

Supporting information for:

A simple method to predict and interpret the formation of azeotropes in binary systems using conventional solvation free energy calculations

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Thermodynamic basis for the formation of azeotropes using limiting activity coefficients

For a binary system at vapor/liquid equilibrium, assuming the vapor phase is an ideal gas and that the liquid phase fugacity is independent of pressure (i.e., that the Poynting correction is negligible and the activity coefficient is independent of pressure), the iso-fugacity condition can be written as¹

$$\begin{aligned} x_1 \gamma_1(T, x_1) P_1^{\text{sat}}(T) &= y_1 P \\ x_2 \gamma_2(T, x_1) P_2^{\text{sat}}(T) &= y_2 P \end{aligned} \quad (1)$$

where x_1 and x_2 are the liquid phase mole fracs of component 1 and 2, respectively, y_1 and y_2 are the vapor phase mole fracs of component 1 and 2, respectively, P is the pressure, P_1^{sat} and P_2^{sat} are the pure component vapor pressures at the equilibrium temperature T , and γ_1 and γ_2 are the Lewis/Randall or Raoult's law normalized activity coefficients of component 1 and 2, respectively. Throughout the derivation, component 1 will correspond to the most volatile component (MVC) and component 2 will correspond to the least volatile component (LVC). From eq. 1 we define the K -value of component i as

$$K_i = \frac{y_i}{x_i} = \frac{\gamma_i(T, x_1) P_i^{\text{sat}}(T)}{P} \quad (2)$$

where $i=\{1 \text{ or } 2\}$, and the relative volatility as

$$\alpha(T, x_1) = \frac{K_1}{K_2} = \frac{y_1/x_1}{y_2/x_2} = \frac{\gamma_1(T, x_1) P_1^{\text{sat}}(T)}{\gamma_2(T, x_1) P_2^{\text{sat}}(T)} \quad (3)$$

where by convention α is defined as the ratio of K -values of the MVC relative to the LVC. In the design of vapor/liquid separation processes (i.e., distillation), the greater the deviation of α from unity, the greater the separation achievable in a single stage^{2,3}. When $\alpha > 1$ the MVC is

concentrated in the vapor phase, when $\alpha < 1$ the LVC is concentrated in the vapor phase, and when $\alpha = 1$ no separation is possible. Specifically, at an azeotrope $x_1 = y_1$ and $x_2 = y_2$ leading to the relationship

$$\alpha(T, x_1^{\text{azeo}}) = 1 = \frac{\gamma_1(T, x_1^{\text{azeo}})}{\gamma_2(T, x_1^{\text{azeo}})} \frac{P_1^{\text{sat}}(T)}{P_2^{\text{sat}}(T)} \quad (4)$$

where the superscript “azeo” is used to indicate properties at the azeotrope.

For a binary system at vapor/liquid equilibrium we have two degrees of freedom. If we consider either isothermal (P_{xy}) or isobaric (T_{xy}) vapor/liquid equilibrium, we are left with just a single degree of freedom. Having just a single degree of freedom, we can make use of the Intermediate Value Theorem to determine if an azeotrope will exist using values of the relative volatility in the limit that $x_1 \rightarrow 0$ and $x_1 \rightarrow 1^4$. Before proceeding, we point out that this will be restricted to identifying mono-azeotropic systems. Additionally, we will restrict our derivation to the isothermal case as our free energy calculations in the present study will be restricted to a single temperature. Of central importance to the isothermal case is that P_1^{sat} and P_2^{sat} are constant, and having assumed γ_1 and γ_2 are independent of pressure, γ_1 and γ_2 are therefore only functions of composition.

Working with Lewis/Randall normalized activity coefficients, we recall the limiting conditions. First, in the infinite dilution limit, the deviations from ideality will be greatest. For a system that exhibits a minimum boiling azeotrope (positive deviations from Raoult’s law, $\gamma_i > 1$), this will correspond to values of $\gamma_{i,j}^\infty$ that are greater than 1 and a maximum, where the subscript notation “ i, j ” is used to indicate i is infinitely dilute in j . Knowing this, we consider the limiting conditions of eq. (4).

