ANALELE UNIVERSITATII BUCUREŞTI

Department of Physical Chemistry
4-12 Regina Elisabeta Blvd, District 3, Bucharest
phone: +40-21-3143508; fax: +40-21-3159249
*p*ISSN: 1220-871X *e*ISSN: 1844-0401

ARS DOCENDI PUBLISHING HOUSE
Sos. Panduri 90, District 5 Bucharest
phone/fax: +40-21-4102575
e-mail: arsdocendi@yahoo.com

NEW ALGORITHM AND PROGRAM FOR SIMPLE EXTRACTION WITH MULTIPLE CONTACTS OPTIMIZATION

T.-M. Sturzu * **and Mirela Marcu** **

abstract: A mathematical algorithm and a Turbo Pascal computer program, allowing to perform some calculations for simple extraction with multiple contacts, using the Gibbs's triangle and a new method of interpolation, simpler than the usual one, are described. The results obtained on the computer are in line with those obtained by hand execution of the graphical constructions, being confirmed by the experimental results. The depicted algorithm obviously simplifies the hand graphic construction work.

key words: simple extraction with multiple contacts; Gibbs's triangle; new interpolation method; simulation; computer program.

received: January 12, 2010 *accepted*: March 22, 2010

1. Introduction

The simple extraction with multiple contacts [1], or the extraction with the circulation of the phases in cross current, consists of the recurrence of the simple extraction with unique contact, which permits a better separation of the components of initial mixture with the same total quantity of extractive solvent. One recommends [2] the using of equal quantities of solvent or of a unitary proportion between the extraction solvent quantity and the quantity of initial mixture or refined mixture. Extraction solvent is mixed successively with the refined mixture resulted in the previous step, that permits to obtain – whether the contact steps are great enough – a refined mixture with a sufficient degree of purity. The purity of the extract increases with increasing the number of extraction steps.

After each addition of solvent, one makes the mixing up of the two phases that is followed by their separation. Each series of operations corresponds to a step of extraction. The procedure can be realized in steps or continuously. When one works in steps, a single extraction unit (that consists in a mixer and a separator apparatus used successively), can

* Department of Chemical Technology, Natural Resources and Environment Protection, "Radu Cernătescu" Scholar Group, 61 A Socola, Iassy, Romania. *corresponding author e-mail*: tibisturzu@yahoo.com
** Department of Chemistry, "Tudor Vianu" National High School of Informatics, 10 Arhitect Ion Mincu Street, Bucharest, Romania.

replace more unities. The scheme of a simple extraction with multiple contact system, in stationary regime, is depicted in Fig. 1.

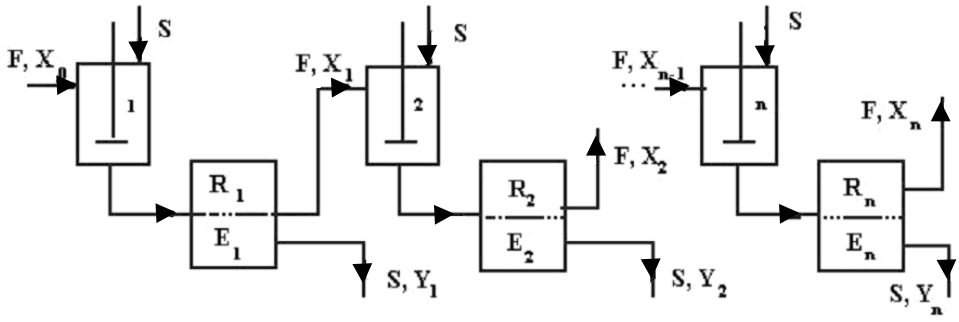

Fig. 1 *Simple extraction with multiple contacts system, in stationary regime: S – mass flow of extractive solvent, in kg/h; F – mass flow of primary solvent, in kg/h; X_0 – mass ratio of the useful component in the primary solvent, in kg B/kg S (B – the useful component); X_i – mass ratios of the useful component in the primary solvent in refined mixture, after the step i, i = 1 ... n, kg B/kg R_i; Y_i – mass ratios of the useful component in the secondary solvent in the extract after the step i, kg B/kg E_i; R_i – mass flows of the primary solvent in refined mixture, after the extractive step i, kg/h; E_i – mass flows of secondary solvent in extract, after the extractive step i, kg/h.*

The calculation of the simple extraction with multiple contacts consists of the determination of the steps number that are necessary for the obtaining of a final refined mixture having an imposed composition, when one specifies the flow rate of the initial mixture and its composition, and the flow rate and the composition of the extractive solvent used in each contact unit [3]. If one respects the Nernst rule, the method of solving the extraction problems is that depicted in the literature [4]. If the extraction solvent is not total immiscible with the primary solvent, the solving of simple extraction with multiple contacts problems is realized using ternary graphics (Gibbs's triangles), in an analogous mode as the solving of simple extraction with unique contact problems, the graphic construction being repeated for more times, until one gets an imposed separation degree, that means a minimum concentration of the useful component in the final refined mixture. For the purification of the wastewaters is necessary to realize – using extraction – a certain composition of the final refined mixture, such as it cannot pollute the receptor river.

