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**SYSTEMATIC 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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Received September 18th, 1987

Accepted November 6th, 1987

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The influence of magnitude of systematic errors in the determination of ternary liquid-liquid equilibrium concentrations on the accuracy of the calculated number of theoretical stages of countercurrent extraction is evaluated on using five hypothetical systems differing in the extent of mutual solubility of components, tie-line slope, and type of binodal curve.

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In one of our recent papers we have treated the problems of the effect of random errors in measured equilibrium composition of ternary liquid-liquid (L-L) systems on the accuracy of the calculated number of stages of countercurrent extraction. A certain group of questions has been discussed which are of interest especially for the users of experimental data, who apply them in computations of designed separating equipments. The problems have been studied on using five hypothetical ternary systems of which three show the closed type of binodal curve with different orientation of tie-lines and two systems have an open binodal curve.

Since also the systematic errors besides the random errors take part in inaccuracies in the experimental determination of equilibrium concentrations, it is quite well-founded to take also note of the quantitative aspects in the relationship of the systematic errors and the results of calculating the separation equipment. These questions form the substantial part of this work. To make possible, in the problems investigated, to interconnect the systematic and random errors in equilibrium L-L composition, both the etalons of equilibrium data of all the systems and the working conditions of the simulated countercurrent extraction given in preceding paper<sup>1</sup> have been retained without any change. As a measure of magnitude of systematic errors in equilibrium composition, the constant value of relative deviation of solute distribution coefficients has been chosen, changing gradually in a certain range of values. In addition to the influence of distribution equilibrium data, the effect of systematic errors on the determination of binodal curve will be evaluated. Already when judging the random errors<sup>1</sup>, it has been shown that the solubility equilibrium data, which

define the form of binodal curve, can influence the number of stages, especially in the systems with open type of binodal curve.

## THEORETICAL

### *Preparation of Equilibrium Data*

When calculating the extraction equipment, the equilibrium data are used in the form of polynomial<sup>2</sup>

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

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

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

is the distribution coefficient. The way of calculating  $a_i$  in Eq. (1) is described in original works<sup>2,3</sup>.

By determining distribution coefficients  $K_i$ , it is possible to calculate composition of equilibrium phases for a value of  $y_2$  chosen in advance. To do so, the following relations are used

$$x_2 = y_2/K_2, \quad (3a)$$

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

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

together with Eq. (2) to obtain the values of  $y_1$  and  $y_3$ .

The accurate data which form the etalon of equilibrium data were expressed in terms of values  $a_i$  in Eq. (1) and their values for all five systems are given in preceding work<sup>1</sup>. Graphical representation of these data is given here as the triangle diagrams in Fig. 1.

The L-L equilibrium data subjected to systematic errors were prepared by a simulated experiment, the measure of their magnitude being chosen a constant value of the relative deviation of mole fraction of solute in some of both equilibrium phases or the relative deviation of the solute distribution coefficient following from it. These data are denoted as distribution ones, and the tie-lines of equilibrium dependences are described by them. The number of tie-lines was always chosen equal to ten. In their simulation, the unchanged form of binodal curve given by the respective values from the etalon of equilibrium concentrations was considered first. From the definition relation of the per cent relative deviation, for the distribution equilibrium

