On the Topology of Ternary VLE Diagrams: Elementary Cells

E. K. Hilmen, V. N. Kiva*and S. Skogestad†

Department of Chemical Engineering, Norwegian University of Science and Technology,
N-7491 Trondheim, Norway

Submitted to *AIChE Journal*
27 Dec. 2000
Revised 06 Oct. 2001

Abstract

The classification of ternary vapor-liquid equilibrium (VLE) diagrams is a key to simple azeotropic distillation analysis. We find that all ternary mixtures so far reported occurring in nature can be qualitatively represented by a combination of only four elementary cells. This greatly reduces the number of VLE diagram structures that need to be analyzed in order to reveal the qualitative characteristics of any ternary azeotropic mixture.

Introduction

Ternary vapor-liquid equilibrium (VLE) diagrams provide a graphical tool to predict qualitatively the feasible separations for multicomponent azeotropic mixtures before detailed simulation or experimental study of their distillation. The various graphical representations of the VLE (residue curve and distillation line maps, isotherm map, equilibrium vector field) are closely related and are equally capable of characterizing the mixture. In this paper, we consider *residue curves* (Schreinemakers 1901, Ostwald 1902, Zharov 1967, Serafimov 1968*a*, Doherty and Perkins 1978), and the topological classification of ternary mixtures into 26 diagrams by Serafimov (1970). Our considerations apply equally well to *distillation lines* (Zharov 1968, Stichlmair 1988). We refer to the review of Widagdo and Seider (1996) and to the literature mentioned for a detailed description of these tools and their application to distillation column profiles. Our contribution is to propose a set of elementary topological cells which are constituents of all feasible ternary VLE diagrams. We show that the until now reported ternary mixtures include only four of these elementary cells.

*Laboratory on Mixtures Separation, Karpov Institute of Physical Chemistry, Moscow 103064, Russia.
†Corresponding author. Tel.: +47-7359-4154; fax: +47-7359-4080; email: skoge@chembio.ntnu.no

1 Classification of ternary VLE diagrams

The number of feasible VLE diagram structures is limited by topological and thermodynamical constraints. A complete classification of these feasible structures for ternary mixtures was given by Serafimov (1970) and Serafimov *et al.* (1971, 1973), and is more recently presented by Serafimov (1996). Serafimov's classification results in the 26 classes of ternary VLE diagrams presented in Figure 1. The classification is

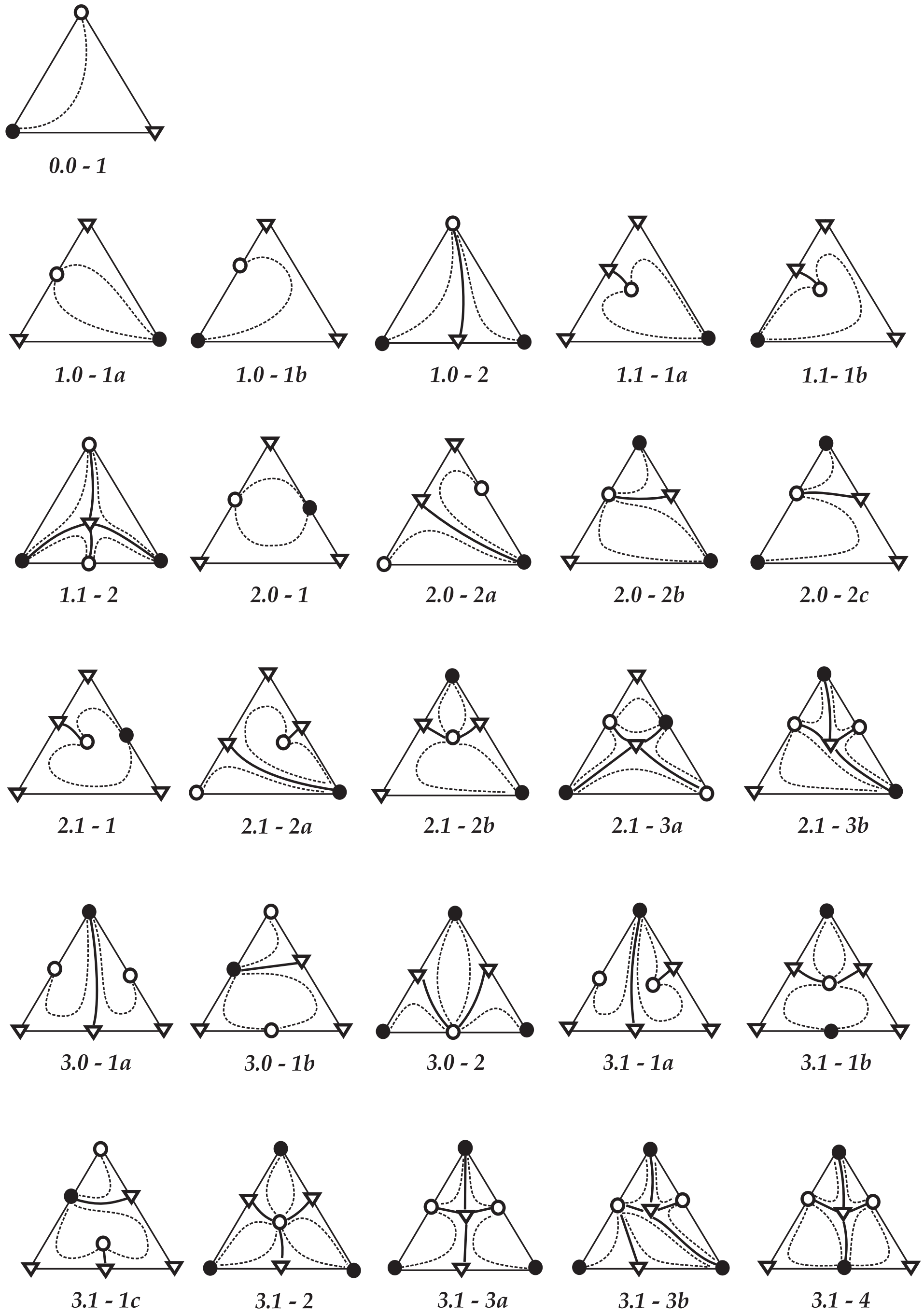

Figure 1: *Serafimov's (1970b) topological classification of ternary mixtures. Structural characteristics of residue curves (or distillation lines) are shown by dashed lines with the singular points indicated by • stable (unstable) node, ∘ unstable (stable) node, and ▽ saddle, and the region boundaries given by bold lines.*

