The solubility of benzene and toluene in water and aqueous salt solutions under pressure

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Abstract. The solubility of benzene in water up to 1.2 kbar at 25-60°C and of toluene in water up to 3 kbar at 25-55°C was determined. Heats of solution are calculated and the bearing of the results on possible changes in the structure of water at high pressures is discussed. The effect of pressure on the solubility of benzene and toluene in aqueous silver nitrate was measured, and is discussed in terms of the formation of hydrocarbon-silver ion complexes.

1 Introduction
We have begun a general study of phase equilibria in systems of aromatic hydrocarbons in water under pressure with a view to investigating the effect of pressure on molecular interactions and the possible influence of the breakdown of the water structure under pressure. In addition, the formation of complexes, under pressure, between aromatic hydrocarbons and aqueous silver nitrate has been studied.

2 Experimental
2.1 Solubility of benzene and toluene in water at atmospheric pressure
Initially we repeated the work on the solubility of benzene in water at atmospheric pressure, using spectrophotometric absorption in the ultraviolet for the determination of concentration. Published results show a wide variation (Andrews and Keefer, 1949, 1950; Bohon and Clausen, 1951; Herington, 1951; Alexander, 1959; Arnold et al., 1958; Franks et al., 1963; McAuliffe, 1963; Reid et al., 1969; Thompson and Snyder, 1964; Worley, 1967); little work has been published on toluene (see the first three references above).

In order to determine solubilities, it is necessary to calibrate the apparatus with hydrocarbon solutions of known concentration. Some of the published work on benzene is open to the criticism that calibrating solutions of concentration too far below that of saturation were used, that departures from Beer’s law have been reported, and that the danger of evaporation of benzene from aqueous calibrating solutions may not have been fully appreciated.

Solutions containing a known concentration of benzene (less than saturated) were prepared:
(a) By freezing with solid CO₂ a sample of A.R. thiophene-free benzene in a weighed glass bulb, which was sealed under vacuum and transferred to a thick-walled glass tube of known weight, 24 mm in diameter and 600 mm long. The tube was partially filled with air-free distilled water in which was placed a small piece of stainless steel. The tube was evacuated, sealed, and weighed, and by breaking the bulb by means of the piece of steel (manipulated with the aid of a magnet) a solution of known concentration could be prepared.
(b) By delivering into a 5 litre flask containing 5 litres of air-free distilled water and 100 ml of mercury an appropriate measured volume of benzene. The flask was quickly stoppered and inverted (the mercury serving to seal the stopper), and allowed to stand with frequent shaking.
(c) By delivering a known volume of benzene into 1 litre of benzene-free ethyl alcohol or
(d) By delivering a known volume of benzene into 5 litres of a mixture of ethyl alcohol and water.

For solutions (c) and (d) much greater concentrations than for (a) and (b) were possible. It has been shown, and we have confirmed, that the extinction coefficient of benzene in ethyl alcohol is not significantly different from that in water; 1 mm silica cells were used in a Unicam SP 500. Solutions prepared by methods (c) and (d) are also useful for revealing any departures from Beer's law at high concentrations. Contrary to reports, no departure was found, provided precautions to minimise evaporation were taken. The extinction coefficient for 254 nm was found to be 146.1 litre mol\(^{-1}\) cm\(^{-1}\). Calibrating solutions of toluene were prepared by methods (b) and (c); an extinction coefficient 227.1 litre mol\(^{-1}\) cm\(^{-1}\) was found at 262 nm.

The solubility of benzene and toluene in water at atmospheric pressure and temperature was determined directly in the 1 mm cell of the Unicam SP 500, using a small magnetically-controlled ball bearing for stirring, and repeating measurements until a constant concentration was reached. A sample was also transferred from a 2 litre batch of solution in contact with hydrocarbon (as for the calibration) for some months.

It was convenient to use the high-pressure apparatus (described later) for studying the solubility of benzene and toluene at atmospheric pressure at higher temperatures, because of the readily available temperature control.

