
RANDOM ERRORS IN EQUILIBRIUM COMPOSITION OF TERNARY LIQUID-LIQUID SYSTEMS AND THEIR EFFECT ON THE CALCULATED NUMBER OF THEORETICAL STAGES OF COUNTERCURRENT EXTRACTION

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The influence of size of random errors in the determination of ternary liquid-liquid equilibrium concentrations on the accuracy of the calculated number of theoretical stages of a counter-current extractor is evaluated by using five hypothetical systems differing in the extent of mutual solubility of components, tie-line slope, and type of binodal curve.

The data on phase equilibria form the needed basis for designing the industrial separating equipments and/or evaluating their operation and optimum working conditions. The L-L equilibrium data can be obtained either by calculating, e.g., by application of group-contribution models or, more often, experimentally. Whereas the data obtained by the former mode represent seldom a sufficiently accurate description of the equilibrium composition of phases, in the latter case, the data determined experimentally are to be correlated before use. The correlation is carried out by some of these two methods:

a) The procedures which are based on thermodynamics and start most often from the dependence of the Gibbs energy of solution on composition. The frequently used equations are especially the Redlich-Kister, NRTL, modified Wilson, and UNIQUAC equations.

b) The procedures whose substance is purely empirical and commonly comprise the dependences of distribution coefficients or in different ways modified ratios of concentrations of components on composition. These are, e.g., the correlations by Hand¹, Othmer and Tobias², Dryden³, Tarasenkov⁴, Ishida⁵, but above all by Rod⁶.

Every set of equilibrium data obtained experimentally is subjected to errors and therefore it will participate, in a certain way and to a certain extent, in the inaccuracies of results of calculating the designed separating equipment. While the qualitative aspects of these connections are well-known, the quantitative aspects, as to the relation of random errors and results of calculations proposed are usually known to the one who tries to solve, only scarcely.

Starting from the assumption that the equilibrium mole fractions will be subjected only to random experimental errors and that the size of these errors is a random quantity with normal probability distribution with a constant value of variance over the whole concentration region, we shall try to obtain some information on the influence of errors in equilibrium composition on the number of extractor stages. For this purpose we shall use the method of simulated measurements of L-L equilibrium composition and their application to the calculation of the number of theoretical stages of countercurrent extractor. The first knowledge of the above-mentioned questions has been obtained on two ternary systems, one of which has exhibited a closed and the second an open binodal curve, which have been reported in one of our previous papers⁷. However, from the view of these two systems it is not possible to draw more general conclusions. They do not enable, e.g., to judge or at least to indicate how will manifest itself the effect of a different slope of tie-lines, different extent of mutual solubility of components (either of solvents mutually or of solute with a solvent). Partly unanswered has remained the question of the effect of error distribution in equilibrium concentrations on the number of extractor stages. And just to some of these problems is drawn attention in this work. For the given purpose five hypothetical ternary systems were chosen. The L-L diagrams of these systems are depicted in Fig. 1a-e.

THEORETICAL

Correlation of Equilibrium Data

To be able to evaluate the effect of errors in equilibrium concentrations on the problems mentioned, it is necessary to dispose partly of an etalon of equilibrium data and partly of "experimental" data obtained in the form of a simulated experiment. On calculating the extraction equipment, the equilibrium data are used processed in the form of a polynomial in the relation recommended by Rod⁶

$$\ln K_i = \sum_k a_{ik} y_2^k, \quad (1)$$

for $k = 0, 1, \dots, n$; $i = 1, 2, 3$ and where

$$K_i = y_i/x_i \quad (2)$$

is the distribution coefficient of component i . The method of calculating the coefficients a_{ik} and the composition of equilibrium phases can be found in original works^{6,8}.