based on the simplifying and common assumption that there exists no more than one binary azeotrope for each binary pair and no more than one ternary azeotrope. Biazeotropy does exist in real mixtures, but it is relatively rare, so this is not a very restrictive assumption. The classification of Serafimov considers topological structures and thus does not distinguish between antipodal diagrams (switching of minimum- and maximum-boiling azeotropes) since they have the same topology. Transition from one antipode to the other can be made by simply changing the sign of the nodes and inverting the direction of the arrows of increasing boiling temperature.

Actually, Gurikov (1958) was the first to derive the rule of azeotropy and propose a thermodynamic topological classification of ternary mixtures. However, his classification was incomplete, and Serafimov (1968*b*) revealed four additional feasible structures and established the 26 topological classes presented in Figure 1. Later, Serafimov's classification of ternary mixtures was refined by distinguishing between antipodes inside each structure class, based on the reasoning that *"minimum- and maximum-boiling azeotropes have dissimilar physical nature and dissimilar behavior during distillation"* (Zharov and Serafimov 1975). This refined classification includes a total of 49 types of ternary VLE diagrams. An even more detailed classification is proposed by Matsuyama and Nishimura (1977) who also rank the components in the order of their boiling temperatures ("light", "intermediate" and "heavy"). This classification includes 113 diagram classes of which 87 are presented graphically by Doherty and Caldarola (1985). Nevertheless, among these 113 classes there are only the 26 topologically distinct structures of Serafimov. Actually, the classification of Matsuyama and Nishimura adds some ambiguity as some of their classes with a ternary saddle azeotrope have two or three possible topological structures. For example, their classification code 112-S can be either of Serafimov's class 3.1-3a or 3.1-3b depending on whether there exists a saddle - saddle separatrix or not. This is also pointed out by Foucher *et al.* (1991) who recommend an extension of the Matsuyama and Nishimura's classification code name in these cases.

In this paper, we use Serafimov's (1970) classification of the topological classes and Zharov and Serafimov's (1975) refinement of the antipodal structure types (referred to as the ZS-type). The relationships between the classifications of Gurikov (1958), Serafimov (1970), Zharov and Serafimov (1975) and Matsuyama and Nishimura (1977) are presented in Table 2. The table is useful when relating publications where the different classifications are used.

2 Elementary cells

There is a great diversity of VLE diagrams for ternary mixtures caused by the variety in physical properties of the components and their molecular interaction. As mentioned, if we assume no biazeotropy and consider only topological differences there are 26 distinct types as presented in Figure 1. Furthermore, there is a far greater diversity in possible shapes (geometry) of the simple phase transformation trajectories such as residue curves and distillation lines. It is possible to reduce this complexity to a combination of a few topological building blocks ("elementary cells") and some basic internal structures (shapes of the simple phase transformation trajectories). We use residue curves to represent the simple phase transformation trajectories in this paper.

We find that among Serafimov's 26 topological classes there are eight elementary topological cells (denoted I, II, III, IV, II', III', IV' and V) that constitute all the ternary diagrams, where a cell is defined as one residue curve region taken with its boundaries (that is, a subspace of the composition space constrained by residue curve boundaries, if any, and the composition simplex). From these eight elementary cells we may construct all the 26 diagrams as shown in Figure 2. Each cell has one unstable and one stable node and some set of saddle points. There are four "primary" diagrams where the composition triangle consists of a single cell (one residue curve region; Serafimov's class 0.0-1, 1.0-1a, 1.0-1b and 2.0-1), and these elementary cells (denoted I, II, III, IV) are also the only so far reported for naturally occurring mixtures. Cells II', III' and IV' are modifications of the primary cells II, III and IV, respectively (with internal nodes), for which there are no reported physical mixtures. Cell V only occurs as an element in Serafimov's class 3.1-1b, and also for this class there is so far no physical mixture reported.

The four primary diagrams and the corresponding elementary cells I, II, III, IV are shown in Figure 3. Each elementary cell is characterized by a certain set and order of the singular points (nodes and saddles) along the contour of its border (that is, by its topology). Accordingly we can name them as given in Figure 3.

