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Solubility of diuron in complex solvent systems

Cheng, Chin-Hwa, M.S.

The University of Arizona, 1989

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SOLUBILITY OF DIURON
IN COMPLEX SOLVENT SYSTEMS

by

Chin-Hwa Cheng

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A Thesis Submitted to the Faculty of the

DEPARTMENT OF PHARMACEUTICAL SCIENCES
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In the Graduate College

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1989

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Date

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ABSTRACT

The solubility of diuron was determined in binary and ternary cosolvent-water systems. The binary systems were composed of a completely miscible organic solvent (CMOS) and water; while, the ternary systems incorporate partially miscible organic solvents (PMOS) into the binary systems.

Due to the low aqueous solubilities of trichloroethylene and toluene, the PMOS's do not behave as cosolvents and they do not play an important role in altering solubility.

CHAPTER 1

INTRODUCTION

Solubility is a major factor which controls the rate of transport of hydrophobic organic chemicals (HOC) from aqueous and aqueous-organic-solvent mixtures and the fate of pollutants. Therefore, prediction of solubility in aqueous solvent mixtures is very important in the environmental area.

At waste disposal areas and land treatment sites, it is likely that the soil solution will consist of a mixture of water and various water miscible organic solvents; therefore, it is necessary to know the solubility of hydrophobic organic chemicals (HOC) in organic solvent-water systems. This information can help characterize the movement of pollutants in contaminated streams and landfills and help in understanding the sorption of HOC's.

For a series of non-hydrogen bonding monosubstituted benzenes in non-hydrogen bonding cosolvents, Chawla et al. (1987) reported a good correlation between log solubility and volume fraction of cosolvent. The data were used to test the log-linear

solubility model of Yalkowsky (1981). The model predicts a linear relationship between the logarithm of the solubility of a solute in a binary solvent system (S_m) and the volume fraction of cosolvent (f_c).

Yalkowsky et al. (EPA Contract No. CR-8125-81) have applied this model to the solubility of organic solutes in multiple solvent systems. In mixed or multiple solvent systems, there is a linear relationship between the solubility of a drug in a mixed solvent system and the fraction of the cosolvent. Normally, the solvents used in mixed systems are completely miscible with water. These solvents are called completely miscible organic solvents (CMOS). A partially miscible organic solvent (PMOS) is defined as a solvent which is not miscible with water in all proportions. A system where both PMOS and CMOS are present is called a complex solvent system.

A reciprocal relationship between the logarithm of the sorption coefficient and the fraction of cosolvent was observed in the solvophobic approach by Rao et al. (1985). Nkedl-Kizza et al. (1985) have shown that the sorption coefficient for diuron decreases log linearly as the fraction of cosolvent increases. The

cosolvents that they chose were methanol and acetone.

In the above studies, anthracene was used to represent an ideal hydrophobic sorbate without any polar functional groups, so that its total surface area (TSA) and hydrocarbonaceous surface area (HSA) were identical. In contrast to anthracene, diuron has polar functional groups and this factor causes the total surface area to be greater than the hydrocarbonaceous surface area.

A model has been proposed by Gupta et al. (1989) for partially miscible organic solvents which act like cosolvents in a binary cosolvent-water mixture, where the solubility of HOC is increased. Anthracence was chosen for this study and the solubility of anthracene can be predicted from the proposed equation which is described in Chapter 2.

Diuron is a substituted urea and is now widely used for industrial weed control, particularly in high rainfall climate regions. Due to its low water solubility and great soil particle absorbancy, diuron can be retained in the upper soil layers for a long period of time. Therefore, smaller amounts of diuron are required compared to other herbicides;

consequently, it has a wide area of application. (White-Stevens, 1977)

The objectives of this research are to determine if diuron in different PMOS's can fit the proposed model and if the PMOS's behave as a cosolvent and alter the solubility of diuron.

CHAPTER 2

BACKGROUND

The expression for solubility in mole fraction for a solute in a liquid is given by Equation 2.1. (Martin, Swarbrick and Cammarata, 1983)

$$\log X = - \frac{\Delta H_f (T_m - T)}{2.303\ RTT_m} - \log ac \qquad (2.1)$$

Where X is the mole fraction solubility of the solute; ΔH_f, the molar enthalpy of fusion; R, the gas constant; T_m, the melting point of the solute in Kelvin; T, the absolute temperature of the solution; and ac, the activity coefficient of the solute in solution. The first term on the right side in the above equation is the expression for the ideal solubility of a solid solute. The ideal solubility of a crystalline chemical is dependent on temperature, the melting point of the solid, and the molar heat of fusion (ΔH_f) of the solid.

If the solute is a liquid (i.e., $T > T_m$), the ideal mole fraction solubility will be unity, which means that the solute and the solvent will be completely miscible if their activity coefficient is unity.

The second term on the right side of Equation 2.1 is the logarithm of the activity coefficient (ac). This represents the decrease in solubility due to the difference in intermolecular interactions of the solute and solvent. This term can be represented by the following equation:

$$\log ac = C_{11} + C_{22} - 2C_{12} \qquad (2.2)$$

Where C_{11} represents the interaction forces between the solvent molecules; C_{22}, the forces of interaction between the solute molecules; and C_{12}, the interaction between solvent and solute molecules. If the solute-solute and solvent-solvent interactions are equivalent to the solute-solvent interactions and there is no change in heat or volume on mixing, then log ac becomes zero and the mole fraction solubility will be the ideal solubility. Thus, the solubility of a crystalline solute is limited by the crystal interactions and the interactions of the solution components.

When the temperature is equal to the melting point, the solid and liquid are in equilibrium and the free energy of fusion (ΔG_f) is equal to zero.

Therefore,

$$\Delta G_f = 0 = \Delta H_f - T_m \Delta S_f \qquad (2.3)$$

and

$$\Delta H_f = T_m \Delta S_f \qquad (2.4)$$

Where ΔS_f is the entropy of fusion. At room temperature (25°C), Equation 2.4 may be substituted into Equation 2.1 with R equal to 1.987 cal./K/mole and T equal to 298 K, this results in the following:

$$\log X = -\frac{\Delta S_f}{1364}(MP - 25) \qquad (2.5)$$

Where the melting point (MP) is in degree Celsius. According to Walden's rule, the entropy of fusion (ΔS_f) for most rigid molecules is relatively constant and is approximately equal to 13.5 entropy units. Entropy of fusion (ΔS_f) is generally more understandable and predictable than heat of fusion (ΔH_f). Therefore, for rigid molecules the above equation can be approximately reduced to:

$$\log X \approx -0.01\,(MP - 25) - \log ac \qquad (2.6)$$

This equation is used to estimate solubility from the chemical structure and melting point of the solute.

Equation 2.6 predicts that if the melting point is increased by 100°C with no change in the partition coefficient, the solubility will be decreased by a factor of 10.

Reducing either the melting point of the solute or increasing the interactions between the solute and solvent will increase the solubility of the chemical. Some other methods used to increase solubility include pH adjustment, salt formation, micelle formation, complexation, solid state manipulation, microemulsion formation and cosolvency.

Cosolvency is one of the most effective methods to increase solubility. The solubility of a chemical can increase by several orders of magnitude if the proper type and suitable amount of cosolvent are used.

Yalkowsky, Flynn and Amidon (1972) observed a linear relationship between the logarithm of the solubility and the fraction cosolvent for a series of alkyl p-aminobenzoates in propylene glycol and water mixtures. In 1981, Yalkowsky and Roseman derived an equation which predicted a log-linear increase in chemical solubility with an increasing volume of cosolvent fraction.

For a binary solvent system composed of a

cosolvent and water, the total solubility of the chemical in the solvent mixture, S_m, can be expressed by Equation 2.7.

$$\log S_m = f \log S_c + (1 - f) \log S_w \qquad (2.7)$$

Where S_m is the solubility of the chemical in the cosolvent-water mixture; f, the volume fraction of the cosolvent; S_c, the solubility of the chemical in pure cosolvent; and S_w, the solubility of the chemical in water. From Equation 2.1, the mole fraction solubility for both cosolvent and water can be written in the following forms:

$$\log S_w = - \frac{\Delta S_f \ (T_m - T)}{1364} - \log ac_w \qquad (2.8)$$

$$\log S_c = - \frac{\Delta S_f \ (T_m - T)}{1364} - \log ac_c \qquad (2.9)$$

In Equations 2.8 and 2.9, ac_w and ac_c are the activity coefficient for the chemical in water and in cosolvent, respectively.

Substituting $\log S_w$ and $\log S_c$ into Equation 2.7 and rearranging the terms, results in the following equation:

$$\log S_m = \log S_w + f(\log ac_w - \log ac_c) \qquad (2.10)$$

This equation assumes that the enthalpy of fusion and the melting point of the chemical remain unchanged during the solubility determination in both water and cosolvent, and in the cosolvent-water mixtures. (This assumption does not hold when the chemical precipitates in a different crystal form when solvents are changed.)

For a given cosolvent-water system, ac_c and ac_w will be constant. Therefore, Equation 2.10 can be changed to the following equation:

$$\log S_m = \log S_w + f\sigma \qquad (2.11)$$

This equation predicts the linear relationship between log S_m and f_c with a slope σ. The slope, σ, is a measure of the solubilizing potential of the cosolvent and also corresponds to the logarithm of the solubility ratio (S_c/S_w).

Rubino (1984) investigated the solubility of some poorly soluble drugs: phenytoin, diazepam, and benzocaine. The solubilities of these drugs can be approximated by the above log linear equation. Chawla et al. (1987) reported a good correlation between log solubility and fraction of cosolvent for a series of non-hydrogen bonding monosubstituted benzenes in non-hydrogen bonding cosolvents.

For multiple cosolvent systems, Equation 2.11

becomes

$$\log (S_m / S_w) = \Sigma_i (f_i \sigma_i) \qquad (2.12)$$

Where f_i is the volume fraction of cosolvent i and σ_i denotes the slope of the corresponding cosolvent-water mixture. The above relationship was also observed by Yalkowsky et al. for a range of pollutants in cosolvent-water systems (E.P.A. Report #CR81852).

Equation 2.12 deals with completely miscible organic solvents (CMOS) only. Gupta et al. (1989) extended Equation 2.12 to include partially miscible organic solvents (PMOS) in water and cosolvent-water mixtures. A model was established to determine the effect of PMOS on the solubility of anthracene in a binary cosolvent-water mixture. The expression becomes:

$$\log S^a_{c,p,w} = \log S^a_w + \sigma^a_c f_c + \frac{\sigma^a_p S^p_w}{D_p} 10^{\sigma^p_c f_c} \qquad (2.13)$$

Where $S^a_{c,p,w}$ represents the solubility of anthracene in a ternary solvent system (CMOS, PMOS, water); S^a_w and S^p_w represent the aqueous solubilities of anthracene and PMOS, respectively; f_c represents the volume fraction of CMOS; D_p is the density of the solute (PMOS); σ^a_c is the slope of the solubility curve of

anthracene in the cosolvent-water mixture without PMOS; σ_c^p is the slope of the solubility curve of PMOS in cosolvent-water mixture; and σ_p^a is the slope of the solubility curve of anthracene in PMOS-water mixture. Each of these slopes can be calculated from the solubility of the solute in the cosolvent and the solubility of the solute in water.

CHAPTER 3

EXPERIMENTAL PROCEDURES

The solubility of diuron[1] has been studied in different solvent systems. These systems are indicated in Table 3.1. As shown in Table 3.1, the four completely miscible organic solvents (CMOS) used are methanol[2], acetone[3] (ACE), acetonitrile[4] (ACN) and propylene glycol[5] (PG). The two partially miscible organic solvents (PMOS) used are trichloroethylene[6] (TCE) and toluene[7]. The cosolvent-water mixtures which contained 0% to 50% (V/V) of a completely miscible organic solvent were prepared using milli-Q water[8].

---

1. Pestanal(R), Riedel - deHaën Company, Wunstorfer Straße D-3016 Seelze 1.
2. American Burdick & Jackson Laboratories, Inc., Muskegan, MI 49442
3. Mallinckrodt, Inc., Paris, KY 40361.
4. Baxter Healthcare Corporation, Burdick & Jackson Division, Muskegon, MI 49442.
5. Fisher Scientific Company, Fair Lawn, NJ 07410.
6. Aldrich Chemical Company, Milwaukee, WI 53201.
7. Fisher Scientific Company, Fair Lawn, NJ 07410.
8. Milli-Q Water System, Model CDOF01205, Millipore.

The solubility of diuron in the presence of PMOS, in the absence of PMOS, and in pure PMOS were determined. The solubility of the PMOS in each CMOS-water systems was also measured. All of the experiments were done at 24 ± 2°C.

SOLUTION PREPARATION

Completely Miscible Organic Solvent (CMOS) Solutions

A series of cosolvent and water mixtures were made as follows: 0, 1, 2, 3, 4, and 5 mls of cosolvent were mixed with 10, 9, 8, 7, 6, and 5 mls of water, respectively. The volumes of cosolvent and water were measured separately to prevent possible volume fraction change of cosolvent upon mixing.

Saturated Partially Miscible Organic Solvent (PMOS) Solutions

PMOS was added dropwise, while manually shaking, to one of the above solutions until a minimum excess amount (20 - 50 microliters) was seen to ensure saturation. The solution was then equilibrated by using a testtube rotator[9] (14 rpm) in the absence of light at

9. Model 400-100 Labindustries, Berkley, CA 94710.

room temperature for 24 hours. After rotating, the solutions were centrifuged for 15 minutes in a Beckman model TJ-6R centrifuge at 3000 rpm. Five milliliters of supernatant was removed and transferred to a 5 ml teflon-lined screw capped vial.

Addition of Diuron

Small increments of solute were added to the saturated PMOS solution, until there was a minimum excess of solute. These solutions were then placed on a testtube rotator in the dark at room temperature for 24 hours to equilibrate and prevent light degradation.

After saturation was achieved, the solutions were centrifuged at 3000 rpm for 20 minutes in a Beckman model TJ-6R centrifuge. The supernatant was then transferred to a small vial. Aliquots of the cosolvent-water phase were analyzed by high performance liquid chromatography (HPLC) after appropriate dilution. Acetonitrile was used for dilutions to prevent phase separations upon dilution. In the higher fraction cosolvent mixtures, the PMOS concentrations after dilution were too low to be determined, thus an analysis of the original sample solution was required.

ANALYTICAL CONDITIONS

A Beckman HPLC system was used with a 110A pump and a Spectroflow 757 variable wavelength UV detector set at 254 nm. A Spectra Physics 8780XR autosampler was used for autoinjection. A volume of 20 µl was used for the injection loop. Chromatograms which include retention time and peak areas were recorded on a Hewlett-Packard 3390A integrator. A 5 µm, 25 cm x 4.6 mm Alltech Econosphere C18 column was used.

The following chromatgraphic conditions were used: the mobile phase was a mixture of acetonitrile and water (70:30), the flow rate was set at 1 ml/min, the sensitivity of the detector was 0.1 a.u.f. and the peak width was 0.04. For the determination of the diuron concentration, the attenuation of the integrator was initially set at 3.0. When toluene and trichloroethylene concentrations were measured, the attenuation was reset at 1.0 because of their low concentrations. The pressure was around 1000 to 1500 psi.

Under these conditions, the retention time for diuron was between 4.22 and 4.37 minutes, for trichloroethylene between 5.95 and 6.29 minutes, and for toluene between 6.42 and 6.61 minutes. The calibration

curve was drawn by plotting the detector response versus the injected known concentrations. At least five standards of known concentrations were injected to make a calibration curve for each set of samples. Sources of variations in the different calibration curve parameters were investigated. A variation greater than 10% was considered unacceptable, and the corresponding standard solution was prepared again.

All samples in each system were done in duplicate. If the difference between the two replicates was greater than 20%, a third replicate was made and the data compared again. Every sample was analyzed three times and the peak areas were within a 5% range.

