Measuring Vapor-Liquid Equilibrium for Aqueous-Organic Systems: Review and a New Technique

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The vapor–liquid equilibrium (VLE) of aqueous–organic mixtures is important in understanding the physical chemistry behind the contamination and remediation of contaminated surface water, ground water and unsaturated soils. The state of the science is assessed, and available VLE and solubility data are reviewed comprehensively for several organic compounds. Benzene, toluene, o-, m-, p-xylene, ethylbenzene, chloroform, 1,1,1-trichloroethane (TCA), and trichloroethylene (TCE) were included in this study. Correlations are provided for estimation of VLE as a function of temperature. A new VLE apparatus was developed to extend experimental techniques found in the literature. Partitioning data for several aqueous–organic systems were measured. The collected data compared very favorably to data available in the literature. The new procedure is capable of providing high-quality data over a wide range of liquid concentrations and temperatures.

Introduction

Until recently, the study of vapor–liquid equilibrium (VLE) of aqueous–organic systems has received relatively little attention. This is especially true of systems with low mutual solubilities (e.g., water–toluene or water–trichloroethylene). Though the initial data for the water–benzene system was collected before the turn of the century, comprehensive data covering a range of temperatures is not available for many of these systems. The techniques for measuring the VLE of these systems are not as fully developed as those for measuring organic–organic mixtures. Many of the procedures and apparatuses available for mutually soluble compounds are inappropriate for systems with low mutual solubilities.

The VLE of aqueous–organic mixtures is important in understanding the physical chemistry behind the contamination of various waters. Major applications of this knowledge include estimation of evaporative losses from wastewater streams, cost-effective design of vapor-stripping operations, *in-situ* vapor extraction, contaminant transport in unsaturated soils, and prediction of activity of dissolved compounds in ground water. The organic species most often involved are typically the monoaromatic species and chlorinated compounds commonly found in fuels and cleaning solutions.

All of these applications require values for the activity coefficients of the dissolved species, the determination of which is compounded by interaction between solutes. The ability to accurately model the activity of these mixtures remains limited due to a lack of reliable data that take into account the many factors affecting their fundamental thermodynamics.

This article presents a review of available VLE and solubility data for several organic compounds, measurement techniques, and an analytical apparatus and procedure for measuring aqueous–organic VLE developed in our laboratory.

Benzene, toluene, *o*-xylene, ethylbenzene, chloroform, 1,1,1-trichloroethane (TCA), and trichloroethylene (TCE) were included in this study. These compounds are ubiquitously used and present widespread containment and disposal problems. Their presence extends throughout surface waters, underground water supplies, and wastewater collection systems. The ability to predict their movement and distribution is necessary to minimize their impact on the environment. Although the aqueous solubilities of these compounds are characterized as low (< 8,000 mg/L), they are still sufficiently high to pose a threat to the health of the environment and are significantly greater than drinking water (DW) standards. Table 1 compares the physical properties and drinking water standards for these compounds.

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Table 1. Physical Properties and DW Standards for Several Organic Compounds at 25°C

Compound	Vapor[*] Pres. mm Hg	Solubility[**] in Water mg/L	Solubility[**] of Water mg/L	Partition[†] Coefficient $(\mathrm{mg/L})^V/(\mathrm{mg/L})^L$	Drinking[‡] Water Std. mg/L
Benzene	94.14	1,760	610.	0.258	0.005
Toluene	28.19	533.	435.	0.273	1.1
Ethylbenzene	9.535	169.	376.	0.361	0.7
o-Xylene	6.606	178.	390.	0.295	10[§]
Chloroform	195.0	7,220	—	0.182	—
1,1,1-TCA	122.9	1,300	—	0.836	0.2
TCE	73.21	1,370	—	0.473	0.005

[*] Daubert and Danner (1993).

[**] Median literature value at 25°C.

[†] This study at 25°C.

[‡] Code of Federal Regulations (1993).

[§] Total xylenes.

SI Unit: kPa = mm Hg × 0.133

Summary of VLE Thermodynamics and Estimation Techniques

The activity coefficient, γ_i, is defined for moderate pressures by

$$y_iP = x_i\gamma_i(x_1,x_2,\ldots,x_n,T)P_i^{\mathrm{sat}}(T). \tag{1}$$

It is a function of both liquid phase composition and temperature and is a property of component i in the liquid phase only. The standard state is pure solute i at the system temperature.

Much of the data in the literature is presented in terms of a partition coefficient, K_i, or Henry's law coefficient, H_i. For low solubility mixtures these two coefficients are essentially equivalent. Strictly speaking, however, Henry's law coefficient is the partition coefficient at infinite dilution of species i:

$$H_i = \lim_{x_i \to 0} K_i, \tag{2}$$

where

$$K_i \equiv \frac{\text{concentration of } i \text{ in the vapor phase}}{\text{concentration of } i \text{ in the liquid phase}}. \tag{3}$$

K_i can be expressed in several different forms. Table 2 lists the common ones. Conversion between forms requires simple units transformations.

When the gas phase is nearly ideal, Eq. 6 leads to a common estimate for the aqueous partition coefficient (Mackay and Shiu, 1981):

$$K_i^{vp} = \frac{P_i^{\mathrm{sat}}}{S_i}. \tag{7}$$

Table 2. Common Forms of the Partition Coefficient

$K_i = K_i^M \equiv \dfrac{C_i^V}{C_i^L}$	(4)
$k_i \equiv \dfrac{y_i}{x_i}$	(5)
$K_i^{vp} \equiv \dfrac{y_iP}{C_i^L}$	(6)

The partition coefficient and the activity coefficient are related to one another. We have from Eq. 1

$$\gamma_i = k_i\frac{P}{P_i^{\mathrm{sat}}}. \tag{8}$$

The infinite dilution activity coefficient can also be estimated as the reciprocal of the solubility in mole fractions (Walas, 1985). This is valid for reasonably small solubilities and solvent activity coefficients of 1.0.

Review of VLE Measurement Techniques

All VLE measurement techniques have in common the ability to ascertain the temperature, pressure, and concentrations of one or both phases at equilibrium. In principle, there are five distinct experimental procedures:

(1) Static methods
(2) Mechanical recirculation methods
(3) Separate measurement of solubility and pure species vapor pressure
(4) Ebulliometry
(5) Perturbation chromatography.

Ebulliometry and perturbation chromatography are not suitable methods for low solubility aqueous–organic systems. Ebulliometry would utilize much too large a volume of solution to be feasible due to the low aqueous solubilities. Perturbation chromatography requires the solvent to be distributed as a thin film on a chromatographic support. The vapor pressure of water is too high to be stable in such an environment. Useful general reviews of VLE measurement techniques without focus on dilute aqueous systems have been provided elsewhere (Malanowski and Andevko, 1990; Williamson, 1975; Marsh, 1978).

Static and mechanical recirculation methods: General

Static and mechanical recirculation methods have several aspects in common. The system is driven to equilibrium in some suitable container. One or both phases are then analyzed to determine equilibrium concentrations. A mass balance may be written for the sample at equilibrium:

$$M_i^{\mathrm{charged}} - [C_i^LV_i^L + C_i^VV_i^V] = M_i^{\mathrm{loss}}. \tag{9}$$

The term M_i^{loss} is the amount of compound i not accounted for by the measured concentrations of each phase. It is the result of leakage from the sample container, adsorption to container surfaces, loss during sampling, and/or faulty measurement. If only one phase is sampled, the mass balance is *required* to calculate the concentration of the second. For instance, if only the liquid phase is sampled, the mass balance becomes

$$M_i^{\text{charged}} - C_i^L V_i^L = C_i^{V*} V_i^V = [C_i^V V_i^V + M_i^{\text{loss}}]. \quad (10)$$

C_i^{V*} is the calculated vapor concentration and C_i^V is the actual vapor concentration accounting for losses, M_i^{loss}. Significant errors may go unnoticed if M_i^{loss} is not known. Reverse the superscripts V and L for vapor phase sampling.

If the concentrations of both phases are measured, M_i^{loss} can be calculated. It still incorporates losses from all possible sources. Though not needed to determine the equilibrium point, knowing the magnitude of M_i^{loss} helps indicate the integrity of the experimental technique. Losses from leakage and adsorption to container surfaces also become less important. Losses during sampling and due to faulty measurements are still important. Sampling techniques are discussed below. Gas chromatography (GC) and spectrography are the most applicable analysis methods. Analytical measurement techniques are an issue beyond the scope of this discussion. A principal goal in technique development is the reduction of M_i^{loss} to zero.

To determine when equilibrium has been reached, system concentrations or pressure are repetitively measured until no significant change between sequential measurements is noted. Concentration measurement may require the sacrifice of some samples to determine the minimum equilibrium time. All other samples are then equilibrated for at least that period of time.

The liquid phase from an equilibrated vapor–liquid system can be manually syringe sampled, transferred via a sample loop and valving directly to a GC, or collected in a suitable container for handling otherwise, for example, by an autosampler. However accomplished, the size of the sample should be small so as not to appreciably disturb the system from equilibrium. Replicate liquid samples and vapor samples may then be taken if needed.

Sampling of the vapor phase is not as straightforward. Vapor samples should be analyzed immediately after collection. Gas-tight syringes can be used, but care must be taken to assure that the sampling is done precisely and accurately. Manual syringe sampling is very sensitive to temperature fluctuations and syringe condition. Vapor samples can also be collected in sample loop and valve assemblies.

Static methods

Static methods tend to be the simplest in design. An aliquot of the mixture is sealed in a suitable container. The container is placed in a thermostator held at the desired temperature. One or both phases are then analyzed to determine the equilibrium concentrations.

Various means of improving mass-transfer rates are available by providing mechanical agitation to the system. Stirring bars driven by magnetically coupled motors or reciprocating shakers are two common examples. Care should be taken to prevent the agitation from causing a significant temperature rise.

