

## NOMENCLATURE

- $a$  = constant, Equation 5,  $\text{cp.}^{-1}$   
 $b$  = constant, Equation 5,  $\text{cp.}^{-1}$   
 $\Delta G$  = activation energy for viscous flow, cal. per mole  
 $h$  = Planck's constant  
 $k_1$  = constant,  $\text{cp. per (gram per ml.) (sec.)}$   
 $k_2$  = constant,  $(\text{cp.}) (\text{sec.}^2)$  per (gram mole)  
 $n$  = number of points  
 $N$  = Avogadro's number  
 $t$  = temperature,  $^{\circ}\text{C.}$   
 $v$  = molal volume, ml. per mole  
 $V_G$  = geometric mean molal volume, ml. per mole  
 $X$  = mole fraction bromododecane  
 $\eta$  = absolute viscosity,  $\text{cp.}$   
 $\theta$  = time,  $\text{sec.}$   
 $\nu$  = kinematic viscosity,  $\text{cp. per (gram per ml.)}$   
 $\Sigma$  = summation operator

## Superscripts

- 0 = pure component

## Subscripts

- 1,2 = species 1, species 2  
 $C$  = calculated value  
 $E$  = experimental value

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RECEIVED for review June 28, 1968. Accepted May 19, 1969. This work was supported by the National Science Foundation under Grant GK 686.

# Solubility of $\text{C}_6\text{-C}_8$ Aromatic Hydrocarbons in Liquid $\text{CO}_2$

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Solubility data of benzene, toluene, ethylbenzene, *o*-, *p*-, and *m*-xylene in liquid  $\text{CO}_2$  are given for temperatures from  $-15^{\circ}$  to  $-55^{\circ}\text{C.}$

THE SOLUBILITY of hydrocarbons in liquid  $\text{CO}_2$  was studied by Gore (14) as early as 1861, and the first comprehensive review on the subject dates back to 1906 (7). Although several decades have since gone by, there are only a few investigators who have published additional data on this subject (2-16). Of these, the work of Francis (8-13) stands out as being the most comprehensive, covering the solubility behavior of several hundred binary and ternary systems of liquid  $\text{CO}_2$ .

Interest in the subject has been reawakened recently because of the possible use of liquid  $\text{CO}_2$  as a gentle refining and extracting agent—e.g., in the manufacture of extractable oils and natural products (1) and in the isolation of *p*-xylene from a mixture of  $\text{C}_8$  aromatic hydrocarbons. The following study has been carried out to obtain more accurate data on the solubility behavior of these aromatic hydrocarbons in this particular solvent.

## MATERIALS

$\text{CO}_2$  was obtained from siphon tube cylinders (Air Reduction Co., Richmond, Calif.) and passed through a  $\text{CaSO}_4$  drying tube prior to use. This  $\text{CO}_2$  is at least 99.99% pure.

The aromatic hydrocarbons were obtained from different commercial suppliers and further purified by silica gel treatment and distillation, where necessary. Purity analyses were carried out by determining the freezing point with a platinum resistance thermometer calibrated by the National Bureau of Standards and/or analysis with a Perkin-Elmer 900 gas chromatograph equipped with a flame-ionization detector on a 100-foot by 0.02-inch i.d. support-coated capillary column coated with an MBM-Apiezon-Igepal liquid substrate. Additional analyses with an Aerograph 1520 gas

chromatograph equipped with a thermal conductivity detector using a 5-foot by  $\frac{1}{4}$ -inch Porapak R column showed that there cannot be more than 0.01% water in the investigated compounds. The purity of the hydrocarbons and the identified impurities are shown in Table I.

## EXPERIMENTAL

A sketch of the apparatus is given in Figure 1. A 7.5-inch long, 1-inch i.d. Lab-Crest glass pressure reaction vessel (Fischer and Porter Co., Warminster, Pa.) is connected to a manifold and immersed in an acetone bath. Stirring in the tube is provided by a  $\frac{1}{2}$ -inch diameter Teflon-covered finned magnetic stirring bar, which is driven by a 2-inch by 1.75-inch U-shaped magnet. A thermocouple, which is inserted through the cross into the glass tube, is used to determine the temperature of the solution.  $\text{CO}_2$  is introduced into the system from the cylinder by opening valves *A* and *C*. Excess  $\text{CO}_2$  from the vessel is vented into the atmosphere through the side arm via valves *A* and *B*. The dry nitrogen at the end of valve *B* prevents moisture from entering the unit when the system is at atmospheric or subatmospheric pressure. The volume of the solution in the tube is determined with a cathetometer. Liquid levels are measured relative to reference lines which are inscribed on the tube.

