Solubility of Alkylbenzenes in Distilled Water and Seawater at 25.0°C

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The solubilities of a number of alkylbenzenes are measured in distilled water and seawater at 25.0°C. Saturation is achieved by equilibrating water with aromatic hydrocarbon vapor at the equilibrium vapor pressure of the alkylbenzene involved. Results indicate that for monosubstituted alkylbenzenes, the size of the alkyl substituent is important in determining the solubility, whereas for polysubstituted alkylbenzenes, the positions of the substituents on the benzene ring are also important.

An understanding of the solubility behavior of oil in aqueous solutions of different ionic strength is important in understanding the mechanisms of oil reservoir formation. Moreover, solubility studies of oil in different ionic strength aqueous media are important because salting in or salting out processes may alter geochemical pathways as oil is transported through salinity gradients such as those in estuaries. However, since oil is a complex mixture of organic compounds, it is doubtful whether the solubility behavior of oil in freshwater or brines can ever be thoroughly understood until the solubility behavior of the individual organic compounds composing it is thoroughly understood. As a step in this direction, the solubilities of a number of substituted alkylbenzenes were determined in distilled water and in artificial seawater. Alkylbenzenes were chosen to see how substituent size and substituent positions on the benzene ring influence solubilities.

Experimental

Solubility values were obtained by equilibrating water with aromatic hydrocarbon vapor in an all-glass equilibrating apparatus consisting of a 1-liter Erlenmeyer flask with an insert tube. Several milliliters of pure aromatic hydrocarbon were placed in the bottom of the insert tube, which was capped with a ground glass stopper. The hydrocarbon was completely isolated from its surroundings except for perforations in the insert which allowed the hydrocarbon vapor to enter the air space above the water in the Erlenmeyer equilibration flask. The vapor could not escape the equilibration flask, as the male ground glass joint at the outside of the top of the insert tube fitted the female ground glass joint in the inside of the neck of the Erlenmeyer flask precisely. The flask contained 500 ml of seawater or distilled water.

The flask was placed in a constant-temperature shaking bath. Thus, the hydrocarbon vapor in the flask was the equilibrium vapor pressure of the pure hydrocarbon at whichever temperature the shaking bath was set. All solubility values in this work were taken at 25.0° ± 0.1°C. The water was equilibrated by shaking for 48 hr. However, for most of the molecules studied, equilibration was complete within 35 hr. Figures 1 and 2 demonstrate approach to equilibrium from undersaturation and oversaturation for two alkylbenzenes in distilled water. In the approach from supersaturation, the flasks were shaken for 24 hr at 75°C and then allowed to cool gradually to 25°C while being sampled periodically. The supersaturation values are all undoubtedly a bit high, since the aromatics formed droplets which rose to the surface and dispersed throughout the water upon coming out of solution. Some of these droplets were probably sampled as well as the dissolved hydrocarbons.

Exactly 100-ml aliquots were removed from the flask by volumetric pipet for analysis. The volumetric pipet containing the aliquot was allowed to drain into a 250-ml separatory funnel containing 10 ml of hexane. After draining, the volumetric pipet was immediately rinsed with several milliliters of hexane, which was also allowed to drain into the separatory funnel. By draining the volumetric pipet into the 10 ml of hexane in the bottom of the separatory funnel, any amounts of hydrocarbon which degassed should have dissolved in the hexane. Each aliquot was extracted three times with 10-ml portions of hexane (the 10 ml initially present in the bottom of the separating funnel was the first).

The 10 ml of hexane initially present in the bottom of the separatory funnel contained an internal standard. The internal standard was another aromatic molecule with a vapor pressure similar to that of the compound under investigation. For example, *m*-xylene was an internal standard for toluene, whereas 1,2,4-trimethylbenzene served as an internal standard for *m*-xylene. The use of an internal standard insured that any loss of the hydrocarbon being analyzed subsequent to removal from the equilibration vessel could be compensated for.

