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## **APPENDICES**

### **Appendix A Chemical Properties**

#### Nonionic surfactant (t-octylphenolpolyethoxylate, OP(EO)7)

#### Benefits

## 1

- Excellent wetting & detergency
- Excellent for use at low temperatures
- Readily biodegradable (OECD 301E)

# Applications

- Cleaners
- Paints & coatings
- Pulp & Paper
- Oilfield
- Textile
- Agrochemicals
- Metalworking fluids

## **Typical physical properties**

Name: Octylphenol Ethoxylate Cloud Point (at 1 wt% actives aqueous solution): 25°C HLB: 12.3 Moles EO: 7.5 Molar mass: 537 g/mole CMC (Critical micelle concentration: 25°C): 120 ppm Surface Tension (at 1% actives, 25°C):31 dynes/cm Foam Height (Ross-Miles foam height: at 0.1 wt% actives): 55/40 mm Pour Point: -14°C Form (at 25°C): Liquid pale yellow Viscosity at 25°C (77°F): 260 cP Density at 25°C (77°F): 1.052 g/mL Flas Pt, Closed Cup, ASTM D93: 254°C, 490°F

## Volatile organic compounds

## Table A1 Properties of VOCs

VOCs	BEN	TOL	ETB	DCE	TCE	PCE
CAS number	71-43-2	108-88-3	100-41-4	107-06-2	79-01-6	127-18-4
Molecular formula	$C_6H_6$	C <sub>7</sub> H <sub>8</sub>	$C_{8}H_{10}$	$C_2H_4Cl_2$	C <sub>2</sub> HCl <sub>3</sub>	$C_2Cl_4$
Molar mass (g/mol)	78.1	92.1	106.2	99.0	131.4	165.8
Density (g/cm <sup>3</sup> )	0.877	0.867	0.866	1.253	1.460	1.622
Melting point (°C)	5.5	-93	-95	-35	-73	-19
Boiling point (°C)	80.1	110.6 °C	136.0	83.5-84.0	87.0	121.1
Solubility in water (g/L)	0.800	0.470	0.015	0.870	0.100	0.015
Viscosity at 20°C (cP)	0.652	0.590	0.669	0.840	0.580	0.890

**Remarks**: CAS (Chemical Abstracts Service registry number) = a unique number for each chemical in the format xxx-xx-x., BEN = Benzene, TOL = Toluene, ETB = Ethylbenzene, DCE = 1,2 Dichloroethane, TEC = Trichloroethylene, and PCE = Tetrachloroethylene.

#### Appendix B Sample of Calculation

#### Batch experiment

 Table B1 Equilibrium data in water system: 50–200 ppm toluene and 30°C.

	[toluene] <sub>Equilibrium</sub> (ppm)		
[toluene] <sub>initial</sub> (ppm)	Liquid phase	Vapor phase	
52.0	25.5	892749.2	
86.7	35.2	1352041.9	
121.4	54.2	1972300.7	
164.7	74.6	2609153.0	

**Table B2** Equilibrium data in OP(EO)<sub>7</sub> system: 100–800 ppm toluene, 300 mM OP(EO)<sub>7</sub>, and 30°C.

	[toluene] <sub>Equilibrium</sub> (ppm)		
[toluene] <sub>initial</sub> (ppm)	Liquid phase	Vapor phase	
102.8	82.5	102655.7	
205.6	196.2	226339.8	
499.1	464.8	554153.7	
807.0	790.6	938694.3	
990.2	907.3	1109021.0	

Form Table B1, the correlation between GC peak area of toluene concentration in vapor phase and toluene concentration in liquid phase (unsolubilized toluene concentration) was observed as

$$C_u = (2.8 \times 10^{-5}) \cdot (GC \text{ peak area of toluene})$$
 with  $R^2 = 0.9919$  (B1)

Combining equation (B1) with the Henry's law constant of toluene in water at

 $30^{\circ}$ C (*H* =  $6.8 \times 10^{-5}$  tm/ppm) yields

$$p_t = (1.9 \times 10^{-9}) \cdot (GC \text{ peak area of toluene})$$
(B2)

This correlation is used for converting the GC peak area of toluene in vapor phase in Table B2 to toluene partial pressure as shown in Table B3.

**Table B3** Apparent Henry's law constant data of OP(EO)<sub>7</sub> system: 100–800 ppm toluene, 300 mM OP(EO)<sub>7</sub>, and 30°C.

