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VISUALIZATION METHODS FOR EVALUATION OF FEASIBLE SEPARATIONS OF AZEOTROPIC MIXTURES

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Abstract

In this study the visualization system AVS (Application Visualization System) is applied. This tool is provided with a module library for userfriendly modelling of systems under study. Three data viewers are implemented: Image Viewer, Graph Viewer and Geometry Viewer allowing the graphical representation of multidimensional data fields as the boiling and dew temperatures as a function of the composition. By using special modules the graphical representations can be characterized by colours, brightness and other effects; by the zoom module the scale can be varied; there are also possibilities for the animation of the objects under study, the representation of isolines, for example of temperature or driving forces, as well as the calculation and representation of vector fields. The last option makes it possible to construct representation combining information about the residue curve map and the temperature surface.

Keywords: separations of azeotropic mixtures.

1. Introduction

Highly nonideal mixtures are characterized by strong interactions between the molecules of components as hydrogen bonding, dispersion forces, dipole-dipole interaction which cause deviations from Raoult's law and result in such phenomena as homogeneous or heterogeneous azeotropes. Azeotrope forming compounds are quite common. There was published recently a two-volume compilation with data of more than 18 800 azeotropic systems involving about 1700 compounds (GMEHLING, 1994). There are different types of azeotropes as binary azeotropes, ternary, quaternary and even two quinary azeotropes, further minimum, maximum or saddle azeotropes.

The topology of binary azeotropic mixtures appears in various graphic representations in the following way :

- Minimum or maximum boiling temperatures under constant pressure conditions,
- Minimum or maximum total vapor pressure at constant temperature,

- The vapor–liquid equilibrium diagram is such that an intersection between the equilibrium curve and the 45°-line can be observed.

2. Ternary and Higher Dimensional Azeotropic Mixtures

In binary systems the situation and the topology is simple and obvious and the synthesis of optimal separation schemes can be carried out without complications. But the separation of binary azeotropic mixtures needs often the involving of a third compound – an entrainer – and this results finally in a ternary mixture.

The complications in the process synthesis are connected with ternary and higher dimensional systems. Depending on the number of components involved in a mixture and on the order of azeotropic points a great variety of topologies studied by many investigators appears, see for example (MATSUYAMA and NISHIMURA, 1977).

In *Fig. 1* a ternary system is presented showing the great variety of topologies in the boiling temperature vs. composition diagrams of such mixtures as binary and ternary azeotropic points, distillation boundaries and saddle points. The composition of a mixture containing N species with L_i $(i = 1, 2, \ldots, N)$ moles of each is uniquely defined by a state vector of $N-1$ mole fractions $x = (x_1, \ldots, x_{N-1})$ and can be represented as a point in a $(N-1)$- dimensional composition simplex or concentration plane called a composition (or Gibbs) diagram.

For the graphical representation of the behavior of an azeotropic system, on the following constructions can be used:

1. The residue curve map representation based on the residue curve approach,

2. The boiling (and dew) temperature surfaces based on the representation of the boiling (and dew) temperatures vs. mixture composition. The concept of the residue curve was introduced by SCHREINEMAKERS (1901). Let us assume that an amount of dL moles of composition y_i $(i = 1, 2, \ldots, N)$ is vaporized in equilibrium with the liquid. The amount of the residual liquid, $L - dL$ will have the composition $x_i + dx_i$. The material balance for the i-th component gives:

$$Lx_i = y_i dL + (L - dL)(x_i + dx_i). \tag{1}$$

By ignoring the second-order differential, this becomes

$$Lx_i = dL(x_i - y_i). \tag{2}$$

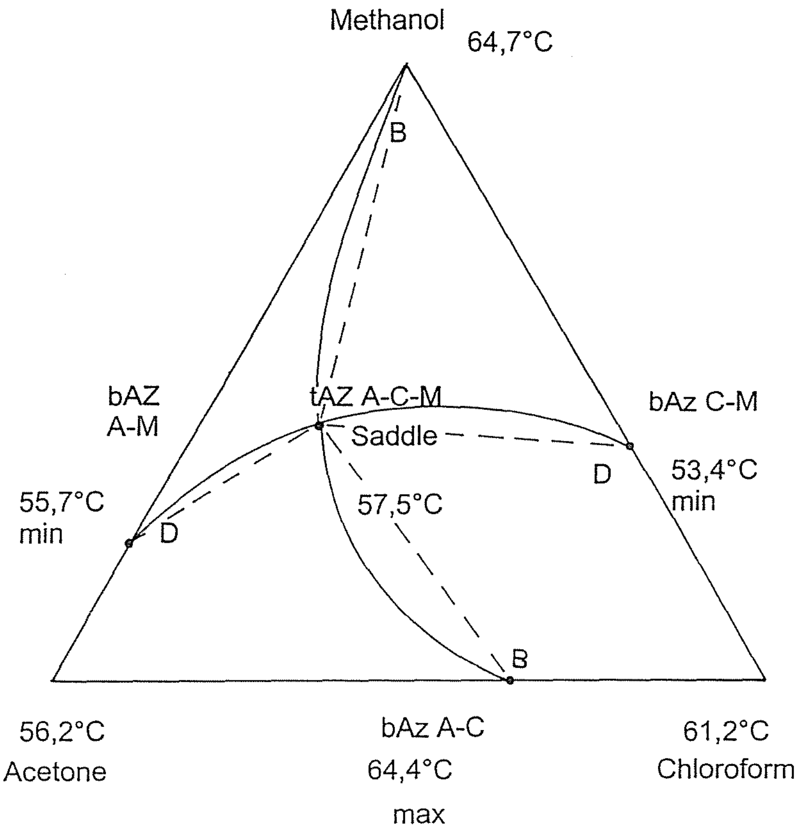

Fig. 1. Azeotropic points and their characteristics, distillation regions, boundaries and their approximation by the konovalov's rule (B – bottom product, D – distillate product, bAz – binary azeotrope, tAz – ternary azeotrope)

The mole fractions in *Eq.* (2) are not all independent since they must satisfy the conditions:

$$\sum_{i=1}^{N} x_i = 1; \qquad \sum_{i=1}^{N} y_i = 1. \tag{3}$$

Setting $dt = dL/L$ this can be rewritten as

$$\frac{dx_i}{dt} = x_i - y_i. \tag{4}$$

The compositions in the vapor and liquid phase are determined by the thermodynamic equilibrium relationship $y = f(x)$.

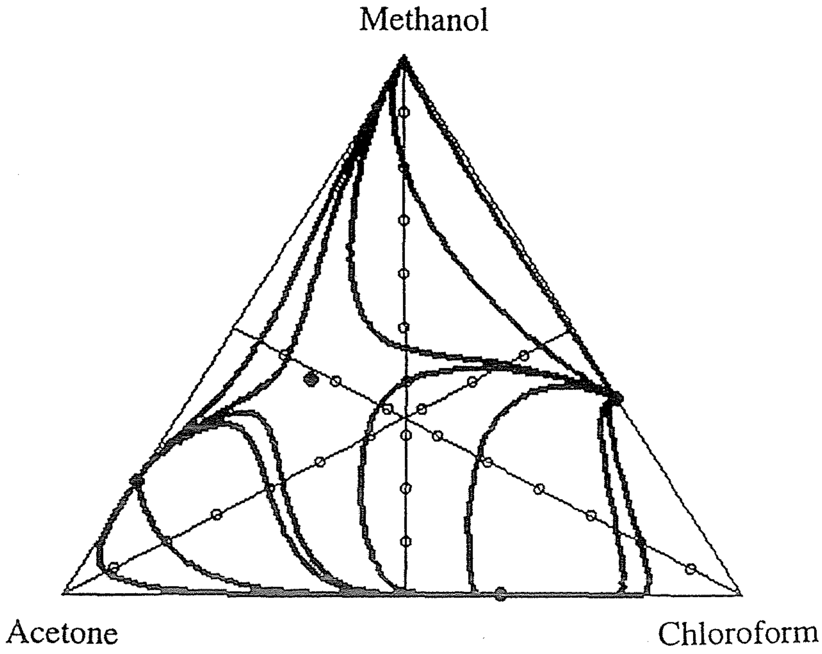

Fig. 2. Residue curve map for the mixture acetone–chloroform–methanol (1 bar, azeotrope points are designed by.)

