complex mixture is assumed to be a mixture of hypothetical components 1 and 2, called "soluble" and "insoluble" for convenience. The solvent is component 3. The values of R , E , S , z_1 , and z_2 can all be measured. The problem is to determine values for the hypothetical compositions by use of the measured data.

By writing material balances for the system, one can obtain the following equations:

$$z_1 + z_2 = 1 \quad (1)$$

$$x_1 + x_2 + x_3 = 1 \quad (2)$$

$$y_1 + y_2 + y_3 = 1 \quad (3)$$

$$z_1 = x_1R + y_1E \quad (4)$$

$$z_2 = x_2R + y_2E \quad (5)$$

$$S = x_3R + y_3E \quad (6)$$

TABLE 1. AMOUNTS AND COMPOSITIONS IN A ONE-STAGE BATCH EXTRACTION OF A COMPLEX MIXTURE

Component	Complex mixture		Solvent	
	Fraction	Amount	Fraction	Amount
Soluble	z_1	z_1		
Insoluble	z_2	z_2		
Solvent	—	—	1	S
Total	1	1	1	S

Component	Raffinate		Extract	
	Fraction	Amount	Fraction	Amount
Soluble	x_1	x_1R	y_1	y_1E
Insoluble	x_2	x_2R	y_2	y_2E
Solvent	x_3	x_3R	y_3	y_3E
Total	1	R	1	E

TABLE 2. DERIVATION OF A_3 FROM EXPERIMENTAL DATA ON THE ONE-STAGE BATCH SOLVENT EXTRACTION OF A MIDCONTINENT NEUTRAL OIL WITH NITROBENZENE AT 50°F.

S	Raffinate oil °A.P.I.	Extract oil °A.P.I.	x_3	y_3	$Y =$ $R(1 - x_3)$	E	$\log K_3$	$A_3 = \log K_3/(y_3 - x_3)$
	24.4							
0.7504	—	18.0	0.2757	0.6563	0.7581	0.7038	0.3766	0.989
1.000	27.5	18.1	0.250	0.705	0.672		0.450	0.989
1.500	28.9	18.4	0.223	0.763	0.586		0.534	0.989
2.000	29.5	18.8	0.210	0.800	0.534		0.581	0.985
2.500	30.4	19.3	0.195	0.812	0.461		0.619	1.003
3.000	29.9	19.8	0.205	0.842	0.429		0.614	0.964
4.000	31.1	20.4	0.195	0.859	0.357		0.644	0.970
5.000	31.5	21.6	0.198	0.877	0.304		0.646	0.951
7.000	32.1	22.5	0.152	0.891	0.221		0.768	1.039

Note: All quantities and fractions are by weight.

Written by analogy with the conventional vapor-liquid equilibrium equations, the following equations define equilibrium ratios for the system:

$$y_1 = K_1 x_1 \quad (7)$$

$$y_2 = K_2 x_2 \quad (8)$$

and

$$y_3 = K_3 x_3 \quad (9)$$

In order to relate the K 's to the phase compositions, observed values of K ($= y/x$) were plotted against various functions of composition. It was found that the variation of the K 's could practically all be accounted for by variation in solvent concentrations, and of course at the plait point all three K 's are equal to unity. A number of empirical equations that express this behavior were examined; the following equations give the best agreement with the experimental data:

$$\log K_1 = A_1(y_3 - x_3) \quad (10)$$

$$\log K_2 = A_2(y_3 - x_3) \quad (11)$$

and

$$\log K_3 = A_3(y_3 - x_3) \quad (12)$$

These equations define three constants, A_1 , A_2 , and A_3 , which are fundamental

tions (9) and (12):

$$A_3 = \log (y_3/x_3)/(y_3 - x_3) \quad (13)$$

To find values for A_1 , A_2 , and z_1 , Equation (7) is substituted into Equation (4) to give