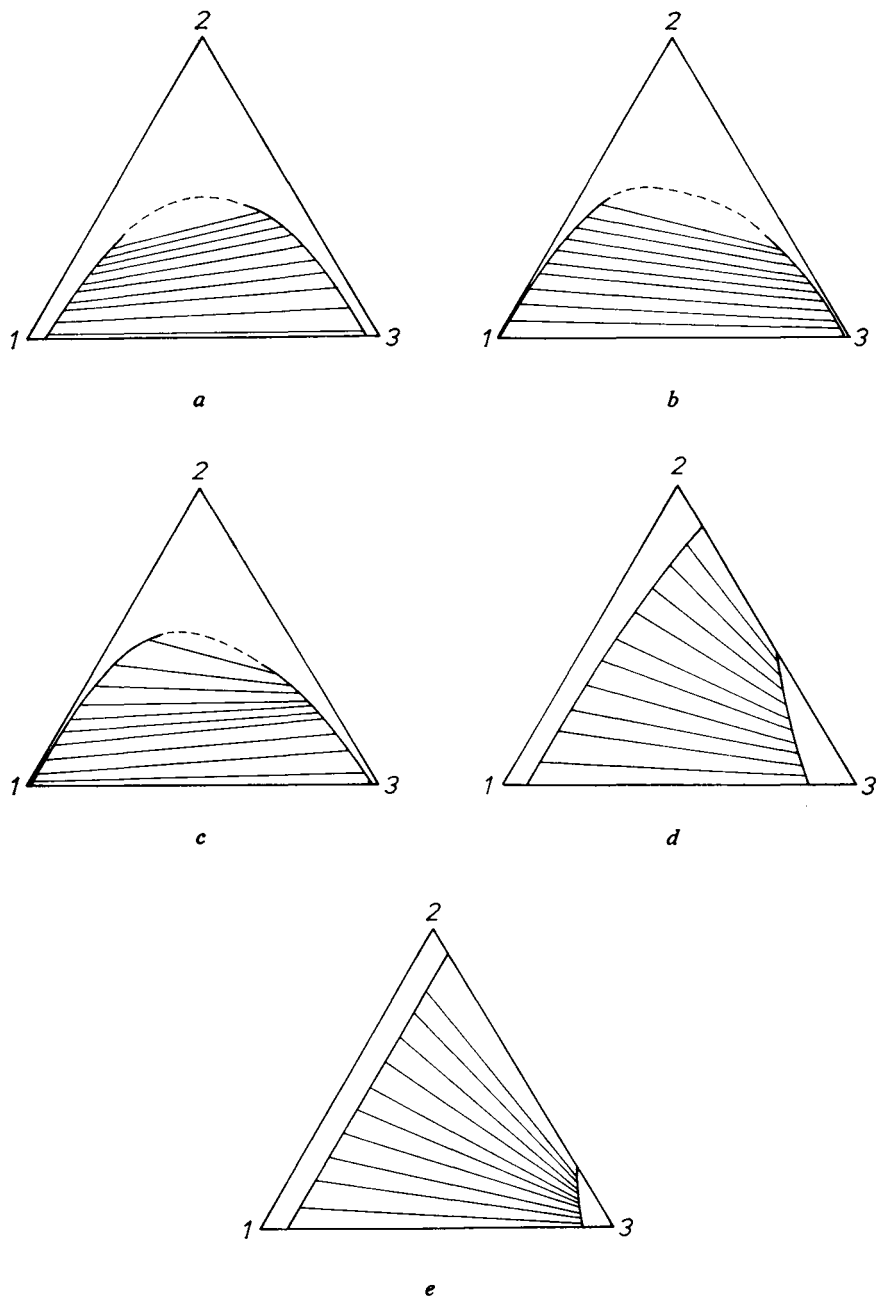


FIG. 1
Equilibrium L-L diagrams of hypothetical systems. *a* System I, *b* system II, *c* system III, *d* system IV, *e* system V