The static technique has been used by many researchers. Olsson (1980) described an experimental system consisting of a 1-L glass bulb sealed with a Teflon-coated septa. A small glass cup containing a portion of the liquid phase was suspended below the seal to facilitate sampling. The bulb with sample was immersed in a thermostatically controlled water bath for 24 hours. Both liquid and vapor phases were sampled. Hussam and Carr (1985) used a more elaborate apparatus. A small glass vial was thermostated in a waterbath. A calibrated sample loop was in communication with the headspace of the vial. A series of valves could isolate the sample loop, which was then evacuated by a vacuum pump. Valves then coupled the vial to the loop into which a small amount of headspace vapor was drawn by the vacuum and the loop was switched into the carrier gas flow of a GC for analysis. Hussam and Carr measured only the vapor phase directly. The liquid phase was calculated by mass balance. Freitag and Robinson (1986) sampled both phases with this procedure. Anderson and Prausnitz (1986) developed a static apparatus with which to measure aqueous partition coefficients of a number of organic solvents at high pressure. The sampling system consisted essentially of three calibrated syringe pumps. One was used for sampling each of the equilibrated phases, drawing the sample into a sample loop. The third moved in tandem with the other two, closing as either of the others opened. The volume thus remained constant throughout the sampling process. The equilibrium cell was a commercially available sight glass. Two ovens maintained isothermal conditions.

Marsh (1989) reviewed several static systems. One by Gaube et al. (1987) was "designed primarily for measurements on binary mixtures with limited miscibility." This apparatus was based on the design of Gibbs and van Ness (1972). Degassed liquid compounds were metered into an evacuated, thermostated equilibrium cell. A pressure gauge measured total system pressure. Concentrations were determined from the metered amounts of liquid to obtain Px data. The coexistence equation was used to calculate vapor phase concentrations. Many others have used similar apparatuses of varying sophistication; they include Kolbe and Gmehling (1985), Price and Kobayashi (1959), Weber et al. (1984), and Wilsak et al. (1986). A simple assembly of this type was used by Wilding et al. (1987). It consisted of a 500-mL flask immersed in a beaker of water maintained at a constant temperature by a hot plate. Liquids were introduced to the equilibrium flask and degassed using vacuum. A mercury manometer measured the pressure. PTx and $PTxy$ data could be collected. Liquid phase concentrations were determined from the amounts added, accounting for losses during degassing. The vapor phase was sampled and analyzed to determine vapor phase concentrations. With appropriate sampling ports, both vapor and liquid phases can be sampled for any of the apparatuses just given.

Filoneko and Korol (1976) described experiments using a magnetically stirred solution. Temperature control was realized by a cooling and heating jacket. Manual syringe sampling of only the vapor phase was carried out.

A technique known as headspace gas chromatography

(HSGC) has been investigated by several researchers. In HSGC, the headspace of sealed vials is sampled by an automated mechanism onto a GC. The second phase may be either solid or liquid. Weidlich and Gmehling (1985) clearly described the procedure. In a separate paper, Weidlich et al. (1986) concluded that HSGC "is a technique which allows the measurement of vapor-liquid equilibrium data of widely differing systems within a very short time." Schoene and Steinhauses (1985) provide data for several binary systems studied using HSGC.

One concern with HSGC was not addressed by the literature. The saturated vapor phase will partially condense when the sample vial is pressurized to 30+ psia (207+ kPa). The condensed material will flash again when the vial is depressurized onto the GC column. However, the concentration gradients induced within the vial by the condensation/flash sequence may affect the amount of volatile components charged onto the column. In short, the system may not be at equilibrium at the time the sample is actually taken. This aspect was not discussed in the literature and was not investigated further here. Also, no provisions are available for sampling the equilibrated liquid phase. A mass balance is required and leads to the problems discussed earlier. Furthermore, the commercially available injection systems are designed only for operation above ambient temperatures (> 30°C). An external cooling source is needed to maintain temperatures near or below ambient. To accommodate this, modifications to the apparatus are required.

McAuliffe (1971) reported a method based on successive GC analysis after repeated equilibrations of an inert gas with an aqueous sample containing dissolved hydrocarbon. A 50-mL glass hypodermic syringe was used to hold the sample. The syringe was flushed with the aqueous sample several times and 25 mL was retained. Twenty-five mL of inert gas was added. The vapor was sampled and analyzed after equilibrium was achieved. The entire vapor phase was then discharged and replaced with fresh inert gas. The sample was then reequilibrated and the vapor phase was again analyzed. Plotting the vapor phase concentration vs. the number of equilibrations on semilog paper produced a straight line. McAuliffe derived the following equation, from which both the partition coefficient and solubility could be determined:

$$\log[C_{i,n}^V] = -n\log[K_i+1] + \log[K_i C_{i,0}^L]. \tag{11}$$

Brown and Wasik (1974) described a similar procedure that eliminated the manual vapor syringe. A valve and sample loop assembly provided direct injection of the vapor onto a GC. They measured the concentrations from only two successive equilibrations.

A method following the same general logic is known as equilibrium partitioning in closed systems (EPICS) (Gossett, 1987). The concentrations are determined for the vapor phase above two samples with differing solvent volumes. If the ratio between the masses of solute in each sample is known, the partition coefficient is calculated by

$$K_i = \frac{V_2^L - rV_1^L}{rV_1^V - V_2^V}, \tag{12}$$

where

$$r = \left(\frac{C_{i,1}^V}{C_{i,2}^V}\right)\left(\frac{M_{i,2}}{M_{i,1}}\right). \tag{13}$$

Mechanical recirculation

Mechanical recirculation techniques provide mechanical mixing of the vapor and liquid phases with each other to increase the rates at which samples equilibrate. The increase in surface area from the bubbling or spraying results in increased mass-transfer rates. The concurrent mixing further assures intraphase homogeneity. In many ways these techniques are similar to the static equilibrium methods already discussed and many of the same concerns apply. The differences generally lie in the sampling techniques, and the apparatuses are typically more sophisticated. An advantage of mechanical recirculation is that the recirculated phase can be circulated through the sampling apparatus.

The simplest mechanical recirculation device found in the literature (Kieckbusch and King, 1979) recirculated the headspace vapor. A 2-mL syringe and three-way valve functioned as a small hand pump. The suction side drew vapor through a gas-sampling syringe and discharged below the liquid surface. Only the vapor concentration was measured directly. Brown et al. (1988) and Freitag and Robinson (1986) also both described vapor-recirculating apparatuses. Brown's device pumped the vapor through a sample loop. The Freitag system allowed sampling of both phases by vacuum suction into a sample loop.

Ohgaki et al. (1988) used two equilibrium cells with communication between the vapor and liquid phases of each cell via flexible tubes. One cell was moved vertically with respect to the other. Hydrostatic forces transferred the sample from one cell to the other, agitating the sample in the process. Both the vapor and liquid phases were sampled.

Mackay et al. (1979) described measurement of pressure and concentration during an equilibrium air–water exchange process. It was a continuous version of McAuliffe's batch, static procedure. Air was bubbled through a column of water containing the dissolved hydrocarbon. The solute was continuously stripped from the water. The concentration of the liquid phase was measured at discrete times. Assuming equilibrium was established between the water phase and the bubbling vapor, the following linear relationship exists:

$$\ln\left(\frac{C_i^L(t)}{C_i^L(0)}\right) = -\left(\frac{K_i F^V}{V^L RT}\right)t. \tag{14}$$

By incorporating an appropriate mass-transfer coefficient the assumption of equilibrium can be relaxed.

Leroi et al. (1977) discussed a similar setup and gave references for its background as a GC calibration technique.

Sventlanov et al. (1971) used a method described by Treger et al. (1964). Nitrogen gas saturated with the organic compound was bubbled through a thermostated cell filled with water until the water was saturated. Escaping vapors were collected with a refluxing condenser and apparently returned to the cell. The concentration of the equilibrated liquid was determined by a colorimetric analysis. The data were then

Table 3. Vapor–Liquid Partition and Activity Coefficients for the Benzene–Water System

Temp. °C	Partition Coeff. in Reported Units	Reported Units*	Partition Coeff. $(mg/L)^V/(mg/L)^L$	Activity** Coeff.	Reference
Benzene					
1.0	97.5	$(mf)^V/(mf)^L$	0.0780	2,690	(Leighton and Calo, 1981)
1.3	95.2	$(mf)^V/(mf)^L$	0.0761	2,620	(Leighton and Calo, 1981)
4.50	12.33	$(mg/L)^L/(mg/L)^V$	0.08110	2,391	(Brown and Wasik, 1974)
5.00	12,500	kPa/mf	0.0974	2,720	(Sanemasa et al., 1982)
6.33	11.10	$(mg/L)^L/(mg/L)^V$	0.09009	2,396	(Brown and Wasik, 1974)
7.06	10.45	$(mg/L)^L/(mg/L)^V$	0.09569	2,418	(Brown and Wasik, 1974)
8.96	9.52	$(mg/L)^L/(mg/L)^V$	0.105	2,530	(Brown and Wasik, 1974)
10.0	**0.122**	$\mathbf{(mg/L)^V/(mg/L)^L}$	**0.122**	**2,660**	**(This Work)**
11.0	153.7	$(mf)^V/(mf)^L$	0.1190	2,468	(Leighton and Calo, 1981)
11.75	8.17	$(mg/L)^L/(mg/L)^V$	0.122	2,550	(Brown and Wasik, 1974)
12.10	8.03	$(mg/L)^L/(mg/L)^V$	0.125	2,460	(Brown and Wasik, 1974)
13.0	181.0	$(mf)^V/(mf)^L$	0.1392	2,623	(Leighton and Calo, 1981)
15.0	**0.163**	$\mathbf{(mg/L)^V/(mg/L)^L}$	**0.163**	**2,790**	**(This Work)**
15.00	21,500	kPa/mf	0.162	2,780	(Sanemasa et al., 1982)
15.10	6.91	$(mg/L)^L/(mg/L)^V$	0.145	2,480	(Brown and Wasik, 1974)
17.93	6.18	$(mg/L)^L/(mg/L)^V$	0.162	2,540	(Brown and Wasik, 1974)
20.	0.29	$(mg/L)^V/(mg/L)^L$	0.29	4,000	(Howe et al., 1987)
20.06	5.51	$(mg/L)^L/(mg/L)^V$	0.181	2,480	(Brown and Wasik, 1974)
21.0	257.7	$(mf)^V/(mf)^L$	0.1932	2,520	(Leighton and Calo, 1981)
22.0	264.3	$(mf)^V/(mf)^L$	0.1975	2,465	(Leighton and Calo, 1981)
25.	0.5345	$kPa/(mol/m^3)$	0.2156	2,362	(Howe et al., 1987)
25.	0.00555	$atm/(mol/m^3)$	0.227	2,490	(Mackay et al., 1979)
25.0	**0.258**	$\mathbf{(mg/L)^V/(mg/L)^L}$	**0.258**	**2,830**	**(This Work)**
25.00	33,800	kPa/mf	0.247	2,700	(Sanemasa et al., 1982)
27.2	327.6	$(mf)^V/(mf)^L$	0.2409	2,425	(Leighton and Calo, 1981)
30.	5.3	mm Hg/(mmol/kg)	0.2787	2,500	(Saylor et al., 1938)
30.	2.890	mm Hg/mf	0.274	2,431	(Tucker et al., 1981)
30.01	2,402.	Activity Coeff.	0.2722	2,417	(Hussam and Carr, 1985)
35.	6.2	mm Hg/(mmol/kg)	0.3203	2,300	(Saylor et al., 1938)
35.0	**0.385**	$\mathbf{(mg/L)^V/(mg/L)^L}$	**0.385**	**2,800**	**(This Work)**
35.00	50,300	kPa/mf	0.356	2,590	(Sanemasa et al., 1982)
45.00	73,400	kPa/mf	0.505	3,200	(Sanemasa et al., 1982)

*mf = mol fraction; V = vapor phase; L = liquid phase.
**$f_i^o = P_i^{sat}$.

reported as the solubility of chloroform in water below a hypothetical vapor with a chloroform partial pressure of 760 mm Hg (101 kPa). It is believed that their data were offset by a factor of 10. See the discussion under Reviewed Data as a Function of Temperature below.