STATISTICAL ANALYSIS

The duplicate solubility data points were averaged before taking the logarithm. The calibration curve was determined by linear regression with a zero intercept which is the relationship of no-sample-and-no-response. Sample concentrations were then determined from the slopes of the standard calibration curves. The regressions were done with Lotus 123[10].

10. 123 Lotus Development Corporation, Cambridge, MA 02142.

TABLE 3.1

SUMMARY OF SYSTEMS STUDIED

PMOS CMOS	TRICHLORO- ETHYLENE	TOLUENE
METHANOL	*	*
ACETONITRILE	*	*
PROPYLENE GLYCOL	*	*
ACETONE	*	*

TABLE 3.2

STRUCTURES OF SOLUTE AND SOLVENTS

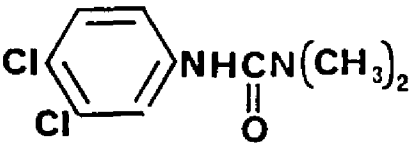
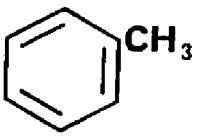
	COMPOUND	STRUCTURE
SOLUTE	DIURON	
CMOS	METHANOL	CH_3OH
	ACETONE	$CH_3C(=O)CH_3$
	ACETONITRILE	CH_3CN
	PROPYLENE GLYCOL	$CH_3CH(OH)CH(OH)H$
PMOS	TRICHLOROETHYLENE	$Cl_2C{=}CHCl$
	TOLUENE	

TABLE 3.3

PHYSICAL PROPERTIES OF SOLUTES AND SOLVENTS

TYPE	COMPOUND	MOL. WT.	DENSITY¥	MP(^{o}C)
SOLUTE	DIURON	233.10	-	158
CMOS	ACETONE	58.08	0.788*	-94
	ACN	41.05	0.787**	-54
	PG	76.09	1.0361	-59
	METHANOL	32.04	0.7915	-97.8
PMOS	TCE	131.40	1.4904	-84.8
	TOLUENE	92.4	0.8669	-95

¥ d^{25}_{4} * d^{25}_{25} ** d^{15}_{4}

PG: Propylene Glycol ACN: Acetonitrile

TCE: Trichloroethylene

CHAPTER 4

RESULTS

The solubility of diuron has been studied in various CMOS-PMOS systems. These systems are indicated in Table 3.1. As listed in the table, four completely miscible organic solvents (CMOS) were studied: methanol, acetone, acetonitrile and propylene glycol; and two partially miscible organic solvents (PMOS): toluene and trichloroethylene (TCE).

COMPARISON OF THE SOLUBILITY OF DIURON IN VARIOUS COSOLVENT-WATER MIXTURES

CMOS-Water Systems

Figure 4.1 shows the solubility of diuron in four CMOS-water systems in the absence of PMOS. Higher solubilities of diuron are found in the acetonitrile-water and the acetone-water systems compared to the methanol-water and propylene glycol-water systems. The acetonitrile-water system has the highest solubility followed by acetone-water, methanol-water and finally propylene glycol-water with the lowest. The log solubility increases as the fraction of CMOS increases.

CMOS-PMOS-Water Systems

The solubility of diuron in four CMOS-water systems saturated with different PMOS's are shown in Figures 4.2 to 4.5. In all cases, an approximately linear relationship is seen in each system. A comparison between the solubility of diuron in the presence and absence of PMOS is shown in Figures 4.6 to 4.13. Appendix A includes the log solubility of diuron versus fraction of CMOS graphs for every PMOS in each of the four systems.

I. Effect of PMOS on the Solubility of Diuron

A) Methanol-Water System

Figure 4.2 illustrates a comparison between the solubility of diuron in the methanol-water system with and without PMOS (TCE, toluene). The addition of TCE did not produce an increase in solubility. However, toluene increased the solubility of diuron as much as five times.

B) Acetone-Water System

Figure 4.3 shows the solubility of diuron in the acetone-water system with different PMOS's. A linear relationship is observed between the fraction of

acetone-water and the log solubility with different PMOS's. This figure shows that TCE decreased the solubility; while toluene only slightly affected the solubility of diuron.

C) Acetonitrile-Water System

Figure 4.4 shows the solubility of diuron in the acetonitrile-water system with different PMOS's. At higher fractions of acetonitrile-water mixtures (0.4 - 0.5) the solubility of diuron levels off. This phenomenon maybe due to the volume change upon mixing or mutual solubility. During the experiment an expansion of the PMOS layer is seen after rotation.

D) Propylene Glycol-Water System

Figure 4.5 represents the effect of the presence of PMOS on the solubility of diuron in the propylene glycol-water system. The diuron solubilities with and without the addition of PMOS are similar for this system.

E) Effect of the Presence of TCE

Figures 4.6 to 4.9 show the comparison of the solubility of diuron with the presence and absence of

TCE in the methanol-water, acetone-water, acetonitrile-water and propylene glycol-water systems. Similarities in the solubility of diuron in the absence and the presence of TCE are observed in both the methanol-water and propylene glycol-water systems. TCE does not increase the solubility of diuron in the propylene glycol-water and methanol-water systems. In the acetone-water and acetonitrile-water systems, the addition of TCE results in a decrease of the solubility of diuron.

F) Effect of the Presence of Toluene

Figures 4.10 to 4.13 compare the solubility of diuron in the presence and absence of toluene in the methanol-water, acetone-water, acetonitrile-water and propylene glycol-water systems. Only in the methanol-water system is the solubility of diuron significantly increased. No great differences are seen in the solubility of diuron in the absence and presence of toluene in the other three CMOS-water systems.

Appendix B contains the graphs for the log solubility of diuron versus fraction of CMOS for trichloroethylene (TCE) and toluene in all four of the CMOS-water systems. The solubility of diuron is highest

in the acetonitrile-water system and is followed, in descending order, by acetone-water, methanol-water and propylene glycol-water systems.

Solubility of PMOS in CMOS-Water Mixtures

Figures 4.14 to 4.15 compare the solubility of both PMOS's in all the CMOS-water systems. Appendix C contains the solubility of both PMOS's in the four CMOS-water systems.

Figure 4.14 shows the log solubility of trichloroethylene versus fraction of CMOS. Except for the acetonitrile-water system, a curvature is observed in all of the systems. Although the acetonitrile-water system shows the highest diuron solubility, the solubility of TCE is highest in the acetone-water system followed by acetonitrile-water, methanol-water and propylene glycol-water systems. After the 0.4 fraction of acetonitrile in the acetonitrile-water system the trichloroethylene concentration increases slowly compared to the TCE concentration in the other systems.

Figure 4.15 compares the log solubility of toluene versus fraction of CMOS. A sigmoidal curve is seen in the propylene glycol-water and acetone-water systems.

The acetone-water system has the highest toluene solubility followed by acetonitrile-water, methanol-water and propylene glycol-water systems. At the higher fractions (0.4 - 0.5) of the acetonitrile-water system, the toluene concentration did not increase as rapidly as in the lower fractions. The previous figure shows that with the addition of toluene the solubility of diuron increases. The amount of toluene in the system did not increase proportionally with the higher fractions and results in a decrease of the cosolvent effect. This may explain why the solubility of diuron levels off in the higher fractions of acetonitrile-water.

Solubility of Diuron in Pure Solvents

Table 4.1 lists the solubility of diuron in pure solvents, including the CMOS's and the PMOS's. The solubility of diuron is highest in acetonitrile, followed in descending order by acetone, methanol and propylene glycol. And diuron is more soluble in TCE than toluene.

Regression Parameters and Aqueous Solubilities

Table 4.2 lists the regression parameters, σ_c^d, σ_c^p, and σ_p^d. These three regression parameters are determined in binary systems. σ_c^d is the slope of the solubility curve of diuron in cosolvent-water mixture in the absence of PMOS; σ_c^p is the slope of the solubility curve of PMOS in cosolvent-water mixture; and σ_p^d is the slope of the solubility curve of diuron in PMOS-water mixture. Table 4.3 lists the aqueous solubilities for diuron, toluene and TCE. Since the solubilities of toluene and trichloroethylene are very low, it is very difficult to determine the solubility of diuron in the PMOS-water mixture. Therefore, the σ_p^d determination is based on two data points only (0% and 100%).

TABLE 4.1

SOLUBILITY OF DIURON IN PURE SOLVENT

SOLVENT		LOG SOLUBILITY*
PMOS	TOLUENE	3.275
	TRICHLORO-ETHYLENE	3.455
CMOS	METHANOL	4.616
	ACETONE	4.482
	ACETONITRILE	4.178
	PROPYLENE GLYCOL	4.144

* µg/ml

TABLE 4.2

BINARY PARAMETERS

SOLUTE (d)	CMOS (c)	SLOPE (σ_c^d)	R^2
DIURON	METHANOL	2.988	0.961
DIURON	ACETONITRILE	4.565	0.995
DIURON	ACETONE	4.385	0.998
DIURON	PROPYLENE GLYCOL	2.217	0.982

SOLUTE (d)	PMOS (p)	SLOPE (σ_p^d)	R^2
DIURON	TOLUENE	1.722	-
DIURON	TCE	3.444	-

SOLUTE (p)	CMOS (c)	SLOPE (σ_c^p)	R^2
TOLUENE	METHANOL	1.373	0.941*
TOLUENE	ACETONITRILE	2.367	0.983
TOLUENE	ACETONE	2.921	0.986
TOLUENE	PROPYLENE GLYCOL	1.452	0.965
TCE	METHANOL	2.032	0.914
TCE	ACETONITRILE	1.631	0.993
TCE	ACETONE	2.202	0.980*
TCE	PROPYLENE GLYCOL	0.744	0.995

* regression based on the first four data points

TABLE 4.3

AQUEOUS SOLUBILITIES (µg/ml)

COMPOUND	LOG SOLUBILITY
DIURON	1.560
TCE	0.011
TOLUENE	-0.369

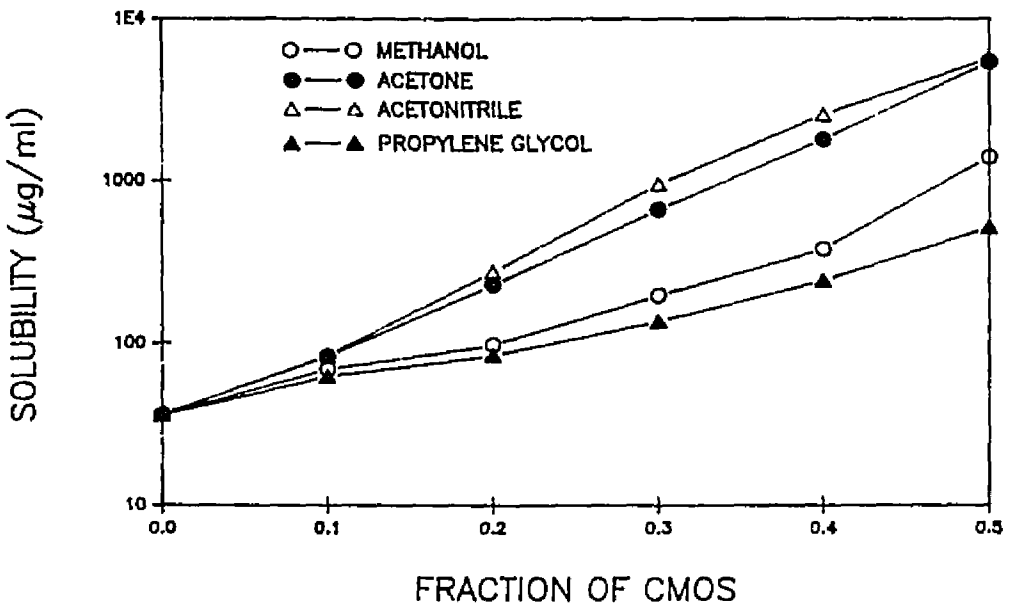


Figure 4.1: Solubility of Diuron in CMOS/water

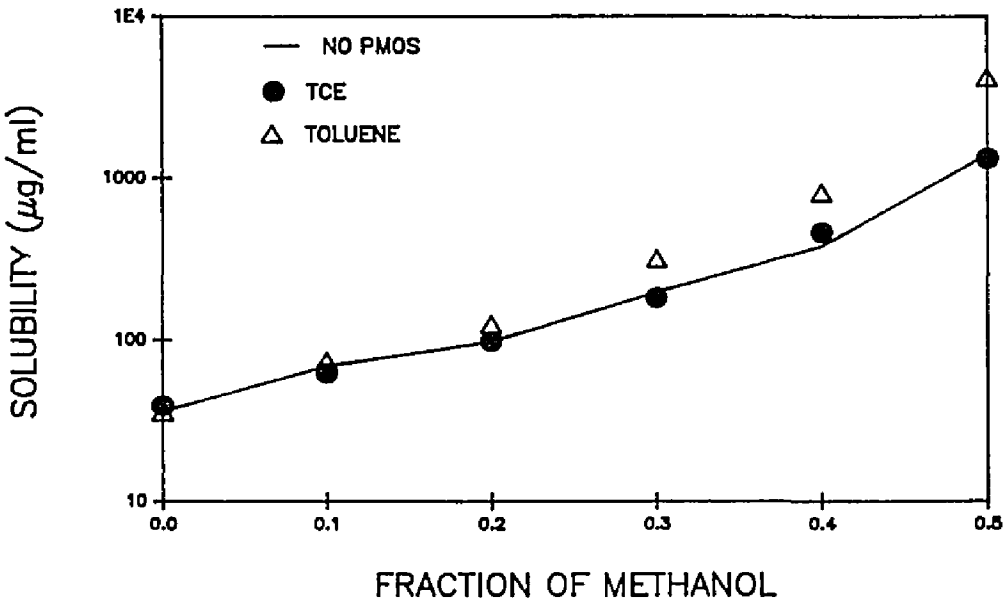


Figure 4.2: Solubility of Diuron in Methanol/water
Effect of the Presence of PMOS

