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Roger F. Sebenik[a]; Brooks M. Sharp[ab]; Morton Smutz[a]
[a] Institute for Atomic Research and Department of Chemical Engineering, Iowa State University, Ames, Iowa [b] McDonnell Aircraft Corporation, St. Louis, Missouri

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Computer Solution of Solvent-Extraction-Cascade Calculations for the Monazite Rare-Earth Nitrates–Nitric Acid–Tributyl Phosphate–Water System*

ROGER F. SEBENIK, BROOKS M. SHARP,† and MORTON SMUTZ

INSTITUTE FOR ATOMIC RESEARCH AND DEPARTMENT OF CHEMICAL ENGINEERING, IOWA STATE UNIVERSITY, AMES, IOWA

Summary

The trial-and-error calculations required to determine the composition and concentration of all streams in an internally fed countercurrent multicomponent solvent-extraction cascade were programmed for an IBM 7074 computer. The method outlined for the monazite rare-earth nitrates–nitric acid–TBP–water system was an adaptation of the Thiele and Geddes technique, in which systematic adjustments of end-stream concentrations were made repetitively for the component most mismatched at the feed stage. The equilibrium data were stored in the memory of the computer in table form, and equilibrium compositions were calculated by an empirical procedure. Although no attempt was made to optimize the matching procedure, rapidly converging solutions were observed.

This paper extends the work of Sharp and Smutz (*12*) on cascade calculations for the five-solute system $La(NO_3)_3$–$Pr(NO_3)_3$–$Nd(NO_3)_3$–$Sm(NO_3)_3$–HNO_3–TBP–H_2O. The problem can be stated as follows: Given (1) the composition, total concentration, and flow rate of an aqueous feed of monazite rare-earth nitrates (with no cerium present), (2) the number of ideal stages in the extract and scrub sections, and (3) the flow rates of the organic and aqueous

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† Present address: McDonnell Aircraft Corporation, St. Louis, Missouri.

solvents, determine the compositions and concentrations of all streams in the cascade at steady state.

The solution presented is an adaptation of the Thiele and Geddes method (*15*) and involves trial-and-error calculations starting with assumed concentrations of all components in one of the exit streams. The problem is solved if the concentrations of all components in the aqueous stream leaving the feed stage are identical when calculated independently stage by stage from the ends of the cascade, and when the over-all material balance is satisfied.

PREVIOUS WORK

Smith (*13*) reviews the techniques of Lewis and Matheson (*9*), Thiele and Geddes (*15*), and Amundson and Pontinen (*1,2*) for distillation calculations and Horton and Franklin (*7*) and Edmister (*4*) for absorption calculations. The available calculation methods for multicomponent extraction are not as common or complete. A graphical approach to quarternary systems has been developed by Powers (*10*). With this method the concentrations of a four-component system are represented on a three-dimensional tetrahedron diagram and the distribution coefficients are plotted versus one-component concentration at constant values of a second. The actual operating lines and tie lines existing within the tetrahedron are then projected onto two of its ternary diagram faces and the graphical constructions are performed on them. The absorption or stripping-factor method, originally developed for absorber and stripper calculations by Kremser (*8*), Brown and Souders (*3*), and Horton and Franklin (*7*), has been applied to multicomponent distillation by Edmister (*4*), and to extraction by Friday (*5*). In a single analytical expression, this method combines the equilibrium and material balance equations for one component, and relates the concentration of that component in a given stage to its concentration in the raffinate. Smith and Brinkley (*14*) proposed a stage-by-stage analytical calculation to solve multicomponent extraction separations. This procedure can be applied to any number of components if the distribution coefficients are available as a function of the phase composition. Neither the Smith and Brinkley technique (*14*) nor the Friday stripping-factor technique (*5*) was used for this work because it has not been possible to express the rare-earth equilibrium calculations in a convenient analytical expression.