Solubility measurement

Methods of solubility measurements can be categorized into three groups that describe the method of creating the saturated solution:

(1) Two liquid-phase contact (TLPC) methods
(2) Turbidity, or cloud point, measurement
(3) Vapor–liquid contact (VLC) methods.

The various analytical techniques available include mixing of known liquid amounts, GC, liquid chromatography (LC), spectrography, K-F titration, scintillation counting of labeled solute, and chemical conversion of the solute to a precipitate or gas with further analysis.

The TLPC method involves mixing excess quantities of the two liquid compounds in a suitable container and allowing the system to come to equilibrium. The two liquid phases are in direct contact with one another. The sample may be agitated to improve mass-transfer rates. The formation of emulsions of suspensions can impair the accuracy of the measurement.

An early study of the water–benzene system metered amounts of one species into the other until a second standing phase was noted (Herz, 1898). This is inherently inaccurate due to the difficulty of determining when saturation has been reached.

Hill (1923) described two TLPC methods, one of which is similar to the EPICS method for VLE measurement described above. Arnold et al. (1958) reported carefully collected TLCP data for the water–benzene systems up to 45°C. UV spectrography was used to measure concentrations. Quality TLCP data at high temperature and pressure were also collected by Anderson and Prausnitz (1986) for several water–aromatic systems. Analysis was done by valve sampling onto a GC.

Generator columns produce a saturated solution by circulating the solvent through a bed of support material coated with the solute of interest (May et al., 1978). By supporting the solute, the dispersion of droplets in the solvent is mini-

Table 4. Vapor–Liquid Partition and Activity Coefficients for the Toluene–Water System

Temp. °C	Partition Coeff. in Reported Units	Reported Units*	Partition Coeff. $(mg/L)^V/(mg/L)^L$	Activity** Coeff.	Reference
Toluene					
1.0	121.8	$(mf)^V/(mf)^L$	0.09748	12,930	(Leighton and Calo, 1981)
3.0	129.2	$(mf)^V/(mf)^L$	0.1027	12,100	(Leighton and Calo, 1981)
4.50	12.92	$(mg/L)^L/(mg/L)^V$	0.07740	8,623	(Brown and Wasik, 1974)
6.33	11.42	$(mg/L)^L/(mg/L)^V$	0.08757	8,692	(Brown and Wasik, 1974)
7.06	10.68	$(mg/L)^L/(mg/L)^V$	0.09363	8,775	(Brown and Wasik, 1974)
8.96	9.61	$(mg/L)^L/(mg/L)^V$	0.104	9,250	(Brown and Wasik, 1974)
11.0	**0.159**	$\mathbf{(mg/L)^V/(mg/L)^L}$	**0.159**	**11,900**	**(This Work)**
11.75	8.05	$(mg/L)^L/(mg/L)^V$	0.124	9,350	(Brown and Wasik, 1974)
12.10	7.92	$(mg/L)^L/(mg/L)^V$	0.126	8,980	(Brown and Wasik, 1974)
12.4	204.6	$(mf)^V/(mf)^L$	0.1576	11,220	(Leighton and Calo, 1981)
12.5	198.1	$(mf)^V/(mf)^L$	0.1526	10,870	(Leighton and Calo, 1981)
15.0	**0.192**	$\mathbf{(mg/L)^V/(mg/L)^L}$	**0.192**	**11,600**	**(This Work)**
15.00	22,000	kPa/mf	0.166	10,000	(Sanemasa et al., 1982)
15.10	6.68	$(mg/L)^L/(mg/L)^V$	0.150	9,070	(Brown and Wasik, 1974)
17.9	251.5	$(mf)^V/(mf)^L$	0.1904	10,420	(Leighton and Calo, 1981)
17.93	5.85	$(mg/L)^L/(mg/L)^V$	0.171	9,360	(Brown and Wasik, 1974)
19.1	278.7	$(mf)^V/(mf)^L$	0.2102	10,360	(Leighton and Calo, 1981)
20.	0.26	$(mg/L)^V/(mg/L)^L$	0.26	12,000	(Schoene and Steinhauses, 1985)
20.06	5.14	$(mg/L)^L/(mg/L)^V$	0.195	9,110	(Brown and Wasik, 1974)
22.7	309.8	$(mf)^V/(mf)^L$	0.2310	9,812	(Leighton and Calo, 1981)
23.0	342.7	$(mf)^V/(mf)^L$	0.2553	10,300	(Leighton and Calo, 1981)
25.	0.6503	$kPa/(mol/m^3)$	0.2623	9,598	(Howe et al., 1987)
25.	0.00664	$atm/(mol/m^3)$	0.271	9,930	(Mackay et al., 1979)
25.0	**0.273**	$\mathbf{(mg/L)^V/(mg/L)^L}$	**0.273**	**9,990**	**(This Work)**
25.00	36,900	kPa/mf	0.269	8,860	(Sanemasa et al., 1982)
35.0	**0.469**	$\mathbf{(mg/L)^V/(mg/L)^L}$	0.469	**10,800**	**(This Work)**
35.00	58,900	kPa/mf	0.417	9,600	(Sanemasa et al., 1982)
36.9	0.66	$(mg/L)^V/(mg/L)^L$	0.66	15,000	(Schoene and Steinhauses, 1985)
41.5	0.87	$(mg/L)^V/(mg/L)^L$	0.87	17,000	(Schoene and Steinhauses, 1985)
45.00	87,300	kPa/mf	0.601	11,800	(Sanemasa et al., 1982)
46.0	1.05	$(mg/L)^V/(mg/L)^L$	1.05	20,700	(Schoene and Steinhauses, 1985)

*mf = mol fraction; ^{V} = vapor phase; ^{L} = liquid phase.
**$f_i^o = P_i^{sat}$.

mized. The generator column used in May's work was packed with 60–80 mesh glass beads. The coating was prepared by pumping pure liquid solute through the column and then purging the excess with water. The generated effluent was analyzed by LC. Generator columns can be used for generating large volumes of saturated solution.

For the turbidity method, the two liquid compounds are placed in a sealed container. The temperature of the system is raised and lowered, and the disappearance or appearance of a turbidity is noted through a refractometer or similar device. The concentrations are determined either by preweighing the solute amounts placed in the container or by post-experiment analysis. This method is generally very accurate. Originally devised by Alexejew (1886), it has also been used by Groschuff (1911) and Pryor and Jentoft (1961) and is useful over a wide range of temperatures and pressures.

In the VLC method, aliquots of the two pure liquids are placed together in a container. The liquid phases are initially separated and not allowed direct contact with each other. Each liquid will vaporize and a portion will redissolve in the other. At equilibrium, the fugacity of each component is the same in all three phases and is the same as if the two liquid phases were in direct contact with each other. The amount of dissolved solute is then determined by spectrography or chromatography.

Vapor pressure

Vapor pressures for most common compounds can be obtained from many sources (Daubert and Danner, 1993; Perry et al., 1984; Riddick et al., 1986). A review of vapor pressure data is not presented here. The vapor pressures used in this study were calculated from the five-parameter equation obtained from Daubert and Danner (1993).

Reviewed Data

A review of the literature was conducted for values of aqueous–organic VLE and solubility data for the organic compounds studied here. The review of solubility data was limited to chloroform, trichloroethane, and trichloroethylene because a comprehensive compilation of solubility data for the aromatic species of interest was available (Kertes, 1989). Three other papers (Mackay and Shiu, 1981; McAuliffe, 1966; Sutton and Calder, 1975) were found that reviewed earlier literature. Several errors were found in the paper by Mackay and Shiu. The table of aromatic data contained incorrect and

Table 5. Vapor–Liquid Partition and Activity Coefficients for the Ethylbenzene–Water System

Temp. °C	Partition Coeff. in Reported Units	Reported Units*	Partition Coeff. $(mg/L)^V/(mg/L)^L$	Activity** Coeff.	Reference
Ethylbenzene					
4.50	12.31	$(mg/L)^L/(mg/L)^V$	0.08123	30,420	(Brown and Wasik, 1974)
6.33	10.70	$(mg/L)^L/(mg/L)^V$	0.09346	30,770	(Brown and Wasik, 1974)
7.06	9.91	$(mg/L)^L/(mg/L)^V$	0.101	31,200	(Brown and Wasik, 1974)
8.96	8.82	$(mg/L)^L/(mg/L)^V$	0.113	33,000	(Brown and Wasik, 1974)
11.75	7.20	$(mg/L)^L/(mg/L)^V$	0.139	33,600	(Brown and Wasik, 1974)
12.10	7.11	$(mg/L)^L/(mg/L)^V$	0.141	31,900	(Brown and Wasik, 1974)
15.00	25,500	kPa/mf	0.192	36,500	(Sanemasa et al., 1982)
15.10	5.85	$(mg/L)^L/(mg/L)^V$	0.171	32,500	(Brown and Wasik, 1974)
17.93	5.04	$(mg/L)^L/(mg/L)^V$	0.198	33,600	(Brown and Wasik, 1974)
20.06	4.36	$(mg/L)^L/(mg/L)^V$	0.229	32,700	(Brown and Wasik, 1974)
25.	0.8024	$kPa/(mol/m^3)$	0.3237	35,010	(Howe et al., 1987)
25.	0.7986	$kPa/(mol/m^3)$	0.3221	34,840	(Howe et al., 1987)
25.	0.00843	$atm/(mol/m^3)$	0.345	37,300	(Mackay et al., 1979)
25.0	**0.361**	$\mathbf{(mg/L)^V/(mg/L)^L}$	**0.361**	**39,000**	**(This Work)**
25.00	44,300	kPa/mf	0.324	35,000	(Sanemasa et al., 1982)
35.00	74,400	kPa/mf	0.527	34,000	(Sanemasa et al., 1982)
45.00	112,000	kPa/mf	0.771	41,600	(Sanemasa et al., 1982)

*mf = mol fraction; V = vapor phase; L = liquid phase.
**$f_i^o = P_i^{sat}$.

missing references, inconsistent reporting of significant figures, incorrect calculations, and incorrect data. It was also unclear how they arrived at their recommended values. Nevertheless, their paper did cover a wide range of organic compounds and should be a starting point for other reviews. Both the McAuliffe, and the Sutton and Calder papers contained a number of references for the aqueous solubility of aromatic compounds. McAuliffe provided references for several olefins and paraffins as well.

