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**RECOMMENDED METHODS FOR
THE PURIFICATION OF SOLVENTS
AND TESTS FOR IMPURITIES
METHANOL and ETHANOL**

Prepared for publication by

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Methanol

Abstract - Specifications for the commercially available solvent, relevant physicochemical and key solvent properties are given. The procedures for purification include removal of water, production of conductivity-grade solvent, and removal of bases and heavy metals. Gas chromatography is best for detection of organic impurities and flameless atomic absorption for heavy metals. Methods for the determination of water depend on its concentration.

INTRODUCTION

The classical method for the production of methanol, the destructive distillation of wood, has long ago been replaced by synthetic methods. These methods yield a quite pure product, and the change has caused one of the more important impurities in the methanol employed in the older literature, namely acetone, to be no longer a pressing problem. The commercial grade A of methanol is nowadays sufficiently pure for practically all synthetic uses and for its use as a solvent, except for very specific requirements. The specifications of manufacturers for their guaranteed reagents generally conform to those in the American Chemical Society "Reagent Chemicals" (ref. 1), see Table 1.

TABLE 1. Examples of specifications for commercially available methanol

	ACS ^a	Merck ^b	Fluka ^c	Baker ^d	AnalaR ^e	
<i>Impurity</i>		<i>Maximal content in ppm</i>				
Free acid, as HCO ₂ H	20	20	25	20	9	
Free alkali, as NH ₃	3	3	1	2	2	
Chloride		0.5				
Heavy metals		0.1	0.5		1	
Magnesium		0.1				
Ethanol		1000				
Acetone	10	1001	10	} 10	50	
Formaldehyde		1	10			
Chloroform			50			
Water	2000	500	500	300	1000	
Nonvolatile substances	10	10	20	3	10	
Substances reducing KMnO ₄ ^f	5 min with 10 μmol/20mL	15 min with 5 μmol/12.6mL	pass test	pass test	20 min with 2.5 μmol/10mL	
<i>Other specifications</i>						
Boiling range ^g , °C	1.0		1.0	2.0(100%)	1.0(95%)	
% Transmittance ^h						
at 210 nm	16	20		16		
at 220 nm	40	50	25	40		
at 240 nm	79		80	79		
at ≥ 280 nm	98	98	99	98		

^aRef. 1; ^bMerck Standards for guaranteed purity reagent; ^cFluka specifications for puriss. p.a. absolute and acetone-free reagent; ^dJ.T. Baker specifications for "Baker Instra-Analyzed" reagent; ^eAnalaR Standards for Laboratory Chemicals, AnalaR Standards Ltd., London, 7th ed., 1977; ^fPink color persists for at least the specified time at 15°C when the specified amount of aqueous KMnO₄ is added to the specified volume of methanol; ^gBracketting the normal boiling point of 64.7°C; ^hMinimal light transmittance in 1 cm light-path cells.

The physical and thermodynamic properties of methanol have recently been critically reviewed (ref. 2). Selected other properties are given in a book dealing with organic solvents (ref. 3). Values for selected properties of methanol taken from these and other sources are listed in Table 2.