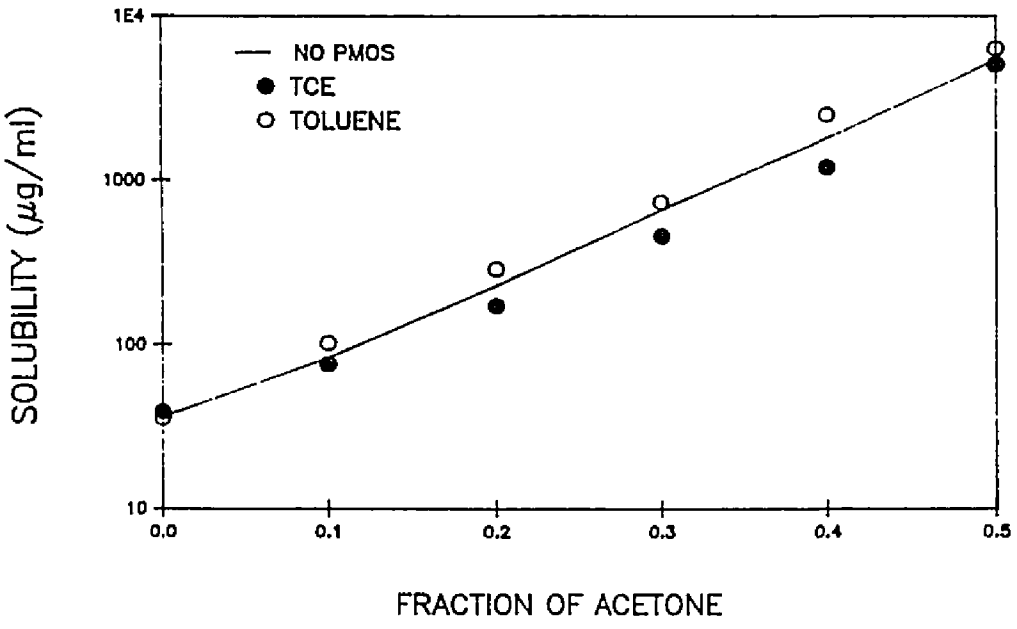


Figure 4.3: Solubility of Diuron in Acetone/water
Effect of the Presence of PMOS

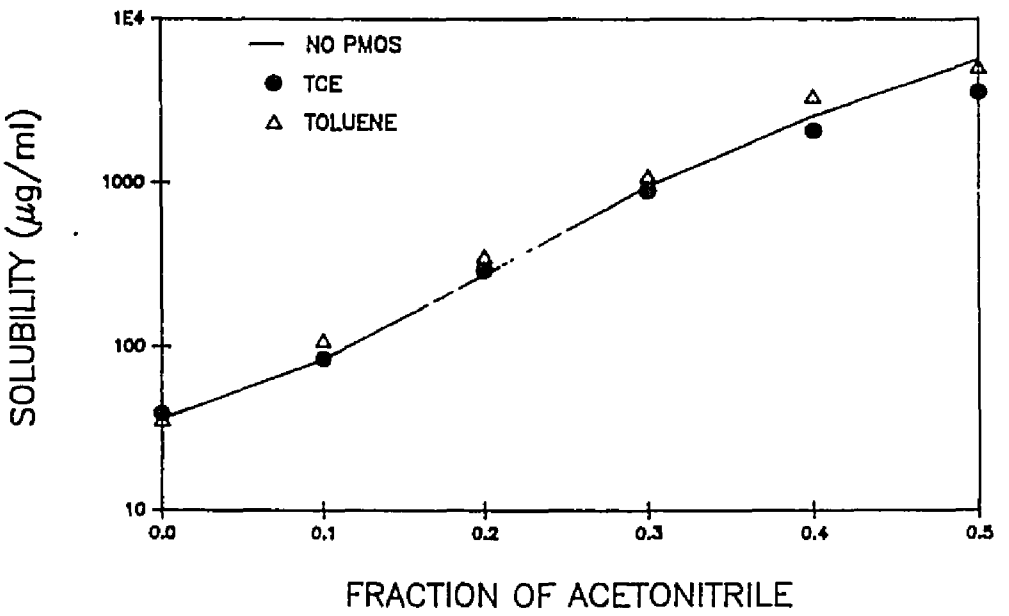


Figure 4.4: Solubility of Diuron in ACN/water
Effect of the Presence of PMOS

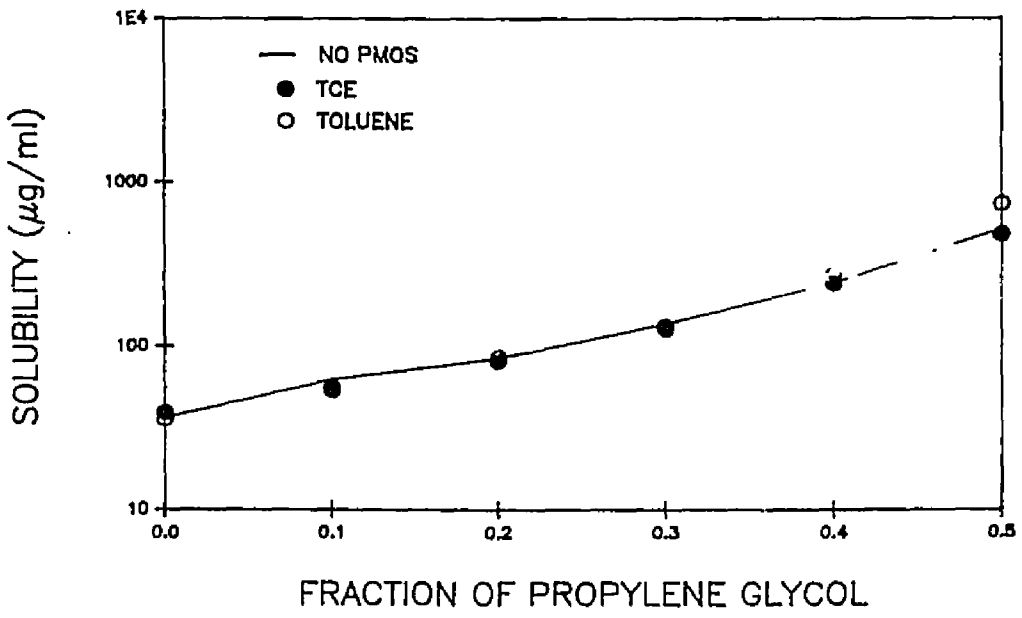


Figure 4.5: Solubility of Diuron in PG/water
Effect of the Presence of PMOS

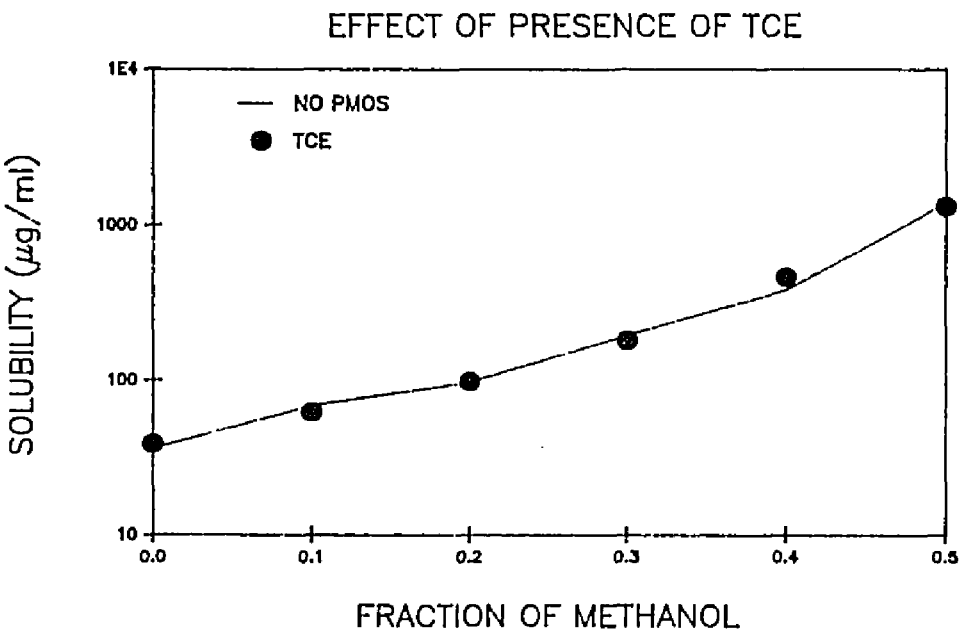


Figure 4.6: Solubility of Diuron in Methanol/water
Effect of the Presence of TCE

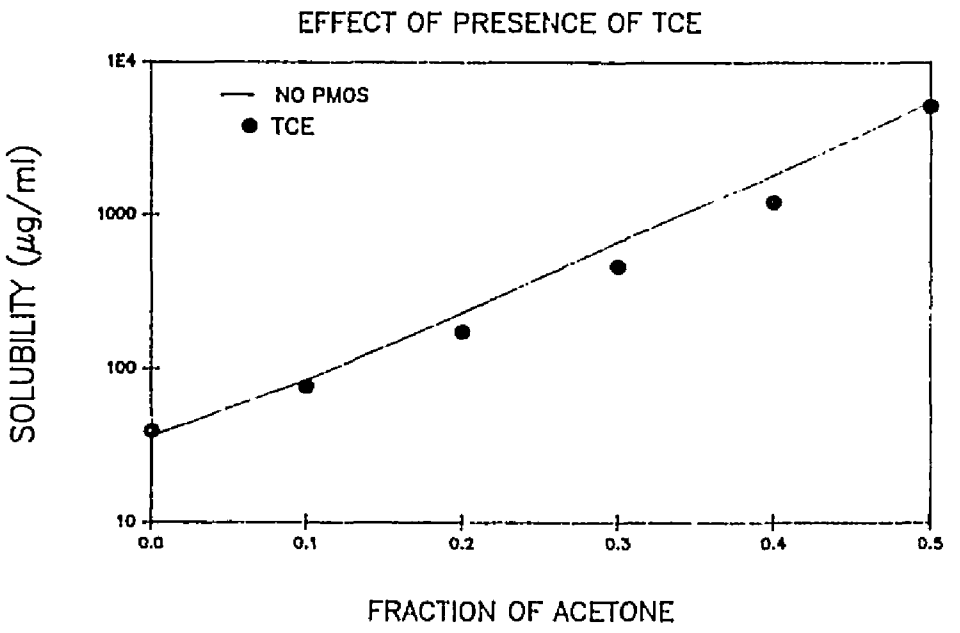


Figure 4.7: Solubility of Diuron in Acetone/water
Effect of the Presence of TCE

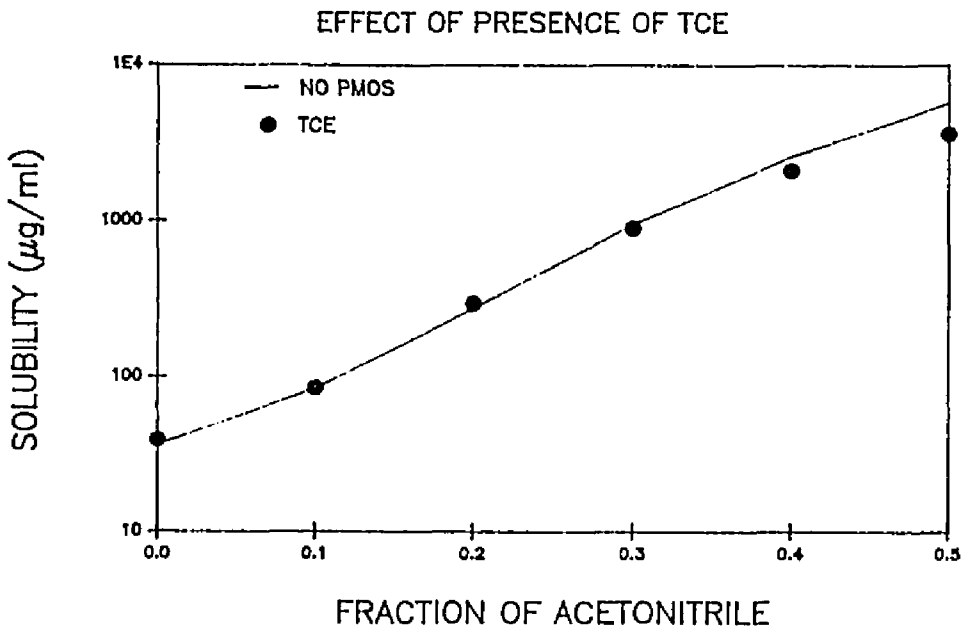


Figure 4.8: Solubility of Diuron in ACN/water
Effect of the Presence of TCE

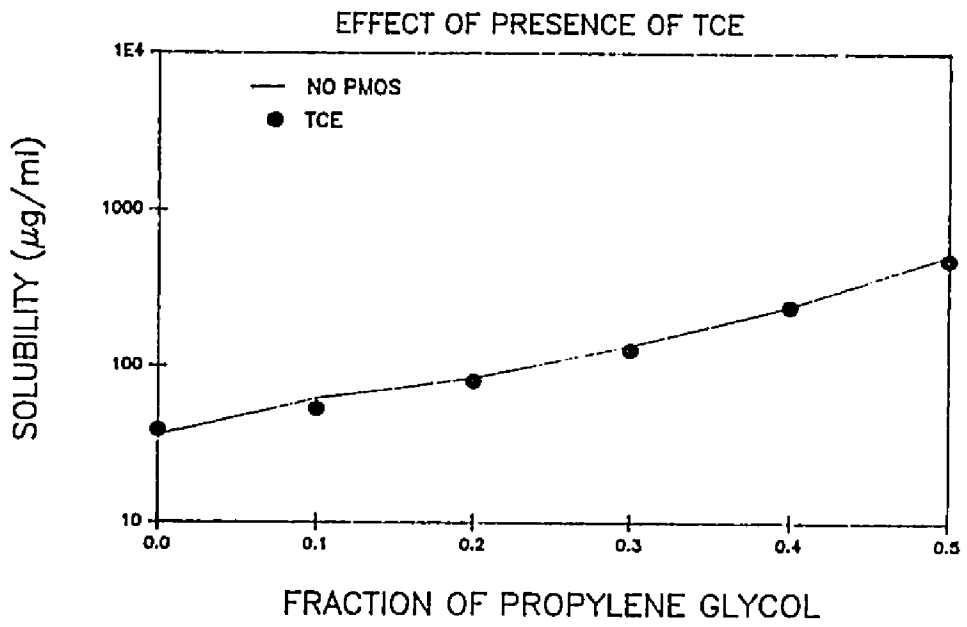


Figure 4.9: Solubility of Diuron in PG/water
Effect of the Presence of TCE

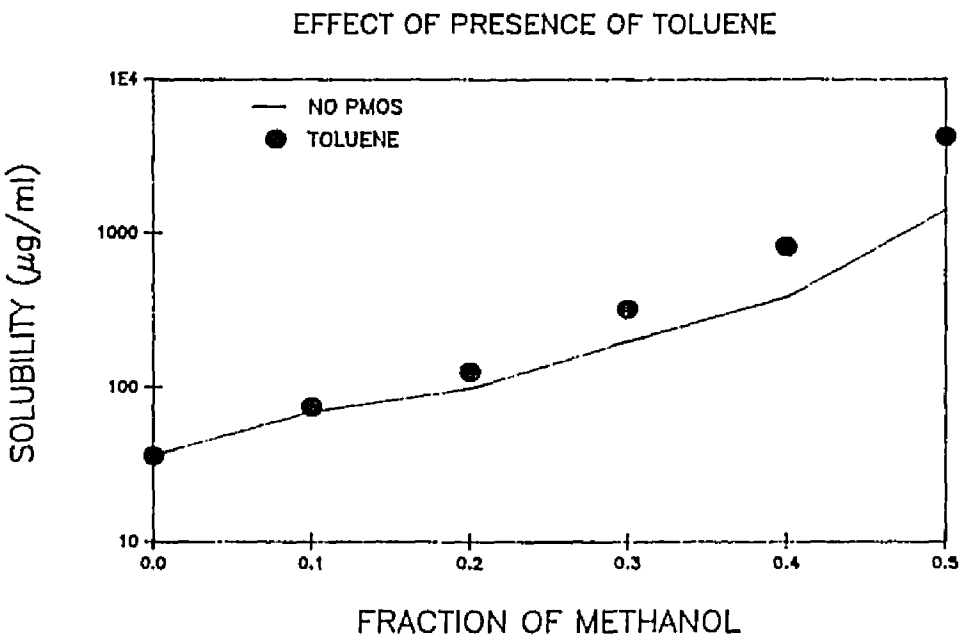


Figure 4.10: Solubility of Diuron in Methanol/water
Effect of the Presence of Toluene