Simulated Experiment

When simulating the experiment with the aim to obtain a set of "experimental" equilibrium data subjected to random errors, the following equations

$$x_{ij,\text{exp}} = \sigma(x_i) N_k + x_{ij}, \quad (3a)$$

$$y_{ij,\text{exp}} = \sigma(y_i) N_k + y_{ij} \quad (3b)$$

can be used for $i = 2, 3$; $j = 1, 2, \dots, l$; $k = 1, 2, \dots, l$, where $x_{ij,\text{exp}}$, $y_{ij,\text{exp}}$ are the experimental values of mole fractions of component i in the raffinate (x) and extract (y) phases; x_{ij} , y_{ij} are the accurate values for which $\sigma(x_i) = \sigma(y_i) = 0$; N_k is a number from the sequence of random numbers with normal distribution with centre $\mu = 0$ and variance $\sigma^2 = 1$; $\sigma(x_i)$, $\sigma(y_i)$ are square roots of variance or root mean square deviations of mole fraction of component i in the raffinate and extract phases. Product $\sigma(x_i) N_k$, $\sigma(y_i) N_k$ gives the random error of single measurement. Subscript j is connected with serial number of tie-lines, subscript k with serial number of random number N . The equations recommended for generating numbers N_k can be found in literature^{9,10}.

Calculation of Number of Stages of Countercurrent Extractor

The basis of analytical determination of number of theoretical stages of countercurrent extractor is the numerical finding of composition of material streams from one stage to another one and the iteration calculation of composition of equilibrium phases of extract and raffinate. The continuous description of equilibrium is mediated by the Rod polynomials whose parameters have been identified for each situation by treating the respective set of "experimental" points. At the beginning of calculations it is necessary to know or choose the composition of raw material and extracting agent, the concentration of extracted component in the raffinate product and the ratio of flow rates of extracting agent and raw material. The fundamental relations and algorithm of calculating the number of stages were given in one of our previous papers⁸.

EXPERIMENTAL

Etalon of Equilibrium Data and Number of Theoretical Stages

The values of coefficients a_{ik} in Eq. (1) for the etalon of equilibrium data of the systems examined here are given in Table I. The form of equilibrium dependences corresponding to accurate equilibrium values can be observed also by means of solid lines in Fig. 1a-e. The dash course of binodal curves with the first three systems is estimated. In each of equilibrium triangles, more tie-lines is drawn to make the mutual comparison of systems easy. So, e.g., system I in Fig. 1a

has tie-lines with positive slopes ($y_2 > x_2$) whereas system *II* in Fig. 1*b* has tie-lines with negative slope ($y_2 < x_2$). System *III* in Fig. 1*c* is of solutropic type. Systems *IV* and *V* in Figs 1*d* and 1*e* have, unlike the foregoing systems, an open binodal curve with unequally large solubility of components 1 and 2 in 3.

To be able to evaluate the effect of errors which are the "experimental" equilibrium concentrations subjected to, the conditions of extraction in countercurrent stagewise equipment were simulated. The chosen conditions of extraction are given in Table II including the calculated number of theoretical stages (NTS) with accurate equilibrium data. The values of parameter E_{n+1}/R_0 were chosen as a multiple of the minimum value. This multiple was with single systems within 1.15 to 1.3. It was presumed that the extracting agent is pure component 3 and extracted material a mixture of components 1 and 2.

Conditions of "Experimental" Determination of Equilibrium Data

When preparing the equilibrium data in the form of simulated experiment, we considered that each set of data should have included ten tie-lines, which is the number common in laboratory determination. The root mean square deviations of mole fractions of components 2 and 3 were chosen from the interval of 0.001 to 0.013. The mole fractions of component 1 were considered as dependent variables and their values were determined from conditions $\sum x_{i,\text{exp}} = 1$ and

TABLE I
Values of coefficients a_{ik} in Eq. (1) representing "accurate" L-L equilibrium data of hypothetical ternary systems