$$z_1 = x_1 R + K_1 x_1 E \quad (14)$$

Solving for x_1 yields

$$x_1 = z_1/(R + K_1 E) \quad (15)$$

Similarly, Equations (5) and (8) give

$$x_2 = z_2/(R + K_2 E) \quad (16)$$

Equations (1) and (2) give

$$z_2 = 1 - z_1 \quad (17)$$

and

$$x_1 + x_2 = 1 - x_3 \quad (18)$$

Substituting Equations (15), (16), and (17) into (18) gives

$$z_1/(R + K_1 E) + (1 - z_1)/(R + K_2 E) = 1 - x_3 \quad (19)$$

Solving Equation (19) for z_1 gives

$$z_1 = \frac{1/(R + K_2 E) - (1 - x_3)}{1/(R + K_2 E) - 1/(R + K_1 E)} \quad (20)$$

Equation (20) contains K_1 and K_2 , which are related to the constants A_1 and A_2 through Equations (10) and (11). Substituting data on three isothermal batch extractions of a mixture at different solvent ratios into Equation (20) gives three simultaneous equations from which values can be determined for the three unknowns.

Since A_1 and A_2 enter into Equation (20) nonlinearly, the three simultaneous equations must be solved by trial and error. This procedure can be systematized by using the Newton-Raphson method as applied to simultaneous equations (6). To use this method a function f is defined:

$$f = z_1 - z_1' \quad (21)$$

where

$$z_1' = \frac{1/(R + K_2 E) - (1 - x_3)}{1/(R + K_2 E) - 1/(R + K_1 E)} \quad (22)$$

Values are assumed for z_1 , A_1 , and A_2 . Substituting these values and the data from each batch extraction into Equations (21) and (22) gives three values of f : f_a , f_b , and f_c . Unless the correct values of the unknowns have been assumed, the values of f_a , f_b , and f_c will not all be zero. Better approximations of the unknowns are then obtained by solving the following equations for h , k , and l :

$$(D_1 f_a - D_1 f_b)k + (D_2 f_a - D_2 f_b)l = f_b - f_a \quad (23)$$

$$(D_1 f_a - D_1 f_c)k + (D_2 f_a - D_2 f_c)l = f_c - f_a \quad (24)$$

and

$$h = -f_a - D_1 f_a k - D_2 f_a l \quad (25)$$

to this method. With values for these constants, one can calculate equilibrium phase compositions over the whole range of compositions for the system composed of components 1, 2, and 3.

The value of A_3 can easily be calculated from experimental data by use of Equa-

where

$$D_1 f = \frac{2.303 K_1 E (y_3 - x_3) z_1' / (R + K_1 E)^2}{1/(R + K_2 E) - 1/(R + K_1 E)} \quad (26)$$

and

$$D_2 f = \frac{2.303 K_2 E (y_3 - x_3) (1 - z_1') / (R + K_2 E)^2}{1/(R + K_2 E) - 1/(R + K_1 E)} \quad (27)$$

The improved assumptions for the unknowns are $z_1 + h$, $A_1 + k$, and $A_2 + l$. The procedure is repeated until the values of f_a , f_b , and f_c are zero. Three to five trials are usually required.

Equilibrium phase compositions can then be calculated by use of A_1 , A_2 , and A_3 . Starting with an assumed value of $(y_3 - x_3)$, values for K_1 , K_2 , and K_3 are calculated by use of Equations (10), (11), and (12). Then Equation (9) gives

$$(y_3 - x_3) = K_3 x_3 - x_3 = (K_3 - 1)x_3 \quad (28)$$

from which

$K_3 = 1$, Equations (29) and (32) are indeterminate. Application of L'Hôpital's rule (1) to these equations gives

$$x_3 = y_3 = 0.4343/A_3 \quad (33)$$

and

$$x_1 = y_1 = \frac{x_3(A_2 - A_3) - A_2}{A_1 - A_2} \quad (34)$$

at the plait point.

With values for the equilibrium phase compositions, the value of z_1 can be used to calculate R , E , and S by use of the material-balance equations (1) to (6).

ratio was obtained, as well as the weight yields of extracts and raffinates. The oil content of each extract and raffinate was determined by distilling off the solvent from a sample of the phase in question. Table 2 summarizes these data.