2. A new graphic interpolation method in Gibbs's triangle

One of the disadvantages of the Gibbs's triangles using for solving the extraction problems is the difficulty of the procedure for the conoda which pass through a certain point constructions. The more used actual procedure [4] of graphic interpolation for the construction of a conodum that passes through a certain point is the following (see Fig. 2):

– being known the ratio between the quantity of extractive solvent and initial mixture, one can establish the position of P point, through it is necessary to draw the conodum using the graphic interpolation;

– one draws the adjacent of point P conoda, being known the equilibrium phases compositions;

- one connects point P with the triangle top which corresponds to the useful component and one prolongs the straight line until it intersects the opposite side in C point;
- one draws parallels to the sides of the triangle trough the intersection points of the given conoda with the refined mixtures branch of the binodal curve and with the drown straight line, respectively;
- through the intersection points obtained one draws a conjunction straight line (interpolation straight line);
- through the point P one draws a parallel to the straight line W – A until this intersects the interpolation straight line;
- through the new intersection point one draws a parallel to A – C straight line, until it intersects the refined mixtures branch of binodal curve;
- the intersection point obtained is connected with the point P, and the straight line is extended until to the intersection with the extract's branch of the binodal curve, thus being obtained the new conodum.

Although on the computer, we can avoid the visualization of the presented graphical construction, even its analytic pursue is intricate. If one tries the graphical construction on graph paper, the density of lines is so great at high number steps of extraction, that the auxiliary construction for the drawing of conoda "muddles the place". Taking into account this reason, the solving of extraction problems using Gibbs's triangle is practically abandoned, other methods being preferred, that uses rectangular equilibrium diagrams and auxiliary interpolation constructions that complicate the calculation. We note here that new geometric and simulation based methods were already proposed for solving extraction problems for mixtures of up to four components [5, 6]. However, we have considered that the method of extraction problems solving using ternary diagrams (Gibbs's triangles) must not be abandoned, even though it is restricted to ternary systems. It is necessary only its improvement and its implementation on the computer.

Owing to this reason, we have suggested a new method of graphical interpolation that uses only three auxiliary straight lines instead of ten auxiliary straight lines. The method consists of the following:

- one draws the conoda adjacent with point P and they are extended until they are intersected in point K,
- one connects point K with point P, extending the straight line until to the intersection with the extracts branch, getting the new conodum.

One can notice in the figure that the superposition of the obtained conoda is almost perfect. We do not have to forget that the classical method is an approximation too. The advantages of the new method are the following:

- the auxiliary construction does not "muddle the place" destined to the main graphical construction, although at little concentrations it needs additional space;

– the new method is simpler for its analytic transposition, having as an aim the simulation of the graphic construction on computer, where it is not absolutely necessary the visualization of the auxiliary construction for conoda's drawing.

Fig. 2 presents the two methods of interpolations for their comparison. Obviously, we continued to use the new interpolation method.

The disadvantage of the method is the great space occupied, on graph paper, outside of the Gibbs's triangle, but this disadvantage is less important than the construction of an illegible graphic owing to the lines' density. At the analytic transposition for the simulation on the computer, this disadvantage disappears and the new method is preferable.

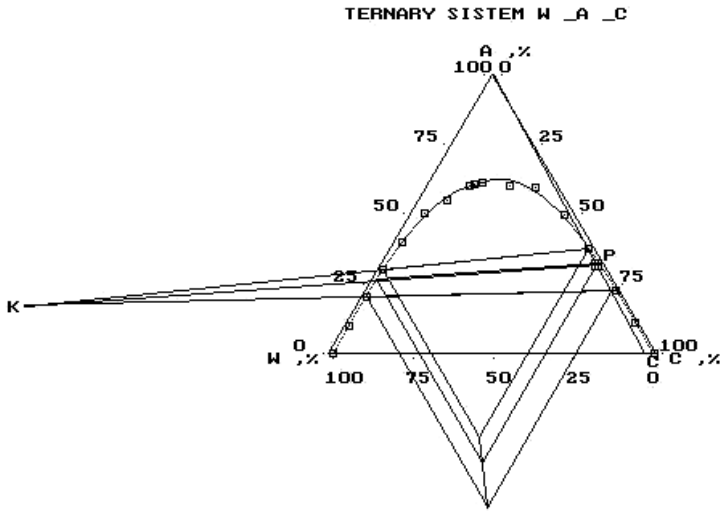

Fig. 2 *Comparison between the classical interpolation method and the new interpolation method for the conoda's drawing that pass trough a certain point, for the ternary system water (W) – acetone (A) – chlorobenzene (C).*

