PROMÉTHÉE

IMPACT OF SOLVENT MIXTURES ON EQUILIBRIUM CONSTANTS

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OUTLINE

- Needs
  - Speciation
- Tools
  - Definitions
  - Models
- Data
  - Conductivity
  - Titration
- Conclusions

Example - Speciation of molybdenum in solution

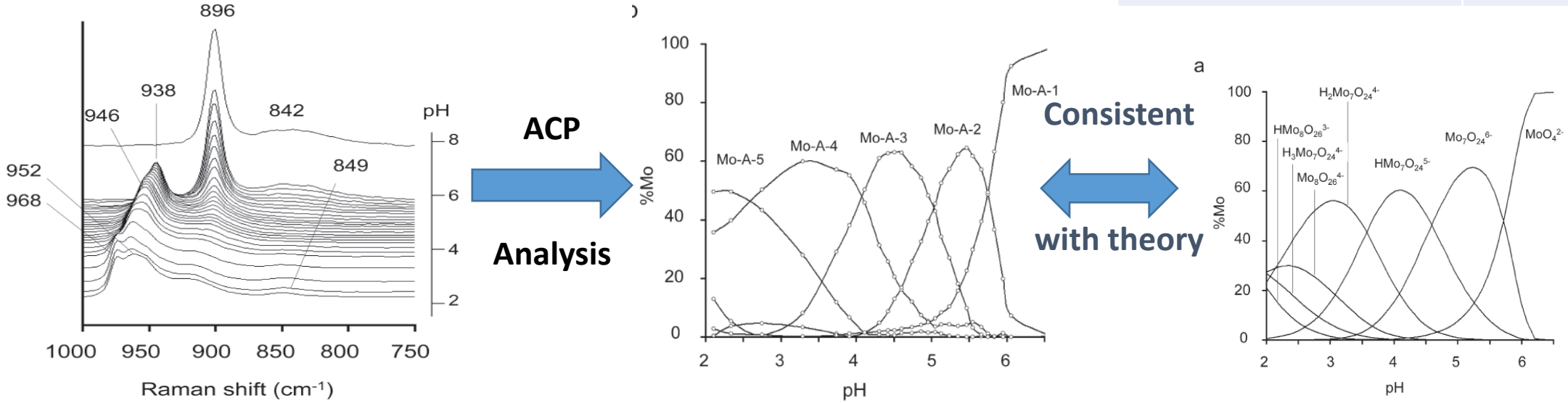
- **Example of polymolybdenate**
  - **In aqueous medium : the speciation is well known (**Cruywagen et al., *Inorg. Chem*. 1980, 19, 552-554)
    - **Determination of the formation constant by potentiometric titration**

$$7MoO_4^{2-} + (8+x)H^+ \leftrightarrow H_xMo_7O_4^{(6-x)-} + 4H_2O$$

$$\beta_{mp} = \frac{[H_xMo_mO_y]}{[MoO_4^{2-}]^m \cdot [H^+]^p}$$

Formula	Log (β_{mp}) @ 25°C
$Mo_7O_4^{6-}$	52.81
$HMo_7O_4^{5-}$	57.40
$H_2Mo_7O_4^{4-}$	60.97
$H_3Mo_7O_4^{3-}$	63.03
$Mo_8O_6^{4-}$	71.19
$HMo_8O_6^{3-}$	73.03

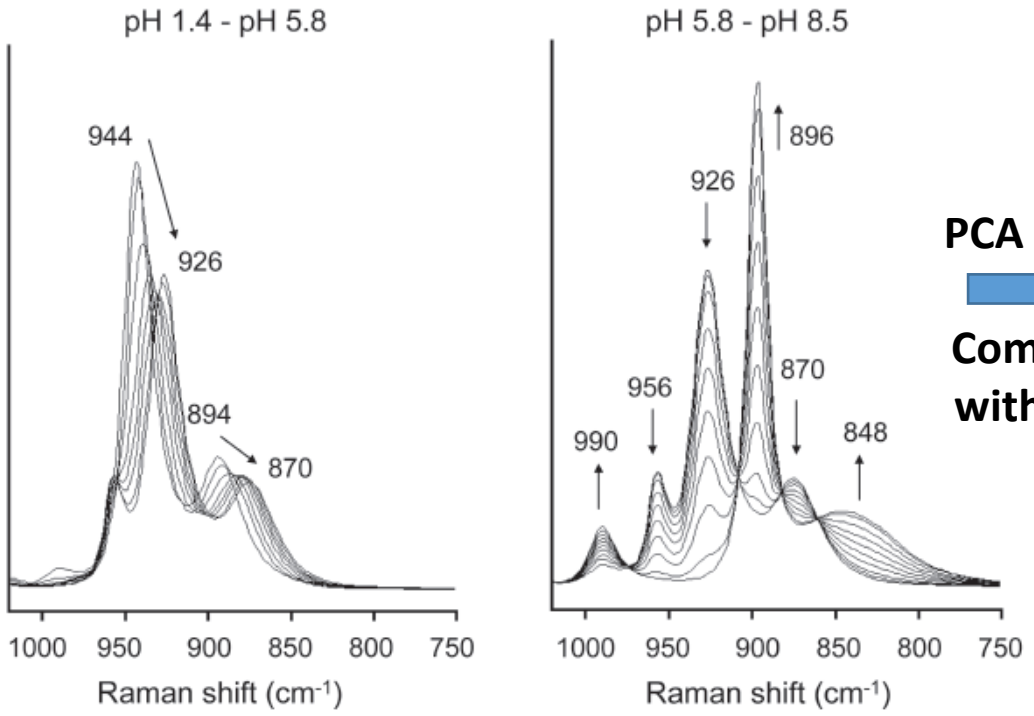
    - **Confirmation by Raman Spectroscopy (Bergwerff Ph-D, 2007)**



Example - Speciation of molybdenum in mixed solvent solution

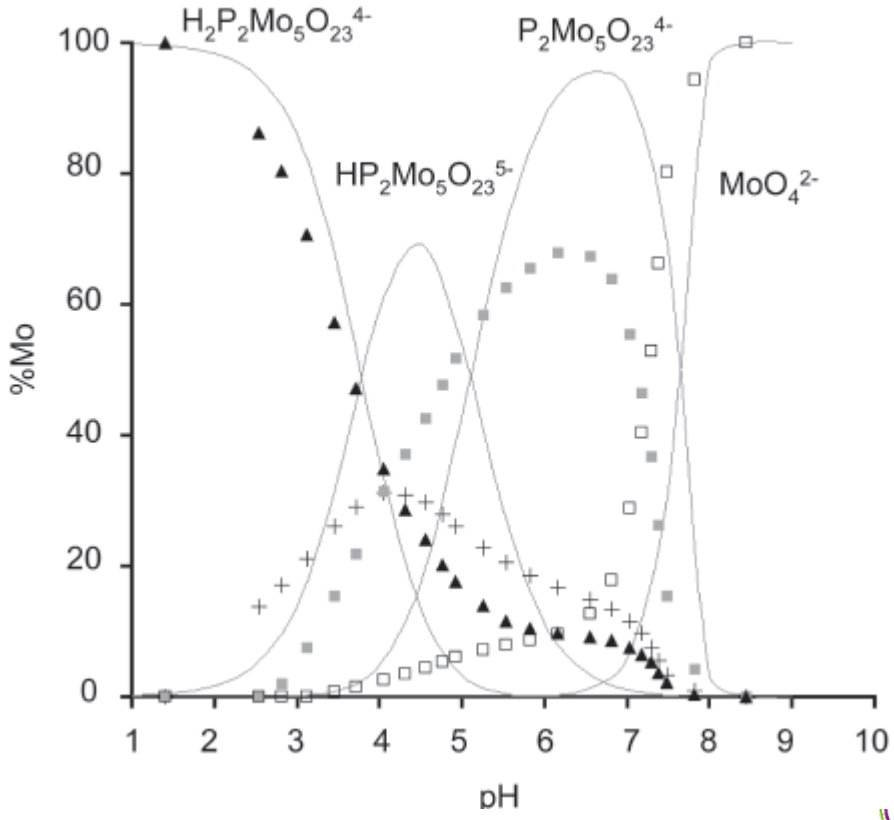
- **With Phosphoric acid : formation of heteropolycompounds (increase of Mo solubility …)**
  - **Constants are known… but analytical datas did not corroborate even in « simple » case(Bergwerff et al)**

