THE EFFECT OF SYSTEMATIC ERRORS OF THE EQUILIBRIUM DISTRIBUTION CONCENTRATIONS ON THE NUMBER OF STAGES OF COUNTERCURRENT EXTRACTION WITH VARIOUS CONSUMPTION OF EXTRACTANT

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On using five hypothetical systems differing in the extent of mutual solubility of components, tie-line slope, and type of binodal curve, the effect is evaluated of systematic errors in the form of absolute deviation in the liquid–liquid equilibrium distribution concentrations on the accuracy of calculated number of theoretical stages of isothermal countercurrent extraction under various operating conditions.

In preceding papers[1,2] we have dealt with the occurrence and distribution of random errors when measuring the tie-lines and binodal curve in liquid–liquid ternary systems and with their influence on the accuracy of the calculated number of theoretical stages of countercurrent extraction. In the next paper[3], which is a continuation of the problems studied, the effect of systematic errors in equilibrium concentrations in the form of percent relative deviation was examined. The group of questions treated and the results obtained may attract attention especially of the users of equilibrium data who apply them in the computations of designed separation equipments.

In this paper we intend to report a number of further knowledge. It was obtained in the study of equilibrium data subjected to systematic errors in the form of absolute deviation and in their application in the extraction calculations. Here we started from the hitherto knowledge according to which the inaccuracies in the determination of binodal curve influence only slightly or to a smaller extent the accuracy of result of the required number of theoretical stages in the process. The accuracy of this results is dependent in a decisive degree on the accuracy of the distribution equilibrium data which determine the position and slope of tie-lines. A simulated experiment was therefore directed exclusively to the distribution equilibrium data. The second group of questions refers to the effect of changes of operating parameters of countercurrent extraction when investigating the absolute systematic errors of equilibrium concentrations. The operating parameters are represented here by the relative consumption of extractant, i.e., the extractant consumption related to a unit amount

of raw material processed. The other optional parameters, such as the composition of raw material, extractant and raffinate product were not changed and remained the same as in preceding works[2,3] so that the same area of concentration region of equilibrium triangles was retained practically in all the calculations.

THEORETICAL

The etalons of equilibrium data of five hypothetical systems with all their details were given in paper[2]. They are expressed in terms of values a_{ik} $(k = 0, 1, ..., 3)$ of the third-order polynomial

$$\ln K_i = a_{i0} + a_{i1}y_2 + a_{i2}y_2^2 + a_{i3}y_2^3 \tag{1}$$

for component $i = 1, 2, 3$, where

$$K_i = y_i/x_i \tag{2}$$

is the distribution coefficient.

The distribution coefficients of components are given by coefficients a_{ik} for each component for the value of y_2 chosen in advance, which makes it possible to calculate the composition of equilibrium phases by means of the relations

$$x_2 = y_2/K_2, \tag{3a}$$

$$x_1 = [1 - K_3 + (K_3 - K_2) x_2]/(K_1 - K_3), \tag{3b}$$

$$x_3 = [1 - K_2 + (K_2 - K_1) x_1]/(K_3 - K_2), \tag{3c}$$

and Eq. (2) for determining the values of y_1 and y_3.

The liquid–liquid equilibrium data subjected to systematic errors were prepared by a simulated experiment. The constant value of absolute deviation of mole fraction of solute in one of two phases was the measure of errors. The data of this kind are denoted as distribution ones, and the position and slope of tie-lines is given by them. The number of tie-lines was always chosen to be ten. The course of binodal curve was not changed in the simulated experiment and remained identical with the binodal curve of "accurate" equilibrium data.

The simulated preparation of the experimental equilibrium mole fractions was carried out by means of the relation

$$x_{2,\mathrm{exp}} = x_2 + \delta(x_2), \tag{4a}$$

$$y_{2,\mathrm{exp}} = y_2 + \delta(y_2), \tag{4b}$$

where x_2 and y_2 are the accurate values of mole fractions of solute in the phase rich

in component 1 (x) and/or in component 3 (y); $\delta(x_2)$, $\delta(y_2)$ are the constant values of absolute systematic errors. The values of $\delta(x_2)$ were chosen in the interval from -0.025 to 0.010 whereas the values of $\delta(y_2)$ in the interval from -0.010 to 0.025. The values of mole fraction $y_{1,exp}$ differ, for errors $\delta(y_2)$ considered, only slightly from the accurate values, and therefore they were determined by linear interpolation. Mole fractions $y_{3,exp}$ were considered to be dependent, and their values were determined by complementing to unity. In simulating the equilibrium composition of the second phase, the values of $x_{3,exp}$ were determined by linear interpolation whereas the values of $x_{1,exp}$ were complemented to unity. Each set of equilibrium data prepared in this way was correlated by means of Eq. (1) before the application itself, by which the continuous description of the experimental equilibrium dependence was obtained.