There is an important difference between an elementary cell of the "primary" diagrams (one residue curve

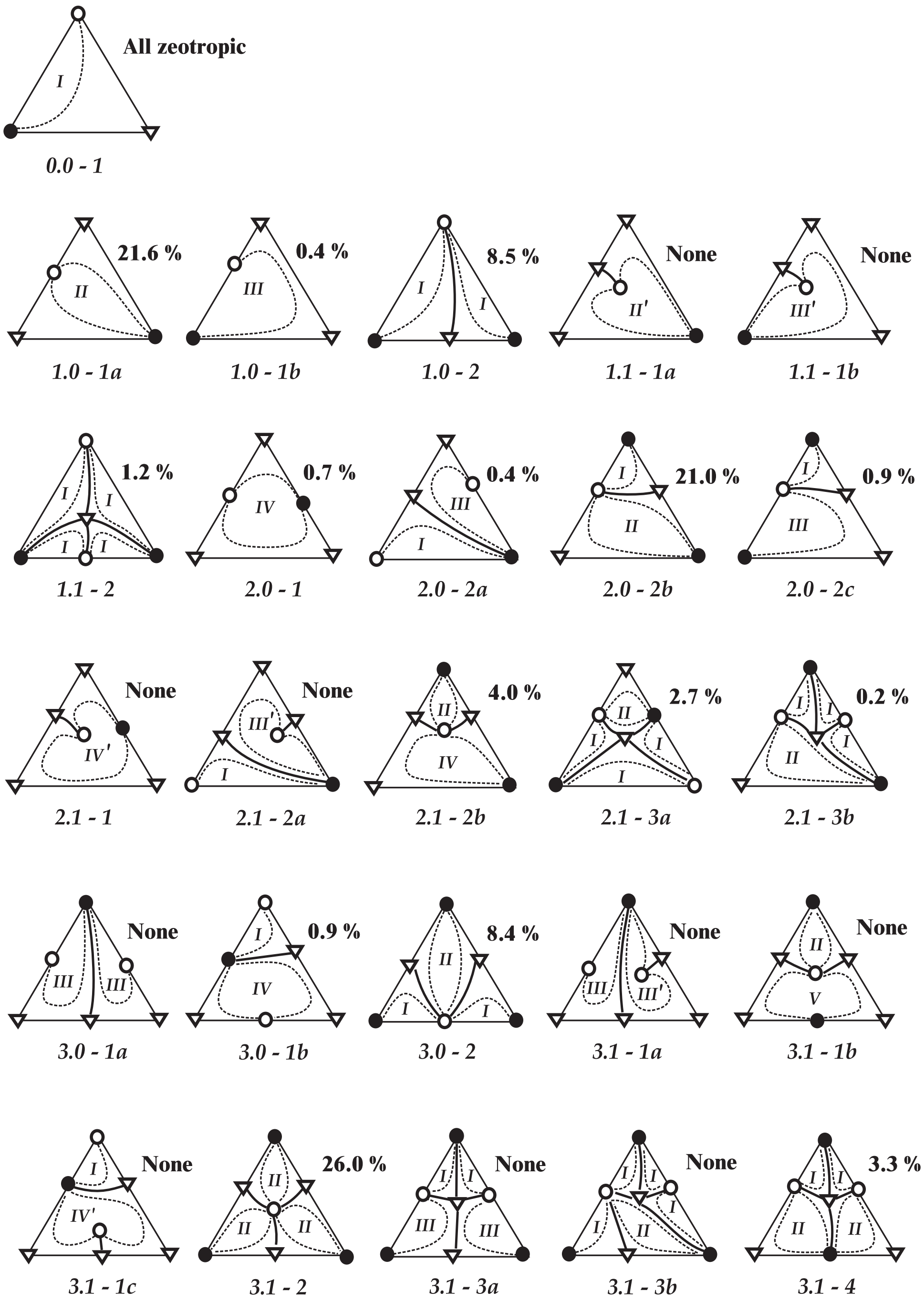

Figure 2: *Elementary cells (I, II, III, IV, II', III', IV' and V) within Serafimov's 26 topological classes. Physical occurrence (%) of azeotropic mixtures reported in the literature according to Reshetov's statistics (based on data from 1965 to 1988).*