Raman spectra with respect to pH



PCA Analysis

Comparison with theory



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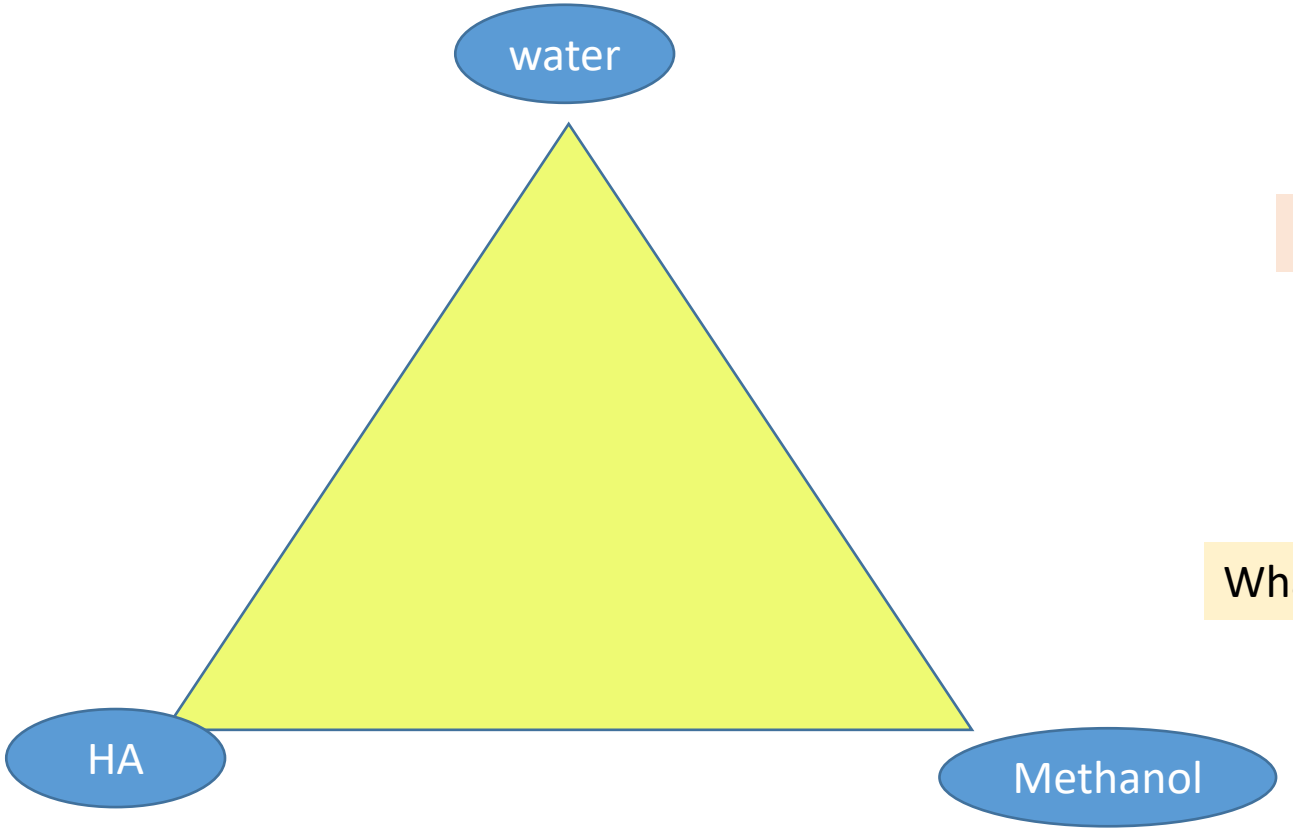
TOOLS

$$HA + H_2O = A^- + H_3O^+$$



$$\prod_i (a_i)^{\nu_i} = K$$

What is activity?

What is the equilibrium constant?

THE CHEMICAL POTENTIAL

$$dG \leq 0$$

$$\sum_i \mu_i \nu_i = 0$$

What is the chemical potential?

$$\mu_i = \left.\frac{\partial G}{\partial N_i}\right|_{P,T,N_{j\neq i}}$$

$$d\mu_i = RTd\ln(f_i)$$

The chemical potential :
- Depends on a reference state
- Logarithmic function of concentration (=>minus infinite at high dilution)

Fugacity (pressure dimension)

THE FUGACITY

$$d\mu_i = RTd\ln(f_i)$$

$$\mu_i^{(1)} - \mu_i^{(2)} = RT \ln \frac{f_i^{(1)}}{f_i^{(2)}}$$

Separately defined for each component

A thermodynamic state is defined from :
- Temperature (necessarily identical in all states)
- Pressure
- Physical state (may be virtual -> careful definition)
- Composition

Fugacity:
- Is a direct measure of chemical potential
- Measures the 'escaping tendency' of a compound
- More or less linear function of concentration (=>definition of activity coefficient)

$$f_i = c_i f_i^{ref} \gamma_i$$

What is c?

What is *ref*?

REFERENCE STATES

$$f_i = c_i f_i^{ref} \gamma_i$$

$$f_i^{ref}$$

- For solvents
- For ions/solutes (x)
- For ions/solutes (m)
- For ions/solutes (c)