In order to obtain a numerical solution in multicomponent

distillation and extraction calculations, the multistage trial-and-error calculations must converge. Although Friday and Smith (*6*) have pointed out that the lack of multicomponent solvent-extraction data has made it difficult to check the rate of convergence of proposed methods, the inherent differences that exist between distillation and extraction processes make extraction calculations more likely to converge rapidly. First, extraction systems normally involve a fixed temperature profile, so that enthalpy balances are not required and the unsettling influence of changing stage temperature from trial to trial is eliminated. Also, because solvent extraction involves two immiscible-liquid phases, the assumption of constant flow rates is more likely to be a safe simplification.

EQUILIBRIUM CALCULATIONS

Sharp and Smutz (*12*) describe the equilibrium calculations in detail and show a sample calculation for predicting the composition of one phase when the other is specified. The procedure is empirical. It involves calculations of the total solute and nitric acid distribution coefficients from the various contributing two-solute systems, calculation of the nitric acid molality and separation factors, and then calculation of the composition and concentration of all components for the unspecified phase. The allowable range of data is from 3 to 16 total molality (nitrate basis) in the aqueous phase and 2 to 4.5 total molality in the organic phase. The results of simulated column runs have shown the method to be a good approximation (*12*).

STAGEWISE CALCULATIONS

The concentration and compositions of streams passing each other between stages in the cascade were determined by material balances. Compositions were expressed in molality units to minimize the errors caused by assuming constant aqueous and organic mass flow rates in each section of the cascade. The resulting errors are small because the TBP is equilibrated with water before use and the solubility of TBP in water is less than 1 gram per liter.

Operating lines for the scrub and extract sections of Fig. 1 are shown in Eqs. (1) and (2), respectively:

$$S_{1'}(\bar{M}_i)_{1'} + R_n(M_i)_n = S_{n+1}(\bar{M}_i)_{n+1} + R_0(M_i)_0 \quad (1)$$

$$S_0(\bar{M}_i)_0 + R_m(M_i)_m = S_{m-1}(\bar{M}_i)_{m-1} + R_1(M_i)_1 \quad (2)$$

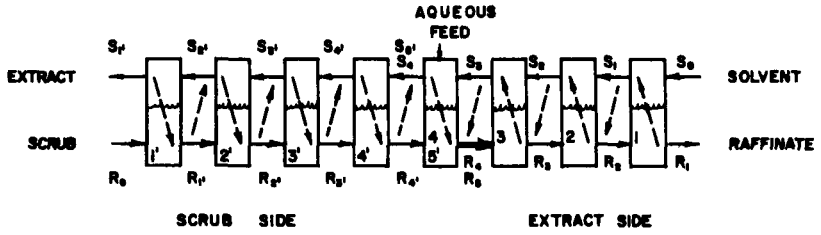

FIG. 1. Schematic diagram of an eight-stage extractor.

COMPUTER PROGRAM

If the composition and concentration of the feed, the flow rates, and the number of stages on each side of the feed stage are specified, the calculation method as programmed can be used to determine the component concentrations of all streams, including the final extract and raffinate, of a countercurrent internally fed solvent-extraction cascade. When the concentration of all components in one of the streams leaving the cascade is arbitrarily specified, the concentration of the other leaving stream is determined, using an over-all material balance. Calculating stage by stage from each end of the cascade by alternate equilibrium and material-balance relationships, one obtains two independent values for the concentration of each component in the aqueous phase (or the organic phase) leaving the feed stage. This is shown by the dashed lines on the cascade of Fig. 1. If the two calculated concentrations for each component in this stream do not agree within a desired tolerance, it is necessary to adjust the specified end concentrations and repeat the calculations. This procedure of adjusting the end-stream concentrations, calculating stage by stage from each end, and then comparing the concentrations of all components in the aqueous phase leaving the feed stage is repeated until the two independent calculations are within the tolerance.

Although it would be possible to make adjustments of end-stream concentrations for more than one component at a time, this procedure did not seem appropriate, because the values obtained for the concentrations of all components in any stream are affected to some extent when an adjustment in concentration for any component is made. Thus it was thought desirable to make adjustments for only one component at a time, and in fact, to adjust only the most mismatched component.

