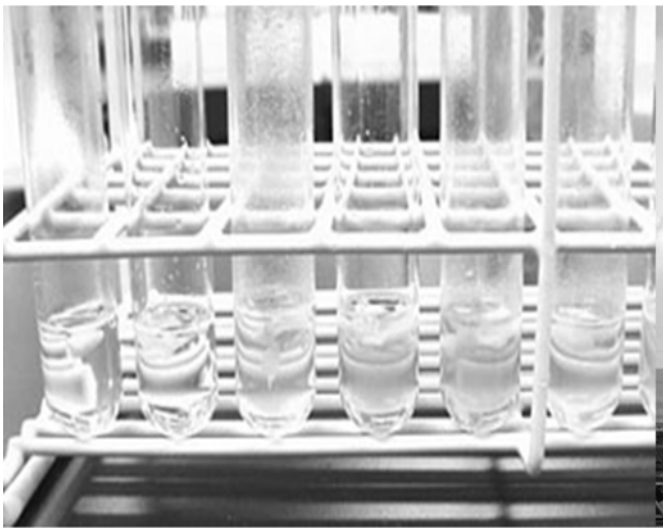
Guidelines for Ternary Azeotropic Points

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Introduction

Although there are many actual measurement data on binary azeotropic mixtures, there are currently few data for ternary systems and prediction is difficult.

It is time-consuming and inefficient to check all regions even when conducting experiments.

Here, we will introduce a rule of the thumb which seems to be effective for the purpose of estimating ternary azeotropic points.

Ewell, Harrison, Berg Liquid Classification Table

- In a binary system, it is possible to get an indication as to what kind of azeotrope is formed by using a liquid classification table in which pure liquids are categorized into five classes in decreasing order of hydrogen bonding capacity.

Group	Characteristics	Examples
I	Compounds having three-dimensional hydrogen	Water, alcohols, glycerin, amino alcohols, hydroxylamines, oxyacids, amides, polyhydric phenols
II	Compounds having active hydrogen atoms and electron donors other than group 1	Alcohols, acids, phenols, primary amines and secondary amines, oximes, nitro compounds and nitriles having a hydrogen atom at the α position, hydrazines, ammonia, HF, HCN
III	Compounds having electron donors but no active hydrogen atom	Ethers, ketones, aldehydes, esters, tertiary amines, pyridines, nitrile compounds and nitriles having no hydrogen atom at the α position
IV	Compounds having active hydrogen atoms but no electron donor	Compounds with two or more chlorine atoms bonded to the same carbon atom ($CHCl_3$, CH_2Cl_2, CH_3CHCl_2), and compounds with chlorine atoms bonded to adjacent carbon atoms (CH_2Cl-CH_2Cl, CH_2Cl-$CHCl$-CH_2Cl, $CHCl_2$- $CHCl_2$)
V	Compounds that cannot form hydrogen bonds	Hydrocarbons, sulfides, mercaptans, group 4 or more halogenated hydrocarbons, nonmetal simple substances (iodine, phosphorus, sulfur)

Ewell, R.H., J.M. Harrison and L. Berg: *Ind. Eng. Chem.*, 36, 871 (1944)

Deviation from Raoult's Law

- As a result of studying 15 kinds of combinations from the liquid classification by Ewell *et al*, Hirata *et al*. reported that they could be divided into five groups.

