Solubility Enhancements of Trichloroethene and Perchloroethene by Mixed Surfactant

BAOWEI ZHAO*, KUN ZHU, CUILING ZHANG
*School of Environmental and Municipal Engineering,
Lanzhou Jiaotong University, Lanzhou 730070 China.*

Summary: Solubility enhancements of trichloroethene (TCE), perchloroethene (PCE) and their mixture (TCE-PCE) by mixed nonionic and anionic surfactant, Triton X-100 (TX100) and sodium dodecylbenzene sulfonate (SDBS) in DNAPL/ water systems were presented. Their solubilization extent of TCE by mixed TX100-SDBS at the total mass ratios of 3: 1, 1: 1 and 1: 3 was much larger than by single TX100 and even larger than by single SDBS at ratios of 1: 1 and 1: 3. The solubilization extent of PCE by mixed TX100-SDBS was between those by single TX100 and single SDBS. In the mixed TCE-PCE system, the solubilization extent of TCE or PCE by mixed TX100-SDBS at the ratios of 1: 1 and 1: 3 was larger than by single SDBS while less than by single TX100 at a greater surfactant concentration. TX100 partitioning into the organic phase dictated the solubilization extent. SDBS reduced greatly the partition loss of TX100 into organic phase. The extent of partition decreased with increasing the amount of SDBS. The mutual affinity of SDBS and TX100 in the mixed micelle controlled the partitioning of TX100 into DNAPL phase.

Introduction

Dense nonaqueous phase liquids (DNAPLs) are more prevalent contaminants found in the subsurface and may migrate below the water table being denser than the surrounding groundwater. Further downward migration of the contaminant can occur due to an increase in the hydraulic potential, lateral spreading of a pool to a vertical fracture, or a reduction in interfacial tension (IFT) due to change in subsurface chemistry, which pose the most significant problem due to their location in the aquifer.

Surfactant injection is a promising technology for enhancing DNAPL remediation, through micelle solubilization and / or mobilization [1-2]. The mobilization mechanism involves the immiscible (two phase) displacement of DNAPL as free product. However, the risk of downward migration of DNAPL as free product into uncontaminated regions of aquifers has been the primary limitation for the implementation of immiscible displacement technologies. Solubilization usually involves the use of micellar surfactant solutions to increase the apparent aqueous solubility of contaminant in a single-phase miscible displacement flood. This approach has been shown to be effective in numerous studies [3-9] and may significantly reduce remediation times compared to pump-and-treat. Solubilization technologies pose less risk of uncontrolled DNAPL migration and are less complex to design.

Ethoxylated nonionic surfactants have high solubilization capacity [10, 11]. However, one concern with these surfactants is their partitioning between aqueous and organic phase during remediation applications [12-14]. The partitioning of nonionic surfactant can, especially in the case of polar DNAPLs, leads to substantial loss of a surfactant, leaving little surfactant remaining in the aqueous solution for solubilization [12, 13], which would greatly reduce the surfactant flushing efficiency and surfactant recovery in post-groundwater extraction recycling operations.

In general, anionic surfactant does not partition into the organic phase [15]. However, their solubilization capability for DNAPLs is significantly less than for nonionic one's [10, 11]. Anionic and nonionic surfactant solutions usually form mixed micelle that frequently exhibit characteristic properties that are remarkable different from those of individual components [15-17], which would result in less partitioning of nonionic surfactant and more aqueous solubility enhancement of DNAPLs.

In this paper, our objectives are: (i) to test and compare the apparent solubilization extents of single and mixed surfactants in TCE, PCE and TCE-PCE/ water systems; (ii) to compare the losses of the nonionic surfactants used individually and in

---

combination with the anionic surfactant; (iii) to investigate mechanisms for reduction of the nonionic-surfactant partition loss of DNAPLs. The results may have implications for aquifer remediatior contaminated by DNAPLs.

