Accounting for cross-association in nonself-associating species using a physically consistent SAFT-VR Mie approach

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BACKGROUND

- Self-associating (SA) molecules have both electron pair donor and acceptor sites, and can form hydrogen bonds with themselves
- Molecules with only donor- or only acceptor sites, such as ethers, ketones, and esters, are nonself-associating (NSA), but can form hydrogen bonds with other molecules → cross-association
- Traditional SAFT parameterisation only treats SA molecules explicitly
- Need approach to obtain association parameters for NSA molecules

OBJECTIVE

To develop a general and physically consistent approach to account for cross-association in a predictive manner for a wide range of components

METHODOLOGY

STEP 1: Select thermodynamic model

- **SAFT-VR Mie-GV** [1] combines SAFT-VR Mie [2] with the dipolar term of Gross & Vrabec [3]
- SAFT-VR Mie-GV accurately describes properties of dipolar molecules, therefore serves as suitable foundation of this work
- A single electron pair donor site (**N scheme**) is assigned to the polar, NSA molecules that will allow them to cross-associate [4,5]

STEP 2: Select tool to determine association parameters

- **Discretised sensitivity analysis** [4,5] is used to determine suitable association parameters
- The SAFT-VR Mie-GV parameters are fixed, and the association parameters (ε^{AB} and r_c) are varied at discrete intervals
- Mixture VLE is calculated at each combination of (ε^{AB}, r_c)
- The deviations are projected onto the (ε^{AB}, r_c)-plane, resulting in contour plots (see Fig. 1(a))
- In this work an "alcohol-first" approach is followed: binary VLE of alcohol + ether/ketone/ester systems are used in the development

STEP 3: Analysing discretisation results

- (ε^{AB}, r_c)-pairs on the same contour give almost identical predictions
- Ketone/ether mixtures: minimum AAD locus (white line in Fig. 1(a)) is similarly located for all investigated systems → can use *global* parameter set for homologous group
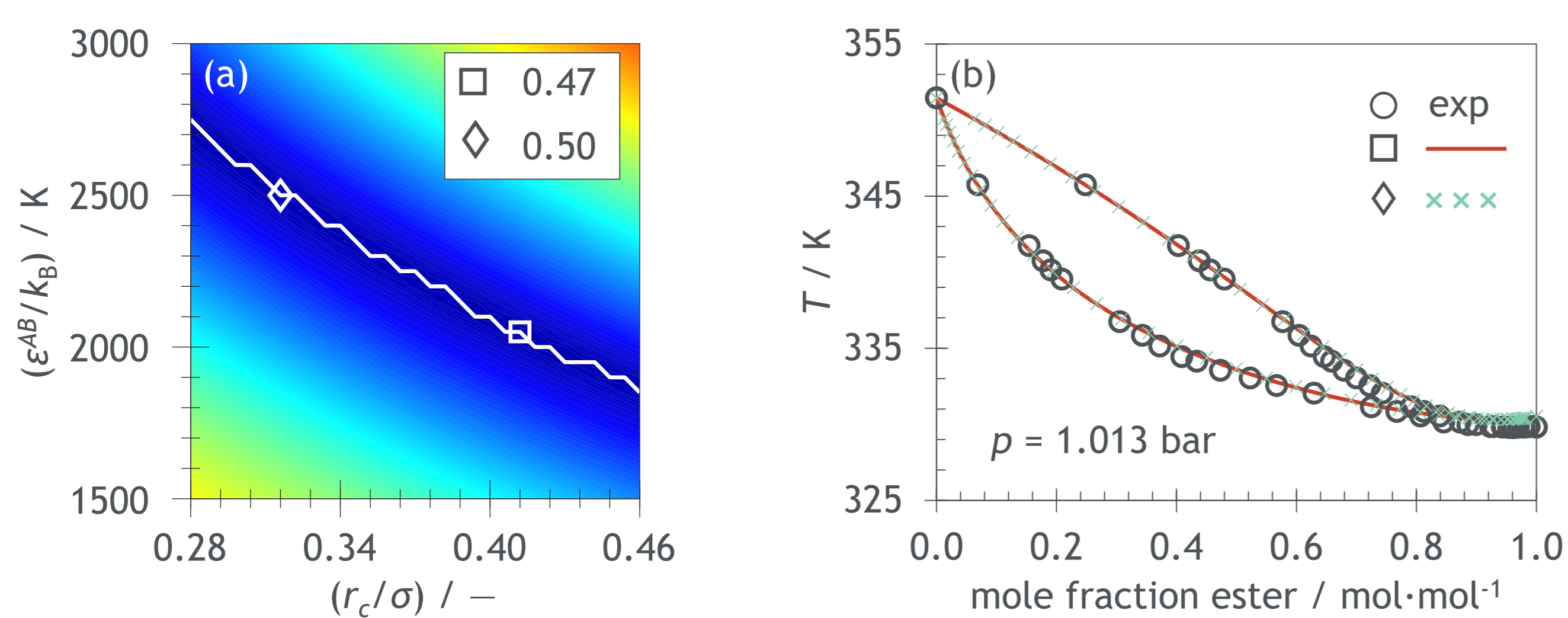- For ester mixtures, $\varepsilon^{AB} = f(r_c^{alcohol}, M_w^{ester})$