2.2 Solubility of benzene at high pressure

The high-pressure optical cell (see figure 1a and 1b) was a modified version of that described by Owen (Bradley, 1969). The Unicam SP 500 was adapted by means of

![Figure 1. (a) High-pressure optical cell; (b) built-in pressure intensifier.](image-url)
With Compliments

D. C. Munro.
a mirror system to accommodate the pressure vessel. All metal components of the pressure vessel coming into contact with the aqueous solution were made of stainless steel. Viton rubber O-ring seals were supported by nylon anti-extrusion rings. The end plug comprised a push-in section A (figure 1a) carrying the O rings and anti-extrusion rings, and a threaded section which could be screwed onto the push-in section until a shoulder made contact with the block, giving a controlled compression on all rings. Oil pressure was delivered to a large piston G (figure 1b) which drove a smaller piston H (figure 1b); the latter terminated in a Bridgman seal B (figure 1a), made from stainless steel, and incorporating copper and Teflon sealing rings; the intensification factor was ~40. The length of the smaller piston was adjusted so that in the event of sample leakage the oil pressure would not force the piston onto the sapphires.

The holders for the sapphire windows were constructed on the same principle as the end plug, i.e. with push-in sections. The sapphires were supported in position in the push-in sections by means of Viton O rings (C in figure 1a) which were compressed by means of stainless-steel 45° chamfer rings. The latter were forced against the O rings by caps which screwed onto the head of the window holders.

The push-in sections were forced into the block by means of the threaded window plug until the shoulders of the sapphire holders came into contact with the shoulders of the block; these sections were sealed by two O rings and two anti-extrusion rings, arranged alternately (D in figure 1a). Dimensions were such that the two sapphires just met when the push-in sections were fully screwed in, and steel spacing washers (E in figure 1a) were then inserted against the shoulders so that any desired gap between the sapphires could be achieved. In fact a gap of 0.8 mm was convenient. A second spacer (F in figure 1a), which could be varied, ensured that the compression in the O rings and anti-extrusion rings was maintained constant. Trial and error showed that the best section for the anti-extrusion rings was rectangular, and the optimum thickness was found by experiment.

The block was heated by asbestos heating tape and the temperature was maintained by means of a thermistor coupled with a resistance bridge, a West ‘Gardsman’ controller, and Sunvic switch. The thermistor was inserted into a hole in the end plug, and was calibrated against internal temperatures with the benzene solutions at 1 atm.

The pressure was calibrated by observing the freezing and melting of a sample of benzene in the block, over a range of pressures, using visible light from the spectrophotometer, a mirror system to observe the crystals, and referring to published data on the freezing point of benzene under pressure (Osugi et al., 1968). The absorption under pressure, as a measure of concentration, was calibrated by the use of solutions of known benzene content under pressure; there was little effect of pressure and temperature on the calibration.

The main difficulty in the determination of solubility, especially for the higher pressures and lower temperatures, was the low rate of solution.

The absorption was monitored daily and was recorded for 3–7 days (in one instance for 12 days, with consistent results), until no further change occurred. Mixing in the bomb occurred most probably by means of convection currents; it is essential that liquid benzene should not touch the faces of the sapphire windows, since the adhering layer gives a spurious high absorption. Results for \( \lg S \) over a range of pressures from atmospheric upwards and for temperatures 25–60°C are given in figure 2a; \( S \) is the solubility in mol litre\(^{-1}\).
2.3 Studies on toluene at higher pressures

The pressure was calibrated by observing the freezing point of bromobenzene and by referring to published data (Deffet, 1940). Concentrations were calibrated as for benzene, and results are given in figure 2b.