The reviewed data are presented in Tables 3–13. The data are reported in the units and significant figures given in the source papers and in the common units $(mg/L)^V/(mg/L)^L$. The partition coefficient and solubilities are also given as activity coefficients.

The required values for vapor pressure and density were calculated from the temperature-dependent equation from Daubert and Danner (1993). The standard state for the activity coefficients was the pure solute vapor pressure at the reported temperature (see Eq. 1).

Graphs of the data as a function of temperature also are

Table 6. Vapor–Liquid Partition and Activity Coefficients for the *o*-, *m*-, and *p*-xylene–Water Systems

Temp. °C	Partition Coeff. in Reported Units	Reported Units*	Partition Coeff. $(mg/L)^V/(mg/L)^L$	Activity** Coeff.	Reference
o-Xylene					
15.0	16,600	kPa/mf	0.125	35,000	(Sanemasa et al., 1982)
25.	0.4930	$kPa/(mol/m^3)$	0.1989	31,050	(Howe et al., 1987)
25.0	29,200	kPa/mf	0.213	33,300	(Sanemasa et al., 1982)
25.0	**0.295**	$\mathbf{(mg/L)^V/(mg/L)^L}$	**0.295**	**46,100**	**(This Work)**
35.0	46,900	kPa/mf	0.332	30,300	(Sanemasa et al., 1982)
45.0	73,500	kPa/mf	0.506	38,400	(Sanemasa et al., 1982)
m-Xylene					
15.0	22,500	kPa/mf	0.170	37,000	(Sanemasa et al., 1982)
25.	0.7538	$kPa/(mol/m^3)$	0.3041	37,570	(Howe et al., 1987)
25.0	40,600	kPa/mf	0.297	36,600	(Sanemasa et al., 1982)
35.0	68,200	kPa/mf	0.483	35,400	(Sanemasa et al., 1982)
45.0	104,000	kPa/mf	0.716	43,800	(Sanemasa et al., 1982)
p-Xylene					
15.0	23,900	kPa/mf	0.180	37,300	(Sanemasa et al., 1982)
25.	0.7538	$kPa/(mol/m^3)$	0.3041	35,780	(Howe et al., 1987)
25.0	42,400	kPa/mf	0.310	36,400	(Sanemasa et al., 1982)
35.0	70,300	kPa/mf	0.498	34,900	(Sanemasa et al. 1982)
45.0	114,000	kPa/mf	0.784	46,000	(Sanemasa et al., 1982)

*mf = mol fraction; V = vapor phase; L = liquid phase.
**$f_i^o = P_i^{sat}$.

Table 7. Vapor–Liquid Partition and Activity Coefficients for the Chloroform–Water System

Temp. °C	Partition Coeff. in Reported Units	Reported Units*	Partition Coeff. (mg/L)^V/(mg/L)^L	Activity** Coeff.	Reference
Chloroform					
1.9	68.9	(mf)^V/(mf)^L	0.0550	846	(Leighton and Calo, 1981)
9.6	0.0645	(mg/L)^V/(mg/L)^L	0.0645	678	(Gossett, 1987)
13.5	128.7	(mf)^V/(mf)^L	0.0988	866	(Leighton and Calo, 1981)
15.	4.8	(g/100 g)/760 mm Hg	0.104	837	(Svetlanov et al., 1971)
15.0	**0.109**	**(mg/L)^V/(mg/L)^L**	**0.109**	**874**	**(This Work)**
15.7	146.7	(mf)^V/(mf)^L	0.1118	899	(Leighton and Calo, 1981)
17.1	155.0	(mf)^V/(mf)^L	0.1176	866	(Leighton and Calo, 1981)
17.5	0.103	(mg/L)^V/(mg/L)^L	0.103	759	(Gossett, 1987)
20.	8.6	(mg/L)^L/(mg/L)^V	0.12	750	(McConnell et al., 1975)
22.0	194.5	(mf)^V/(mf)^L	0.1454	868	(Leighton and Calo, 1981)
24.8	0.150	(mg/L)^V/(mg/L)^L	0.150	828	(Gossett, 1987)
24.9	204.8	(mf)^V/(mf)^L	0.1516	837	(Leighton and Calo, 1981)
25.	0.4263	kPa/(mol/m^3)	0.1720	910	(Howe et al., 1987)
25.	0.4901	kPa/(mol/m^3)	0.1977	1,046	(Howe et al., 1987)
25.	0.162	(mg/L)^L/(mg/L)^V	0.162	857	(Leighton and Calo, 1981)
25.0	0.172	(mg/L)^L/(mg/L)^V	0.172	910	(Lincoff and Gossett, 1981)
25.0	**0.182**	**(mg/L)^V/(mg/L)^L**	**0.182**	**963**	**(This Work)**
30.	3.2	(g/100 g)/760 mm Hg	0.149	651	(Svetlanov et al., 1971)
34.6	0.223	(mg/L)^V/(mg/L)^L	0.223	837	(Gossett, 1987)
45.	2.1	(g/100 g)/760 mm Hg	0.222	709	(Svetlanov et al., 1971)
60.	1.3	(g/100 g)/760 mm Hg	0.335	1,120	(Svetlanov et al., 1971)

*mf = mol fraction; V = vapor phase; L = liquid phase.
**$f_i^o = P_i^{\text{sat}}$.

Table 8. Vapor–Liquid Partition and Activity Coefficients for the 1,1,1-Trichloroethane–Water System

Temp. °C	Partition Coeff. in Reported Units	Reported Units*	Partition Coeff. (mg/L)^V/(mg/L)^L	Activity** Coeff.	Reference
1,1,1-Trichloroethane					
1.0	297.0	(mf)^V/(mf)^L	0.2377	5,994	(Leighton and Calo, 1981)
1.0	297.9	(mf)^V/(mf)^L	0.2384	6,012	(Leighton and Calo, 1981)
1.2	307.0	(mf)^V/(mf)^L	0.2455	6,195	(Leighton and Calo,1981)
2.5	327.8	(mf)^V/(mf)^L	0.2610	6,267	(Leighton and Calo, 1981)
7.0	418.5	(mf)^V/(mf)^L	0.3282	6,147	(Leighton and Calo, 1981)
9.6	0.328	(mg/L)^V/(mg/L)^L	0.328	5,590	(Gossett, 1987)
10.0	504.0	(mf)^V/(mf)^L	0.3914	6,355	(Leighton and Calo, 1981)
12.0	556.8	(mf)^V/(mf)^L	0.4296	6,355	(Leighton and Calo, 1981)
12.0	569.6	(mf)^V/(mf)^L	0.4395	6,501	(Leighton and Calo, 1981)
12.9	586.2	(mf)^V/(mf)^L	0.4509	6,691	(Leighton and Calo, 1981)
14.0	652.7	(mf)^V/(mf)^L	0.5003	6,755	(Leighton and Calo, 1981)
17.5	0.502	(mg/L)^V/(mg/L)^L	0.502	5,940	(Gossett, 1987)
18.0	766.7	(mf)^V/(mf)^L	0.5802	6,556	(Leighton and Calo, 1981)
18.0	793.4	(mf)^V/(mf)^L	0.6004	6,784	(Leighton and Calo,1981)
18.0	802.9	(mf)^V/(mf)^L	0.6076	6,865	(Leighton and Calo, 1981)
19.0	828.3	(mf)^V/(mf)^L	0.6249	6,759	(Leighton and Calo, 1981)
19.2	836.7	(mf)^V/(mf)^L	0.6308	6,828	(Leighton and Calo, 1981)
19.5	788.1	(mf)^V/(mf)^L	0.5935	6,431	(Leighton and Calo, 1981)
20.	0.71	(mg/L)^V/(mg/L)^L	0.71	7,400	(McConnell et al., 1975)
24.3	1,027.6	(mf)^V/(mf)^L	0.7624	6,677	(Leighton and Calo, 1981)
24.8	0.703	(mg/L)^V/(mg/L)^L	0.703	6,170	(Gossett, 1987)
25.	1.7620	kPa/(mol/m^3)	0.71076	5,966	(Howe et al., 1987)
25.0	**0.836**	**(mg/L)^V/(mg/L)^L**	**0.836**	**7,020**	**(This Work)**
25.2	1,094.3	(mf)^V/(mf)^L	0.8096	6,801	(Leighton and Calo, 1981)
25.3	1,110.7	(mf)^V/(mf)^L	0.8215	6,903	(Leighton and Calo, 1981)
26.0	1,090.2	(mf)^V/(mf)^L	0.8047	6,483	(Leighton and Calo, 1981)
26.0	1,131.4	(mf)^V/(mf)^L	0.8351	6,728	(Leighton and Calo, 1981)
26.1	1,073.8	(mf)^V/(mf)^L	0.7923	6,386	(Leighton and Calo, 1981)
34.6	0.987	(mg/L)^V/(mg/L)^L	0.987	5,810	(Gossett, 1987)

*mf = mol fraction; V = vapor phase; L = liquid phase.
**$f_i^o = P_i^{\text{sat}}$.