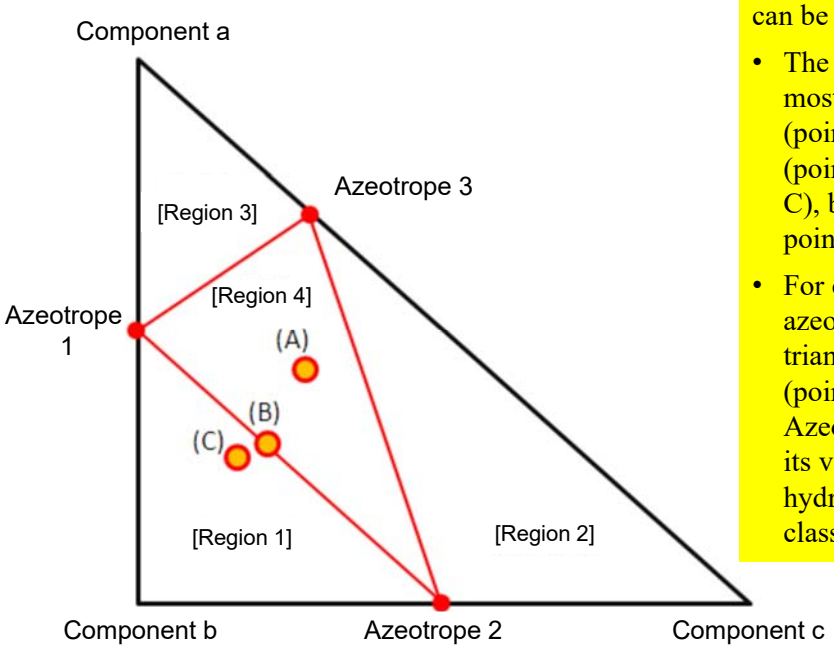
	Binary Systems	Deviation	Hydrogen Bonding	
1	I + V II + V	Always positive deviation; I + V often have a limited solubility.	Hydrogen bonds are broken.	γ>1
2	III + IV	Always negative deviation	Hydrogen bonds are formed.	γ<1
3	I + IV II + IV	Always positive deviation; I + IV often have a limited solubility.	Hydrogen bonds may be broken or formed. However, dissociation of class I or II liquid is an important factor.	γ>1
4	I + I I + II I + III II + II II + III	Normally a positive deviation; Usually these are complex solutions, some of which show a negative deviation to produce maximum azeotropic mixtures.	Hydrogen bonds may be broken or formed.	
5	III + III III + V IV + IV IV + V V + V	Systems close to an ideal solution always with positive deviation or ideal solution behavior. In the cases when azeotropes exist, these are minimum azeotropic mixtures.	There is no hydrogen bonding.	γ≥1

Example: The binary system of methanol (type II) - benzene (type V) that forms a minimum azeotrope belongs to group 1.

"Saishin Jyouryuu Kogaku" (*in Japanese*: Latest Distillation Engineering) Hirata Mitsuho, P. 45, Nikkan Kogyo Shimbunsha

Range of Existence of Ternary Azeotropic Points

- When three binary sets of a ternary system each have an azeotropic point, four regions can be formed by connecting each azeotropic point on a ternary diagram.



At this time, the following empirical facts can be understood

- The ternary azeotropic point is located most frequently within [Region 4] (point A). It can also exist on a side (point B) or outside of [Region 4] (point C), but the probability of it being on point A is by far the largest.
- For cases other than point A, the ternary azeotropic point is at the side of the triangle (point B) or near the base side (point C) in the triangle [Component b - Azeotrope 1 - Azeotrope 2] which has at its vertex the strongest component for hydrogen bonding in the liquid classification of Ewell et al.

Classification of Azeotropic Points

- The classification results of ternary azeotropic mixtures taken from the scientific literature*1) are listed here.