APPLICATION

Calculation of Number of Theoretical Stages in Countercurrent Extraction

A sketch of countercurrent extraction is given in Fig. 1. By using the correlated set of liquid–liquid equilibrium data prepared always for a certain value of absolute deviation $\delta(x_2)$ or $\delta(y_2)$, the number of theoretical stages (N_{TS}) was calculated needed for the countercurrent extraction. The fundamental relations and the algorithm for calculating N_{TS} were given in our preceding work[4]. It is formed by the numerical finding of composition of material streams from stage to stage combined with the iteration calculation of composition of equilibrium phases of extract and raffinate.

The number of theoretical stages $N_{TS,exp}$ calculated in this way with the experimental data is compared with the value of N_{TS} obtained with the etalon of equilibrium data in the form of the relative percent deviation

$$d_{NTS} = 100(N_{TS,exp} - N_{TS})/N_{TS}\,. \tag{5}$$

by which the basis for evaluating the effect of errors on the accuracy of result of chemical-engineering calculation is obtained.
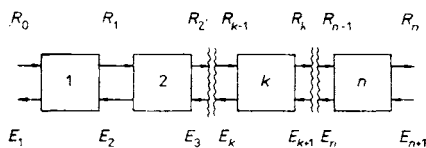

FIG. 1

Sketch of countercurrent extraction

Operating Parameters of Process

One of the optional parameters in countercurrent extraction is the consumption of extractant. On its value depends the number of theoretical stages needed to ensure the required sharpness of separation. Whether or in what way the inaccuracies of equilibrium data will manifest themselves in deviations in N_{TS} just from the point of view of changed operating conditions, this was the question which was examined in each of the five systems. For this purpose, three values of the relative consumption of extractant E_{n+1}/R_0 as a certain multiple of the minimum value $(E_{n+1}/R_0)_{min}$ were chosen for each system. The values of optional parameters of the process and the values of N_{TS} calculated with the etalon of equilibrium data at chosen conditions of extraction are given in Table I.

RESULTS AND DISCUSSION

The form of the ternary liquid–liquid equilibrium dependences was chosen so as to represent various differences of systems applied in practice. *System I* exhibits the

TABLE I

Operating conditions of the countercurrent extraction and the calculated number of theoretical stages with etalon of equilibrium data

System	$x_{2,0}$	$x_{2,n}$	$(E_{n+1}/R_0)_{min}$	$\dfrac{E_{n+1}/R_0}{(E_{n+1}/R_0)_{min}}$	N_{TS}
I	0·26	0·01	0·326	1·15	14·38
				1·32	9·18
				1·45	7·53
II	0·50	0·01	0·923	1·15	16·98
				1·30	11·66
				1·45	9·26
III	0·50	0·005	0·730	1·10	5·02
				1·30	3·94
				1·45	3·67
IV	0·50	0·01	1·77	1·15	16·17
				1·24	12·62
				1·45	8·84
V	0·50	0·01	4·96	1·15	23·36
				1·25	16·57
				1·30	14·65

closed type of binodal curve with tie-lines for which holds $y_2 > x_2$. *System II* has also the closed binodal curve, however, tie-lines with opposite orientation, i.e., $y_2 < x_2$. *System III* is of solutropic type with closed binodal curve which joins tie-lines with positive and negative slope. *System IV* has the open type of binodal curve with limited solubility of components $1-3$ and $2-3$. For its tie-lines holds
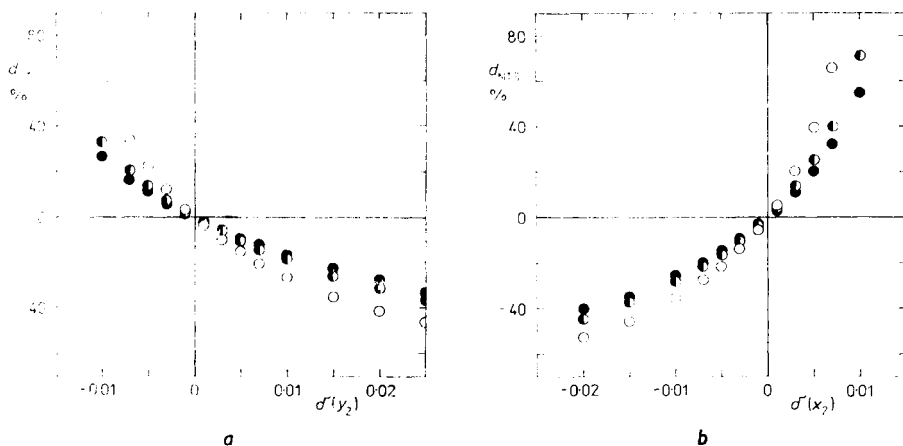

