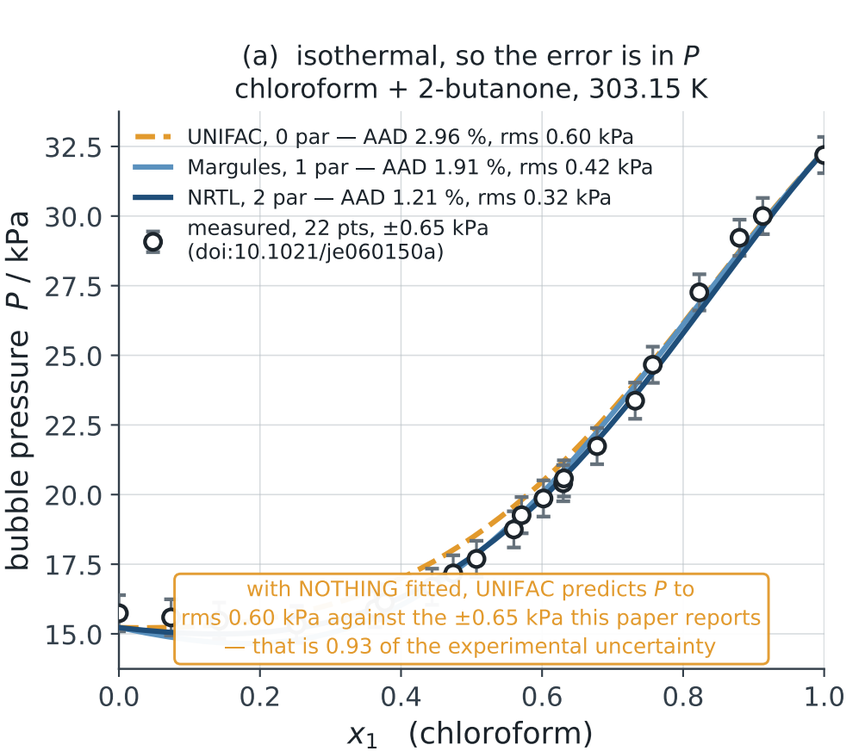
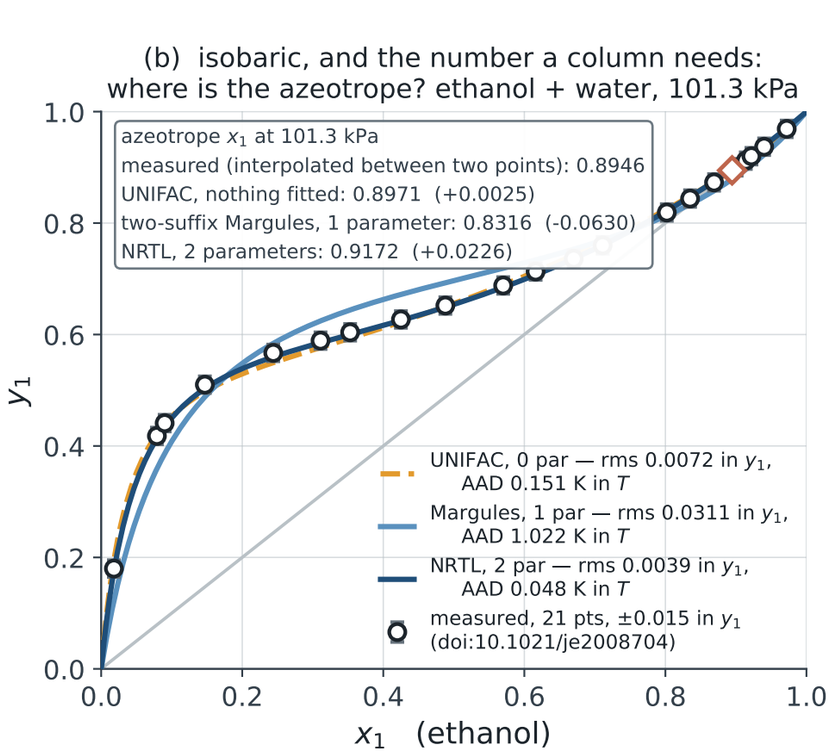
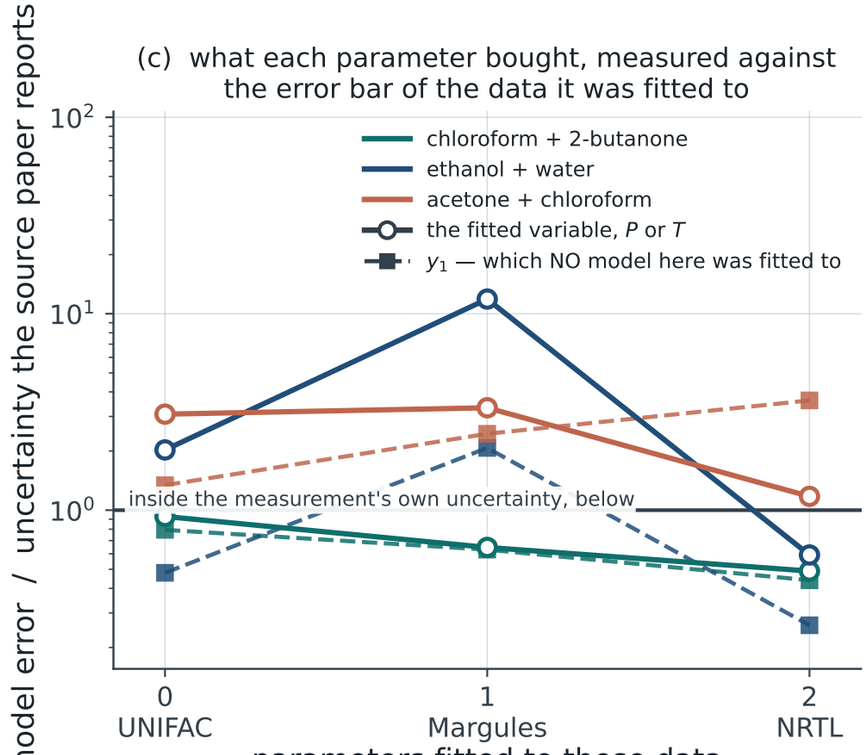
How wrong is UNIFAC, in numbers — and what one or two fitted parameters actually buy over it