Each 30-ml hexane extract was concentrated to 10 ml by evaporation of hexane under a stream of prepurified nitrogen gas. Use of the internal standard assumed that the internal standard and the hydrocarbon under investigation were lost at equal rates during evaporation. In reality, this assumption was not true, and experiments were designed to insure that differential loss during the evaporation step could be compensated for. As this was an important step, one such experiment will be described.

Standards containing both toluene and *m*-xylene in hexane were composed so that the concentration of each compound in the standard was approximately equal. A number of such standards covering a wide concentration range were made up. Ten-ml aliquots of each standard were placed in a beaker, diluted to 30 ml with hexane, and evaporated back to 10 ml under nitrogen. Four duplicates of each standard were run. The concentrations of toluene and *m*-xylene in each standard were determined by gas chromatography before and after evaporation. The loss of toluene relative to *m*-xylene could then be determined as a function of the concentration of toluene in the standard. This type of procedure was carried out for all combinations of alkylbenzenes and internal standards.

The loss of toluene relative to *m*-xylene was 21.9%. The losses of *m*-xylene, *p*-xylene, *o*-xylene, and ethylbenzene relative to 1,2,4-trimethylbenzene were 4.4, 4.7, 5.2, and 4.8%, respectively. The losses of all other compounds relative to their internal standards during evaporation were 1% or less.

The concentration of aromatic hydrocarbons was determined by injection of the concentrated hexane extract into a Hewlett-Packard 5711A dual-column gas chromatograph

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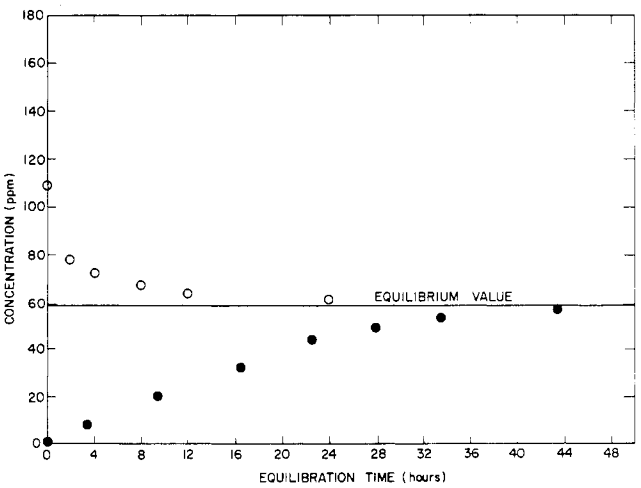

Figure 1. Concentration vs. equilibration time for 1,2,4-trimethylbenzene

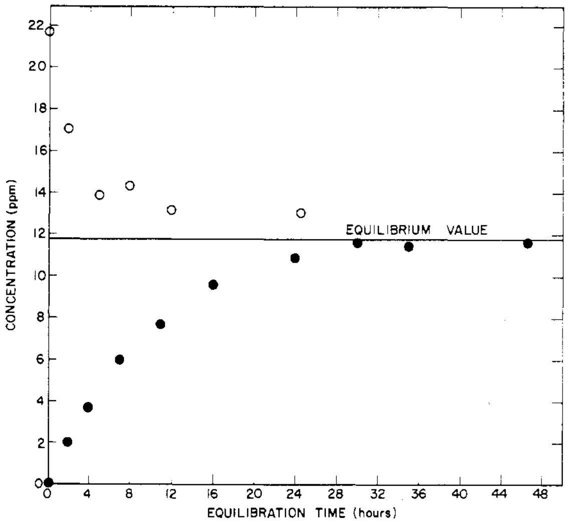

Figure 2. Concentration vs. equilibration time for *n*-butylbenzene

equipped with flame ionization detectors and connected to a strip chart recorder. Peak areas (detector response) were calculated with a Hewlett-Packard 3373B electronic integrator. The columns in the chromatograph were 1-m long by 2-mm i.d. The column packing was 5% didecylphthalate and 5% bentone 34 on Chromosorb W(AW). Detectors were kept at 350°C and the inlet ports at 250°C. The nitrogen carrier gas flow rates were 20 ml/min. The oven temperature and programming rate were variable depending upon the hydrocarbon being analyzed.