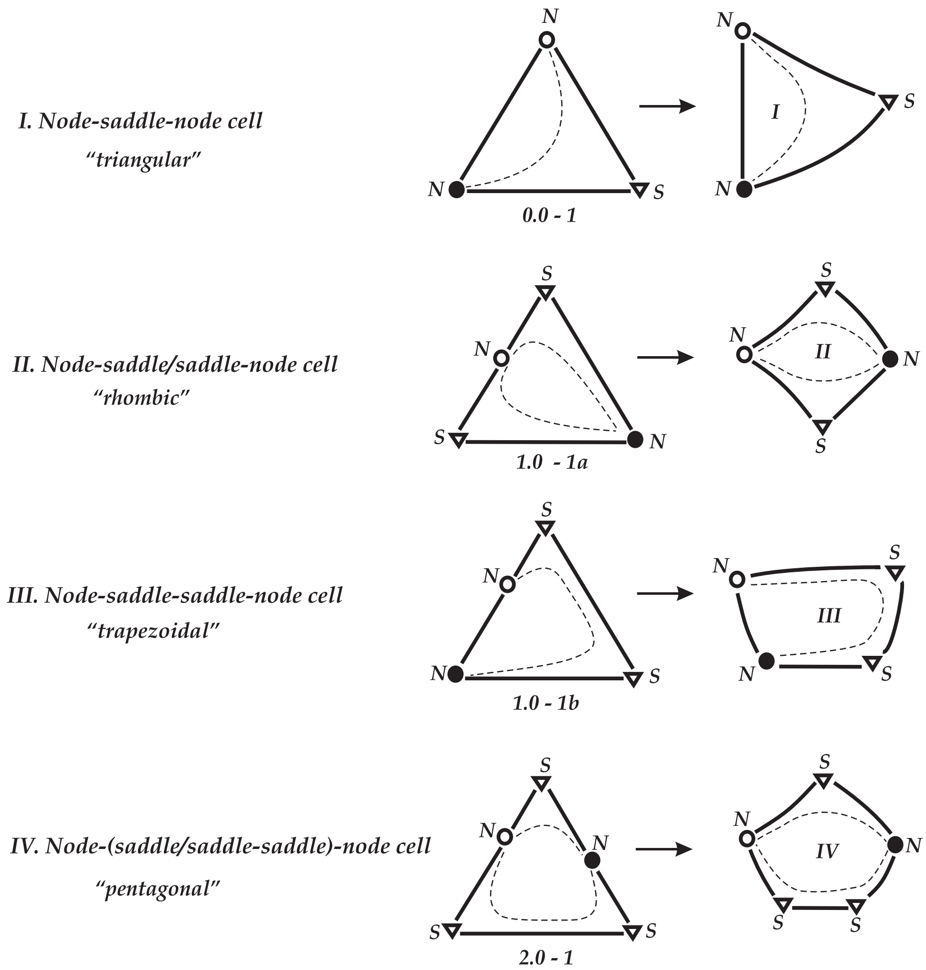

Figure 3: *Generalization of the four elementary topological cells I, II, III, IV from the diagrams with one residue curve region. Each cell is characterized by the set and order of the nodes (N) and saddles (S) along the contour of its border. The singular points are also indicated by • stable (unstable) node, ○ unstable (stable) node, ▽ saddle. The dashed lines indicate the qualitative paths of the residue curves.*

region) and an elementary cell incorporated into more complex diagrams. If an elementary cell is a primary diagram, the saddle point is a pure component point. The borders of the cell are the edges of the composition triangle (linear). The (stable and unstable) nodes are pure component points or points of binary azeotropes. If an elementary cell is a constituent of a complex diagram, at least one of its saddles is a binary or a ternary azeotrope, and, therefore, at least one of the borders of the cell is a residue curve boundary (curved) showed by the solid thick lines in Figure 2. One of the nodes can be a point of a ternary azeotrope. In general, the composition space is broken into several residue curve regions (cells) if there are more than one unstable node or more than one stable node.

Despite these differences, a single elementary cell and an elementary cell incorporated into a complex diagram are topological equivalent. Note, however, that inside similar topological cells there may be various shapes of the residue curves (simple phase transformation trajectories).

3 Occurrence in nature

Even though all the classified diagrams in Figure 2 are topologically and thermodynamically feasible, their occurrence in nature is limited by the probability of certain combinations of molecular interactions. In this section we present data on the occurrence of the different classes among the mixtures reported in the literature. This permits us to exclude rare or improbable diagram classes from consideration.

Serafimov (1968*b*) analyzed the occurrence of different types of VLE diagrams among 418 reported (experimental) data on ternary azeotropic mixtures. Reshetov (1998) made a similar study for 1609 ternary mixtures (in which 1365 are azeotropic) based on thermodynamic data that were published during the period from 1965 to 1988. To the best of our knowledge we have not found any other publications that address this issue. The occurrence of the various classes as reported by Serafimov and Reshetov are given in Table 1. (Reshetov's statistics are also presented in Figure 2). Note that Reshetov (1998) found that the three mixtures reported for class 3.1-1a in the statistics by Serafimov (1968*b*) actually was of another structure class. From Reshetov's data we see that only 16 of Serafimov's 26 classes are reported to occur in nature. If we also differentiate between minimum- and maximum-boiling azeotropes (ZS-type), then we find that 27 of the 48 classes are reported. The distribution reported in these studies does not necessarily reflect the real occurrence in nature. The azeotropic data selection is small and occasional. Moreover, the distribution can be distorted compared to the unknown natural distribution since the published mixture data are results of deliberate searches for entrainers for specific industrial separation problems. Nevertheless, these data are interesting and can be used for some deductions:

- Serafimov's class 3.1-2 with three minimum-boiling binary azeotropes and one minimum-boiling ternary azeotrope has the largest number of reported mixtures. About 26 % of the 1365 ternary azeotropic mixtures in the study by Reshetov are of this class.
- Elementary cells I and II cover more than 90 % of all the reported ternary azeotropic mixtures. The three most common structures are Serafimov's classes 1.0-1a (21.6 %), 2.0-2b (21.0 %) and 3.1-2 (26.0 %). Among these three classes only cells I and II occur.
- Ternary azeotropes are common in nature. About 38% of the reported ternary mixtures have a ternary azeotrope. These are Serafimov's classes 1.1-2, 2.1-2b, 2.1-3a, 2.1-3b, 3.1-2 and 3.1-4.

For each of the reported classes, one may find a great number of (similar) mixtures in nature. However, for those classes with no reported mixtures, and with a structure that requires a set of molecular interactions that are unlikely, we expect that few if any real mixtures will be found. The experimental data for ternary azeotropic mixtures used for the above statistics is rather limited. However, the experimental data for binary azeotropic pairs is considerably more extensive. For example, Gmehling *et al.* (1994) have compiled data for 18 800 binary systems (involving about 1 700 components). From this we can estimate the behavior of a large number of ternary mixtures combinations from a VLE model, but to our knowledge no systematic effort has yet been done.

It is well-known that binary maximum-boiling azeotropes are less abundant than minimum-boiling azeotropes. According to Lecat (1949) the ratio of minimum-boiling versus maximum-boiling azeotropes that occurs in nature is about 9 to 1. The statistics of Reshetov confirm this heuristic rule. Thus, the more maximum-boiling binary azeotropes that are included in the ternary mixture, the less is the probability of its occurrence. This is clearly demonstrated in Table 1. In particular, no ternary mixture with three binary maximum-boiling azeotropes has been found among Reshetov's selection of 1365 mixtures. Ternary maximum-boiling azeotropes are also very rare. As a result, even for the topological structures where the existence is beyond question, the occurrence of antipodes with maximum-boiling azeotropes is much less than that of antipodes with minimum-boiling azeotropes.