The technique of adjusting the end-stream molality of the one component consisted of a series of 0.05, 0.005, 0.0005, 0.0001, and 0.000001 molality changes until the component was matched to within the desired tolerance. It was quite arbitrary that the series of changes started with 0.05 and ended with 0.000001, because a much larger initial change could have been used and the final adjustment could have been as small as the computer would allow. This range was found to be quite adequate, however, and this particular procedure was used because it proved to be efficient and required only a few seconds of computer time per iteration. An iteration was considered to be the process of matching one component at the feed stage and usually consisted of a number of incremental adjustments to an end-stream concentration. A complete calculation usually required a number of iterations, as will be discussed later.

As there may be several stages between the stage where the adjustments are made and the feed stage, small changes in end-stream concentrations may be reflected by relatively large changes in concentrations at the feed stage. For example, a 0.000001 change in an extract stream molality could cause the mismatch at the feed stage to change from 0.10 to −0.10. Under these conditions, an incremental change less than 0.000001 would be necessary if the tolerance were 0.01.

In addition to the specified feed composition, the number of stages, the location of the feed stage, and the flow-rate ratios, the computer program requires input data concerning the initial split, the tolerance, the maximum number of iterations permitted, and the flow rate of any one stream. The split is defined as the ratio of the amount of a component in the extract stream leaving the cascade to the amount of that component in the feed stream. The initial split, then, is the assumed value of this fraction used in the first iteration of the program, and the actual split is the fraction that satisfies all equilibrium and material balances of the cascade. The tolerance is the maximum absolute value permitted for the difference between the two calculated concentrations of the most mismatched component in the matching aqueous stream. The maximum number of iterations is a variable which is specified to stop the calculations at some predetermined number of iterations in case too much computer time is being used.

To make stagewise calculations in a cascade, the flow rates of

the individual streams are needed to convert the moles of each component per unit time to the necessary molality units per unit time. However, the flow rates are actually introduced into the program as ratios, and thus the four flow streams become defined by these three expressions:

$$S/R_1 \qquad R_0/S \qquad R_0 + F = R_1$$

Therefore, by specifying the solvent flow rate, S, the flow rate of all the streams will be obtained for the calculations if S/R_1 and R_0/S are known.

SAMPLE PROBLEM

In this problem the concentrations and compositions of all streams in the extractor illustrated in Fig. 1 are to be determined assuming the following feed-composition and flow-rate ratios:

HNO_3:	3.0850 moles/time
$La(NO_3)_3$:	0.8890 mole/time
$Pr(NO_3)_3$:	0.2962 mole/time
$Nd(NO_3)_3$:	0.6666 mole/time
$Sm(NO_3)_3$:	0.1482 mole/time
Total:	5.0850 moles/time

$$S/R_1 = 1.2121$$
$$R_0/S = 0.1470$$

The value of the program variables for this problem are:

1. Initial split assumed: the ratio of the amount of each component in the extract stream to the amount of the component in the feed stream

HNO_3:	0.7000
$La(NO_3)_3$:	0.0010
$Pr(NO_3)_3$:	0.0010
$Nd(NO_3)_3$:	0.0200
$Sm(NO_3)_3$:	0.0400

2. Tolerance = 0.0100 m, arbitrarily selected
3. Maximum number of iterations = 50, arbitrarily specified
4. Solvent flow rate: S = 1.0 kg/time.

The computer printout of the solution is shown in Fig. 2. The

aqueous composition of each component versus the stage number for the cascade is shown in Fig. 3.

The calculations were programmed in the full Fortran language for the IBM 7074 computer. The program is composed of a main program, which does the preliminary work of inputting and storing necessary data, and three subroutines (Match, Extrac, and Scrub). Sebenic (*11*) gives the Fortran statements of the entire program.