$$f_i = x_i P_i^{\sigma} \gamma_i$$

$$f_i = x_i H_i \gamma_i^{x}$$

$$f_i = m_i \frac{H_i^m}{m^0} \gamma_i^m$$

$$f_i = [i] \frac{H_i^c}{c^0} \gamma_i^c$$

$$P_i^{\sigma}$$

$$H_i = \lim_{x_i \to 0} \frac{f_i}{x_i} = P_i^{\sigma} \gamma_i^{\infty}$$

$$\frac{H_i^m}{m_i^0} = M_s H_i$$

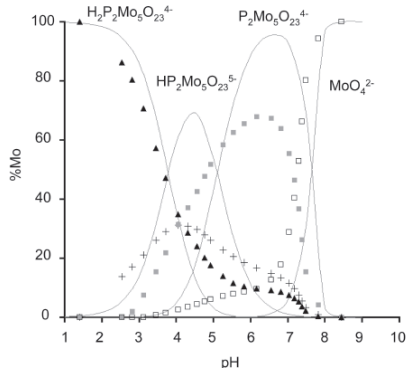
$$H_i^c = c_i^0 v_s H_i$$

$$\gamma_i^x = \frac{\gamma_i}{\gamma_i^{\infty}}$$

$$\gamma_i^m = \gamma_i^x x_s$$

$$\gamma_i^c = \frac{v}{v_s} \gamma_i^x$$

CHEMICAL EQUILIBRIUM

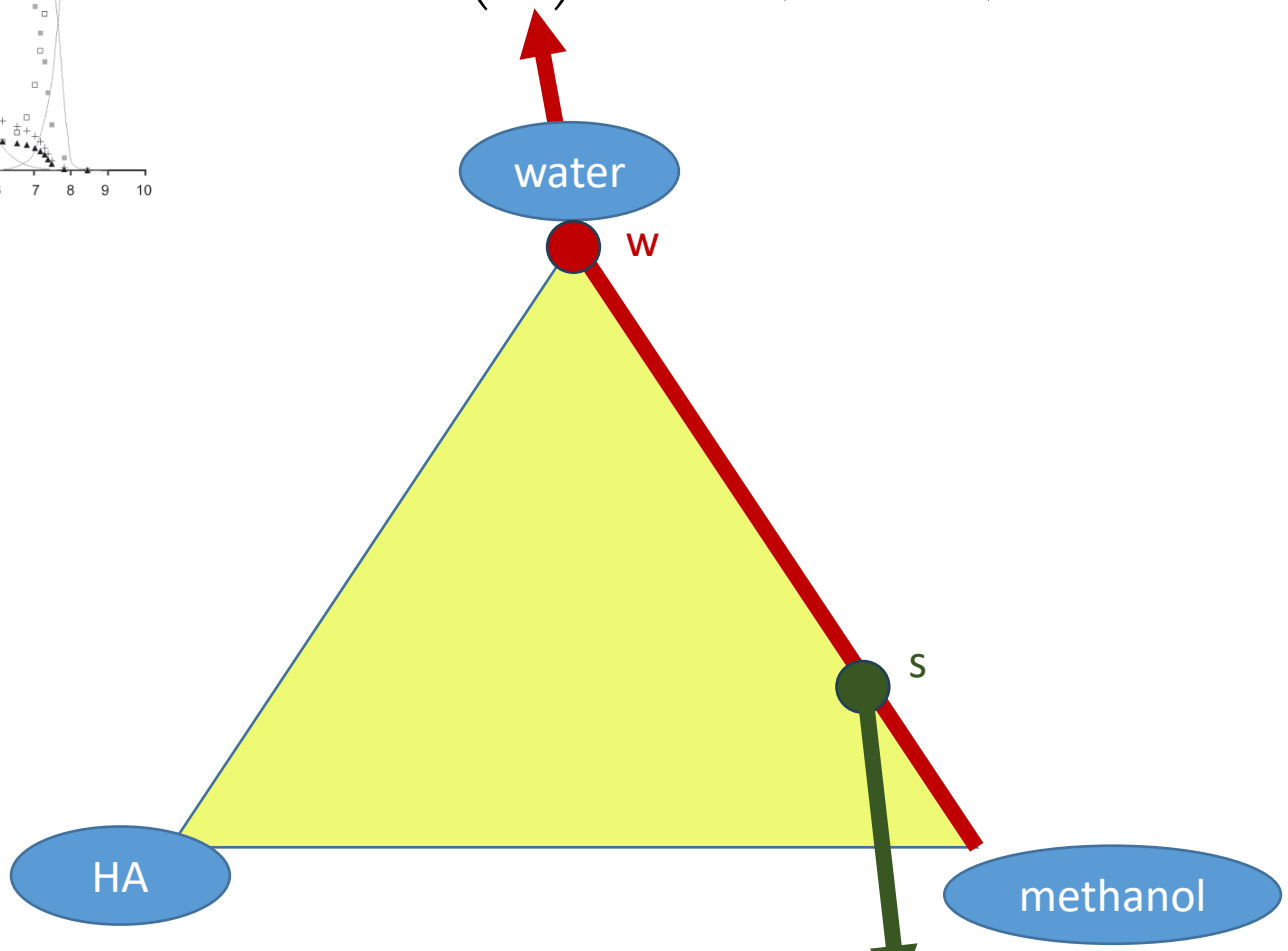


$$\sum_i \mu_i \nu_i = 0$$

$$\sum_i \nu_i \left(\mu_i^{ref} + RT \ln\left(\frac{f_i}{f_i^{ref}}\right)\right) = 0$$

$$\prod_i (a_i)^{\nu_i} = \prod \left(\frac{f_i}{f_i^{ref}}\right)^{\nu_i} = \exp\left(\frac{-\sum_i \nu_i \mu_i^{ref}}{RT}\right) = K$$

$$\prod_i (a_i^{w})^{\nu_i} = \prod \left(\frac{f_i}{f_i^{w}}\right)^{\nu_i} = \exp\left(\frac{-\sum_i \nu_i \mu_i^{w}}{RT}\right) = K^{w}$$

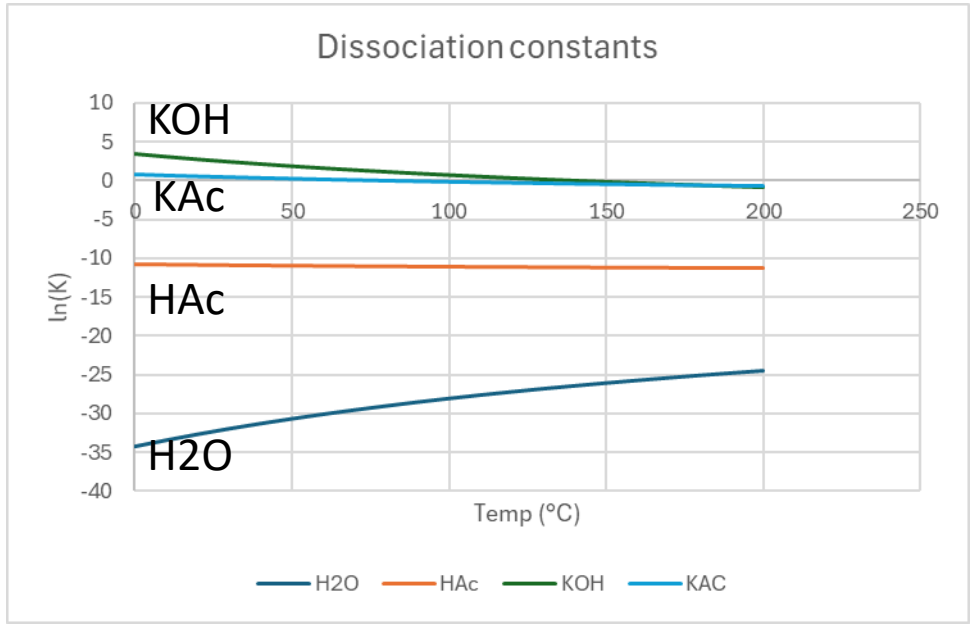


$$\ln\left(\frac{K^{s}}{K^{w}}\right) = \frac{-\sum_i \nu_i (\mu_i{}^{s} - \mu_i{}^{w})}{RT} = \ln \prod \left(\frac{f_i^{s}}{f_i^{w}}\right)^{\nu_i}$$

$$\prod_i (a_i^{s})^{\nu_i} = \prod \left(\frac{f_i}{f_i^{s}}\right)^{\nu_i} = \exp\left(\frac{-\sum_i \nu_i \mu_i^{s}}{RT}\right) = K^{s}$$