![Figure 2. Pressure dependence of the solubility of (a) benzene and (b) toluene in water.](image)

3 Discussion of hydrocarbon–water systems

3.1 Theoretical

If the two components are labelled 1 (water) and 2 (hydrocarbon), and the two phases A (rich in water) and B (rich in hydrocarbon), then the isobaric variation with temperature of the mole fraction $X_2$ of hydrocarbon in the aqueous layer is given by

\[
\left( \frac{\partial X_2}{\partial T} \right)_p = \left( \frac{\partial^2 g}{\partial X_2^2} \right)_p \frac{\Delta H_2}{T} \Delta X_2
\]

(Rowlinson, 1969), where $\Delta H_1 = H_1^A - H_1^B$, i.e. the difference in the partial molar heat content of the water in the two phases; similarly $\Delta H_2 = H_2^A - H_2^B$; $g$ is the Gibbs free energy per mole, i.e. the Gibbs free energy of $n_1$ moles of water and $n_2$ moles of hydrocarbon, divided by $n_1 + n_2$; and $\Delta X_2 = X_2^A - X_2^B$.

Approximations may be introduced into equation (1), since the mole fractions of hydrocarbon in water and water in hydrocarbon are small compared with unity, i.e. where appropriate $X_2^A \approx 0$, $X_1^A \approx 1$, $X_2^B \approx 1$, and $X_1^B \approx 0$. If we take the pure components as standard states, so that they are on the same footing (cf Prigogine, 1957, chapter XXI), this means that $\gamma_2^A \approx 1$, where $\gamma$ is an activity coefficient. It is readily shown that, if the hydrocarbon in water is assumed to obey Henry's law, i.e. $\gamma_2^A = \text{constant}$, then

\[
\left( \frac{\partial^2 g}{\partial X_2^2} \right)_{p,T} = \left( \frac{\partial^2 g}{\partial X_1^2} \right)_{p,T} = \frac{RT}{X_1^AX_2^B}.
\]

Hence we have approximately

\[
\left( \frac{\partial X_2}{\partial T} \right)_p = \frac{\Delta H_2}{RT^2} \frac{X_2^A}{X_2^A X_2^B}
\]

or,

\[
\frac{\Delta H_2}{RT^2} = \left( \frac{\partial \ln X_2^A}{\partial T} \right)_{p,T},
\]

\[
\Delta H_2 = -R \left( \frac{\partial \ln X_2^A}{\partial (1/T)} \right)_{p,T} \approx -R \left( \frac{\partial \ln S}{\partial (1/T)} \right)_{p,T}
\]

where $S$ is the solubility in mol litre$^{-1}$. $\Delta H_2$ may be calculated from the results given in figure 2a.
To be exact, the so-called heat of solution should be called a heat of transference. The variation of $\Delta H_2$ with pressure is given in figure 3. The variation of $\Delta S_2 = \Delta H_2/T$, i.e. the partial molal entropy of transfer, is readily calculated from the mean temperature.

Similarly we have

$$
\left( \frac{\partial X_2}{\partial p} \right)^A_T = \left( \frac{\partial V_1}{\partial X_1} + \frac{\partial V_2}{\partial X_2} \right) T \Delta X_2,
$$

or

$$
\left( \frac{\partial \ln X_2}{\partial p} \right)^A_T \approx -\frac{\Delta V_2}{RT}.
$$

3.2 Discussion of results for benzene and water

It is clear from figure 2a that $-\Delta V_2$ is roughly constant with varying pressure (except at low pressures), with values of 4.7, 4.2, 1.6, and 1.3 cm$^3$ mol$^{-1}$ at 35, 45, 55, and 60°C respectively. Previous work (Kudchadker and McKetta, 1962) on the effect of pressure on solubility corresponds to an impossibly high value of $-\Delta V_2$ (2890 cm$^3$ mol$^{-1}$ at 100°F).

