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PURIFICATION OF SOLVENTS FOR
ELECTROANALYSIS†

BENZONITRILE
DICHLOROMETHANE
1,1-DICHLOROETHANE AND
1,2-DICHLOROETHANE

Prepared for publication by

KARL M. KADISH and JAMES E. ANDERSON
Department of Chemistry, University of Houston, Houston, Texas 77004, USA

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Purification of solvents for electroanalysis: benzonitrile

Abstract. The relevant physicochemical properties of benzonitrile are tabulated and its most important solvent properties are discussed. Examples of typical electrochemical studies in benzonitrile are presented. The impurities present in commercial benzonitrile are listed and a recommended purification method is described.

INTRODUCTION

Benzonitrile (C_6H_5CN) is generally a good solvent for the study of organic, anhydrous inorganic, and organometallic compounds. It is generally similar in its behavior as a solvent to acetonitrile (CH_3CN) (ref. 1, 2). However, one important structural difference between the two solvents is that benzonitrile does not have a labile hydrogen atom in the alpha position to the nitrile. The lack of an α -hydrogen potentially allows for stabilization of species that would react with acetonitrile.

Some of the important physical properties (ref. 2) of benzonitrile are listed in Table 1. Benzonitrile has a relatively large dipole moment for an aromatic solvent and the relative permittivity (dielectric constant) of 25.20 is also large compared to most other aromatic solvents. Benzonitrile has a low vapor pressure (but a strong odor) and hence is a good solvent to use when there is the possibility of concentration changes due to evaporation. Benzonitrile has a high freezing point and therefore does not allow low temperature studies. The Gutmann donor/acceptor numbers (ref. 3) indicate that benzonitrile is not a strongly coordinating solvent.

Numerous electrochemical studies have been carried out in benzonitrile. The solvent has a large cathodic and anodic potential range which, using a Pt electrode and tetrabutylammonium perchlorate (TBAP) as supporting electrolyte, extends between -1.95 V and $+1.8$ V vs SCE. Thus, the solvent is suitable for studying complexes where it is necessary to know both the HOMO and the LUMO under the same solution conditions. For example, mono and dinitrosyl iron(II) porphyrins may be oxidized or reduced by five reversible single electron transfer steps in benzonitrile (ref. 4). These reactions occur at values of $E_{1/2}$ between -1.89 V and $+1.46$ V vs SCE (ref. 4). Benzonitrile has also proven to be one of the best solvents for the study of metalloporphyrins using thin-layer spectroelectrochemistry and ESR techniques (ref. 4-6). The solvent does not readily react with anion or cation radicals. In addition, it is incompletely miscible with water, unlike acetonitrile.

Common supporting electrolytes that have been used in benzonitrile are tetrabutylammonium perchlorate (TBAP), tetrabutylammonium hexafluorophosphate [TBA(PF_6)], tetraethylammonium perchlorate (TEAP), lithium perchlorate, and sodium perchlorate (ref. 1, 4-7). The one-electron reduction of benzonitrile has been reported (ref. 8) to give a red-orange radical that has a half-life of 20 minutes. Mann also reported (ref. 1) that a red product was formed upon reduction of the solvent.

Benzonitrile is reported to be toxic for some people (ref. 9). Exposure to benzonitrile may lead to nausea as well as other effects. However, no chronic effects of benzonitrile have been reported to date.

MANUFACTURE OF BENZONITRILE AND COMMON IMPURITIES

The purity of commercial benzonitrile typically is 99% or better. Common impurities are water, benzoic acid, isonitriles, and different amines. The amount of any one impurity will depend upon the method used in the production.

Benzonitrile is commercially prepared by a number of different ways and a few examples are as follows: One method is to heat sodium benzenesulfonate with a sodium cyanide solution containing copper sulfate, and the product is distilled away from the reaction mixture (ref. 10). Benzonitrile can also be prepared by the reaction of benzoic acid and ammonia; the mixture is heated to approximately $400^\circ C$ over aluminum oxide (ref. 11). It can also be prepared by the reaction of hydrogen cyanide and arylhalide in the vapor phase, over a nickel(II) oxide or nickel catalyst supported on aluminum oxide (ref. 12). One final example for the preparation of benzonitrile is the production from toluene and nitrogen monoxide. This is done in the presence of a dehydration catalyst such as silver on an inert support (ref. 13).