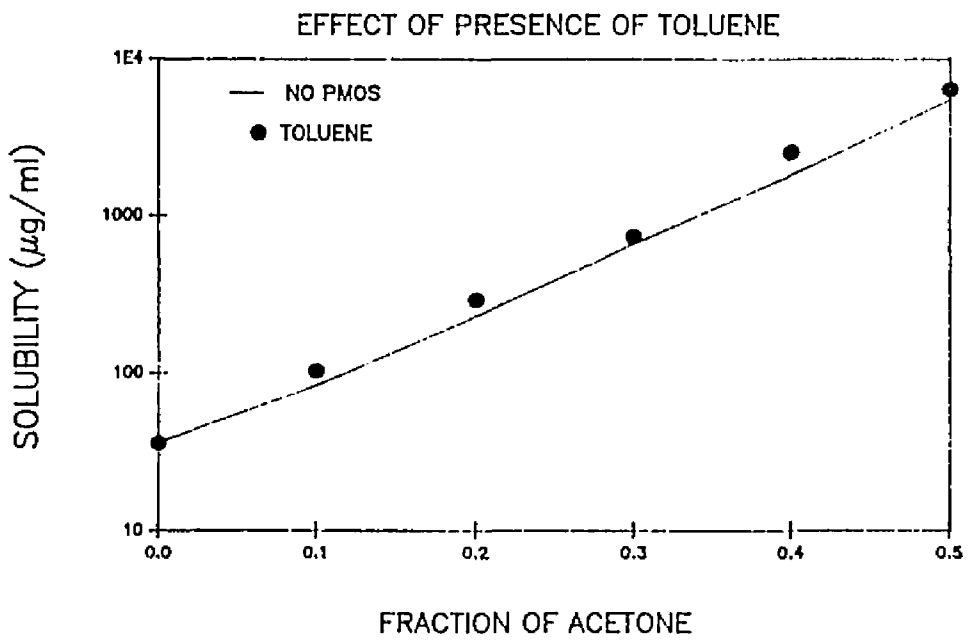


Figure 4.11: Solubility of Diuron in Acetone/water
Effect of the Presence of Toluene

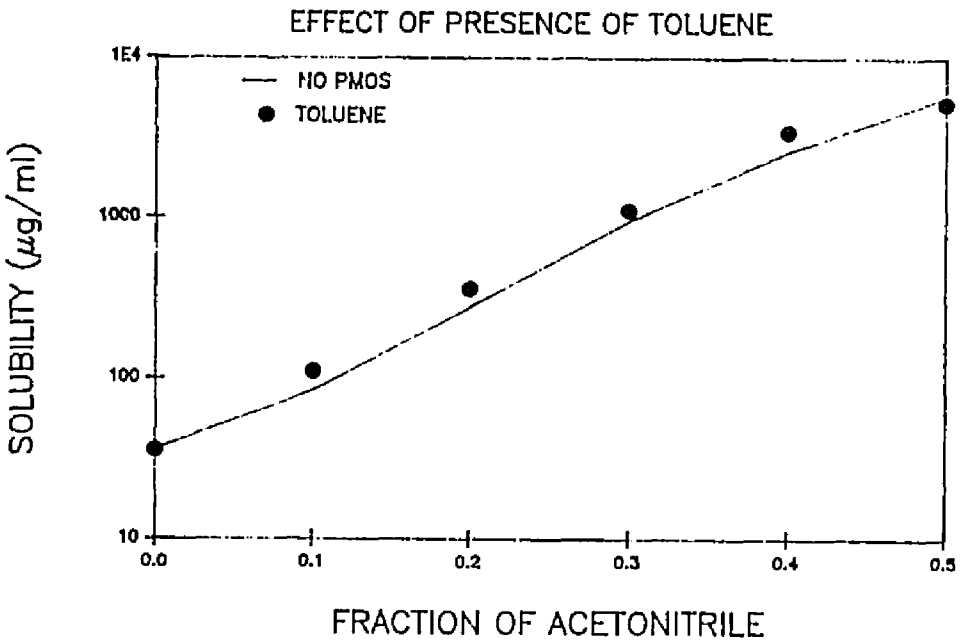


Figure 4.12: Solubility of Diuron in ACN/water
Effect of the Presence of Toluene

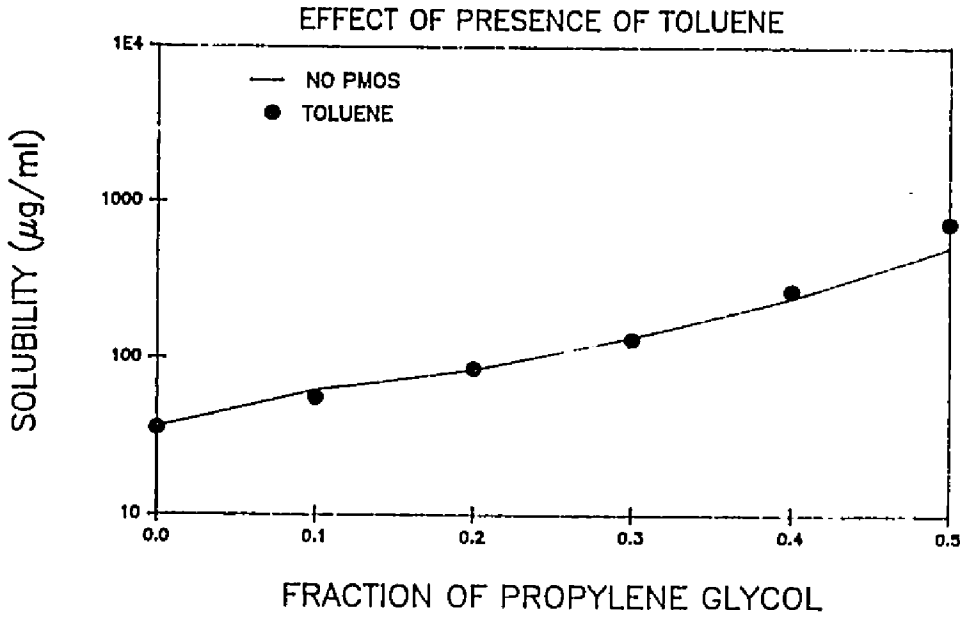


Figure 4.13: Solubility of Diuron in PG/water
Effect of the Presence of Toluene

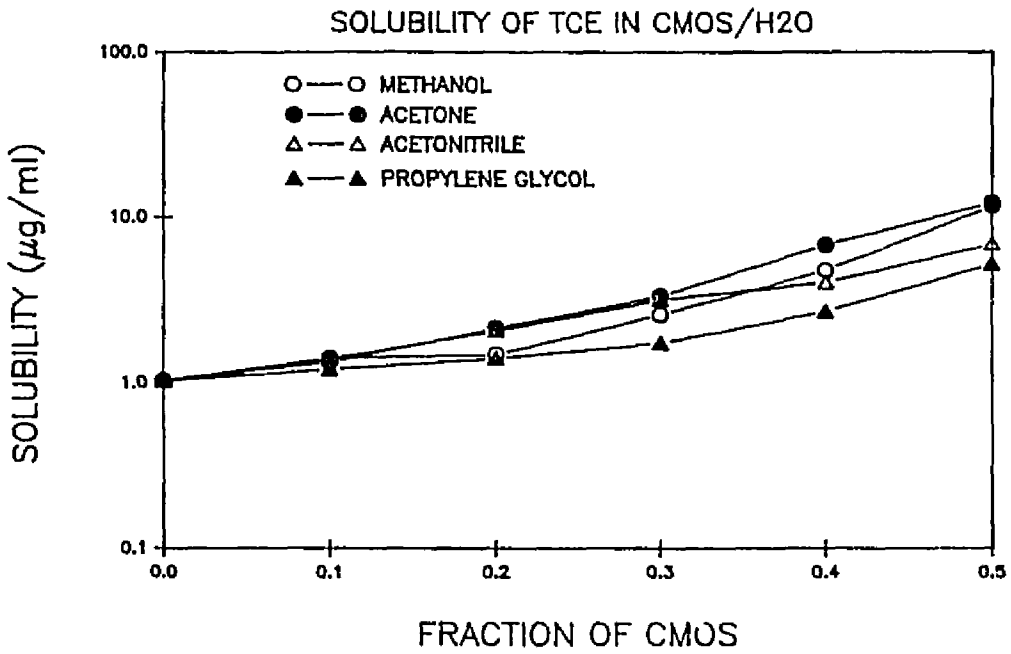


Figure 4.14: Solubility of Trichloroethylene in CMOS/water

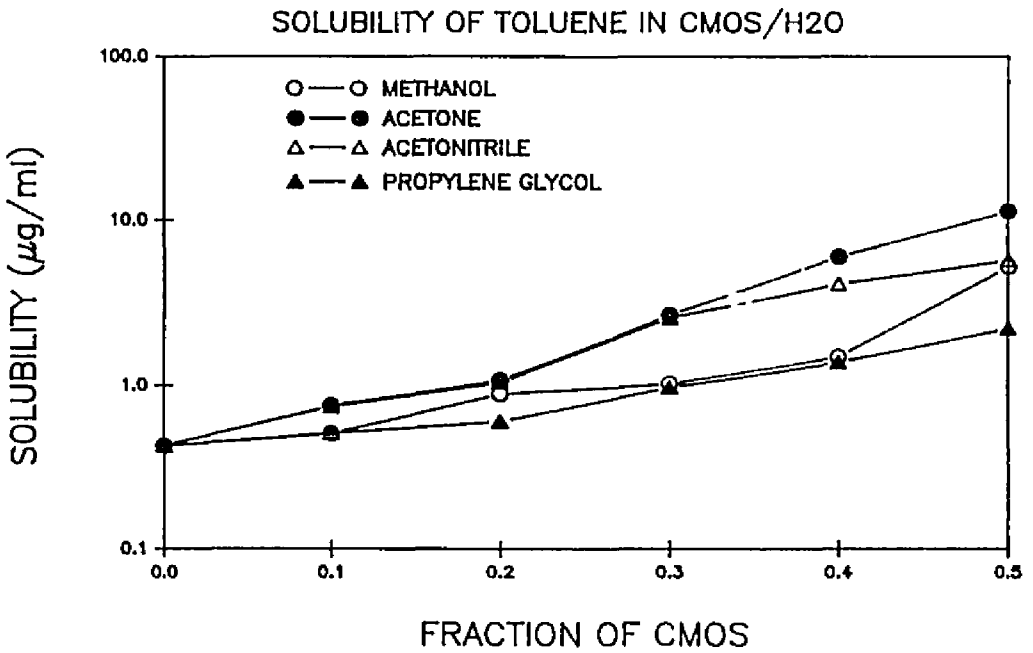


Figure 4.15: Solubility of Toluene in CMOS/water

CHAPTER 5

DISCUSSION

As stated above, a system which includes PMOS, CMOS, and water is called a complex solvent system. As indicated by Equation 2.13, the solubility of a chemical in a complex solvent system can be predicted from its own and the PMOS' solubilities in pure water and with three other binary parameters (i.e. σ_c^d, σ_c^p, σ_p^d). These are listed in Table 4.2, and the aqueous solubilities are listed in Table 4.3. Using the data in Tables 4.2 and 4.3, and Equation 2.13, the following equations can be obtained for predicting the solubility of diuron.

I. CMOS-Water Systems Saturated with <u>Toluene</u>

a) Acetonitrile-Water System

$$\log S^d_{c,p,w} = 1.560 + 4.565\ f_c + (8.493 * 10^{-4}) * 10^{2.367\ f_c} \qquad (5.1)$$

b) Acetone-Water System

$$\log S^d_{c,p,w} = 1.560 + 4.385\ f_c + (8.493 * 10^{-4}) * 10^{2.921\ f_c} \qquad (5.2)$$

c) Methanol-Water System

$$\log S^{d}_{c,p,w} = 1.560 + 2.988\ f_c + (8.493 * 10^{-4}) * 10^{1.971\ f_c} \quad (5.3)$$

d) Propylene Glycol-Water System

$$\log S^{d}_{c,p,w} = 1.560 + 2.217\ f_c + (8.439 * 10^{-4}) * 10^{1.452\ f_c} \quad (5.4)$$

II. CMOS-Water Systems Saturated with <u>TCE</u>

a) Acetonitrile-Water System

$$\log S^{d}_{c,p,w} = 1.560 + 4.565\ f_c + (2.371 * 10^{-3}) * 10^{1.631\ f_c} \quad (5.5)$$

b) Acetone-Water System

$$\log S^{d}_{c,p,w} = 1.560 + 4.385\ f_c + (2.371 * 10^{-3}) * 10^{2.202\ f_c} \quad (5.6)$$

c) Methanol-Water System

$$\log S^{d}_{c,p,w} = 1.560 + 2.989\ f_c + (2.371 * 10^{-3}) * 10^{2.032\ f_c} \qquad (5.7)$$

d) Propylene Glycol-Water System

$$\log S^{d}_{c,p,w} = 1.560 + 2.217\ f_c + (2.371 * 10^{-3}) * 10^{0.744\ f_c} \qquad (5.8)$$

All of the above equations follow the general form:

$$\log S^{D}_{c,p,w} = a + b\ f_c + c\ 10^{d\ f_c} \qquad (5.9)$$

Where "a" is the aqueous solubility of the chemical and is constant in each of the above equations; "b" is also a constant dependent on the CMOS used; "c" is a constant dependent on the particular PMOS used, and is also related to the aqueous solubility and density of PMOS and the slope of the solubility curve of diuron in the PMOS-water mixture; "d" varies in each of the CMOS-water mixtures because it is dependent on both the CMOS and

PMOS used. The constants of each equation for each particular system are listed in Table 5.1.

The second term on the right side of Equation 5.9 predicts the increase of the chemical solubility due to the presence of the CMOS. And the last part of the equation represents the increase of the chemical solubility resulting from the addition of the PMOS. "d" is the exponent of 10, and therefore has a greater influence in determinating the solubility of diuron. A small deviation may cause a large effect on the predicted solubility.

Because of the low aqueous solubilities of TCE and toluene, the "c" term is relatively small. It is not significant in contributing to the predicted solubility. Therefore, instead of a curvature in the predicted solubility graph, a linear predicted solubility curve is obtained. Figure 5.1 shows the observed versus predicted solubility in methanol-water mixture with methyl t-butyl ether as the PMOS for anthracene. The predicted solubility has a curvature in this figure, which implies that the methyl t-butyl ether can behave as a cosolvent and alter the solubility of anthracene. A similar graph was expected from this diuron study. But due to the very low aqueous solubilities of TCE and

toluene, the "c" term is relatively small and will not play an important role on the solubility determination. Therefore, the model equation can be simplified to the following equation:

$$\log S^{d}_{c,p,w} = \log S^{d}_{w} + \sigma^{d}_{c} f_{c} \qquad (5.10)$$

Based on this equation, the solubility of diuron can be predicted. There is no significant difference between the data from Equation 2.13 and Equation 5.10.

Figures 5.2 to 5.5 show the comparison of the observed solubility versus the predicted solubility of diuron. As can be seen in each of the graphs, the predicted solubility in most cases is in good agreement with the experimental value. In the acetone-water and methanol-water systems with TCE as the PMOS (Figures 5.3 and 5.4), the observed data show a curve and the predicted values are higher than the observed values for the middle region of the fractions. According to Rubino and Yalkowsky (1987), the deviations from the log-linear behavior are primarily due to the cosolvent-water interactions. Therefore, the deviations in the two graphs may be explained by the interactions between the solvents. At low cosolvent fractions, water is being restructured with the cosolvents. These water-

cosolvent interactions make the cosolvent a poorer solvent and alter its solubilizing power. Therefore, log S_m is no longer proportional to the volume fraction of cosolvent and produces a lower solubility than expected.

This model assumes that water interacts the same with the solute at all water concentrations. The water which contributes to the solubilization of the solute is assumed to be proportional only to the volume fraction of water. However, water is no longer in the hydrogen bonded lattice and is less able to exclude a nonpolar solute from the solution. At high cosolvent fractions the system is more loosely structured and has less interactions with other water molecules compared to the lower fractions. So, the water is relatively free to interact with the solute and acts like a "better" solvent than is predicted by the model. This may explain why the observed solubility is higher than the predicted solubility in Figure 5.8 for the methanol-water system with toluene at higher fractions (0.4 and 0.5).

