INTERNATIONAL UNION OF PURE AND APPLIED CHEMISTRY

ANALYTICAL CHEMISTRY DIVISION
COMMISSION ON ELECTROANALYTICAL CHEMISTRY*

RECOMMENDED METHODS FOR THE PURIFICATION OF SOLVENTS AND TESTS FOR IMPURITIES

BENZENE AND TOLUENE

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Recommended methods for the purification of solvents and tests for impurities: Benzene and toluene

Abstract. A table of the relevant physicochemical properties of benzene and toluene are presented and the most important solvent properties of both solvents for chemical and electrochemical analysis are discussed. Examples of electrochemical analysis in benzene and toluene are given. The most common impurities found in commercial benzene and toluene are listed and recommended purification procedures are presented.

INTRODUCTION

The use of benzene and toluene as solvents in electrochemical studies can be accomplished by means of microelectrodes. The relatively small current passed by microelectrodes compensates for the large resistance of the low dielectric media (ref. 1-4). One advantage of benzene or toluene as a solvent is that, in most cases, the solvent coordination is eliminated. Also, electrochemical results in benzene and toluene can be directly compared with both spectroscopic and chemical results for a given compound under the same solution conditions.

Benzene and toluene are both excellent solvents for studying a wide variety of organic and organometallic compounds. However, there are several distinct advantages to using toluene rather than benzene as a solvent for electrochemical studies. In particular, the vapor pressure of toluene is less than that of benzene. Hence, changes in concentration due to evaportaion during the experiment are not as significant. The freezing point of toluene (-94.99 °C) is also much lower than that of benzene and this enables low temperature electrochemical studies to be carried out. However, it should be noted that the solubility of most salts used as supporting electrolyte decreases drastically in toluene at lower temperatures.

Some of the important physical properties (ref. 5) of benzene and toluene are listed in Table 1. Benzene has a dipole moment of 0.00 Debye (1 Debye = 3.33564 x 10^{-30} C m) and is used as a reference solvent to measure the dipole moment of other compounds. The relative permittivity (dielectric constant) of benzene is very low. Benzene has a high vapor pressure which presents a significant health concern (see below). The noncoordinating nature of benzene is demonstrated by the Gutmann donor/acceptor numbers (ref. 6). Toluene also has a small dipole moment of 0.31 Debye and a low relative permittivity. The low coordinating nature of toluene is also reflected by the Gutman donor/acceptor numbers (ref. 6).

Benzene has a large cathodic and anodic potential range which extends between -2.7 and +2.0 V vs SCE (ref. 7) with a Pt electrode of 25 μm diameter and 0.1 M (M = mol dm^{-3}) tetrahexylammonium perchlorate as the supporting electrolyte. It should be noted that these values include the liquid junction potential that exists between the aqueous reference electrode and the benzene. A large potential range is useful when it is important to study both the LUMO (lowest unoccupied molecular orbital) and the HOMO (highest occupied molecular orbital) of a given compound under the same solution conditions. In addition, the non-coordinating nature of benzene will minimize solvent interactions with the electrogenerated cations or anions. Tetrahexylammonium perchlorate is a common supporting electrolyte for benzene. The conductivity of this solution and the solubility of the supporting electrolyte can be substantially increased at higher temperatures. A concentration of 0.7 M tetrahexylammonium perchlorate is possible in benzene at 45°C and this allows for the use of larger working electrodes (ref. 3).

Benzene is also a very good solvent to use for the determination of physical and thermodynamic properties such as acid-base constants and dipole moments of organic compounds (ref. 8). This is due to the relative chemical inertness of benzene and the wide range of organic compounds that are soluble in benzene. In addition, the physical and thermodynamic properties of benzene are such that it also allows measurements of a wide range of properties of non-organic complexes.

Similar to benzene, toluene also has a large cathodic and anodic working potential range. Toluene containing 0.1 M tetrahexylammonium perchlorate as supporting electrolyte has been reported to have a potential range of -2.0 to +2.0 V vs a Ag wire pseudoreference electrode for a Pt working electrode having a 10 μm diameter (ref. 3a). The potential of the Ag wire pseudoreference was estimated to be 0.29 V vs SCE and the potential

TABLE 1.   Selected properties of benzene and toluene[a]