Fig. 1. Contour plot (a) and corresponding predictions (b) for methyl ethanoate + ethanol. Data from Ref. [6].

RESULTS

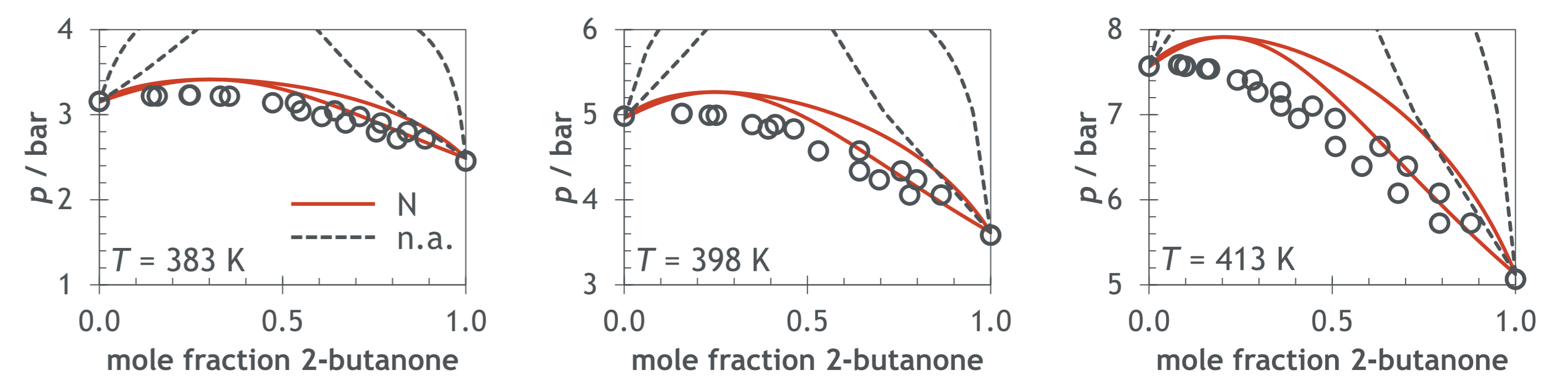### 1. Extended temperature/pressure ranges

Fig. 2. 2-Butanone + ethanol VLE at three temperatures. Data from Ref. [7].

- Results indicate temperature dependence of association parameters
- Highlights potential shortcoming of association term
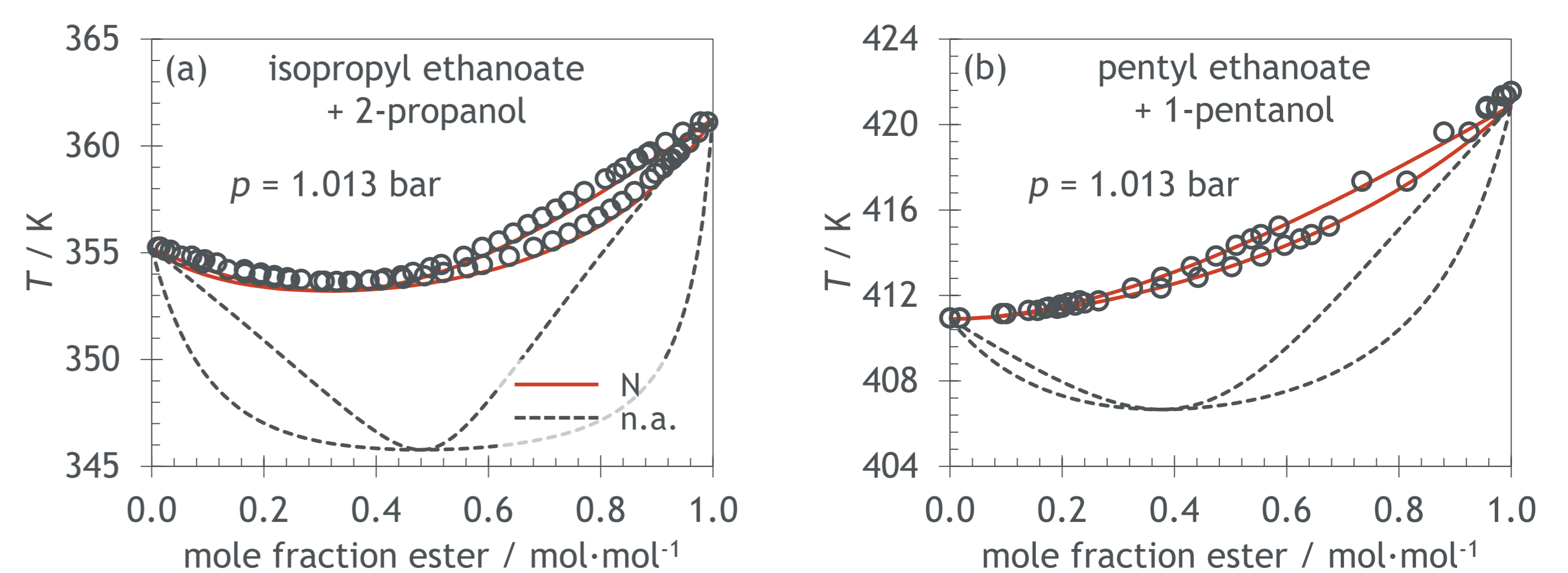
2. Molecules not included in method development