TABLE 1. Selected properties of benzonitrile^a

Freezing temperature, $t_m/^\circ\text{C}$	-12.75
Boiling temperature, $t_b/^\circ\text{C}$, at 0.101325 mPa	191.10
Density, $\rho/\text{kg dm}^{-3}$, at 25°C	1.0006
Vapor pressure, p/kPa , at 28.2°C	0.133
Dynamic viscosity, $\eta/\text{mPa s}$, at 15°C	1.447
Refractive index, n_D , at 20°C	1.52823
Surface tension, $\gamma/\text{mN m}^{-1}$, at 15°C	38.65
Dipole moment, μ/D , at 25°C in benzene ^b	4.05
Enthalpy of vaporization, $\Delta H_V/\text{kJ mol}^{-1}$ at 25°C	55.48
	at t_b
	45.94
Molar heat capacity, $C_p/\text{J K}^{-1} \text{mol}^{-1}$	190.29
Relative permittivity, $D = \epsilon/\epsilon_0$, at 25°C	25.20
Donor number (Gutmann) ^c , $\text{DN}/\text{kcal mol}^{-1}$	11.9
Acceptor number (Gutmann) ^c , AN	15.5
Solvatochromic parameters ^d (Kamlet-Taft)	
(a) Polarity parameter, π^*	0.90
(b) Hydrogen bond acceptor number, β	0.41
(c) Hydrogen bond donor number, α	0.00

^a Reference 2

^b D = Debye = $3.33564 \times 10^{-30} \text{ C m}$

^c Reference 3, 1 cal = 4.184 J

^d Reference 23 and 24

PURIFICATION OF BENZONITRILE

Benzonitrile can be purified by pre-drying the solvent followed by either fractional distillation or distillation from phosphorous pentoxide under an inert atmosphere. Generally, these distillations are performed at reduced pressure. Larson and Iwamoto (ref. 14) reported that benzonitrile which is suitable for polarographic studies can be prepared by pre-drying commercial grade benzonitrile with calcium sulfate. The solvent is then repeatedly distilled from phosphorous pentoxide under an inert atmosphere and only the middle fractions is collected from each distillation. Some modifications of their technique are to distill the solvent "many times" from phosphorous pentoxide (ref. 15), to dry the solvent with calcium oxide and fractionally distill many times (ref. 16), or to reflux the solvent over phosphorous pentoxide for 24 hours followed by distillation prior to use (ref. 17).

In some cases, benzonitrile was washed prior to drying. Perrin reports (ref. 18) that benzonitrile can be washed with concentrated hydrogen chloride followed by drying with potassium carbonate. The benzonitrile is then dried with calcium chloride followed by distillation from phosphorous pentoxide under an inert atmosphere. The pre-wash treatment is for the removal of isonitriles and amines. This same technique was reported by Koval (ref. 19).

Conductivity grade benzonitrile was prepared by Van Dyke and Harrison (ref. 20) as follows: Commercially available benzonitrile is treated with aluminum chloride and rapidly distilled at 40°C - 50°C under a reduced pressure. The solvent is then washed with alkali and dried

with calcium chloride. Next, it is distilled under a reduced pressure from calcium chloride and then at 35°C under a reduced pressure several times. The benzonitrile is then fractionally crystallized several times by partial freezing. Finally, the benzonitrile is stored over finely divided activated alumina and withdrawn as required.

One method for the purification of benzonitrile for electrochemical studies is as follows (ref. 21): Commercial grade benzonitrile is dried with activated 4A molecular sieves. The solvent is then refluxed over sodium under vacuum and eventually distilled. The benzonitrile is then washed successively with dilute sulfuric acid, water, potassium bicarbonate solution and finally twice with water. The solvent is dried over magnesium sulfate and then with activated molecular sieves. Finally, it is fractionally distilled at a high reflux ratio. With 0.2 M ($M = \text{mol dm}^{-3}$) TBA(PF₆) as supporting electrolyte, the cathodic potential of the solvent is reported to be -2.2 V vs SCE .

RECOMMENDED PROCEDURE FOR PURIFICATION OF BENZONITRILE

The recommended method for the purification of benzonitrile is a modification of the technique described by Larson and Iwamoto (ref. 14). The benzonitrile is pre-dried with a mild drying agent such as calcium chloride. The calcium chloride is decanted and the benzonitrile is transferred to a distillation apparatus containing phosphorous pentoxide. It can be stored over phosphorous pentoxide under an inert atmosphere and distilled as needed under reduced pressure. The first 10-15% and the last 20% should be discarded.

TEST FOR RESIDUAL IMPURITIES

A technique to test the overall purity of benzonitrile has been reported by Witschonke (ref. 22) based on the freezing point of the purified solvent. As expected, this technique is not very sensitive to low concentration levels of impurities. Water can be determined by a Karl Fischer titration. Probably the best technique for the determination of impurities is to analyze the solvent by GC or GC/MS techniques. In addition, infrared spectroscopy can be used to determine the purity of the solvent.

