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## RECOMMENDED METHODS FOR THE PURIFICATION OF SOLVENTS AND TESTS FOR IMPURITIES

### 1,2-ETHANEDIOL AND 2,2,2-TRIFLUOROETHANOL

*Prepared for publication by*

Y. MARCUS

Department of Inorganic and Analytical Chemistry  
Hebrew University of Jerusalem, Jerusalem 91904, Israel

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# Recommended methods for the purification of solvents and tests for impurities: 1,2-Ethandiol and 2,2,2-Trifluoroethanol

## 1,2-ETHANEDIOL

**Abstract** - Specifications for the commercially available solvent, relevant physiochemical and key solvent properties are given. The procedures for the purification include the removal of oxidation products and of water. Gas chromatography is best for the detection of organic impurities.

## INTRODUCTION

Ethylene glycol - 1,2-ethandiol - is, next to the rather unstable hydrogen peroxide, the most water-like nonaqueous solvent. It is, therefore, of interest to solution chemists and electrochemists, in particular also since its fairly high relative permittivity allows good solubility and complete dissociation of uni-univalent electrolytes.

The solvent is manufactured nowadays in large quantities, and is used as an intermediate in the plastics industry, as a plasticizer, as an antifreeze and as a solvent. It is made by the hydration of ethylene oxide, resulting in a product of high purity, the commercial product assaying at >99%. The main impurities are diethylene glycol (3-oxapentane-1,5-diol) and triethylene glycol (3,6-dioxaoctane-1,8-diol), as well as methanol and aldehydic oxidation products, and, of course, water. The solvent is extremely hygroscopic, and absorbs in a week 30% of its mass of atmospheric water (ref. 1).

Fractional distillation is the method generally employed for the preparation of a reagent-grade solvent. The specifications of manufacturers for their reagents generally pertain to >99.5% assay solvent, see Table 1. No entries for 1,2-ethandiol have been made, however, in specification listings such as the American Chemical Society's "Reagent Chemicals" (ref. 2, but see ref. 3).

The physical and thermodynamic properties of 1,2-ethandiol are given in Riddick and Bunger's book "Organic Solvents" (ref. 4), and these (updated where necessary) and a few other properties, mainly polarity indices, are presented in Table 2.

1,2-Ethandiol is a glass-forming liquid, and the determination of its freezing temperature is difficult. Several authors have commented on this point, and of the more recent determinations,  $-13.2^{\circ}\text{C}$  (ref. 15),  $-12.6^{\circ}\text{C}$  (ref. 5), and  $-12.3^{\circ}\text{C}$  (ref. 6), the highest appears to be the most accurate. The vapor pressure at ambient temperatures is quite low and difficult to measure accurately. A better estimate of it for 298.15 K is obtained from the (non-linear) extrapolation of very careful measurements at higher temperatures, 374 to 495 K (ref. 7) than from those made in the range 283 to 373 K (ref. 10).

The relative permittivity of 1,2-ethandiol is quoted in ref. 4 as 37.7 at  $25^{\circ}\text{C}$ , from the work of several authors in the 1930s. More recent work (refs. 16-19) yielded values >40 for this temperature. The value in ref. 16 for  $30^{\circ}\text{C}$ , 39.41, agrees well with that interpolated from the data in ref. 17, 39.53. The value in ref. 19 for  $20^{\circ}\text{C}$ , 41.20, agrees fairly well with that given in ref. 17, 41.82. Hence the value interpolated from ref. 17 for  $25^{\circ}\text{C}$  is taken to represent the best value at this temperature, and is presented in Table 2.

1,2-Ethandiol offers few hazards to its users. It presents negligible hazards to health by inhalation at ambient temperatures, low acute oral toxicity (except when used in massive doses in the adulteration of wine!), and insignificant irritation from skin contact. However, toxic amounts can be absorbed through the skin on prolonged contact (ref. 20).