	Benzene	Toluene
Freezing temperature, t_m/°C	5.533	-94.991
Boiling temperature, t_b/°C, at 0.101325 MPa	80.094	110.630
Density, ρ/kg dm^{-3}, at 25°C	0.87360	0.86219
Vapor pressure, p/kPa, at 25°C	12.7	3.8036
Dynamic viscosity, η/mPa s, at 25°C	0.6028	0.5525
Refractive index, n_D, at 25°C	1.49792	1.49413
Surface tension, γ/mN m^{-1}, at 25°C	28.20	27.92
Dipole moment, μ/D[b]	0.00[c]	0.31
Enthalpy of vaporization, ΔH_v/kJ mol at 25°C	33.843	37.990
at t_b	30.726	33.183
Molar heat capacity, C_p/J K^{-1} mol at 25°C	135.760	157.29
Relative permittivity, $D = \varepsilon/\varepsilon_0$, at 25°C	2.27401	2.3807
Donor number (Gutmann)[d], DN/kcal mol^{-1}	0.1	e
Acceptor number (Gutmann)[d], AN	8.2	e
Solvatochromic parameters[f] (Kamlet-Taft)		
(a) Polarity parameter, $\pi*$	0.59	0.54
(b) Hydrogen bond acceptor number, β	0.10	0.11
(c) Hydrogen Bond Donor number, α	nil	nil

[a] Reference 5

[c] By definition (refence solvent).

[e] These values have not been reported in the literature. However, calculations indicate they are close to benzene[46].

[b] D = Debye = 3.33564×10^{-30} C m.

[d] Reference 5, 1 cal = 4.184 J

[f] Reference 45,46

window of toluene is reported to be -2.3 to +1.7 V vs SCE (ref. 3). Other workers have observed a potential range for toluene of -2.7 to +2.0 V vs SCE with a Pt electrode and the same supporting electrolyte (ref. 7). These values include the liquid junction potential that exists between toluene and the agueous reference electrode.

Several electron transfer processes which are well characterized in acetonitrile have also been investigated in toluene in order to determine how this solvent would change the electrochemistry. In general, the data were consistent with other results obtained by changing from a coordinating to a non-coordinating solvent. However, some significant differences in the chemistry and electrochemistry of the electron transfer processes were observed. For example, the two one-electron transfer steps which are observed for oxidation of (TPP)H$_2$, (TPP)Ni or (TPP)Cu (where TPP = the dianion of tetraphenyl-porphyrin) in CH$_2$Cl$_2$ are condensed into a single two-electron step in toluene (ref. 3). The chemical reaction of electrogenerated [(TPP)Co]$^-$ with the "non-bonding solvent" CH$_2$Cl$_2$ to give the metal-carbon bonded complex (TPP)Co(CH$_2$Cl) has been reported (ref. 9) and this chemical reaction can be eliminated when the electrochemical analysis is carried out in toluene (ref. 10).

Tetrahexylammonium perchlorate has been used as a supporting electrolyte for toluene (ref. 3,10). A sufficiently large concentration (0.1 M) of this salt can be dissolved in toluene at room temperature. In addition, the electrolyte concentration and the conductivity of this solution can be substantially increased upon warming the solution. A concentration of 0.7 M tetrahexylammonium perchlorate can be reached in toluene at 45 °C (ref. 3).

Both the acute and chronic effects of exposure to benzene are well documented. The 9th Edition of the Merck Index (ref. 11) states that acute exposure to benzene from either ingestion or inhalation of benzene can cause irritation of the mucous membranes, convulsions and possibly death. Chronic exposure to benzene may result in changes in the

blood and can lead to leukemia (ref. 12-15). A full report on the relationship between exposure to benzene and leukemia is given in the 1981 Second Annual Report on Carcinogens (ref. 16). Benzene is classified as a carcinogen by IARC (International Agency for Research on Cancer) and as a hazardous substance and a hazardous waste by EPA (the Environmental Protection Agency, U.S.A.) (ref. 12). Regulations on the permissible exposure limits in air were set in 1977 by the United State government OSHA (Occupational Safety and Health Administration) to be no more than 1 ppm as a time weighted average for an eight hour working day (ref. 12) with a ceiling level of 5 ppm for a maximum duration of 15 minutes. Benzene is also a flammable substance with a substantial vapor pressure (ref. 5,12). Hence appropriate precautions should be used to avoid both exposure to and ignition of benzene.