In the limit that $x_1 \rightarrow 0$ and $x_2 \rightarrow 1$, $\gamma_1 \rightarrow \gamma_{1,2}^\infty$ and $\gamma_2 \rightarrow 1$. In the context of eq. (4), $\gamma_1/\gamma_2 \rightarrow \gamma_{1,2}^\infty$. For a system that exhibits a minimum boiling azeotrope, $\gamma_{1,2}^\infty$ will be larger than the corresponding value at the azeotrope composition, and $\gamma_2 = 1$ will be less than the corresponding value at the azeotropic composition. As a result, for a system with a minimum boiling azeotrope

$$\alpha(T, x_1 \rightarrow 0) = \gamma_{1,2}^{\infty}(T) \frac{P_1^{\text{sat}}(T)}{P_2^{\text{sat}}(T)} > 1 \quad (5)$$

Considering next the limit that $x_1 \rightarrow 1$ and $x_2 \rightarrow 0$, $\gamma_1 \rightarrow 1$ and $\gamma_2 \rightarrow \gamma_{2,1}^{\infty}$. This leads to $\gamma_1/\gamma_2 \rightarrow 1/\gamma_{2,1}^{\infty}$. For a system that exhibits a minimum boiling azeotrope, $\gamma_1 = 1$ will be less than the corresponding value at the azeotrope composition, and $\gamma_{2,1}^{\infty}$ will be larger than the corresponding value at the azeotrope composition. As a result, for a system with a minimum boiling azeotrope

$$\alpha(T, x_1 \rightarrow 1) = \frac{1}{\gamma_{2,1}^{\infty}(T)} \frac{P_1^{\text{sat}}(T)}{P_2^{\text{sat}}(T)} < 1 \quad (6)$$

Putting it together, for a system with a minimum boiling azeotrope

$$\alpha(T, x_1 \rightarrow 0) > 1 \wedge \alpha(T, x_1 \rightarrow 1) < 1 \quad (7)$$

This tells us that at low concentrations of the MVC, $\alpha > 1$ and the MVC will be concentrated in the vapor phase. Then past the azeotropic composition, $\alpha < 1$ and the LVC will be concentrated in the vapor phase. Further, since T is constant and α is a continuous function with respect to x_1 , the Intermediate Value Theorem states that there exist a value of x_1 such that $\alpha = 1$, confirming the existence of an azeotrope.

Using the same analysis, we can obtain an equivalent expression for the case of a maximum boiling azeotrope. The difference is for a system that exhibits a maximum boiling azeotrope (negative deviations from Raoult's law, $\gamma_i < 1$), the limiting conditions will correspond to values of $\gamma_{i,j}^{\infty}$ that are less than 1 and a minimum. This results in the following expression for a system with a maximum boiling azeotrope

$$\alpha(T, x_1 \rightarrow 0) < 1 \wedge \alpha(T, x_1 \rightarrow 1) > 1 \quad (8)$$

which is the opposite of the minimum boiling case. We find that for the case of a maximum boiling azeotrope, at low concentrations of the MVC, $\alpha < 1$ and the LVC will be concentrated in the vapor

phase. Then, past the azeotropic composition, $\alpha > 1$ and the MVC will be concentrated in the vapor phase.

Table S1: The 146 unique compounds which make-up the 2,366 studied binary systems, along with their CAS and SMILES.

Compound	CAS	SMILES
1-butanol	71-36-3	CCCCO
1-decanol	112-30-1	CCCCCCCO
1-hexanol	111-27-3	CCCCCCO
1-octanol	111-87-5	CCCCCCCO
1-pentanol	71-41-0	CCCCO
1-propanol	71-23-8	CCCO
2,2,2-trifluoroethanol	75-89-8	C(C(F)(F)F)O
2,2,4-trimethylpentane	540-84-1	CC(C)CC(C)(C)C
2,6-dimethylpyridine	108-48-5	CC1=NC(=CC=C1)C
2-heptanone	110-43-0	CCCCCC(=O)C
2-methylpentane	107-83-5	CCCC(C)C
2-methylpyridine	109-06-8	CC1=CC=CC=N1
2-propanol	67-63-0	CC(C)O
3-methylpyridine	108-99-6	CC1=CN=CC=C1
4-heptanone	123-19-3	CCCC(=O)CCC
4-methyl-2-pentanone	108-10-1	CC(C)CC(=O)C
acetone	67-64-1	CC(=O)C
acetonitrile	75-05-8	CC#N
benzene	71-43-2	C1=CC=CC=C1
benzonitrile	100-47-0	C1=CC=C(C=C1)C#N
benzyl alcohol	100-51-6	C1=CC=C(C=C1)CO
bromobenzene	108-86-1	C1=CC=C(C=C1)Br
carbon tetrachloride	56-23-5	C(Cl)(Cl)(Cl)Cl
chlorobenzene	108-90-7	C1=CC=C(C=C1)Cl
cyclohexane	110-82-7	C1CCCC1
cyclopentane	287-92-3	C1CCCC1
cyclopentanol	96-41-3	C1CCC(C1)O
dibutyl ether	142-96-1	CCCCOCCCC
dichloromethane	75-09-2	C(Cl)Cl
diethyl ether	60-29-7	CCOCC
diethylamine	109-89-7	CCNCC
dimethyl sulfoxide	67-68-5	CS(=O)C
ethanol	64-17-5	CCO
isobutanol	78-83-1	CC(C)CO
methanol	67-56-1	CO
m-xylene	108-38-3	CC1=CC(=CC=C1)C
heptane	142-82-5	CCCCCC
hexadecane	544-76-3	CCCCCCCCCCCCCCCC
hexane	110-54-3	CCCCCC
nitroethane	79-24-3	CC[N+](=O)[O-]