The threshold limit in air is 100 ppm,  $274\text{ mg/m}^3$  (ref. 21). The flashpoint is rather high,  $115^{\circ}\text{C}$ , and the temperature of spontaneous ignition in air is  $\geq 413^{\circ}\text{C}$  (ref. 22).

## STRUCTURE OF LIQUID 1,2-ETHANEDIOL

The existence of a highly pronounced structure in 1,2-ethandiol can be inferred from its high viscosity ( $\eta = 16.13\text{ Pa}\cdot\text{s}$  at  $25^{\circ}\text{C}$ ) and its high Trouton's constant,  $\frac{v_s}{v_l} = \frac{H}{T_b}$  (at  $T_b$ )/ $T_b = 13.0\text{ R} = 108\text{ J K}^{-1}\text{ mol}^{-1}$ , compared with  $10.7 \pm 0.7\text{ R}$  for non-associated liquids. It has also a high dipole correlation parameter (Kirkwood's  $g = 4.56$  at  $20^{\circ}\text{C}$ , ref. 17), indicative of cooperative dipole orientation and of self-association.

This structure is brought about by a three-dimensional network of hydrogen bonds, each molecule being capable of donating two and accepting two hydrogen bonds, just as in liquid water.

The isolated molecule appears to exist predominantly in the *gauche*-form, with an internal hydrogen bond (ref. 23). In the liquid, the extensive hydrogen-bonded network is confirmed by Raman- and infrared spectral measurements. These show a preponderance of intermolecularly-bonded OH-groups (the  $3353\text{ cm}^{-1}$  band) and a minority of monomeric molecules, with internally bonded OH-groups (the  $3604\text{ cm}^{-1}$  band, ref. 24). Nuclear magnetic resonance measurements of the effects of urea and tetramethylurea on the chemical shift of the hydroxyl protons show the former to be structure-making and the latter to be structure-breaking (ref. 25).

### KEY SOLVENT PROPERTIES OF 1,2-ETHANEDIOL

Because of the two hydroxyl groups, 1,2-ethanediol is highly structured (see section on STRUCTURE above) and water-like. This fact is manifested in its unlimited miscibility with water on the one hand, and limited miscibility with non-polar organic solvents (e.g. 5.51 wt.% benzene in the saturated solution at  $20\text{ }^{\circ}\text{C}$ , ref. 26) or even polar ones, such as diethyl ether, on the other. The limits of the mutual solubilities of 1,2-ethanediol and water are well below the freezing points of the two liquids, extending down to  $-60\text{ }^{\circ}\text{C}$  (ref. 27).

The solubilities of only a few salts in 1,2-ethanediol have been reported (refs. 27,28). Most of the known values are shown in Table 3. The solubilities of  $\text{LaF}_3$  and  $\text{LaCl}_3$  at  $25\text{ }^{\circ}\text{C}$  are  $1.10^{-3}$  and  $0.56\text{ mol/kg}$  respectively (ref. 32). The solvation power of 1,2-ethanediol towards ions is more similar to that of water than that of most other solvents. This is manifested in low standard molar Gibbs free energies of transfer of the ions from water to 1,2-ethanediol. Typical values are 0 to  $-2\text{ kJ/mol}$  for the alkali metal ions and 3 to  $9\text{ kJ/mol}$  for the halide ions (ref. 33). This is due to the greater overall similarity between the relevant solvent properties (the polarity indices, the solubility parameter, see Table 2) of 1,2-ethanediol to those of water than those of other solvents. It should also be pointed out that the relatively high value of  $\epsilon = 40.7$  supports complete ionic dissociation of all 1:1 electrolytes, just as in water.