There is considerable evidence that the quasi-structure of water is broken down by an increase in pressure or temperature (Lawson and Hughes, 1963). $\Delta H_2$ (equal to $H^A_2 - \overline{H^p_2}$) is compounded of a number of terms. $\overline{H^p_2}$ is very nearly equal to $H^A_2$, the molar enthalpy of benzene. $\overline{H^A_2}$ may be split into three terms: (a) a negative term arising from an exothermic heat of 'reaction' between hydrocarbon and water, with the electrons of the benzene becoming attracted to the protons of the water and causing solvation of the benzene; this term will be almost pressure independent; (b) a positive term arising from the breakdown of the water structure prior to interaction; this term will decrease as the pressure increases, since an increase in pressure will tend to break up the open structure of water; (c) a positive term arising from the energy needed to form a cavity in the water large enough to hold a benzene molecule; this term will increase with increase in pressure and will become particularly important at high pressures. If term (c) does not have an overriding effect for benzene in water up to 1.2 kbar, then $\Delta H_2$, which is positive, should decrease with increase in pressure, as observed (except at low pressures).

![Figure 3. Variation of $\Delta H_2$ for benzene and toluene with pressure.](image-url)
3.3 Discussion of results for toluene and water

With toluene it is possible to go to higher pressures than with benzene, before solidification occurs. As shown in figure 2b, the behaviour up to ~1.2 kbar is similar to that with benzene, $-\Delta V_2$ having mean values 9.6, 9.2, and 7.3 cm$^3$ mol$^{-1}$ at the respective temperatures 35, 45, and 55°C. Above 1.3 kbar, however, $\Delta V_2$ becomes zero and then changes sign. It is probable that the effect of pressure on the structure of water is decreasing at higher pressures. If the dissolution of toluene in 'structureless' water is accompanied by an increase in volume, then $\Delta V_2$ will become positive at sufficiently high pressures, as observed. In contrast to the behaviour with benzene, $\Delta H_2$ for toluene shows a minimum, but this again is probably due to an extension of the range of pressure. The increase in $\Delta H_2$ with increasing pressure after the minimum may well arise from the effect of pressure on the energy of cavity formation.

4 The solubility of benzene and toluene in aqueous silver nitrate and potassium nitrate

As shown by Andrews and Keefer (1949, 1950), silver ion greatly increases the solubility of benzene in water, owing to the formation of the complexes AgC$_6$H$_6$ and Ag$_2$C$_6$H$_6$$^{++}$, the proportion of the latter increasing with increasing concentration of silver ion. We have determined spectrophotometrically the solubility of benzene and toluene in aqueous silver nitrate at 25°C, as described earlier; the absorption peak is not appreciably shifted by the silver nitrate and potassium nitrate (the latter being added to maintain the concentration of uni-univalent salt at 1 M). Absorption studies with known concentrations of benzene and toluene (less than saturation) in the presence of KNO$_3$ (1 M) showed that the salt has a negligible effect on the calibration.

The equilibrium constants $K_1$ and $K_2$ for benzene are given by

$$K_1 = \frac{[\text{AgC}_6\text{H}_6]}{[\text{Ag}][\text{C}_6\text{H}_6]} , \quad K_2 = \frac{[\text{Ag}_2\text{C}_6\text{H}_6^{++}]}{[\text{Ag}^2][\text{AgC}_6\text{H}_6]}.$$  

It follows that the total benzene (determined spectrophotometrically) is equal to $S$:

$$S = [\text{C}_6\text{H}_6] + K_1[\text{Ag}^+] [\text{C}_6\text{H}_6] + K_1 K_2 [\text{Ag}^+]^2 [\text{C}_6\text{H}_6].$$  

(6)

Since liquid benzene is present, $[\text{C}_6\text{H}_6] = \text{constant} = S_0$; also $[\text{Ag}^+] \gg [\text{AgC}_6\text{H}_6]$ and $[\text{Ag}^+] \gg [\text{Ag}_2\text{C}_6\text{H}_6^{++}]$. Hence we have approximately

$$S = S_0 (1 + K_1[\text{total Ag}]+ K_1 K_2[\text{total Ag}]^2).$$  

(7)

Similar equations apply to the toluene system.