Pure components and azeotropes are singular points of the vector field defined by the right hand side of *Eq.* (4), which vanishes simultaneously at pure and azeotropic compositions, i.e. satisfying $x_i = y_i$. MATSUYAMA (1977) and DOHERTY (1978) have shown that these singular points are elementary (saddles or nodes) and isolated in the composition space.

The residue curve is defined as an integral curve of the set of simultaneous nonlinear differential equations (4). The continuous distillation profiles are constrained to lie within certain subregions of the composition simplex, and it is precisely this fact which distinguishes azeotropic distillation from ideal distillations. According to the Konovalov's second rule a residue curve runs monotonously in the direction of rising temperature (at constant pressure).

Therefore, knowing the boiling temperatures of the pure components and the azeotropes it is possible to indicate approximately the subregions and the boundaries between them. In *Fig. 1* the azeotropic points and the connecting lines between them are shown. Each subregion represents a new distillation region (a so-called simple distillation region, SDR) with the properties of an ideal mixture. The azeotropic mixture plays the role of a new or pseudocomponent. That means a feed lying in a given subregion can be separated only into the components representing the corners of this subregion (accounting the boiling temperatures of the components). The separatrices representing special residue curves divide the different simple distillation regions. *Fig. 2* shows the total reflux distillation paths (or residue curves) for one of the most investigated systems, the homogeneous azeotropic mixture methanol–acetone–chloroform.

Residue curves and rectification trajectories coincide only in the case of total reflux. Under distillation conditions the rectification trajectories can differ from the residue curves (VOGELPOHL 1993).

3. Process Systems for the Separation of Azeotropic Mixtures

For the separation of azeotropic mixtures different approaches can be used, see for example (SIMMROCK):

a) methods without external components (entrainers)
  - Two-pressure rectification (in some mixtures the azeotrope can be broken by changing system pressure);
  - For systems showing minimum azeotropic behaviour and two liquid phases (with no miscibility gap) a combination of column and decanter can be applied;

b) methods with external components (entrainers)
  - Azeotrope rectification: Using an external component forming a new azeotrope with one of the components with the highest or lowest boiling temperature of the system. The entrainer recovery can be carried out either by a decanter for heterogeneous azeotropic mixtures or by additional separation operations for homogeneous azeotropic mixtures.
  - Extractive rectification: Adding an entrainer with a high boiling temperature which overcomes the azeotrope it is possible to recover the entrainer after separation in an additional column.
  - Reactive rectification: Combining the separation process with a chemical reaction in some cases high efficient separation schemes can be obtained.

For the optimal choice of the separation scheme the identification and location of the continuous azeotropic distillation region boundaries (which are boundaries only in the case of distillation with total reflux, in other cases the rectification lines can cross these boundaries) is one of the most important aspects for the synthesis.

4. The Temperature Surface and the Residue Curve Map Approach for the Separation Scheme Synthesis

Although a qualitative overview of the different subregions and the boundaries can be obtained applying the second Konovalov's rule, this information is only necessary but not sufficient for a synthesis procedure. For a more exact analysis of the distillation regions more sophisticated tools are needed: the residue curve map, the temperature surfaces and their derivatives. A numerical procedure for the exact calculation of the separatrices has been proposed recently (MEKIFFER, HARTMANN, 1992).