In addition to these data, experimental results from similar studies found in the literature (7 to 10) were used.

DISCUSSION OF RESULTS

Starting with the experimental data in Table 2, the first step is to determine a value of A_3 by use of Equation (13). This calculation is summarized in Table 2. Calculated values of the empirical

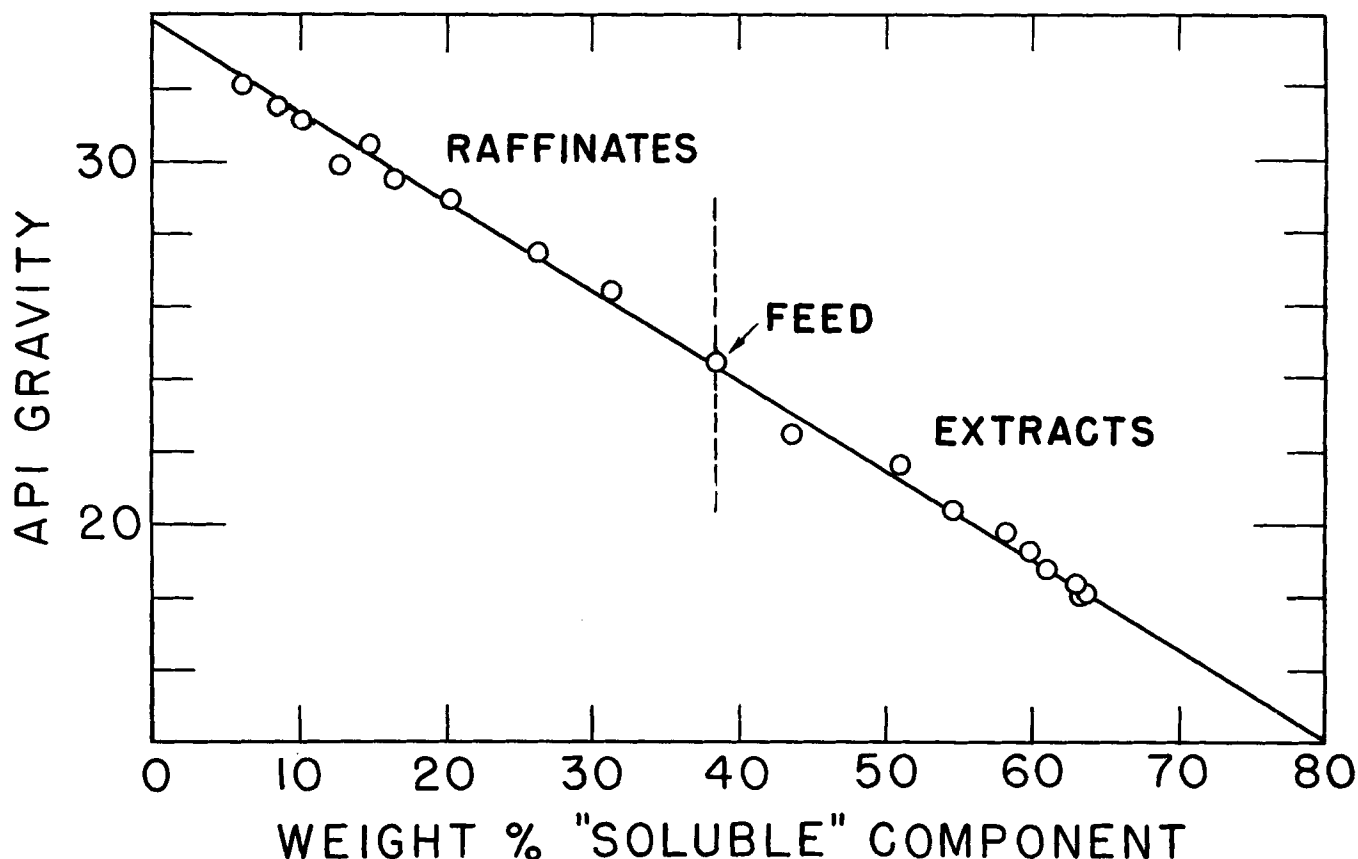


Fig. 1. Gravity vs. composition.