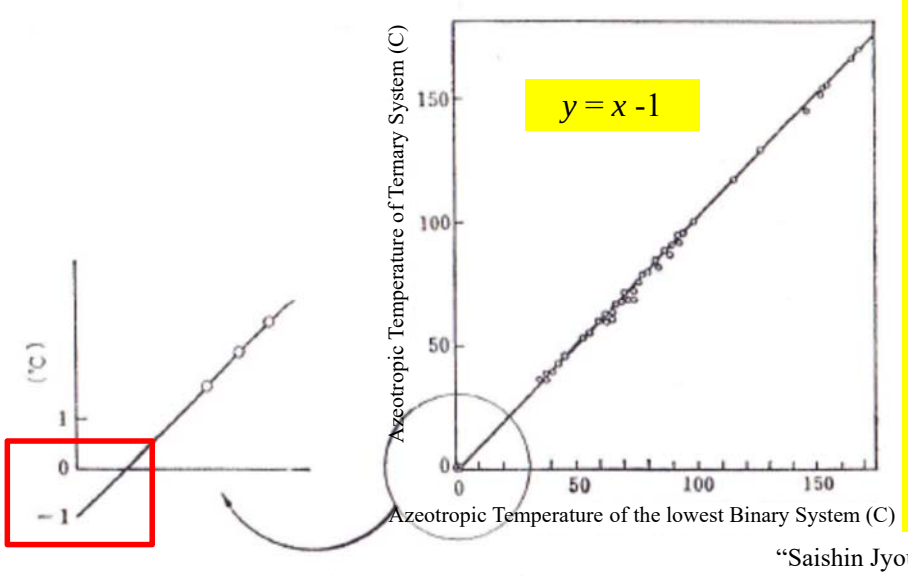
Approximately 70% of azeotropic points are A, and when B is included on the side, it is found that 80% or more of the ternary azeotropic points are in the A region or on its side.

No.	Ternary Systems	Ewell Classification	Position of Azeotrope
1	Water, ethanol, carbon tetrachloride	I - II - V	A
2	Water, allyl alcohol, carbon tetrachloride	I - II - V	A
3	Water, n-propyl alcohol, carbon tetrachloride	I - II - V	A
4	Water, butanone, 2-carbon tetrachloride	I - III - V	A
5	Water, s-butanol, carbon tetrachloride	I - II - V	A
6	Water, t-butanol, carbon tetrachloride	I - II - V	A
7	Water, ethanol, carbon disulfide	I - II - V	A
8	Water, n-propyl alcohol, nitromethane	I - II - III	A
9	Water, iso-propyl alcohol, nitromethane	I - II - III	A
10	Water, nitromethane, pentanone-3	I - III - III	C
11	Water, acetonitrile, trichloroethylene	I - II - IV	A
12	Water, acetoalcohol, trichloroethylene	I - II - IV	A
13	Water, ethanol, trichloroethylene	I - II - IV	B
14	Water, n-propyl alcohol, trichloroethylene	I - II - IV	A
15	Water, acetonitrile, benzene	I - III - V	A
16	Water, ethanol, 1,2-dichloroethane	I - II - IV	C,A
17	Water, ethanol, ethyl acetate	I - II - III	B
18	Water, ethanol, 1 chlor-2 methyl propane	I - II - IV	C
19	Water, ethanol, pentanone-2	I - II - III	C
20	Water, ethanol, benzene	I - II - V	A
21	Water, ethanol, cyclohexane	I - II - V	A
22	Water, allyl alcohol, benzene	I - II - V	A
23	Water, allyl alcohol, cyclohexane	I - II - V	A
24	Water, n-propyl alcohol, propyl acetate	I - II - III	C
25	Water, n-propyl alcohol, benzene	I - II - V	A
26	Water, n-propyl alcohol, cyclohexane	I - II - V	A
27	Water, iso-propyl alcohol, iso-propyl acetate	I - II - III	A
28	Water, iso-propyl alcohol, benzene	I - II - V	A
29	Water, iso-propyl alcohol, cyclohexane	I - II - V	A
30	Water, iso-propyl alcohol, butanone-2	I - II - III	A
31	Water, butanone-2, benzene	I - II - V	B
32	Water, n-butyl alcohol, n-butyl formate	I - II - III	B
33	Water, n-butyl alcohol, n-butyl acetate	I - II - III	C
34	Water, s-butyl alcohol, benzene	I - II - V	A
35	Water, tert-butyl alcohol, benzene	I - II - V	A
36	Water, tert-butyl alcohol, cyclohexane	I - II - V	A
37	Water, iso-amyl alcohol, iso-amyl formate	I - II - III	B
38	Carbon disulfide, methanol, ethyl bromide	II - V - V	C
39	Methanol, acetone, chloroform	II - III - IV	C
40	Methanol, acetone, cyclohexane	II - III - V	A
41	Ethyl ether, methyl formate, pentane	III - III - V	B
42	n-butyl alcohol, toluene, pyridine	II - III - V	A

Note *1):
- Horsley, L.H : Azeotropic Data I & II, American Chemical Society
- Kagaku kogaku kyokai hen : Bussei teisu 1-shu (*In Japanese*: Chemical Engineering Association Edition: Physical Property Constants vol. 1)

Temperatures of Ternary Azeotropic Points

- In the cases where each of the three binary sets of the components constituting a ternary system has an azeotropic point, plotting the azeotropic temperature of the ternary system versus the azeotropic temperature of the lowest binary system gives the linear relationship $y = x - 1$.