System	Component (i)	a_{i0}	a_{i1}	a_{i2}	a_{i3}
<i>I</i>	1	-3.1482	1.9558	-6.7962	26.336
	2	0.76432	-1.0225	2.2224	-5.1594
	3	2.9961	-2.2044	7.9799	-24.857
<i>II</i>	1	-4.3647	8.2197	-13.166	31.679
	2	-0.78381	1.9093	-1.2887	-2.9283
	3	5.2257	-15.143	53.910	-123.92
<i>III</i>	1	-3.8499	5.6011	-12.202	39.879
	2	0.79366	4.1258	-41.052	59.484
	3	4.3264	-5.9143	26.130	-78.718
<i>IV</i>	1	-2.0060	2.8432	-11.204	20.679
	2	-1.1643	2.8872	-7.7976	8.8215
	3	2.5142	-1.9338	0.96067	-4.8615
<i>V</i>	1	-2.4202	5.1118	-21.421	75.691
	2	-2.0941	8.4412	-60.257	172.16
	3	2.5259	-1.0475	-11.656	56.259

$\sum y_{i,\text{exp}} = 1$. The random errors were calculated for σ being constant in the entire concentration region corresponding to the solid course of binodal curve. Once when preparing the "experimental" values x_i , y_i it was assumed that for the errors in mole fractions held $\sigma(x_2) = \sigma(x_3) = \sigma(y_2) = \sigma(y_3)$, another time $\sigma(x_2) = \sigma(y_2)$, $\sigma(x_3) = \sigma(y_3)$ taking $\sigma(x_2) \neq \sigma(x_3)$.

Random errors $\sigma(x_i) N_k$ and $\sigma(y_i) N_k$ for a chosen $\sigma(x_i)$ and $\sigma(y_i)$ take differently large positive and negative values, which is connected with alternating the sign of numbers N_k . For a system with ten tie-lines, ten random numbers N_k were prepared by generating and by means of them also the same number of random errors for each considered component in the raffinate and extract points. Retaining the chosen order of tie-lines ($j = 1, 2, \dots, l$) and so also the order of accurate values x_{ij} and y_{ij} , it was, however, possible to choose or change optionally the order of numbers N_k ($k = 1, 2, \dots, l$) and/or by means of them also the order of simulated random errors which are attached according to Eq. (3) to the accurate values of mole fractions. However, so a situation arose making it possible to prepare a great number of sets of "experimental" equilibrium data showing the same value of $\sigma(x_i)$ and $\sigma(y_i)$ but differing mutually in various regrouping of errors of single measurement. This regrouping of errors during the preparation of "experimental" equilibrium values of x_2 and y_2 appeared to influence to a certain extent the calculated number of theoretical stages while the effect of regrouping the errors when generating values of x_3 and y_3 on the number of theoretical stages is insubstantial.

On the basis of this finding we chose, when preparing the sets of "experimental" equilibrium concentrations with a constant value $\sigma(x_i) = \sigma(y_i)$, such an order of errors that the calculated number of theoretical stages should be close to the average value of NTS determined from a greater number of sets of equilibrium data having the same constant value $\sigma(x_i) = \sigma(y_i)$ but showing always other order of errors in simulated formation of equilibrium concentrations. Some data on this procedure are given for illustration in Table III. We started from the value $\sigma(x_2) = \sigma(y_2) = \sigma(x_3) = \sigma(y_3) = 0.003$. By various regrouping of errors when generating the mole fractions of component 2 in the raffinate and extract phases, about thirty rounded-off sets of "experimental" composition were gradually prepared. By using each such set correlated by the Rod polynomials (I), the number of theoretical stages was calculated for the given conditions of extraction, their average value and also their selective root mean square deviation s_{NTS} were found. Those sets of equilibrium composition for which the calculated number of stages differed more and less than three times the value s_{NTS} were left out. In the end, the single values of relative deviation in the number of theoretical stages were compared with its average value.