Pöllmann and Blass (1994) propose to reduce the number of ternary VLE diagrams by considering only ”physically meaningful” structures. Their list includes 19 of Serafimov’s 26 classes, excluding 1.1-1a, 1.1-1b, 2.1-1, 2.1-2a, 3.1-1a, 3.1-1c, and 3.1-3b. However, it is impossible in principle to state that some classes of ternary mixtures cannot exist in nature or are “physically meaningless”, because all the structures in Figure 2 are thermodynamically and topologically feasible. We can only discuss the *probability* of the existence of some types of the VLE diagram structures.

Table 1: *Occurrence of ternary VLE diagram structures found in published mixture data*

Serafimov's class	Occurrence Serafimov (until 1968)	ZS-type	Set of azeotropes [a]	Occurrence Reshetov (1965-1988)
0.0-1	-	1	zeotropic	244
1.0-1a	13	3a	min	283
		7a	max	12
1.0-1b	2	3b	min	4
		7b	max	1
1.0-2	20	4	min	95
		8	max	21
1.1-1a	None	2a	min + min Az_3	None
		6a	max + max Az_3	None
1.1-1b	None	2b	min + min Az_3	None
		6b	max + max Az_3	None
1.1-2	7	5	min + S_3	8
		9	max + S_3	8
2.0-1	1	15	min + max	9
2.0-2a	None	17	min + max	2
		18	max + min	3
2.0-2b	77	11a	min + min	280
		21a	max + max	6
2.0-2c	2	11b	min + min	10
		21b	max + max	2
2.1-1	None	13	min + max + min Az_3	None
		14	min + max + max Az_3	None
2.1-2a	None	16a	min + max + min Az_3	None
		16b	min + max + max Az_3	None
2.1-2b	3	10	min + min + min Az_3	55
		20	max + max + max Az_3	None
2.1-3a	14	19	min + max + S_3	37
2.1-3b	5	12	min + min + S_3	2
		22	max + max + S_3	1
3.0-1a	None	29	min + min + max	None
		33	max + max + min	None
3.0-1b	None	28	min + min + max	9
		34	max + max + min	3
3.0-2	85	24	min + min + min	114
		37	max + max + max	None
3.1-1a	3	27b	min + min + max + min Az_3	None
		32b	max + max + min + max Az_3	None
3.1-1b	None	26	min + min + max + min Az_3	None
		31	max + max + min + max Az_3	None
3.1-1c	None	27a	min + min + max + max Az_3	None
		32a	max + max + min + min Az_3	None
3.1-2	171	23	min + min + min + min Az_3	355
		36	max + max + max + max Az_3	None
3.1-3a	None	25a	min + min + min + S_3	None
		38a	max + max + max + S_3	None
3.1-3b	None	25b	min + min + min + S_3	None
		38b	max + max + max + S_3	None
3.1-4	15	30	min + min + max + S_3	41
		35	max + max + min + S_3	4

[a] min - minimum boiling binary azeotrope; max - maximum boiling binary azeotrope; Az_3 - ternary node azeotrope; S_3 - ternary saddle azeotrope.

4 Use of elementary cells

The concept of elementary topological cells is a simplification which primarily is made to reduce the number of structures of ternary VLE diagrams. It is useful for preliminary analysis of azeotropic distillation (presynthesis). Based on the knowledge of the distillation behavior of azeotropic mixtures of the primary diagrams elementary cells in Figure 3, or combinations of these, we also have information about what behavior to expect from other more complex mixtures. It is important to recognize that each real mixture has its own specific thermodynamic characteristics and should therefore be analyzed in detail in a later step of the separation synthesis.

The concept of elementary cells is even more important when using the classification of Matsuyama and Nishimura with its less surveyable 113 classes.

The elementary cell concept may be extended to mixtures with more than three components, but grahical visualization is then more difficult. Of course, for a multicomponent mixture one can analyze each ternary subsystem. For example, each of the four triangles of a four-component tethrahedon is one of the 26 ternary classes and (for the real mixtures reported so far) four elementary ternary cells.

4.1 The album

One goal underlying the classification of ternary mixtures is to have a complete album of possible VLE diagram structures with their corresponding scheme of separation by distillation. But this is not established knowledge. Prediction of feasible distillation product compositions for even some of the simplest diagram structures is still under development. Furthermore, methods or separation schemes to separate all classes of (ternary) azeotropic mixtures are not established. One reason is that there are many possible structures with deformation of the simple phase transformation paths due to regions with different volatility order within the composition space, making this an almost impossible task. Instead, we propose to consider selected VLE diagrams and specific mixtures of these diagrams in detail:

1. Zeotropic mixture, ideal and nonideal with univolatility line(s)
   (Serafimov's class 0.0-1: cell I);

2. Mixture with one separatrix (one binary azeotrope)
   (Serafimov's class 1.0-2: combination of two cell I's);

3. Mixture without separatrix, but with one binary azeotrope
   (Serafimov's class 1.0-1a: cell II and 1.0-1b: cell III);

4. Mixture without separatrix, but with two binary azeotropes nodes
   (Serafimov's class 2.0-1: cell IV).

An illustration of a ternary mixture with one binary saddle azeotrope (Class 1.0-2) consisting of two elementary cell I's is given in Figure 4. The left cell has "C-shaped" residue curves, and the right cell has "S-shaped" residue curves (inflection) caused by the univolatility line α_{23}. Although both cells are of type I, this difference in shape may have a large effect on the actual separation process. For details on the internal structure ("shape") of ternary VLE diagrams, the reader is referred to Hilmen (2000) and Reshetov *et al.* (1999).