The acid-base properties of 1,2-ethanediol are not very different from those of water. The autoprotolysis constant,  $K_s/\text{mol}^2\text{ dm}^6$ , is given by  $\text{p}K_s = 15.65$  at  $25\text{ }^{\circ}\text{C}$  (ref. 34), with similar values (in the range 15.57 to 15.72) given in refs. 34-37. The acidity constant in dilute aqueous solutions  $K_a/\text{mol dm}^3$ , was determined long ago (ref. 38) as  $\text{p}K_a = 14.77$  at  $25\text{ }^{\circ}\text{C}$ . On the other hand, it must be realized that 1,2-ethanediol is an ampholytic protic solvent, so that it should have a leveling effect on the reactivities of acids and bases.

### PURIFICATION OF 1,2-ETHANEDIOL

Because of the high reactivity of the two hydroxyl groups, the effect of monofunctional impurities should generally be less than proportional to their concentration, whereas that of water should be proportional to it (perhaps on the volume fraction base, which makes it about 3 times as effective as on the mole fraction base). The purity of the reagent grade solvent is, therefore, sufficient for a wide range of applications. Only for the most exacting physical property measurements is further purification required. This is generally achieved by drying over anhydrous sodium sulfate and subsequent rectification under nitrogen, for avoidance of oxidation.

#### Procedure

Step 1. Dry the solvent 1,2-ethanediol over freshly dehydrated sodium sulfate (refs. 17,40).

Step 2. Fractionally distill the solvent at least twice in vacuum (refs. 40,42), at  $1.1\text{ kPa}$  (ref. 17), or under a blanket of nitrogen at this pressure (ref. 41), for avoidance of oxidation to aldehydes. The middle fraction is collected. A reflux ratio of 1:10 was specified (ref. 41).

Step 3 (optional). A double fractional recrystallization was used for the final purification step in ref. 17. The necessity of this step was, however, not demonstrated.

For special purposes special treatments have been proposed. Thus, treatment of the hydration product of ethylene oxide at  $150\text{ }^{\circ}\text{C}$  with a mixture containing 12%  $\text{NaBH}_4$ , 38%  $\text{NaBH}$ , and 50%  $\text{H}_2\text{O}$  was said to produce a high purity 1,2-ethanediol with particularly low absorbance in the UV (ref. 43).

## DETECTION OF IMPURITIES

Water in 1,2-ethanediol is generally determined by Karl-Fischer titration. Thus  $0.07 \pm 0.01\%$  water was found (ref. 41) in a fractionally distilled solvent, which was not first dried over sodium sulfate. New reagents for the Karl-Fischer titration, applicable specifically also in 1,2-ethanediol, have been proposed (ref. 44).

Organic impurities (also water) are determined by chromatography. Gas-liquid chromatography was used for the determination of  $\geq 0.1\%$  diethylene glycol (3-oxapentane-1,5-diol),  $\geq 0.05\%$  water, and  $\geq 0.05\%$  methanol (ref. 45, see also ref. 46). High performance/pressure liquid chromatography (HPLC) was applied more for the determination of 1,2-ethanediol in the presence of other polyols, but the methods employed (e.g., refs. 47,48) could presumably also be used for the determination of impurities in this solvent.

Special methods have been employed for the determination of specific impurities. Glycolaldehyde (2-hydroxyethanal) was determined above a detection limit of 60 ppm in 1,2-ethanediol by the formation of its adduct with 3-methyl-2-benzthiazolinone hydrazone, extraction of the adduct with tetrachloromethane, and oxidative formation of the osazone with 2,4-dinitrophenyl-hydrazine. The osazone was determined spectrophotomerically at 616 nm (ref. 49). Chloride was determined above a detection limit of 0.5 ppm by potentiometric titration with 0.01 M silver nitrate of the sample dissolved in ethanol or 75% acetone in water, containing 0.2 M nitric acid (ref. 50).

