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APPENDICES

Appendix A Chemical Properties

Nonionic Surfactant Properties

Chemical Description

Name: Branched Secondary Alcohol Ethoxylate

Surfactant Type: Nonionic

Benefits

- Superior wetting agent
- Penetrant & dispersant
- Narrow gel range
- Silicone emulsifier

Applications

This product is suitable for use in applications such as:

- Paper & textile processing
- Pigment & wax/resin dispersants
- Hard surface cleaners
- Agrochemicals
- Paints & coatings

Typical physical properties

Actives, wt%: 90
Diluent: Water
Cloud Point: 36°C
HLB: 13.1
Moles EO: 8
Pour Point: <-40°C
Appearance: Pale yellow liquid
pH: 5.4
Viscosity (25°C): 71 cP
Density (20°C): 0.994
CMC: (25°C): 800 ppm
Surface Tension (25°C): 27 dynes/cm

Solubility and compatibility

- Soluble in water
- Soluble in most polar and non-polar solvents and oils
- Chemically stable in the presence of dilute acids, bases and salts
- Compatible with soaps, anionic and cationic surfactants, and many organic solvents

Solute properties

The solute can be classified into 2 types; aromatic and chlorinated hydrocarbon series. The aromatic hydrocarbon series are benzene (BEN), toluene (TOL), and ethyl benzene (ETB). While the chlorinated hydrocarbon consist of 1,1-dichloroethylene (DCE), trichloroethylene (TCE), and tetra chloroethylene (PCE).

Table A1 Physical and chemical properties of all solutes.

Solutes	Molecular weight	Density (g/cm^3)	Water solubility (mg/l)	Log octanol water partition coefficient. log K_{ow}	Molar volume V_x (cm^3/mol)*	Henry's law constant (Pa m^3/mol)
BEN	78.11	0.8786	1770	2.13	89.1	576
TOL	92.14	0.8669	533	2.69	106.3	673
ETB	106.18	0.867	169	3.15	122.4	854
DCE	96.94	1.213	2500	1.32	79.46	2675
TCE	131.39	1.465	1370	2.29	89.02	970.7
PCE	165.83	1.623	151	3.4	102	1852

* observed at 20 °C

Reference : U.S. Environmental Protection Agency, 2002.
Yalkowsky, 1999.
Turner *et al.*, 1996.
Mackay, 2006.
Staudinger *et al.*, 2001.

Appendix B Sample of Calculation

Batch experiment

Table B1 Equilibrium data in water system: 100-800 ppm toluene and 40°C

Initial toluene (ppm)	GC peak area of toluene at equilibrium	
	Liquid Phase	Vapor Phase
100	184.40	5301.1
250	288.85	8036.8
500	395.13	10683.5
700	466.55	12916.2
800	546.58	15039.30

Table B2 Equilibrium data in Tergitol TMN-6 system: 500-2000 ppm toluene, 450 mM, and 40°C

Initial toluene (ppm)	GC peak area of toluene at equilibrium	
	Liquid Phase	Vapor Phase
500	576.48	6054.47
1000	1286.05	11954.30
1500	1790.95	16280.17
1750	2080.45	18994.60
2000	2361.28	21539.87

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

$C_u = (3.63\times10^{-2})\times(\text{GC peak area of toluene})$ with $R^2 = 0.9983$ (B1)

Combining equation (B1) with the Henry's law constant of toluene in water at 40°C ($H = 1.20\times10^{-4}$ atm/ppm)

$p_t = (4.34\times10^{-6})\times(\text{GC peak area of toluene})$ (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 Tergitol TMN-6 system: 100-2000 ppm toluene, 450 mM Tergitol, and 40°C

Initial toluene	GC peak area of toluene at equilibrium		
	Liquid Phase	Vapor Phase	Toluene partial pressure (atm)
500	576.48	6054.47	2.63×10^{-2}
1000	1286.05	11954.30	5.19×10^{-2}
1500	1790.95	16280.17	7.07×10^{-2}
1750	2080.45	18994.60	8.24×10^{-2}
2000	2361.28	21539.87	9.35×10^{-2}

From Table B3, the toluene partial pressure and total toluene concentration in liquid phase is plotted together. The slope of the plot is consider to be the apparent Henry's law constant that is 3.98×10^{-5}.