3. Distinctive features for the simulation of problems solving of simple extraction with multiple contacts using graphical methods

For the computer solving of simple extraction with multiple contacts problems we used *the rectangular-triangular model for liquid-liquid equilibrium in ternary system*, model that is based on a change of variable such as, both in Gibbs's triangle and in associated rectangular system, the graphical representations are identical [7].

The simulation of simple extraction with multiple contacts problems follows the graphical construction from Fig. 3, in line with the following algorithm:

– one determines the polynomial regressive equation' degrees both for the extracts branch and for the refined mixtures branch, that are the branches of binodal curve;

– one determines the polynomial regressive equations' coefficients for the two branches of binodal curve, such as the form of binodal curve to be identical in the two

representation systems, being possible both the analytic solving and the drawing of Gibbs's triangle on the computer's screen;

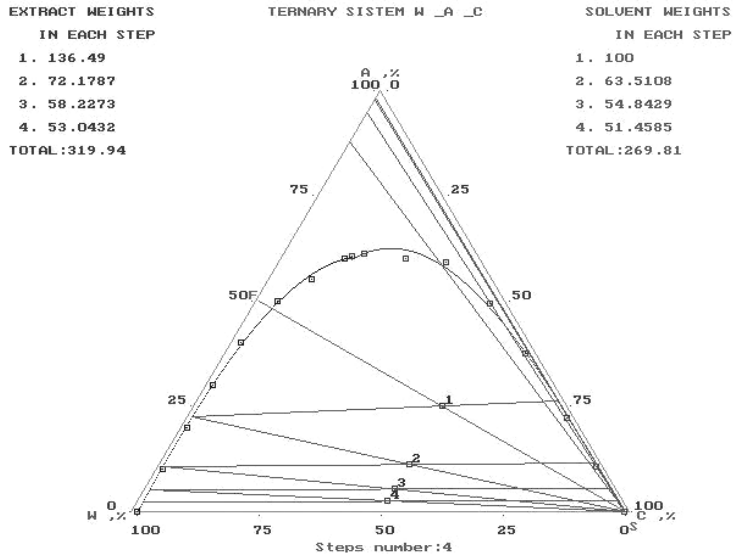

Fig. 3 *The solving of simple extraction with multiple contacts problems in Gibbs's triangle (the result of the computer program for the analysed example, for 100 g initial mixture).*

- one determines the equation of the straight line which passes through the figurative points that corresponds to the initial mixture (F) and to the solvent (C) and draws the straight line;
- one determines the position of point (1) on the drawn straight line, knowing that the initial ratio mixture: solvent is 1:1, ratio considered optimal by some authors [4];
- through point (1) one draws the conodum using the new interpolation method;
- one determines the intersection points of the conodum with the extracts branch and the refined mixtures branch, respectively; for the determination of the intersection point between a straight line with a curve we used the halving interval method, because one cannot know *a priori* the degree of curve equation;
- one connects the intersection point of the curve with extracts branch with the point which figurate the solvent and determines the equation of this straight line;
- one determines the position of point (2), knowing the ratio solvent-to-refined mixture etc.;
- the graphic construction is finished whether the conodum intersects the refined mixtures branch in a lower or equal point with that imposed;
- one calculates the quantities (flow rates) of solvent for each extractive step and the quantities (flow rates) of extract and refined mixture, using the lever's rule;

– one determines the compositions of free solvent extracts for each extractive step and the medium composition of free solvent extract.

