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Prediction of the fluid phase behavior of the quaternary system ethylene oxide + air by molecular simulation

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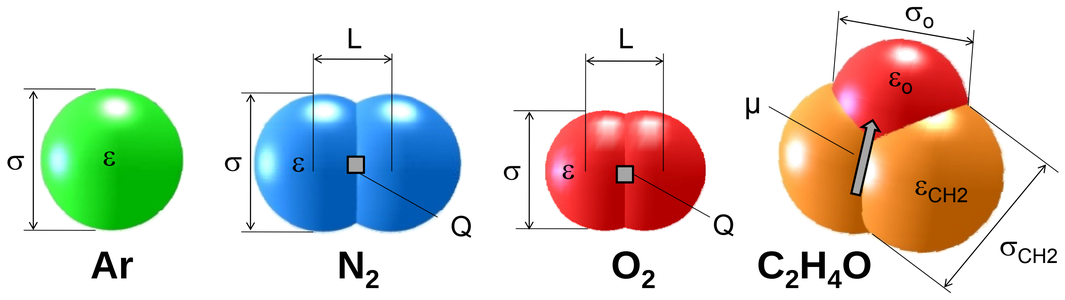
Motivation

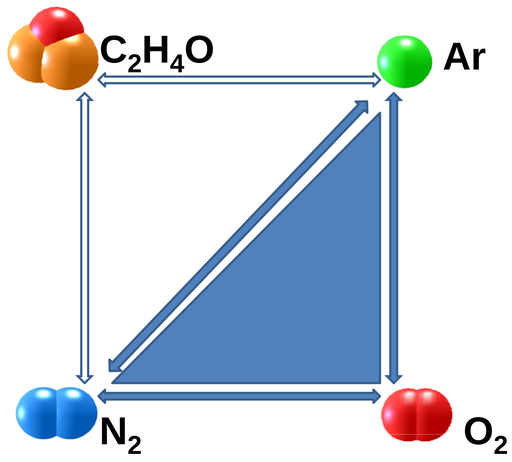
According to the vision of the Industrial Fluid Property Simulation Collective (IFPSC), “molecular simulation will become a breakthrough technology that is widely accepted in the chemical industry and applied (…) to meet the industry's evolving fluid property data needs” [1]. This is of particular interest for hazardous fluids which are economically vital, but often little explored experimentally. In 2007, The IFPSC has therefore challenged the development of new molecular models for such a substance, i.e. ethylene oxide (EO) [2]. The response of the community has shown that state-of-the-art molecular models are indeed capable of quantitatively covering a wide range of thermodynamic properties in a predictive manner. The present contribution is built upon the EO model developed in our group [3], which was the first entry of the challenge. It agrees almost throughout with the available reference data, taking the combined error bars into account.

In this work, the molecular model for EO [3] is combined with a ternary model for air [4]. Two of the three unlike interactions affecting EO (with nitrogen and with argon) were calibrated to experimental Henry’s law data, altering the dispersion energy by less than 4% from the Lorentz-Berthelot rule. On the basis of this model, the vapor-liquid equilibrium was predicted for the quaternary system and all its binary and ternary subsystems for a broad range of temperatures and pressures. Furthermore, compressed liquid densities are predicted as well. In order to facilitate the use of these data for subsequent work, cubic equations of state were parameterized to the whole set of simulation data. In total, this case study aims to present a straightforward route to include molecular simulation into industrial applications.