TABLE 1. Examples of specifications for commercially available 1,2-ethanediol

	Merck <sup>a</sup>	Fluka <sup>b</sup>	Baker <sup>c</sup>	AnalaR <sup>d</sup>
Impurity	Maximal content in ppm (mass)			
Water	1000	1000	2000	1000
Free acid, as CH <sub>3</sub> CO <sub>2</sub> H	10	10	100	5
Chloride	0.2	10	5	0.2
Sulfate		10		20
Iron	0.5	0.5	0.2	1
Copper		0.05		0.1
Cadmium, zinc		0.05		
Other heavy metals <sup>e</sup>		0.1		
Residue on ignition	0.005		0.005	0.003
Formaldehyde	0.005			
Substances reducing KMnO <sub>4</sub>	3			
<b>Other specifications</b>				
Boiling range, °C		195-197	194-200	195-199
Melting range, °C		-11- -9		

\* <sup>a</sup> Merck (Darmstadt, F.R. Germany) guaranteed purity reagent; <sup>b</sup> Fluka (Switzerland) specifications for puriss reagent; <sup>c</sup> J.T. Baker (U.S.A.) specifications for "Baker Analyzed" reagent; <sup>d</sup> B.D.H. (London, UK) specifications for AnalaR reagent; <sup>e</sup> Pb, Co, Ni, Cr, and Mn.



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## 2,2,2-TRIFLUOROETHANOL

**Abstract** - The purity expected for the commercially available solvent, relevant physicochemical and key solvent properties are given. The procedures for the purification include drying and fractional distillation. Gas chromatography is best for the detection of organic impurities.

### INTRODUCTION

Trifluoroethanol (TFE), or more exactly 2,2,2-trifluoroethanol, is a protic solvent that has very strong hydrogen bond donating abilities but very weak electron pair donating abilities. Hence it is an excellent solvating solvent for anions and a poor one for cations. Its uses as a solvent in organic reactions and in electrochemistry are based on these facts. Beyond these uses, it is widely used as a working fluid in refrigeration systems.

The solvent is manufactured by catalytic reduction of trifluoroacetic acid. It is available commercially from dealers in laboratory chemicals, but these do not, generally, provide specifications of their product, in terms of its purity, beyond stating its assay to be >99% (Aldrich, Milwaukee, Catalog 1986/7). The only specially pure reagent found in catalogs of the major manufacturers is the Uvasol reagent for spectroscopy (Merck, Darmstadt, Catalog 1984), which assays at 99.7%, and has <0.2 water as the major impurity. This reagent should permit in 1 cm cells, against a reference of water, 15% transmittance at 190 nm, 85% at 220 nm, and 98% at 250 nm.

The physical and thermodynamic properties of trifluoroethanol are not given in standard reference books of solvents, such as Riddick and Bunger's "Organic Solvents" (ref. 1), and must be obtained from the original research literature. These properties and the polarity indices are presented in Table 1.

### STRUCTURE OF LIQUID 2,2,2-TRIFLUOROETHANOL

The existence of self-association and structure in trifluoroethanol can be inferred from its high Trouton's constant,  $\Delta_v S = \Delta_v H$  (at  $T_b$ )/ $T_b = 12.6 R = 105 J K^{-1} mol^{-1}$ , compared with  $10.7 \pm 0.7 R$  for non-associated liquids. It has also a high dipole correlation parameter (Kirkwood's  $g = 3.0$  at 25 °C, ref. 15), indicative of cooperative dipole orientation and of self-association.

This structure of trifluoroethanol is ascribed to intermolecular hydrogen bonding, which has been observed both in the gas phase and in the liquid. Association to dimers in the gas phase was inferred from the dependence of the thermal conductance on the pressure of the vapor (ref. 16, but see ref. 17, where vapor density data are interpreted in terms of higher oligomers and not dimers). The self-association in liquid trifluoroethanol is comparable to that of ethanol, since although it is a much stronger hydrogen bond donor, it is also a much weaker hydrogen bond acceptor. Internal hydrogen bonding in the *gauche*-form of the monomer accounts for the major fraction of the intensity of the OH stretching band in the infrared spectrum (Ref. 18).