The volume of the tube is calibrated with distilled water by weighing in incremental amounts of water and determining the resultant level with a cathetometer. Since measurements are carried out at levels well above the bottom curvature of the tube, the volume of the tube between this point and the top can be computed from

$$V = aH + b$$

Table I. Solubility of C<sub>6</sub>-C<sub>8</sub> Aromatic Hydrocarbons in Liquid CO<sub>2</sub>

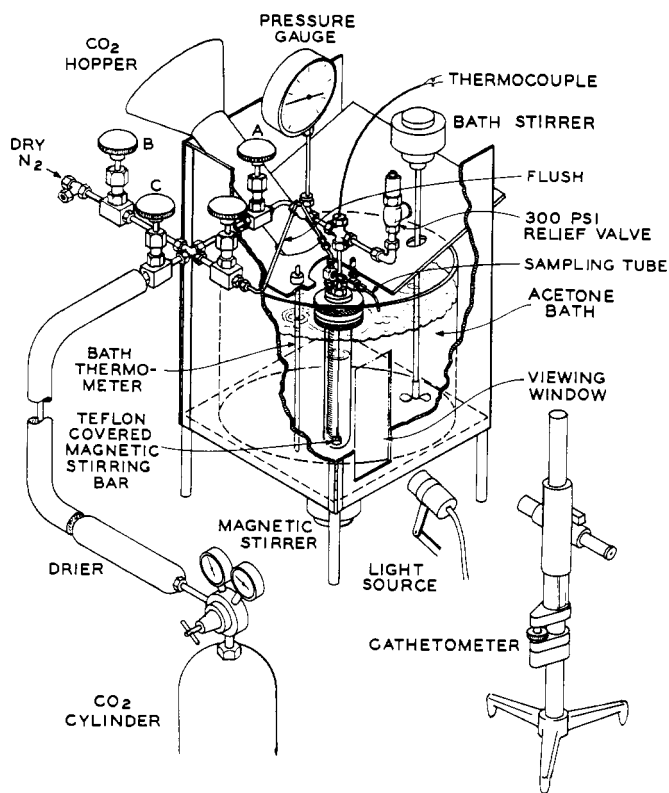
Compound	Temp., ° C.	Gram Hydrocarbon per Ml. Soln.	% Purity	Impurities
Benzene	-14.5	0.703	99.8	
	-17.2	0.642		
	-20.9	0.534		
	-28.4	0.367		
	-29.3	0.338		
	-31.6	0.297		
	-32.4	0.278		
	-33.4	0.256		
	-40.0	0.169		
	-40.2	0.167		
	-40.6	0.163		
	-44.5	0.130		
	-47.6	0.110		
	-52.7	0.083		
Toluene	-10 to -56	Miscible in all proportions	> 99.9	
Ethylbenzene	-10 to -56	Miscible in all proportions	99.6	Lower-boiling compounds
<i>m</i> -Xylene	-59.1	0.797	99.4	0.5% <i>p</i> -xylene 0.1% <i>o</i> -xylene
<i>o</i> -Xylene	-29.0	0.891	> 99.9	0.06% cumene 10 p.p.m. <i>p</i> -xylene
	-32.8	0.854		
	-35.4	0.807		
	-37.2	0.779		
	-37.8	0.781		
	-39.8	0.690		
	-42.0	0.492		
	-43.4	0.404		
	-44.3	0.312		
	-45.2	0.225		
	-45.3	0.252		
	-46.2	0.194		
	-46.5	0.194		
	-47.0	0.178		
	-48.5	0.141		
	-49.2	0.131		
	-49.6	0.135		
	-49.8	0.128		
-55.1	0.045			
-56.1	0.043			
-56.4	0.043			
<i>p</i> -Xylene	-16.2	0.247	> 99.9	73 p.p.m. ethylbenzene, 121 p.p.m. <i>m</i> -xylene
	-16.9	0.228		
	-18.4	0.188		
	-21.4	0.147		
	-22.0	0.136		
	-22.4	0.133		
	-22.8	0.129		
	-24.5	0.119		
	-27.1	0.106		
	-28.9	0.093		
	-32.9	0.073		
	-37.2	0.052		
	-39.5	0.046		
	-42.7	0.036		
	-44.2	0.035		
	-46.5	0.036		

where  $V$  is the volume of the tube at the level  $H$ . Coefficients  $a$  and  $b$  are computed by the method of the least squares from the calibration points. The standard error of the volume determinations is 0.11 ml. Determined volumes range from 15 to 60 ml. The volume of the solution is obtained by subtracting the volume of the stirrer and the immersed portion of the thermocouple. Since the coefficient of expansion for borosilicate glass is  $3 \times 10^{-6}$  per °C. and  $\Delta T_{\max}$  is 80°C., the contraction correction is negligibly small. The thermocouple used has been calibrated against a platinum resistance thermometer calibrated by the National Bureau of Standards. The standard

deviation between these two systems is 0.13°C. This is also the standard deviation of the observed temperatures, since the standard deviation of the platinum resistance thermometer is less than 0.02°C.