The solution of several trial problems showed that the number of iterations required to obtain a match of all components within a specified tolerance may not be large, even though the end-stream concentrations initially assumed were in error by several orders of magnitude. For example, note in Table 1 that 12 iterations were required for this sample problem when the molality of $La(NO_3)_3$ was assumed to be 0.000088 (run 6) instead of the correct value of 0.0105, and the other assumed concentrations were also quite low.

INTERNALLY FED CASCADE WITH FEED STAGE MATCH OF ALL COMPONENTS

NUMBER OF ITERATIONS= 9 TOLERANCE= 0.0100

S= 1.0000 R1= 0.8250 RO= 0.1470 F= 0.6780

RO/S= 0.1470 S/R1= 1.2121 N= 5 M= 4

MOLALITY

	TOTAL	HNO3	LA	PR	ND	SM	RE
F	7.4998	4.5501	1.3112	0.4369	0.9832	0.2186	2.9498
S*	2.2817	2.0221	0.0105	0.0326	0.1393	0.0772	0.2596
R1	3.3979	1.2883	1.0649	0.3195	0.6391	0.0860	2.1096

MOLES

	TOTAL	HNO3	LA	PR	ND	SM	RE
F	5.0850	3.0850	0.8890	0.2962	0.6666	0.1482	2.0000
S*	2.2817	2.0221	0.0105	0.0326	0.1393	0.0772	0.2596
R1	2.8033	1.0629	0.8785	0.2636	0.5273	0.0710	1.7404

FRACTION OF FEED

	TOTAL	HNO3	LA	PR	ND	SM	RE
S*	0.4487	0.6555	0.0118	0.1100	0.2090	0.5210	0.1298
R1	0.5513	0.3445	0.9882	0.8900	0.7910	0.4790	0.8702

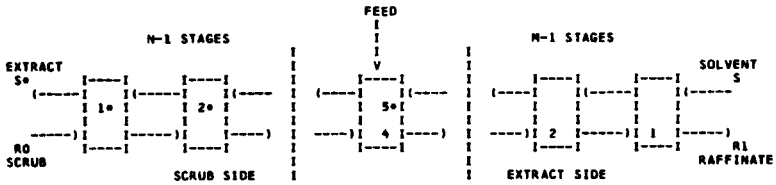

FIG. 2. Computer printout of the solution of the sample problem (part 1).

EXTRACT SIDE CALCULATION S/R1= 1.2121 M= 4

	STAGEWISE MOLALITIES							STAGEWISE COMPOSITIONS									
	TOTAL	HNO3	LA	PR	ND	SM	RE	ACFR	LAFR	PRFR	NDFR	SMFR	REFR	LA/RE	PR/RE	ND/RE	SM/RE
S 0	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
R 1	3.3979	1.2883	1.0649	0.3195	0.6391	0.0860	2.1096	0.379	0.313	0.094	0.188	0.025	0.621	0.505	0.151	0.303	0.041
S 1	1.9333	1.3506	0.2003	0.0994	0.2456	0.0375	0.5827	0.699	0.104	0.051	0.127	0.019	0.301	0.344	0.171	0.421	0.064
R 2	5.7412	2.9254	1.3076	0.4400	0.9368	0.1315	2.8159	0.510	0.228	0.077	0.163	0.023	0.490	0.464	0.156	0.333	0.047
S 2	2.8309	2.1742	0.1648	0.1097	0.3092	0.0731	0.6567	0.768	0.058	0.039	0.109	0.026	0.232	0.251	0.167	0.471	0.111
R 3	6.8292	3.9237	1.2646	0.4524	1.0139	0.1746	2.9055	0.575	0.185	0.066	0.148	0.026	0.425	0.435	0.156	0.349	0.060
S 3	3.1450	2.5580	0.1221	0.0928	0.2819	0.0902	0.5870	0.813	0.039	0.030	0.090	0.029	0.187	0.208	0.158	0.480	0.154
R 4	7.2100	4.3889	1.2129	0.4320	0.9808	0.1954	2.8211	0.609	0.168	0.060	0.136	0.027	0.391	0.430	0.153	0.348	0.069