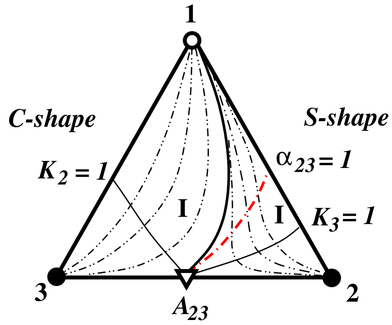

Figure 4: *Ternary azeotropic mixture with one binary saddle azeotrope (Class 1.0-2 consisting of two Cell I's). Residue curves; unidistribution (solid) and univolatility (dash-dotted) lines are given.*

4.2 Multiple steady states

As an example of the use of elementary cells we may consider the possibility for multiple steady states in (homogeneous) azeotropic distillation. Such multiplicities may lead to problems in column operation and control, as well as problems in column design and simulation. When two or more multiple steady states exists for the same inputs it is possible that, for some disturbance, the column profile jumps from the desirable (in terms of product specifications) to an undesirable steady state. However, such catastrophic jumps may be avoided by proper control of the column, and the separation schemes for such mixtures may well be feasible and economical. The possibility of multiple steady states at infinite efficiency of the distillation (infinite reflux, infinite theoretical equilibrium trays, and D/F from 0 to 1) was first noted by Balashov *et al.* (1970). They considered a mixture of Serafimov's class 1.0-1b (primary diagram of elementary cell III with U-shaped residue curves) with a binary maximum-boiling azeotrope (ZS-type 7b), and found that for these mixtures it is feasible to have multiple products for the same value of the parameter D/F. Later, Petlyuk and Avet'yan (1971) analyzed this issue in more detail and included bifurcation analysis. This analysis is also included in the textbook by Petlyuk and Serafimov (1983), where Petlyuk writes *"the existence of more than one saddle along a distillation line for sharp (infinite reflux, infinite column) separation going from an unstable node to a stable node leads to multiplicity of the separation products for the same feed composition and the same value of parameter D/F"*. The geometrical considerations given by Petlyuk and coworkers are also found in Serafimov *et al.* (1971). This is a sufficient, but not a necessary condition for multiplicity of the mixture. Bekiaris *et al.* (1993) give a similar condition, roughly that the *existence of two or more neighboring saddles* may lead to output multiplicity. Bekiaris *et al.* (1993) also identify other structural characteristics that may induce multiple steady states, such as highly curved distillation boundaries ("pseudosaddles"), as for the mixture of acetone-chloroform-methanol.

The elementary cells that may lead to output multiplicity are III, III', IV and IV'. From this we can predict the *possibility* of multiple steady states (sufficient condition) for any given mixture that is caused by these structural characteristics. From Figure 2 we see that 14 of the 26 diagrams include these elementary cells (1.0-1b, 1.1-1a, 1.1-1b, 2.0-1, 2.0-2a, 2.0-2c, 2.1-1, 2.1-2a, 2.1-2b, 3.0-1b, 3.1-1a, 3.1-1b, 3.1-1c, 3.1-3a). From the statistics by Reshetov we find that about 7 % of the reported VLE diagram structures include these cells. Serafimov's class 2.1-2b, which includes cell IV, is relatively common (4 %), and this class may give multiplicities for feeds in the region with U-shaped residue curves.

The significance of multiplicities for column operation have been studied by Morari and coworkers (Laroche *et al.* 1992*a*, Laroche *et al.* 1992*b*, Bekiaris *et al.* 1993, Bekiaris and Morari 1996, Güttinger and Morari 1996, Güttinger and Morari 1997). Mixtures with one binary minimum-boiling azeotrope of Serafimov's class 1.0-1b (primary diagram of cell III with U-shaped residue curves) has been the focus, in particular the mixture of acetone - heptane - benzene. However, from the occurrence statistics we see that Serafimov's class 1.0-1b is not very common.

Bekiaris and Morari (1996) found multiple steady states for the mixture ethanol - ethyl propanoate - toluene (Serafimov's class 2.0-2a, ZS-type 18, which includes cells I and III) for a specific feed region. The specific feed region corresponds exactly to elementary cell III.

5 Pseudo-component subsystem

An idea related to the concept of elementary cells is the concept of pseudo-components. This approach is known to many engineers working with azeotropic distillation. Vogelpohl (1999) proposes to analyze real azeotropic mixtures as subsystems approximated by zeotropic mixtures where each azeotrope is represented by a pseudo-component. A residue curve region with k singular points (pure component and azeotropes) is thus represented as a k-component zeotropic mixture by assuming constant relative volatilities between the real components and the pseudo-components (azeotropes). *Ideal distillation lines* are calculated for each subsystem. However, this strong simplification has major pitfalls. The ideal distillation lines (or residue curves) diverge from the real (exact) ones as azeotropic mixtures necessarily have univolatility lines that deform the simple phase transformation trajectories and cause S-, Ω-, and even more complex shapes (internal structures) of the distillation lines (residue curves). For example, a ternary azeotropic mixture of Serafimov's class 1.0-2 (Figure 4) may be considered to be a quaternary system with the binary saddle azeotrope as an intermediate boiling pseudo-component. From this, for both of the cells I in the diagram, C-shaped ideal distillation lines are calculated. However, this is not true for the real mixture. Furthermore, the approach results in straight line distillation boundaries which in general are curved (Schreinemakers 1902).

We argue that when only the *qualitative* shape of the curves are needed, one can sketch the residue curve map (by hand) rather than calculate the exact, but incorrect, ideal subsystems map based on the constant relative volatility assumption. For example, we know that for mixtures of Serafimov's class 1.0-2 (Figure 4) with one binary azeotrope saddle and a separatrix that splits the composition space into two cells I, one of these cells must have a univolatility line extending from the azeotrope and to one of the binary edges resulting in an inflection point of the residue curves (S-shape).