MODELING : CHEMICAL EQUILIBRIUM

	type	Equation considérée	Mu (298.15)	pK
H2O	solvent	2 H2O = H3O+ + OH-	-40050.0823	14.03
HAc	solvent_refmolality	HAc + H2O = H3O+ + Ac-	-27083.8843	4.75
Methanol	solvent			
KOH	solute_refmolality	KOH = K+ + OH-	6472.7881	-1.13
KAc	solute_refmolality	KAc = K+ + Ac-	1303.94124	-0.23
H3O+	ion			
K+	ion			
OH-	ion			
Ac-	ion			

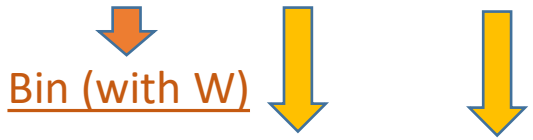


$$pK = -\log\left(\exp\left(-\frac{\Delta g_{react}}{RT}\right)\right) = -\log\left(\exp\left(\frac{\mu_i}{RT}\right)\right)$$

ACTIVITY COEFFICIENT MODEL : ENRTL

1. Take parameters from Aspen
2. Revisit some parameters to allow simultaneous Psat and MIAC
3. Interactions between ions and cosolvents (MeOH et HAC) must be regressed on ternary data (partial pressures)
4. Other parameters are either default or nul

	W	MeOH	HAc	KAc	KOH
MeOH	NISTV100				
HAc	NISTV100	APV100			
KAc	NISTV100	NISTV100	NISTV100		
KOH	Fit Bin MIAC	Fit Bin + Ter	0	0	
K+/OH-	Fit Bin MIAC	Fit Bin + Ter	0	0	0
H3O+/OH-	ENRTL-RK	Defaut	0	0	0
K+/Ac-	Fit Bin MIAC	Fit Bin + Ter	Fit Bin + Ter	0	0
H3O+/Ac-	Defaut	Fit pKa	0	0	0



Bin (with M/A) + Ter

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ELECTRIC CONDUCTIVITY MEASUREMENTS

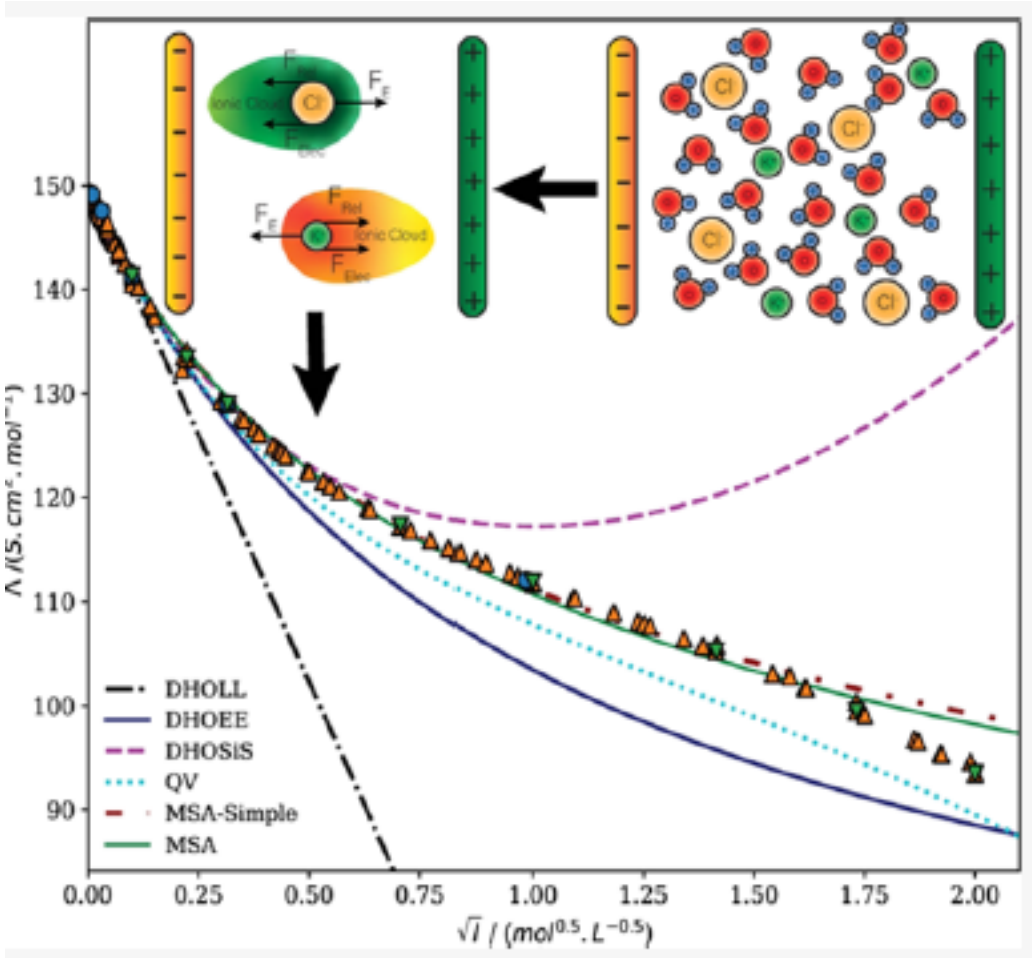
Forces électrophorèse + relaxation => modèle théorique

$$AB = A^- + B^+$$

$$\Lambda = \Lambda^\infty \alpha(c, K) h(c, \sigma, T, \varepsilon_r, \rho)$$

$$\alpha = \frac{n_{A-}}{n^0} = \frac{n_{B+}}{n^0} \qquad \text{avec} \qquad K = \frac{c\,\alpha^2}{1-\alpha}\gamma_\pm^2(c)$$

- A model is required (not a direct measurement)
- One salt at a time
- Cover a large concentration range (min 4 points)



Naseri et al. (2022) Ind. Eng Chem. Res. 61, 3168-3185

CONFRONT MODEL AND DATA

$$HAc + H_2O \rightleftharpoons H_3O^+ + Ac^-$$

$$\ln\left(\frac{K^s}{K^w}\right) = \frac{-\sum_i \nu_i(\mu_i{}^s - \mu_i{}^w)}{RT} = \ln\prod\left(\frac{f_i^s}{f_i^w}\right)^{\nu_i}$$

