**Registry No.** 1,3-Dioxolane, 646-06-0; acetonitrile, 75-05-8.

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# Solubility of Aromatic Hydrocarbons in Water and Sodium Chloride Solutions of Different Ionic Strengths: Benzene and Toluene

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**The solubilities of benzene and toluene in aqueous sodium chloride solutions having ionic strengths ranging from 0 to 5.00 have been determined at 25.00 °C. The solubilities were determined by headspace analysis using a multiple injection interrupted flow (MIIF) technique. The values for the Henry's law constants and partition coefficients for benzene and toluene in the solutions studied are also given. The activity coefficients of benzene and toluene in the solutions studied can be calculated from the solubility data.**

Determining solubilities of substances with appreciable vapor pressures can be complicated by the partition of such substances between the solvent and free gas space present above the solvent. A modification of the headspace analysis technique developed by Massaldi and King (*1*) was selected as the method used for this study because of its ease of execution and because solute partition is not a problem since headspace methods make use of partition.

## Theory

Volatile solutes tend to obey Henry's law

$$p = kx \qquad (1)$$

The Henry's law constant is dependent upon the solute, solvent, and temperature but is independent of $x$ over the range for which the law holds. Since conformity with Henry's law increases as $x \rightarrow 0$, substances of limited solubilities tend to obey it over their solubility range.

When a sample from above a solution of a volatile solute, which obeys Henry's law, is analyzed by gas chromatography (GC) the peak area of the solute is directly proportional to its mole fractions in both the vapor and solution through the relationship

$$A = Cy = Cx/K_p \qquad (2)$$

The total number of moles of solute in the system is given by

$$n_s = n_x + n_y \qquad (3)$$

Table I. Symbols Employed[a]

| | |
|---|---|
| $p$ | partial pressure of substance in the vapor |
| $x$, $y$ | mole fraction of substance in the solution and vapor, respectively |
| $k$ | Henry's law constant |
| $A_x$, $A_y$ | integrated GC peak area of vapor from above solution samples and from vapor-only samples, respectively |
| $K_p$ | partition coefficient ($=x/y$) |
| $C$ | GC correlation constant |
| $n_x$, $n_y$, $n_s$ | moles of substance in the solution, vapor, and system, respectively |
| $v_x$, $v_y$, $v_s$ | liquid volume of substance in the solution, vapor, and system, respectively |
| $S$ | solubility in any units |
| $\gamma$ | activity coefficient |
| $\mu$ | ionic strength |

[a] Zeroed quantities refer to system as well as solvent saturation.

If $n_s^0$ and $n_y^0$ can be determined then $n_x^0$ can be computed. The method of Massaldi and King was modified, in part, in the way $n_s^0$ was determined. Table I defines the terms used in the determinations.

## Experimental Section

***Instrumentation.*** Measurements were made using a headspace attachment constructed specifically for a Varian Model 3700 gas chromatograph (*2*).

***Materials.*** Benzene and toluene (Baker Instra-Analyzed grade) were analyzed by gas chromatography and were 99.97 and 99.83% pure, respectively. Sodium chloride (Baker Analyzed Reagent grade) was dried at 110 °C prior to use. The deionized water used had a conductivity of $<10^{-6}$ (ohm cm)$^{-1}$ at 20 °C.

***Sample Preparation.*** Samples were prepared in 125-mL septum bottles (Wheaton "400" clear glass) which have a mean volume of 160.10 ± 0.87 mL at room temperature. Two types of samples were used: one contained 50.00 mL of water or aqueous NaCl solution plus the hydrocarbon of interest, added from a microliter syringe (Hamilton Model 700 RN); the other contained only hydrocarbon vapor. A small 6.4 mm by 22.2 mm Pyrex glass coated magnetic stirring bar with a mean volume of 0.70 mL (Bel-Art Products) was present in the liquid