Fig. 2

Dependence of d_{NTS} on a $\delta(y_2)$, b $\delta(x_2)$ for system *I*. Ratio $(E_{n+1}/R_0)/(E_{n+1}/R_0)_{min}$: ○ 1·15, ◐ 1·32, ● 1·45
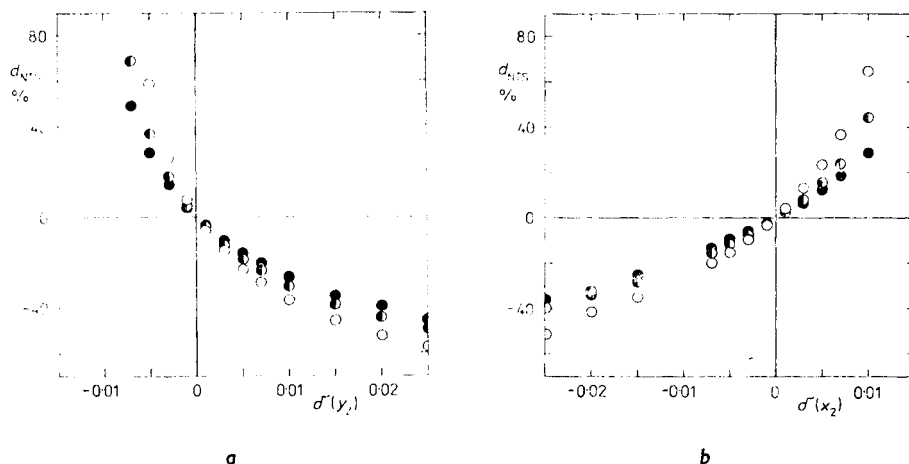

Fig. 3

Dependence of d_{NTS} on a $\delta(y_2)$, b $\delta(x_2)$ for system *II*. Ratio $(E_{n+1}/R_0)/(E_{n+1}/R_0)_{min}$: ○ 1·15, ◐ 1·30, ● 1·45

$y_2 < x_2$. *System V* is of the same type as system *IV*, it differs from it by a lower solubility of components 1 and 2 in component 3.

The calculated results obtained for all five systems are demonstrated in Figs 2 — 6 in the form of graphical representation of the dependence of relative deviation in the number of theoretical stages d_{NTS} on the absolute systematic error of equilibrium
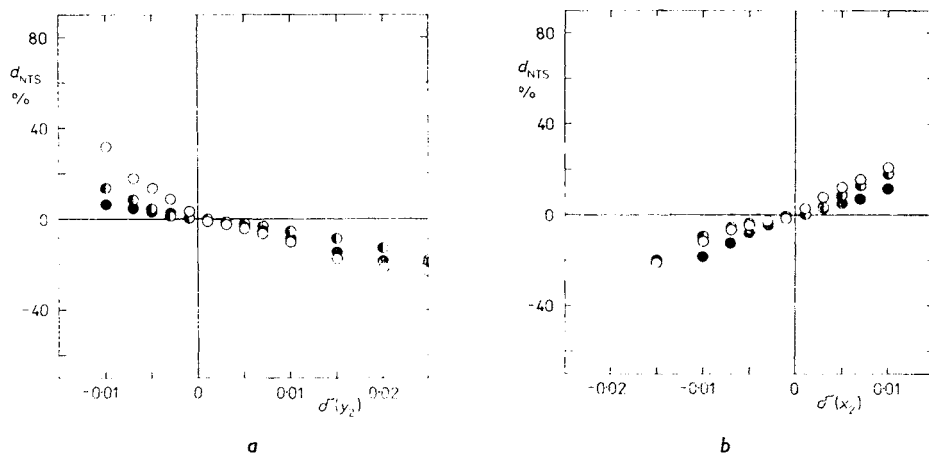