From equation (B1) and (B2), the unsolubilized toluene concentration in 450 mM Tergitol TMN-6 can be calculated. Therefore, the solubilization constant (K_s) is then calculated and tabulated in Table B4.

From $p_t = H_{app}C_{tot} = HC_u$

Therefore, $Cu = (H/H_{app})\ C_{total}$

Table B4 Solubilization and unsolubilization toluene concentration in liquid phase at equilibrium: 100-2000 pmm toluene, 450 mM Tergitol TMN-6, and 40°C

Peak area of toluene at equilibruin	Unsolubilized toluene	Solubilized toluene	K_s (M^{-1})
576.48	191.85	384.62	4.41
1286.05	428.00	858.05	4.36
1790.95	596.04	1194.91	4.33
2080.45	692.38	1388.07	4.31
2361.28	785.84	1575.43	4.29

From Table B4, the solubilization constant of toluene in 450 mM Tergitol TMN-6 at 40°C is considered to be 4.35 M^{-1}.

Continuous experiment

Initial toluene concentration	2010.43	ppm
Final toluene concentration	136.71	ppm
Toluene removal (%)	93.20	%
Initial Surfactant concentration	450	mM
Final Surfactant concentration	499	mM
Vapor pressure of water at 40°C	0.0726	atm
H at 40°C	560.4	atm/ mole fraction

Calculation of the overall liquid phase volumetric mass transfer coefficient of toluene, $K_x a$.

From $$z = \frac{L_0}{K_x a} \ln\left(\frac{x_{i,t} - x_i^*}{x_{f,t} - x_i^*}\right) \qquad \text{(B4)}$$

1. Height of packing, Z

   Packing height = 30 cm.

2. The molar liquid flux. *L_0*

Volume flux or superficial velocity

the volume flow rate of feed solution = 1.1 cm^3/min

the cross section area of column = 33.2 cm^2

So, the volume flux of feed solution = 3.31×10^{-2} cm^3/cm^2 min

from final toluene concentration = 136.7 ppm (mg/l)

and final surfactant concentration = 498.96 mM

Volume of A = concentration of A / Density of A

So, Volume of toluene per 1 litre = 2.32 cm^3

Volume of surfactant per 1 litre = 1.04×10^{2} cm^3

Volume of water per 1 litre = 8.94×10^{-2} cm^3

Volume fraction of A = Volume of A / Total volume

Volume fraction of toluene in feed solution = 2.32×10^{-3}

Volume fraction of surfactant in feed solution = 1.04×10^{-1}

Volume fraction of water in feed solution = 8.93×10^{-1}

The volume flux of A = (Volume fraction of A)×(the volume flux of feed solution)

The volume flux of toluene in product solution = 5.22×10^{-6} cm^3/cm^2 min

The volume flux of surfactant in product solution = 3.83×10^{-3} cm^3/cm^2 min

The volume flux of water in product solution = 2.93×10^{-2} cm^3/cm^2 min

The molar flux of A = (The volume flux of A)×(Density of A)/(MW of A)

The molar flux of toluene in product solution = 4.91×10^{-8} mol/cm^2×min

The molar flux of surfactant in product solution = 1.65×10^{-5} mol/cm^2×min

The molar flux of water in product solution = 1.63×10^{-3} mol/cm^2×min

The molar liquid flux, *L_0*

$= (4.91\times10^{-8} + 1.65\times10^{-5} + 1.63\times10^{-3}) = 1.64\times10^{-3}$ mol/cm^2×min