TABLE 2. Selected properties of methanol

Property	Value	Ref.
Molar mass, $M/\text{Kg mol}^{-1}$	0.032042	
Freezing temperature, $t_m/^\circ\text{C}$	-97.56	2
Boiling temperature at 0.101325 M Pa, $t_b/^\circ\text{C}$	64.70	2
Flash point, $t_{f1}/^\circ\text{C}$	12	3
Density at 25 $^\circ\text{C}$, $\rho/\text{kg dm}^{-3}$	0.78664	2
Thermal expansivity, isobaric, at 20 $^\circ\text{C}$, α_p/K^{-1}	1.182×10^{-3}	4
Compressibility, isothermal, at 25 $^\circ\text{C}$, κ_T/Pa^{-1}	1.195×10^{-9}	4
Surface tension at 25 $^\circ\text{C}$, $\gamma/\text{N m}^{-1}$	0.02212	5
Dynamic viscosity at 25 $^\circ\text{C}$, $\eta/\text{Pa}\cdot\text{s}$	0.5445×10^{-3}	3
Vapor pressure at 25 $^\circ\text{C}$, p/kPa	16.725	2
Enthalpy of vaporization $\Delta H^V/\text{kJ mol}^{-1}$ at 25 $^\circ\text{C}$.	37.40	2
at normal boiling temperature	34.48	2
Standard molar entropy at 25 $^\circ\text{C}$, $S^\circ/\text{JK}^{-1}\text{mol}^{-1}$	239.7	2
Molar heat capacity at 25 $^\circ\text{C}$, $c_p/\text{JK}^{-1}\text{mol}^{-1}$	81.17	2
Relative permittivity at 25 $^\circ\text{C}$, ϵ	32.70	3
Volume susceptibility at 25 $^\circ\text{C}$, $\chi_V/\text{cm}^3 \text{mol}^{-1}$	-21.42×10^{-6}	5
Refractive index, D-line, at 25 $^\circ\text{C}$, n_D	1.32652	2
Electrolytic conductivity at 25 $^\circ\text{C}$, $\kappa/\text{S cm}^{-1}$	1.5×10^{-9}	3
Dipole moment, μ/D	2.87*	3
Polarizability, $\alpha/\text{m}^3 \text{molecule}^{-1}$	3.26×10^{-30}	5
Intermolecular potential energy minimum (divided by Boltzmann's constant), $(u/k)/\text{K}$	255	5
Collision diameter, σ/nm	0.371	5
Polarity index, Reichardt, $E_T/\text{kcal mol}^{-1}$	55.5**	6
Polarity index, Kosower, $Z/\text{kcal mol}^{-1}$	83.6**	7
Acceptor number, Gutmann, AN	41.3	8
Donor number, Gutmann, $DN/\text{kcal mol}^{-1}$	33.8**	9
Polarity index, Taft Kamlet, π^*	0.586	10
Hydrogen bond donor power, Taft Kamlet, α	0.990	11

* $1\text{D} = 3.33564 \times 10^{-30} \text{C m}$.** $1 \text{ cal} = 4.184 \text{ J}$.

Methanol, being a protic solvent but having also electron-pair donation capabilities, is an amphoteric solvent, similar in many respects to water. It is capable of solvating both cations and anions, and although its dielectric constant (relative permittivity) is modest (32.7 at 25 $^\circ\text{C}$), in comparison with water (78.5 at 25 $^\circ\text{C}$), it supports the ionic dissociation of most electrolytes. On the other hand, it is well miscible with most organic solvents, except the higher alkanes and perfluoroalkanes, and is a good solvent for organic compounds in general. These properties have made methanol a very extensively utilized and studied solvent.

The low freezing point of methanol (-97.6 $^\circ\text{C}$) permits the study of electrolytes by, e.g., n.m.r. techniques, at low temperatures, where line widths are much reduced and solvent exchange is considerably slowed down compared with room temperature. The relatively low normal boiling point of methanol (64.7 $^\circ\text{C}$) can be turned into an advantage, when it permits the ready removal of the solvent from temperature-sensitive reaction products. The low viscosity of methanol is an advantage too.

Since methanol itself is a rather reactive solvent, in terms of reversible donor-acceptor interactions with solutes, it requires a relatively high concentration of even more reactive impurities (water, acids, bases) to falsify the results obtained with methanol of ordinary purity. For certain very demanding purposes, however, these impurities must be removed, and precautions must be taken against their re-introduction from the atmosphere.

These and other properties, such as ready availability, inexpensiveness, and low toxicity of moderate concentrations of the vapors ($< 260 \text{ mg m}^{-3}$, contrasted with high toxicity of the ingested substance) contribute to the general utility of methanol as a solvent.

STRUCTURE OF LIQUID METHANOL

The main feature of the structure of liquid methanol is its association by hydrogen bonding. Unlike water molecules, which can both donate and accept two hydrogen bonds and therefore produce an extensive three-dimensional associated network, methanol molecules can donate one and accept two hydrogen bonds. As a consequence, chain-like associates are formed in the liquid. It is remarkable, though, that the angular correlation factor g has the value 0.99, i.e., nearly unity, which is characteristic of non-associated liquids (compare with $g = 2.67$

in water and $g = 3.01$ in ethanol, all the values pertaining to 25 °C) (ref. 12). On the other hand, the entropy of vaporization at the normal boiling point, $\Delta S^V = 102.06 \text{ JK}^{-1}\text{mol}^{-1}$, is definitely higher than the expectation value from Trouton's rule, $\sim 86 \text{ JK}^{-1}\text{mol}^{-1}$, and this is in agreement with the associated nature of the liquid.