The module of Turbo-Pascal program that realises the comparison between the classical method and the new interpolation method, using user's procedures [7], is presented below.

```
  'n':BEGIN
  writelc(11,10,lightgreen,'x a dat
  (% weight):');read(cmag);
  writelc(13,10,lightgreen,'x b dat
  (% weight,>20%):');read(cmb);
  cma:=100-cmag-cmb/2;
  writelc(15,10,lightmagenta,'Fond
 (0-black,1-white):');read(cb);
  initgraph(gd,gm,pdriver);if cb>0 then
  setbkcolor(white);
  xcen:=round(getmaxx/2)-100;ycen:=250;
  triangle(2,3);cold(cb,blue);
  points(2,xa,xb);cold(cb,magenta);
  points(2,ya,yb);cod:=3;
  coefficients(xa,xb,br,grr);
  cod:=4;coefficients(ya,yb,be,gre);
  curve(2,1,n,grr,br,xa);
  curve(2,n,1,gre,be,ya);
  if cb=0 then cul:=lightred else cul:=red;
  square(xcen+round(2*cma),ycen+round
  (2*cmb*sin(pi/3)),6,cul);
  writexy(xcen+round(2*cma)+5,
  ycen+round(2*cmb*sin(pi/3))+9,0,1,'P');

{CLASICAL METHOD PROGRAMMING}
  pr:=0;xbl1:=0; for j:=2 to n-1 do begin
   ecdr2p(xa[j],xb[j],ya[j],yb[j],a0,a1);
   xbl2:=a0+a1*cma;
   if (cmb>=xbl1) and (cmb<xbl2) then pr:=j-1;
  xbl1:=xbl2;end;
  if cb=0 then col(white) else col(darkgray);
  linieh(2,xa[pr],xb[pr],ya[pr],yb[pr]);
  linieh(2,xa[pr+1],xb[pr+1],
  ya[pr+1],yb[pr+1]);
  if cma=50 then begin d0:=50;d1:=0;
  end else begin
   ecdr2p(50,100,cma,cmb,d0,d1); end;
  if cma=50 then begin cx:=50;cy:=0;
  end else pint2d(d0,d1,0,0,cx,cy);
  plot(xcen+100,ycen+round(200*sin(pi/3)));
  dr(round(2*cx-100), round((2*cy-200)*sin(pi/3)));
  writexy(xcen+round(2*cx)+2,ycen-2, 0,1,'C');
  ecdr2p(xa[pr+1],xb[pr+1],ya[pr+1],yb[pr+1],b0,b1);
  ecdr2p(xa[pr],xb[pr],ya[pr], yb[pr],c0,c1);
  pint2d(b0,b1,d0,d1,dx,dy);
  pint2d(c0,c1,d0,d1,ex,ey);ecdr1ppd(2,dx,dy,e0,e1);
  ecdr1ppd(-2,xa[pr+1],xb[pr+1],f0,f1);
  pint2d(e0,e1,f0,f1,fx,fy);
  linieh(2,xa[pr+1],xb[pr+1],fx,fy);
linieh(2,dx,dy,fx,fy);ecdr1ppd(2,ex,ey,g0,g1);
  ecdr1ppd(-2,xa[pr],xb[pr],h0,h1);
  pint2d(g0,g1,h0,h1,gx,gy);
```

```
  linieh(2,xa[pr],xb[pr],gx,gy);
  linieh(2,ex,ey,gx,gy);readkey;
  ecdr2p(fx,fy,gx,gy,f0,f1);
  linieh(2,fx,fy,gx,gy);readkey;
  ecdr1ppd(2,cma,cmb,h0,h1);
  pint2d(f0,f1,h0,h1,dx,dy);
  linieh(2,cma,cmb,dx,dy);readkey;
  ecdr1ppd(-2,dx,dy,g0,g1);
  intdrcb(1,grr,br,g0,g1,ex,ey);
  linieh(2,dx,dy,ex,ey);readkey; cold(cb,red);
  ecdr2p(cma,cmb,ex,ey,h0,h1);{conoda}
  intdrcb(2,gre,be,h0,h1,dx,dy);
  linieh(2,ex,ey,dx,dy);{e conoda}

  {PROGRAMMING FOR THE NEW METHOD}
  pint2d(b0,b1,c0,c1,kx,ky);
  linieh(2,ya[pr+1],yb[pr+1],kx,ky);
  linieh(2,ya[pr],yb[pr],kx,ky);
  writexy(xcen+round(2*kx,10,
  ycen+round(2*ky*sin(pi/3))+3,0,1,'K');
  readkey;
  ecdr2p(cma,cmb,kx,ky,f0,f1);
  intdrcb(2,gre,be,f0,f1,fx,fy);
  linieh(2,kx,ky,fx,fy);
  readkey;closegraph;
END;
```

The program realises the correlative analysis between the variables of the process [8], and the determination of the coefficients of regressive equations for the two branches of binodal curve [9]. It also uses user's procedures from a personal library of procedures [7].