FIG. 4

Dependence of d_{NTS} on *a* $\delta(y_2)$, *b* $\delta(x_2)$ for system *III*. Ratio $(E_{n+1}/R_0)/(E_{n+1}/R_0)_{min}$: ○ 1·10, ◐ 1·30, ● 1·45
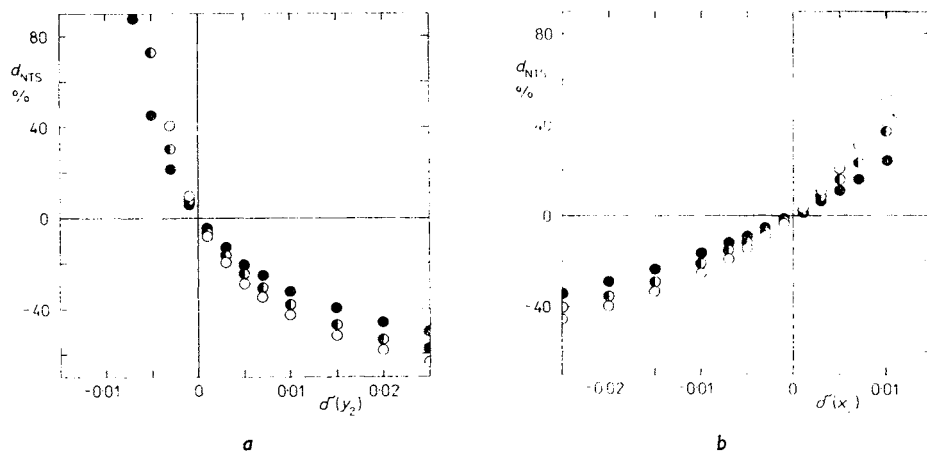

FIG. 5

Dependence of d_{NTS} on *a* $\delta(y_2)$, *b* $\delta(x_2)$ for system *IV*. Ratio $(E_{n+1}/R_0)/(E_{n+1}/R_0)_{min}$: ○ 1·15, ◐ 1·24, ● 1·45

mole fraction of solute in the extract phase $\delta(y_2)$ and the raffinate phase $\delta(x_2)$. In each figure, it is possible to observe the dependences for three values of relative consumption of extractants E_{n+1}/R_0.

As it follows from the figures, the common feature of all the systems examined is that errors $\delta(y_2) > 0$ and $\delta(x_2) < 0$ which cause an increase in the values of distribution coefficient of solute, K_2, diminish N_{TS} in agreement with expectation. The relative deviations in the number of theoretical stages d_{NTS} acquire then negative values. If, however, the errors are of opposite signs, $\delta(y_2) < 0$ and $\delta(x_2) > 0$, the deviations in the number of stages acquire positive values.

It follows from the comparison of deviations d_{NTS} brought about by errors in y_2 and x_2 that the calculated number of stages is largely influenced by the errors causing the decrease of K_2 values, i.e., errors $\delta(y_2) < 0$ and $\delta(x_2) > 0$. By comparing the results of systems I and II in Figs 2 and 3, it follows that errors $\delta(y_2)$ influence the deviations in N_{TS} largely in system II, the tie-lines of which have negative slope whereas in system I with a positive tie-line slope, errors $\delta(x_2)$ bring about larger deviations in N_{TS}.

Similar behaviour can be observed in further system with closed binodal curve, viz. solutropic system III. The effect of systematic errors $\delta(y_2)$ and $\delta(x_2)$ on the calculated number of theoretical stages is in this case, however, much smaller (Fig. 4) in comparison with systems I and II.

The deviations in N_{TS} in systems IV and V with open type of binodal curve (Figs 5 and 6) are more sensitive to the errors in the determination of distribution mole fractions x_2 and y_2 to a larger extent than the systems with closed type of binodal
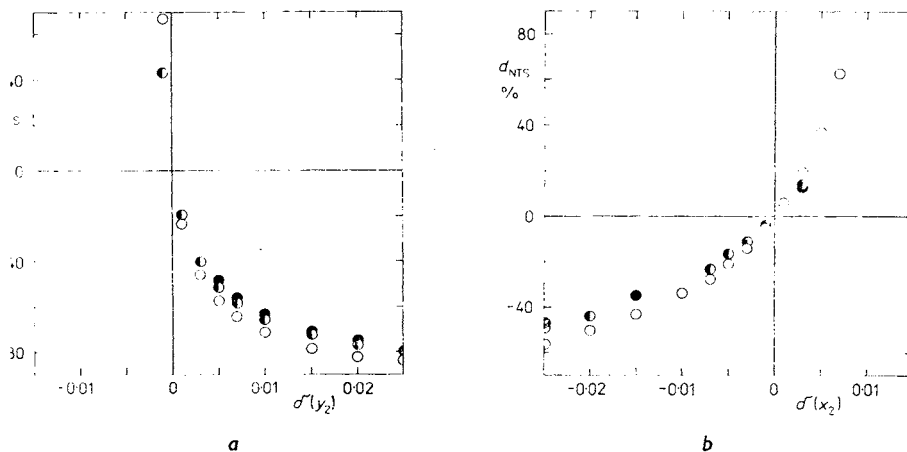