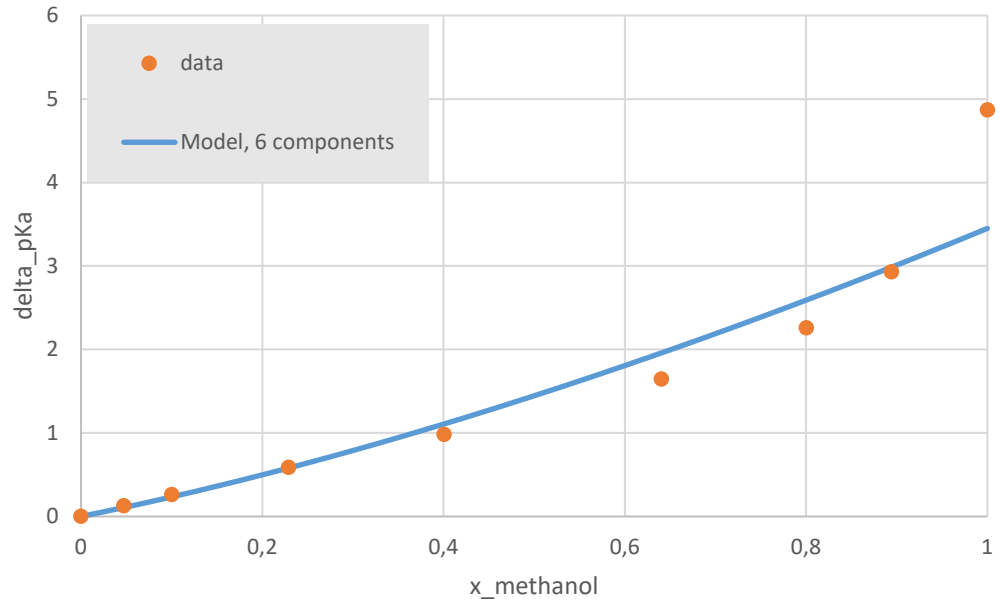
Feb., 1956 IONIZATION CONSTANT OF ACETIC ACID IN WATER–METHANOL 151

THE IONIZATION CONSTANT OF ACETIC ACID IN WATER–METHANOL MIXTURES AT 25° FROM CONDUCTANCE MEASUREMENTS

BY THEODORE SHEDLOVSKY AND ROBERT L. KAY

Contribution from the Laboratories of the Rockefeller Institute for Medical Research, New York, N. Y.

Received August 17, 1955



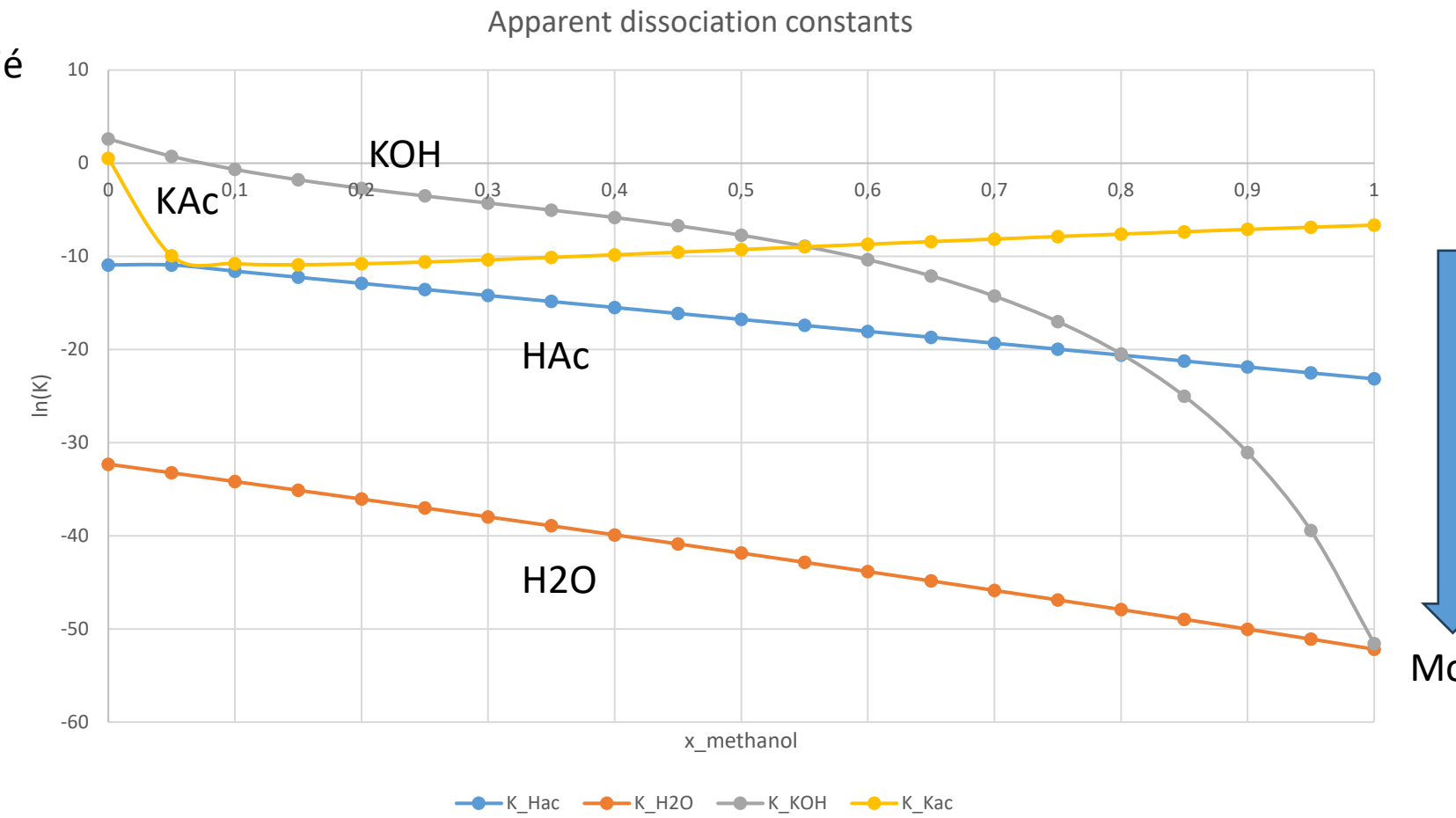
Ions, HAc: $$\left(\frac{f_i^s}{f_i^w}\right) = \left(\frac{v_s}{v_w}\frac{\gamma_i^{s,\infty}}{\gamma_i^{w,\infty}}\right)$$

H2O (solvant): $$\left(\frac{f_i^s}{f_i^w}\right) = \left(\frac{\gamma_i^{s,\infty}}{\gamma_i^w = 1}\right)$$

$$pK_a^s - pK_a = log_{10}\left(\frac{\gamma_{Ac^-}^{s,\infty}\gamma_{H3O^+}^{s,\infty}}{\gamma_{HAc}^{s,\infty}} \Big/ \frac{\gamma_{HAc}^{w,\infty}\gamma_{H2O}^{s,\infty}}{v_w}\right)$$

DISSOCIATION CONSTANTS VS SOLVENT COMPOSITION (ACCORDING TO ENRTL)