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Purification of solvents for electroanalysis: dichloromethane

Abstract - Values are tabulated for the relevant physicochemical properties of dichloromethane and the most important properties of this solvent are discussed. Examples of typical electrochemical studies in dichloromethane are presented. The impurities present in commercial dichloromethane are listed and a recommended purification method is described.

INTRODUCTION

Dichloromethane (which is commonly called methylene chloride) is one of the most widely used chlorinated solvents. It is a very weakly coordinating solvent, but dissolves many organic and organometallic compounds. Dichloromethane has been used as a "nonbonding" solvent for studies by a wide variety of techniques. These include photochemical studies, electrochemical studies, and studies of homogeneous reaction chemistry. Dichloromethane is not totally unreactive since it is known to undergo chloride extraction in the presence of certain highly oxidized or highly reduced inorganic or organometallic complexes (ref. 1, 2) and it may also directly react with metal centers in a few organometallic compounds (ref. 2).

The most important physical properties of dichloromethane are listed in Table 1 (ref. 3). Of note is the small relative permittivity (dielectric constant) and the low Gutmann donor number of this solvent. Due to its relatively low freezing temperature, dichloromethane is also a convenient solvent for low temperature work.

Dichloromethane was first used in the mid 1960's for studies of organometallic electrochemistry (ref. 4, 6), but only recently has this solvent become widely used as an electrochemical solvent. Its nonbonding nature and lack of Lewis base properties make dichloromethane an appropriate solvent to study inorganic and organometallic complexes when one wishes to minimize the effect of solvent on electrochemical reactivity. It has a working potential range of -1.8 V to $+1.7$ V vs SCE using tetrabutylammonium perchlorate and a Pt electrode and -1.9 to $+0.8$ V vs SCE using tetrabutylammonium perchlorate and an Hg electrode (ref. 9). Thus, this solvent is ideal for studying both reductions and oxidations of a given compound at a Pt electrode under the same solution conditions.

Several good examples of electrochemistry in dichloromethane have been provided with metalloporphyrins (ref. 7, 8). These complexes may undergo the reversible formation of anion radicals, dianions, cation radicals, and dications as well as metal centered reactions, all of which may occur within the potential range of dichloromethane. Many oxidations of porphyrins have been carried out in dichloromethane. Since porphyrin cation radicals and dications are produced at relatively positive potentials and are attacked by nucleophiles to yield an isoporphyrin, the best solvent of choice is often dichloromethane. There is also an added advantage in that comparisons may be made directly between electrochemical and/or electrochemical/ESR results obtained in this solvent and chemical results obtained in other "nonbonding" solvents such as carbon tetrachloride or chloroform.

Common supporting electrolytes for dichloromethane in addition to tetrabutylammonium perchlorate are the tetrabutylammonium salts (TBAX), such as TBACl (ref. 9), TBABr (ref. 9), TBAI (ref. 9), and TBA(PF₆) (ref. 7, 8). Mann (ref. 4) reports that tetraethylammonium perchlorate is not sufficiently soluble to be used as a supporting electrolyte. The use of TBAX where X = Cl⁻, Br⁻ or I⁻ leads to a decrease in the anodic potential range of the solvent/supporting electrolyte system.

Many electrochemical studies in dichloromethane are now carried out using the technique of cyclic voltammetry. The resistivity of dichloromethane is fairly high, 7.25 ohm-m with TBAP and 7.22 ohm-m with tetrapropylammonium perchlorate (TPAP), using 0.1 M (M = mol dm⁻³) supporting electrolyte (ref. 10) but with the correct cell geometry and with higher concentrations of supporting electrolytes, dichloromethane may be used in thin-layer spectroelectrochemistry (ref. 7, 8) where it is usually not necessary to correct for IR loss. Dichloromethane is also an excellent solvent for low temperature electrochemistry. Its freezing temperature is -95.14°C and as such, measurements using dry ice or low temperature slush baths can easily be carried out. This will lead to larger IR losses than at room temperature but the lower temperature will often stabilize otherwise highly reactive oxidized or reduced products of an electrode reaction.

Patty (ref. 11) has reported that dichloromethane is the least toxic of the four chlorinated methanes. The 9th edition of the Merck Index (ref. 12) states that dichloromethane is a narcotic in large concentrations. In addition, dichloromethane has recently been reported to be a potential carcinogen (ref. 13). Thus, care should be used with this solvent.