Table 9. Vapor–Liquid Partition and Activity Coefficients for the Trichloroethylene–Water System

Temp. °C	Partition Coeff. in Reported Units	Reported Units*	Partition Coeff. $(\text{mg/L})^V/(\text{mg/L})^L$	Activity** Coeff.	Reference
Trichloroethylene					
1.0	131.6	$(\text{mf})^V/(\text{mf})^L$	0.1053	4,655	(Leighton and Calo, 1981)
1.0	139.5	$(\text{mf})^V/(\text{mf})^L$	0.1116	4,934	(Leighton and Calo, 1981)
1.2	138.8	$(\text{mf})^V/(\text{mf})^L$	0.1110	4,909	(Leighton and Calo, 1981)
2.5	168.4	$(\text{mf})^V/(\text{mf})^L$	0.1341	5,634	(Leighton and Calo, 1981)
7.0	200.9	$(\text{mf})^V/(\text{mf})^L$	0.1576	5,123	(Leighton and Calo, 1981)
9.6	0.163	$(\text{mg/L})^V/(\text{mg/L})^L$	0.163	4,810	(Gossett, 1987)
10.0	232.7	$(\text{mf})^V/(\text{mf})^L$	0.1807	5,067	(Leighton and Calo, 1981)
12.0	254.8	$(\text{mf})^V/(\text{mf})^L$	0.1966	5,005	(Leighton and Calo, 1981)
12.0	265.8	$(\text{mf})^V/(\text{mf})^L$	0.2051	5,221	(Leighton and Calo, 1981)
12.9	287.0	$(\text{mf})^V/(\text{mf})^L$	0.2207	5,637	(Leighton and Calo, 1981)
14.0	309.9	$(\text{mf})^V/(\text{mf})^L$	0.2376	5,499	(Leighton and Calo, 1981)
17.5	0.265	$(\text{mg/L})^V/(\text{mg/L})^L$	0.265	5,340	(Gossett, 1987)
18.0	375.0	$(\text{mf})^V/(\text{mf})^L$	0.2838	5,457	(Leighton and Calo, 1981)
18.0	379.6	$(\text{mf})^V/(\text{mf})^L$	0.2873	5,524	(Leighton and Calo, 1981)
18.0	375.0	$(\text{mf})^V/(\text{mf})^L$	0.2838	5,457	(Leighton and Calo, 1981)
19.0	393.5	$(\text{mf})^V/(\text{mf})^L$	0.2969	5,454	(Leighton and Calo, 1981)
19.2	417.3	$(\text{mf})^V/(\text{mf})^L$	0.3146	5,784	(Leighton and Calo, 1981)
19.5	396.5	$(\text{mf})^V/(\text{mf})^L$	0.2986	5,495	(Leighton and Calo, 1981)
20.	2.74	$(\text{mg/L})^L/(\text{mg/L})^V$	0.365	6,410	(McConnell et al., 1975)
20.	0.34	$(\text{mg/L})^V/(\text{mg/L})^L$	0.34	6,000	(Schoene and Steinhauses, 1985)
24.3	537.1	$(\text{mf})^V/(\text{mf})^L$	0.3985	5,869	(Leighton and Calo, 1981)
24.8	0.392	$(\text{mg/L})^V/(\text{mg/L})^L$	0.392	5,780	(Gossett, 1987)
25.	1.0286	$\text{kPa}/(\text{mol/m}^3)$	0.41492	5,846	(Howe et al., 1987)
25.0	**0.473**	$\boldsymbol{(\text{mg/L})^V/(\text{mg/L})^L}$	**0.473**	**6,660**	**(This Work)**
25.2	539.9	$(\text{mf})^V/(\text{mf})^L$	0.3995	5,632	(Leighton and Calo, 1981)
25.3	545.7	$(\text{mf})^V/(\text{mf})^L$	0.4036	5,692	(Leighton and Calo, 1981)
26.0	551.1	$(\text{mf})^V/(\text{mf})^L$	0.4068	5,489	(Leighton and Calo, 1981)
26.0	563.8	$(\text{mf})^V/(\text{mf})^L$	0.4161	5,616	(Leighton and Calo, 1981)
26.1	558.1	$(\text{mf})^V/(\text{mf})^L$	0.4118	5,559	(Leighton and Calo, 1981)
34.6	0.591	$(\text{mg/L})^V/(\text{mg/L})^L$	0.591	5,730	(Gossett, 1987)
36.9	0.88	$(\text{mg/L})^V/(\text{mg/L})^L$	0.88	7,900	(Schoene and Steinhauses, 1985)
41.5	1.08	$(\text{mg/L})^V/(\text{mg/L})^L$	1.08	8,640	(Schoene and Steinhauses, 1985)
46.	1.41	$(\text{mg/L})^V/(\text{mg/L})^L$	1.41	11,400	(Schoene and Steinhauses, 1985)

*mf = mol fraction; V = vapor phase; L = liquid phase.
**$f_i^o = P_i^{\text{sat}}$.

presented as Figures 1–12. Data presentation in these figures was not transformed to activity coefficients and polynomial regressions were used to be consistent with IUPAC presentation (Kertes, 1989). The reviewed data were quite consistent both for a particular binary system and among homologues. Each reviewed data set was empirically fit as a function of temperature. The majority of the data sets were best fit with a second-order polynomial. The coefficients of the fitted data sets are shown in Table 14. In general, box plots were used to initially identify outlier data. Statistically, this defines an outlier as a value that is greater than the upper fourth plus 1.5 times the fourth-spread or less than lower fourth plus 1.5

Table 10. Solubilities and Activity Coefficients of Chloroform in Water

Temp. °C	Solubility in Water Reported Unit	Reported Units	Solubility in Water mg/L	Activity* Coeff.	Reference
Chloroform					
15.	8.52	g/kg	8,500	779.	(Gross and Saylor, 1931)
20.	8,200	ppm wt.	8,200	810	(McConnell et al., 1975)
20.	8,000	mg/L	8,000	830	(Neely, 1976)
25.	60,500	μM	7,220	917.	(Banerjee et al., 1980)
25.0	0.90	mL/100 mL	13,000	510	(Booth and Everson, 1948)
30.	7.71	g/kg	7,660	865.	(Gross and Saylor, 1931)

*$f_i^o = P_i^{\text{sat}}$.

Table 11. Solubilities and Activity Coefficients of 1,1,1-Trichloroethane in Water

Temp. °C	Solubility in Water Reported Units	Reported Units	Solubility in Water mg/L	Activity* Coeff.	Reference
1,1,1-Trichloroethane					
20.	480	ppm wt.	480	15,000	(McConnell et al., 1975)
20.	0.00675	mol/L	900	8,230	(Pavlovskaya et al., 1977)
25.	10,000	μm	1,30	5,700	(Banerjee et al., 1980)
37.	950	mg/L	950	7,800	(Neely, 1976)

*L = liquid phase.
**$f_i^o = P_i^{sat}$.

Table 12. Solubilities and Activity Coefficients of Trichloroethylene in Water

Temp. °C	Solubility in Water Reported Units	Reported Units	Solubility in Water mg/L	Activity* Coeff.	Reference
Trichloroethylene					
25.	1,000	mg/L	1,000	7,300	(Neely, 1976)
20.	1,100	ppm wt.	1,100	6,600	(McConnell et al., 1975)
25.	0.0104	mol/L	1,370	5,320	(Tewari et al., 1982)
25.	11,200	μM	1,470	4,960	(Banerjee et al., 1980)

*L = liquid phase.
**$f_i^o = P_i^{sat}$.

times the fourth-spread (Hoaglin et al., 1983). When insufficient data were available or a single data set was visibly inconsistent with the remaining literature data, a subjective determination was made.

One of the data sets, the partition coefficient of chloroform in water, was fit with a straight line. The distribution of data did not support the use of a higher order function.

Fitting was not done for three data sets: the solubility of chloroform in water, of TCA in water, and of TCE in water. With the exception of the data point collected by Booth and Everson (1948), the data for the solubility of chloroform in water was fairly consistent. However, not enough data were available over a wide enough range of temperatures to allow curve fitting. The data for the solubilities of TCA and TCE in water were too widely scattered to permit a valid fit to be obtained.

The validity of the chloroform partition data collected by Sventlanov et al. (1971) may be questioned. The data were suspiciously offset by a factor of 10 from the rest of the literature. It was assumed that this was a translation error of the units from the Russian.

Experimental Section

Apparatus

A new VLE apparatus was developed to overcome the perceived deficiencies in previous experimental techniques found in the literature. A VLE cell was designed with the following criteria in mind: measurement of concentrations in both phases so that system closure need not be assumed, but rather would serve as a verification of data accuracy; quantitative transfer of vapor samples to the analytical instrument; rapid

Table 13. Solubilities and Activity Coefficients of Water in Chloroform, 1,1,1-Trichloroethane, and Trichloroethylene

Temp. °C	Solubility of Water in Organic Reported Units	Reported Units	Solubility of Water in Organic mg/L	Activity* Coeff.	Reference
Chloroform					
25.	0.0930	g/100 g	1,380	162	(Staverman, 1941)
1,1,1-Trichloroethane					
25.	0.034	g/100 g	450	400	(Staverman, 1941)
Trichloroethylene					
25.	0.32	g/100 g	4,700	43	(Kirk-Othmer, 1947–1951)

*$f_i^o = P_i^{sat}$.

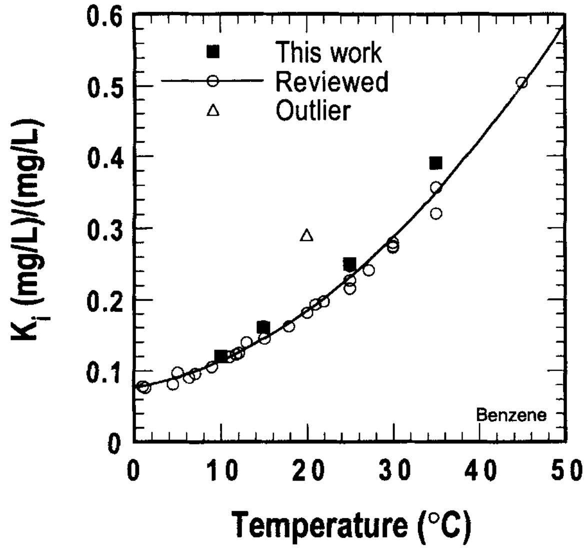

Figure 1. Vapor-liquid partition coefficient of benzene vs. temperature.