Plus dissocié



Moins dissocié

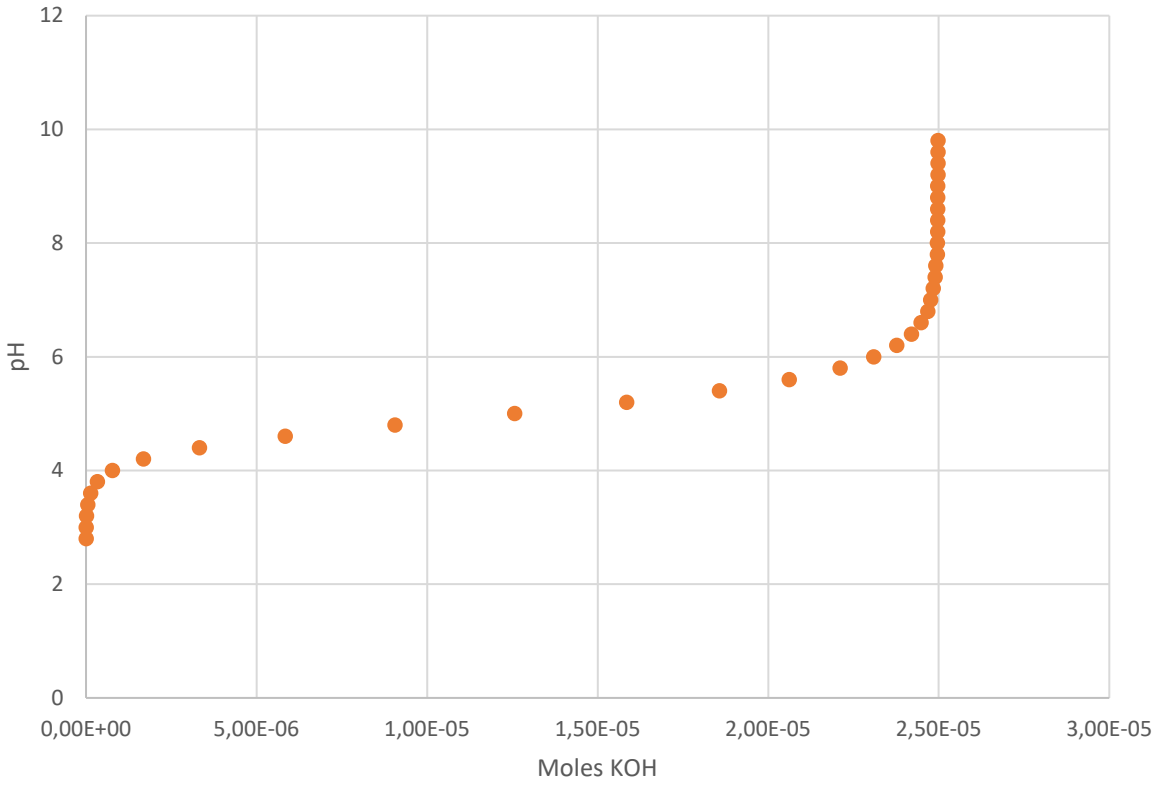
TITRATION

0.2M HAc

$$HAc + H_2O \rightleftharpoons H_3O^+ + Ac^-$$

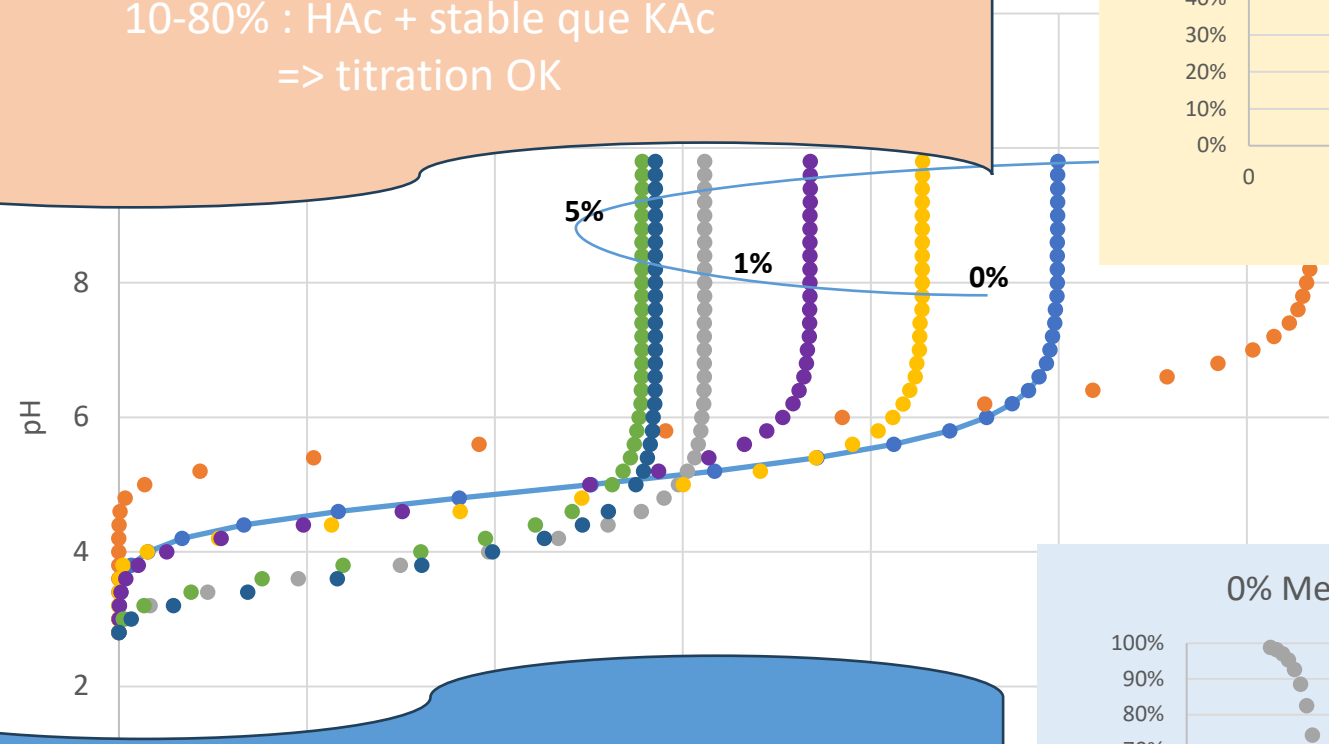
Titration de HAC par KOH

- Point d'équivalence = pKa
- Hypothèse: l'ajout de la base (« forte ») n'impacte pas les coefficients activités (faibles dilution)