### KEY SOLVENT PROPERTIES OF 2,2,2-TRIFLUOROETHANOL

Trifluoroethanol is miscible with water in all proportions (ref. 5) and is mutually miscible with other solvents to a similar extent to ethanol, but interacts more strongly with basic solvents than its alkanol analog. The liquid-vapor equilibrium diagrams in the binary mixtures of trifluoroethanol with water, methanol, ethanol, and 2-butanol have been determined (ref. 17), and they exhibit deviations from ideality positive for water, negative for methanol and ethanol).

Little has been published concerning the solubilities of electrolytes in trifluoroethanol. The rather low relative permittivity,  $\epsilon_r = 26.67$  at 25 °C (ref. 5,8) and the poor cation solvating power (see below) cause salts of small cations not to be particularly soluble. The solubility products of potassium chloride and perchlorate,  $pK_s = 4.0$  and 7.2, respectively (ref. 19), are indicative of this trend. The solubility of hydrogen chloride, 0.06 moles per mole solvent (ref. 13), is also very low, and can be used for the estimation of the

hydrogen bond acceptance or electron pair donicity of trifluoroethanol (ref. 14), which is very low. Conductivity data for dilute electrolyte solutions in trifluoroethanol (ref. 15) show extensive ion pair formation to be the rule.

The standard Gibbs free energies of transfer of ions from water to trifluoroethanol (ref. 20) show fairly high positive values for cations and negative values for anions:  $\Delta \text{tr}G^\circ / \text{kJmol}^{-1}$  is 39 for  $\text{K}^+$ , 50 for  $\text{Ag}^+$ , -10 for  $\text{Cl}^-$  and  $\text{ClO}_4^-$  and -8 for  $\text{Br}^-$  and  $\text{I}^-$  (see also ref. 9 and 19). This behavior is ascribed to the low electron pair donicity of the solvent (expressible as a negligible value of the Kamlet-Taft  $\beta$  parameter) on the one hand, and the very high hydrogen bond donating ability (expressible as the Kamlet-Taft  $\alpha$  parameter) on the other.

The hydrogen bond donating ability of trifluoroethanol being intermediate between those of formic and acetic acids (ref. 21), it is also manifested in terms of the acidity of the solvent. The autoprotolysis constant is low,  $K_s / \text{dm}^6 \text{ mol}^{-2} = 10^{-15}$  (ref. 22), due to the reluctance of the solvent to accept a proton (from itself) to form  $\text{CF}_3\text{CH}_2\text{OH}_2^+$ . However, the acidity in water is high,  $K_a = 4.3 \cdot 10^{-13}$  at 25 °C (ref. 23, see also 24 and 25), much higher than the analogous alkanol, ethanol.

Trifluoroethanol being a relatively new solvent, its toxic effects have not yet been fully investigated (ref. 25). The threshold limit in air has been set at 2.5 ppm and the solvent is able to penetrate intact skin. Toxic effects were not seen in production workers possibly exposed to it, but were seen in animal experiments, where it caused intoxication, narcosis and death at increasing doses. An antidote is ethanol (ref. 26).

## PURIFICATION OF 2,2,2-TRIFLUOROETHANOL

The purification of reagent grade trifluoroethanol has been mentioned in the literature in connection with the accurate measurement of its physical properties. The main impurities are traces of stronger acids (perhaps trifluoroacetic acid that has escaped reduction) and water. Therefore the means of purification are mainly drying over a basic drying agent and fractional distillation.

### Procedure

Step 1. Dry the reagent grade solvent trifluoroethanol over anhydrous potassium carbonate overnight (ref. 5,9,15).

Step 2. Fractionally distil the solvent at a reflux ratio of 10:1 at atmospheric pressure. Collect the middle fraction.