TABLE 5.1

Summary of the Coefficients

$$\log S^{d}_{c,p,w} = a + b\, f_c + c\, 10^{d\, f_c}$$

CMOS	PMOS	a	b	$c*10^4$	d
ACN	TOL	1.560	4.565	8.493	2.367
ACE	TOL	1.560	4.385	8.493	2.921
MeOH	TOL	1.560	2.989	8.493	1.971
PG	TOL	1.560	2.217	8.493	1.452
ACN	TCE	1.560	4.565	23.71	1.631
ACE	TCE	1.560	4.385	23.71	2.202
MeOH	TCE	1.560	2.989	23.71	2.032
PG	TCE	1.560	2.217	23.71	0.744

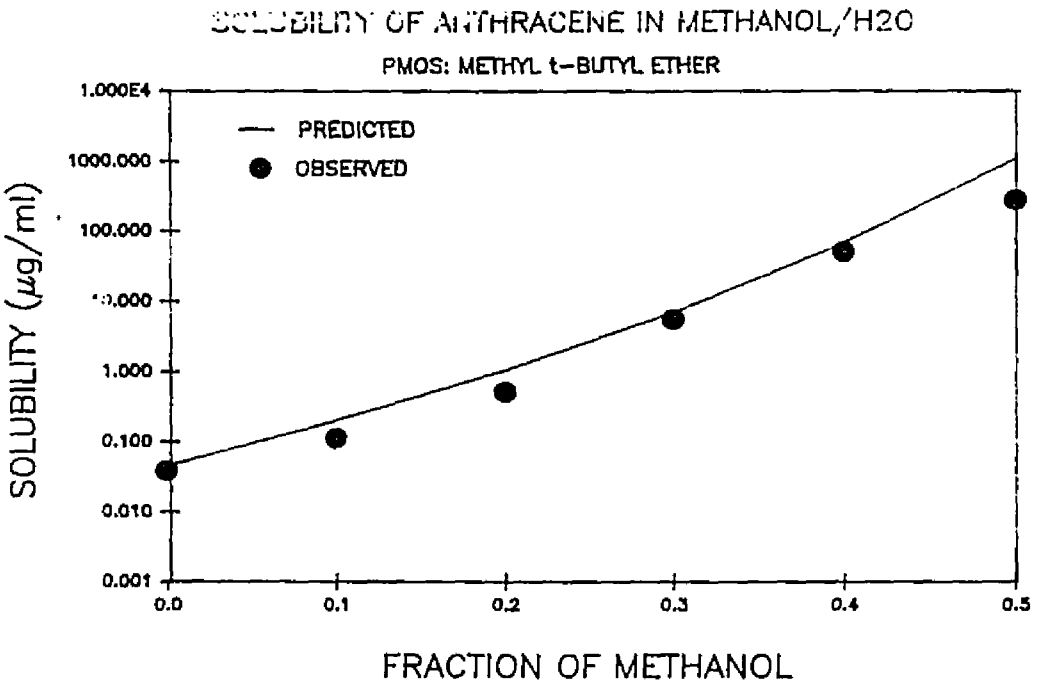


Figure 5.1: Observed versus Predicted Solubility Solubility of Anthracene in Methanol-water System with Methyl t-Butyl Ether

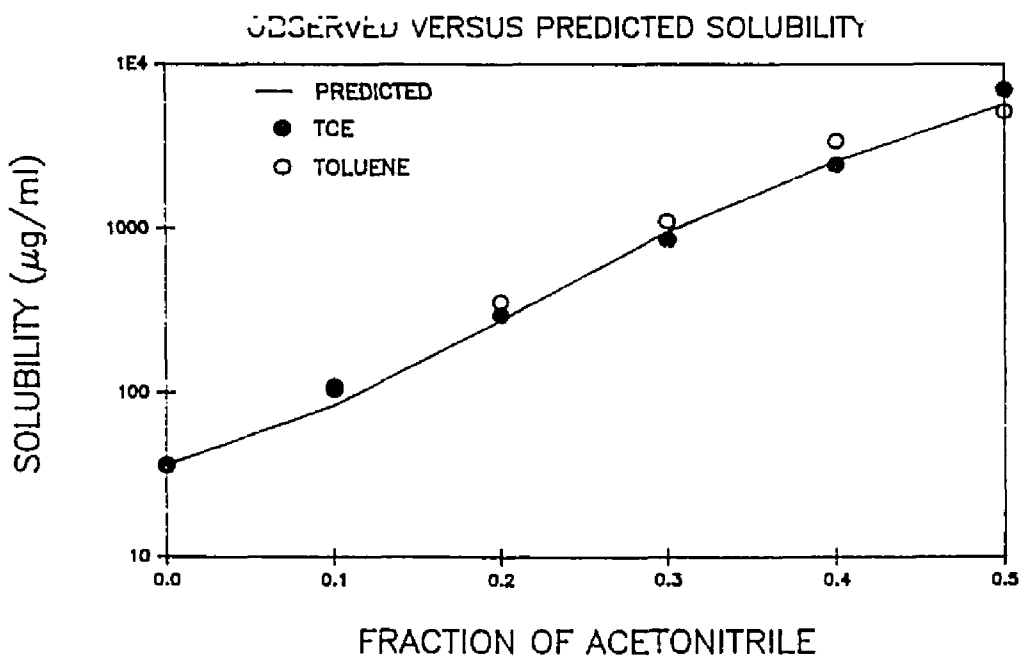


Figure 5.2: Observed versus Predicted Solubility
Effect of PMOS in Acetonitrile/water

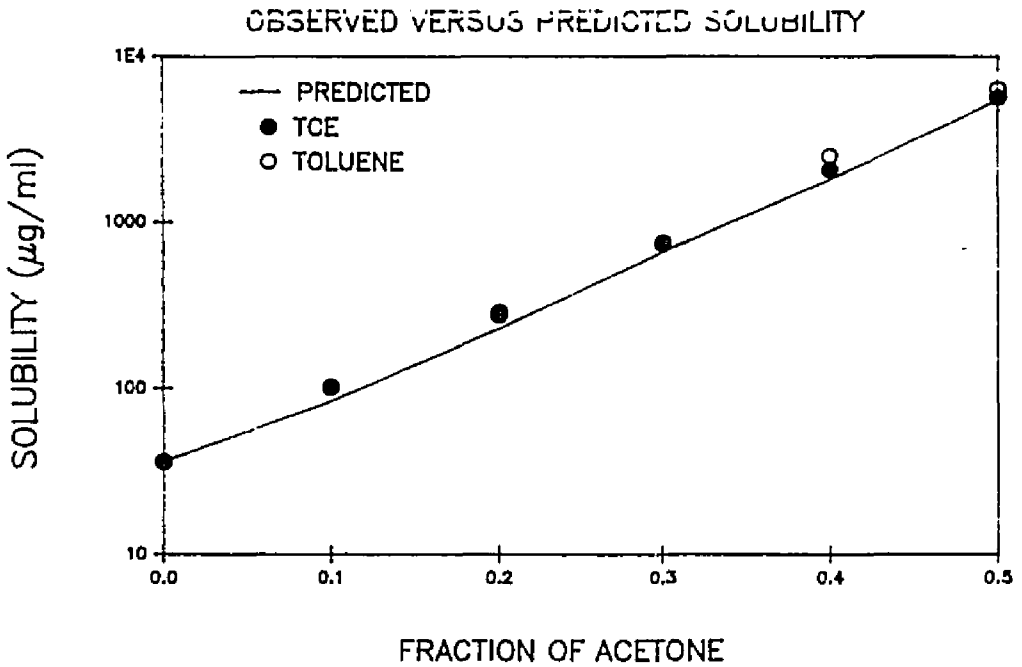


Figure 5.3: Observed versus Predicted Solubility
Effect of PMOS in Acetone/Water

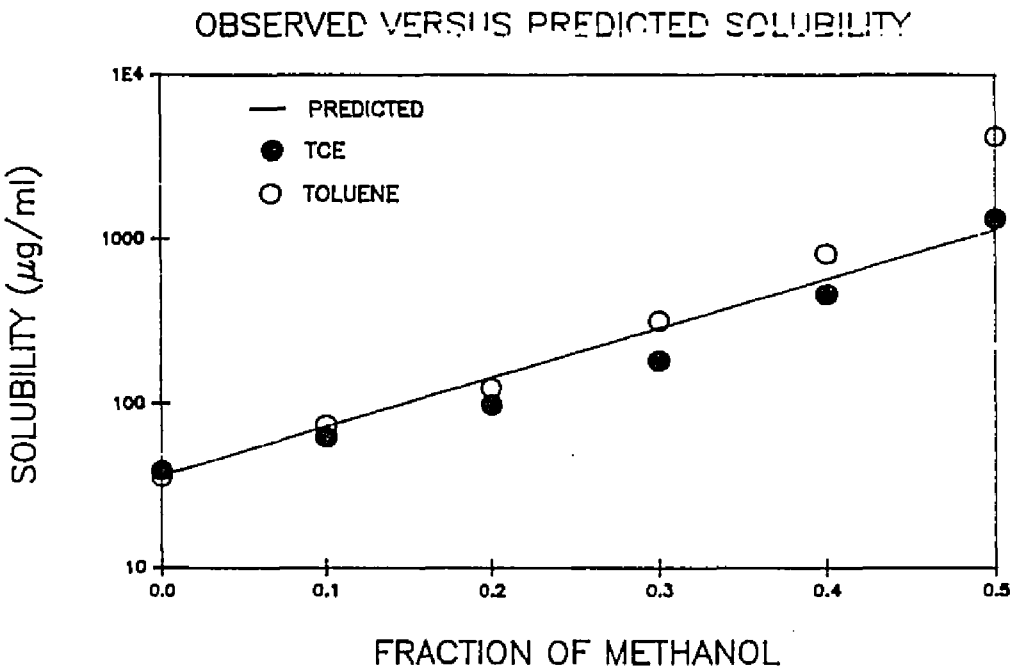


Figure 5.4: Observed versus Predicted Solubility
Effect of PMOS in Methanol/Water

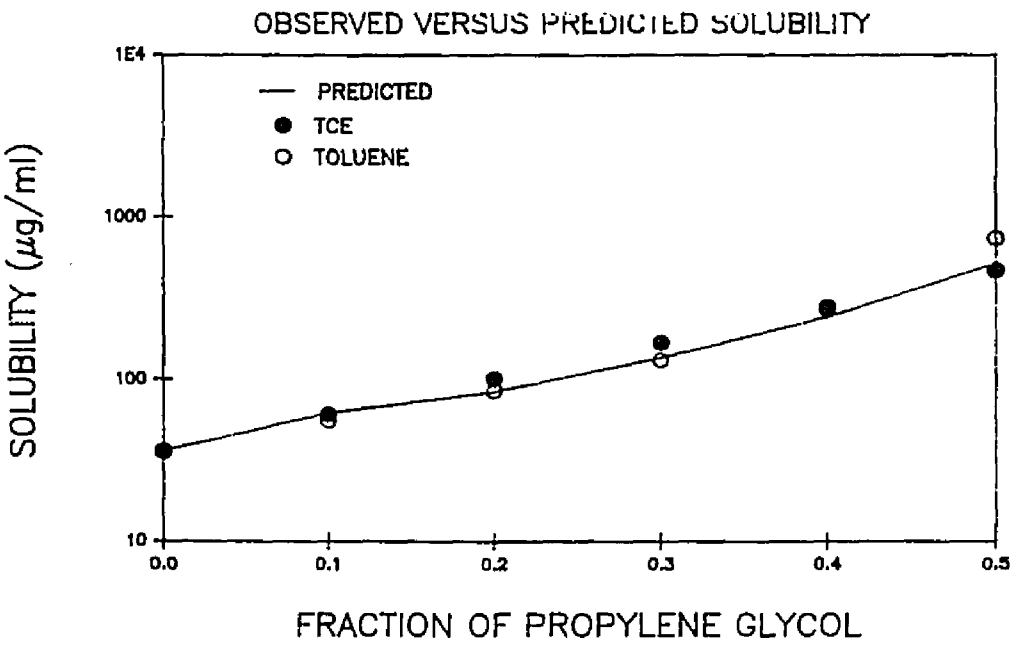


Figure 5.5: Observed versus Predicted Solubility
Effect of PMOS in Propylene Glycol/Water

CHAPTER 6

CONCLUSION

The following model, which was proposed for the solubility of anthracene, is now applied to the solubility of diuron.

$$\log S^{d}_{c,p,w} = \log S^{d}_{w} + f_c \sigma^{d}_{c} + \frac{S^{p}_{w} 10^{f_c \sigma^{p}_{c}}}{D_p} \sigma^{d}_{p}$$

According to this model, the solubility of diuron can be determined from six parameters. They are: the aqueous solubility of diuron ($S^{d}_{c,p,w}$), the slope of the solubility curve of diuron in the CMOS-water mixture (σ^{d}_{c}), the aqueous solubility of the PMOS (S^{p}_{w}), the slope of the solubility curve of PMOS in the CMOS-water mixture (σ^{p}_{c}), the slope of the solubility curve of diuron in the PMOS-water mixture (σ^{d}_{p}), and the density of the PMOS (D_p).

In the sorption study, anthracene is used to represent an ideal hydrophobic sorbate since it does not have any polar functional groups and its total surface area (TSA) is identical to its hydrocarbonaceous surface area (HSA). In contrast to anthracene, diuron has polar

functional groups and this factor causes the total surface area (TSA) to be smaller than the hydrocarbonaceous surface area (HSA).

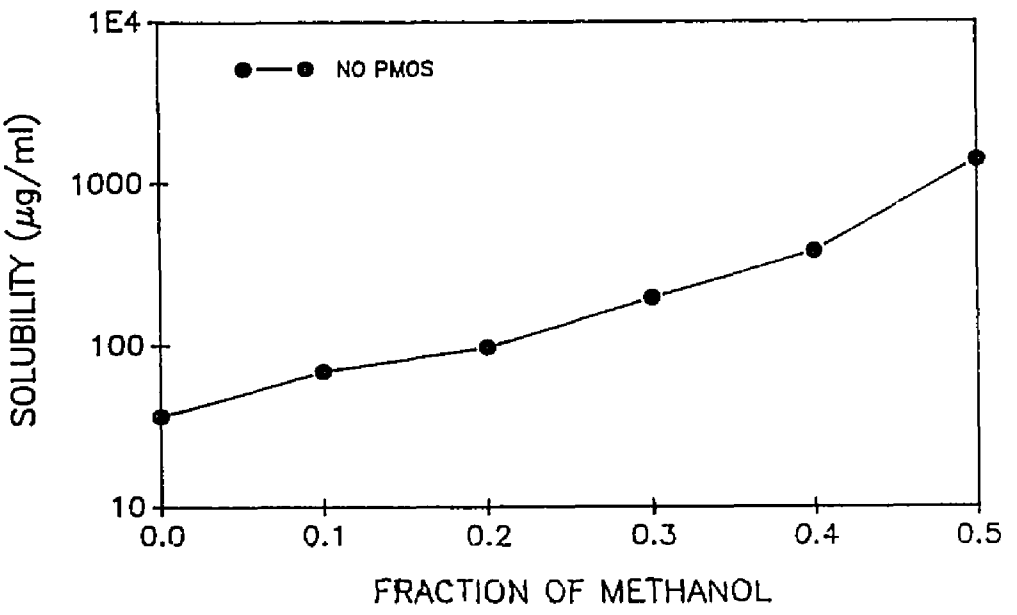
Due to the low aqueous solubilities of TCE and toluene, the "c" term is relatively small and can be omitted. This implies that TCE and toluene do not behave as cosolvents and the solubility of diuron can be predicted from its aqueous solubility and fraction of CMOS. The predicted values agree well with the data obtained from this study.