The 9th Edition of the Merck Index states that toluene is less toxic than benzene but that it is a narcotic in high concentrations (ref. 11). Other reports state that toluene is more acutely toxic than benzene (ref. 5,17), with the greatest danger from inhalation. Exposure to toluene can cause irritation to the eyes, respiratory tract and skin. Prolonged exposure will result in a loss of lipids from the skin (ref. 12). Long term exposure to toluene apparently does not lead to the same effects on the blood that occur upon long term exposure to benzene (ref. 18). Toluene is classified as a hazardous substance and a hazardous waste by EPA. It is also classified as a flammable liquid (ref. 5,12,19-21). Appropriate care should be taken with the use of this solvent.

MANUFACTURE OF BENZENE AND COMMON IMPURITIES

Benzene is produced primarily from petroleum. Although benzene is found in most crude oils, its concentration is relatively low. The amount of benzene in crude oils can be increased by a number of different processes after which extraction and purification can be carried out. Benzene is also produced by a reforming-separation process in conjunction with the production of toluene and xylenes, or BTX (benzene/toluene/xylene) processing (ref. 22,23). Benzene can also be made from coal (ref. 22-24), but this process is currently not as significant as the preparation from petroleum. Common impurities found in benzene are water, thiophene, toluene, cyclohexane, methylcyclohexane, heptanes, saturated hydrocarbons, free hydrogen sulfide and sulfur dioxide (ref. 22,25,26).

Benzene can be purchased in a relatively pure form (ref. 21). The typical grade available for research applications meets the specifications required by the American Chemical Society (ref. 27). Some of these specifications are that the concentration of thiophene be less than 1 ppm, that the total concentration of sulfur compounds be less than 0.005% and that the concentration of water be less than 0.05%. An ACS spectral grade of benzene is also available. In this case, the maximum absorbance of the benzene sample in a 1.0 cm cell with water as a reference is defined over the spectral range of 280 to 400 nm. The absorbance should not exceed 1.00 at 280 nm, 0.30 at 290 nm, 0.10 at 300 nm, 0.04 at 330 nm, 0.02 at 350 nm and 0.01 at 380 nm to 400 nm (ref. 27).

MANUFACTURE OF TOLUENE AND COMMON IMPURITIES

The primary source of toluene is petroleum which accounts for approximately ninety percent of the toluene produced. The other ten percent is made by a variety of processes including recovery as a side product in the production of ethylene, propylene and styrene. A small percentage (about one percent) of the toluene produced is from the separation of coal tars (ref. 20). The common impurities found in toluene are water, methylthiophenes, other sulfur containing hydrocarbons, saturated hydrocarbons, free hydrogen sulfide and sulfur dioxide (ref. 5,20,26).

Toluene is commercially available in a relatively pure form (ref. 20,21) which meets the specifications required by the American Chemical Society (ref. 27). Some of these specifications are that there be a well-defined boiling point (110.6 ± 0.1 °C), that the total concentration of sulfur compounds be less than 0.003% and that the concentration of water be less than 0.03%. An ACS spectral grade definition of toluene is based on the maximum absorbance of the toluene sample in a 1.0 cm cell with water as a reference over the spectral range of 286 to 400 nm. The absorbance should not exceed 1.00 at 286 nm, 0.50 at 288 nm, 0.20 at 293 nm, 0.10 at 300 nm, 0.05 at 310 nm, 0.02 at 335 nm and 0.01 at 350 nm to 400 nm (ref. 27).

PURIFICATION OF BENZENE

There are numerous ways to purify benzene (ref. 5,26). The level of purity necessary for a given experiment must be considered before the purification method is selected. Some of the methods described include the National Bureau of Standards method for the purification of benzene. This method is a combination of crystallization and filtration with silica gel. A benzene/ethanol composition is made and then cooled to -10°C, followed by collection of the solid benzene. The benzene is then washed three times with distilled water followed by filtration through silica gel to remove any water or remaining ethanol (ref. 28). Another method is to recrystallize the benzene several times, discarding

approximately 25% each time as the liquid fraction. The benzene is then dried with phosphorus pentoxide followed by fractional distillation (ref. 29). Other methods of purification involve distilling the benzene from an active reagent such as sodium or calcium hydride under an inert or dry atmosphere (ref. 30,31). In addition, after distillation, the benzene may be fractionally crystallized up to three separate times (ref. 32).

Sulfuric acid is used to remove thiophene and various olefins from benzene by a number of different methods (ref. 5,26,33). In general, the benzene is shaken with concentrated sulfuric acid followed by washes with water, dilute sodium hydroxide, and water again. At that point the benzene is pre-dried with calcium chloride or another mild drying agent, followed by more rigorous drying with any one of a number of materials such as phosphorus pentoxide, sodium, lithium aluminum hydride, calcium hydride or calcium. The benzene may then be further purified by distillation under an inert atmosphere from a drying agent or by recrystallization methods.