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**Table II. GC Response for Toluene in 50.0 mL of Water at 25.00 °C**

| solute, μL | time, min | | | | | | |
|---|---|---|---|---|---|---|---|
| | 2 | 3 | 4 | 5 | 6 | zero | $R$ |
| 8 | 154 342 | 156 297 | 158 200 | 160 190 | 162 355 | 150 309 | 1.000 |
| 16 | 308 654 | 314 154 | 319 225 | 323 508 | 327 382 | 299 861 | 0.997 |
| 24 | 472 932 | 479 951 | 485 355 | 490 065 | 496 379 | 462 133 | 0.998 |
| 32 | 635 610 | 641 182 | 648 660 | 655 351 | 662 436 | 621 907 | 1.000 |
| 40 | 806 111 | 814 576 | 822 442 | 830 434 | 839 307 | 789 674 | 1.000 |

samples. Pyrex rather than poly(tetrafluoroethylene) (PTFE) coated stirring bars were used when it was observed that PTFE in the system absorbed benzene which lead to high solubility values (*3*). The bottles were sealed by using PTFE-coated silicone septa (Ace Tuf-Bond) and aluminum seals (Wheaton). Tin foil was placed between the septum and the bottle's contents in order to preclude absorption of hydrocarbon by the PTFE-coated septa. All preparations were carried out in an air-conditioned laboratory at 20 °C. The densities of the brine solutions were determined at 20 and 25 °C and the density ratio was employed to adjust the results from preparative to experimental temperature. The bottles were thermostated (25.00 ± 0.01 °C) and shaken for 72 h prior to analysis. For analysis each bottle was transferred to a tempering beaker and pressurized to 15.00 ± 0.02 psig with chromatographic grade nitrogen.

***Analytical Procedure.*** Bottles were attached to the headspace attachment by piercing their septa with a side-port needle (Precision Sampling Corp.), an integral part of the headspace unit. Bottle and tempering beaker were supported on a magnetic stirrer (Cole-Parmer Micro-V). Vapor flow, 2–3 mL/min, through the sampling valve (Valco, 6-port) and sample loop (430 μL) was controlled by a fine metering valve (Nupro M series with vernier handle). The sampling valve was connected to a 1 m by 3.2 mm stainless steel GC column (5% SP-1200, 1.75% Bentone-34 on 100/120 mesh Supelcoport (Supelco Inc.)) and then to a flame ionization detector (FID).

To determine the hydrocarbon solubility the concentrations of hydrocarbon in the vapor in equilibrium with hydrocarbon in solution must be known (eq 2). Any vapor removal produces a pressure drop which disturbs this equilibrium. To obtain the equilibrium concentration, a multiple injection interrupted flow technique (MIIF) was developed. A series of vapor aliquots were taken at known flow times and a linear extrapolation of their GC responses made to obtain the GC response at equilibrium. The pneumatic compartment of the GC and the headspace attachment were heated to 60 °C to minimize hydrocarbon condensation or adsorption in the system.

Sampling schedules and integrator events were time coordinated to assure optimum integrator operation. Table II gives GC data for a typical run using the MIIF technique. The increase in peak area with flow time results from the partial pressure drop with vapor removal and desorption of solute from solution to reestablish equilibrium. The increase in mole fraction of hydrocarbon in the vapor occurs since other gases present are not replenished. Column "zero" under "Time" in Table II is from linear least-squares analysis of the time data. Column "*R*" are the linear correlation coefficients of the data that produced each "zero" time value. The mean correlation coefficients for the "zero" time versus hydrocarbon volume plots used in this study was 0.9996 ± 0.0005 (sdm).

Analysis of samples that contained only hydrocarbon vapor was carried out using the same procedure. The absence of liquid gave peaks of essentially constant size, and mean peak areas were used.