APPENDIX A

Solubility of Diuron with and without the Partially Miscible Organic Solvent

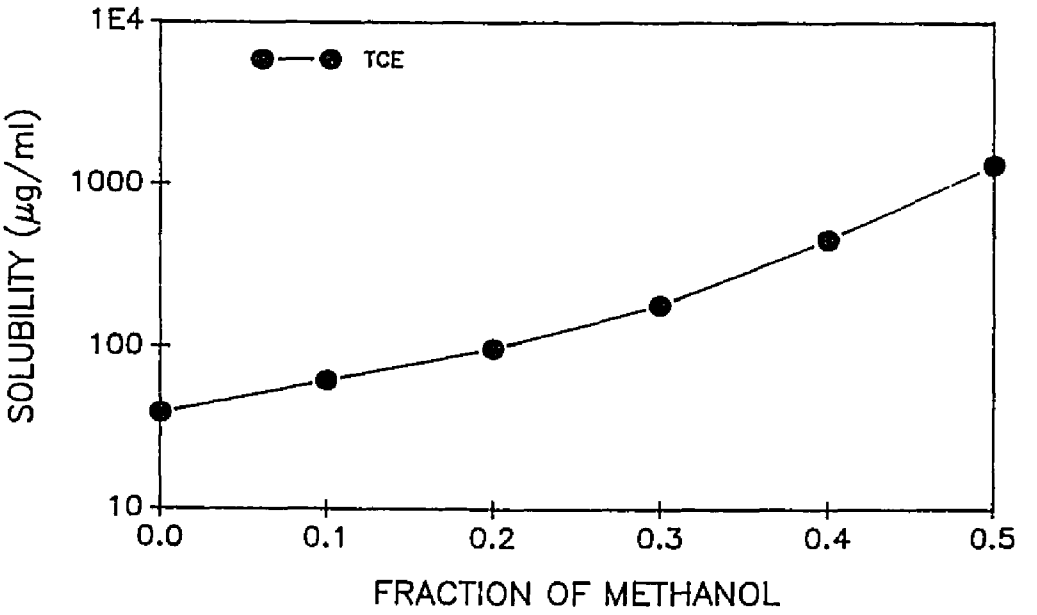
SOLUBILITY OF DIURON IN METHANOL/WATER
PMOS:NONE

Fraction of MeOH	Log Solubility (µg/ml)
0	1.560
0.1	1.838
0.2	1.989
0.3	2.294
0.4	2.580
0.5	3.146



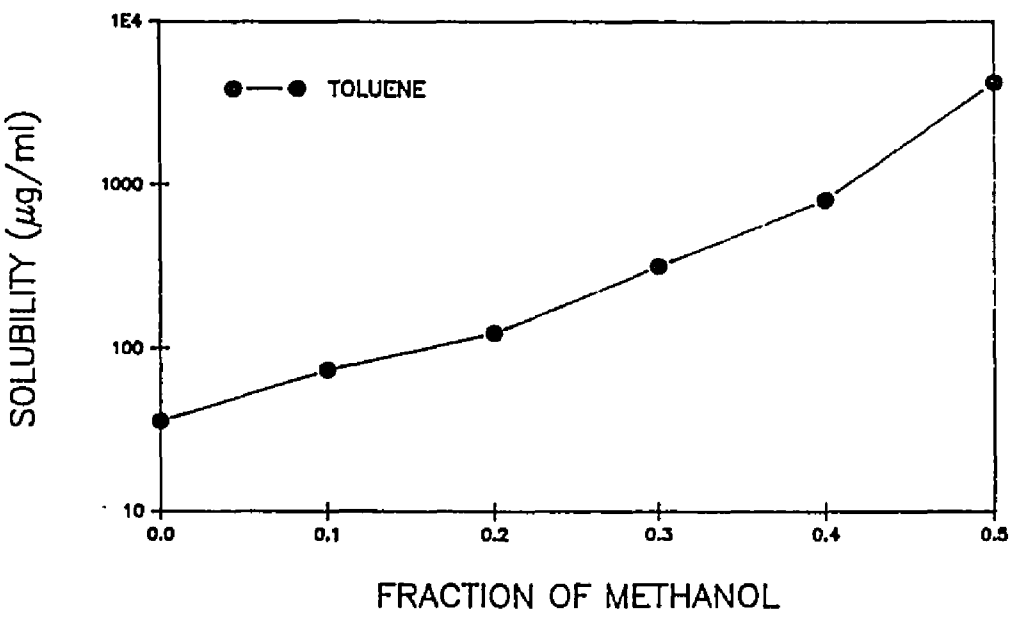
SOLUBILITY OF DIURON IN METHANOL/WATER
PMOS:TRICHLOROETHYLENE

Fraction of MeOH	Log Solubility (µg/ml)
0	1.591
0.1	1.792
0.2	1.990
0.3	2.259
0.4	2.662
0.5	3.121



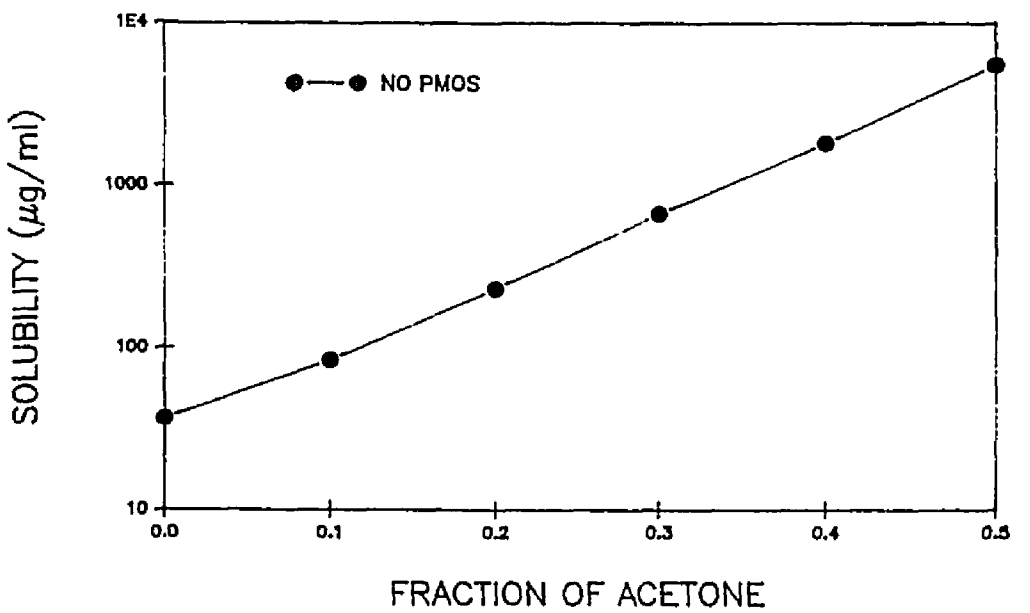
SOLUBILITY OF DIURON IN METHANOL/WATER
PMOS:TOLUENE

Fraction of MeOH	Log Solubility (µg/ml)
0	1.553
0.1	1.866
0.2	2.094
0.3	2.501
0.4	2.907
0.5	3.623



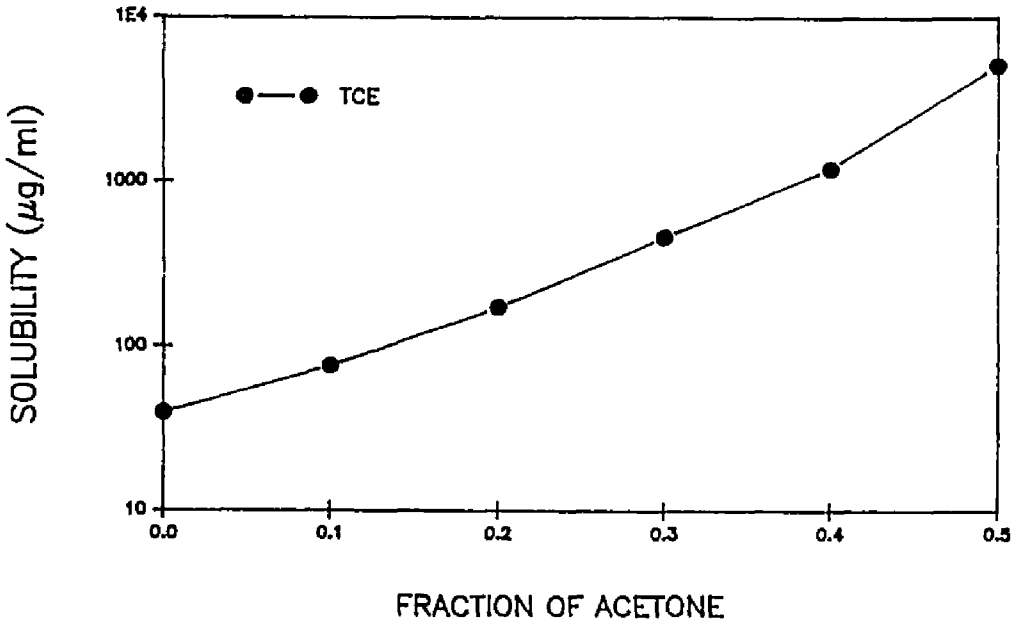
SOLUBILITY OF DIURON IN ACETONE/WATER
PMOS:NONE

Fraction of ACE	Log Solubility (µg/ml)
0	1.560
0.1	1.919
0.2	2.359
0.3	2.821
0.4	3.256
0.5	3.735



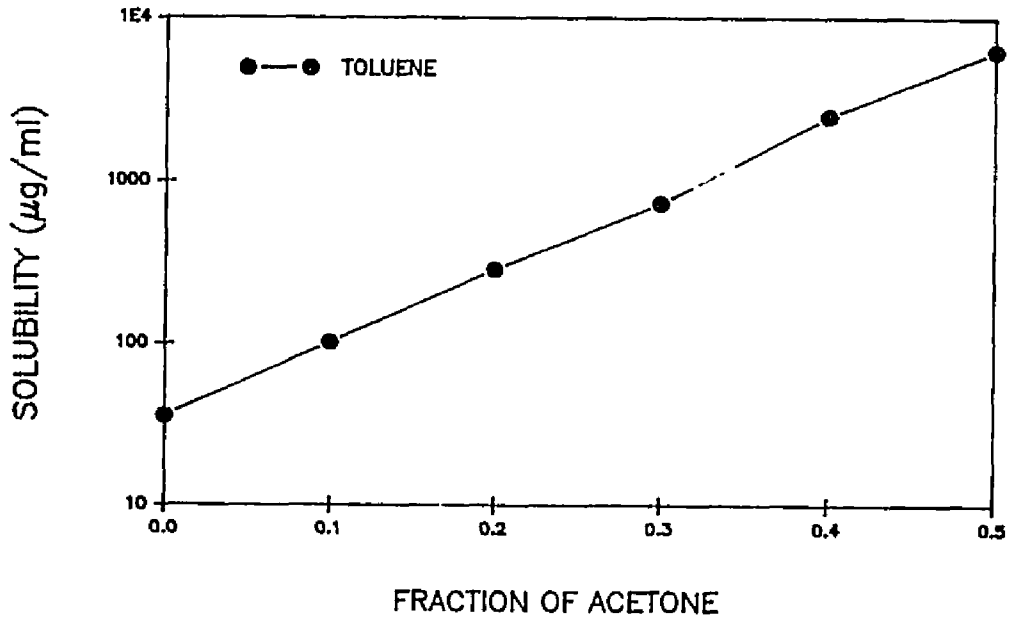
SOLUBILITY OF DIURON IN ACETONE/WATER
PMOS:TRICHLOROETHYLENE

Fraction of ACE	Log Solubility (µg/ml)
0	1.592
0.1	1.878
0.2	2.235
0.3	2.661
0.4	3.077
0.5	3.706



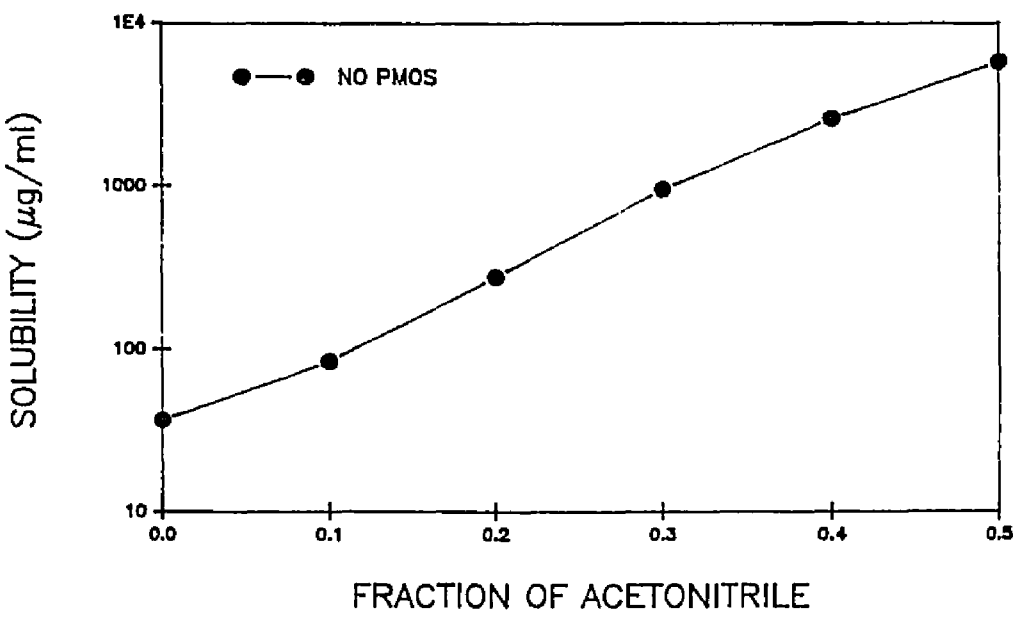
SOLUBILITY OF DIURON IN ACETONE/WATER
PMOS:TOLUENE

Fraction of ACE	Log Solubility (µg/ml)
0	1.553
0.1	2.009
0.2	2.460
0.3	2.865
0.4	2.399
0.5	3.801



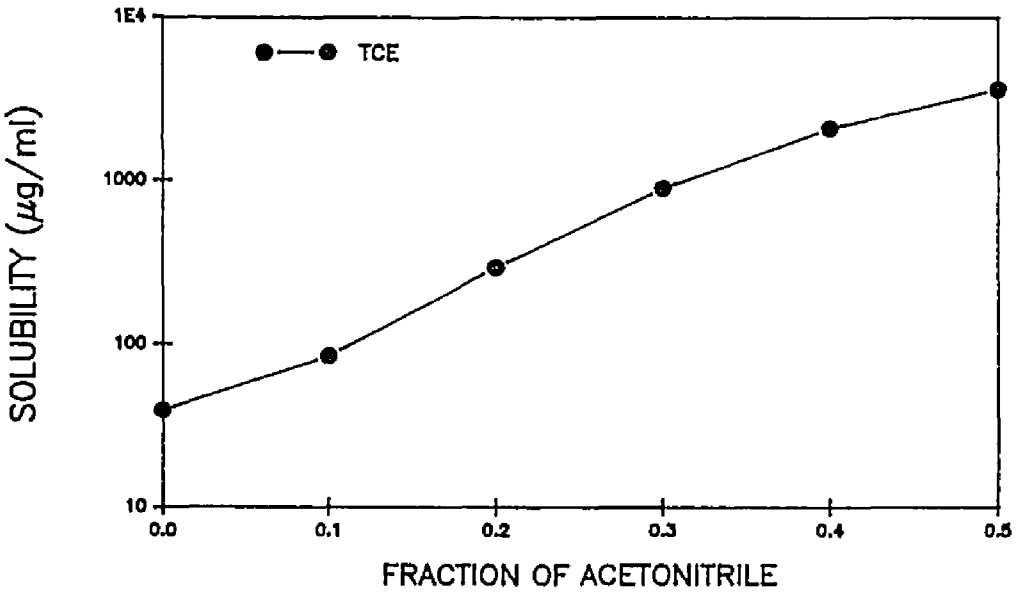
SOLUBILITY OF DIURON IN ACETONITRILE/WATER
PMOS:NONE

Fraction of ACN	Log Solubility (µg/ml)
0	1.560
0.1	1.922
0.2	2.439
0.3	2.977
0.4	3.410
0.5	3.755