$$x_3 = (y_3 - x_3)/(K_3 - 1) \quad (29)$$

Then

$$y_3 = (y_3 - x_3) + x_3 \quad (30)$$

Substituting Equations (7) and (8) into (3) gives

$$K_1 x_1 + K_2 x_2 = 1 - y_3 \quad (31)$$

Solving Equations (18) and (31) for x_1 gives

$$x_1 = \frac{(1 - y_3) - K_2(1 - x_3)}{K_1 - K_2} \quad (32)$$

Equation (7) gives y_1 . The values of x_2 and y_2 are found by Equations (2) and (3).

At the plait point where $K_1 = K_2 =$

These equations give

$$R = (z_1 y_2 - z_2 y_1)/(x_1 y_2 - x_2 y_1) \quad (35)$$

$$E = (x_1 z_2 - x_2 z_1)/(x_1 y_2 - x_2 y_1) \quad (36)$$

and

$$S = R + E - 1 \quad (37)$$

EXPERIMENTAL DATA

In order to test the theory developed above, experimental data on the solvent extraction of a variety of complex mixtures with different solvents were required. Among the data used was a series of one-stage batch solvent extractions of a Mid-continent neutral oil carried out at a temperature of 50°F. The solvent-to-feed weight

constant A_3 are derived for each batch extraction. Since the values of x_3 for S above 2.5 are plainly erratic, these values were omitted in arriving at the final value for A_3 . Because these erratic values badly affect further calculation, the data were smoothed by use of the value of A_3 just determined. To smooth the data the experimental values of S and $Y = R(1 - x_3)$ were accepted as correct. A value of $(y_3 - x_3)$ was assumed, and x_3 and y_3 were calculated by Equations (29) and (30). Then values were calculated for R and Y by means of the material-balance equations. This procedure was repeated until the calculated value of Y matched the experimental value. The value of E was found by

TABLE 4. COMPARISON OF EXPERIMENTAL AND CALCULATED EXTRACTIONS OF A MIDCONTINENT NEUTRAL OIL WITH NITROBENZENE AT 50°F.

	Treat 1: Multibatch			Treat 2: Multibatch			Treat 3: Countercurrent			Treat 4: Countercurrent		
	Lab.	Calc.	H—N	Lab.	Calc.	H—N	Lab.	Calc.	H—N	Lab.	Calc.	H—N
Stages	2	2	2	4	4	4	2	2	2	4	4	4
Wt. % solvent	100	100	100	100	100	100	100	100	100	100	100	100
Wt. % yield	47.3	46.3	47.4	28.8	29.9	31.0	53.5	50.2	53.7	45.0	43.3	43.4
Raffinate gravity, °A.P.I.	30.5	30.8	30.6	32.8	33.3	32.9	29.6	29.8	29.9	31.2	32.5	32.5
Raffinate solvent, wt. %	20.5	19.1	18.8	20.2	15.9	13.5	20.8	20.7	20.5	19.7	16.9	14.4

	Treat 5: Multibatch			Treat 6: Multibatch			Treat 7: Countercurrent			Average deviation	
	Lab.	Calc.	H—N	Lab.	Calc.	H—N	Lab.	Calc.	H—N	Calc.	H—N
Stages	2	2	2	4	4	4	2	2	2		
Wt. % solvent	75	75	75	75	75	75	75	75	75		
Wt. % yield	54.0	53.0	53.7	34.5	35.5	36.9	57.8	61.6	56.9	1.8	1.1
Raffinate gravity, °A.P.I.	29.3	29.6	29.6	32.2	32.9	32.4	28.6	28.0	28.8	0.6	0.4
Raffinate solvent, wt. %	21.3	21.0	21.1	19.3	16.5	14.7	21.9	23.8	22.7	1.9	2.6

Note: The countercurrent extractions were run by the batch (pseudo) countercurrent extraction method (5).