data of mole fraction of component 2 then follows

$$y_{2,\text{exp}} = y_2(1 + d(y_2)/100), \quad (4a)$$

$$x_{2,\text{exp}} = x_2(1 + d(x_2)/100). \quad (4b)$$

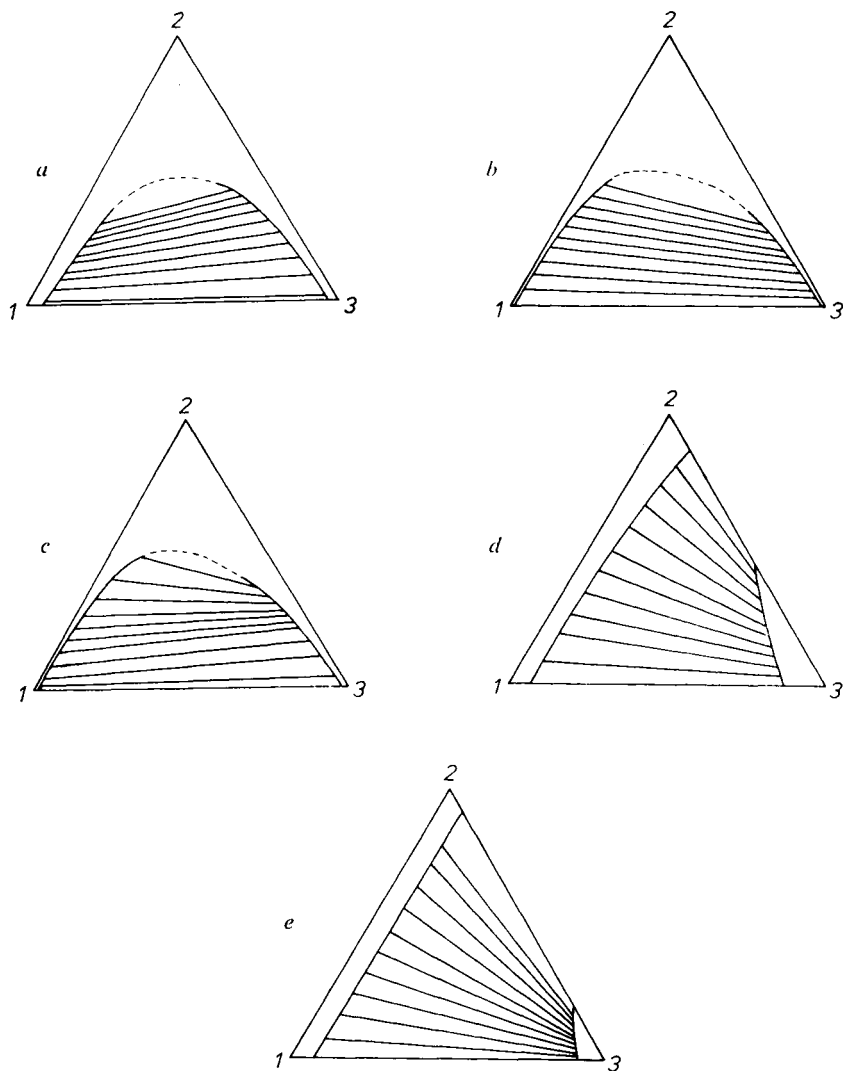


FIG. 1  
Equilibrium L-L diagrams of hypothetical systems. *a* System I, *b* system II, *c* system III, *d* system IV, *e* system V

In Eq. (4),  $y_2$ ,  $x_2$  are the accurate values of mole fractions of solute 2 in the phase rich in component 3 or component 1,  $d(y_2)$  and  $d(x_2)$  are the constant values of per cent relative deviation of mole fractions of component 2 chosen from the interval  $\pm 2\%$  to  $\pm 15\%$ . The values of mole fraction  $y_1$  change, in case of the deviation  $d(y_2)$  considered, only slightly and therefore they were determined by linear interpolation. Mole fraction  $y_3$  was considered as dependent, and its values were established by complementing to unity. When simulating the values of mole fraction  $x_2$ , the values of  $x_3$  were determined by linear interpolation whereas  $x_1$  were complemented to unity. Each set of distribution equilibrium data prepared in this way and corresponding to ten tie-lines was correlated by Eq. (1) before the application, a continuous description of equilibrium dependences being obtained.

For calculating the number of stages in countercurrent extraction, the "experimental" equilibrium data are replaced by the correlated data. Therefore, when evaluating the effect of magnitude of systematic errors, it will be given in the form of average per cent relative deviation of correlated values of distribution coefficient of solute

$$\langle d(K_2) \rangle = (100/n) \sum_l [(K_{2,l,corr} - K_{2,l})/K_{2,l}] \quad (5)$$

for  $l = 1, 2, \dots, n$ , where  $n = 10$ . The values of  $\langle d(K_2) \rangle$  have either positive or negative value. The positive value of  $\langle d(K_2) \rangle$  is connected with such systematic errors which bring about an increase of values  $K_{2,corr}$  either by increasing  $y_{2,exp}$  or decreasing  $x_{2,exp}$  in comparison with the accurate data of these quantities. In case of the negative value of  $\langle d(K_2) \rangle$ , the situation is opposite.