The infrared and n.m.r. spectra of methanol, too, indicate its associated nature, in that few "free" OH groups, but many hydrogen-bonded ones, are seen (ref. 13). The shifts produced by solutes, whether polar aprotic solvents or anions, in the relative populations of these two classes of OH groups are typical for the interactions.

KEY SOLVENT PROPERTIES OF METHANOL

Methanol is a good solvent for polar organic substances. Nonpolar substances, as far as the solubility can be judged from the solubility parameter $\sigma = [\rho(\Delta H^V - RT)/M]^{1/2} = 29.3 \text{ J}^2 \text{ cm}^{-3/2}$ (ref. 12), should be dissolved in methanol to at least 1 mole % for substances which have solubility parameters above 18.6. The practical limit seems to be a little lower, say 16.5. This limit excludes the alkanes and perfluoroalkanes, which indeed are not well soluble in methanol, but includes haloalkanes and aromatic hydrocarbons, which are generally well soluble in, or completely miscible with, methanol.

Methanol is a good solvent for electrolytes. Its dielectric constant and solvating power for ions are adequate for producing complete ionic dissociation of a dissolving electrolyte, although some ion pairing may occur. For 1:1 electrolytes ion pairing will occur (ref. 14) when the sum of the radii of the solvated ions of opposite charge is less than 0.857 nm. The radii of solvated ions in methanol are generally in the range 0.3 to 0.5 nm, so that ion pairing should not be a rare occurrence.

The solvation power of methanol towards ions is similar to that of water. The standard Gibbs free energy of transfer of monovalent ions from water to methanol is generally $<15 \text{ kJ mol}^{-1}$. (ref. 15). The solubility of sparingly soluble 1:1 electrolytes should therefore be at most 400 times smaller than in water, and, for example, in the case of silver chloride the factor is 53 (ref. 16). Electrolytes which are well soluble in water are generally also soluble in methanol, with some noteworthy exceptions, such as sodium fluoride, potassium chloride, and the sulfates. The solubilities of some salts of the alkali metals are shown in Table 3.

Methanol is less acidic than water. In aqueous solutions at 25 °C $pK_a = 15.553 \pm 0.016$ (one standard deviation) (ref. 19) (K_a in mol/dm^3). A more recent but less precise estimate is $pK_a = 15.2 \pm 0.3$ (ref. 20). The autoprotolysis constant has been reported as $pK_s = 16.70$ (ref. 21 and 22), and a more recent determination has given $pK_s = 16.91$ (ref. 23) (K_s in $\text{mol}^2 \text{ dm}^{-6}$). Since methanol is a typical ampholytic protic solvent it has a levelling effect on the reactivities of acids and bases.

TABLE 3. Molal solubilities of some salts of the alkali metals, (mol/kg solvent) at 25 °C (ref. 17)

	F	Cl	Br	I	NO ₃	CO ₃	SO ₄
Li ⁱ	0.0068	4.95	3.95	vs ^a	6.23	0.0075	0.0115
Na	0.0055	0.240	1.56	4.17	0.345	0.0293	0.0008
K	0.394	0.071	0.175	1.029	0.0376	0.447	3×10^{-5}
Rb		0.111 ^b					
Cs		0.215			0.0121		

^aVery soluble

^bFrom ref. 18.

PURIFICATION OF METHANOL

In view of the fact that commercial methanol is now sufficiently pure for most applications, the purification methods that have been utilized in the past for precise laboratory work are generally no longer required. These methods have been listed in ref. 3 and 24 and need to be applied only under exceptional circumstances.

Still, one of the more common impurities, water, is present in commercial pure methanol to an appreciable extent (ca. 500 ppm, see Table 1). This amount of water is not expected to have a profound effect on dilute solutions of solutes in methanol, in view of the hydroxylic nature of this solvent itself and its low molar volume, hence high concentration of hydroxyl groups. There are 24.55 mol/dm³ of OH groups in methanol, and only 0.022 mol/dm³ of water molecules (at the level of 500 ppm). For those applications where this impurity is still critical, following is a recommended method of purification.

Procedure I (removal of water) (ref. 25)

Step 1. Distill the methanol with a good fractionating column under the exclusion of moisture. The water content is reduced to ca. 100 ppm. From this step proceed to either step 2 or step 3, according to requirements.