Equation (37). The smoothed data are given in Table 3.

To determine the values of z_1 , A_1 , and A_2 , the smoothed data at values of $S = 1, 3$, and 5 were chosen. Application of the procedure given above to solve Equation (20) gave these values for the unknowns:

$$z_1 = 0.382$$

$$A_1 = -0.035$$

$$A_2 = -1.570$$

$$A_3 = 0.990$$

obtained by use of a phase diagram which was calculated from the constants A_1 , A_2 , A_3 , and z_1 . The calculated values of A.P.I. gravities were taken from Figure 1. The agreement is very good. The results calculated by the usual Hunter-Nash method (2, 3, 4) are shown too for comparison.

On application of the algebraic method to a variety of systems, it was found that either volume fractions or weight fractions could be used, as long as the same basis was used throughout. A straight line was given by A.P.I. gravity with weight fractions and by specific gravity with volume fractions.

R = raffinate amount per unit amount of feed

S = solvent amount per unit amount of feed

x = raffinate composition

y = extract composition

$Y = R(1 - x_2)$ = yield of refined oil

z = feed composition

Subscripts

a, b, c = each of three simultaneous equations

1 = soluble component

2 = insoluble component

3 = solvent

TABLE 5. SOLVENT-EXTRACTION CONSTANTS FOR VARIOUS SYSTEMS

Complex mixture	Solvent	Temp., °F.	z_1	A_1	A_2	A_3	Ref.
Midcontinent neutral oil	Nitrobenzene	50	0.382 wt.	-0.035	-1.570	0.99	
Light gas oil	Sulfur dioxide	70	0.258 vol.	-0.002	-1.794	1.042	7
Dewaxed Asiatic crude residuum	Propane	70	0.433 wt.	0.696	-1.870	1.023	8
Heavy lube oil base	Phenol	110	0.264 vol.	0.469	-1.628	1.123	9
Heavy lube oil base	Phenol + 5% H ₂ O	110	0.261 vol.	-0.149	-1.835	1.153	9
Heavy lube oil base	Phenol + 10% H ₂ O	110	0.262 vol.	-0.472	-1.988	1.172	9
Stock 2	Furfural	208	0.330 wt.	-0.090	-1.593	0.986	10
Stock 2	Nitrobenzene	32	0.268 wt.	0.817	-1.450	1.066	10
Stock 2	Nitrobenzene	50	0.457 wt.	0.144	-1.620	1.003	10
Stock 2	Aniline	149	0.436 wt.	-0.166	-1.917	0.960	10
Stock 2	Acetone	86	0.788 wt.	-0.802	-2.539	0.973	10

With these values, the phase compositions were calculated for each of the extractions in Table 3. In Figure 1 the solvent-free compositions are shown plotted against the A.P.I. gravities of the oils. The resulting straight-line relation is just what one would expect from a true binary mixture—the Midcontinent neutral oil behaving as if it were a binary mixture of a 9.3°A.P.I. "soluble" component and a 33.8°A.P.I. "insoluble" component. For all systems for which data were available, this straight-line relation between hypothetical composition and a corresponding additive property was found.

Table 4 gives experimental data on four batch cocurrent multistage extractions and three batch countercurrent multistage extractions of the Midcontinent neutral. Also given are the results

Table 5 gives the derived constants for the systems studied. These results show that the hypothetical binary composition of a given mixture is not invariant under all conditions. Although the data are too few to warrant a firm conclusion, the indications are that the hypothetical composition of a given stock will be the same with closely similar solvents, but it will be quite different with a quite different type of solvent.

NOTATION

A = empirical constant

$D = \partial/\partial A$ = differential operator

E = extract amount per unit amount of feed

f = defined function

h, k, l = corrections to assumed values of unknowns

K = equilibrium ratio

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