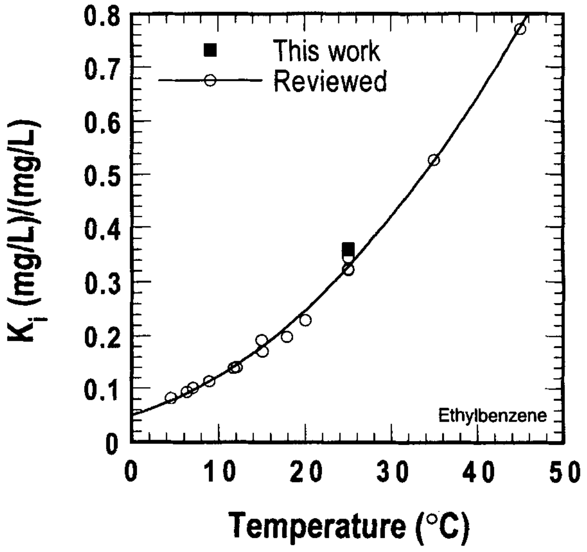

Figure 3. Vapor-liquid partition coefficient of ethylbenzene vs. temperature.

equilibration; assurance of isothermal conditions; measurement of system pressure; sampling of each phase without significantly disturbing the system; and ease of operation.

The VLE apparatus (Figure 13) consisted of a main reservoir that was partially filled with liquid, and two circulation pathways (one for liquid, one for vapor). The liquid phase was mechanically pumped from the bottom of the reservoir through the liquid recirculation pathway (righthand side of Figure 13). The liquid was returned to the main reservoir through a venturi eductor at the top of the main reservoir. The motive force for the vapor phase flow was provided by the educting effect of the liquid flow through the venturi eductor. The vapor phase was drawn off the top of the main reservoir, through the vapor recirculation pathway, and also returned to the main reservoir through the venturi eductor (lefthand side of Figure 13). The two phases were intimately mixed in the eductor. Sampling assemblies for each fluid were provided within each recirculation loop. The pressure and temperature of the system were monitored. The temperature was controlled ±2.0°C. Improved temperature control reduced excursions to within 0.5°C. All wetted parts were stainless steel (main reservoir, all tubing, and pump body), glass (rotometer bodies), Teflon (liquid-sampling assembly, gaskets, and pump O-rings), Viton (rotometer and liquid-sampling assembly O-rings), Ryton (pump gears), carbon-filled PTFE (valve rotors), chromium-plated brass (venturi eductor), or Nitronic-60 (valve body). Adsorption was found to not be a problem. Carryover of organic solute between experiments

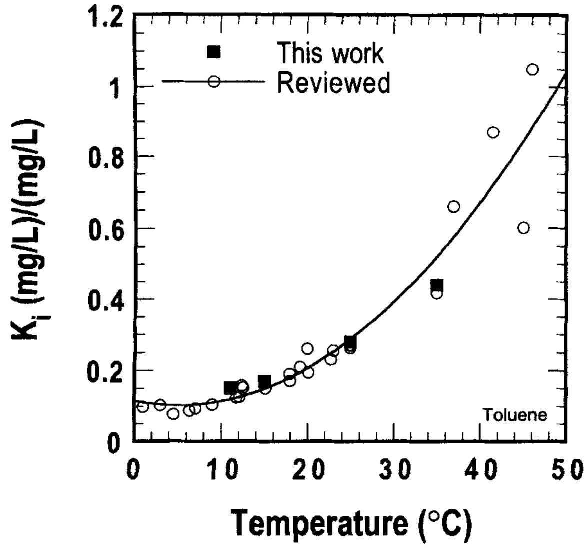

Figure 2. Vapor-liquid partition coefficient of toluene vs. temperature.

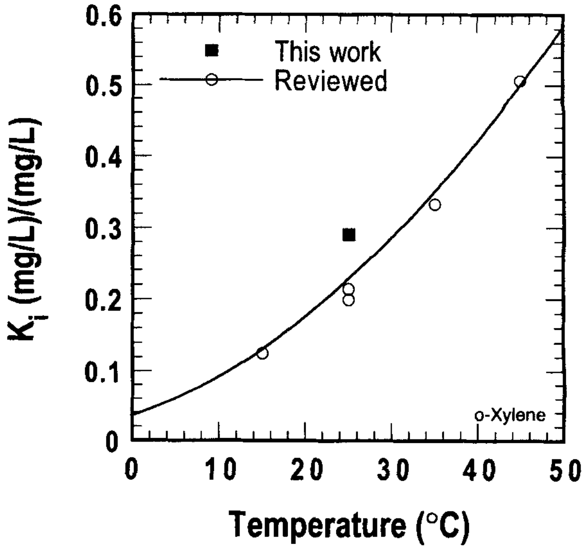

Figure 4. Vapor-liquid partition coefficient of o-xylene vs. temperature.

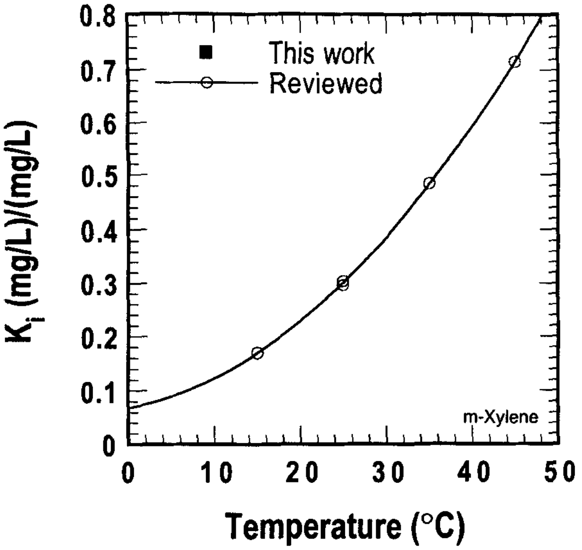

Figure 5. Vapor–liquid partition coefficient of *m*-xylene vs. temperature.

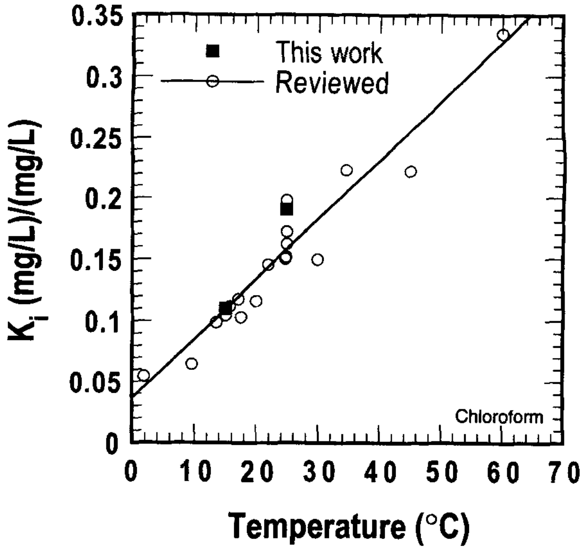

Figure 7. Vapor–liquid partition coefficient of chloroform vs. temperature.

and difficulty in cleaning would have resulted if significant amounts of organic solute had adsorbed to the cell components.

Liquid sampling was achieved by flushing the equilibrated liquid phase through a GC autosampler vial held in the liquid flowpath by the liquid-sampling assembly. The vial was then removed, capped, and labeled for later analysis by GC. The vapor phase was sampled directly from the vapor flowpath onto the GC via a 107-μL sample loop and valve assembly.

The equilibrium cell was shown to meet each of the seven design criteria mentioned earlier. Specific design details are described in the following paragraphs.

The reservoir was constructed of an 8-in. (203-mm) length of 2-in. (51-mm) 304 SS schedule 40 pipe with male pipe threads on either end. The pipe was sealed with 316 SS standard and blind flanges and Teflon mating gaskets at both ends. The pipe and flanges were obtained from Middlesex Stainless Steel, New Brunswick, NJ. The gaskets were obtained from Raritan Supply Co., New Brunswick, NJ. All connections to the reservoir were made through the blind flanges that were drilled and tapped to accommodate fittings with male pipe threads as needed.

The liquid circulation path began with a drawoff tube from the bottom end of the reservoir. The drawoff tube extended into the reservoir and ended in a 180° bend so that the inlet pointed down. This design was used to minimize vapor entrainment that might have been caused by drawdown of the liquid surface while placing the tubing entrance centrally in the liquid phase. Tubing from the reservoir then routed the liquid through a 40-μm screen filter, a pump, a sintered metal

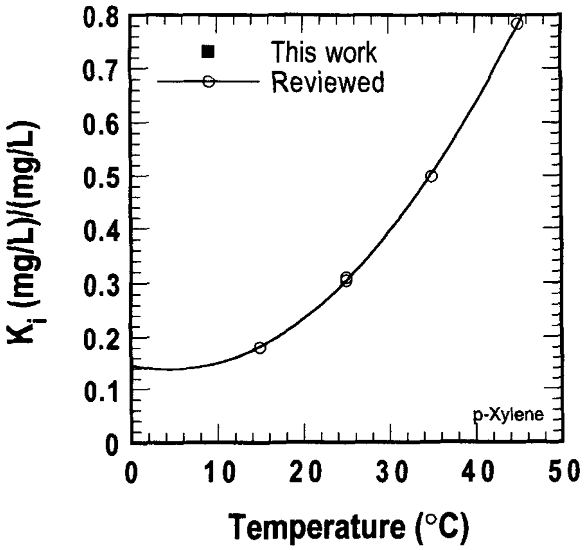

Figure 6. Vapor–liquid partition coefficient of *p*-xylene vs. temperature.

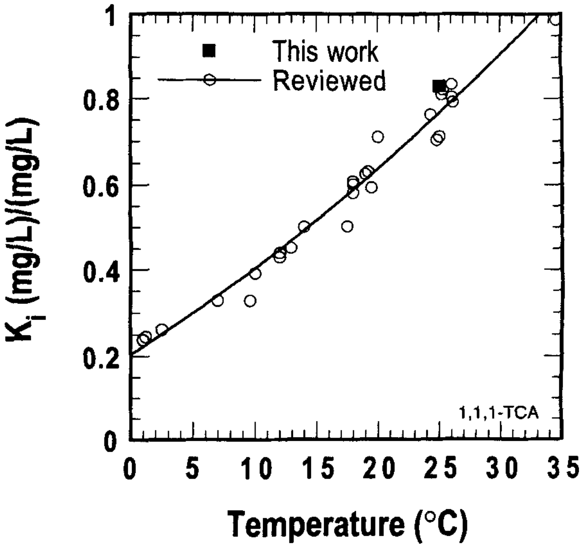

Figure 8. Vapor–liquid partition coefficient of 1,1,1-trichloroethane vs. temperature.