Molecular models



Available experimental data on phase coexistence

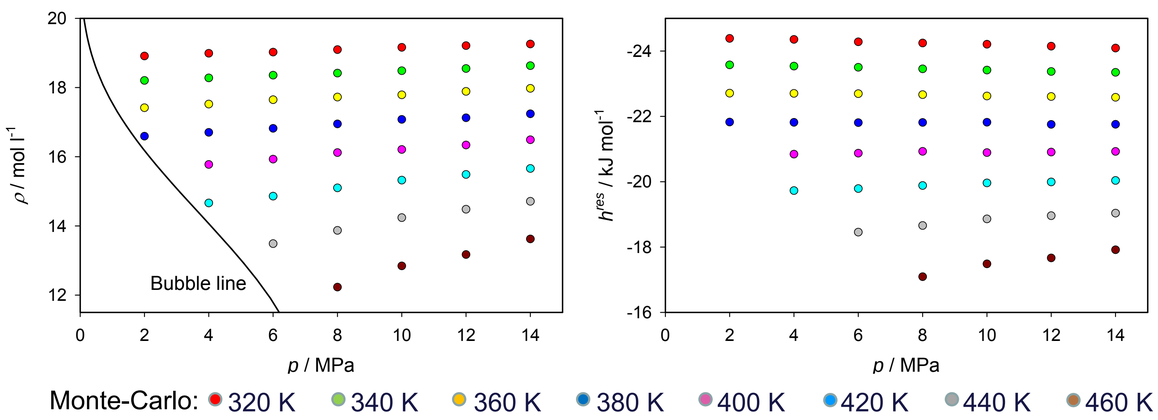


experimental binary VLE available

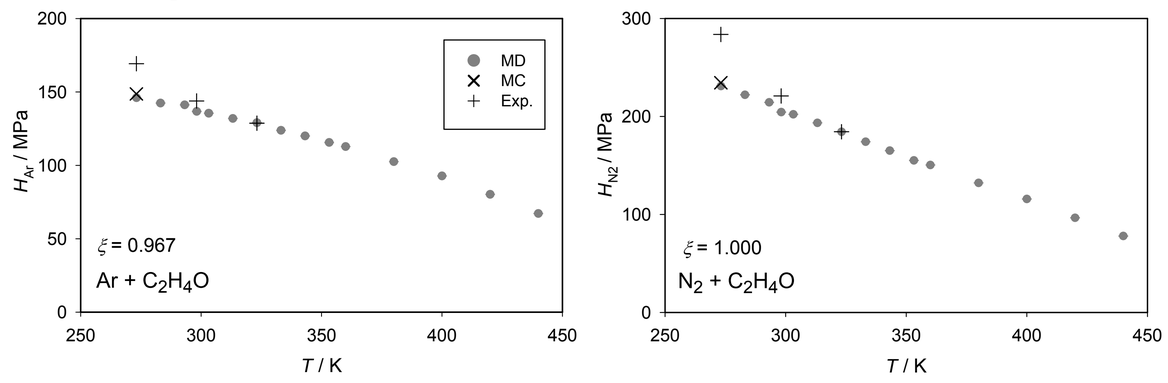
experimental Henry’s law constant available