FIG. 6

Dependence of d_{NTS} on a $\delta(y_2)$, b $\delta(x_2)$ for system V. Ratio $(E_{n+1}/R_0)/(E_{n+1}/R_0)_{min}$: ○ 1·15, ◑ 1·25, ● 1·30

curve. The exceptionally strong influence occurs in case of errors $\delta(y_2)$. System V which differs from system IV especially in a shorter extract branch of binodal curve reacts even to relatively small errors $\delta(y_2)$ by large deviations in the number of theoretical stages.

It can be observed in all the systems that with increasing consumption of extractant, the effect of systematic errors in equilibrium concentrations x_2 and y_2 on the calculated number of theoretical stages in the process is reduced.

The demands on the accuracy of equilibrium distribution data follow from the importance of result of the calculation itself. So, e.g., for the design calculation of N_{TS} in countercurrent extraction, the result determined with the accuracy of about $\pm 20\%$ is considered satisfactory. This requirement may be apparently fulfil when systematic errors $\delta(x_2)$ and $\delta(y_2)$ acquire values from a certain interval. The width of this interval depends on the type of system and on the extractant consumption. So, in case that the extractant consumption is about 30% higher than the minimum value and the system is of the type of system I, the error range of $\delta(x_2)$ is $(-0.008, 0.004)$, and the error range of $\delta(y_2)$ is $(-0.007, 0.012)$. For the type of system II, the range $\delta(x_2)$ is $(-0.011, 0.006)$, and the interval of $\delta(y_2)$ $(-0.003, 0.006)$. For the solutropic system III, these intervals are widest, $\delta(x_2)$ $(-0.015, 0.011)$ and $\delta(y_2)$ $(-0.012, 0.025)$. The systems with the open type of binodal curve compared to those with closed type of binodal curve have much narrower range of errors $\delta(y_2)$. So, in system IV, the range of $\delta(x_2)$ is $(-0.01, 0.006)$ and the range of $\delta(y_2)$ $(-0.0025, 0.004)$ and in system V with much shorter extract branch of binodal curve, the range of $\delta(x_2)$ is $(=0.006, 0.007)$, and the range of $\delta(y_2)$ $(-0.0005, 0.001)$.

CONCLUSION

We assume that the results presented will complement suitably the results of our preceding works[2,3] and yield useful information for all who will apply equilibrium data in calculations of diffusion separation equipments. The demands on the accuracy of equilibrium distribution data may appear many a time to be higher than our possibilities. If we dismiss the rare occurrence of solutropic systems then for non-solutropic systems with closed type of binodal curve we will accept as satisfactory the systematic error in equilibrium distribution concentrations of solute of the magnitude about 0.5 mole %. The equilibrium data with systematic error larger than 1 mole % often appear to be of low quality. In case of the systems with open type of binodal curve, the demands on the accuracy of equilibrium data are still higher. It concerns the data of the extract branch of binodal curve whose systematic error should be near-by 0.1 mole %.

LIST OF SYMBOLS

a_i	coefficient in Eq. (*I*)
d_{NTS}	relative deviation in number of theoretical stages
E_k	mole flow of extract from k-th stage
E_{n+1}	mole flow of extractant in process
E_{n+1}/R_0	relative consumption of extractant
K_i	distribution coefficient
N_{TS}	number of theoretical stages
R_0	mole flow of raw material
R_k	mole flow of raffinate from k-th stage
$x_i, x_{i,exp}$	accurate or experimental value, respectively, of equilibrium mole fraction in phase rich in component 1
$x_{2,0}, x_{2,n}$	mole fraction of solute in raw material or in raffinate, respectively, from the last stage
$y_i, y_{i,exp}$	accurate or experimental value, respectively, of equilibrium mole fraction in phase rich in component 3
$\delta(x_2), \delta(y_2)$	absolute systematic error in equilibrium mole fractions x_2 and y_2, respectively

Subscripts

exp	experimental
i	component of system
k	arbitrary stage
min	minimum
n	last stage
NTS	referring to number of theoretical stages
TS	referring to theoretical stages
1, 2, 3	components of system: 1 initial solvent, 2 solute, 3 extractant

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