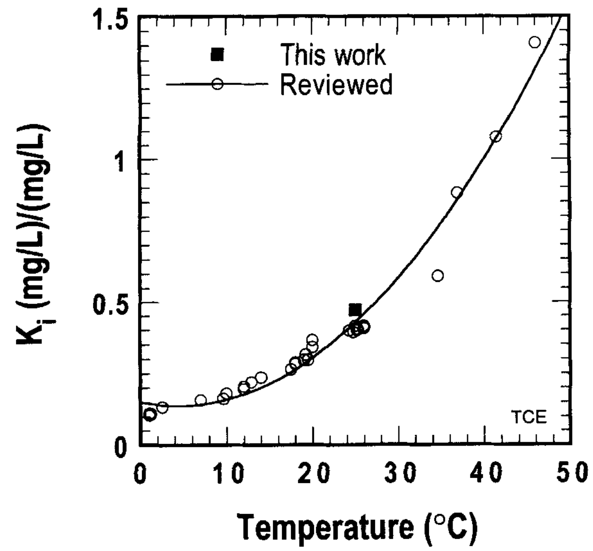

Figure 9. Vapor–liquid partition coefficient of trichloroethylene vs. temperature.

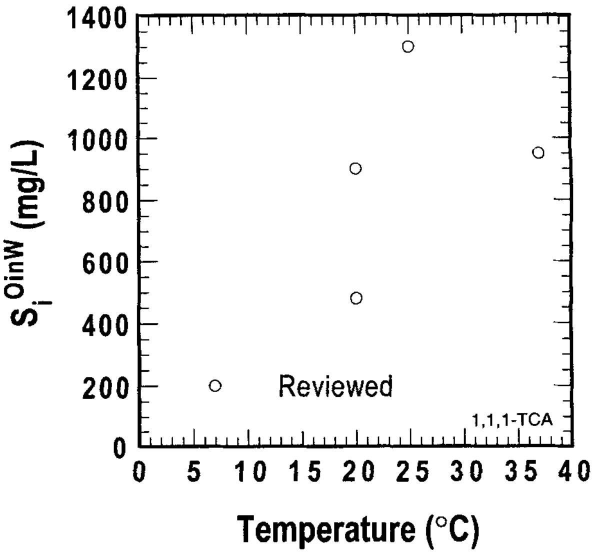

Figure 11. Solubility of 1,1,1-trichloroethane in water vs. temperature.

filter (2 or 7 μm), a sampling valve assembly, and an eductor pump at the top of the reservoir where the liquid recirculated into the reservoir. The pump (Barish Pump Co., Bohemia, NY, model 1830-346) was a sealed gear pump magnetically coupled to the driving motor. The pump body was 316 stainless steel with Ryton gears and a Teflon O-ring seal. The gears were one of the few wearable parts.

The sampling assembly allowed collection of a liquid sample directly into a 1.85-mL GC autosample vial. The vial was held in place by a bracket that compressed the lip of the vial against a fitted Teflon seal. A Viton O-ring was later inserted between the vial lip and the Teflon to improve sealability. The Teflon seal mated to the male pipe threads of a stainless steel male run tee (R. S. Crum, Morningside, NJ, part #SS-200-3TMT). The run of the tee was enlarged to accommodate the passage of a section of 1/8-in. (3.2-mm) tubing, which was set such that it ended flush with the top of the sample vial. Liquid entered the vial assembly through this section of tubing. The exit from the assembly was through the branch of the tee. This design assured thorough flushing of the sample vial with liquid. A small pocket (less than 1 cm^3) of trapped air was left above the branch of the tee and below the tubing seal in the annulus between the tee and the extended section of tubing. The effect of this air pocket was not studied and was assumed negligible. The entire sampling assembly could be isolated from the rest of the system with a six-port valve configured for four-port use (Valco Instrument Co., Houston, TX, model 6UWP). Thus, the pump did not need to be turned off to remove the liquid sample and replace the sample vial.

A section of coiled tubing of known volume was placed in

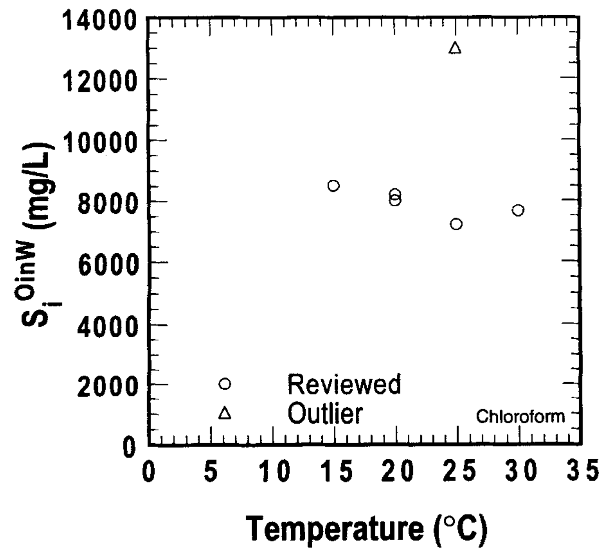

Figure 10. Solubility of chloroform in water vs. temperature.

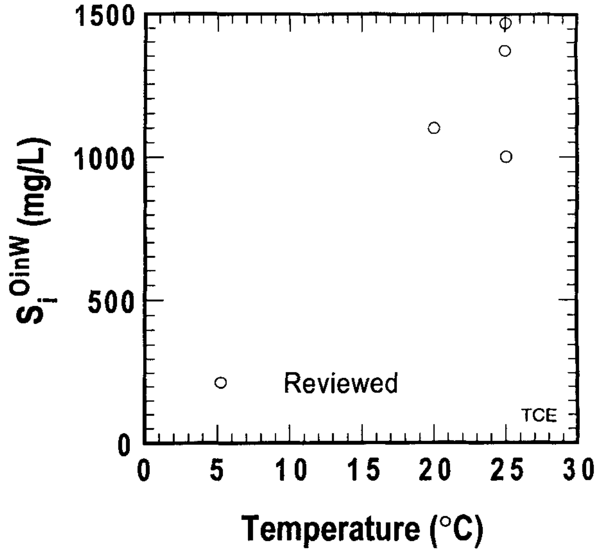

Figure 12. Solubility of trichloroethylene in water vs. temperature.

Table 14. Empirical Fit of the Partition Coefficient vs. Temperature: $K_i = a + b * T + c * T^2$

Compound	Temp. °C	a	b	c	r
Benzene	0–50	0.0763	0.00211	0.000162	0.9922
Toluene	0–50	0.115	−0.00474	0.000466	0.9544
Ethylbenzene	5–45	0.0500	0.00487	0.000250	0.9976
o-Xylene	15–45	0.0353	0.00444	0.000131	0.9694
m-Xylene	15–45	0.0683	0.00292	0.000255	0.9999
p-Xylene	15–45	0.146	−0.00349	0.000392	0.9998
Chloroform	0–60	0.0394	0.00486	—	0.9559
1,1,1-TCA	0–35	0.204	0.0182	0.000173	0.9849
TCE	5–45	0.151	−0.00597	0.000680	0.9867

the liquid flow path between the liquid sample assembly and the eductor. Three-way valves at both ends of the section allowed the section to be isolated from the rest of the cell. The original "put/take" loop was made of two sections of 1/4-in. (6.4-mm) tubing (total volume 100 mL). This was replaced with a single section of 3/16-in. (4.8-mm) SS tubing (volume 130 mL). The loops allowed the quantitative removal, "take," of liquid at the system concentration and replacement, "put," with liquid at another concentration (either solute-saturated deionized water or neat deionized water). The effect was an overall increase or decrease of solute mass in the cell. This allowed data to be collected at a number of concentrations with ease. The pump must be turned off during the put/take operation.

The liquid was returned to the top of the reservoir through the venturi eductor pump. The liquid was utilized as the motive fluid for driving the vapor through the circulation loop.

Vapor was drawn off the top of the reservoir. The vapor tubing was routed down to a 6-port valve (Valco Instrument Co., Houston, TX, model 6UWP). The valve was configured to switch a sample loop between the vapor flow path of the cell (sampling mode) and the carrier gas line of the GC (injection mode). The sample loop (Valco, Houston, model SL1008UW) and valve assembly had a calibrated sample volume of 107 μL. The body of the valve was Nitronic-60 stainless steel and the rotor was a carbon-filled PTFE compound. After the valve, the vapor passed through a rotometer for flow rate measurement (Matheson, Bridgeport, NJ, Tube Cube 601). The original Buna-N O-rings deteriorated steadily over time and were replaced with Teflon and then Viton. The vapor then entered the sidearm of the eductor. The liquid jet entrained the vapor, driving it through the sample loop and flowmeter. The two phases mixed intimately in the eductor mixing section before discharge back into the reservoir.