Vogelpohl (1999) emphasizes that his main point is not to approximate the distillation lines of real mixtures by the distillation lines of ideal systems, but to show that the distillation behavior of real (zeotropic and azeotropic) mixtures is not fundamentally different from the distillation behavior of ideal systems, and that, therefore, the large body of knowledge developed from the theory of multicomponent distillation may be applied to better understand the distillation of real multicomponent mixtures. This is in line with the idea behind elementary cells presented in this paper.

6 Conclusion

The concept of elementary topological cells of ternary VLE diagrams is a key to a simple and surveyable azeotropic distillation analysis. Any real ternary mixture can be qualitatively represented by a combination of only four elementary cells. This greatly reduces the number of VLE diagram structures that need to be analyzed in order to reveal the qualitative characteristics of any ternary azeotropic mixture.

Acknowledgments

Dr. S.A. Reshetov at the Karpov Institute of Physical Chemistry in Moscow is greatfully acknowledged for providing the statistics on the occurrence of Serafimov's classes for reported ternary azeotropic mixtures.

Table 2: *Relationship between different classifications of ternary VLE diagrams*

	Gurikov (1958)	Serafimov (1970)	ZS-type[a]	Matsuyama & Nishimura (1977)
Zeotropic	1	0.0-1	1	000
One binary azeotrope	4a	1.0-1a	3a	100
			7a	030
	4b	1.0-1b	3b	001
			7b	003
	3	1.0-2	4	020
			8	400
One binary and one ternary azeotrope	2a	1.1-1a	2a	200-m
			6a	040-M
	2b	1.1-1b	2b	002-m
			6b	004-M
	5	1.1-2	5	010-S
			9	300-S
Two binary azeotropes	9	2.0-1	15	031, 103, 130
	8a	2.0-2a	17	023, 320
			18	401, 410
	8c	2.0-2b	11a	102, 120, 021
			21a	043, 430, 403
	8b	2.0-2c	11b	201, 210, 012
			21b	034, 304, 340
Two binary and one ternary azeotrope	7	2.1-1	13	032-m, 230-m, 203-m
			14	041-M, 140-M, 104-M
	-	2.1-2a	16a	420-m, 402-m
			16b	024-m, 420-M
	6	2.1-2b	10	022-m, 220-m, 202-m
			20	044-M, 440-M, 404-M
	10a	2.1-3a	19	013-S, 310-S, 301-S
	10b	2.1-3b	12	011-S, 110-S, 101-S
			22	033-S, 330-S, 303-S
Three binary azeotropes	14a	3.0-1a	29	411
			33	323
	14b	3.0-1b	28	123, 321, 132, 213, 312, 231
			34	413, 314, 431, 341, 134, 143
	13	3.0-2	24	212, 122, 221
			37	434, 344, 443
Three binary and one ternary azeotrope	-	3.1-1a	27b	421-m, 412-m
			32b	423-M, 324-M
	12	3.1-1b	26	232-m, 223-m, 322-m
			31	414-M, 441-M, 144-M
	-	3.1-1c	27a	142-M, 241-M, 124-M, 214-M, 421-M, 412-M
			32a	423-m, 324-m, 432-m, 342-m, 234-m, 243-m
	11	3.1-2	23	222-m
			36	444-M
	15	3.1-3a	25a	121-S, 112-S, 211-S
			38a	343-S, 334-S, 433-S
	-	3.1-3b	25b	121-S, 112-S
			38b	343-S, 334-S, 433-S
	16	3.1-4	30	131-S, 113-S, 311-S
			35	133-S, 313-S, 331-S

[a] ZS-type refers to the refined classification of the 49 antipodal structures by Zharov and Serafimov (1975), p. 96-98

References

Balashov, M.I., A.V. Grishunin, A.V. Ryazanova and L.A. Serafimov (1970). On the Investigation of Continuous and Batch Distillation Regions (in Russian). *Book: Physical-Chemical Foundations of Distillation, Moscow Lomonosov Institute of Fine Chemical Technology, Moscow* pp. 205–215.

Bekiaris, N. and M. Morari (1996). Multiple Steady States in Distillation: ∞/∞ Predictions, Extensions, and Implications for Design, Synthesis, and Simulation. *Ind. End. Chem. Res.* **35**, 4264–4280.

Bekiaris, N., G.A. Meski, G.A. Raudu and M. Morari (1993). Multiple Steady States in Homogeneous Azeotropic Distillation. *Ind. Eng. Chem. Res.* **32**(9), 2023–2038.

Doherty, M.F. and G.A. Caldarola (1985). Design and Synthesis of Homogenous Azeotropic Distillations 3. The Sequencing of Columns for Azeotropic and Extractive Distillation. *Ind. Eng. Chem. Fundam.* **24**(4), 474–485.

Doherty, M.F. and J.D. Perkins (1978). On the Dynamics of Distillation Processes I. The Simple Distillation of Multicomponent Non-Reacting, Homogeneous Liquid Mixtures. *Chem. Eng. Sci.* **33**, 281–301.

Foucher, E.R., M.F. Doherty and M.F. Malone (1991). Automatic Screening of Entrainers for Homogeneous Azeotropic Distillation. *Ind. Eng. Chem. Res.* **30**, 760–772.

Gmehling, J., J. Menke, J. Krafczyk and K. Fischer (1994). *Azeotropic Data, Part I and Part II*. VCH-Publishers, Weinheim, New York.

Gurikov, Y.V. (1958). Structure of the Vapor-Liquid Equilibrium Diagrams of Ternary Homogeneous Solutions (in Russian). *Russ. J. Phys. Chem.* **32**(9), 1980–1996. Abstract in English.

Güttinger, T.E. and M. Morari (1996). Multiple Steady States in Homogeneous Separation Sequences. *Ind. Eng. Chem. Res.* **35**(12), 4597–4611.