SCRUB SIDE CALCULATION RO/S= 0.1470 N= 5

	STAGEWISE MOLALITIES							STAGEWISE COMPOSITIONS									
	TOTAL	HNO3	LA	PR	ND	SM	RE	ACFR	LAFR	PRFR	NDFR	SMFR	REFR	LA/RE	PR/RE	ND/RE	SM/RE
R*0	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000										
S*1	2.2817	2.0221	0.0105	0.0326	0.1393	0.0772	0.2596	0.886	0.005	0.014	0.061	0.034	0.114	0.040	0.126	0.537	0.297
R 1	3.6683	2.7528	0.0823	0.1451	0.4886	0.1996	0.9155	0.750	0.022	0.040	0.133	0.054	0.250	0.090	0.159	0.534	0.218
S 2	2.8209	2.4268	0.0226	0.0539	0.2111	0.1066	0.3941	0.860	0.008	0.019	0.075	0.038	0.140	0.057	0.137	0.536	0.270
R 2	5.2555	3.8267	0.2078	0.2518	0.7450	0.2242	1.4288	0.728	0.040	0.048	0.142	0.043	0.272	0.145	0.176	0.521	0.157
S 3	3.0542	2.5846	0.0410	0.0696	0.2488	0.1102	0.4696	0.846	0.013	0.023	0.081	0.036	0.154	0.087	0.148	0.530	0.235
R 3	6.1196	4.3145	0.3999	0.3263	0.8667	0.2122	1.8051	0.705	0.065	0.053	0.142	0.035	0.295	0.222	0.181	0.480	0.118
S 4	3.1812	2.6563	0.0692	0.0806	0.2667	0.1084	0.5249	0.835	0.022	0.025	0.084	0.034	0.165	0.132	0.153	0.508	0.207
R 4	6.7019	4.4520	0.7136	0.3876	0.9443	0.2044	2.2499	0.664	0.106	0.058	0.141	0.030	0.336	0.317	0.172	0.420	0.091
S 5	3.2668	2.6765	0.1154	0.0896	0.2781	0.1073	0.5903	0.819	0.035	0.027	0.085	0.033	0.181	0.195	0.152	0.471	0.182
R 5	7.1924	4.3864	1.2078	0.4289	0.9741	0.1953	2.8060	0.610	0.168	0.060	0.135	0.027	0.390	0.430	0.153	0.347	0.070
S 6	3.3389	2.6669	0.1880	0.0956	0.2825	0.1059	0.6720	0.799	0.056	0.029	0.085	0.032	0.201	0.280	0.142	0.420	0.158

FIG. 2. Computer printout of the solution of the sample problem (part 2).