Fig. 3. (a) Isopropyl ethanoate + 2-propanol [8]; (b) Pentyl ethanoate + 1-pentanol [9].

- Application *beyond* components used in the method development support validity of approach and correlation used for esters
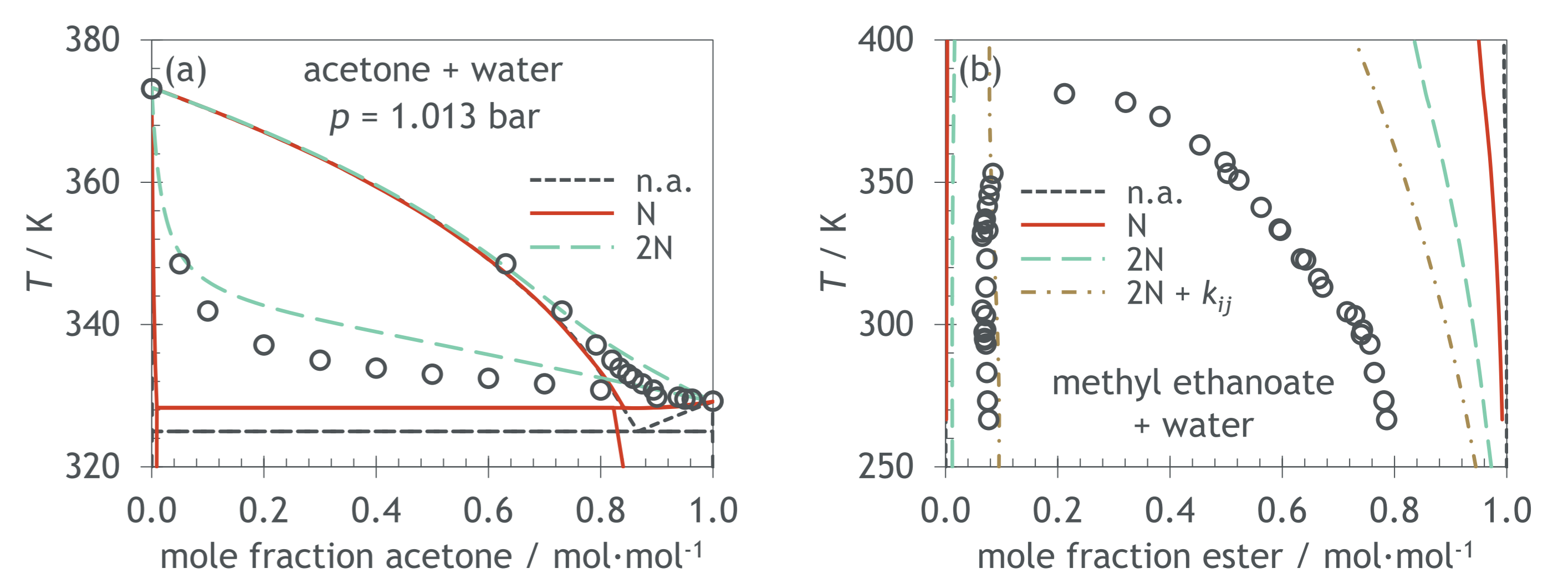
3. Aqueous mixtures

Fig. 4. (a) Acetone + water VLE [10]; (b) Methyl ethanoate + water LLE [11,12].