TABLE 1. Selected properties of dichloromethane^a

Freezing temperature, $t_m/^\circ\text{C}$	-95.14
Boiling temperature, $t_b/^\circ\text{C}$, at 0.101325 mPa	39.75
Density, $\rho/\text{kg dm}^{-3}$, at 25°C	1.3168
Vapor pressure, p/kPa , at 25°C	58.102
Dynamic viscosity, $\eta/\text{mPa s}$, at 15°C	0.449
Refractive index, n_D , at 25°C	1.4212
Surface tension, $\gamma/\text{mN m}^{-1}$, at 20°C	28.12
Dipole moment, μ/D , in cyclopentane ^b	1.14
Enthalpy of vaporization, $\Delta H_V/\text{kJ mol}^{-1}$ at 25°C	28.556
at t_b	27.983
Molar heat capacity, $C_p/\text{J K}^{-1} \text{mol}^{-1}$, at 19.3°C	100.88
Relative permittivity (dielectric constant), $D = \epsilon/\epsilon_0$, at 25°C	8.93
Donor number (Gutmann) ^c , $\text{DN}/\text{kcal mol}^{-1}$	0.0
Acceptor number (Gutmann) ^c , $\text{AN}/\text{Dimensionless}$	20.4
Solvatochromic parameters ^d (Kamlet-Taft)	
(a) Polarity parameter, π^*	0.80
(b) Hydrogen bond acceptor number, β	0.0
(c) Hydrogen bond donor number, α	0.22

^a Taken from reference 3^c Reference 30, 1 cal = 4.184 J^b $D = \text{Debye} = 3.33564 \times 10^{-3} \text{ C m}$ ^d Reference 31 and 32

MANUFACTURE OF DICHLOROMETHANE AND COMMON IMPURITIES

Dichloromethane is produced by two different methods (ref. 14). The first is direct reaction of excess methane with chlorine at high temperatures. This process produces all of the chlorinated methanes as well as hydrogen chloride. Some methane remains in the product, as well as several longer chain chlorocarbon compounds which are due to impurities in the methane reactant. The dichloromethane is separated from these other compounds by fractional distillation. The second and predominant method has as a first step the reaction of hydrogen chloride and methanol in the presence of a catalyst to give methyl chloride. The methyl chloride is then chlorinated in a similar way as for methane. All of the chloromethanes are produced in this process. In addition, methanol is present as an impurity. The dichloromethane is separated by fractional distillation. Common reported impurities in commercial dichloromethane are hydrogen chloride, alcohols, small amounts of water, and some decomposition products such as formaldehyde (ref. 14, 15).

The following specifications are representative of commercial grade (ref. 14) dichloromethane:

distillation range (101.3 kPa)	39.4 - 40.4°C
density 25°C	1.319 - 1.322 kg/dm^3
acidity (as hydrogen chloride)	5 mg/kg
non-volatile matter	10 mg/kg
water	100 mg/kg

Although dichloromethane is considered to be relatively stable, small amounts of stabilizers may be used at the time of production and are found in the commercial product. Common stabilizers are phenolic compounds (phenol, hydroquinone, p-cresol for example), epoxides, amines, and a mixture of nitromethane and 1,4-dioxane (ref. 14).

The initial decomposition of dichloromethane occurs at 120°C in dry air (ref. 16). The primary product is hydrogen chloride, with small amounts of phosgene produced. On prolonged contact with water, dichloromethane hydrolyzes to produce hydrogen chloride and formaldehyde (ref. 14). Dichloromethane will react with either iron or aluminum to dechlorinate, especially if the dichloromethane contains water or other halogenated solvents, by a Friedel-Crafts reaction.

The American Chemical Society standards for reagent grade dichloromethane include the following requirements (ref. 17): density, 1.321 to 1.315 kg/dm³; acidity (as hydrogen chloride), less than 0.001%; water, less than 0.02%. In addition, ACS spectroscopic grade dichloromethane standards require that the absorbance in a 1 cm cell not exceed 1.00 at 235 nm, 0.35 at 240 nm, 0.10 at 250 nm, 0.40 at 260 nm and 0.01 at 340 nm to 500 nm referred to water in a matched cell. Furthermore, the absorption curve should be smooth over the entire range of wavelengths.

PURIFICATION TECHNIQUES

The reported methods for the purification of dichloromethane are quite varied and reflect the different levels of purity needed for the particular experiment. For example, Lowry (ref. 18) fractionally distilled commercial dichloromethane many times until the conductivity of the middle fraction was constant, while Gray (ref. 19) reports that dichloromethane can be purified by vacuum distillation onto activated 4A molecular sieves and distilled again when needed.