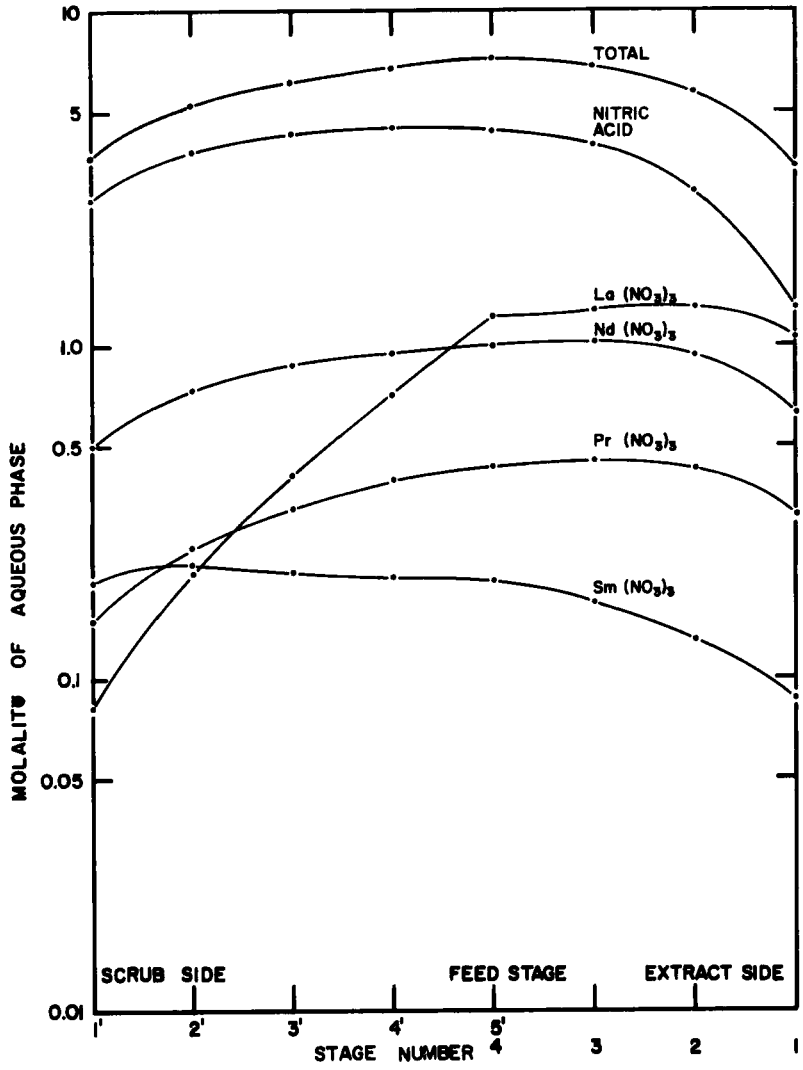

FIG. 3. Stagewise concentrations of each component in the aqueous stream.

In run 2, 14 iterations were needed when some of the initially assumed values were very low and others were very high. Note also that although the initially assumed extract stream molalities of run 4 were closer to the correct values than those for run 5, 21 iterations were required for run 4 while only 11 were required for run 5.

TABLE 1
Effect of Initial Assumptions on the Number of Iterations Required for the Sample Problem

		Initially assumed extract-stream molalities					
	Correct extract-stream molalities	Run 1	Run 2	Run 3	Run 4	Run 5	Run 6
HNO_3	2.0221	2.1595	1.8510	1.8510	2.3137	2.4680	2.4680
$La(NO_3)_3$	0.0105	0.000088	0.0889	0.0889	0.000889	0.000088	0.000088
$Pr(NO_3)_3$	0.0326	0.0888	0.0296	0.000296	0.00296	0.00296	0.00148
$Nd(NO_3)_3$	0.1393	0.000666	0.26664	0.1333	0.0133	0.0133	0.00333
$Sm(NO_3)_3$	0.0772	0.0741	0.0014	0.0148	0.0741	0.05428	0.00148
No. of iterations required		13	14	14	21	11	12

For those problems where the calculations went outside the available equilibrium data, the computer stopped and printed the stagewise concentrations for the last legitimate calculation. In all other cases, the calculations rapidly converged to values within the prescribed tolerance. The entire calculation normally required less than a minute of computer time.

DISCUSSION OF RESULTS

Because of the empirical nature of the equilibrium data and the fact that the simplifying assumptions of Sharp and Smutz's (*12*) equilibrium model are not, in general, applicable to other extraction systems, the method of multicomponent solvent extraction described herein applies only to the rare-earth system presented. The computer program and technique may be useful to those wishing to determine the number of ideal stages required to make a desired separation of these solutes.

The calculation method and computer program used in this research has demonstrated convergence each time the program has been run, except for those cases in which regions of incomplete equilibrium data were encountered.