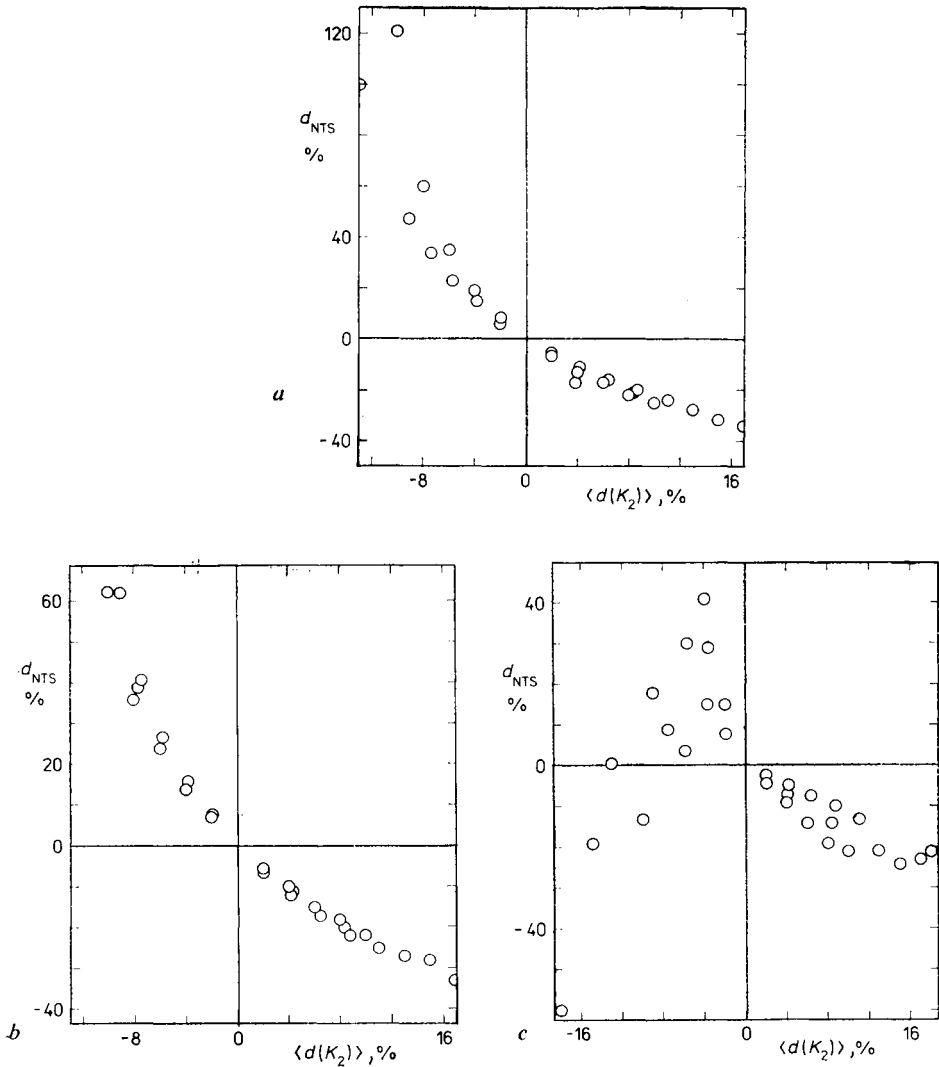
In other series of the experiments, only the solubility data were subjected to systematic errors, with which the form of binodal curve was adequately adapted. The branches of binodal curve were in this way shifted either closer to the sides of triangle diagram which a larger heterogeneous region corresponds to in comparison with the etalon of equilibrium data or in the opposite direction which a larger mutual solubility of solvents 1 and 3 corresponds to. In such a way adapted positions of branches of binodal curve were calculated from the chosen constant values of relative deviation of mole fraction of component 1 in mixtures rich in solvent 3,  $d(y_1)$ , and from values  $d(x_3)$  in mixtures rich in initial solvent 1. The values of deviations  $d(y_1)$  and  $d(x_3)$  were chosen gradually in the range of  $\pm 2\%$  up to  $\pm 10\%$ . The mole fractions of solute  $y_2$ ,  $x_2$  and therefore also the values of distribution coefficient  $K_2$  remained unchanged for single tie-lines and consequently identical with "accurate" values.

#### *Application of Equilibrium Data*

The number of theoretical stages (NTS) needed in countercurrent extraction was calculated by using the correlated set of equilibrium data prepared always for a cer-

tain constant value of relative deviation  $\langle d(K_2) \rangle$ . All the optional parameters of calculation, such as they had been given in preceding paper<sup>1</sup>, remained unchanged. The fundamental relations and the algorithm of calculation of NTS had been given in paper<sup>3</sup>. The calculated number of theoretical stages  $N_{TS,exp}$  for the "experimental" equilibrium data were compared with the value of  $N_{TS}$  obtained with the "accurate" equilibrium data in the form of per cent relative deviation

$$d_{NTS} = 100(N_{TS,exp} - N_{TS})/N_{TS} \quad (6)$$



The values of  $N_{TS}$  for single systems had been given in paper<sup>1</sup>. By means of Eq. (6), the results of calculation were also evaluated in which the solubility equilibrium data were subjected to systematic error taking a constant value of  $d(y_1)$  and  $d(x_3)$  always the same as to the magnitude and sign.