	[toluene] <sub>Equilibrium</sub> (ppm)				
[toluene] <sub>initial</sub>	Liquid phase	Vapor phase	Toluene partial		
(ppm)			pressure (atm)		
102.8	82.5	102655.7	$1.94 \times 10^{-4}$		
205.6	196.2	226339.8	$2.29 \times 10^{-4}$		
499.1	464.8	554153.7	$1.05 \times 10^{-3}$		
807.0	790.6	938694.3	$1.78 \times 10^{-3}$		
990.2	907.3	1109021.0	$2.10 \times 10^{-3}$		

From Table B3, the toluene partial pressure and total toluene concentration in liquid phase is plotted together. The slope of this plot is considered to be the apparent Henry's law constant that is  $2.3 \times 10^{-6}$ .

From equation (B1) and (B2), the unsolubilized toluene concentration in 300 mM OP(EO)<sub>7</sub> can be calculated. Therefore, the solubilization constant ( $K_s$ ) is then calculated and tabulated in Table B4.

From 
$$p_t = H_{App} C_{tot} = H C_u$$
  
Therefore,  $C_u = (H/H_{App}) C_{total}$  (B3)

[toluene] <sub>Equilibrium</sub> (mM)	Unsolubilized [toluene] (mM)	Solubilized [toluene] (mM)	$K_s(\mathbf{M}^{-1})$
0.896	$3.28 \times 10^{-2}$	0.863	87.5
2.045	$7.48 \times 10^{-2}$	1.970	87.2
5.045	$1.84 \times 10^{-1}$	4.860	86.4
7.943	$2.90 \times 10^{-1}$	7.653	85.6
10.155	$3.71 \times 10^{-1}$	9.783	85.1

**Table B4**Solubilized and unsolubilized toluene concentration in liquid phase atequilibrium: 100–800 ppm toluene, 300 mM OP(EO)7, and 30°C.

From Table B4, the solubilization constant of toluene in 300 mM OP(EO)<sub>7</sub> at  $30^{\circ}$ C is considered to be 87 M<sup>-1</sup>.

## Continuous experiment

Condition: 300 ppm toluene feed, 300 mM OP(EO)<sub>7</sub> feed, 1.1 mL/min feed flow rate, 38 Torr column pressure, 5-hole distributor, and 30°C.

Experimental data

Initial toluene concentration (ppm):	304.7
Final toluene concentration (ppm):	32.4
Toluene removal (%):	89.4
Initial Surfactant concentration (mM):	300.1
Final Surfactant concentration (mM):	303.6
Vapor pressure of water at 30°C (atm):	0.0419
<i>H</i> at 30°C (atm/mole fraction):	321

From 
$$Z = \frac{L_0}{K_x a} \ln(\frac{x_{i,t} - x_t^*}{x_{f,t} - x_t^*})$$
(B4)

- 1. Height of packing, Zpacking height = 25.4 cm.
- 2. The molar liquid flux,  $L_0$

#### Volume flux or superficial velocity

	the volume flow rate of feed solution	=	1.1	cm <sup>3</sup> /min
	the cross section area of column	=	30.7	$cm^2$
so,	the volume flux of feed solution	=	$3.58 \times 10^{-2}$	$cm^3/cm^2 min$
	from final toluene concentration	=	32.4	ppm (mg/l)
	and final surfactant concentration	=	303.6	mM

Volume of A = concentration of A / Density of A

So,	Volume of toluene per 1 litre	=	$3.74 \times 10^{-2}$	cm <sup>3</sup>
	Volume of surfactant per 1 litre	=	$1.68 \times 10^{2}$	$cm^3$
	Volume of water per 1 litre	=	$8.22 \times 10^2$	$cm^3$

Volume fraction of A = Volume of A / Total volume So, Volume fraction of toluene in feed solution =  $3.77 \times 10^{-5}$ Volume fraction of surfactant in feed solution =  $1.70 \times 10^{-1}$ Volume fraction of water in feed solution =  $8.30 \times 10^{-1}$ 

The volume flux of  $A = (Volume fraction of A) \cdot (the volume flux of feed solution)$ 

The volume flux of toluene in outlet stream	=	$1.35 \times 10^{-6}$	cm <sup>3</sup> /cm <sup>2</sup> .min
The volume flux of surfactant in outlet stream	=	6.09× 10 <sup>-3</sup>	cm <sup>3</sup> /cm <sup>2</sup> .min

The volume flux of water in outlet stream =  $2.97 \times 10^{-2}$  cm<sup>3</sup>/cm<sup>2</sup>.min

The molar flux of A = (The volume flux of A)·(Density of A)/(MW of A) The molar flux of toluene in outlet stream =  $1.27 \times 10^{-8}$  mol/cm<sup>2</sup>.min The molar flux of surfactant in outlet stream =  $1.20 \times 10^{-5}$  mol/cm<sup>2</sup>.min The molar flux of water in outlet stream =  $1.65 \times 10^{-3}$  mol/cm<sup>2</sup>.min