As shown in figure 4 (for 1 atm at 25°C), the plot of $S$ against [total Ag] is sufficiently linear at low concentrations of Ag to give $K_1$; correction can be made for the fact that $[\text{Ag}^+] \neq$ [total Ag] by an iterative process.

Data for the solubility of benzene in these salt solutions are given in table 1. Our values at 25°C and 1 atm compare with Andrews and Keefer's values of $K_1 = 2.4$ litre mol$^{-1}$ and $S_0$ (in 1 M KNO$_3$) = 0.0165 mol litre$^{-1}$. Although no allowance has been made for activity coefficients, it should be noted that $K_1 = [\text{AgC}_6\text{H}_6]/[\text{Ag}^+][\text{C}_6\text{H}_6]$. The benzene has an activity coefficient near unity, since the liquid benzene layer is present, and the activity coefficients of the Ag$^+$ and AgC$_6$H$_6^+$ ions in aqueous solution cancel to a considerable extent.

For benzene solutions the change of $K_1$ with temperature corresponds to a heat of complex formation ($\text{Ag}^++\text{C}_6\text{H}_6 = \text{AgC}_6\text{H}_6^+$) of $\Delta H = -8.25$ kcal mol$^{-1}$ at 1 atm, and $\Delta H = -19.7$ kcal mol$^{-1}$ at 625 bars. The behaviour of $K_1$ with pressure corresponds to a volume change on formation of the complex ion of 8.7 cm$^3$ mol$^{-1}$ at 45°C, and 24.6 cm$^3$ mol$^{-1}$ at 55°C.
For toluene solutions (table 1) our values at 25°C and 1 atm compare with Andrews and Keefer's value of $K_1 = 2.95 \text{ mol}^{-1} \text{ litre}^{-1}$ and $0.0043 \text{ mol} \text{ litre}^{-1}$. The decrease of $K_1$ with increased temperature corresponds to a heat of formation for the complex ion $\text{AgC}_6\text{H}_5\text{CH}_3$ of $-5.6 \text{ kcal mol}^{-1}$ at 1 atm, and $-15.3 \text{ kcal mol}^{-1}$ at 1 kbar. The change of $K_1$ with pressure corresponds to a volume increase on formation of the complex of $11.0 \text{ cm}^3 \text{ mol}^{-1}$ at 45°C, and $5.9 \text{ cm}^3 \text{ mol}^{-1}$ at 55°C.

At all the temperatures and pressures considered the presence of 0.1 M AgNO$_3$ caused an increase in the solubility of the hydrocarbon over that measured when the solvent was 1 M KNO$_3$, the percentage increase for toluene being greater than for benzene. This percentage increase in solubility was progressively reduced with increased temperature at all pressures.

The salting-out coefficients in 1 M KNO$_3$, i.e. $S_w/S_K$, where $S_w$ is the solubility in water and $S_K$ the solubility in 1 M KNO$_3$, are equal to the activity coefficients of the hydrocarbon in 1 M KNO$_3$. Results are reasonable in comparison with the effect of other electrolytes on the solubility of benzene (Conway et al., 1964).

![Graph showing solubility of benzene and toluene as a function of the total concentration of silver at 25°C and atmospheric pressure.]

**Figure 4.** Solubility of benzene and toluene as a function of the total concentration of silver at 25°C and atmospheric pressure.

**Table 1.** Data for the solubility of benzene and toluene in aqueous salt solutions.

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<th>$T$ (°C)</th>
<th>$p$ (bars)</th>
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<th>$S_K$ (mol litre$^{-1}$)</th>
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<th>$K_1$ (litre mol$^{-1}$)</th>
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$S_w$ = solubility in water,
$S_K$ = solubility in 1 M KNO$_3$,
$S_{Ag}$ = solubility in 0.1 M AgNO$_3$/0.9 M KNO$_3$. 

Aqueous solubility of hydrocarbons under pressure
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References