TABLE II

Conditions of countercurrent extraction and calculated number of theoretical stages N_{TS} with "accurate" equilibrium concentrations

Basic information	System				
	<i>I</i>	<i>II</i>	<i>III</i>	<i>IV</i>	<i>V</i>
Composition of raw material ($x_{2,0}$)	0.26	0.50	0.50	0.50	0.50
Composition of extracting agent ($y_{3,n+1}$)	1	1	1	1	1
Composition of raffinate ($x_{2,n}$)	0.01	0.01	0.005	0.01	0.01
E_{n+1}/R_0	0.430	1.20	0.803	2.20	5.70
N_{TS}	9.18	11.66	5.02	12.62	23.36

The order of errors on generating this set of equilibrium data for which the obtained value of relative deviation in NTS was nearest the average value of deviations in NTS was then used also for simulating further sets of equilibrium data for the same system. We remark here that such a procedure need not always lead to the most probable order of errors in simulated determination of equilibrium composition; the possible number of variants with different order of errors is much higher than that applied in our work but from the point of view of consumption of computer time the time of computation is significantly shortened.

RESULTS AND DISCUSSION

The calculated number of the extractor theoretical stages based on the "experimental" equilibrium concentrations $N_{TS,exp}$ was compared with the value of N_{TS} obtained with the etalon of equilibrium data in the form of per cent relative deviation

$$D_{NTS} = \frac{N_{TS,exp} - N_{TS}}{N_{TS}} 100. \quad (4)$$

The results obtained are presented in the form of graphic representation of the relative deviation in NTS on σ in Figs 2a–e and 3a–e.

It follows from the comparison of dependences in Fig. 2a–e that the deviations in the determination of stages increase with increasing value of $\sigma(x_i) = \sigma(y_i)$ regardless of the form of binodal curve and slope of tie-lines. But if the systems are judged with respect to the magnitude of deviations in NTS, then the greatest changes are showed by systems *I* and *II*. Even though these systems differ in opposite slope of tie-lines and in values of mutual solubilities of solvents *1* and *3*, the influence of random errors on NTS manifests itself in them nearly to the same extent. Solutropic

TABLE III

Values of arithmetic average $\bar{N}_{TS,exp} = \sum N_{TS,exp}/n$, selective root mean square deviation $s_{NTS} = \sqrt{\sum (N_{TS,exp} - \bar{N}_{TS,exp})^2/n}$, average relative deviation $S_{NTS} = (100/n) \sum (|N_{TS,exp} - N_{TS}|/N_{TS})$ of theoretical stages of countercurrent extraction, and number n of considered sets of equilibrium data for evaluating the influence of order of random errors of simulated equilibrium composition for constant value $\sigma(x_i) = \sigma(y_i) = 0.003$

Quantity	System				
	<i>I</i>	<i>II</i>	<i>III</i>	<i>IV</i>	<i>V</i>
$\bar{N}_{TS,exp}$	9.82	12.20	5.16	12.75	21.98
s_{NTS}	0.74	1.3	0.26	2.2	2.4
S_{NTS}	8.5	9.4	4.6	13	9.1
n	27	27	30	26	15

