

High-Pressure Solubility Data of Methane in Aniline and Aqueous Aniline Systems

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Alternative approaches to the reduction of nitrobenzene for the aniline production using methane are being investigated. Solubility data of gases in aniline or aqueous aniline solutions are very scarce. In this work, high-pressure equilibrium data were measured for methane–aniline and methane–aniline–water systems at temperatures ranging from 293.15 to 373.15 K and pressures up to 100 MPa using a visual static method for detection of phase transitions. The influence of the temperature, pressure, and water on the solubility of methane in aniline was studied. It is shown that the solubility of methane in aniline increases with temperature and pressure and strongly decreases with the water content of the system.

Introduction

The application of high pressures to industrial processes has led to engineering operations that frequently require knowledge of solubilities of gases in liquids at pressures higher than those for which such data are ordinarily available. The production of aniline by reduction of nitrobenzene is such a process.

Aniline is a synthetic organic chemical with a broad range of applications which include polyurethane manufacturing, rubber chemicals, dyes and pigments, drugs, agrochemicals, and specialty fibers. The efficient design, scale-up, optimization, and control of a chemical process such as aniline's production require the understanding of the process's kinetic and thermodynamic behavior inasmuch detail as possible. In fact, the catalytic reduction of nitrobenzene to aniline is a complex chemical process where a number of competing processes contribute to the final product. Changes in process conditions with the possible formation of intermediates can act as catalyst poisons that change the process's efficiency. Moreover, the actual more restraining safety and environmental concerns and the continuous search for optimized process technologies require the development and application of new or alternative processes to meet efficiency, quality, and environmental goals.

The production of aniline was originally carried through the reduction of nitrobenzene by reaction with HCl in the presence of dispersed iron generating aniline and iron oxide sludge.¹ This process produces large quantities of waste and was thus replaced by the catalytic hydrogenation of nitrobenzene.¹ A further step for the improvement of the production process was proposed in the 70s when Polinski and Harvey² suggested that the hydrogen, used for the reduction of the nitrobenzene, could be simultaneously generated in the main reactor avoiding the external production, storage, and transport of hydrogen. This process was later optimized and patented,^{3,4} and it can be

summarized by the following reactions.



Having in mind that these reactions occur simultaneously, it becomes clear the importance of studying the solubility of methane in aniline and in its aqueous solutions. These processes are carried out at high temperature, between 420 and 450 K, and at high pressures, around 1.5–2.0 MPa.

Literature data regarding the systems studied in this work are scarce or even nonexistent. To our knowledge, data exist for the mutual solubility of the aniline/water system⁵ and for the solubility of methane in aniline at atmospheric pressure at a single temperature.⁶ Data for the solubility of methane on water are far more frequent.^{7,8} To improve the thermodynamic knowledge of these systems, the solubility of methane in pure aniline and in an aniline–water mixture with 5 % (w/w) water content was studied in this work to evaluate the influence of water on the methane's solubility in aniline.

Experimental Section

Chemicals used for the measurements were methane (4.0) from Linde Gas and aniline (99.5 %) from Aldrich.

Figure 1 shows a schematic diagram of the variable-volume high-pressure cell which was previously described in the literature.^{9,10} It consists of a horizontal hollow stainless steel cylinder closed at one end by a movable piston. One sapphire window closes the other end allowing visual observation of the entire fluid in the study. A video acquisition system made up of an endoscope plus a video camera is placed behind the sapphire windows to display on the screen of a computer what happens inside the measuring cell. A small magnetic bar is placed inside the cell for the homogenization of the mixture by means of an external magnetic stirrer. Due to the presence of this magnetic stirring bar as well as of the second window, the

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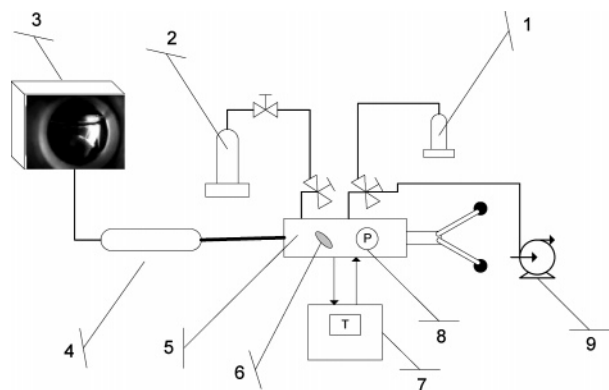


Figure 1. Schematic apparatus: 1, aniline; 2, methane; 3, screen; 4, endoscope plus a video camera; 5, high-pressure variable-volume cell; 6, magnetic bar; 7, thermostat bath circulator; 8, piezoresistive pressure transducers; 9, vacuum pump.

minimum internal volume is limited to 8 cm³, whereas the maximum volume was fixed to 30 cm³ to limit the size of the cell and thus to reduce thermal inertia and temperature gradients within the cell.