RECOMMENDED PROCEDURE FOR PURIFICATION OF BENZENE

The recommended purification method of benzene for chemical and electrochemical analysis requires removal of thiophene with sulfuric acid followed by drying and distillation from a reactive metal. Laboratory grade benzene 200 ml (ml = cm^3) is vigorously stirred with concentrated 50 ml sulfuric acid for one hour to remove any thiophene. The presence of thiophene is noted by a change in the color of the sulfuric acid from colorless to yellow. The benzene is separated from the sulfuric acid and washed with water, 0.1 M sodium hydroxide, and several times with water again. The benzene is then pre-dried with calcium chloride or sodium sulfate followed by refluxing over sodium under an inert atmosphere (nitrogen or argon) for one hour. The benzene is then fractionally distilled under an inert atmosphere, discarding the first ten percent and the last twenty percent.

TEST FOR RESIDUAL IMPURITIES OF BENZENE

The best technique to determine the purity of benzene is gas chromatography (ref. 5,22,34). Other methods to test the purity of benzene are based on various physical properties of the solvent. Tests based on the freezing point, the specific gravity and the distillation range are all relatively sensitive (ref. 5,22,35). For example, it has been demonstrated by gas chromatography that no more than 0.2% hydrocarbon impurities are present in benzene which has a boiling range less than 1°C. Water in benzene can be determined to 0.05% by a Karl Fischer titration. Thiophene and sulfur compounds can also be determined to 1 ppm and 0.005% respectively by standardized ACS methods (ref. 27). In addition, an ASTM (American Society for Testing Materials) standardized test for carbon disulfide is also available (ref. 36).

PURIFICATION OF TOLUENE

Toluene can be purified by a number of methods (ref. 5,26). The level of purity necessary for a given experiment must be considered before the purification method is selected. Unlike benzene, fractional crystallization cannot be easily performed with toluene. This is due to the low melting point of the solvent. Toluene is typically purified by a combination of chemical treatments and fractional distillation. It may be pre-dried with agents such as calcium chloride or sodium sulfate followed by a more complete removal of water with active reagents such as sodium, calcium hydride or phosphorus pentoxide. At this point the toluene is fractionally distilled from the drying agent under an inert atmosphere (ref. 5,26). Another method is to distill commercially available toluene from phosphorus pentoxide and to store it over activated 4Å molecular sieves (ref. 3).

Methylthiophenes, other sulfur containing compounds and various other petroleum side products can be removed with sulfuric acid (ref. 5,26,37-40). In general, the toluene is shaken with concentrated sulfuric acid followed by washes with water, dilute sodium hydroxide, and water again. It is important to keep the temperature of the concentrated sulfuric acid below 30 °C when washing the toluene in order to avoid a sulfonation reaction (ref. 26). The toluene is then treated by the method described above. It is pre-dried with a mild drying agent, followed by more rigorous drying with a material such as phosphorus pentoxide, sodium or calcium hydride. The toluene is then further purified by distillation under an inert atmosphere from the drying agent. Some methods utilize either mercury or sodium amalgam to further aid the removal of sulfur containing compounds (ref. 37,38).

RECOMMENDED PROCEDURE FOR PURIFICATION OF TOLUENE

The recommended method for the purification of toluene for chemical and electrochemical analysis is similar to that for benzene. Laboratory grade toluene (200 ml) is vigorously stirred with 50 ml concentrated sulfuric acid for one hour at a temperature below 30 °C. The toluene is separated from the sulfuric acid and then washed with water, 0.1 M sodium hydroxide, and several times with water again. The toluene is then pre-dried with

calcium chloride or sodium sulfate followed by refluxing over sodium under an inert atmosphere (nitrogen or argon) for one hour. Finally, it is fractionally distilled under an inert atmosphere, discarding the first ten percent and the last twenty percent.

TESTS FOR RESIDUAL IMPURITIES OF TOLUENE

Gas chromatography is the best method to test for impurities in toluene (ref. 5,20,34,41,42). Other methods to test the purity of toluene are based on various physical properties such as the freezing curve and the density (ref. 5,35,43). It has been stated that the boiling point is not a sensitive method to determine the purity of toluene (ref. 5,44). Water can be determined to 0.03% by a Karl Fischer titration and sulfur compounds can be determined to 0.003% by the standardized ACS methods (ref. 27).

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