Güttinger, T.E. and M. Morari (1997). Predicting Multiple Steady States in Distillation: Singularity Analysis and Reactive Systems. *PSE '97-ESCAPE-7, 25-29 May, 1997, Trondheim, Norway, Supplement to Computers Chem. Engng.* **21**, S995–S1001. See C97-2.

Hilmen, E.K. (2000). Separation of Azeotropic Mixtures: Tools for Analysis and Studies on Batch Distillation Operation. PhD thesis. Norwegian University of Science and Technology, Trondheim, Norway.

Laroche, L., N. Bekiaris, H.W. Andersen and M. Morari (1992*a*). Homogeneous Azeotropic Distillation: Separability and Flowsheet Synthesis. *Ind. Eng. Chem. Res.* **31**(9), 2190–2209.

Laroche, L., N. Bekiaris, H.W. Andersen and M. Morari (1992*b*). The Curious Behavior of Homogeneous Azeotropic Distillation - Implications for Entrainer Selection. *AIChE J.* **38**(9), 1309–1328.

Lecat, M. (1949). *Tables Azéotropiques, Azéotropes Binaries Orthobares*. Brussels.

Matsuyama, H. and H. Nishimura (1977). Topological and Thermodynamic Classification of Ternary Vapor-Liquid Equilibria. *J. Chem. Eng. Jpn.* **10**(3), 181–187.

Ostwald, W. (1902). *Lehrbuch der Allgemeinen Chemie. Verwandtschaftslehre. Erste Teil (In German)*. Verlag von Wilhelm Engelmann, Leipzig, Germany.

Petlyuk, F.B. and L.A. Serafimov (1983). *Multicomponent Distillation. Theory and Design (in Russian) [Mnogokomponentnaya Rektifikatsiya: Teriyo I. Raschet]*. Chemistry Publishing Co, Moscow.

Petlyuk, F.B. and V.S. Avet'yan (1971). Investigation of the Rectification of Three-Component Mixtures with Infinite Reflux. *Theor. Found. Chem. Eng.* **5**(4), 499–507.

Pöllmann, P. and E. Blass (1994). Best Products of Homogeneous Azeotropic Distillations. *Gas Sep. Purif.* **8**(4), 194–228.

Reshetov, S.A. (1998). Private communications. Karpov Institute of Physical Chemistry, Moscow.

Reshetov, S.A., I.B. Zhvanetskij and E.V. Orlova (1999). Modeling of Continuous Distillation of Ternary Mixtures with Phase Diagrams Containing One-Side Unity α-Lines. *Theor. Found. Chem. Eng.* **33**(2), 149–155.

Schreinemakers, F.A.H. (1901). Dampfdrucke Ternärer Gemische. Theoretischer Teil: Zweite Abhandlung (In German). *Z. Phys. Chem.* **36**(4), 413–449.

Schreinemakers, F.A.H. (1902). Einige Bemerkungen über Dampfdrucke Ternärer Gemische (In German). *Z. Phys. Chem.* **43**, 671–685.

Serafimov, L.A. (1968*a*). Separation Technology of Azeotropic Mixtures (in Russian). *Book: Azeotropy and Polyazeotropy, Chapter XX1 (additional chapter in Russian edition), W. Świętosławski (Ed.), Chemistry Publishing Co., Moscow* pp. 186–224.

Serafimov, L.A. (1968*b*). Theoretical Principles of Distillation Sequences Design and Synthesis for Nonideal Multicomponent Mixtures (in Russian). PhD thesis. Lomonosov Institute of Fine Chemical Technology, Moscow.

Serafimov, L.A. (1970). The Azeotropic Rule and the Classification of Multicomponent Mixtures VII. Diagrams for Ternary Mixtures. *Russ. J. Phys. Chem.* **44**(4), 567–571 [1021–1027].

Serafimov, L.A. (1996). Thermodynamic and Topological Analysis of Liquid-Vapor Phase Equilibrium Diagrams and Problems of Rectification of Multicomponent Mixtures. *Book: Mathematical Methods in Contemporary Chemistry, S.I. Kuchanov (Ed.) Gordon and Breach Publishers, Amsterdam* pp. 557–605.

Serafimov, L.A., V.S. Timofeyev and M.I. Balashov (1973). Rectification of Multicomponent Mixtures II. Local and General Characteristics of the Trajectories of Rectification Processes at Infinite Reflux Ratio. *Acta Chemica Acad. Sci. Hung.* **75**(2), 193–211.

Serafimov, L.A., V.T. Zharov and V.S. Timofeyev (1971). Rectification of Multicomponent Mixtures I. Topological Analysis of Liquid-Vapor Phase Equilibrium Diagrams. *Acta Chemica Acad. Sci. Hung.* **69**(4), 383–396.

Stichlmair, J. (1988). *Distillation and Rectification.* Vol. B3. Ullmann's Enc. Ind. Chem.

Vogelpohl, A. (1999). On the Relation between Ideal and Real Systems in Ternary Distillation. *Trans. IChemE* **77**(9), 487–492.

Widagdo, S. and W.D. Seider (1996). Journal Review: Azeotropic Distillation. *AIChE J.* **42**(1), 96–128.

Zharov, V.T. (1967). Free Evaporation of Homogeneous Multicomponent Solutions. *Russ. J. Phys. Chem.* **41**(11), 1539–1543.

Zharov, V.T. (1968). Phase Transformations [*Distillation Lines*] and Rectification of Multicomponent Solutions. *Russ. J. Appl. Chem.* **41**(12), 2530–2536.

Zharov, V.T and L.A. Serafimov (1975). *Physicochemical Foundations of Simple Distillation and Rectification (in Russian).* Chemistry Publishing Co., Lenningrad.