Results and Discussion

Solubilization tests

The aqueous-phase solubilities of TCE and PCE as a function of total surfactant concentrations (TSC) are shown in Fig. 1. The mass ratios of TX100 to SDBS were 3: 1, 1: 1 and 1: 3. At low TSC ($\leq$ 1000 mg/ L), no significant solubility enhancements for TCE and PCE by both single and mixed surfactants were observed. For TCE/ water systems (Fig. 1a), single TX100 showed no TCE solubity enhancemnet even at 10000 mg/ L, while single SDBS enhanced the TCE solubility linearly with the SDBS concen-tration above 1000 mg/ L (the CMC of

SDBS is 963.2 mg/L). The aqueous solubilities of TCE with 3:1 TX100-SDBS were intermediate between those with single TX100 and SDBS.The solubilization extents of TCE by 1: 1 and 1: 3 TX100-SDBS were greater than that by single SDBS, as clearly indicated by the slopes of solubilization curve above 1000 mg/ L concentration. 1: 3 TX100-SDBS exhibited the largest effect for TCE. As for PCE/ water systems (Fig. 1b), the most significant solubility enhancement was observed when the amount of single TX100 reached above 4000 mg/ L. The apparent solubilities of PCE by 3: 1, 1: 1 and 1: 3 TX100-SDBS were higher than those by single SDBS above 1000 mg/L of TSC. As for TCE-PCE/water systems (Fig.1c-d), no TCE and PCE solubility enhancement occurred when the amount of single TX100 was less than 4000 mg/ L. The situation by 3: 1 TX100-SDBS were essentially the same as by single SDBS while the situation by 1: 1 and 1: 3 TX100-SDBS were superior to by single SDBS.
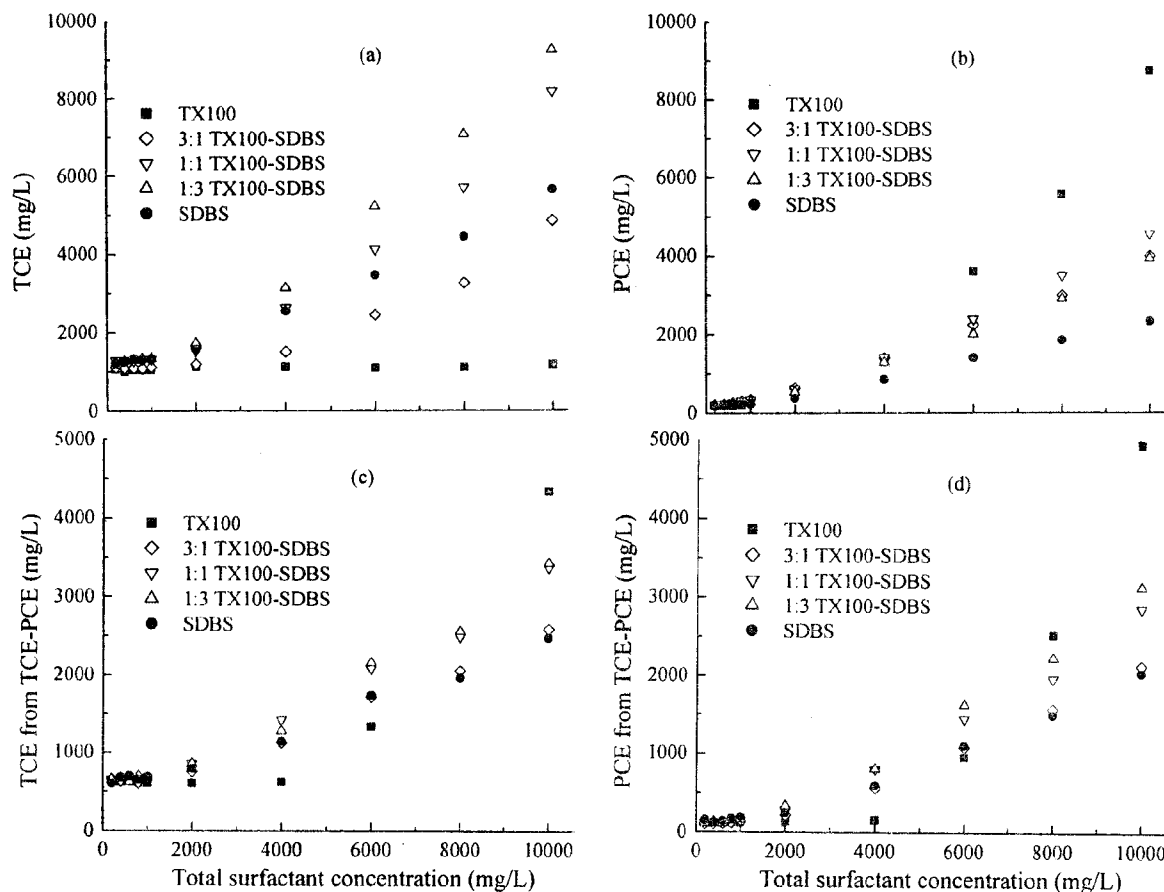