4. Results and discussion

Having as an aim the validation of the calculation algorithm and of the proposed program we considered the extraction of acetone out of an initial mixture acetone-water, with 50 % (weight) acetone, using as extractive solvent pure chlorobenzene. We worked with 100 g initial mixture. The equilibrium data for the ternary system water-acetone-chlorobenzene was taken from the literature [4]. It was imposed that the refined mixture must contain maximum 2.5 % acetone. We draw then the graphics manually and simulated them on the computer. For the branches of saturation isotherm we got the regressive equations coefficients in rectangular system axis associated with Gibbs's triangle.

Using the computer program we obtained the construction from Fig. 3. The program can be used for any input valid data. For the considered example, we got four contact steps and the quantities of extractive solvent and extract for each contact step. The quantities of the refined mixture and the compositions of the free of solvent extracts (% weight of acetone) are given in Table 1.

Comparable results were obtained doing the experiments and from the manually elaborated graphics. We could remark that the graphic construction time on the graph paper is great enough, while on the computer the results were got in only few seconds, and that, at little values of the concentrations, graphical constructions are considerable influenced by the

executor's ability, being subjective and generating errors. The new interpolation method that was proposed, having great advantages on the computer simulation, is not so practicable using hand construction, because it necessitates a huge graph paper surface for the auxiliary constructions for conoda's interpolation.

Table 1 *Results obtained at the simulation of simple extraction with multiple contacts for water-acetone-chlorobenzene system.*

Contact step	Quantity of the refined mixture in each step (g)	Composition of the free of solvent extract (% weight of acetone)	Average composition of the free of solvent extract (% weight of acetone)
0	100	-	97.1361
1	63.5108	97.7513	
2	54.8429	97.4308	
3	51.4585	94.2541	
4	49.8739	87.5154	

The dosage of acetone from the phases of extract and refined mixture for the four extractive steps has been done by titration with $KMnO_4$ in alkaline medium, when acetic acid, carbon dioxide and water were obtained. For accuracy, titrations with $K_2Cr_2O_7$ in acid medium have also been done, the results being roughly the same. Reproducible results were also obtained using the iodometric method, using a solution of KI – KIO_3 in a KOH medium, the excess of iodine being titrated with a solution of $Na_2S_2O_3$ 0,1 n, in the presence of starch [10].

5. Conclusions

One can get the following conclusions:

a) We elaborated a mathematical algorithm and a *Turbo-Pascal* computer program that permits the effectuation of some calculations on the computer for simple extraction with multiple contacts;

b) We elaborated a new graphical interpolation method for the drawing of conoda which pass through a point with a certain composition; the method is more advantageous both for hand graphic constructions, because the auxiliary construction is simpler and is placed in the exterior of Gibbs's triangle, and for the simulation of the graphical constructions on the computer, because it simplifies very much the algorithm for the drawing of new conoda;

c) The obtained results are in line with that we obtained experimentally and by hand execution of graphical constructions;

d) The elaborated program can be used both in industry and research units for calculations and in educational units, as a didactic facility.

REFERENCES

1. Mămăligă, I. and Petrescu, S. (2007) **Operații de transfer de masă şi utilaje specifice**, Ed. Ceremi, Iași, 263-92.

2. Kafarov, V. (1975) **Fundamentals of Mass Transfer**, Mir Publishers, Moscow, 85-105.

3. Florea, O. şi Dima, R. (1984) **Procese de transfer de masă şi utilaje specifice**, Editura Didactică si Pedagogica, Bucureşti, 89-103.

4. Pavlov, C. F., Romankov, P.G. and Noskov, A.A. (1981) **Procese şi aparate în ingineria chimică**, Editura Tehnică, Bucureşti, 351-89.

5. Minotti, M., Doherty, M.F. and Malone, M.F. (1996) *Ind. Eng. Chem. Res.* **35**, 2672-81.

6. Marcilla, A., Gomez, A., Reyes, J.A. and Olaya, M.M. (1999) *Ind. Eng. Chem. Res.* **38**, 3083-95.

7. Sturzu, T.M. and Marcu, I.C. (2004) *Analele Universităţii Bucureşti. Chimie* **13**(1-2)**,** 303-8.

8. Bakhalov, N. (1976) **Méthodes numériques – Analyse, algebre, équations différentielles ordinaires**, Éditions Mir, Moscow, 61-6.

9. Sturzu, T.M. (1989) *Bul. Fiz. Chim.* **XII-XIII**, 105-8.

10. Albert, F. and Greff, C. (2002) **Analiză chimică organică**, Editura Tehnică, Bucureşti, 240-1.