The residue curve map approach allows to determine the SDR and the separatrices between them approximately. For this aim a user-friendly tool was invented which solves the following operations:

- Integration of the system of differential *Eqs.* (3)–(4) for mixtures of arbitrary dimension and pressure
- Graphical representation of the residue curves map and various projections for higher dimensional systems
- Calculation of the azeotropic points
- Determination of the character of the azeotropic points (in the sense of Lyapunov)
- Computation of the pinch points

The representation of the boiling and dew temperature surfaces of azeotropic mixtures gives some other insights into the topology than the residue curve map. It implies more information about the complex relationships in these systems including subregions of distillation, distillation boundaries, driving forces, temperature surface isotherms, minimum separation work as a function of the composition and distillation course in a column.

Although the valleys and ridges on the temperature surface are not the boundaries (separatrices) of simple distillation regions and can be crossed by rectification trajectories, they join approximately the singulary points of the mixture (*Fig. 3*). The valley and/or ridge lines arise in each binary positive or binary negative azeotrope. They arrive at a binary point on another edge of the system being is not an extremum. In the case of a ternary azeotrope the valley and/or ridge lines cross the point of the ternary azeotrope.

For a comprehensive overview of these very complicated relationships one needs a sophisticated graphical representation tool allowing different user-friendly operations with the boiling (and dew) temperature surfaces. For this aim different computer-aided graphic tools can be used.

Graphical based design and representation environments are extensively used in different fields of chemical engineering. The design of chem-

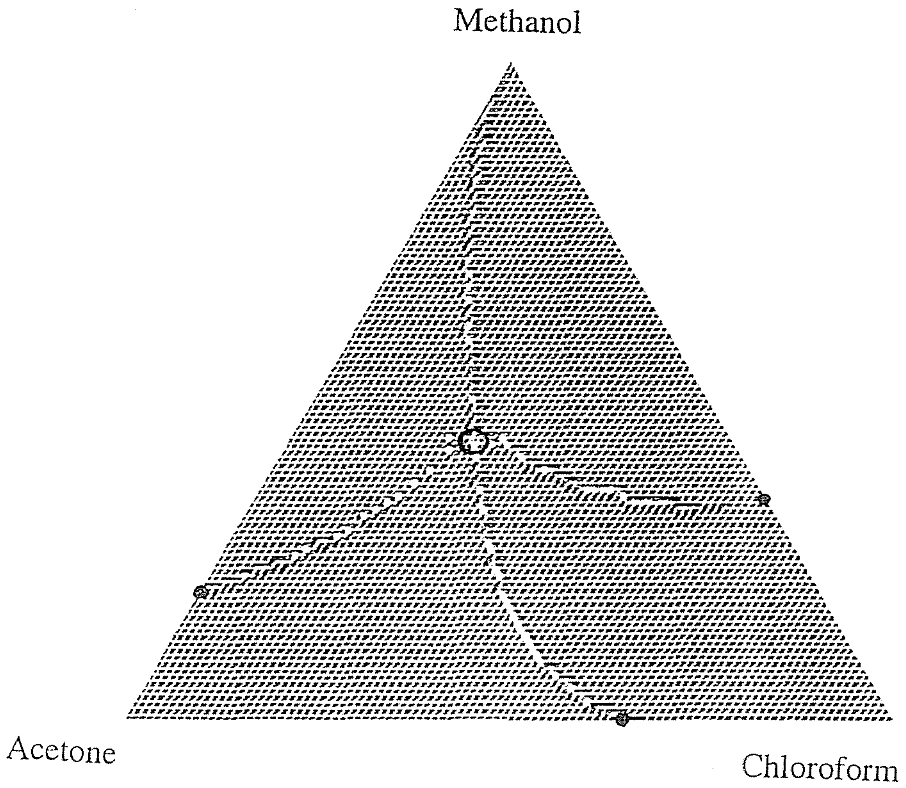

Fig. 3. Azeotropic points, valleys and ridges of the boiling temperature surface for the mixture acetone–chloroform–methanol (1 bar)

ical process systems, especially the separation sequence synthesis for multicomponent mixtures with nonideal behaviour requires a deep insight in the topology of distillation regions, the course of the distillation boundaries and their dependence on pressure, the influence and choice of external compounds as entrainers, etc. It requires the ability to interpret the complex relationships, to represent special views what concerns isolines of the temperatures or other variables, peaks and valleys of the surfaces, boundaries, vector fields and interconnection of different surfaces, further the animation of the graphical representations for better views in the multidimensional space, the projections on given planes, zooming of interesting areas and so on. The aim of presenting information in this way is to provide instruments of exploring all the relevant details and connections so as to be able to extract data for synthesizing optimal process systems .