Step 2. Pass the methanol slowly through a column of dry molecular sieves (Linde type 4A), store the methanol over a lump of calcium hydride. As long as the calcium hydride retains its lump form, the water content is <7 ppm.

Step 3. For a reduction of the water content to 0.5 ppm, the methanol is distilled twice in an all-glass still from metallic sodium. Freshly cut pieces, 1-2 g per L methanol are used, the first few tens of mL of distillate are discarded, and the rest, boiling within 0.01 °C of the boiling point, is used immediately (ref. 26).

Caution: Anhydrous magnesium perchlorate is not suitable for the drying of methanol: danger of EXPLOSION! Nor are drierite or calcium oxide effective drying agents for methanol. Calcium metal is apt to contaminate the methanol with ammonia from its calcium nitride impurity.

Procedure II (conductivity grade) (ref. 27)

Step 1. Reflux 4.5 L methanol for 24h over 50 g magnesium. Distill 4 L and reflux these over silver nitrate for 24h, under exclusion of atmospheric moisture and carbon dioxide.

Step 2. Distill the methanol and shake it with activated alumina for 24h. Filter through a sintered glass filter into a vessel which contains an atmosphere of pure nitrogen, from which the methanol is distilled again in an all-glass system.

Specific conductances of 5×10^{-9} S are readily obtained with this method. With a conductivity cell sealed between the condenser and receiver in the last distillation step, the minimal specific conductance observed was 1.5×10^{-9} S \cdot cm $^{-1}$.

Procedure III (removal of bases and heavy metals) (ref. 28 and 29)

Step 1. Condition a dry macroporous (e.g. Amberlyst 15) or macro-porous sulfonated-polystyrene-type cation exchange resin in the hydrogen-ion form for 24h with methanol to pre-swallow it and eliminate the removable water.

Step 2. Prepare a 1:2 mixture (by volume) of a strongly acidic cation exchange resin (e.g., Duolite C-20, pretreated successively with 2 NHCl, 1.5N NaOH, and 2N HCl) and a strongly basic anion exchange resin (e.g., Duolite A-162, pretreated successively with 1.5N NaOH, 2N HCl, and 1.5N NaOH), wash with water, dry and pre-swallow it in methanol for 24h.

Step 3. Pass the methanol to be purified successively through a 6 to 10 cm column of the mixed exchanger from Step 2, then through a 6 to 10 cm column of the conditioned resin from Step 1 at a rate of 3 mL/min.

This treatment reduces the concentration of amines, that produce an obnoxious odor in the methanol, to <0.1 ppm, and removes this odor (ref. 28). The concentration of ions, such as Na $^{+}$, K $^{+}$, Mg $^{2+}$, Ca $^{2+}$, Cl $^{-}$, NO $_{3}^{-}$, and SO $_{4}^{2-}$ is reduced from 2-10 ppm to <0.02 ppm each (ref. 29). Many heavy metal ions will also be retained on these columns. Specific removal of Fe $^{3+}$, Cu $^{2+}$, Co $^{2+}$, Pb $^{2+}$, etc., on polymers with anchored chelating agents, such as tiron, is described in ref. 30 and 31.

Other impurities are either not obnoxious and can be tolerated at the levels at which they are present in high grade commercial methanol, or, like carbon dioxide and other acidic impurities, are removed by procedures I or III. For the removal of other impurities, such as acetone or formaldehyde, from technical grade methanol, consult ref. 3, 24, or 26. Purified methanol should be prevented from being oxidized to formaldehyde by exclusion of air.

DETECTION OF IMPURITIES

Gas chromatography is the generally useful method for the determination of the residual impurities in methanol. High sensitivity detectors, such as flame ionization, are required for the determination of the impurities at the <10 ppm level. As a stationary phase, a mixture of 67% polyethylene glycol 4000 and 33% diethyl sebacate, applied as 5% on silanized kieselguhr, has been recommended; as the operating temperature 60 °C (ref. 32). See also ref. 33 for a study of several column packings for the gas chromatography of methanol, and ref. 34 for the analysis of methanol by high performance liquid chromatography.

Ethanol can be detected in methanol down to a level of 3 ppm by gas chromatography (ref. 35). Amines and other reactive impurities can be detected by means of a copper(II)-ion-selective electrode (ref. 37).