experimental ternary VLE available

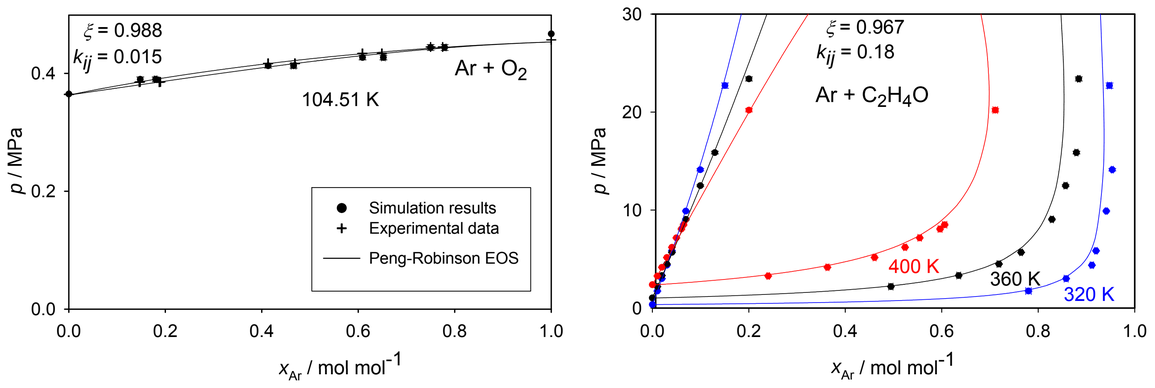
Pure ethylene oxide

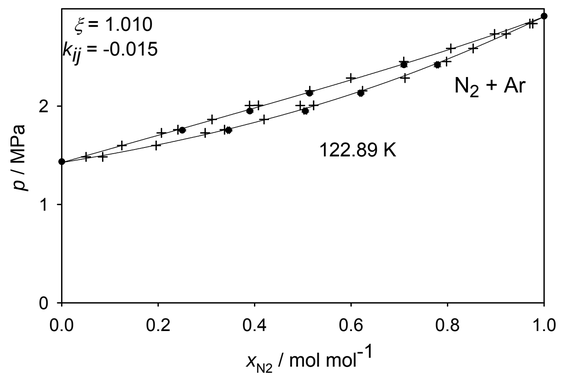


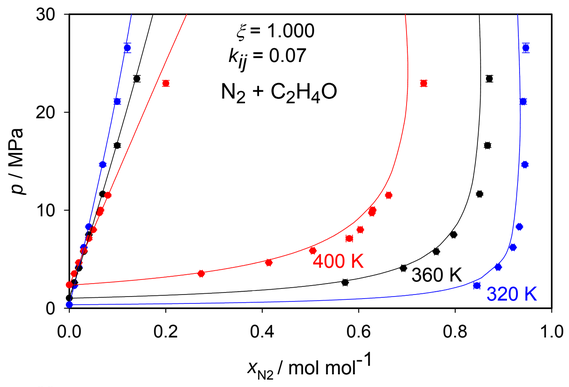
Henry’s law constant

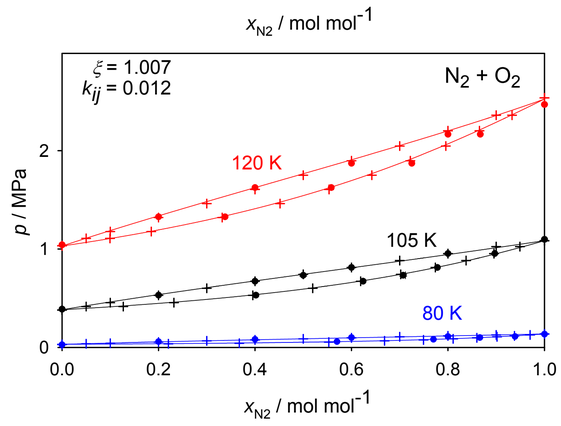