The most common method for purification of dichloromethane is to reflux the solvent under an inert gas over a drying agent, such as phosphorous pentoxide or calcium hydride, followed by distillation as needed (20-23). Molecular sieves (4A) are frequently used for storing and drying the dichloromethane rather than phosphorous pentoxide or calcium hydride. A variation of the same technique described above is to distill the solvent from lithium aluminum hydride under argon (ref. 24) or to doubly distill dichloromethane from phosphorous pentoxide under argon followed by a final distillation from potassium carbonate (ref. 25).

A more rigorous purification method involves pre-washing dichloromethane, followed by distillation. For example, Maryott (ref. 26) washed commercial dichloromethane with concentrated sulfuric acid, then with aqueous sodium hydroxide, followed by water. The dichloromethane was then dried by leaving overnight over sodium hydroxide and calcium chloride. Finally, the product was fractionally distilled. Perrin (ref. 27) reports a method for the purification of dichloromethane that is similar to Maryott's. Perrin's method is to shake the dichloromethane with concentrated sulfuric acid until the acid layer remains colorless, wash with water, 5% aqueous sodium carbonate and then water again. The dichloromethane is pre-dried with calcium chloride, distilled from calcium hydride or phosphorous pentoxide, and stored over activated 4A molecular sieves. This method is used quite frequently (ref. 28, 29).

RECOMMENDED PROCEDURE FOR DICHLOROMETHANE

The recommended procedure is based on Perrin's technique, but with some modification. Shake reagent grade dichloromethane with concentrated sulfuric acid until the acid layer remains colorless. Wash with water, saturated aqueous sodium carbonate, and then with water again. Pre-dry with calcium chloride. Reflux for two hours over phosphorous pentoxide and distill onto fresh phosphorous pentoxide under inert atmosphere, discarding the first 10% and the last 20% of the solvent. The dichloromethane can then be stored over phosphorous pentoxide and distilled as needed.

TEST FOR RESIDUAL IMPURITIES

Residual water can be determined by Karl Fischer titration. The method is described as follows in the A.C.S. Reagent Chemicals (ref. 17) book:

Place 25 ml of methanol in a dry titration flask and add Karl Fischer reagent to a visually or electrometrically determined end point. Add 25 ml (33 g) of the sample, taking care to protect the sample and contents of the flask from moisture. Stir vigorously and titrate with Karl Fischer reagent to the same end point. Calculate the water content of the sample from the titer and volume of Karl Fischer reagent consumed by the sample.

The test for residual acidity in the A.C.S. Reagent Chemicals (ref. 17) book is given as follows:

To 25 ml of alcohol in a 100-ml glass-stopped flask, add 0.10 ml of phenolphthalein indicator solution and 0.01N sodium hydroxide solution until a pink color persists for at least 30 seconds after vigorous shaking. Add 25 ml (33 g) of sample from a pipet and mix thoroughly with the neutralized alcohol. If no pink color remains, titrate with 0.01N sodium hydroxide to the end point where the pink color persists for at least 30 seconds. Not more than 0.90 ml of 0.01N sodium hydroxide should be required. Great care should be taken in the test during the addition of the sample and the titration to avoid contamination from carbon dioxide.

The test for free halogens in the A.S.C. Reagent Chemicals (ref. 17) book is described as follows:

Shake 10 ml vigorously for 2 minutes with 10 ml of 10% potassium iodide reagent solution and 1 ml of starch indicator solution. A blue coloration should not be present in the water layer.

In general, the purity of dichloromethane is commonly monitored by both infrared spectroscopy and gas chromatographic techniques (ref. 14)

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Purification of solvents for electroanalysis: 1,1-dichloroethane and 1,2-dichloroethane

Abstract - Values are tabulated for the relevant physicochemical properties of 1,1-dichloroethane and 1,2-dichloroethane and the most important solvent properties of these two solvents are discussed. Examples of typical electrochemical studies in these two solvents are presented. Common impurities present in commercial 1,1-dichloroethane and 1,2-dichloroethane are listed and recommended purification procedures are described.

INTRODUCTION

1,1-Dichloroethane and 1,2-dichloroethane are good solvents for studying the reactions and physical properties of organic and organometallic compounds. Both compounds are very weak electron donors. Of the two, 1,2-dichloroethane is more frequently used. 1,2-Dichloroethane is a good solvent for photochemical (ref. 1) and electrochemical (ref. 2-8) studies. However, neither solvent is as commonly used as dichloromethane, perhaps due to their potential health hazard (see below) as well as to the fact that dichloromethane has long been established as a good nonbinding electrochemical solvent.