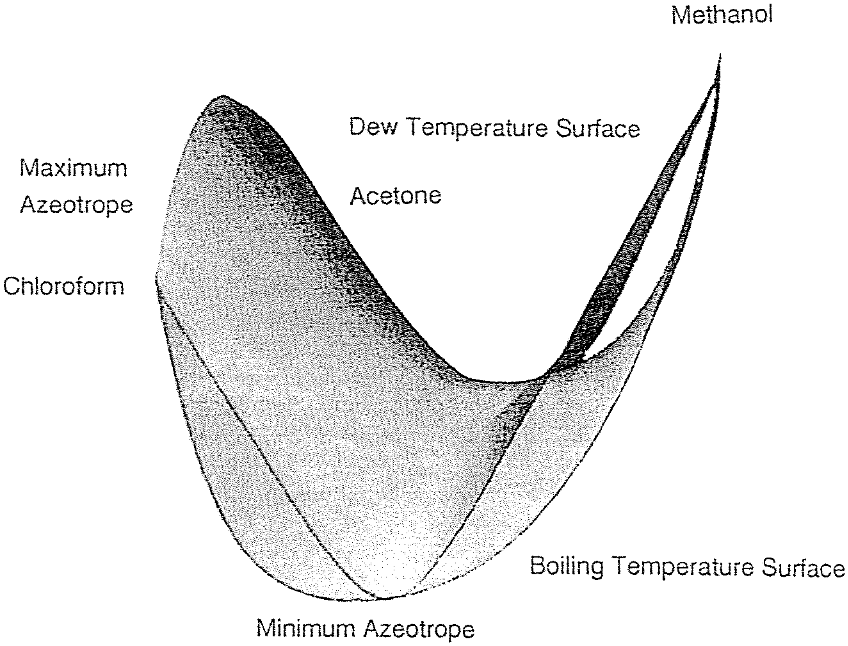

Fig. 4. Equilibrium diagram for the ternary mixture acetone– chloroform–methanol (1 bar)

The use of colours for the representation of different levels of values (for example of temperatures), for highlighting of regions of interest as well as for the construction of contour values is a necessary component of a computer-aided graphical tool. The use of such techniques as graphical potentiometers to specify a range of smooth parameter change an animated observation of different shapes and states of a system under study is possible. Thus, the chemical engineer is able to generate a much more rapid graphical representation of the actual state and situation of the parameter space. A wider and deeper knowledge of the variety of behaviour is possible because the tools allow to acquire information more readily and in a manner more suitable for knowledge retention (McGreavy 1991).