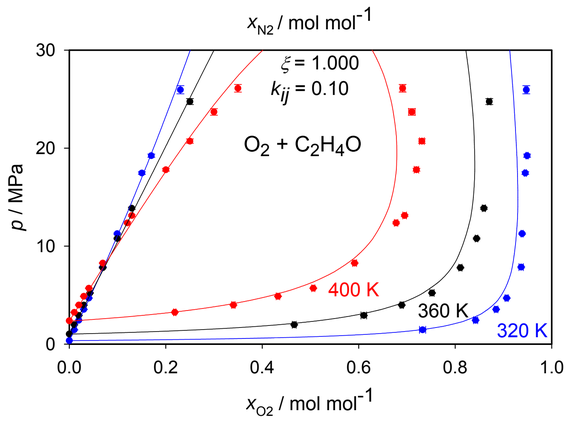
Binary VLE



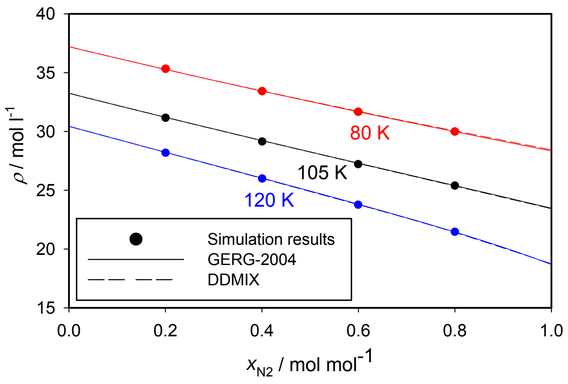


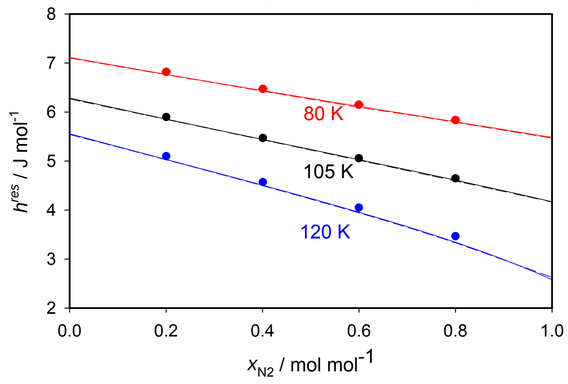




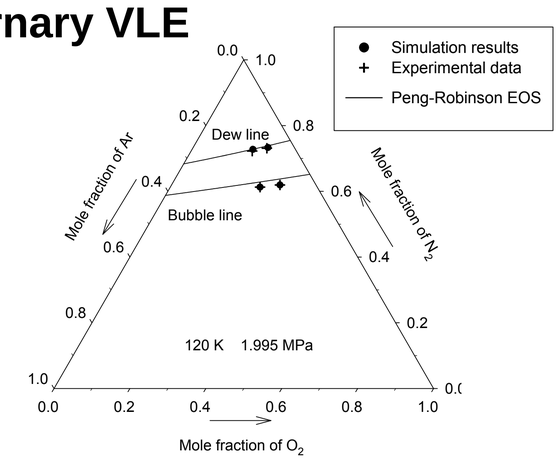


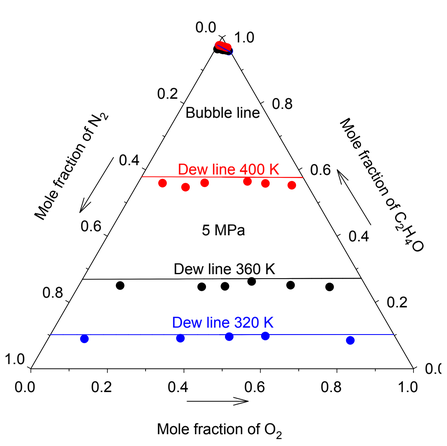
Binary bubble density and enthalpy of Nitrogen + Oxygen