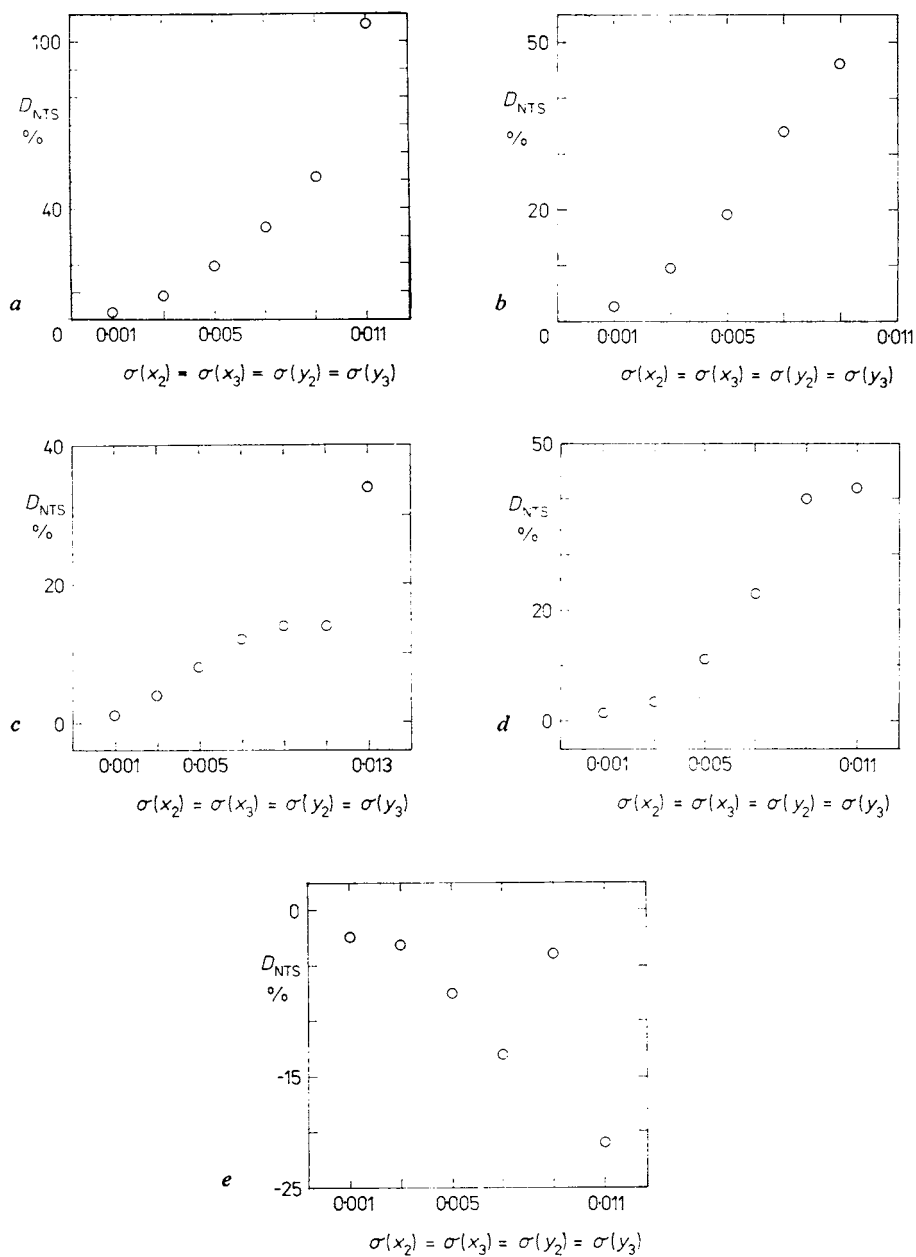


FIG. 2

Per cent relative deviation in determining the number of theoretical stages of extractor in dependence on the magnitude of random errors in equilibrium concentrations (denotation a–e as in Fig. 1)