The maximum error in the weight of the hydrocarbon is a few milligrams. Sample sizes range from 2 to 20 grams.

After weighing the organic compound into the glass tube, the vessel is mounted on the manifold and immersed in the cooling bath. Valves  $A$  and  $B$  are left open to maintain the contents of the tube at atmospheric pressure, while the bath is cooled to around -20°C. With benzene or *o*-xylene, it is advisable to stir the organic compound vigor-



1. Solubility apparatus

ously during cooling, so the product will solidify in a spongy mass which will dissolve easier in the  $\text{CO}_2$ . Valve *B* is then closed, and valve *C* is slowly opened to introduce liquid  $\text{CO}_2$  into the system until the desired level in the tube is reached. After the hydrocarbon is dissolved, which, in the case of benzene and *p*-xylene, may take some time, the temperature of the bath is slowly decreased until crystal formation is observed. The temperature of the system is then allowed to rise slowly under vigorous stirring of the product mixture in the tube. At the point where the last crystals are dissolving, stirring is stopped and the temperature and level in the tube are measured. To ensure accurate readings, the heating rate of the solution is always maintained at  $0.5^\circ\text{C}$ . per minute or less at the time of measurement.

To reduce the amount of  $\text{CO}_2$  in the measuring tube, valves *A* and *B* are carefully opened and the  $\text{CO}_2$  is allowed to boil off and escape into the atmosphere. Some organic crystals may be deposited on the walls during this process, but the addition of small amounts of fresh (warm) liquid  $\text{CO}_2$  is sufficient to melt and dissolve all these crystals back into the bulk solution.

## RESULTS AND DISCUSSION

The results of these measurements are given in Table I and Figure 2. Both toluene and ethyl benzene are miscible in all proportions with liquid  $\text{CO}_2$  above its triple point ( $-56.6^\circ\text{C}$ ). *m*-Xylene is also highly soluble in liquid  $\text{CO}_2$ . Although the melting point of this compound lies much higher than that of  $\text{CO}_2$ , the freezing point depression in the presence of small amounts of  $\text{CO}_2$  is sufficiently large to result in a mutual solubility in all proportions at temperatures above  $-56.6^\circ\text{C}$ . for  $\text{CO}_2$  levels of a few per cent or more. To obtain an indication of the high solubility, one data point was obtained at  $-59.1^\circ\text{C}$ ., where the solution contains 0.80 gram of *m*-xylene per ml. of solution. The disappearing solid phase in this case was  $\text{CO}_2$ .

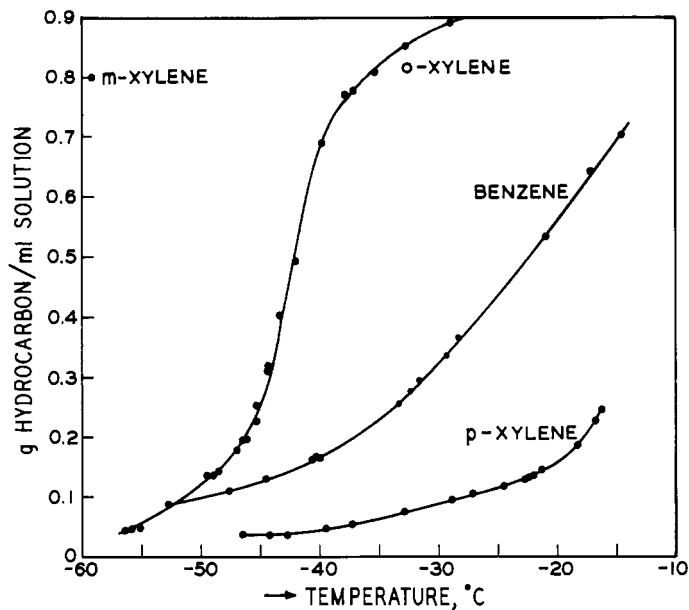


Figure 2. of  $\text{C}_6$ - $\text{C}_8$  aromatic hydrocarbons in liquid  $\text{CO}_2$

*p*-Xylene shows the lowest solubility. A gradual increase in solubility up to  $-20^\circ\text{C}$ . is observed, after which the rise in solubility becomes more pronounced. Benzene shows a gradual increase in solubility over the whole observed temperature range. *o*-Xylene, on the other hand, demonstrates a marked increase in solubility between  $-45^\circ$  and  $-35^\circ\text{C}$ .

The reported solubilities are valid only for the pure organic compounds in liquid  $\text{CO}_2$ .  $\text{CO}_2$  has a very strong homogenizing action, rendering miscible most pairs of partially miscible liquids (9). We may, therefore, also expect a strong increase in solubility when mixtures of these investigated organic compounds are dissolved in liquid  $\text{CO}_2$ .

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RECEIVED for review January 9, 1969. Accepted June 9, 1969.