Electronic Supplementary Material (ESI) for Reaction Chemistry & Engineering.

Supplementary Materials

Enhanced hydroformylation of 1-Octene in *n*-butane expanded solvents with Co-based Complexes

Dupeng Liu,[1,2] Zhuanzhuan Xie,[2] William Kirk Snavely,[2] Raghunath Chaudhari,[1,2] and Bala Subramaniam[1,2]

[1]Department of Chemical & Petroleum Engineering, [2]Center for Environmentally Beneficial Catalysis, University of Kansas
Lawrence, KS 66047

Submitted to

Reaction Chemistry & Engineering

February 2018

[1] Correspondence concerning this article should be addressed to B. Subramaniam at bsubramaniam@ku.edu

S1. Volumetric expansion simulation.

The volumetric expansion data are predicted by Peng-Robinson equation of state (PR-EoS) with van der Waals' mixing rules embedded in Aspen Plus® software (see Equation S1). The critical parameters and acentric factor are taken from NIST Standard Reference Database.[1] Since experimental VLE data for 1-octene+*n*-butane binary system is not available in the literature, we use published VLE data on 1-octane+*n*-butane binary[2] to estimate the binary interaction parameters for $k_{1\text{-octene}/n\text{-butane}}$ as an approximation (Table S1). The simulation method used here has been previously demonstrated to satisfactorily predict the volumetric expansion as well as VLE data for CO_2- and propane-expanded solvent systems.[3,4,5]

$$P = \frac{RT}{(V-b)} - \frac{a(T)}{V(V+b)+b(V-b)} \qquad \text{(Equation S1)}$$

where the variables a and b are defined for pure components as follows:

$$a(T) = a_c\alpha$$

$$a_c = 0.45723553\frac{R^2{T_c}^2}{P_c}$$

$$\alpha = [1 + (0.37464 + 1.54226\omega - 0.26993\omega^2)(1 - \sqrt{T_r})]^2$$

$$b = 0.07779607R\frac{T_c}{P_c}$$

$$T_r = \frac{T}{T_c}$$

where T_c, P_c and ω represents the critical temperature, critical pressure and acentric factor, respectively

For multicomponens system, the van der Waals' mixing rules and binary interaction parameters are used for the mixtures as follows.

$$a = \sum_i \sum_j x_i x_j a_{ij}$$

$$b = \sum_i x_i b_i$$

where $a_{ij} = \sqrt{a_i a_j}(1 - k_{ij})$

and k_{ij} is the binary interaction parameter.

Table S1: Critical temperature T_c, critical pressure P_c, acentric factor ω and binary interaction parameters of the binary components

Substance	T_c (°C)	P_c (MPa)	ω	*kij*
n-butane	152.01	3.794	0.199	-0.088
1-Octene	293.43	2.675	0.395	

S2. Calculation of carbon and hydrogen balance deficit

The carbon balance deficit is estimated by calculating the moles of syngas consumed (from the observed pressure drop in the syngas reservoir) and comparing the value with the moles of hydrogen and carbon added in the products. Each mole of nonanol formed consumes 2 moles of hydrogen and 1 mole of carbon monoxide. Each mole of nonanal formed consumes 1 mole of hydrogen and 1 mole of carbon monoxide. Each mole of octane formed consumes 1 mole of hydrogen. A sample calculation for carbon and hydrogen balances at 180°C and 6.0 MPa (Table 3, Entry #6) is shown below.

The moles of syngas depletion were calculated from the pressure decrease (ΔP) in the reservoir and the reservoir temperature. The volume of the external reservoir (V_{res}) is 300 ml. The reservoir exists at room temperature (T_{res}). R is the gas constant.

$$N_{syngas} = \frac{\Delta P * V_{res}}{R * T_{res}} = \frac{1573\ kPa * 0.3\ L}{8.314\ \left(L{\cdot}kPa{\cdot}K^{-1}{\cdot}mol^{-1}\right) * 293.15K} = 193.6\ mmol$$

Table S2: Sample calculation of carbon and hydrogen balance deficit

Compound		Measured value	CO	H_2
Syngas depletion from reservoir / mmol		193.6	-	-
Measured nonanal formation/ mmol		0	0	0
Measured nonanol fomation/ mmol		58.2	58.2	116.4
Measured octane formation / mmol		11.2	0	11.2
H_2 and CO addition to the product / mmol	CO		58.2	
	H_2			127.6
	H_2 + CO	185.8		

carbon and hydrogen balance deficit:

$$n_{deficit=} \frac{193.6 - 185.8}{193.6} * 100\% = 3.99\ \%$$

T=180°C, P = 6.0 MPa, H_2/CO = 2:1; [Co] = 1000 ppm,

The carbon and hydrogen balance deficit for all the runs are summarized in Table S3.

System	H_2 and CO addition to the product, mmol	Syngas depletion from reservoir, mmol	$n_{deficit}$, %
Table 2 in Main Text			
Entry 1	184.6	189.4	2.55
Table 3 in Main Text			
Entry 1	73.6	75.1	1.95
Entry 2	182.7	187.8	2.76
Entry 3	184.9	191.0	3.20
Entry 4	127.3	129.0	1.38
Entry 5	165.3	167.7	1.43
Entry 6	185.9	193.6	3.99
Entry 7	118.0	122.4	3.57
Entry 8	183.8	189.8	3.19
Entry 9	147.5	153.6	3.92
Entry 10	182.8	187.7	2.62
Entry 11	190.2	194.9	2.44
Table 4 in Main Text			
Entry 1	186.7	192.4	2.98
Entry 2	189.5	196.1	3.35
Entry 3	191.6	195.5	1.95
Entry 4	136.7	139.9	2.28
Table 5 in Main Text			
Entry 1	205.0	207.2	1.08
Entry 2	206.8	211.3	2.13
Entry 3	203.3	208.1	2.30
Entry 4	202.8	209.3	3.10
Entry 5	173.1	176.2	1.75

Table S3. Carbon and hydrogen balance deficits for various runs

References

1. P.J. Linstrom and W.G. Mallard, Eds., NIST Chemistry WebBook, NIST Standard Reference Database Number 69, National Institute of Standards and Technology, Gaithersburg MD, 20899, doi:10.18434/T4D303

2. Kay W B, Genco J, Fichtner D A. Vapor-liquid equilibrium relations of binary systems propane-n-octane and butane-n-octane[J]. Journal of Chemical and Engineering Data, 1974, 19(3): 275-280.

3. Jin, H., & Subramaniam, B. (2004). Homogeneous catalytic hydroformylation of 1-octene in CO2-expanded solvent media. *Chemical engineering science*, *59*(22-23), 4887-4893.

4, Ye, K., Freund, H., Xie, Z., Subramaniam, B., & Sundmacher, K. (2012). Prediction of multicomponent phase behavior of CO2-expanded liquids using CEoS/GE models and comparison with experimental data. *The Journal of Supercritical Fluids*, *67*, 41-52.

5. Liu, D., Chaudhari, R.V., Subramaniam, B., 2017. Enhanced solubility of hydrogen and carbon monoxide in propane- and propylene-expanded liquids. AIChE Journal 107, 2666. doi:10.1002/aic.15988