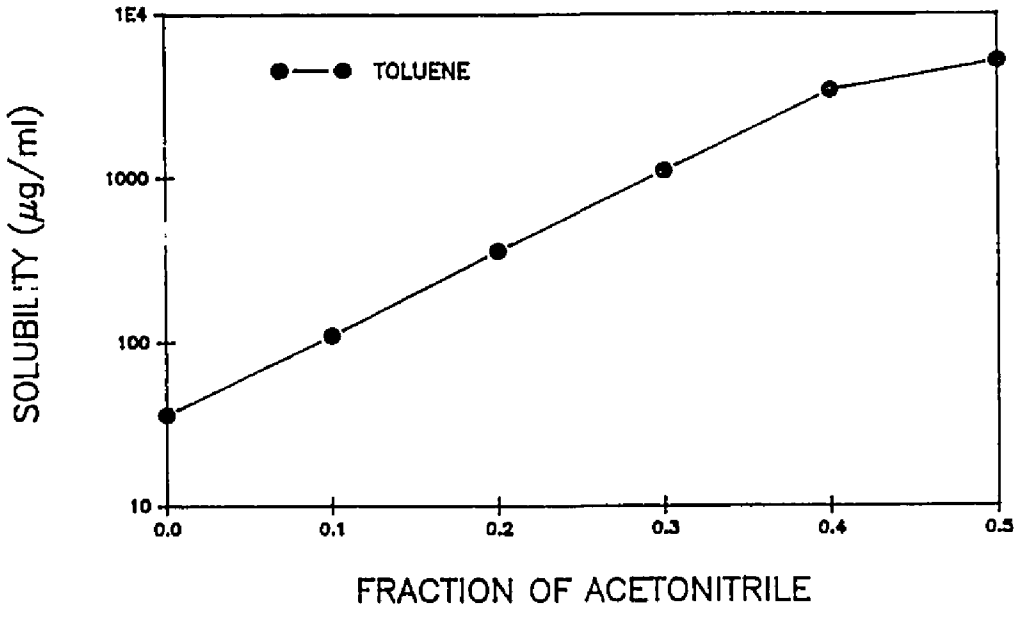
SOLUBILITY OF DIURON IN ACETONITRILE/WATER
PMOS:TRICHLOROETHYLENE

Fraction of ACN	Log Solubility (µg/ml)
0	1.592
0.1	1.926
0.2	2.468
0.3	2.951
0.4	3.318
0.5	3.556



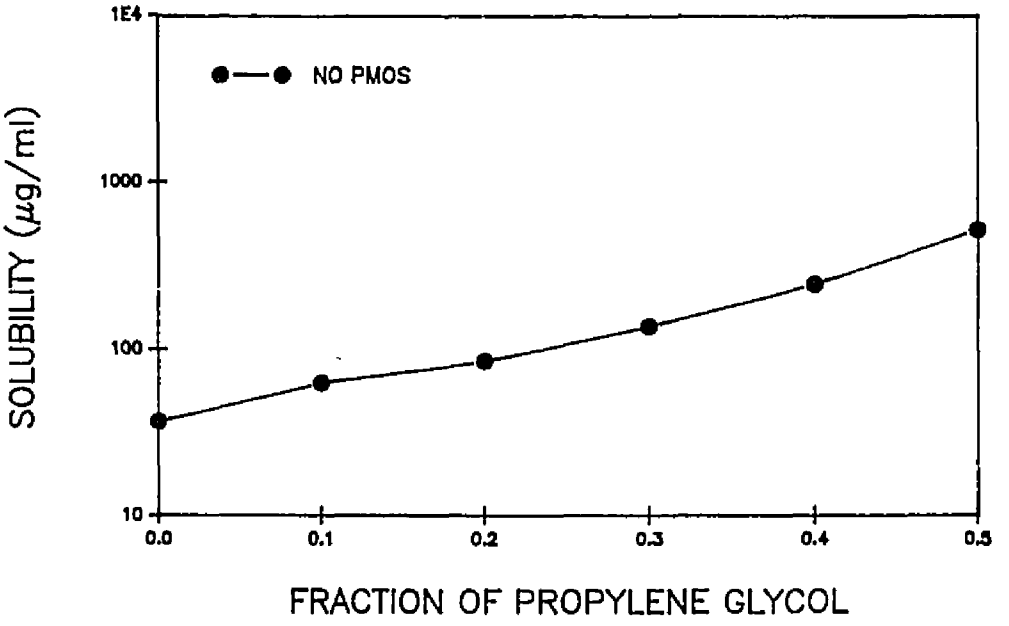
SOLUBILITY OF DIURON IN ACETONITRILE/WATER
PMOS:TOLUENE

Fraction of ACN	Log Solubility (µg/ml)
0	1.553
0.1	2.038
0.2	2.552
0.3	3.040
0.4	3.530
0.5	3.710



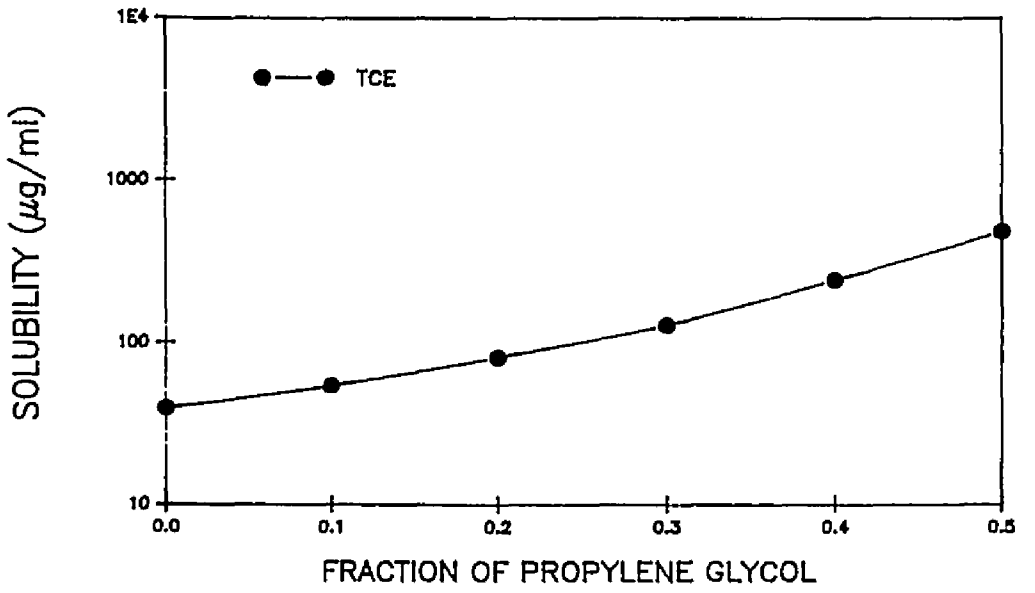
SOLUBILITY OF DIURON IN PROPYLENE GLYCOL/WATER
PMOS:NONE

Fraction of PG	Log Solubility (µg/ml)
0	1.560
0.1	1.794
0.2	1.925
0.3	2.135
0.4	2.386
0.5	2.714



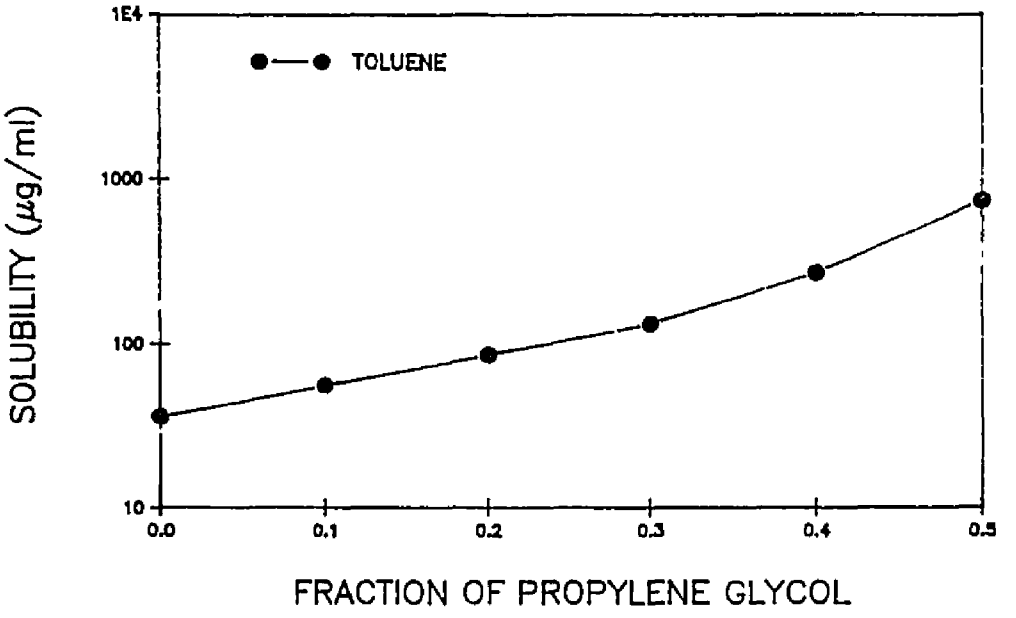
SOLUBILITY OF DIURON IN PROPYLENE GLYCOL/WATER
PMOS:TRICHLOROETHYLENE

Fraction of PG	Log Solubility (µg/ml)
0	1.592
0.1	1.728
0.2	1.904
0.3	2.102
0.4	2.380
0.5	2.681



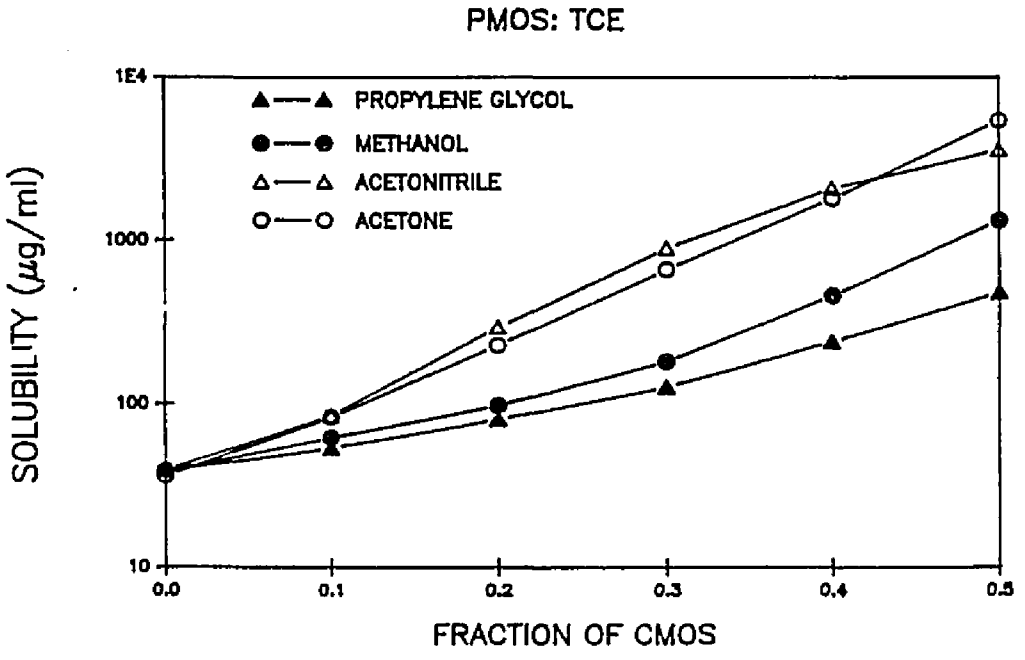
SOLUBILITY OF DIURON IN PROPYLENE GLYCOL/WATER
PMOS:TOLUENE

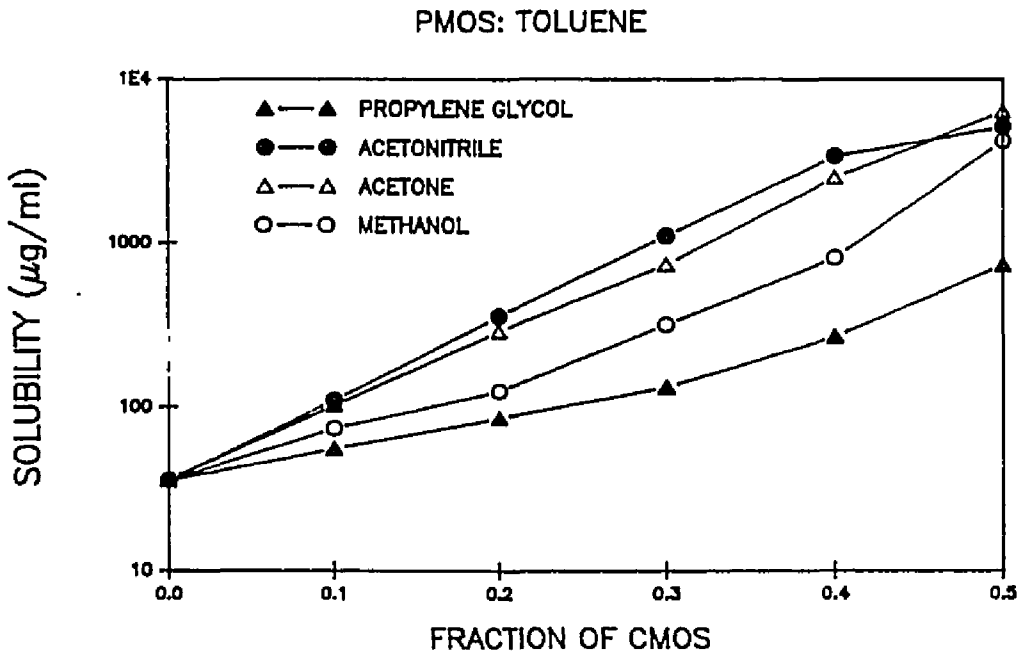
Fraction of PG	Log Solubility (µg/ml)
0	1.553
0.1	1.743
0.2	1.930
0.3	2.119
0.4	2.429
0.5	2.866



APPENDIX B

Solubility of Diuron in Cosolvent-Water Systems


PMOS: TCE
PROPYLENE GLYCOL
METHANOL
ACETONITRILE
ACETONE
SOLUBILITY (μg/ml)
1E4
1000
100
10
0.0
0.1
0.2
0.3
0.4
0.5
FRACTION OF CMOS

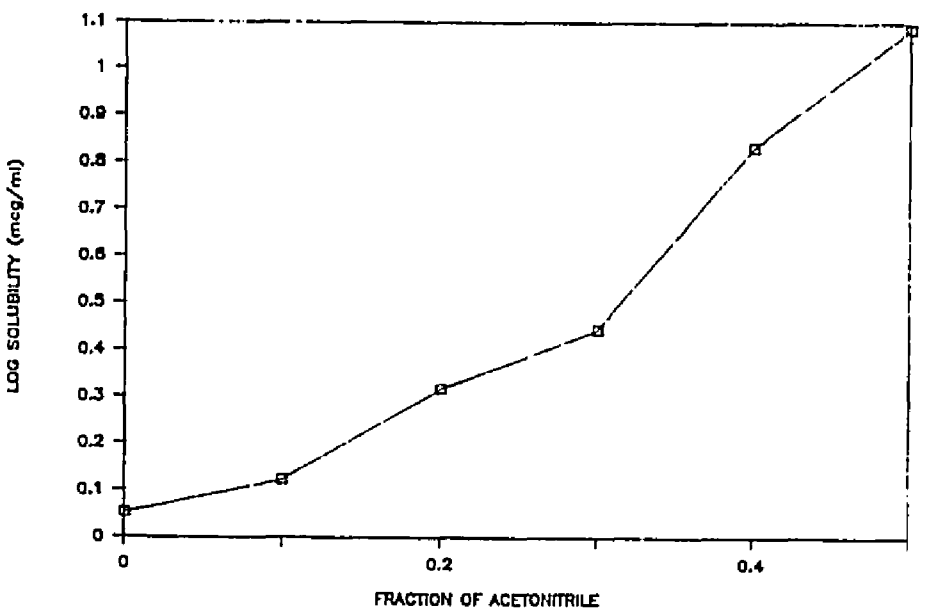

PMOS: TOLUENE
PROPYLENE GLYCOL
ACETONITRILE
ACETONE
METHANOL
SOLUBILITY (μg/ml)
1E4
1000
100
10
0.0
0.1
0.2
0.3
0.4
0.5
FRACTION OF CMOS