The solubility of a given hydrocarbon was determined by comparing its peak area in the hexane extract (after being corrected for evaporation loss) to the peak area of the same compound in an external standard. The same compound was used for comparison rather than the internal standard compound because of possible differences in detector response for the two compounds.

All freshwater was doubly distilled. The seawater was made according to the formula of Lyman and Fleming (*3*), which gave a salinity of 34.5 parts per thousand.

All glassware was rinsed with double-distilled hexane to remove any contaminants. The glassware was then soaked for 24 hr in a concentrated chromic acid bath, rinsed with double-distilled water, and dried for 12 hr or more in an oven at 200°C. The glassware was not removed from the oven until just prior to use.

The chemicals were bought either from Aldrich Chemical Co. or Matheson Coleman & Bell. All were 99%+ pure except 1,2,3-trimethylbenzene, which was purified by distillation through a Vigreaux column until its purity was 98.4% as determined by gas chromatography.

Experimental Results

Table I shows solubilities of individual aromatic hydrocarbons in distilled water and seawater at 25°C. Values obtained in this work are compared with those of McAuliffe (*4*), Price (*7*), Hermann (*1*), and Polak and Lu (*6*). In general, agreement is quite good. The isopropylbenzene, however, shows serious disagreement with literature values. No reason for this is known. All measurements give the precision as the standard deviation of the mean for six replicates. The precision is excellent for most measurements.

Table I. Solubility of Individual Compounds at 25.0°C

Compound	Soly distd water at 25°C, ppm	Soly seawater at 25°C, ppm	Lit values (distd water, 25°C)	
Toluene	534.8 ± 4.9	379.3 ± 2.8	515 ± 17[a] 554 ± 15[b]	573[c]
Ethylbenzene	161.2 ± 0.9	111.0 ± 1.3	152 ± 8[a] 131 ± 1.4[b]	177[c]
o-Xylene	170.5 ± 2.5	129.6 ± 1.8	175 ± 8[a] 167 ± 4[b]	213[c]
m-Xylene	146.0 ± 1.6	106.0 ± 0.6	134 ± 2[b]	162[c] 157[d]
p-Xylene	156.0 ± 1.6	110.9 ± 0.9	157 ± 1[b]	185[c] 163[d]
Isopropylbenzene	65.3 ± 0.8	42.5 ± 0.2	50 ± 5[a] 48.3 ± 1.2[b]	
1,2,4-Trimethylbenzene	59.0 ± 0.8	39.6 ± 0.5	57 ± 4[a] 51.9 ± 1.2[b]	
1,2,3-Trimethylbenzene	75.2 ± 0.6	48.6 ± 0.5		
1,3,5-Trimethylbenzene	48.2 ± 0.3	31.3 ± 0.2		
n-Butylbenzene	11.8 ± 0.1	7.09 ± 0.07		
s-Butylbenzene	17.6 ± 0.2	11.9 ± 0.2		
t-Butylbenzene	29.5 ± 0.3	21.2 ± 0.3		

[a] McAuliffe (*4*). [b] Price (*7*). [c] Polak and Lu (*6*). [d] Hermann (*1*).