The molar liquid flux, 
$$L_0$$
  
=  $(1.27 \times 10^{-8} + 1.20 \times 10^{-5} + 1.65 \times 10^{-3}) = 1.66 \times 10^{-3}$  mol/cm<sup>2</sup>.min

3. Inlet mole fraction of toluene,  $x_{i,i}$ 

From inlet coacervate phase solution,						
Inlet surfactant conce	=	300.0	mM			
Inlet toluene concenti	ration	=	304.7	ppm		
mole of surfactant	=	3.00×	10 <sup>-1</sup>	М		
mole of toluene	=	3.31×	10-3	М		
mole of water	=	4.66×	10 <sup>1</sup>	М		

So,

mole fraction of toluene ( $x_{i,t}$ ) =  $7.05 \times 10^{-5}$ 

# 4. Outlet mole fraction of toluene, $x_{f,t}$

From outlet coacervate phase solution,

Outlet surfactant concentration	=	303.6	mM
Outlet toluene concentration	-	32.4	ppm

mole of surfactant		$3.03 \times 10^{-1}$	Μ
mole of toluene	=	$3.52 \times 10^{-4}$	Μ
mole of water	=	$4.66 \times 10^{1}$	М

So,

mole fraction of toluene  $(x_{f,t}) = 7.50 \times 10^{-6}$ 

5. The equilibrium mole fraction of toluene in the coacervate solution from flash calculation,  $x_t^*$ 

From flash equation,

$$\sum x_i^* - \sum y_i^* = 0,$$

Therefore,

$$\sum_{n=1}^{n=i} \frac{z_i (1 - K_i)}{1 + \frac{V}{F} (K_i - 1)} = 0$$
(B5)

5.1 Calculation of the vapor-liquid equilibrium partition coefficient  $(K_i)$ 

For toluene,

$$K_{t} = \frac{H}{P(1 + K_{s}C_{m})} = 236$$

where H = 321 atm/mole fraction, P = 38 Torr = 0.051 atm, K<sub>s</sub> = 87 M<sup>-1</sup>, C<sub>m</sub> = 300 mM.

For water,

$$K_w = \frac{y_w}{x_w^*} = 1$$

For surfactant,

$$K_{surf} = \frac{y_{surf}}{x_{surf}^{*}} = \frac{0}{x_{surf}^{*}}$$

5.2 Calculation of the equilibrium mole fraction of toluene  $(x_t^*)$ 

From inlet coacervate phase solution,

Inlet surfactant concentration	=	300.0	mM
Inlet toluene concentration	=	304.7	ppm

mole of surfactant in feed	=	3.00>	< 10 <sup>-1</sup>	М
mole of toluene in feed	=	3.31>	< 10 <sup>-3</sup>	М
mole of water in feed	=	4.66>	< 10 <sup>1</sup>	Μ
mole fraction of surfactant	in feed (z <sub>surf</sub> )	=	6.40×	10-3
mole fraction of toluene in	feed (z <sub>t</sub> )	=	7.05×	10-5
mole fraction of water in fe	$ed(z_w)$	=	9.94×	10-1

So,

Substituting  $K_i$  and  $z_i$  values for toluene, water, and surfactant in equation (B5), then the  $\frac{V}{F}$  was calculated by iteration. The obtained  $x_i^*$  as well as the calculated Z,  $L_0$ ,  $x_{i,i}$ , and  $x_{f,i}$  values were then substituted in equation (B4) for  $K_x a$  calculation. The calculated data from  $\frac{V}{F}$  variation are tabulated in Table B5. The satisfied  $\frac{V}{F}$  value is the minimum  $\frac{V}{F}$  value that can be used to calculate  $K_x a$ .

$\frac{V}{F}$	sum (x-y)	$x_{\iota}^{*}$	sum x	sum y	$K_x a ({ m mol/cm}^3{ m min})$
1	#DIV/0!	2.99×10 <sup>-7</sup>	#DIV/0!	#DIV/0!	1.49×10 <sup>-4</sup>
0.8	0.032	3.74×10 <sup>-7</sup>	1.026	0.994	1.50×10 <sup>-4</sup>
0.4	0.010	7.44×10 <sup>-7</sup>	1.004	0.994	1.53×10 <sup>-4</sup>
0.2	0.008	1.47×10 <sup>-6</sup>	1.002	0.994	$1.60 \times 10^{-4}$
0.1	0.006	2.88×10 <sup>-6</sup>	1.001	0.994	$1.76 \times 10^{-4}$
0.038	0.005	7.11×10 <sup>-6</sup>	1.000	0.995	3.35×10 <sup>-4</sup>
0.036	0.005	7.47×10 <sup>-6</sup>	1.000	0.995	5.02×10 <sup>-4</sup>
0.035	0.005	7.66×10 <sup>-6</sup>	1.000	0.995	#NUM!
0.006	0.000	2.93×10 <sup>-5</sup>	1.000	1.000	#NUM!
0	-0.010	7.05×10 <sup>-5</sup>	1.000	1.010	#NUM!