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

From inlet coacervate phase solution,

Inlet surfactant concentration = 450.0 mM

Inlet toluene concentration = 2010.43 ppm

mole of surfactant = 4.50×10^{-1} M

mole of toluene = 2.18×10^{-2} M

mole of water = 4.97×10^{1} M

So, mole fraction of toluene (Z_{tou}) = 4.35×10^{-4}

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

From outlet coacervate phase solution,

Final toluene concentration = 136.7 ppm

Final surfactant concentration = 498.96 mM

mole of surfactant = 4.99×10^{-1} M

mole of toluene = 1.48×10^{-3} M

mole of water = 4.92×10^{1} M

So, mole fraction of toluene = 2.99×10^{-5}

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

From flash equation,

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

Therefore,

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

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

For toluene,

$$K_t = \frac{H}{P(1 + K_s C_m)} = 2442.65$$

Where H = 560.4 atm/mole fraction, P=38 Torr = 0.051 atm, K_s = 4.35 M^{-1}, C_m = 450 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,

Initial Surfactant concentration	=	450	mM
Initial toluene concentration	=	2010.43	ppm
mole of surfactant in feed	=	$4.50\times10\text{-}^{1}$	M
mole of toluene in feed	=	2.18×10^{-2}	M
mole of water in feed	=	4.97×10^{1}	M

So,

mole fraction of surfactant in feed (Z_{surf})	=	8.97×10^{-3}
mole fraction of toluene in feed (Z_{tou})	=	4.35×10^{-4}
mole fraction of water in feed (Z_{water})	=	9.91×10^{-1}

Substitute 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 $Z, L_0, x_{i,t}$ and $x_{f,t}$values were then substituted in equation (B4) for K_xa 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 use to calculate K_xa.

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

V/F	SUM(x-y)	x*	sum x	sum y	NTU	K_xa (mol/cm^{3}min)
1	-	1.78×10^{-7}	-	-	2.684	1.47×10^{-4}
0.6	0.022	2.97×10^{-7}	1.013	0.991	2.688	1.47×10^{-4}
0.2	0.009	8.89×10^{-7}	1.002	0.993	2.707	1.48×10^{-4}
0.07	0.003	2.53×10^{-6}	1.000	0.997	2.761	1.51×10^{-4}
0.056	0.002	3.16×10^{-6}	1.000	0.998	2.783	1.53×10^{-4}
0.054	0.001	3.27×10^{-6}	1.000	0.999	2.787	1.53×10^{-4}
0.052	0.001	3.40×10^{-6}	1.000	0.999	2.791	1.53×10^{-4}
0.05	0.001	3.53×10^{-6}	1.000	0.999	2.796	1.53×10^{-4}
0.049	0.001	3.61×10^{-6}	1.000	0.999	2.799	1.53×10^{-4}
0.048	0.000	3.68×10^{-6}	1.000	1.000	2.801	1.54×10^{-4}
0.045	0.000	3.92×10^{-6}	1.000	1.000	2.810	1.54×10^{-4}
0.04	-0.001	4.41×10^{-6}	1.000	1.001	2.828	1.55×10^{-4}
0.036	-0.003	4.89×10^{-6}	1.000	1.003	2.846	1.56×10^{-4}
0.0355	-0.003	4.96×10^{-6}	1.000	1.003	2.848	1.56×10^{-4}
0.035	-0.003	5.03×10^{-6}	1.000	1.003	2.851	1.56×10^{-4}
0.03	-0.005	5.86×10^{-6}	1.000	1.005	2.883	1.58×10^{-4}
0.02	**-0.012**	**8.73×10^{-6}**	**1.000**	**1.012**	**3.004**	**1.65×10^{-4}**
0	-1.053	4.35×10^{-4}	1.000	2.053	-	-

From Table B5, the satisfied $\frac{V}{F} = 0.02$, $x_t^* = 8.73\times10^{-6}$, and $K_xa = 1.65\times10^{-4}$ mol/cm^{3}min.

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