***Data Reduction.*** The GC area response of the vapor-only samples was analyzed by least-squares as a function of volume of hydrocarbon to obtain

$$A_y = m_y v_y + b_y \qquad (4)$$

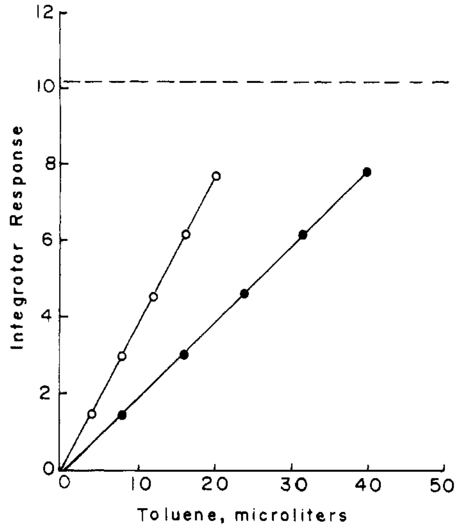

Figure 1. Typical "zero" flow time GC response as a function of microliters of hydrocarbon added to the sample bottle: (○) vapor-only samples; (●) liquid-containing samples. The dashed line corresponds to the computed response at system saturation.

**Table III. Solubility of Benzene and Toluene in Aqueous Solutions of Different Ionic Strengths at 25.00 °C**

| ionic strength | solubility[a] | | |
|---|---|---|---|
| | ppm | mole fractn × $10^4$ | mol/L × $10^2$ |
| | | Benzene | |
| 0 | 1696 ± 1 | 3.91 ± 0.00 | 2.17 ± 0.00 |
| 1 | 1012 ± 2 | 2.33 ± 0.01 | 1.29 ± 0.00 |
| 2 | 721 ± 3 | 1.66 ± 0.01 | 0.921 ± 0.004 |
| 3 | 479 ± 1 | 1.11 ± 0.00 | 0.613 ± 0.001 |
| 4 | 289 ± 7 | 0.666 ± 0.017 | 0.369 ± 0.009 |
| 5 | 201 ± 2 | 0.465 ± 0.004 | 0.257 ± 0.002 |
| | | Toluene | |
| 0 | 580 ± 3 | 1.13 ± 0.01 | 0.629 ± 0.003 |
| 1 | 344 ± 2 | 0.699 ± 0.005 | 0.386 ± 0.003 |
| 2 | 189 ± 0 | 0.400 ± 0.001 | 0.221 ± 0.000 |
| 3 | 124 ± 2 | 0.272 ± 0.004 | 0.150 ± 0.002 |
| 4 | 71.7 ± 1.3 | 0.163 ± 0.030 | 0.0892 ± 0.0016 |
| 5 | 49.7 ± 1.1 | 0.117 ± 0.002 | 0.0638 ± 0.0014 |

[a] Value ± standard deviation of the mean.

The value of $A_y^0$ was obtained from eq 4 by using $v_y^0$ computed, assuming ideal behavior, from vapor volume (160.1 mL), hydrocarbon density, and vapor pressure of pure hydrocarbon, $p^0$, calculated from the Antoine equation (*4*). A least-squares analysis of data for vapor from above the solutions gave a similar relationship

$$A_x = m_s v_s + b_s \qquad (5)$$

At system saturation $A_x = A_y^0$, $v_s = v_s^0$, and $v_x^0 = v_s^0 - v_y^0$. The value of $v_y^0$ for solution samples was computed by using the reduced vapor volume (109.4 mL). Concentrations were computed from $v_x^0$, compound and solution densities, and solution volume and composition. Figure 1 is a typical plot of the GC responses for vapor only and for liquid-containing samples used to calculate $A_y^0$ and $v_s^0$.

***Results.*** The solubility of benzene and toluene in water and aqueous sodium chloride solutions with ionic strengths up to

**Table IV. Partition Coefficients and Henry's Law Constants for Benzene and Toluene in Aqueous NaCl Solutions of Various Ionic Strengths at 25.00 °C**

| ionic strength | benzene | | toluene | |
|---|---|---|---|---|
| | $K_p$ | $10^{-5}k$, Torr | $K_p$ | $10^{-5}k$, Torr |
| 0 | 4.23 | 2.44 | 4.10 | 2.52 |
| 1 | 2.52 | 4.09 | 2.52 | 4.07 |
| 2 | 1.80 | 5.73 | 1.44 | 7.12 |
| 3 | 1.20 | 11.6 | 0.975 | 10.46 |
| 4 | 0.720 | 14.3 | 0.582 | 17.46 |
| 5 | 0.503 | 20.5 | 0.416 | 24.33 |