Azeotropic Temperatures of Ternary Systems

In other words, the azeotropic temperature of the ternary system is approximately -1C lower than the lowest azeotropic temperature among those of the binary systems.

Example: for water, isopropyl alcohol and nitromethane:

The lowest azeotropic temperature is 79.3C for isopropyl alcohol and nitromethane, and the ternary azeotropic temperature is 78C.

"Saishin Jyouryuu Kogaku" (*in Japanese*: Latest Distillation Engineering) Hirata Mitsuho, P. 49, Nikkan Kogyo Shimbunsha

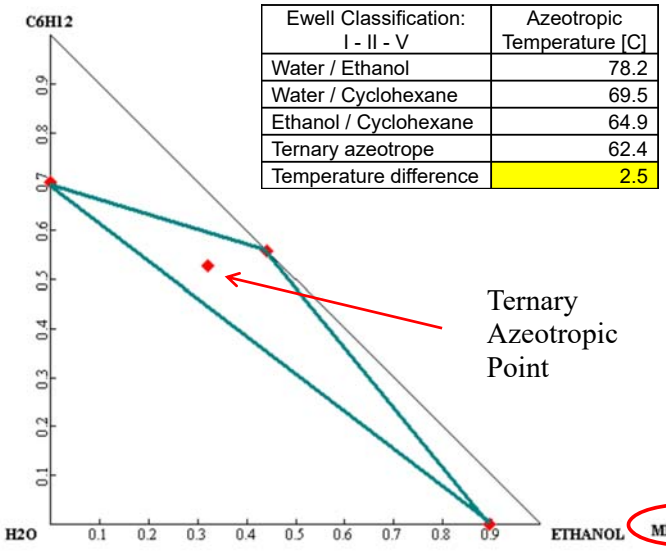
Solutions for R&D to Design

Verifications with Systems of Various Classes

Calculations were carried out to confirm that the empirical rule applies for multiple classes of systems.

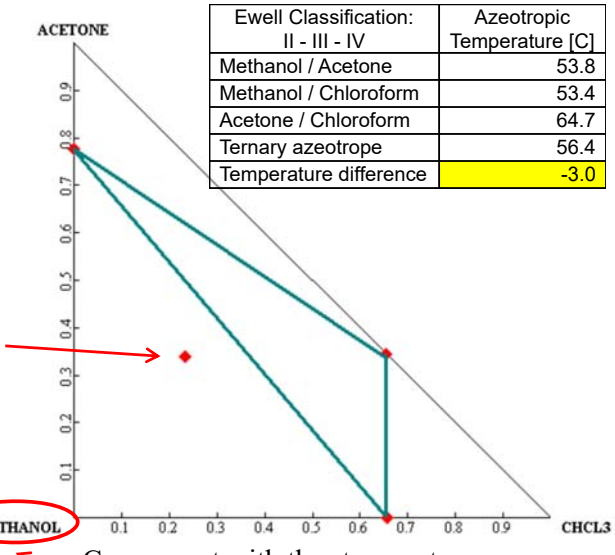
- Water, ethanol, cyclohexane system [I - II - V]
- Methanol, acetone, chloroform system [II - III - IV]

Ewell Classification: I - II - V	Azeotropic Temperature [C]
Water / Ethanol	78.2
Water / Cyclohexane	69.5
Ethanol / Cyclohexane	64.9
Ternary azeotrope	62.4
Temperature difference	2.5