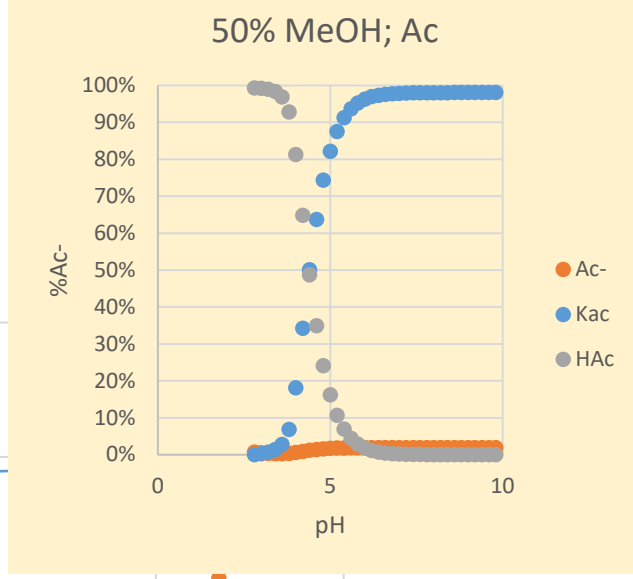


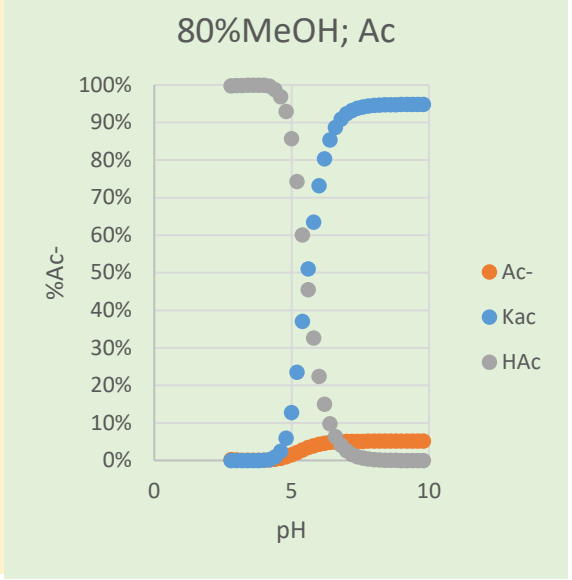
TITRATION EN SOLVANT MIXTE

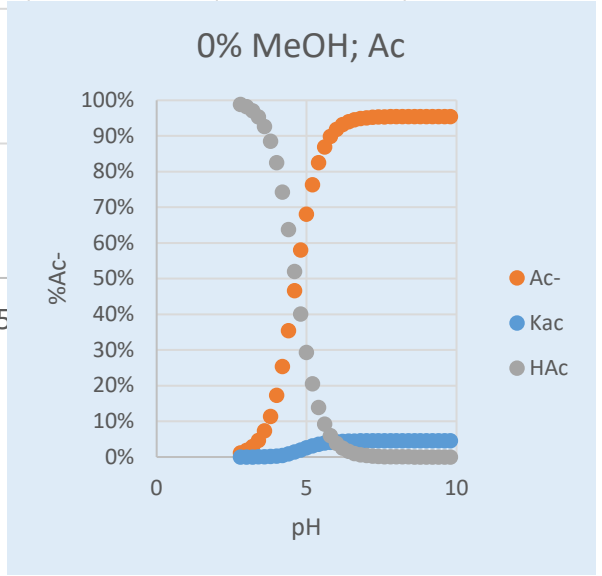
10-80% : HAc + stable que KAc
=> titration OK

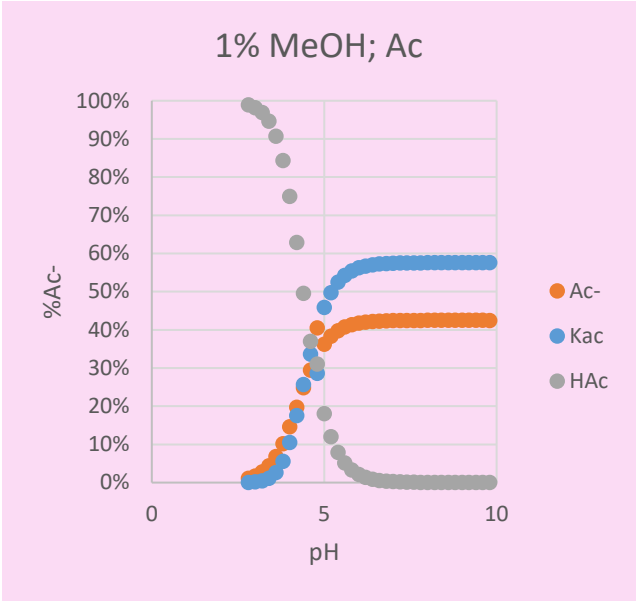


1-5% : KAc et HAc même stabilité
KOH + HAc -> KAc + H+ + OH-
=> pH monte trop vite







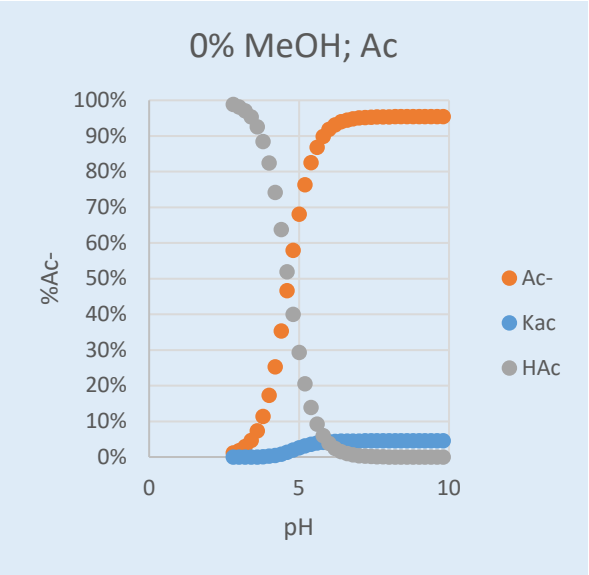


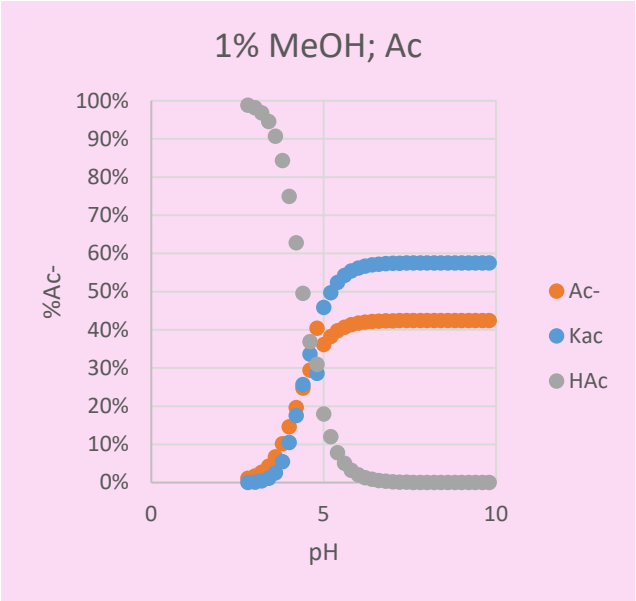
CONCLUSION

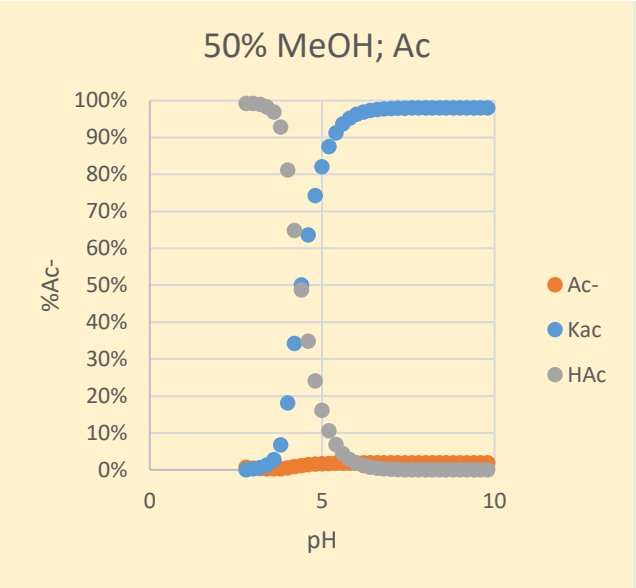
- Passing from one reference state to another is feasible but requires attention
  - Molality => needs to distinguish solvents and solutes
  - Molarity (concentration) => implies knowing the molar volume of the system.