**Table B5** The calculated mole fraction of toluene in vapor and liquid phase and  $K_x a$  as a function of  $\frac{V}{F}$ .

From Table (B5), the satisfied  $\frac{V}{F} = 0.036$ ,  $x_i^* = 7.47 \times 10^{-6}$ , and

 $K_x a = 5.02 \times 10^{-4} \text{ mol/cm}^3 \text{min.}$ 

## Appendix C Experimental Results

## Batch experiments

 Table C1
 Viscosity of OP(EO)7 solution

Condition: 300 ppm toluene feed and 30°C.

[OP(EO)7] (mM)	Viscosity (cP)
300	118.0
450	159.3
550	187.7
630	205.7

# Table C2 Viscosity of OP(EO)7 solution

Condition: 300 ppm toluene feed and 630 mM OP(EO)7.

Temperature (°C)	Viscosity (cP)
30	205.7
40	88.5
45	61.1
50	42.6

[OP(EO) <sub>7</sub> ] (mM)	Henry's law constant, <i>H</i> (atm/ppm)	Apparent Henry's law constant, H <sub>App</sub> (atm/ppm)	Solubilization constant, $K_s$ (M <sup>-1</sup> )
300	$6.8 \times 10^{-5}$	$2.3 \times 10^{-6}$	87
400	$6.8 \times 10^{-5}$	$1.9 \times 10^{-6}$	90
500	$6.8 \times 10^{-5}$	$1.3 \times 10^{-6}$	91
630	$6.8 \times 10^{-5}$	$1.2 \times 10^{-6}$	93

**Table C3** Henry's law, apparent Henry's law, and solubilization constant. Condition:100–1000 ppm toluene and 30°C.

**Table C4** Henry's law, apparent Henry's law, and solubilization constant. Condition:250–2000 ppm toluene and 630 mM OP(EO)7.

Temperature (°C)	Henry's law constant, <i>H</i> (atm/ppm)	Apparent Henry's law constant, H <sub>App</sub> (atm/ppm)	Solubilization constant, $K_s$ (M <sup>-1</sup> )
30	$6.8 \times 10^{-5}$	$1.2 \times 10^{-6}$	91
40	$1.2 \times 10^{-4}$	$1.8 \times 10^{-6}$	99
45	$1.3 \times 10^{-4}$	$2.0 \times 10^{-6}$	102
50	$1.6 \times 10^{-4}$	$2.5 \times 10^{-6}$	106

**Table C5** The structure, Henry's law constant, apparent Henry's law constant, and solubilization constant of all VOCs in batch experiments. Condition: 20–800 ppm VOC in water, 100–2 000 ppm VOC in 450 mM OP(EO)<sub>7</sub>, and 40°C.

VOCs	Structure of the VOCs	Henry's law constant, <i>H</i> (atm/ppm)	Apparent Henry's law constant, $H_{App}$ (atm/ppm)	Solubilization constant, K <sub>s</sub> (M <sup>-1</sup> )
BEN		1.1×10 <sup>-4b</sup>	6.8×10 <sup>-6</sup>	34
TOL	CH3	1.2×10 <sup>-4a</sup>	2.2×10 <sup>-6</sup>	108
ETB	C <sub>2</sub> H <sub>5</sub>	1.5×10 <sup>-4b</sup>	1.2×10 <sup>-6</sup>	294
DCE	CI H H-C-C-H H CI	2.0×10 <sup>-5c</sup>	3.5×10 <sup>-6</sup>	10
TCE	CI CI C=C - I CI H	1.3×10 <sup>-4a</sup>	4.9×10 <sup>-6</sup>	59
PCE	$\begin{array}{ccc} CI & CI \\ I & I \\ C = C \\ I & I \\ CI & CI \end{array}$	2.0×10 <sup>-4a</sup>	3.8×10 <sup>-6</sup>	113

#### Continuous operation

**Table C6** Effect of feed flow rate on vacuum stripping of tolueneCondition: 300 ppm toluene feed, 300 mM OP(EO)7 feed, 54 Torr column pressure,1-hole distributor, and 30°C.