APPENDIX C

Solubility of the Partially Miscible Organic Solvent in Cosolvent-Water System

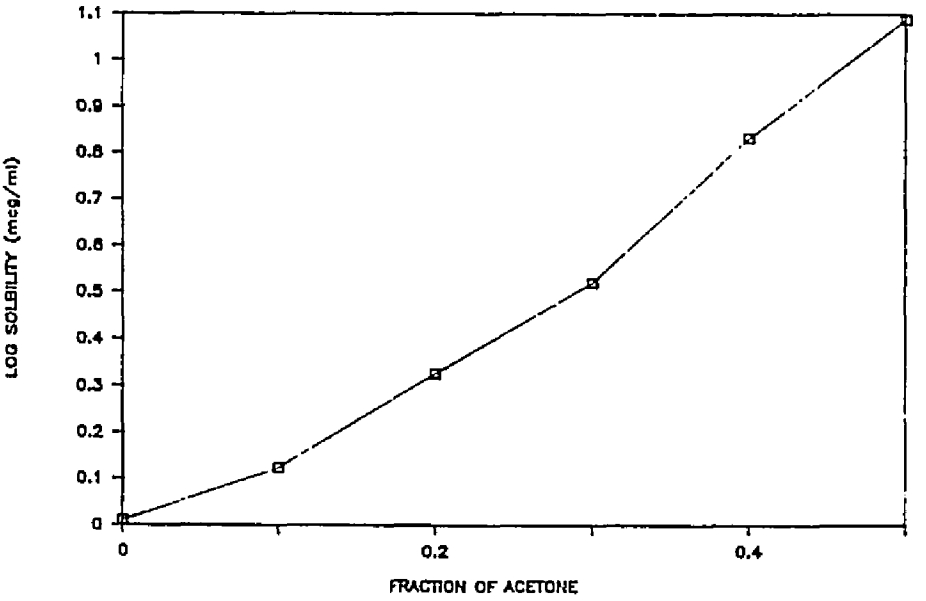
SOLUBILITY OF TRICHLOROETHYLENE
IN ACETONITRILE/WATER

Fraction of ACN	Log Solubility (µg/ml)
0	0.011
0.1	0.143
0.2	0.313
0.3	0.499
0.4	0.604
0.5	0.839



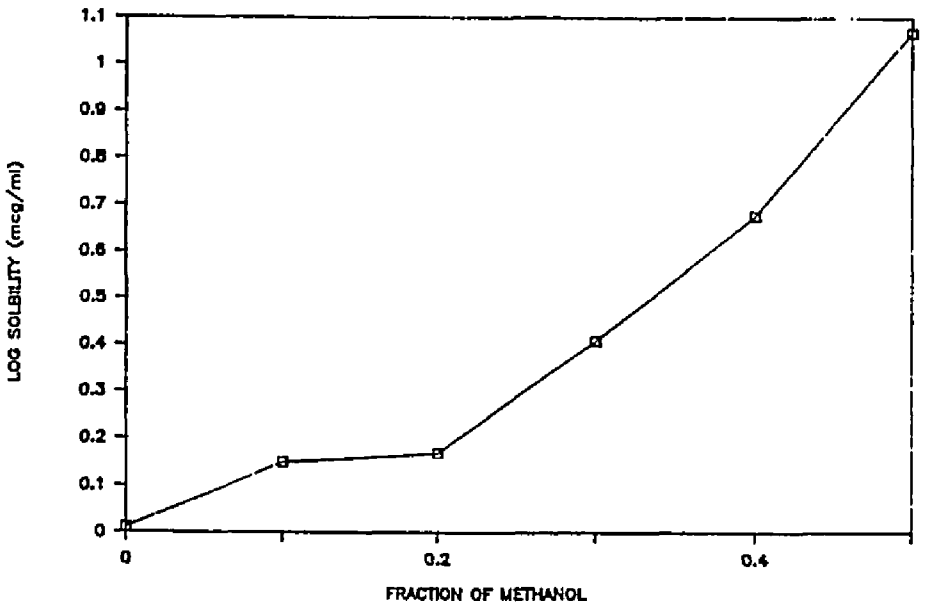
SOLUBILITY OF TRICHLOROETHYLENE
IN ACETONE/WATER

Fraction of ACE	Log Solubility (µg/ml)
0	0.011
0.1	0.124
0.2	0.328
0.3	0.522
0.4	0.833
0.5	1.088



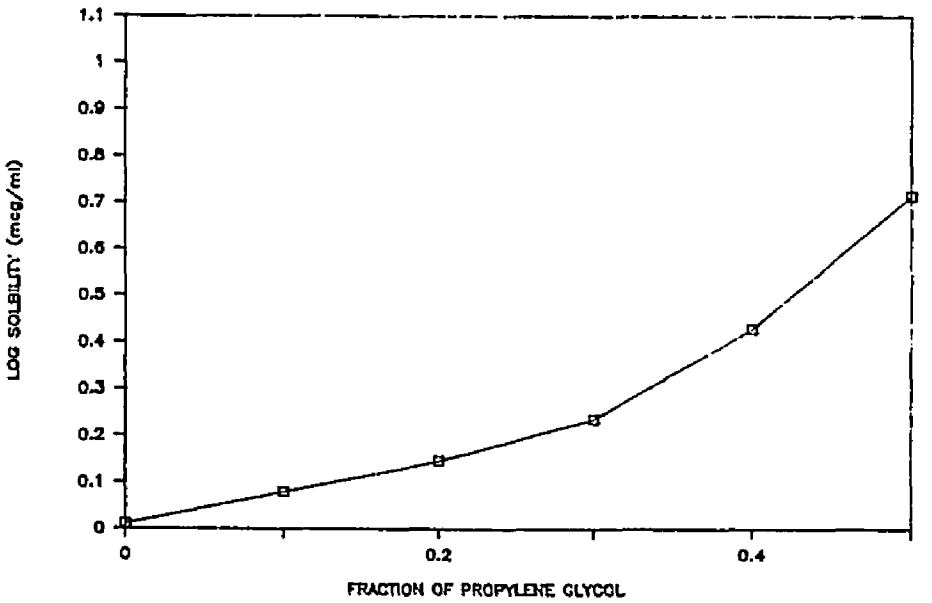
SOLUBILITY OF TRICHLOROETHYLENE
IN METHANOL/WATER

Fraction of MeOH	Log Solubility (µg/ml)
0	0.011
0.1	0.150
0.2	0.169
0.3	0.409
0.4	0.678
0.5	1.068



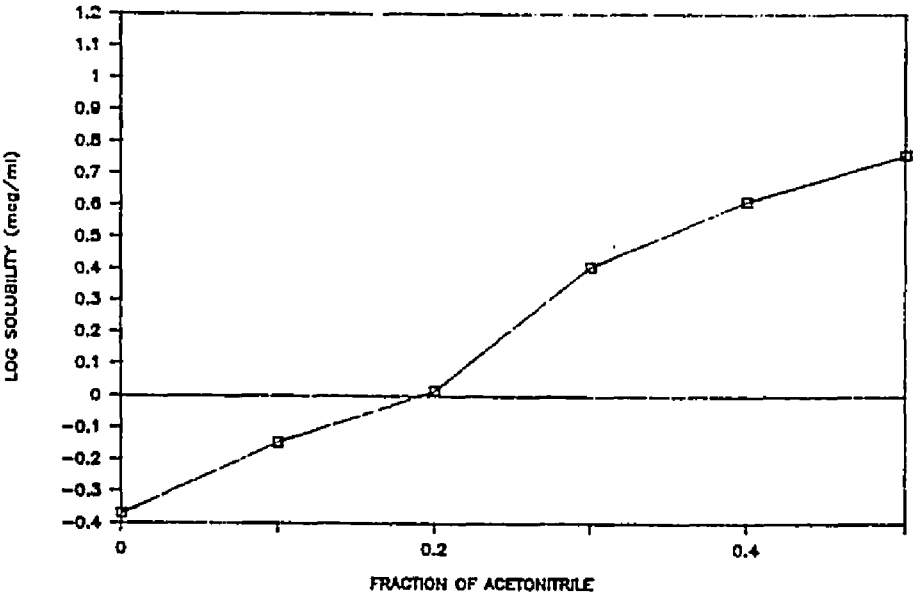
SOLUBILITY OF TRICHLOROETHYLENE
IN PROPYLENE GLYCOL/WATER

Fraction of PG	Log Solubility (µg/ml)
0	0.011
0.1	0.079
0.2	0.147
0.3	0.237
0.4	0.429
0.5	0.716



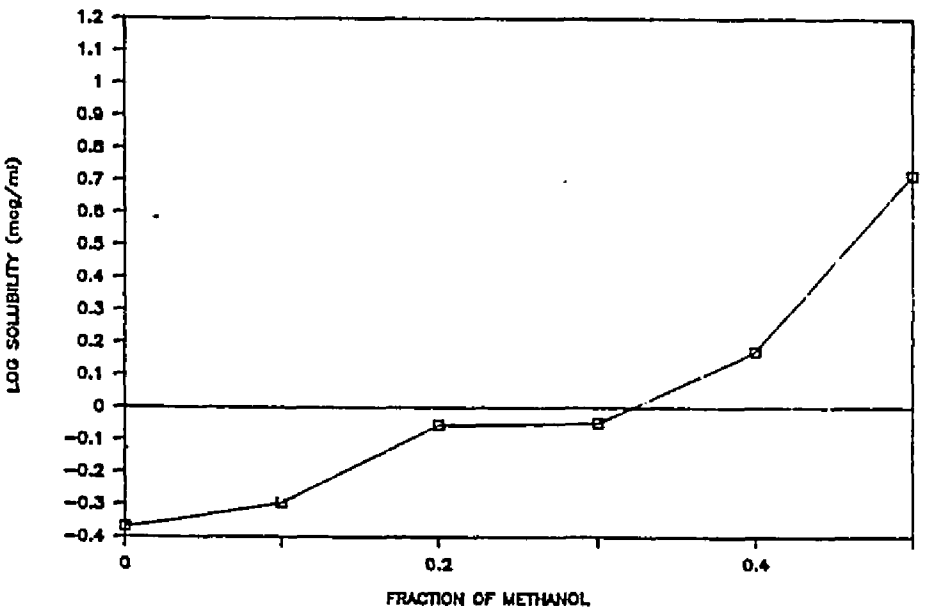
SOLUBILITY OF TOLUENE IN ACETONITRILE/WATER

Fraction of ACN	Log Solubility (µg/ml)
0	-0.369
0.1	-0.146
0.2	0.017
0.3	0.408
0.4	0.614
0.5	0.759



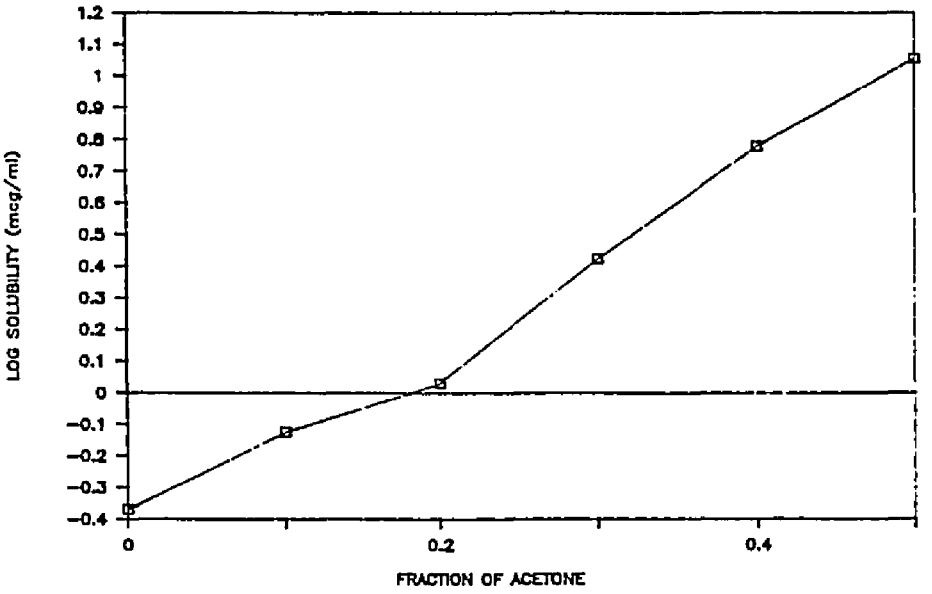
SOLUBILITY OF TOLUENE IN METHANOL/WATER

Fraction of MeOH	Log Solubility (µg/ml)
0	-0.369
0.1	-0.294
0.2	-0.054
0.3	0.009
0.4	0.173
0.5	0.718



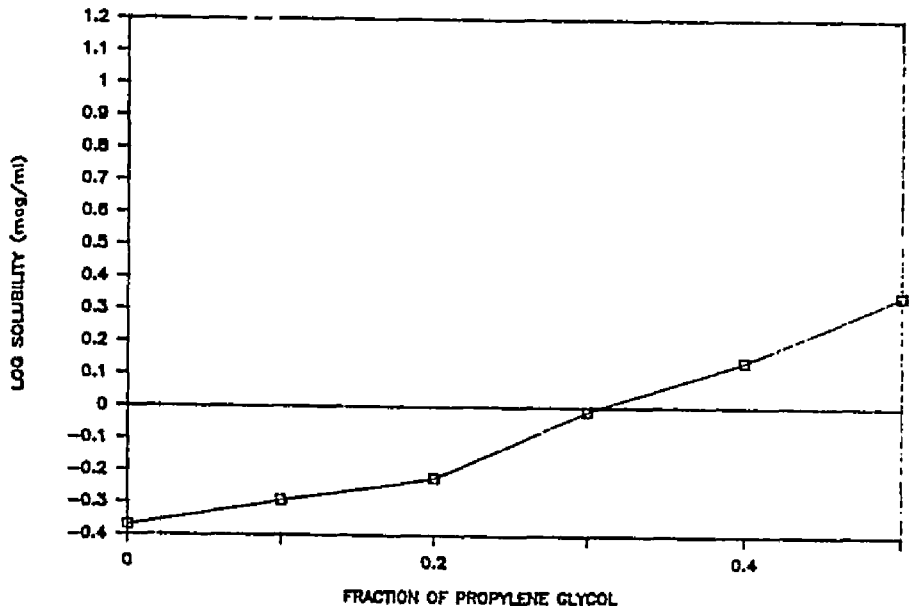
SOLUBILITY OF TOLUENE IN ACETONE/WATER

Fraction of ACE	Log Solubility (µg/ml)
0	-0.369
0.1	-0.124
0.2	0.031
0.3	0.424
0.4	0.779
0.5	1.055



SOLUBILITY OF TOLUENE IN PROPYLENE GLYCOL/WATER

Fraction of PG	Log Solubility (µg/ml)
0	-0.369
0.1	-0.291
0.2	-0.222
0.3	-0.013
0.4	0.141
0.5	0.346



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