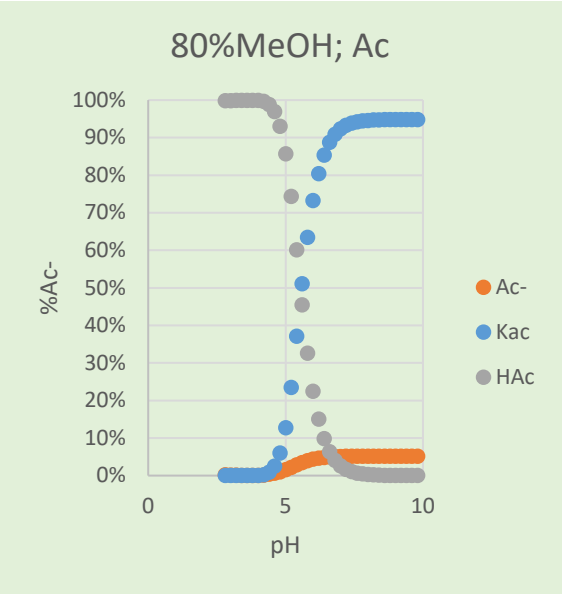
- eNRTL activity model allows computing activity coefficients, but
  - Many parameteres and few data
  - Allows describing the change of the equilibrium constant with solvent composition
  - Parameterisation needs to be revisited (KAc behaviour is unphysical); lack of data!

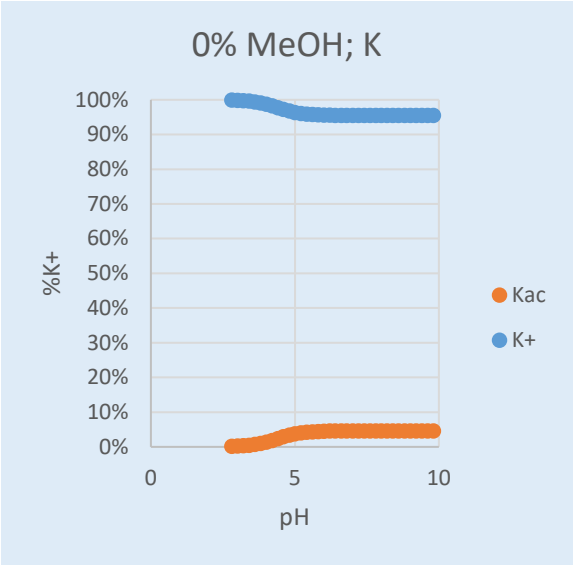
- La conductimetry
- Interpretation of titration in mixed solvents requires attention

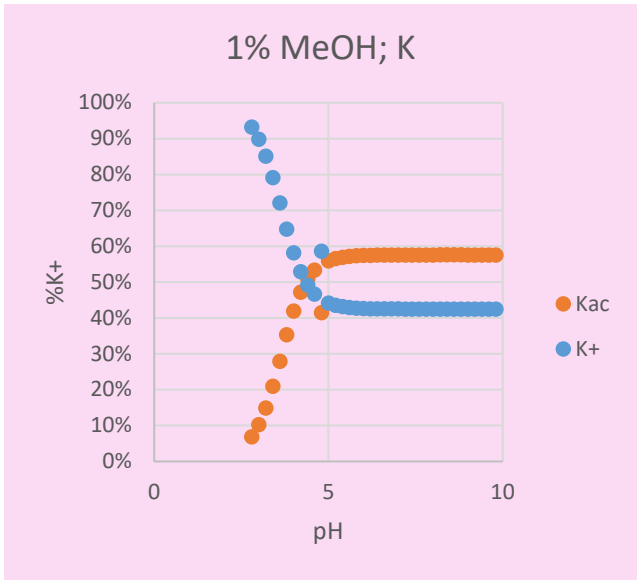

0% MeOH; Ac
%Ac-
pH
Ac-
Kac
HAc

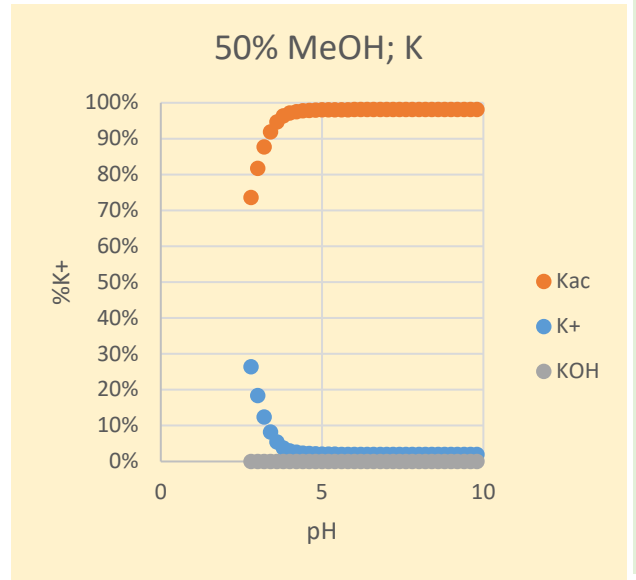

1% MeOH; Ac
%Ac-
pH
Ac-
Kac
HAc

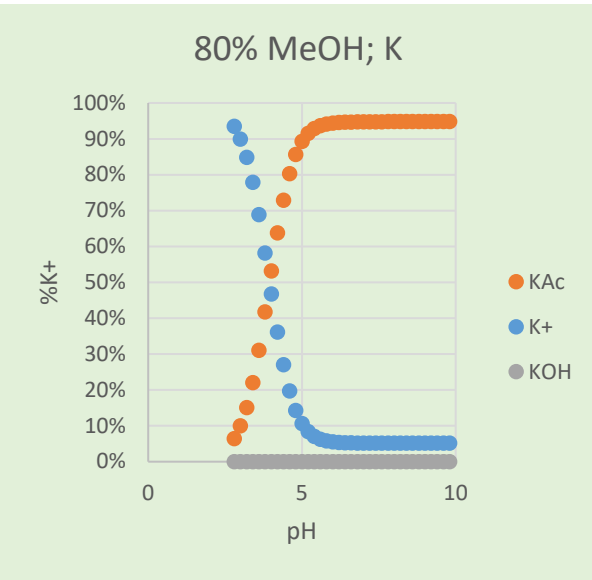

50% MeOH; Ac
%Ac-
pH
Ac-
Kac
HAc


80%MeOH; Ac
%Ac-
pH
Ac-
Kac
HAc


0% MeOH; K
%K+
pH
Kac
K+


1% MeOH; K
%K+
pH
Kac
K+


50% MeOH; K
%K+
pH
Kac
K+
KOH


80% MeOH; K
%K+
pH
KAc
K+
KOH

PH EN SOLVANT MIXTE

$$2H_2O \rightleftharpoons H_3O^+ + OH^-$$

$$pH = -log(a_{H^+}) = -log\left(a_{H_3O^+}\right) + log\left(a_{H_2O}\right)$$

$$2H_2O \rightleftharpoons H_3O^+ + OH^-$$

$$pH = log(K_S) - log(a_{SH^+}) + log(a_S)$$

J.J. Kosinski, P. Wang, R.D. Springer, A. Anderko, Fluid Phase Equilib. 256 (2007) 34–41.