An indication of the rate of convergence for the solution of the sample problem is given by Fig. 4. This is a plot of the sum of the absolute values of the amount of mismatch of all components

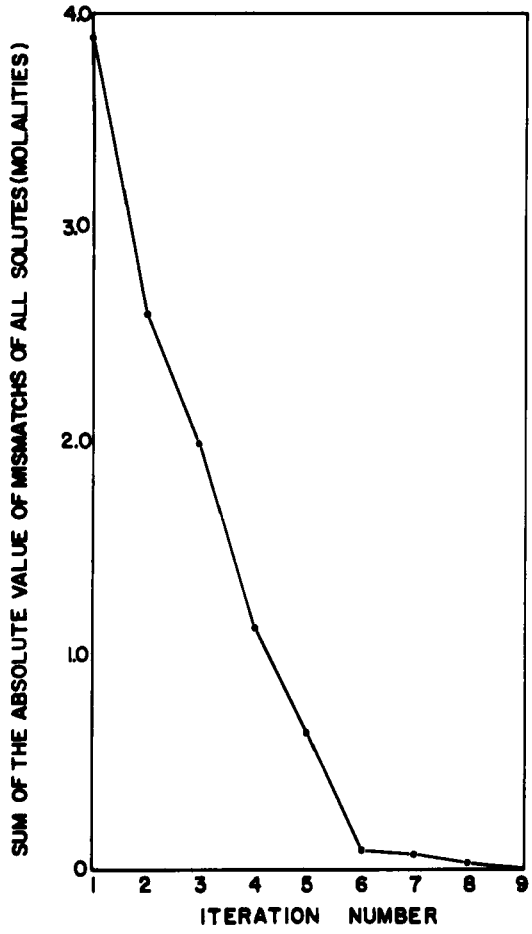

FIG. 4. Rate of convergence for the iterative solution of the sample problem.

versus the iteration number. Note that the rate of convergence is not uniform. Similar plots for other problems have shown that the trend of the curves is downward, but the "sum of the absolute values of mismatch" does not always decrease from iteration to iteration. This suggests the possibility that there may be cases in which convergence to a specified tolerance is not attainable.

Nomenclature

F	flow rate of solvent in a feed stream, kg H_2O/unit time
m	arbitrary stage in the extract section

M molality, moles of a solute per kilogram of water, nitrate basis
$\bar{M}$ molality, moles of a solute per kilogram of TBP, nitrate basis
n arbitrary stage in the scrub section
R flow rate of solvent in an aqueous stream, kg H_2O/unit time
S flow rate of solvent in an organic stream, kg TBP/unit time

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REFERENCES

1. N. R. Amundson and A. J. Pontinen, *Ind. Eng. Chem.*, **50,** 730 (1958).
2. N. R. Amundson and A. J. Pontinen, *A. I. Ch. E. J.*, **5,** 295 (1959).
3. G. G. Brown and M. Souders, Jr., *Ind. Eng. Chem.*, **24,** 519 (1932).
4. W. C. Edmister, *A. I. Ch. E. J.*, **3,** 165 (1957).
5. J. R. Friday, unpublished Ph.D. thesis, Purdue Univ. Library, Lafayette, Ind., 1963.
6. J. R. Friday and B. D. Smith, *A. I. Ch. E. J.*, **10,** 698 (1964).
7. G. Horton and W. B. Franklin, *Ind. Eng. Chem.*, **32,** 1384 (1940).
8. A. Kremser, *Natl. Petrol. News*, **22,** 43 (1930).
9. W. K. Lewis and G. L. Matheson, *Ind. Eng. Chem.*, **24,** 494 (1932).
10. J. E. Powers, *Chem. Eng. Progr.*, **50,** 291 (1954).
11. R. F. Sebenik, M.S. thesis in chemical engineering, Iowa State University, Ames, 1965.
12. B. M. Sharp and M. Smutz, *Ind. Eng. Chem. Process Design Develop.*, **4,** 49 (1965).
13. B. D. Smith, *Design of Equilibrium Stage Processes*, McGraw-Hill, New York, 1963.
14. B. D. Smith and W. K. Brinkley, *A. I. Ch. E. J.*, **6,** 451 (1960).
15. E. W. Thiele and R. L. Geddes, *Ind. Eng. Chem.*, **25,** 289 (1933).

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