Fig. 1   Aqueous phase solubility of TCE and PCE v DNAPL: water (v/ v).   is total surfactant concentration at 1:40 phase ratio of

The results above illustrate that mixed TX100-SDBS with the ratios tested enhance much more significantly the aqueous phase solubility of TCE than does single TX100. Furthermore, mixed TX100-SDBS resulted in larger apparent solubility for TCE and PCE at the ratios of 1:1 and 1: 3, compared with single SDBS. At high TSC, the most significant solubility enhancement of PCE occurred by single TX100. Mixing polar TCE with PCE affected solubilization extents. Several factors may influence the efficiency of contaminated-soil flushing with surfactant [1, 2]. The greater the apparent solubilization for a given systems, the fewer pore volumes of surfactant solution are needed, which reduces capital expenditure and the operation cost.

Many nonionic surfactants have a high intrinsic solubilization capacity for nonaqueous phase liquids compared with anionic one [10, 11]. However, in DNAPL/ water system, the solubilization of DNAPL in the aqueous phase depends on the effecttive concentration of surfactants in the aqueous phase. As shown above, no significant solubilization of TCE by single TX100 occurred, suggesting that the concentration of TX100 in the aqueous phase was significantly reduced. Partitioning of ethoxylated nonionic surfactants into the excess organic phase and the resulting effects on the solubilization of DNAPLs in surfactant solutions have been reported [12-14]. The partitioning extent depends on the properties of surfactants and DNAPLs. Great losses of aqueous TX100 were found in TCE/ water systems (see section followed), rendering TX100 less efficient for solubilization. In contrast, there appeared to be no significant loss of SDBS because solubilization began near its nominal CMC. For TX100-SDBS tested, TX100 partitioning into organic phase had a large effect on the apparent solubilization capacity. Therefore, the extent of TX100 partitioning in mixed-surfactant systems must be different from that for single TX100.

Partitioning losses of TX100

Fig. 2 shows the partition losses of TX100 into TCE, PCE and TCE-PCE phase in solubilization tests.

When single TX100 was used, the losses were larger than 99 %, 15 % and 75 %, respectively. The CMC in the aqueous solution was not attained in TCE/ water system while attained in PCE/ water and TCE-PCE/ water systems by single TX100 at 2000
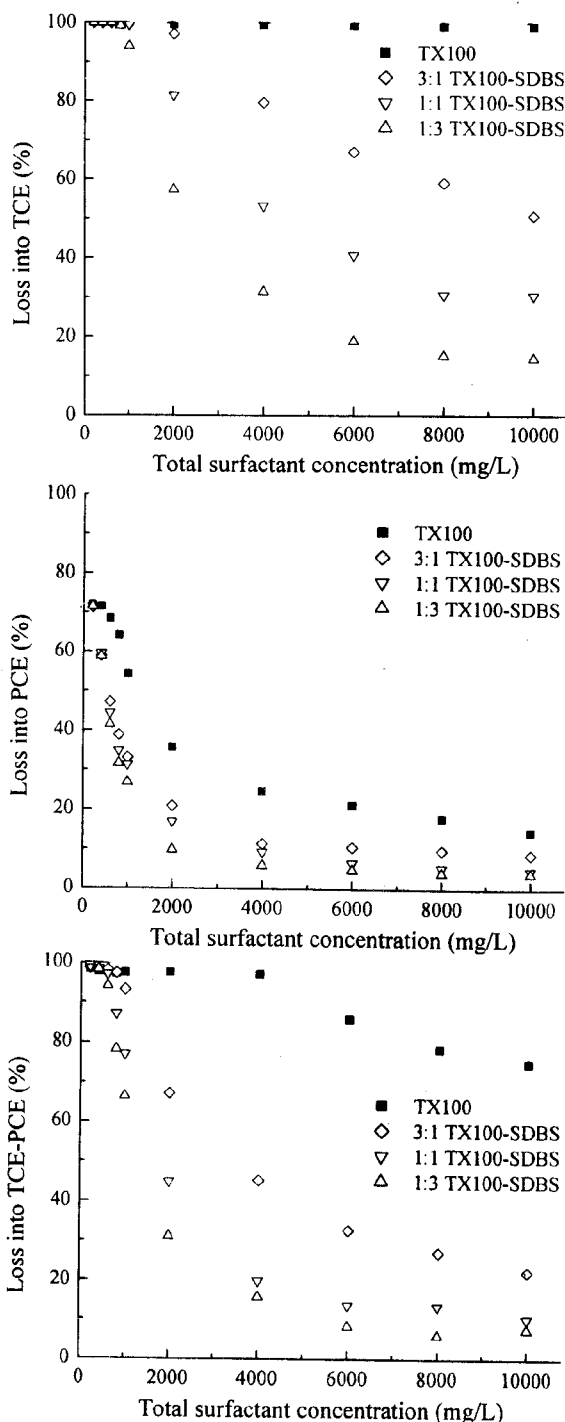