The temperature is kept constant by circulating a heat-carrier fluid through three flow lines directly managed in the cell. This heat-carrier fluid is thermoregulated with temperature stability of 0.01 K by means of a thermostat bath circulator (Huber Ministat CC1). The temperature is measured with a high-precision thermometer, model PN 5207, with an accuracy of 0.01 K connected to a calibrated platinum resistance inserted inside the cell close to the sample.

The pressure is measured by a piezoresistive silicon pressure transducer (Kulite) fixed directly inside the cell to reduce dead volumes. The accuracy of the transducer in the experimental range studied is 0.2 MPa.

The experimental procedure can be described as follows. First, a fixed amount of liquid is introduced in the cell, by vacuum extraction. In the case of the 5 % (w/w) water/aniline solution, this was first prepared and then introduced in the equilibrium cell by the same method. The exact mass introduced is determined by weighting the liquid holder during its introduction with a precision balance (Ohaus) with an accuracy of 0.1 mg. Methane is then introduced under pressure. For this purpose, the gas is initially loaded at saturation pressure in an aluminum reservoir tank (Gerzat) fixed in the plate of a high-weight/high-precision balance having a maximum weighting capacity of 2000 g with an accuracy of 1 mg (Sartorius) and connected to the measuring cell by means of a flexible high-pressure capillary.

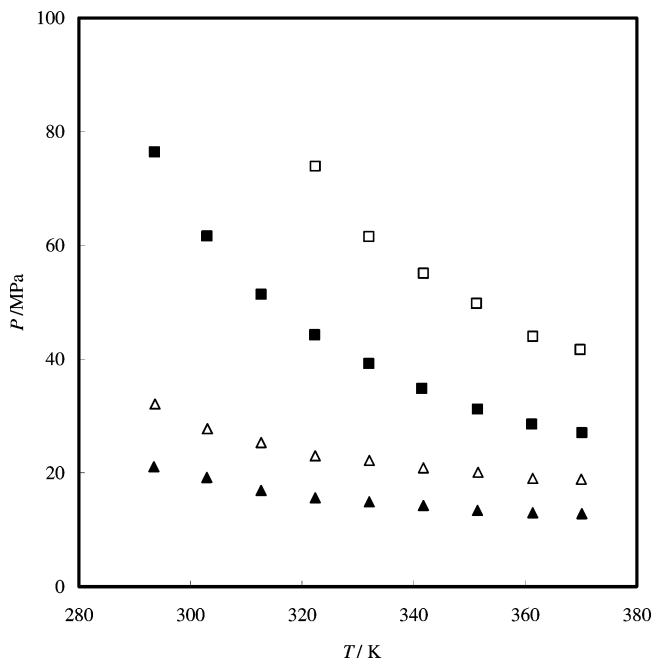


Figure 2. Pressure-temperature diagram for the solubility of methane in pure aniline and aqueous aniline at different mole fractions of the gas: □, 12.58 %; ■, 12.37 %; △, 6.06 %; and ▲, 6.35 %. Open symbols represent the solubility of methane for the ternary system.

The exact mass of gas injected into the measuring cell is determined by weighing the reservoir tank while filling. After preparation of a mixture of known composition, this is allowed to reach the desired temperature at low pressure; the pressure is then slowly increased at constant temperature until the system becomes homogeneous. The pressure at which the last bubble disappears represents the equilibrium pressure for the fixed temperature.

Results and Discussion

Experimental results obtained for the solubility of methane in aniline and in the 5 % (w/w) water/aniline mixture are reported in Table 1.

The temperature dependence of the experimental solubility of methane in both systems is similar, and data for the solubility of methane in pure and hydrated aniline are shown in Figure 2. It can be seen that at low pressures, corresponding to methane's mole fractions up to 6 %, the solubility is a weak function of the temperature. However, the equilibrium pressure needed to solubilize higher amounts of gas is much more markedly

Table 1. Experimental $P(\text{MPa})-x_{\text{CH}_4}-T(\text{K})$ Data Measured for Methane-Aniline and Methane-Aniline-Water Mixtures at Temperatures from 303 to 370 K