Feed flow rate (mL/min)	Toluene removal (%)	The overall liquid phase volumetric mass transfer coefficient, <i>K<sub>x</sub>a</i> (mol/cm <sup>3</sup> min)
1.1	57.9	$2.43 \times 10^{-4}$
2.4	45.0	$3.98 \times 10^{-4}$
5.4	25.6	$4.89 \times 10^{-4}$
7.0	25.8	$8.93 \times 10^{-4}$
9.8	21.6	$1.16 \times 10^{-3}$

**Table C7** Effect of column pressure on vacuum stripping of tolueneCondition: 300 ppm toluene feed, 300 mM OP(EO)7 feed, 1.1 mL/min feed flow rate,1-hole distributor, and 30°C.

Pressure (Torr)	Toluene removal (%)	The overall liquid phase volumetric mass transfer coefficient, $K_x a$ (mol/cm <sup>3</sup> min)
125.0	34.6	$2.04 \times 10^{-4}$
99.6	40.6	$2.43 \times 10^{-4}$
74.2	41.6	$2.38 \times 10^{-4}$
53.9	57.9	$2.65 \times 10^{-4}$
38.6	67.7	$3.17 \times 10^{-4}$

Table C8 Effect of liquid distribution on vacuum stripping of toluene
Condition: 300 ppm toluene feed, 300 mM OP(EO)<sub>7</sub> feed, 1.1 mL/min feed flow rate,
38 Torr column pressure, and 30°C.

Number of distributor hole (Holes)	Toluene removal (%)	The overall liquid phase volumetric mass transfer coefficient, $K_x a$ (mol/cm <sup>3</sup> min)
1	67.7	$3.17 \times 10^{-4}$
2	79.7	$3.77 \times 10^{-4}$
3	87.3	$4.47 \times 10^{-4}$
4	88.0	$3.82 \times 10^{-4}$
5	89.7	$4.82 \times 10^{-4}$

Table C9 Effect of surfactant concentration on toluene vacuum stripping
Condition: 300 ppm toluene feed, 300 mM OP(EO)<sub>7</sub> feed, 1.1 mL/min feed flow rate,
38 Torr column pressure, and 30°C.

[OP(EO)7] (mM)	Toluene removal (%)	The overall liquid phase volumetric mass transfer coefficient, <i>K<sub>x</sub>a</i> (mol/cm <sup>3</sup> min)
300	90.19	$3.36 \times 10^{-4}$
400	80.09	$2.93 \times 10^{-4}$
500	73.13	$2.26 \times 10^{-4}$
630	57.93	$1.47 \times 10^{-4}$

 Table C10 Effect of temperature on toluene vacuum stripping

Condition: 300 ppm toluene feed, 630 mM OP(EO)<sub>7</sub> feed, 1.1 mL/min feed flow rate, 94 Torr column pressure, and 3-hole distributor.

Temperature (mM)	Toluene removal (%)	The overall liquid phase volumetric mass transfer coefficient, $K_x a$
		(mol/cm <sup>3</sup> min)
30	19.68	$8.63 \times 10^{-5}$
40	36.43	$1.48 \times 10^{-4}$
45	55.73	$1.69 \times 10^{-4}$
50	89.24	$2.87 \times 10^{-4}$

 Table C11 Effect of Solute Type on Vacuum Stripping

Condition: 2 000 ppm VOC feed, 450 mM OP(EO)<sub>7</sub> feed, 1.1 mL/min feed flow rate, 59 Torr column pressure, 3-hole distributor, and 40°C.

VOCs	Structure of the VOCs	VOC removal (%)	The overall liquid phase volumetric mass transfer coefficient, $K_x a$ (mol/cm <sup>3</sup> min)
BEN		97.7	4.4×10 <sup>-4</sup>
TOL	CH3	90.6	3.3×10 <sup>-4</sup>
ETB	C2H5	87.3	3.1×10 <sup>-4</sup>
DCE	CI H i   H-CC-H i   H CI	95.5	3.9×10 <sup>-4</sup>
TCE	CI CI C=C CI H	96.4	3.8×10 <sup>-4</sup>
PCE	CI CI C=C CI CI	91.3	3.1×10 <sup>-4</sup>

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- Kungsanant, S., Kittisrisawai, S., Kitiyanan, B., Osuwan, S., and Scamehorn, J.F. (2008, October 20-21) Effect of solute type on volatile organic compound removal from nonionic surfactant coacervate phase solutions by vacuum stripping. <u>Proceedings of The 18th Thailand Chemical Engineering and Applied Chemistry Conference</u>, Pattaya, Thailand.

#### **Presentations:**

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