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Compound	CAS	SMILES
nitromethane	75-52-5	C[N+](=O)[O-]
nonane	111-84-2	CCCCCC
octane	111-65-9	CCCCCC
o-xylene	95-47-6	CC1=CC=CC=C1C
perfluorobenzene	392-56-3	C1(=C(C(=C(C(=C1F)F)F)F)F)F
propanal	123-38-6	CCC=O
p-xylene	106-42-3	CC1=CC=C(C=C1)C
pyridine	110-86-1	C1=CC=NC=C1
sec-butanol	78-92-2	CCC(C)O
tert-butanol	75-65-0	CC(C)(C)O
tetrahydrofuran	109-99-9	C1CCOC1
trichloromethane	67-66-3	C(Cl)(Cl)Cl
triethylamine	121-44-8	CCN(CC)CC
water	7732-18-5	O
1,4-dioxane	123-91-1	C1COCCO1
butanonitrile	109-74-0	CCCC#N
ethyl ethanoate	141-78-6	CCOC(=O)C
1-chloropentane	543-59-9	CCCCCl
1-hexyne	693-02-7	CCCC#C
1,1,1-trichloroethane	71-55-6	CC(Cl)(Cl)Cl
3-pentanone	96-22-0	CCC(=O)CC
butylamine	109-73-9	CCCCN
butyraldehyde	123-72-8	CCCC=O
carbon disulfide	75-15-0	C(=S)=S
cyclohexanone	108-94-1	C1CCC(=O)CC1
cyclopentanone	120-92-3	C1CCC(=O)C1
ethylbenzene	100-41-4	CCC1=CC=CC=C1
pentane	109-66-0	CCCC
tribromomethane	75-25-2	C(Br)(Br)Br
1-hexene	592-41-6	CCCC=C
1-nitropropane	108-03-2	CCC[N+](=O)[O-]
1-pentene	109-67-1	CCCC=C
2-nitropropane	79-46-9	CC(C)[N+](=O)[O-]
aniline	62-53-3	C1=CC=C(C=C1)N
decalin	91-17-8	C1CCC2CCCC2C1
decane	124-18-5	CCCCCC
dodecane	112-40-3	CCCCCCCCCCCC
isopropylbenzene	98-82-8	CC(C)C1=CC=CC=C1
n-methylaniline	100-61-8	CNC1=CC=CC=C1
nitrobenzene	98-95-3	C1=CC=C(C=C1)[N+](=O)[O-]
pentadecane	629-62-9	CCCCCCCCCCCCCCC
pyrrolidine	123-75-1	C1CCNC1

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Table S1: Continued from previous page