Various variants of this procedure have been published: the drying agent contained a little magnesium sulfate (ref. 3,8) or a large amount of calcium sulfate in addition to the potassium carbonate (ref. 27) or in conjunction with sodium hydrogencarbonate (ref. 23). The drying lasted several days (ref. 8) or was effected by reflux for 2h (ref. 27). Other variants involved drying by molecular sieves (ref. 17,28) or by calcium hydride (ref. 24), the latter for removal of remaining trifluoroacetic acid in particular. The solubility of the molecular sieve in the solvent should be checked before its use.

Preparative gas chromatography was also proposed as a method for the purification of trifluoroethanol. Celite-supported 30% triglycerol was used in ref. 28 and PoropakQ at 150 °C in ref. 29. The latter procedure yielded a product suitable for spectral studies in the far ultraviolet region, the first band peaking at 166 nm with a molar absorptivity of only  $290 \text{ L mol}^{-1} \text{ cm}^{-1}$ .

## DETERMINATION OF THE IMPURITIES

Gas chromatography was the method of choice for the determination of impurities in trifluoroethanol, since the presence of metal ion impurities was of no consequence in the studies carried out so far with this solvent. Some of the examinations of the purified solvent with this method either showed no impurities at all (i.e., they were below the limits of detection, ref. 30) or showed contamination by water, ethanol, and an unknown component, to a total amount of 0.3% (ref. 3). In more recent studies the impurities detected (mainly remnant water) amounted to only 200 (ref. 9) or 300 (ref. 5) ppm.

Water was determined in purified trifluoroethanol also by the Karl-Fischer titration method (ref. 5).

TABLE 1. Selected properties of 2,2,2-trifluoroethanol

Property	Value	Ref.
Molar mass, $M/Kg\ mol^{-1}$	0.100004	
Freezing temperature, $t_m/^{\circ}C$	-43.5	2
Boiling temperature at 0.101325 MPa, $t_b/^{\circ}C$	73.8	3
Density at 25 $^{\circ}C$ , $\rho/kg\ dm^{-3}$	1.38335	4
Thermal expansivity, isobaric, at 25 $^{\circ}C$ , $\alpha_p/K^{-1}$	$1.25 \cdot 10^{-3}$	5
Compressibility, adiabatic, at 20 $^{\circ}C$ , $\kappa_s/Pa^{-1}$	$10.0 \cdot 10^{-10}$	6
Dynamic viscosity at 25 $^{\circ}C$ , $\eta/mPa \cdot s$	1.780	5
Vapor Pressure at 25 $^{\circ}C$ , $p/kPa$	10.09	7
Molar enthalpy of vaporization, $\Delta_v H/kJ\ mol^{-1}$		
at 25 $^{\circ}C$	43.97	7
at normal boiling temperature	36.3	7
Solubility parameter, $\delta/J^{1/2}\ cm^{3/2}$	23.9	***
Relative permittivity at 25 $^{\circ}C$ , $\epsilon_r$	26.67	5,8
Refractive index, D-line, at 25 $^{\circ}C$ , $n_D$	1.291	8
Electrolytic conductance at 25 $^{\circ}C$ , $\kappa/S\ cm^{-1}$	$3.9 \cdot 10^{-7}$	9
Dipole moment (in benzene), $\mu/D$	2.28*	10
Polarizability, $\alpha/m^3\ molecule^{-1}$	$\cdot 10^{-30}$	***
Polarity index, Reichardt, $E_T/kcal\ mol^{-1}$	59.5**	11
Polarity/polarizability index, Taft Kamlet, $\pi^*$	0.73	12
Hydrogen bond donor power, Taft Kamlet, $\alpha$	1.51	12
Hydrogen bond acceptor power, Taft Kamlet, $\beta$	0.00	13,14

\*  $D = 3.33564 \cdot 10^{-30}\ C\ m$ ; \*\*  $1\ cal = 4.184\ J$ ; \*\*\* derived from other entries in this table.

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