Fig. 2: TX100 losses into TCE, PCE and TCE-PCE organic phases versus total surfactant concentration at 1: 40 phase ratio of DNAPL: water (v/ v).

and 4000 mg/ L of the total surfactant concentrations. Solubilization of TCE and PCE by single SDBS began soon after the initial concentration surpassed 1000 mg/ L in Fig. 1, due to its negligible partitioning losses (no data shown in Fig. 2). The extent of loss of TX100 decreased significantly with increasing amount of SDBS in mixed surfactants. At lower surfactant concentrations ($\leq$ 1000 mg/ L), the amounts of SDBS were low and the loss fractions of TX100 were great.

Mechanism of loss reduction by SDBS

Extensive research has been performed on the partitioning of nonionic ethoxylated alkylphenol surfactants into saturated hydrocarbon phase. Harusawa *et al.*, [18] reported that partitioning is a process for surfactant monomers and micelle formation limits surfactant partitioning. It may be postulated that the reduction in TX100 partition in mixed surfactant systems was attributed to formation of mixed micelles in the aqueous solution. Surface tension measurement and nonideal solution theory [19-21] were applied to investigate the micelle formation of TX100 and SDBS.

Nonionic and anionic surfactants generally form mixed micelle in solution. The CMC of the binary surfactant on the basis of ideality, single nonionic surfactant and single anionic surfactant is expressed by C^*_{12}, C_1 and C_2, respectively. The molecular interaction parameters (β) between nonionic and anionic surfactants in mixed micelles the actual CMC of mixed surfactant, C_{12}, can be evaluated [19-21]. At fixed mass ratios 1: 9, 2: 8, 3: 7, 4: 6, 5: 5, 6: 4, 7: 3 and 8: 2 of TX100 to SDBS, the CMCs for single TX100 solution, C_1, single SDBS solution, C_2, and their mixture solutions, C_{12}, were determined from surface tension-log surfactant concentration curves and the values of β were calculated, as listed in Table-1. It can be seen from the differences between C^*_{12} and C_{12} that the binary TX100-SDBS systems deviated significantly from ideality. This implied the TX100-SDBS systems form mixed micelles. The negative values of β, with an average value −3.35, indicated an attractive interaction between TX100 and SDBS in their mixed micelles. The fundamental hypothesis directing this research was that the competition of TX100 momomers between the mixed micellar pseudo-phase and the organic phase controlled the partitioning of TX100 in DNAPL/ water systems.

Table-1: The theoretical and experimental CMCs for mixed TX100-SDBS at different mass ratio and the interaction parameters (β)

Mass ratio of TX100:SDBS	C^*_{12} (mmol/L)	C_{12} (mmol/L)	β
0: 10		2.76	
1: 9	1.79	0.618	-4.33
2: 8	1.29	0.522	-3.67
3: 7	0.988	0.491	-3.03
4: 6	0.784	0.404	-3.14
5: 5	0.638	0.373	-2.89
6: 4	0.527	0.329	-2.93
7: 3	0.441	0.276	-3.35
8: 2	0.372	0.253	-3.45
10: 0		0.268	