Water is generally determined by Karl-Fischer titration down to <500 ppm (ref. 32). For a determination at the 70 ppm level, by measurements in the UV of the displacement of the keto-ketal equilibrium after acidification with HBr, see ref. 36. For determinations by means of physico-chemical measurements at the <10 ppm level (ebullimetry and critical solution temperature of cyclohexane) see ref. 26.

Trace concentrations of heavy metals can be determined by flameless atomic absorption or by X-ray fluorescence, after concentration of these impurities on chelating ion exchangers based on cellulose (ref. 31).

Ethanol

Abstract - Specifications for the commercially available solvent, relevant physicochemical and key solvent properties are given. The procedures for purification include the removal of water and of organic impurities. The latter are best detected by gas chromatography and heavy metals by flameless atomic absorption. Water is determined by coulometric Karl Fischer titration at >5 ppm.

INTRODUCTION

Ethanol is produced either by fermentation or synthetically, and the impurities it is likely to contain depend somewhat on the source. Ethanol produced by fermentation may contain higher alcohols ("fusel oil", mainly pentanol isomers), whereas that produced synthetically may contain diethyl ether, in addition to aldehydes, ketones and esters that may be present in the products from both methods. A ubiquitous impurity, of course, is water, and since it is often removed by azeotropic distillation with benzene, this hydrocarbon may also be present as an impurity that is troublesome for spectroscopic studies in the ultraviolet region.

Ethanol is available commercially in quite pure form, either as the azeotrope with water (containing ca. 5% water) or as so-called "absolute" ethanol, containing only 0.2% water. The specifications of manufacturers for their purest grades generally conform to those in the American Chemical Society "Reagent Chemicals" (ref. 1), see Table 1.

The physical and thermodynamic properties of ethanol have recently been reviewed (ref. 2). Selected other properties are given in a book dealing with organic solvents (ref. 3) and in a few other sources. Values for selected properties of ethanol taken from these sources are listed in Table 2.

TABLE 1. Examples of specifications of commercially available ethanol

	ACS ^a	Merck ^b	Fluka ^c	AnalaR ^d
<i>Impurity</i>	<i>Maximal content in ppm</i>			
Free acid, as CH ₃ CO ₂ H	30	10	5	10
Free base, as NH ₃ Chloride	3	3		5
Heavy metals ^e		0.1	0.1	≤0.05
Iron		0.1	0.5	0.05
Light metals ^f				≤0.05
Methanol	1000	500	2000	500
Higher alcohols	30 ^j	500		100 ^j
Formaldehyde		10	10	
Aldehydes, as CH ₃ CHO		10	10	
Ketones, as CH ₃ COCH ₃	10	500	100	10
Water	2000	2000	2000	2000
Nonvolatile substances	10	5	10	5
Substances reducing KMnO ₄	k	3		4 ^k
<i>Other specifications</i>				
Boiling range ^g , °C			2	1
% Transmittance ^h				
at 210 nm		35		30
at 220 nm		55		52
at 230 nm		72		73
at 250 nm		90		90
at >270 nm		98		

^aRef. 1; ^bMerck Standards for guaranteed purity reagent; ^cFluka specifications for puriss. reagent; ^dAnalaR specifications for ARISTAR grade reagent (except for higher alcohols and substances reducing KMnO₄, not specified)

there but specified for AnalaR grade reagent which also has a boiling range of only 0.5°C); ⁶Mn, Co, Ni, Cu, Zn, Cd, Pb, Hg (most stringent specification for ARISTAR grade reagent: Hg 0.002 ppm, Pb 0.01 ppm, Cd 0.005 ppm); ⁷Mg, Al, K, Ca, but for Na the limit is 0.5 ppm; ⁸Bracketing the normal boiling temperature of 78.3°C; ⁹Minimal light transmittance in 1 cm light-path cells; ¹⁰The 30 ppm limit applies specifically to isopropyl alcohol; the test for fusel oil is the absence of odor, after 10 cm³ ethanol has been mixed with 5 cm³ water and 1 cm³ glycerol, the mixture placed on a filter paper and left to evaporate; ¹¹The pink color should persist for >5 min. when 20 cm³ are treated with 0.1 cm³ of 0.1 N KMnO₄ at 15°C.