## RESULTS AND DISCUSSION

The obtained results of calculation are given in Fig. 2 in the form of graphical representation of the dependence between the relative deviation in NTS and the average relative deviation in  $K_2$  on evaluating the effect of systematic errors of distribution equilibrium concentrations. The dependences of relative deviation in NTS on the average relative deviation of  $y_1$  and  $x_3$  expressing the influence of systematic errors in solubility equilibrium concentrations are given in Fig. 3.

The positive values of  $\langle d(K_2) \rangle$  in Fig. 2 are connected with the error causing the increase in values of  $K_2$  in comparison with the etalon of equilibrium data. As expected, the systematic errors in the indicated direction manifest themselves in reducing the required number of stages in countercurrent extraction and consequently in negative values of  $d_{NTS}$ . The course of this decrease is approximately the same in systems *I*, *II*, and *IV* whereas in solutropic system *III*, this decrease is a little

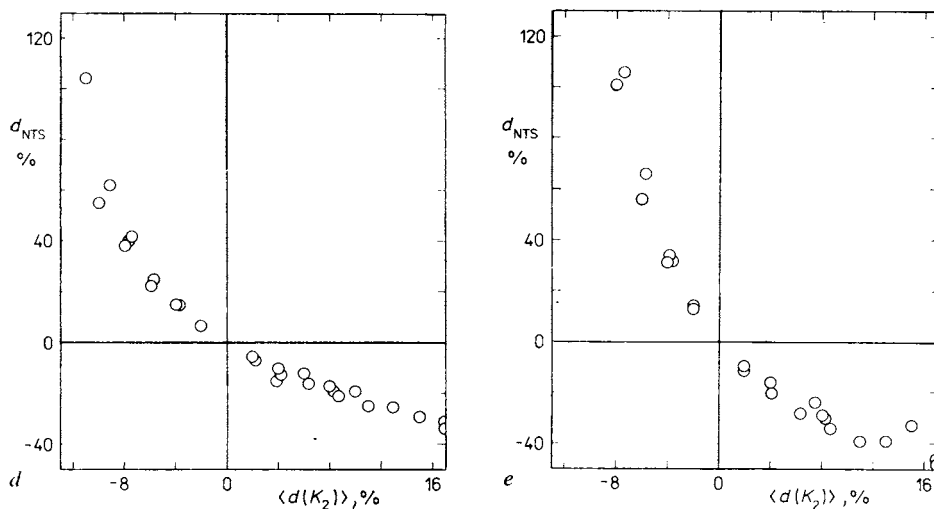


FIG. 2

Dependence of  $d_{NTS}$  on  $\langle d(K_2) \rangle$  for different systems. *a I*, *b II*, *c III*, *d IV*, *e V*

smaller and in system *V* a little larger. On the left-hand side of Fig. 2 one can see the effect of systematic errors manifesting themselves in decreasing the equilibrium  $K_2$  values which negative values of  $\langle d(K_2) \rangle$  correspond to. Systems *I*, *II*, and *IV* behave also in this region in a very similar way, which only confirms that the deviations in NTS do not depend so strongly on the tie-line slope of equilibrium dependence (system *I* has  $y_2 > x_2$ , system *II* has  $y_2 < x_2$ , and system *IV* has  $y_2 < x_2$  and open type of binodal curve) as on the magnitude of changes in  $K_2$ .

The behaviour of solutropic system in Fig. 2c is different from the other systems. The relative deviations in NTS increase at first with decreasing  $\langle d(K_2) \rangle$  and after exceeding a certain value of  $\langle d(K_2) \rangle$  (about  $-5\%$  to  $-7\%$ ) a decrease even in  $d_{\text{NTS}}$  occurs. The observed changes take place apparently owing to a considerable reorientation of arrangement of tie-lines. As to the solutropic systems, it is well-known that, unlike the azeotropic systems in distillation, they can be separated altogether without limitations even though also here difficulties may occur, e.g., in determining the suitable consumption of solvent.