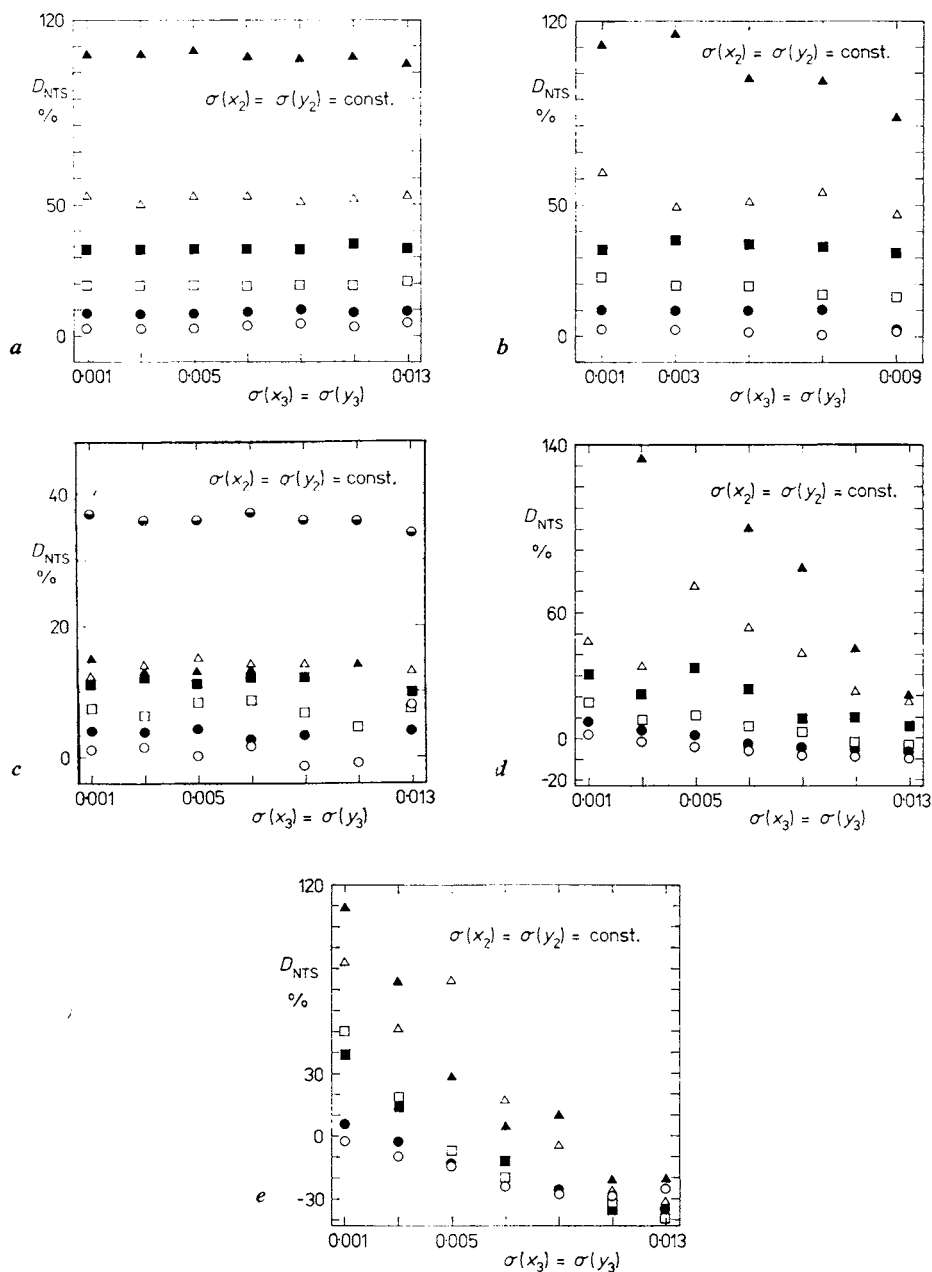


FIG. 3

Per cent relative deviation in determining the number of theoretical stages of extractor in dependence on $\sigma(x_3) = \sigma(y_3)$ for these constant $\sigma(x_2) = \sigma(y_2)$: ○ 0.001, ● 0.003, □ 0.005, ■ 0.007, △ 0.009, ▲ 0.011, ⊙ 0.013 (denotation a—e as in Fig. 1)

system *III* is in comparison with systems *I* and *II* less sensitive to inaccuracies in the determination of equilibrium data and exhibits about half as lower deviations in the number of stages. Similarly behave both the systems with open binodal curve.