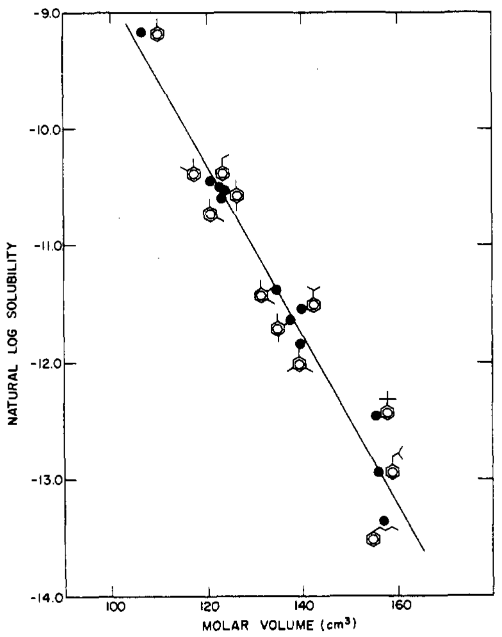

Figure 3. Relation between natural log solubility (as mole fraction) and molar volume

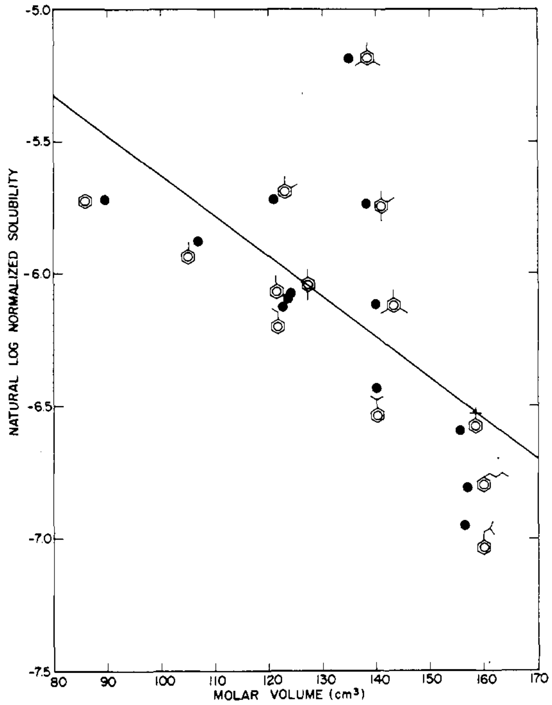

Figure 4. Relation between natural log normalized solubility (as mole fraction) and molar volume

Discussion

To understand the dissolution process, different investigators have attempted to correlate various properties of the aromatics with their solubilities. The most commonly and successfully correlated properties are the molar volume and the molar surface area (*1, 2, 4*). For example, McAuliffe (*4*) found that a plot of the logarithm of the solubility of aromatics against the molar volume of the aromatic yielded a straight line. Figure 3 shows a plot of the natural logs of the solubilities (as mole fractions) in distilled water against molar volume for the aromatics studied. The correlation coefficient is −0.98, which is significant at the 95% confidence level. As with the work of McAuliffe, there is an obvious linear relation between the molar volumes and the natural logs of the solubility.

However, Henry's law states that the solubility of a gas in solution is directly proportional to the vapor pressure of the gas above the solution at equilibrium. Since the smaller aromatics have higher vapor pressures than the larger aromatics, it is quite likely that some of the linear relation between natural log solubility and molar volume is due to differences in the equilibrium vapor pressure of the various aromatics. If the solubilities of the aromatics in distilled water are normalized to 1 atm equilibrium vapor pressure, a plot of the natural log of the normalized solubility against molar volume should be a better indication of the functional dependence of solubility upon molar volume. Figure 4 shows such a plot with benzene included for the sake of completeness. The solubility of benzene was taken from McAuliffe (*4*). The correlation coefficient for the line fitted to the points is −0.63. Thus, while there is still some functional dependence of normalized solubility upon the molar volume, other factors are also significant. These factors include nonspecific dispersion, induction, repulsion, and dipole–dipole interactions between the solute molecules and surrounding solvent molecules (*5*), as well as specific solute–solvent molecular complexes (*8*). Examination of Figure 4 shows that for monosubstituted alkylbenzenes, such interactions seem to be related to the size of the alkyl substituent. For polysubstituted alkylbenzenes, such interactions are also influenced by the positions of the substituents on the benzene ring.

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