- Two negative sites (2N) required for qualitative VLE description
- LLE description lacking, even with inclusion of k_{ij}
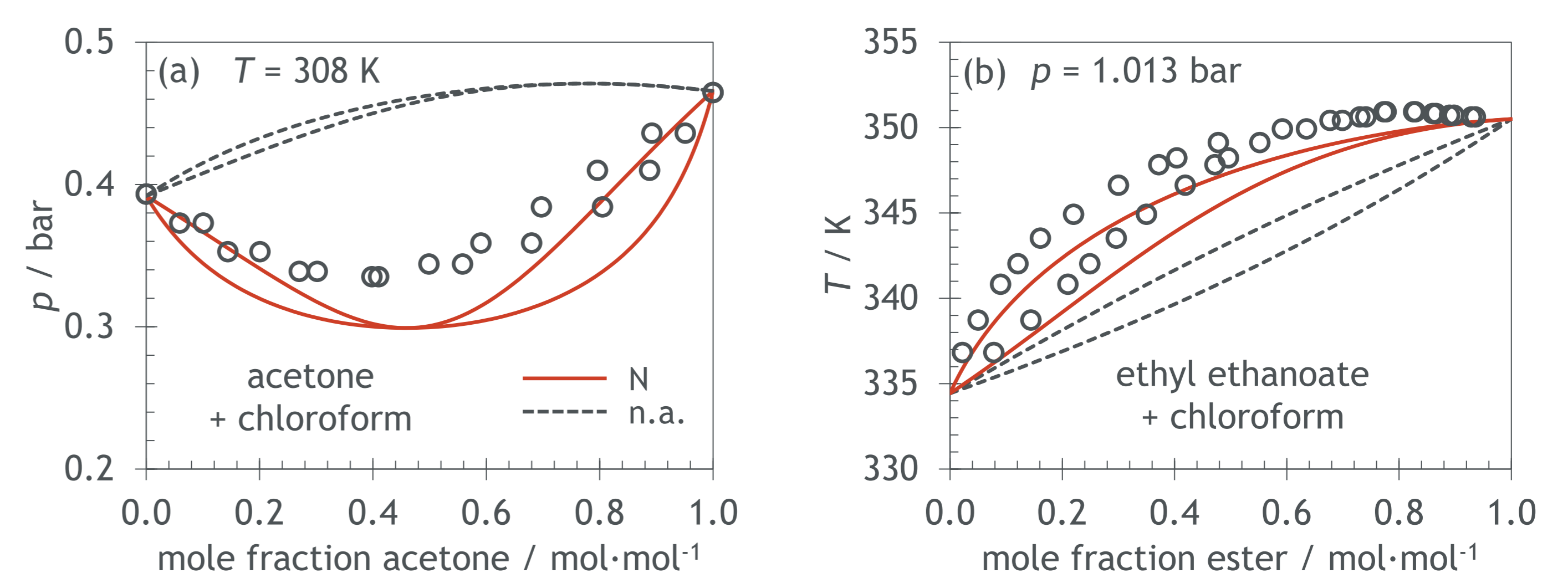
4. Mixtures with chloroform

Fig. 5. (a) Acetone + chloroform [13]; (b) Ethyl ethanoate + chloroform [14].

- Obtain correct qualitative description using P-scheme for chloroform

CONCLUSIONS

- Cross-association offers predictive approach for solvating systems
- Approach can extrapolate to components not involved in development
- Temperature dependence of association contribution evident
- Description of aqueous mixtures remains difficult

References: [1] *Fluid Phase Equilib.* **455** (2018): 24-42; [2] *J. Chem. Phys.* **139** (2013): 154504; [3] *AIChE J.* **52** (2006): 1194-1204; [4] *Fluid Phase Equilib.* **483** (2019): 1-13; [5] *Fluid Phase Equilib.* **569** (2023): 113775; [6] *J. Chem. Eng. Data* **35** (1990): 350-352; [7] *J. Chem. Eng. Data* **58** (2013): 1280-1287; [8] *Fluid Phase Equilib.* **287** (2010): 84-94; [9] *J. Chem. Eng. Data* **55** (2010): 2349-2354; [10] *J. Chem. Eng. Jpn.* **4** (1971): 311-318; [11] *International Critical Tables* **3** (1928): 387; [12] *Pol. J. Chem.* **54** (1980): 1101-1104; [13] *Fluid Phase Equilib.* **56** (1990): 285-301; [14] *J. Chem. Eng. Data* **7** (1962): 367-373.