From analysis of the methods of calculating the countercurrent extractor follows that the number of stages is influenced partly by solubility equilibrium data x_1 , x_3 and y_1 , y_3 which determine the course of binodal curve and also distribution data x_2 , y_2 on which depend the position and slope of tie-lines. When evaluating the influence of inaccuracies of determining the equilibrium composition from the point of view of the distribution and solubility data separately, a number of further knowledge has been obtained. In Fig. 3*a-e* points are plotted which in the vertical direction for constant values $\sigma(x_3) = \sigma(y_3)$ express the effect of distribution data whereas the points for constant values $\sigma(x_2) = \sigma(y_2)$ in the direction of increasing values $\sigma(x_3) = \sigma(y_3)$ express the effect of solubility data on the number of extractor stages. As it follows from Figs 3*a-c*, systems with closed binodal curve behave in a different way than systems with open binodal curve in Figs 3*d* and 3*e*. With systems *I-III*, the effect of magnitude of errors in solubility equilibrium data is practically negligible and the deviations in the number of stages are mostly caused by inaccuracies in distribution data regardless of the tie-line slope and course of binodal curves.

The effect of magnitude of errors in solubility equilibrium data manifests itself to a more significant extent just in the systems with open binodal curve. As it follows from Figs 3*d* and 3*e*, the errors in the determination of solubility data influence NTS in an opposite direction than the errors in distribution data, viz. in the direction of reducing the number of extractor stages. This reduction in NTS is larger with system *V*, and is probably connected with a lower solubility of component *1* and *2* in *3* (the extract branch of binodal curve is shorter than in system *IV*), which results in the fact that the changes in composition of extract streams from one stage to another one will be so small that even very small errors in the determination of not only the distribution but also the solubility equilibrium data may bring about considerable deviations in number of stages. This effect cannot be observed only by means of the results plotted in Figs 2*d* and 2*e* just because of the compensation effect of inaccuracies of solubility data on the deviations in NTS caused by errors of the distribution equilibrium data.

From the results of the systems studied follows simultaneously that, when obtaining the equilibrium dependences, the demands on the accuracy of their determination should be higher for systems with open binodal curve and that these demands grow with decreasing solubility of components in extracting agents.

LIST OF SYMBOLS

a_{ik}	coefficients of Eq. (1)
D_{NTS}	per cent relative deviation of number of theoretical stages

E_{n+1}/R_0	ratio of mole flows of extracting agent and raw material
K_i	distribution coefficient
l	number of tie-lines and/or number of numbers from the sequence of random numbers
n	degree of polynomial given by Eq. (1) and/or number of considered sets of equilibrium data
N_k	random number of normal distribution with $\mu = 0$ and $\sigma^2 = 1$
$N_{TS}, N_{TS,exp}$	number of theoretical stages
s_{NTS}	selective root mean square deviation
S_{NTS}	average relative deviation
x_i	mole fraction of component in raffinate phase
$x_{2,0}; x_{2,n}$	mole fraction of solute in raw material and/or in raffinate product
$x_{ij}; x_{ij,exp}$	accurate and/or experimental value of mole fraction in raffinate
y_i	mole fraction of component in extract phase
$y_{3,n+1}$	mole fraction of component 3 in extracting agent entering extractor
$y_{ij}; y_{ij,exp}$	accurate and/or experimental value of mole fraction in extract
μ	expected value of random quantity
$\sigma^2; \sigma$	variance and/or root mean square deviation of random quantity

Subscripts

exp	experimental
i	component of system
j	ordinal number of experimental point and/or tie-line
k	ordinal number of coefficient in Eq. (1) and/or number determining order of random number N
NTS	related to number of theoretical stages
TS	related to theoretical stages
$1, 2, 3$	denote components of system: 1 initial solvent, 2 solute, 3 extracting agent
$1, 2, \dots, n$	designation of stages of countercurrent extractor

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