Both 1,1-dichloroethane and 1,2-dichloroethane have similar physical properties to those of dichloromethane (ref. 9). Table 1 lists some selected physical properties of 1,1-dichloroethane and 1,2-dichloroethane. Both solvents have a low relative permittivity (dielectric constant) and 1,2-dichloroethane is the reference solvent for the Gutmann donor number scale. Neither Gutmann donor/acceptor numbers nor Kamlet-Taft solvent parameters have been reported for 1,1-dichloroethane. An important difference between 1,1-dichloroethane and 1,2-dichloroethane is the freezing temperature of the two solvents. 1,1-Dichloroethane has a freezing temperature that is fairly low (similar to dichloromethane) making it a convenient solvent for low temperature work. In contrast, 1,2-dichloroethane has a freezing temperature that is much higher. However, 1,2-dichloroethane has a higher boiling point (and hence, a lower vapor pressure) than either 1,1-dichloroethane or dichloromethane.

Both 1,1-dichloroethane and 1,2-dichloroethane are suitable for electrochemical studies at room temperature, but 1,2-dichloroethane has been the most widely used of the two solvents (ref. 2-6). Both solvents have similar working potential ranges which may extend from -1.8 V to +1.7 V vs SCE using tetrabutylammonium perchlorate and a Pt electrode. This range is similar to that of dichloromethane with the same supporting electrolyte. The working potential range of 3.5 V enables one to observe both the reductions and the oxidations of a given compound under the same solution conditions. This is especially important when it is necessary to compare the HOMO and the LUMO of a given complex in the same solvent system. For example, five reversible electrode reactions are observed for monomeric iron(III) tetraphenylporphyrin (ref. 4). These electrode reactions involve three reductions and two oxidations, all of which occur within the potential range of dichloroethane (ref. 4).

Tetrabutylammonium perchlorate is a commonly used supporting electrolyte for both solvents. The resistivity of the dichloroethanes is fairly high (ref. 11) and for 1,2-dichloroethane ranges from 69.40 Ω m in solutions containing 0.01 M ($M = \text{mol/dm}^{-3}$) tetrabutylammonium perchlorate to 2.15 Ω m in solutions containing 1.0 M tetrabutylammonium perchlorate. The resistivity has also been measured in solutions of 0.01 M tetraethylammonium perchlorate (66.90 Ω m) and in 0.01 M tetrapropylammonium perchlorate (65.80 Ω m) and 0.05 M tetrapropylammonium perchlorate (15.60 Ω m). For solutions of 1,2-dichloroethane with all three supporting electrolytes the obtained values are slightly but not significantly higher than for solutions of dichloromethane containing the same supporting electrolytes.

One disadvantage of both 1,1-dichloroethane and dichloromethane is their low boiling points. Depending on the cell design, this may present special problems in normal cells during deoxygenation as well as in some thin-layer spectroelectrochemical cells where time-resolved measurements over a long time are difficult due to solvent evaporation under the influence of a light source. In order to avoid this problem, porphyrin researchers have often switched to 1,2-dichloroethane in place of dichloromethane (ref. 2-8). Because of its higher boiling point (83.48°C), fewer problems are encountered due to solvent evaporation. The relative permittivity of 1,2-dichloroethane is 10.36 compared to 8.93 for dichloromethane, and its donor number is defined as 0.0, similar to dichloromethane. The electrochemical mechanisms and ligand-binding properties of different metalloporphyrins appear to be identical in these two solvents, so that results can be used interchangeably (ref. 4, 6). There are, however, slight differences in absolute potential measurements between the two solvents. These exist even after correction for liquid junction potential by use of ferrocene as an internal standard (ref. 11) and may be due in part to the different relative permittivities of the two solvents.

TABLE 1. Selected properties of 1,1- and 1,2-dichloroethane^a

	1,2-Dichloroethane	1,1-Dichloroethane
Freezing Temperature, $t_m/^\circ\text{C}$	-35.66	-96.98
Boiling Temperature, $t_b/^\circ\text{C}$, at 0.101325 mPa	83.48	57.28
Density, $\rho/\text{kg dm}^{-3}$, at 25°C	1.2458	1.1680
Vapor Pressure, p/kPa , at 20°C	11.112	30.358
Dynamic Viscosity, $\eta/\text{mPa s}$, at 15°C	0.887	0.505
Refractive Index, n_D , at 25°C	1.4421	1.4138
Surface Tension, $\gamma/\text{mN m}^{-1}$, at 20°C	32.23	24.75
Dipole Moment, μ/D , at 25°C in benzene ^b	1.86	1.98
Enthalpy of Vaporization, $\Delta H_v/\text{kJ mol}^{-1}$ at 25°C	34.267	30.999
	at t_b	32.024
Molar Heat Capacity, $C_p/\text{J K}^{-1} \text{mol}^{-1}$, at 27°C	129.12	126.27
Relative Permittivity, $D = \epsilon/\epsilon_0$, at 25°C	10.36	10.0
Donor Number (Gutmann) ^c , $\text{DN}/\text{kcal mol}^{-1}$	0.00 ^d	
Acceptor Number (Gutmann) ^c , AN	16.7	
Solvatochromic Parameters ^e (Kamlet-Taft)		
(a) Polarity Parameter, π^*	0.81	
(b) Hydrogen Bond Acceptor Number, β	0.00	
(c) Hydrogen Bond Donor Number, α	0.00	