For TX100-SDBS systems as presented, significant different properties were observed for the surfactant pairs. SDBS is more hydrophilic with little tendency to partition into TCE, PCE and TCE-PCE, while TX100 is more hydrophobic and partitions strongly to TCE/ water and TCE-PCE/ water systems. Prior to the formation of mixed micelles, TX100 in mixed TX100-SDBS systems partitioned linearly into DNAPL, as illustrated by TCE-PCE/ water system in Fig. 3, due presumably to the weak interaction between the monomers of TX100 and SDBS. When the total amount of TX100-SDBS increased, the selective partitioning of TX100 proceeded with a progressively lower rate when the SDBS level in the aqueous phase increased. Since SDBS showed a negligible partitioning, the levels of mixed TX100-SDBS reached CMCs before the level of single TX100 could reach the CMC as the total
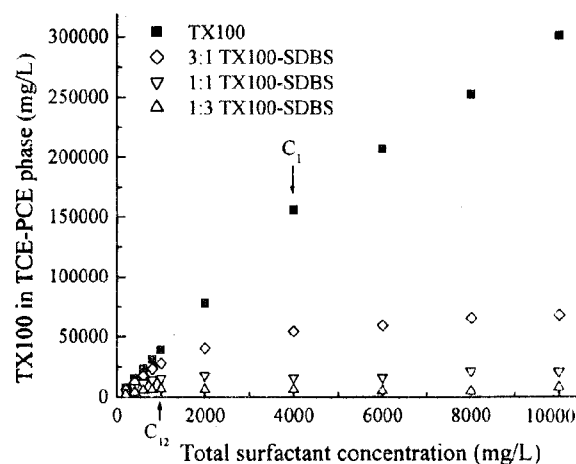

Fig. 3: The relation between the equilibrium concen-trations of TX100 in organic phase and the total surfactant concentration in TCE-PCE/ water system.

surfactant level increased. The incipient mixed micelles should compose mainly of SDBS molecules. However, as the mixed micelles were formed, competition of TX100 monomers between the mixed micellar pseudo-phase and organic phase occurred, reducing the TX100 partition into TCE-PCE and thus producing a break in the partition curves. Since the CMC of single TX100 in aqueous phase was reached at a much later stage because of its high partition loss, the concentration of TX100 in TCE-PCE did not level off until the total concentration was up to 4000 mg/ L. The more is the amount of SDBS in mixed surfactants, the less is the total amount needed to reach the partitioning plateau. The reduction in TX100 partition loss to DNAPLs by the addition of SDBS can thus be attributed to the poor SDBS partition into DNAPL and to the formation of TX100-SDBS mixed micelles.

Experimental

Chemicals

TX100 was obtained from Sigma Chemical Company and SDBS (purity $\geq$ 98 %) was purchased from Tokyo Kasei Kogyo Co., LTD, respectively, used as received. TCE and PCE, with analytical grade, were obtained from Shanghai Chemical Company, China. The characteristics of the selected chemicals are given in Table-2.

Solubilization tests

The surfactant solutions were prepared as single or in mixtures with the concentrations, 200, 400, 600, 800, 1000, 2000, 4000, 6000, 8000 and 10000 mg/ L in water. A series of 20 mL of single or mixed surfactant solutions were placed into 25-mL Corex centrifuge tubes with Teflon cap liners. 500 μL of pure TCE, PCE, or TCE-PCE mixture (1: 1 v: v) was added into each tube. Duplicate samples were prepared for each surfactant concentration solution. These samples were equilibrated on a reciprocating shaker for 72 h at 25 ± 1 °C and then were subsequently centrifuged on a Model Biofuge Prima R centrifuger (Hanau, Germany) for 1 h at the speed of 5000 rpm. An appropriate aliquot of the

supernatant was then carefully withdrawn and diluted to 10 mL in flasks with 8.0 mL of methanol, with the rest by water. The diluted samples were analyzed for TX100, SDBS, TCE and PCE using Hitachi HPLC (Hitachi, Japan), which was equipped with two pumps, an autosampler, and an ultraviolet spectrophoto detector. 100 μL of the sample solution was injected into a reverse-phase C18 column (Waters Spherisorb S5ODS2, 4.6 x 250 mm). The elution was carried out by pumping methanol and water (80: 20 v/ v) isocratically at a flow rate of 1.0 mL/ min. The temperature of column was kept at 40 °C. The absorbency was measured at a wavelength of 224, 224, 200 and 200 nm for SDBS, TX100, TCE and PCE and the retention time was 2.72, 11.85, 5.75, and 7.63 min, respectively. The quantitation limits of the method, defined as the concentrations that gave a signal-to-noise ratio of 10:1, were 0.2, 0.06, 0.015, and 0.023 mg/ L for SDBS, TX100, TCE and PCE.TX100, SDBS TCE and PCE were quantified from the calibration. The amounts of surfactant in organic phase were evaluated by the difference between the initial and equilibrium concentration of surfactant in aqueous phase.