Table 2. Selected properties of ethanol

Property	Value	Ref.
Molar mass, $M/\text{kg mol}^{-1}$	0.046068	
Freezing temperature, $t_m/^\circ\text{C}$	-114.1	2
Boiling temperature at 0.101325 MPa		
$t_b/^\circ\text{C}$	78.29	2
Flash point, $t_{fl}/^\circ\text{C}$	13	3
Density at 25°C, $\rho/\text{kg dm}^{-3}$	0.78509	2
Thermal expansivity, isobaric, at 25°C, α_p/K^{-1}	1.063×10^{-3}	5
Compressibility, isothermal, at 25°C, κ_T/Pa^{-1}	1.187×10^{-9}	
Surface tension at 25°C, $\gamma/\text{N m}^{-1}$	0.02189	5
Dynamic viscosity at 25°C, $\eta/\text{Pa}\cdot\text{s}$	1.078×10^{-3}	3
Vapor pressure at 25°C, p/kPa	7.969	2
Enthalpy of vaporization, $\Delta H^V/\text{kJ mol}^{-1}$, at 25°C	42.30	2
at normal boiling temperature	38.72	
Standard molar entropy at 25°C, $S^\circ/\text{JK}^{-1} \text{mol}^{-1}$	161.04	2
Molar heat capacity at 25°C, $c_p/\text{JK}^{-1} \text{mol}^{-1}$	111.96	2
Relative permittivity at 25°C, ϵ_r	24.55	3
Volume susceptibility at 25°C, $\chi_V/\text{cm}^3 \text{mol}^{-1}$	-33.61×10^{-6}	5
Refractive index, D-line, at 25°C, n_D	1.35941	2
Electrolytic conductivity at 25°C, $\kappa/\text{S cm}^{-1}$	1.35×10^{-9}	3
Dipole moment, μ/D	1.66*	3
Polarizability, $\alpha/\text{m}^3 \text{molecule}^{-1}$	5.12×10^{-30}	5
Intermolecular potential energy minimum (divided by Boltzmann's constant) (u/k)/K	324	5
Collision diameter, σ/nm	0.434	5
Polarity index, Reichardt, $E_T/\text{kcal mol}^{-1}$	51.9**	6
Polarity index, Kosower, $Z/\text{kcal mol}^{-1}$	76.6**	7
Acceptor number, Gutmann, AN	37.1	8
Donor number, Gutmann, $DN/\text{kcal mol}^{-1}$	30.4**	9
Polarity index, Taft Kamlet, π^*	0.54	10
Hydrogen bond donor power, Taft Kamlet, α	0.85	11

* $1 \text{ D} = 3.33564 \times 10^{-30} \text{ C m}$ ** $1 \text{ cal} = 4.184 \text{ J}$.

Ethanol, being a protic solvent but having also electron-pair donating capabilities, is an amphoteric solvent, and is capable of solvating both cations and anions. It has only a modest dielectric constant (relative permittivity), 24.55 at 25°C, hence most electrolytes, when not too dilute, will be extensively ion-paired in it. Ethanol is miscible with most organic solvents, including alkanes, and is a good solvent for organic compounds in general. Mixtures of ethanol with water are better solvents for electrolytes than neat ethanol, and have been used extensively for the investigation of many properties of electrolytes in mixed aqueous solvents.

Ethanol is fairly reactive regarding reversible donor-acceptor interactions with solutes, hence many impurities need be present at relatively high concentrations in order to affect appreciably measurements on solutions in ethanol. A notable exception is water, which may still have adverse effects on many properties even in so-called "absolute" ethanol, where it is present to the extent of 0.2 mass %, or 0.5 mole %.

The physical properties of ethanol, its properties as a solvent, and its ready availability in pure form contribute to its general utility as a solvent. The vapors are non-toxic even

at moderately high concentrations, at which they are readily detectable by their odor (ref. 3). The physiological effects of ingestion, of course, need not be described here, but they place some legal restrictions on the free use of ethanol.

STRUCTURE OF LIQUID ETHANOL

Ethanol is an associated liquid, and forms short chains by hydrogen bonding. Ethanol molecules can donate one but accept two hydrogen bonds, hence the aggregates formed are irregular. Evidence for the association arises from many properties of liquid ethanol. For example, the entropy of vaporization at the normal boiling temperature is $\Delta S^{\circ} = 110.18 \text{ JK}^{-1} \text{ mol}^{-1}$, much higher than the value given by Trouton's rule for nonassociated liquids, $\sim 86 \text{ JK}^{-1} \text{ mol}^{-1}$. The angular correlation factor g has the value of 3.01 at 25°C, compared with 2.67 for water (ref. 12), typical of highly associated liquids (nonassociated ones have $g = 1$).