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5. Applications

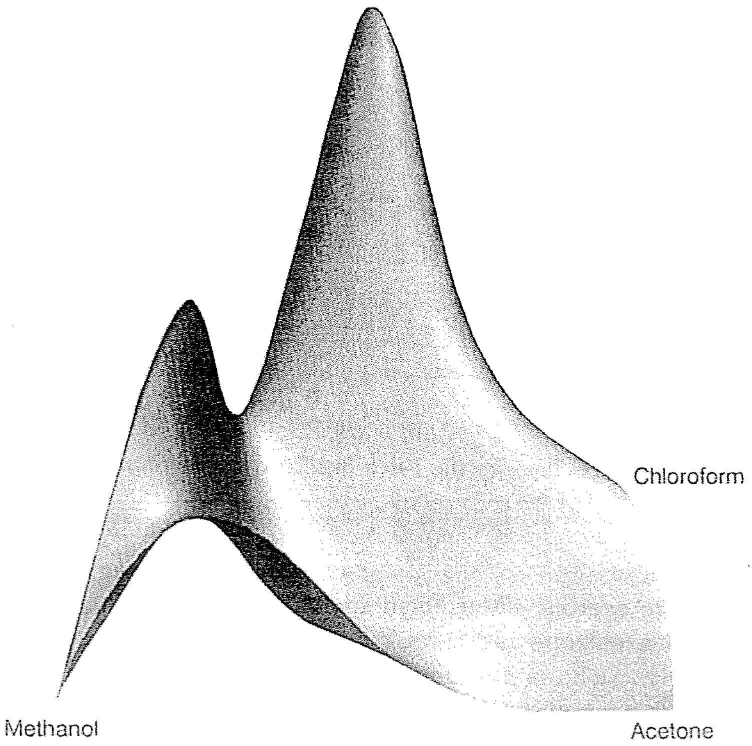

Fig. 5. 3D-view of the driving forces for the batch distillation of the mixture acetone–chloroform–methanol (1 bar)

For an exact synthesis procedure the knowledge of the residue curve map as well as the temperature surfaces are important. In the following the

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[1] In this paper it was impossible to include coloured figures, therefore the information level of the selected black and white figures is limited, also the animation effect cannot be reproduced.

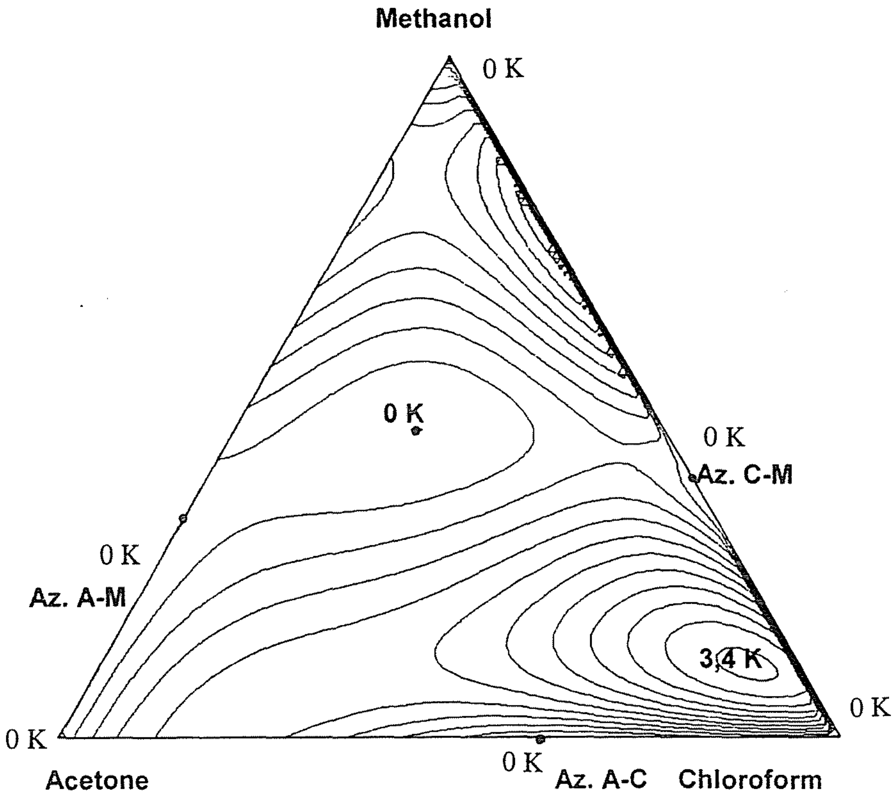

Fig. 6. Driving forces isolines for the batch distillation of the mixture acetone–chloroform–methanol (1 bar)