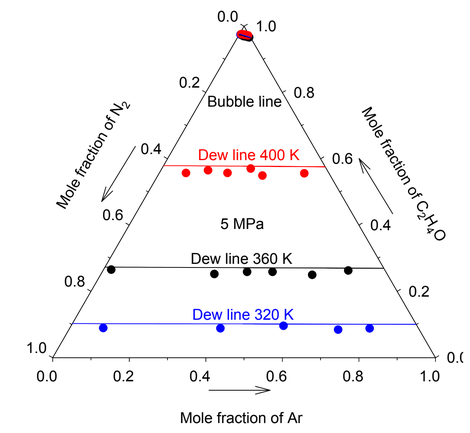


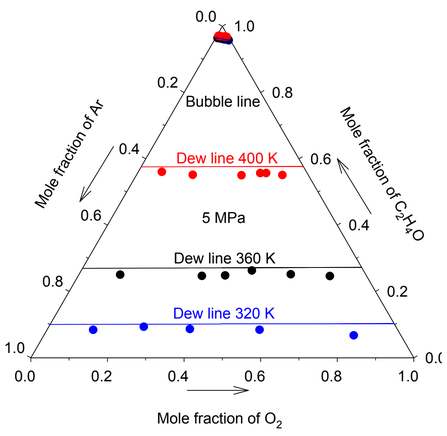


Ternary VLE









Quaternary VLE

	T K	x_{EO} mol/mol	x_{Ar} mol/mol	x_{N2} mol/mol	p MPa	y_{EO} mol/mol	y_{Ar} mol/mol	y_{N2} mol/mol	y_{O2} mol/mol	ρ' mol/l	ρ'' mol/l	Δh^v kJ/mol
Sim.	320	0.9694	0.0102	0.0102	4.83 (4)	0.100 (5)	0.280 (7)	0.396 (4)	0.224 (3)	18.94 (1)	1.87 (1)	22.93 (1)
EOS	320	0.9694	0.0102	0.0102	4.74	0.107	0.279	0.397	0.217	18.30	1.87	
Dev./%					-1.9	0.007	-0.001	0.001	-0.007	-3.4	-0.4	
Sim.	320	0.9388	0.0204	0.0204	9.45 (6)	0.066 (3)	0.291 (5)	0.408 (3)	0.235 (2)	19.08 (1)	3.67 (3)	21.74 (2)
EOS	320	0.9388	0.0204	0.0204	9.41	0.074	0.292	0.407	0.227	18.52	3.75	
Dev./%					-0.5	0.008	0.001	-0.001	-0.008	-2.9	2.1	
Sim.	320	0.9082	0.0306	0.0306	14.2 (1)	0.050 (3)	0.296 (5)	0.408 (3)	0.246 (3)	19.23 (2)	5.46 (4)	20.61 (2)
EOS	320	0.9082	0.0306	0.0306	14.4	0.067	0.297	0.404	0.232	18.76	5.76	
Dev./%					1.5	0.017	0.001	-0.004	-0.014	-2.5	5.4	
Sim.	360	0.9694	0.0102	0.0102	4.77 (2)	0.266 (3)	0.229 (5)	0.306 (3)	0.199 (2)	17.38 (1)	1.71 (1)	20.84 (2)
EOS	360	0.9694	0.0102	0.0102	4.64	0.288	0.225	0.300	0.187	16.68	1.69	
Dev./%					-2.7	0.022	-0.004	-0.006	-0.012	-4.0	-1.2	
Sim.	360	0.9388	0.0204	0.0204	8.55 (5)	0.175 (4)	0.263 (5)	0.335 (3)	0.226 (2)	17.47 (1)	3.02 (2)	19.87 (2)
EOS	360	0.9388	0.0204	0.0204	8.36	0.198	0.254	0.334	0.213	16.85	3.03	
Dev./%					-2.2	0.023	-0.009	-0.001	-0.013	-3.6	0.5	
Sim.	360	0.9082	0.0306	0.0306	12.18 (7)	0.139 (4)	0.273 (5)	0.350 (3)	0.238 (3)	17.52 (2)	4.25 (2)	18.87 (3)
EOS	360	0.9082	0.0306	0.0306	12.16	0.167	0.266	0.344	0.224	17.02	4.41	
Dev./%					-0.1	0.028	-0.007	-0.006	-0.014	-2.9	3.8	
Sim.	400	0.9694	0.0102	0.0102	5.25 (3)	0.538 (3)	0.136 (4)	0.189 (2)	0.137 (2)	15.47 (2)	1.88 (1)	17.64 (3)
EOS	400	0.9694	0.0102	0.0102	5.21	0.563	0.140	0.174	0.124	14.54	1.90	
Dev./%					-0.9	0.025	0.004	-0.015	-0.013	-6.0	1.1	
Sim.	400	0.9388	0.0204	0.0204	8.12 (5)	0.379 (4)	0.200 (6)	0.241 (3)	0.180 (2)	15.45 (2)	2.77 (2)	17.09 (5)
EOS	400	0.9388	0.0204	0.0204	8.06	0.427	0.183	0.226	0.163	14.63	2.89	
Dev./%					-0.7	0.048	-0.017	-0.015	-0.017	-5.3	4.1	
Sim.	400	0.9082	0.0306	0.0306	11.39 (7)	0.348 (3)	0.212 (4)	0.251 (2)	0.188 (2)	15.51 (3)	3.95 (2)	15.85 (4)
EOS	400	0.9082	0.0306	0.0306	10.91	0.366	0.204	0.248	0.182	14.72	3.87	
Dev./%					-4.2	0.018	-0.008	-0.003	-0.006	-5.1	-2.0	

Literature

[1] http://www.fluidproperties.org

[2] F. H. Case, J. Brennan, A. Chaka, K. D. Dobbs, D. G. Friend, P. A. Gordon, J. D. Moore, R. D. Mountain, J. D. Olson, R. B. Ross, M. Schiller, V. K. Shen, and E. A. Stahlberg, *Fluid Phase Equilib.* **274**: 2-9 (2008).

[3] B. Eckl, J. Vrabec, and H. Hasse, *Fluid Phase Equilib.* **274**: 16-26 (2008).

[4] J. Vrabec, G. K. Kedia, and H. Hasse, *Cryogenics* **45**: 253-258 (2005).