The association of ethanol has also been studied spectroscopically, mainly by infrared (ref. 38) and n.m.r. (ref. 39) methods. The relaxation time of the ethyl group has been found to be shorter than that of the hydroxyl group, since the latter is hydrogen bonded to other similar groups.

KEY SOLVENT PROPERTIES OF ETHANOL

Many organic liquids are completely miscible with ethanol, including the alkanes on the one hand and highly polar liquids such as glycol on the other. The solubility parameter of ethanol, calculated as $\delta = [\rho(\Delta H^{\circ} - RT)/M]^{\frac{1}{2}} = 26.1 \text{ J}^{\frac{1}{2}} \text{ cm}^{-3/2}$, is sufficiently near those of nonpolar substances (e.g., tin tetrachloride, $\delta = 17.8 \text{ J}^{\frac{1}{2}} \text{ cm}^{-3/2}$ or iodine, $\delta = 28.8 \text{ J}^{\frac{1}{2}} \text{ cm}^{-3/2}$) to make it a good solvent for these.

The ability of ethanol to solvate both cations and anions is related to its polarity as measured by the donor number $DN = 30.4 \text{ kcal mol}^{-1}$ and the acceptor number $AN = 37.1$, (see Table 2) which makes it a fairly good solvent for electrolytes. The standard Gibbs free energy of the transfer of monovalent ions from water to ethanol is 5 to 20 kJ mol^{-1} (ref. 15), so that the solvation of the ions by ethanol is only to that extent worse than by water. However, the solvated ions are apt to associate in ethanol to solvent-shared and contact ion pairs, since the sum of the radii of the ions rarely exceeds the maximal distance of 1.14 nm for two oppositely single charged ions to be counted as an ion pair (ref. 14), in this solvent having $\epsilon = 24.55$ at 25°C.

These considerations are relevant to the solubility of electrolytes in ethanol. For electrolytes that have an appreciable solubility in water, the ionic interactions are too complicated for the present state of the theory to permit a prediction of what the solubility should be in ethanol. For electrolytes of low solubility such predictions are more nearly feasible. For example, silver chloride should be 139 times less soluble in ethanol than in water (ref. 16) whereas the actual ratio is 149 (ref. 40). The solubilities of some salts in ethanol are given in Table 3.

Table 3. Molal solubilities of some salts of the alkali metals, ammonium and tetraethylammonium (mol/kg solvent) at 25°C (ref. 41)

	OH	F	Cl	Br	I	ClO ₄	CO ₃	B(C ₆ H ₅) ₄
Li			5.83	8.35	18.74	14.26		
Na	4.31 ^a	0.024	0.031	0.225	2.84			
K	6.90 ^a	0.0174	0.0288	0.0405	0.1054 ^b	8.9x10 ⁻³		
Rb			0.0065			5.1x10 ⁻⁴		
Cs			0.0232 ^c			5.1x10 ⁻⁴	0.0318 ^b	0.0014 ^b
NH ₄				0.354		0.162	0.34 ^b	0.0010 ^b
(C ₂ H ₅) ₄ N			8.51	2.76	0.048		0.28	0.0124 ^b

^aAt 28°C; ^bAt 20°C; ^cRef. 17.

Ethanol is less acidic than water, the equilibrium constants for the reactions $\text{C}_2\text{H}_5\text{OH} + \text{H}_3\text{O}^+ = \text{C}_2\text{H}_5\text{OH}_2^+ + \text{H}_2\text{O}$ and $\text{C}_2\text{H}_5\text{OH} + \text{OH}^- = \text{C}_2\text{H}_5\text{O}^- + \text{H}_2\text{O}$ being 6×10^{-3} and 63, respectively (ref. 21). The acidity constant has been estimated as $\text{pK}_a = 16$ for ethanol in aqueous solutions (ref. 19). The autoprotolysis constant has been given as $\text{pK}_s = 19.1$ (ref. 21), 18.95 (ref. 22), 18.75 or 19.28 (ref. 23) and 18.67 (K in $\text{mol}^2 \text{ kg}^{-2}$) and 18.88 (K in $\text{mol}^2 \text{ dm}^{-6}$) at 25°C (ref. 42).