^a Reference 9^b $D = \text{Debye} = 3.33564 \times 10^{-3} \text{ C m}$ ^c Reference 10; 1 cal = 4.184 J^d By definition (reference solvent)^e Reference 35 and 36

One additional advantage to the use of both 1,1-dichloroethane and 1,2-dichloroethane is that some of their properties are similar to those of the other chlorinated solvents. Thus, chemical and spectroscopic (for example NMR) results obtained in solvents such as carbon tetrachloride and chloroform may be directly compared to electrochemical and electrochemical/ESR results obtained in 1,1-dichloroethane and 1,2-dichloroethane.

Both 1,1-dichloroethane and 1,2-dichloroethane are a health hazard. Heppel (ref. 12) reports that 1,1-dichloroethane is somewhat less toxic than carbon tetrachloride. The most important effect seems to be on the liver. The 9th Edition of the Merck Index (ref. 13) states that 1,1-dichloroethane is a narcotic in high concentrations. A later report (ref. 14) states that 1,1-dichloroethane causes liver and kidney damage. The 9th Edition of the Merck Index (ref. 13) states that the vapor of 1,2-dichloroethane causes irritation of the respiratory track and corneal clouding, as well as additional disorders. However, at low concentrations one becomes adapted to the odor which therefore is not a reliable warning (ref. 15). In addition, 1,2-dichloroethane is carcinogenic (ref. 16). Care should be taken while using either of these solvents.

MANUFACTURE OF 1,1-DICHLOROETHANE AND 1,2-DICHLOROETHANE AND COMMON IMPURITIES

1,2-Dichloroethane is prepared commercially by the catalytic vapor or liquid phase chlorination of ethylene (ref. 17). The purity of the ethylene will have a direct effect on the purity of the 1,2-dichloroethane that is produced (ref. 13). Iron(III) chloride is the most frequently used catalyst for the liquid phase chlorination (ref. 17). However, aluminum chloride, antimony pentachloride, and copper(II) chloride are other known catalysts for this process. 1,2-Dichloroethane is also produced by the oxidation/chlorination of ethylene with hydrogen chloride and oxygen. Common impurities found in 1,2-dichloroethane are water, acid (as hydrogen chloride) as well as other chlorinated hydrocarbons resulting from the chlorination process.

1,2-Dichloroethane will decompose at 60°C if heated with water under an inert atmosphere (ref. 17). The main product is hydrogen chloride. Atmospheric oxidation of 1,2-dichloroethane will occur at room temperature generating HCl and resulting in solvent discoloration.

1,1-Dichloroethane is produced commercially from hydrogen chloride and vinyl chloride at 20 to 55°C with an aluminum, iron(III) or zinc chloride catalyst (ref. 17, 18). Common impurities in 1,1-dichloroethane are water, acid (as hydrogen chloride) and other chlorinated hydrocarbons. Commercial 1,1-dichloroethane frequently is stabilized with dioxane (see 1985-1986 Aldrich catalog for example). Dioxane is suspected to be carcinogenic.

1,1-Dichloroethane decomposes from 356 to 453°C by a homogeneous, first order reaction to give hydrogen chloride and vinyl chloride (ref. 19). However, 1,1-dichloroethane will decompose in the presence of metals or metal salts. The decomposition has been studied on activated alumina (ref. 20) as well as on magnesium sulfate and anhydrous alumina (ref. 17).

PURIFICATION TECHNIQUES OF 1,1-DICHLOROETHANE AND 1,2-DICHLOROETHANE

1,1-Dichloroethane was purified by Barton (ref. 21) by extraction with concentrated sulfuric acid and then fractional distillation. Instead of sulfuric acid, aqueous potassium permanganate can be used. Perrin (ref. 22) describes a similar method for the purification of 1,1-dichloroethane, but with some modifications. The solvent is shaken with either concentrated sulfuric acid or aqueous potassium permanganate, washed with water, saturated aqueous sodium hydrogen carbonate, and with water a second time. The 1,1-dichloroethane is then dried with potassium carbonate. Finally, the solvent is distilled from calcium hydride or phosphorous pentoxide under inert atmosphere.