**Table V. Reported Values for the Molar Solubility of Benzene and/or Toluene in Water at 25.00 °C**

| reference | solubility, (mol/L) × $10^2$ | |
|---|---|---|
| | benzene | toluene |
| this work | 2.17 | 0.629 |
| Andrew and Keefer (*9*) | 2.23 | 0.58 |
| Klevens (*10*) | 2.38 | 0.54 |
| Bohon and Clausen (*11*) | 2.29 | 0.681 |
| Hayashi and Sasaki (*12*) | 2.30 | |
| Arnold et al. (*13*) | 2.23 | |
| McAuliffe (*14*) | 2.279 | 0.5599 |
| Taha et al. (*15*) | 2.2 | |
| Worley (*16*) | 2.78 | |
| Polak and Lu (*17*) | 2.247 | 0.622 |
| Price (*18*) | | 0.601 |
| Mackay and Shiu (*19*) | 2.2782 | 0.5639 |
| Sutton and Calder (*20*) | | 0.5805 |
| Schwarz (*21*) | 2.33–2.47 | 0.716–0.727 |
| Sanemasa et al. (*22*) | 2.06 | 0.561 |
| May et al. (*26*) | 2.29 | |

5.00 at 25.00 °C is summarized in Table III.

Since at constant temperature the chemical potential of a solute is the same in all of its saturated solutions, the activity coefficients for the substance in two solutions with different solubilities obey the relationship

$$\gamma_1/\gamma_2 = S_2/S_1 \tag{6}$$

If for one solution the solvent is water, then for a solute with limited solubility

$$\gamma_i = S_{aq}/S_i \tag{7}$$

The assumption implicit in eq 7 is that the solute activity coefficient is 1.00 in the saturated aqueous solution. The validity of this assumption increases as $S^0 \rightarrow 0$. Since the mole fraction solubilities of benzene and toluene in aqueous solution are $3.91 \times 10^{-4}$ and $1.10 \times 10^{-4}$, eq 7 can be used to compute the activity coefficients from the solubility values obtained in this study. Plots of ln $\gamma$ or ln $S$, for benzene or toluene, as a function of ionic strength are linear with correlation coefficients of 0.998 (5–8). These plots yield salting out coefficients, d ln $S$/d$\mu$, of −0.423 and −0.464 for benzene and toluene, respectively.

Partition coefficients and Henry's law constants for benzene and toluene are listed in Table IV for all solutions studied.

Tables V–VII list the results of this work and earlier studies of solubilities, Henry's law constants, and partition coefficients for benzene and for toluene in water at 25.00 °C.

**Table VI. Reported Values for the Henry's Law Constant for Benzene and/or Toluene in Water at 25.00 °C**

| reference | $10^{-5}k$, Torr | |
|---|---|---|
| | benzene | toluene |
| this work | 2.44 | 2.52 |
| Taha et al. (*15*) | 2.40 | |
| Green and Frank (*23*) | 2.30 | |
| Mackay et al. (*24*) | 2.35 | 2.81 |

**Table VII. Reported Values for the Partition Coefficient, $K_p$, for Benzene and Toluene in Water at 25.00 °C**

| reference | $K_p$ | |
|---|---|---|
| | benzene | toluene |
| this work | 4.23 | 4.10 |
| Tsibulskii et al. (*25*) | 4.0 | 3.6 |

## Conclusions

The MIIF headspace analysis technique is a simple, sensitive, and accurate method for determining solubilities, Henry's law constants, partition coefficients, and activity coefficients of nonelectrolytes that have appreciable vapor pressures. There is little system manipulation after sample preparation, which avoids problems associated with solute partition. The MIIF technique does not require the solvent be saturated and thus avoids the complexity the presence of a third solute-rich phase can introduce.

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**Registry No.** NaCl, 7647-14-5; $C_6H_6$, 71-43-2; PhMe, 108-88-3.

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