PURIFICATION OF ETHANOL

Ethanol is available nowadays in highly pure form, see Table 1, so that the methods that have been used in the past (ref. 3, 24) for the purification of this solvent for most laboratory work are generally no longer required.

Of the impurities remaining in the best reagent grade ethanol are the other alcohols (methanol, propanol), acetone, and water. The last mentioned is the most reactive and likely to interfere, and procedures for its removal have been recommended (see below). Benzene is an impurity not normally encountered, but it may be present in a sample dried by ternary azeotropic distillation. It can be removed from dry ethanol by careful fractional distillation, forming an azeotrope with a normal boiling temperature of 68.2°C (ref. 24). Aldehydes, if present, can be removed by the passage of the ethanol through a column of a strong base anion exchange resin in the HSO_3^- form (ref. 43).

Procedure I (removal of organic impurities) (ref. 44)

Step 1. Add carefully concentrated sulfuric acid to the ethanol, and distill the ethanol. The H_2SO_4 acts as an oxidizing agent for aldehydes, and this step also reduces the content of amines.

Step 2. Redistill the ethanol from solid sodium hydroxide, to remove entrained sulfuric acid and acidic impurities.

Step 3. Fractionally distill the ethanol with a good rectification column.

This combined treatment is said to reduce the content of aldehydes and ketones to <1 ppm, and make the ethanol a solvent suitable for spectroscopic studies of solutes in the ultraviolet region.

For the removal of water from so-called "absolute" ethanol, containing about 2000 ppm of water, the following procedures are recommended.

Procedure II (removal of water) (ref. 45)

Step 1. Dehydrate "absolute" ethanol down to <1000 ppm water by reflux over calcium oxide, and distill it, taking precautions to exclude water.

Step 2. Treat a portion of 200 cm^3 of the dehydrated ethanol with 3.5 g calcium hydride crushed to a powder until all of it dissolves by gentle boiling. This treatment produces calcium ethoxide. Distill two thirds of the alcohol off, to remove ammonia originating in calcium nitride possibly present in the hydride.

Step 3. Transfer the remaining solution of calcium ethoxide in ethanol into 2 dm^3 of dehydrated ethanol in a distilling apparatus provided with a double condenser. Boil the solution gently for 20 h, allowing 100 cm^3 to distill over in a slow current of dried pure hydrogen. Discard this distillate.

Step 4. Distill the bulk of the ethanol slowly in the current of hydrogen, discarding the last 100 cm^3 .

The purity of the ethanol so obtained is checked by its density, being 0.789334 + 0.000003 gm cm^{-3} at 20°C (ref. 45), compared with the accepted value of 0.78934 + 0.00007 gm cm^{-3} (ref. 2).

Procedure III (removal of water) (ref. 3)

Step 1. Add about 5% of hexane, cyclohexane, or 2,2,4-trimethyl-1-pentane to "absolute" ethanol, and fractionate to remove the aqueous azeotrope containing the water. This step reduces the water content to <500 ppm.

Step 2. Pass the dehydrated ethanol slowly through a column of dry molecular sieves (Linde type 4A). This step reduces the water content further (a similar treatment reduces the water content of methanol to 7 ppm).

DETECTION OF IMPURITIES

Trace concentrations of heavy metals can be determined by flameless atomic absorption, using a graphite furnace and a tantalum boat (ref. 46), or by anodic stripping voltammetry in the residue after evaporation (ref. 47).

Organic impurities are generally determined by gas chromatography, with a stationary phase made up of 2 portions of polyethyleneglycol 1000 to one portion of bis(2-ethylhexyl)sebacate, applied 15% on silanized kieselguhr (ref. 47), or of polyethyleneglycol 300, applied 25% on Chromosorb W (ref. 48). In the latter case the limit of determination is 5 ppm. Flame

ionization detection is used at these low levels.

Water can be qualitatively detected down to 500 ppm by the formation of a precipitate when aluminum ethoxide in benzene is added to a sample of the ethanol. Quantitative determination of water is carried out by Karl Fischer titration. An automated coulometric Karl Fischer titration has been described (ref. 49) that has a limit of determination of 5 ppm. Some commercial instruments have by now an even better performance.

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