1,1-Dichloroethane has also been purified by repeated fractional distillation, checking both the density and boiling point for purity (ref. 23). In addition to fractional distillation of 1,1-dichloroethane, three crystallizations were employed to further purify the solvent (ref. 24). Vogel (ref. 25) treated 1,1-dichloroethane with saturated aqueous sodium hydrogen carbonate, dried the solvent, and then fractionally distilled it in order to obtain pure solvent.

There are many reported methods for the purification of 1,2-dichloroethane. The most direct method is fractional distillation (ref. 26). One report states that a better quality solvent is obtained by discarding at least the first 10% of the first distillation, and then by fractionally distilling the solvent a second time (ref. 27). A fractional distillation can be followed by several crystallizations, as reported by Tokuhiko (ref. 28).

An additional step to the distillation method for purification of 1,2-dichloroethane is to pre-dry the solvent and then to distill it from either calcium hydride or phosphorous pentoxide. Michelin (ref. 29) used an unspecified drying agent and then distilled from calcium hydride. Walden (ref. 30) used repeated distillation from sodium sulfate to pre-dry and eventually distilled from phosphorous pentoxide.

A more rigorous procedure for the purification of 1,2-dichloroethane requires washing the solvent, pre-drying and finally distilling from phosphorous pentoxide or calcium hydride. Vogel (ref. 31) washed 1,2-dichloroethane with 5% sodium hydroxide, dried it with calcium chloride, and finally distilled the solvent. Other workers have washed the solvent with dilute potassium hydroxide, water, and then dried with calcium chloride (ref. 32, 33). The 1,2-dichloroethane was then distilled from phosphorous pentoxide under inert atmosphere.

Finally, a general method of purification has been described in several publications (ref. 7-9, 22). In this method 1,2-dichloroethane is shaken with concentrated sulfuric acid, washed with water, and then with dilute potassium hydroxide or saturated aqueous sodium carbonate. The solvent is pre-dried with calcium chloride and then refluxed over phosphorous pentoxide under an inert atmosphere.

RECOMMENDED PROCEDURE FOR 1,1-DICHLOROETHANE AND 1,2-DICHLOROETHANE

The purification procedure is the same for both solvents. It is basically the method described by Perrin (ref. 22), but with a few modifications. The solvent is shaken with concentrated sulfuric acid until the acid layer remains colorless. The solvent is washed with water, saturated aqueous sodium carbonate, and water again. The solvent is pre-dried over calcium chloride followed by distillation from phosphorous pentoxide, discarding the first 10% and the last 20%. The purity of the solvent can be monitored by the boiling range.

TESTS FOR RESIDUAL IMPURITIES

Water can be determined by Karl Fischer titration described as follows in the A.C.S. Reagents Chemicals (ref. 34) book:

Place 25 ml of methanol in a dry titration flask and add Karl Fischer reagent to a visually or electrometrically determined end point. Add 25 ml (31 g) of the sample, taking care to protect the sample and contents of the flask from moisture. Stir vigorously and titrate with Karl Fischer reagent to the same end point. Calculate the water content of the sample from the titer and volume of Karl Fischer reagent consumed by the sample.

In addition, a titration for residual acidity is described (ref. 34) as follows:

To 25 ml of alcohol in a 100-ml glass-stoppered flask, add 0.10 ml of phenolphthalein indicator solution and 0.01N sodium hydroxide until a faint pink color persists after shaking for 30 seconds. Add 25 ml (31 g) of sample, mix well, and titrate with 0.01N sodium hydroxide until the pink color is restored. Not more than 0.85 ml of 0.01N sodium hydroxide should be required. Special care should be taken during the addition of the sample and titration to avoid contamination from carbon dioxide.

The ACS standards (ref. 34) for 1,2-dichloroethane include the following: density between 1.241 and 1.251 kg/dm³; a boiling range entirely within 2.0°C including 83.5° ± 0.1°C; acidity (as hydrogen chloride) < 0.001%; and water < 0.03%. ACS spectroscopic grade 1,2-dichloroethane also requires the following UV-visible behavior: In a 1.00 cm cell, with water as a standard, the absorbance should not exceed 1.00 at 226 nm, 0.50 at 230 nm, 0.20 at 235 nm, 0.10 at 240 nm, 0.05 at 245 nm, 0.02 at 250 nm, and 0.01 at 255 nm to 400 nm. In addition, the absorbance curve should be smooth over the entire range with no extra peaks.

The purity of both solvents can be generally checked with infrared spectroscopy as well as by gas chromatographic techniques (ref. 17). These methods are probably the quickest and most reliable to determine the purity of the solvent.

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