Original VLE UNIFAC (Fredenslund, Jones & Prausnitz; group interaction table of Hansen et al.), the subset embedded in vlekit.unifac and checked parameter by parameter against the thermo package in the test suite. NOT modified UNIFAC (Dortmund): no temperature-dependent a_{mn}, no revised combinatorial. Nothing in the UNIFAC curves was fitted to anything. The two fits use Barker's method on the same points, so y_1 was withheld from every model on this figure. Ideal vapour, $\Phi_i = 1$, throughout; end points dropped because γ from data is 0/0 there.

THE NUMBERS. chloroform + 2-butanone: UNIFAC 2.96 % in P (rms 0.60 kPa, 0.93 of the reported ±0.65 kPa) against 1.21 % for two fitted parameters. ethanol + water: UNIFAC 0.151 K, one parameter 1.022 K, two parameters 0.048 K — the group prediction beats the one-parameter fit by 6.7x, and places the azeotrope at $x_1 = 0.8971$ against 0.8946 measured, while the fitted NRTL puts it at 0.9172. acetone + chloroform: the fitted NRTL is better in T (0.087 K vs 0.251 K) and WORSE in y_1 (0.0072 vs 0.0027), because T is what it was fitted to and y_1 is not.

WHEN IS IT GOOD ENOUGH. Read panel (c): a point below the heavy line is a model whose error is smaller than the uncertainty of the measurement judging it, and no further fitting can be shown to help with these data. UNIFAC is already there for chloroform + 2-butanone in P and for two of the three systems in y_1. It is not there for ethanol + water in T, where the two fitted parameters are worth having.

The honest summary is that a group prediction costs a factor of two to five against a good fit on these systems — and that the fit only wins on the variable it was fitted to.