Compound	CAS	SMILES
tetrachloroethylene	127-18-4	C(=C(Cl)Cl)(Cl)Cl
thiophene	110-02-1	C1=CSC=C1
diethyl sulfide	352-93-2	CCSSCC
ethanethiol	75-08-1	CCS
propylamine	107-10-8	CCCN
1,1,2-trichloroethane	79-00-5	C(C(Cl)Cl)Cl
1,1-dichloroethane	75-34-3	CC(Cl)Cl
1,2,4-trimethylbenzene	95-63-6	CC1=CC(=C(C=C1)C)C
1-bromo-2-methylpropane	78-77-3	CC(C)CBr
1-bromopentane	110-53-2	CCCCCCBr
1-bromopropane	106-94-5	CCCBr
1-chloropropane	540-54-5	CCCCl
1-heptanol	111-70-6	CCCCCCO
1-nonal	143-08-8	CCCCCCCCCO
1-pentyne	627-19-0	CCCC#C
2,4-dimethylpentane	108-08-7	CC(C)CC(C)C
2-bromopropane	75-26-3	CC(C)Br
2-chlorobutane	78-86-4	CCC(C)Cl
2-hexanone	591-78-6	CCCCC(=O)C
2-octanone	111-13-7	CCCCCCC(=O)C
2-pantanone	107-87-9	CCCC(=O)C
2-propen-1-ol	107-18-6	C=CCO
4-methylpyridine	108-89-4	CC1=CC=NC=C1
5-nonenone	502-56-7	CCCCC(=O)CCCC
acetic acid	64-19-7	CC(=O)O
anisole	100-66-3	COC1=CC=CC=C1
benzaldehyde	100-52-7	C1=CC=C(C=C1)C=O
bromoethane	74-96-4	CCBr
butanoic acid	107-92-6	CCCC(=O)O
butanone	78-93-3	CCC(=O)C
butyl ethanoate	123-86-4	CCCCOC(=O)C
butylbenzene	104-51-8	CCCCC1=CC=CC=C1
dibromomethane	74-95-3	C(Br)Br
dimethyldisulfide	624-92-0	CSSC
dimethylacetamide	127-19-5	CC(=O)N(C)C
dipropylamine	142-84-7	CCCNCCC
E-1,2-dichloroethene	156-60-5	C(=CCl)Cl
E-2-pentene	646-04-8	CCC=CC
ethyl methanoate	109-94-4	CCOC=O
ethylphenyl ether	103-73-1	CCOC1=CC=CC=C1
ethylene glycol	107-21-1	C(CO)O
fluorobenzene	462-06-6	C1=CC=C(C=C1)F

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Table S1: Continued from previous page

Compound	CAS	SMILES
formamide	75-12-7	C(=O)N
formic acid	64-18-6	C(=O)O
hexanoic acid	142-62-1	CCCCCC(=O)O
m-cresol	108-39-4	CC1=CC(=CC=C1)O
mesitylene	108-67-8	CC1=CC(=CC(=C1)C)C
o-chlorotoluene	95-49-8	CC1=CC=CC=C1Cl
o-cresol	95-48-7	CC1=CC=CC=C1O
o-dichlorobenzene	95-50-1	C1=CC=C(C(=C1)Cl)Cl
o-nitrotoluene	88-72-2	CC1=CC=CC=C1[N+](=O)[O-]
pentanal	110-62-3	CCCCC=O
pentanoic acid	109-52-4	CCCCC(=O)O
pentyl ethanoate	628-63-7	CCCCCOC(=O)C
pentylamine	110-58-7	CCCCN
propanoic acid	79-09-4	CCC(=O)O
propanonitrile	107-12-0	CCC#N
propyl ethanoate	109-60-4	CCCOCC(=O)C
tert-butylbenzene	98-06-6	CC(C)(C)C1=CC=CC=C1
sulfolane	126-33-0	C1CCS(=O)(=O)C1
tetralin	119-64-2	C1CCC2=CC=CC=C2C1
trichloroethene	79-01-6	C(=C(Cl)Cl)Cl
undecane	1120-21-4	CCCCCCCCCC
Z-1,2-dichloroethene	156-59-2	C(=CCl)Cl

References

- (1) Prausnitz, J. M.; Lichtenthaler, R. N.; de Azevedo, E. G. *Molecular Thermodynamics of Fluid-phase Equilibria*, 2nd ed.; Prentice-Hall, Inc.: Englewood Cliffs, NJ, 1986.
- (2) Kister, H. Z. *Distillation Design*; McGraw Hill, Inc.: New York, NY, 1992.
- (3) Wankat, P. C. *Separation Process Engineering: Includes Mass Transfer*, 3rd ed.; Pearson Education, Inc.: Upper Saddle River, NJ, 2012.
- (4) Larson, R. E.; Hostetler, R. P.; Edwards, B. H. *Calculus*, 6th ed.; Houghton Mifflin Company: New York, NY, 1998.