		CH ₄ + Aniline							
x_{CH_4}		302.99 K	312.68 K	322.51 K	332.19 K	341.79 K	351.59 K	361.16 K	370.06 K
0.034		8.27	7.97	7.64	7.50	7.35	7.17	6.89	6.73
0.064		19.18	18.21	15.62	16.00	14.25	13.39	13.00	12.69
0.092		30.04	25.72	21.22	21.95	18.63	17.41	17.02	16.54
0.122		61.65	53.16	44.27	40.66	34.82	31.20	28.57	25.20
0.130		66.30	59.82	48.03	46.00	37.23	33.66	30.49	28.80
0.167			74.42	59.75	57.54	45.58	41.07	37.58	36.36
		CH ₄ + Aniline + Water							
x_{CH_4}		303.08 K	312.68 K	322.37 K	332.05 K	341.73 K	351.43 K	361.35 K	369.97 K
0.030		13.11	12.54	11.91	11.08	10.61	10.09	9.50	9.14
0.061		27.73	25.31	22.98	22.17	20.87	20.08	19.02	18.88
0.090		55.99	48.01	42.62	38.58	34.95	30.44	29.37	29.18
0.116				61.89	53.62	46.17	43.83	40.35	36.55
0.126				73.91	61.54	55.09	49.79	43.99	41.67

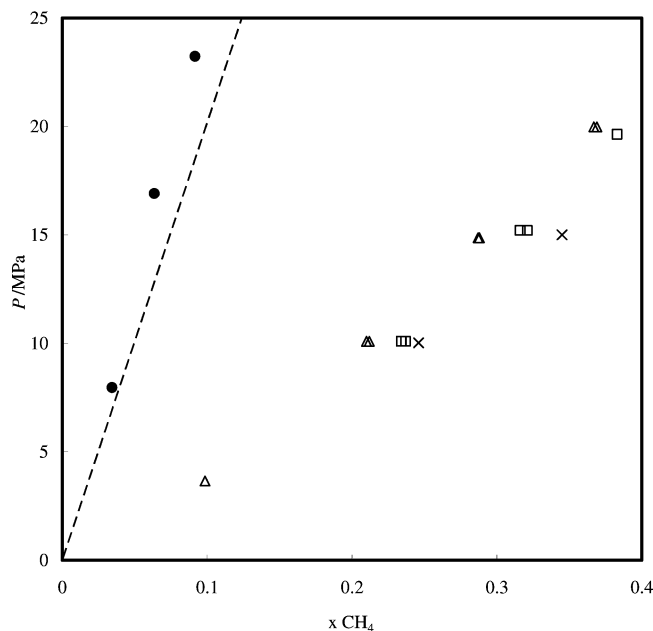


Figure 3. Experimental solubility data for methane in four aromatic compounds around 315 K: ●, data measured in this work for aniline; and Δ, data taken from the literature¹² for benzene; □, toluene; ×, *m*-xylene; and ---, phenol.⁶ The solubility in phenol was estimated from its Henry constant at atmospheric pressure.

dependent on the working temperature. Moreover, it was observed that the solubility of methane in aniline increases with temperature. It is interesting to notice that this behavior is opposite to what usually happens with the solubility of gases in liquids. However the same tendency was found by other authors when studying the solubility of methane in amines.¹¹

The figure also makes clear the influence of water on the solubility of methane in aniline. The solubility of methane in aniline decreases in the presence of water, considering a fixed methane molar fraction. This behavior can be explained by the solvation of water by the aniline through hydrogen bonds that reorganize the bulk allowing fewer interactions between aniline and methane.

Attempting a better understanding of the solubility process of the methane–aniline system, the data measured in this work were compared with experimental data taken from the literature^{6,12} for the solubility of methane in four different aromatic compounds, namely, benzene, toluene, *m*-xylene, and phenol. In this last case, as no data were found for direct comparison, the solubility of methane in phenol was derived from its constant of Henry at atmospheric pressure.⁶ The aim of the comparison is to see the influence of different substitute groups and their consequently different bulk structures on the solubility of methane.

The data shown in Figure 3 indicate that the solvents presented here fall into two different groups. One group is made up of benzene, toluene, and *m*-xylene, showing similar solubilities for methane, whereas the other group contains aniline and phenol. Although the methane solubility obtained as an extrapolation from the atmospheric pressure Henry constants is not valid within the entire pressure range presented, the dashed

lined in Figure 3 can be seen as an upper limit for the solubility of methane in phenol. The much lower solubility of methane in the polar compounds compared to the nonpolar hydrocarbons suggests that both the misfit of interactions between the solute and solvent molecules and the more organized liquid structure that exists in those compounds due to polar interactions or hydrogen bonding, increasing the energy required for cavity formation, will contribute to the much lower solubility observed for methane on these solvents.

Conclusions

New high-pressure equilibrium data for methane in aniline and methane in 5 % (w/w) water/aniline systems were measured at temperatures ranging from 293.15 to 373.15 K and pressures up to 100 MPa.

It has been shown that the solubility of methane in aniline increases with temperature and decreases with the water content of the system. A comparison with literature data for other aromatic compounds indicates that the solubility of methane in aniline is lower than on other aromatic compounds most probably because of the more organized bulk structure of liquid aniline favored by the hydrogen bonds.

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Received for review January 31, 2007. Accepted March 7, 2007.

JE7000528