Ternary Azeotropic Point

Ewell Classification: II - III - IV	Azeotropic Temperature [C]
Methanol / Acetone	53.8
Methanol / Chloroform	53.4
Acetone / Chloroform	64.7
Ternary azeotrope	56.4
Temperature difference	-3.0



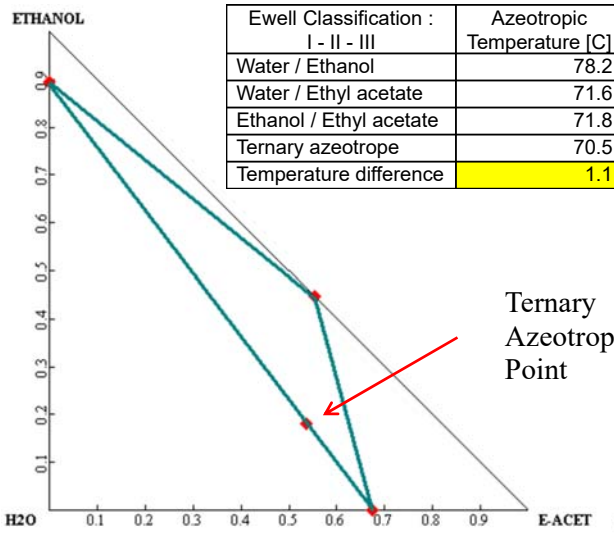
Component with the strongest hydrogen bonds in the system

Solutions for R&D to Design

Verifications with Systems of Various Classes

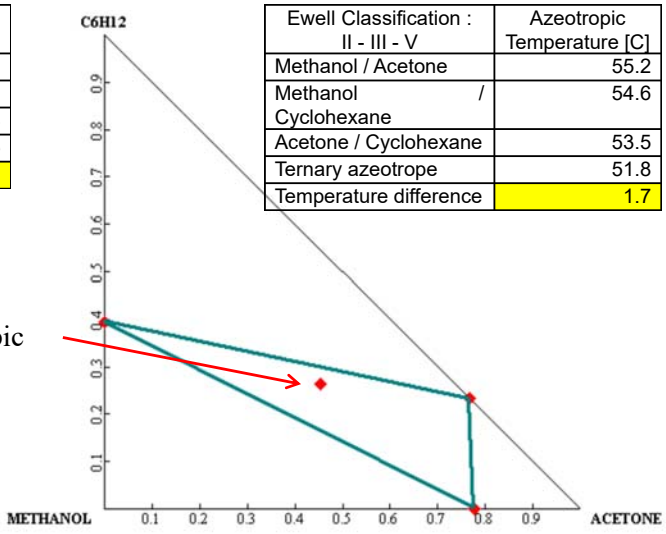
- Water, ethanol, ethyl acetate system [I - II - III]
- Methanol, acetone, cyclohexane system [II - III - V]

Ewell Classification : I - II - III	Azeotropic Temperature [C]
Water / Ethanol	78.2
Water / Ethyl acetate	71.6
Ethanol / Ethyl acetate	71.8
Ternary azeotrope	70.5
Temperature difference	1.1



Ternary Azeotropic Point

Ewell Classification : II - III - V	Azeotropic Temperature [C]
Methanol / Acetone	55.2
Methanol / Cyclohexane	54.6
Acetone / Cyclohexane	53.5
Ternary azeotrope	51.8
Temperature difference	1.7



It is safer to think that the ternary azeotropic temperature is close to the lowest azeotropic temperature among those of the binary systems.

Conclusion

- When each of the three binary sets of the components constituting a ternary system has an azeotropic point, the ternary azeotropic point has a high probability of being present in the region connecting the binary azeotropic points. Also, when it is outside this region, it will be either on the side of the triangle with the strongest hydrogen bonding component in the liquid classification of Ewell et al. (point B) or near the base side of the triangle (point C).
- When each of the three binary sets of the components constituting a ternary system has an azeotropic point, the azeotropic temperature of the ternary system is close to the azeotropic temperature of the lowest binary system (About -1C lower except for systems containing maximum azeotropes).