The results for system *V* with open binodal curve and with comparatively low solubility of component 2 in 3 (which a short extract branch of binodal curve corresponds to) are illustrated in Fig. 2e. This system reacts in the most sensitive way to systematic errors of the distribution equilibrium quantities. So, e.g., at 6% decrease in  $K_2$  values as much as 60% increase in NTS occurs.

A common feature of the systems examined here (partly with the exception of the solutropic one) is that the systematic errors causing a decrease in  $K_2$  values influence the inaccuracies of NTS determination in much greater degree than the errors causing an increase in  $K_2$  values. This effect is made deeper with increasing the absolute

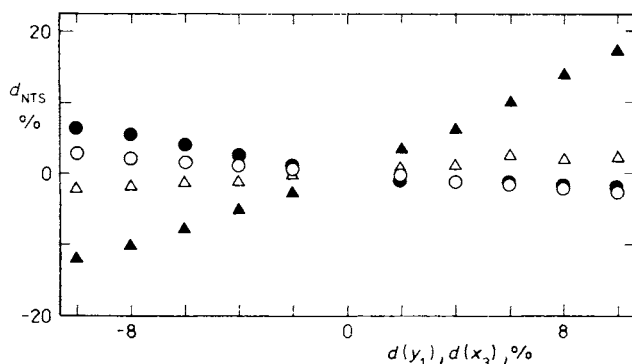


FIG. 3

Dependence of  $d_{\text{NTS}}$  on  $d(y_1), d(x_3)$ .  $\circ$  System *II*,  $\bullet$  system *III*,  $\triangle$  system *IV*,  $\blacktriangle$  system *V*

value of  $\langle d(K_2) \rangle$ . So, e.g., in system II in Fig. 2b,  $d_{NTS}$  is about  $-20\%$  for  $\langle d(K_2) \rangle = 8\%$  whereas for  $\langle d(K_2) \rangle = -8\%$  the value of  $d_{NTS}$  changes to  $+40\%$ . This knowledge can be useful, e.g., in some methods of the experimental determination of tie-lines when the concentration of component 2 is determined only in one of equilibrium phases, the form of binodal curve and composition of heterogeneous mixture being known.

Whereas the inaccuracies in tie-line determination influence NTS in counter-current extraction conspicuously, the effect of systematic errors in binodal curve manifests itself only slightly. Fig. 3, which is an evidence of this, confirms this observation already when investigating the effect of random errors in the given problems<sup>1</sup>. Perhaps only in system V, mild influence on the resulting number of theoretical stages is observed.

We assume that the results given here complete suitably those reported formerly<sup>1</sup>, and that together can provide useful information for all those who will apply the L-L equilibrium data in different calculations of separation equipments as well as for those who take part in the preparation of L-L equilibrium data and many a time must decide upon the suitability of a method of their determination (not only experimental one), quality of experimental technique, purity of substances used, etc.

## LIST OF SYMBOLS

|                          |   |
|--------------------------|---|
| $a_i$                    | coefficients in Eq. (1)   |
| $d(x_i), d(y_i)$         | relative deviation of mole fractions  |
| $d(K_i)$                 | relative deviation of distribution coefficient  |
| $d_{NTS}$                | relative deviation in number of theoretical stages  |
| $\langle d(K_i) \rangle$ | average relative deviation  |
| $K_i$                    | distribution coefficient  |
| $n$                      | number of tie-lines   |
| $N_{TS}$                 | number of theoretical stages  |
| $x_i, x_{i,exp}$         | accurate or experimental value, respectively, of mole fraction in phase rich in component 1 |
| $y_i, y_{i,exp}$         | accurate or experimental value, respectively, of mole fraction in phase rich in component 3 |

## Subscripts

|         |   |
|---------|---|
| corr    | correlated  |
| exp     | experimental  |
| i       | component of system   |
| l       | serial number of tie-line   |
| NTS     | referred to number of theoretical stages  |
| TS      | referred to theoretical stages  |
| 1, 2, 3 | designate components of system: 1 initial solvent, 2 solute, 3 solvent (extracting agent) |



## REFERENCES

1. Dojčanský J., Bafrncová S., Surový J.: Collect. Czech. Chem. Commun. 53, 34 (1988).
2. Rod V.: Chem. Eng. J. 11, 105 (1976).
3. Dojčanský J., Surový J., Bafrncová S.: Collect. Czech. Chem. Commun. 47, 550 (1982).

Translated by J. Linek.