ternary mixture acetone–chloroform–methanol as a system characterized by one ternary azeotrope and three binary minimum azeotropes will be investigated. *Fig. 4* shows the boiling temperature and the dew temperature surfaces as a function of the composition (equilibrium diagram for a ternary mixture). The 3*D*-temperature difference surface (*Fig. 5*) presents the driving forces for the distillation process. The driving forces vanish for the azeotropes and the pure compounds. Using filter modules it is possible to determine the 'valleys' and the 'ridges' on the temperature surface and to identify approximately the boundaries of the different distillation regions. The boundaries between the regions are highly nonlinear (curved), their knowledge is very important for the synthesis of the separation scheme. Applying special slice operation isolines for example for a given temperature (*Fig. 6*). New and very important insights in the very complicated structure of these surfaces give the inference operation carried out on the driving

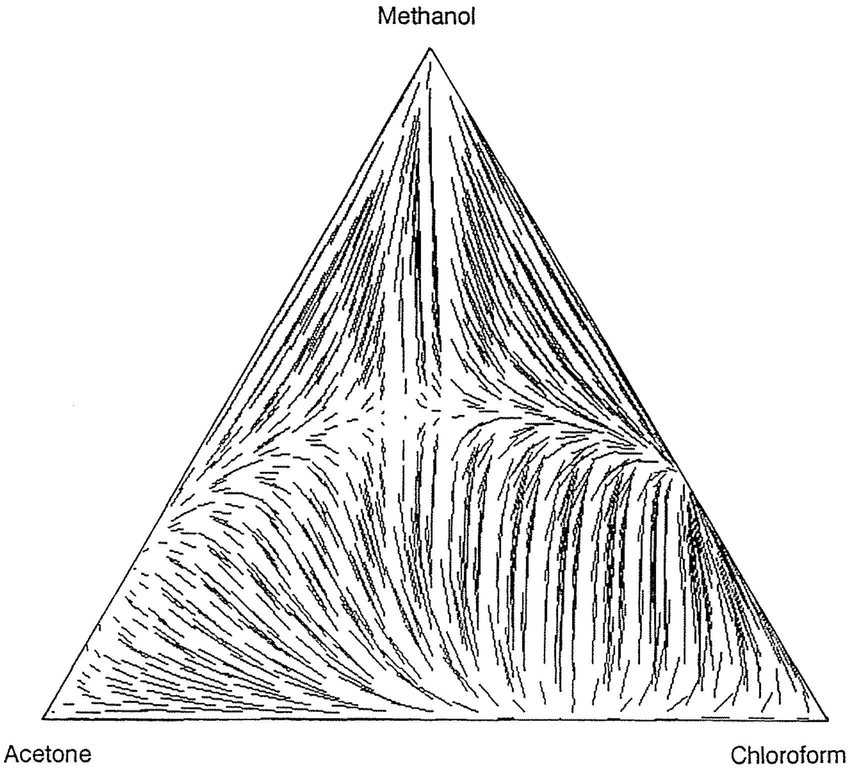

Fig. 7. Inference lines map for the driving forces of the mixture acetone–chloroform–methanol (1 bar)

forces surfaces. *Fig. 7* shows this inference response surface which is a link between the residue curve map and the driving force surface. The residue curve – like representation shows clearly the different subregions and the main directions of the residue curves as well as the azeotropic points and the separatrices. That means it is possible to transform one representation type in another using only the information about the temperature. But the temperature representation and the derived representations based on the temperature contain much more information for the synthesis than the residue curve map only: the driving forces, fine structure of the subregions, the approximate location of the boundaries and their dependence on the pressure. Solving the residue curve *Eq.* (4) it is possible to combine this procedure with a stability analysis according Lyapunov determining the type of singular points and other characteristics. Varying the system pressure it is possible to investigate how the locations of the azeotropic points change. Using some simple transformations new important insights can be generated for example relative volatility surfaces and minimum separation work surface. These graphical tools are very important for the synthesis of energy-efficient separation schemes. For mixtures containing more than three compounds the described procedure can be applied in the same manner using the different projections. Combining these tools with balance and flowsheet simulation packages a high-sophisticated synthesis approach is available.

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