Measurement of surface tension and CMC

Surface tensions of surfactant solutions were determined with a Model 20 tensionmeter (Fisher Science Instrument Co., USA). This instrument operates on the DuNouy principle, in which a platinum ring is suspended from a torsion balance, and the force (in mN/ m) necessary to pull the ring free from the surface film is measured. The critical micelle concentration (CMC) was determined by measuring the surface tension versus surfactant concentration; the plotted surface tension value was taken when stable reading was obtained for a given surfactant concentration, as indicated by at least three consecutive measurements having nearly the same value.

Acknowledgements

Table-2: Characteristics of the selected chemicals

Chemicals	Molecular formula	Molar weight (g/ mol)	IFT[a] (mN/ m)	Aqueous solubility[b] (mg/L, 25 °C)	CMC[c] (mg/ L)
TCE	C₂HCl₃	131.39	34.5	1100	
PCE	C₂Cl₄	165.83	47.5	150.9	
TX100	C₈H₁₇C₆H₄(OCH₂CH₂)₉.₅OH	625			164.7
SDBS	C₁₂H₂₅C₆H₄SO₃Na	348.48			963.2

a. Interfacial tension, reported by Zimmerman [12]; b. Aqueous solubility, reported by Yaws [22]. c. The critical micelle concentration, measured in this work

References

1.   C. C. West and J. H. Harwell, *Environ. Sci. Technol.*, **26**, 2324 (1992).

2.   J. H. Harwell, D. A. Sabatini and R. C. Knox, *Colloids and Surface A*, **151**, 255 (1999).

3.   L. Zhong, A. S. Mayer and G. A. Pope, *J. Contam. Hydro.*, **60**, 55 (2003).

4.   K. D. Pennell, A. M. Adinolfi and L. M. Abriola, *Environ. Sci. Technol.*, **31**, 1382 (1997).

5.   D. J. Prak and L. H. Pritchard, *Water Research*, **36**, 3463 (2002).

6.   T. B. Boving and M. L. Brusseau, *J. Contam. Hydro.*, **42**, 51 (2000).

7.   J.W. Jawitz, D. Dai and P. C. Rao, *Environ. Sci. Technol.*, **37**, 1983 (2003).

8.   K. D. Pennell, L. M. Abriola and W. J. Weber, *Environ. Sci. Technol.*, **27**, 2332 (1993).

9.   J. C. Fountain, A. Klimek and M. G. Beikirch, *J. Hazard. Mater.*, **28**, 295 (1991).

10. M. Zhou and R. D. Rhue, *Environ. Sci. Technol.*, **34**, 1985 (2000).

11. D. E. Kile and C. T. Chiou, *Environ. Sci. Technol.*, **23**, 832 (1989).

12. J. B. Zimmerman, T. G. Kibbey and M. A. Cowell, *Environ. Sci. Technol.*, **33**, 169 (1999).

13. M. A. Cowell, T. G. Kibbey and J. B. Zimmerman, *Environ. Sci. Technol.*, **34**, 1583 (2000).

14. E. C. Butler and K. M. Hayes, *Water Research*, **32**, 1345 (1998).

15. M. J. Rosen, Surfactants and Interfacial Phenomena. 2nd ed. New York: John Wiley & Sons (1989).

16. L. Zhu and S. Feng, *Chemosphere*, **53**, 459 (2003).

17. B. Zhao, L. Zhu and W. Li, *Chemosphere*, **58**, 33 (2005).

18. F. Harusawa, S. Taeko and H. Nakajima, *J. Colloid Inter. Sci.*, **74**, 435 (1980).

19. K. L. Mittal, Solubilization Chemistry of Surfactants 1, New York: Plenum (1979).

20. P. M. Holland and D. N. Rubingh, *J. Phys. Chem.*, **87**, 1984 (1983).

21. M. J. Rosen and X. Y. Hua, *J. Colloid Interface Sci.*, **86**, 164 (1982).

22. C. L. Yaws, Chemical Properties Handbook. New York: McGraw-Hill Book Co. (1999).