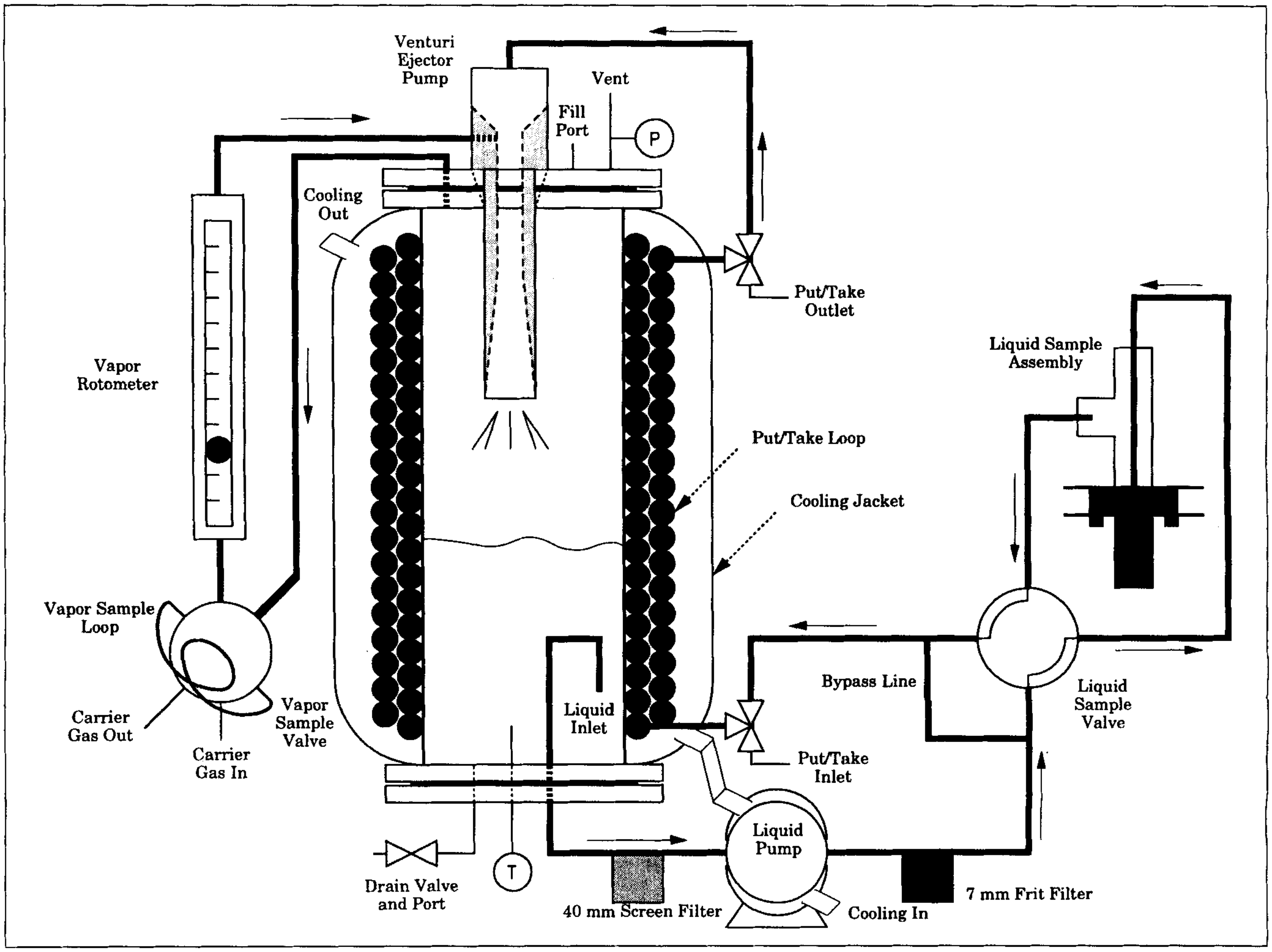

Figure 13. Diagram of the vapor–liquid equilibrium apparatus.

The performance of the eductor (Fischer Scientific, Springfield, NJ, part #09-956) was evaluated to determine its possible effects on the vapor analysis. Under operating conditions, the maximum pressure differential created was 6 mm Hg. This was less than 1% of the prevailing system pressure of 760 mm Hg. No pressure correction was deemed necessary.

Analytical methods

All analysis was carried out on an HP 5880 GC with flame ionization detection. Two columns were used to provide different retention time ranges for the compounds studied. They were a 1% SP 1000 60/80 Carbopack 6′×1/8″ column and a 5% SP 1200 1.75% Bentone 100/120 Supelcoport 6′×1/8″ column. Since FID does not detect water, no separation protocol was necessary. Therefore, the oven temperature was selected to give the shortest possible retention time. The aqueous liquid samples were injected directly onto the GC by a HP 7073 autosampler. Vapor samples were injected as described earlier. All samples were calibrated against liquid phase standards.

Data

Initially, the accuracy of the apparatus was verified by measurement of the pure-component vapor pressure of toluene, isopropyl alcohol, and 1-propanol. Observed vapor pressures were within 5% of reported literature values. Subsequently, the VLE of seven low-solubility, aqueous–organic systems were studied at 25°C. The organic compounds were benzene, toluene, ethylbenzene, *o*-xylene, chloroform, TCA, and TCE. All compounds were of anhydrous grade, 99% or higher purity (Aldrich, Milwaukee, WI), and diluted quantitatively into ultrapure deionized water. Data for three of the compounds (benzene, toluene, and chloroform) were collected over a range of temperatures. Between 10 and 50 data points at different solute mass loadings were collected for each system. The vapor and liquid concentrations were linearly regressed against each other. The slope of the regressed line represented the partition coefficient, K_i. The regressions were preformed with the statistical package S (Becker et al., 1988) using the robust routine *rreg*, which executes an iteratively reweighted least squares regression.

Some data sets exhibited a nonlinearity near the solubility limit. For these data sets, the regression coefficients were determined from the linear portion of the data. The region of linearity was determined by successively eliminating the highest ranked data points from the data set and recalculating the regression coefficients. This was done until a satisfactory regression was obtained, as determined by noting changes in the regression coefficients between successive regressions and by inspection of the residual plots.

The reason for the nonlinearity is not known. It is possible that, near the solubility limit, condensation of organic-laden vapor could have occurred in the vapor sample loop of the equilibrium cell. Modifications to the equilibrium cell are being implemented to eliminate this as a possibility in future studies.

All of the collected data are highlighted in boldface type in Tables 3–9. The collected data agree favorably with the reviewed literature. Characteristic data sets for chloroform at 25°C are plotted in Figure 14. Each "data set" refers to a set of data obtained during an operational sequence for the apparatus (different data sets were determined on different days with freshly prepared stock solutions and standards).

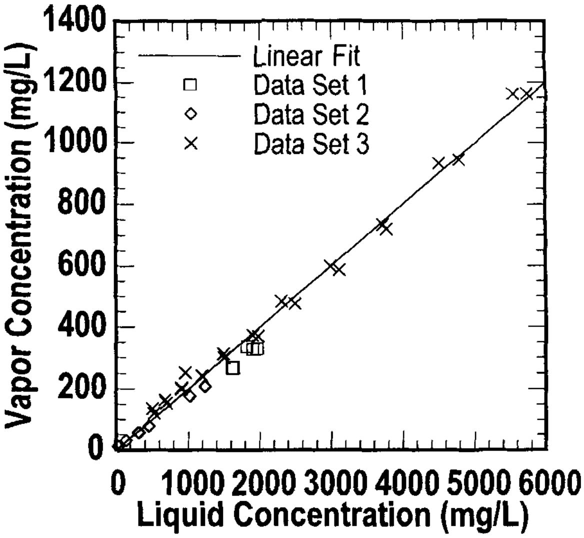

Figure 14. Vapor–liquid equilibrium data for the chloroform–water system collected with the new VLE apparatus at 25°C.

Mass balances

Mass balances could be calculated for individual experimental runs due to the design of the experimental apparatus. The discrepancy in mass was calculated after each put/take as

$$\%\ \text{Mass discrepancy} = \left(\frac{M_m^T - M_c^T}{M_c^T}\right) * 100\%, \tag{15}$$

where

$$M_m^T = C_m^L V^L + C_m^V V^V \tag{16}$$

and

$$M_{c,j}^T = M_{c,j-1}^T - \frac{M_{c,j-1}^T}{V_{j-1}^L + K_i V_{j-1}^V} + C^S V_{j-1}^{(PT)}. \tag{17}$$

It was found that the discrepancies in mass were generally less than 5% for a single experiment. Figure 15 presents boxplots of the mass balance for two experiments.

Conclusions

The literature review turned up consistent sets of data for the compounds studied. By far, water–benzene has been the most studied system. There is a need for data on other systems covering a range of temperatures. This is particularly true of the water-chlorinated organic mixtures. No data were found for the solubilities of water in the chlorinated organics studied. The partition coefficients and mutual solubilities of

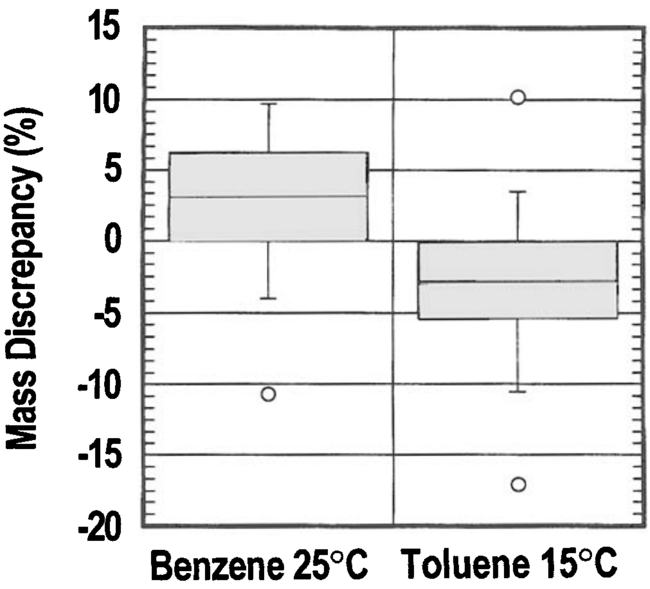

Figure 15. Boxplots of the mass balance discrepancies for the benzene and toluene data collected with the new VLE apparatus at 25°C.

aqueous solutions of the organic compounds studied depend significantly on temperature.

A new experimental VLE apparatus was designed constructed, and tested. Partitioning data for several aqueous–organic systems were measured. Comparison of the collected data to data available in the literature was very favorable. The new procedure is capable of providing high-quality data over a range of concentrations and temperatures.

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Notation

F = volumetric flow rate, L/s
G = Gibb's free energy, J
k = partition coefficient, $(\mathrm{mol/mol})^V/(\mathrm{mol/mol})^L$
K^M = partition coefficient, $(\mathrm{mol/L})^V/(\mathrm{mol/L})^L$
n = number of equilibrations
P = pressure, atm or mm Hg
r = regression coefficient
R = universal gas constant, 0.08206 L·atm/mol·K
S = solubility, mg/L
T = temperature, K or °C
t = time, s
x = liquid-phase mole fraction, mol/mol
y = vapor-phase mole fraction, mol/mol

Greek letters

γ = activity coefficient with Raoult's law standard state, dimensionless
ρ = density, g/mL

Superscripts and subscripts

PT = put/take
S = stock
sat = saturation condition
T = total
$1,2,\ldots,n$ = component in a mixture or sample number
c = calculated quantity
j = sample number
m = measured quantity

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