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

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Recommended methods for the purification of solvents and tests for impurities: nitromethane

The most significant solvent properties of nitromethane are discussed. Values are tabulated for its most relevant physicochemical properties and of its solvation parameters. Examples are given of typical electrochemical studies carried out in this solvent. Impurities present in commercial nitromethane are listed, and a recommended purification procedure is described. Precautions dictated by the potential explosion hazard of nitromethane are discussed.

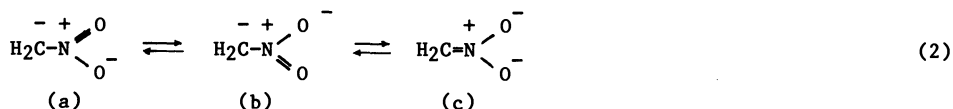
INTRODUCTION

Among those dipolar aprotic solvents having sufficiently high relative permittivities (dielectric constants) to allow straightforward electrochemical measurements, nitromethane occupies a unique position in that its electron donor ability is the weakest. Consequently, it is a particularly useful reference solvent for correlations of solvent effects on acidic properties of solutes, and also for differential titrations of bases. On the other hand, its electron acceptor properties are more strongly developed; furthermore, these properties are complicated by the existence of a nitronic acid (aci) tautomer in equilibrium with the nitro form. Nitromethane also suffers from other limitations. Its purification for critical applications involving acidic solutes and particularly such singly-charged d^{10} ions as copper(I) and silver(I) is difficult owing to the presence of a persistent basic impurity, propionitrile. A particularly significant problem is that under certain conditions nitromethane presents a serious explosion hazard.

Properties and solvation parameters of nitromethane are summarized in Table 1.

KEY SOLVENT PROPERTIES OF NITROMETHANE

1. Nitromethane differs from the majority of dipolar aprotic solvents having comparatively high relative permittivities in that it is incompletely miscible with water; data for various temperatures are in ref. 1.
2. Nitromethane is a very weak proton acceptor, as shown by a pK_a - value near -12 for its conjugate acid in aqueous sulfuric acid (ref. 4,5); cf. acetonitrile, $pK_a = -9.5$. It is also a very weak acceptor of other acids as shown, for example, by its exceptionally low donor number of 2.7 with respect to antimony pentachloride as reference acid (Table 1).
3. By comparison, nitromethane is by no means a very weak proton donor, as shown by its pK_a - value of 10.2 in aqueous solution (ref. 4,5). The cause of this considerable acidity is evident from a consideration of the resonance forms of nitromethane (1) and of its conjugate base (2):



All structures show the inductive effect of the formal positive charge on nitrogen. The major resonance stabilization of the anion derives from the tautomeric structure (c). It is also necessary to explicitly consider the effect of tautomerism in the determination of the pK_a - values of nitroalkanes.

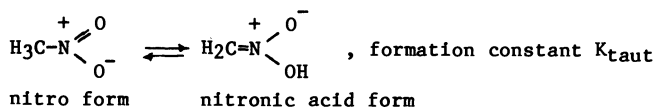


TABLE 1 Selected properties and parameters of nitromethane

Freezing temperature, T/K -273.15 ($t_m/^\circ\text{C}$)	- 28.55
Boiling temperature at 101.325 kPa (1 atm), T/K -273.15 ($t_b/^\circ\text{C}$)	101.20
Flash point, $t_{f1}/^\circ\text{C}$	44
Vapor pressure, p/kPa	4.888
Density, $\rho/\text{kg dm}^{-3}$	1.13124
Dynamic viscosity, $\eta/\text{mPa s}$	0.610
Surface tension, $\gamma/\text{mN m}^{-1}$, at 20°C	37.48
Enthalpy of vaporization, $\Delta H_v/\text{kJ mol}^{-1}$, at t_b	38.27
Molar heat capacity, $C_p/\text{J K}^{-1} \text{mol}^{-1}$, at 23.97 °C	105.8
Refractive index, n_D	1.37964
Dipole moment, μ/D , in hexane at 20°C	3.56
Relative permittivity (dielectric constant), $D = \epsilon/\epsilon_0$	35.94
Donor number (Gutmann), $DN/\text{kcal mol}^{-1}$ <u>a</u>	2.7
Acceptor number (Mayer-Gutmann), $AN/\text{dimensionless}$	20.5
Solvatochromic parameters (Kamlet-Taft) <u>b</u>	
-- polarity parameter, π^*	(0.85)
-- hydrogen bond acceptor parameter, β	-
-- hydrogen bond donor number, α	(0.23)

Values of properties are from Ref. 1 and are for 25 °C, except where otherwise noted. Donor and acceptor numbers are from Ref. 2 and solvatochromic parameters are from Ref. 3; values are for 25 °C.

a 1 cal = 4.184 J

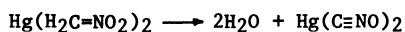
b Somewhat uncertain; see Ref. 3.

Representing the acid dissociation constant of the nitro form (C-acid) by K_C and that of the nitronic acid form (O-acid) by K_O , conventional (potentiometric, spectrophotometric) methods for the determination of the dissociation constant will give an apparent value, K' , which is related to K_C and K_O by

$$K' = K_C / (1 + K_{\text{taut}})$$

For nitromethane in aqueous solution, $\text{p}K_C = 10.2$, $\text{p}K_O = 3.3$, and $\text{p}K_{\text{taut}} = -6.9$ (ref. 5). In spite of the relatively low concentration of the nitronic acid form, not only K_C but also K_O could be determined by rapidly adding, for example, a half equivalent of strong acid to a solution of the nitronate ion, when $\text{pH} = \text{p}K_O$. After allowing equilibrium with the nitro form to be established, $\text{pH} = \text{p}K'$. It is to be noted that this procedure is viable because the nitronate ion is protonated rapidly at oxygen but very slowly at carbon. The rates of proton transfer reactions of nitroalkanes have been discussed (ref. 5).

4. Many nitronate salts are shock sensitive explosives. If they are allowed to form in nitromethane a serious explosion hazard will exist because they may detonate the nitromethane. The problem is aggravated by the presence of heavy metal ions. An example is the decomposition of the mercury(II) salt into the well-known detonator mercury fulminate:



TYPICAL ELECTROCHEMICAL STUDIES IN NITROMETHANE

Transport properties

Unni, Elias and Schiff (ref. 6) and Coetzee and Cunningham (ref. 7) carried out high-precision conductance measurements (on mainly quarternary ammonium salts). Coetzee and Cunningham synthesized the salt tetraisoamylammonium tetraisoamylborate and compared single-ion conductivities predicted by assuming that the cation and anion of this reference electrolyte have equal mobilities with conductivities derived from Blum and Schiff's transference numbers (ref. 8); agreement was virtually within experimental error.

Voltammetry and direct potentiometry

The cathodic limit of the voltammetric "window" of nitromethane occurs early owing to the ease of electrochemical reduction of this solvent. At the dropping mercury electrode the window is restricted to the range +0.55 to -0.8 V vs. SCE (aq.) (ref.9). Schmid and Gutmann (ref. 9) measured the half-wave potentials of a few metal ions which can be reduced in this solvent, and Gritzner (ref. 10) used these potentials (and similar data for a variety of other solvents) to predict free energies of transfer of single ions based on the bisbiphenylchromium(I/O) extrathermodynamic assumption. Badoz-Lambling and Bardin (ref. 11) measured (potentiometrically) the standard potentials of the $\text{Cu}^{2+}/\text{Cu}^+$, Cu^+/Cu , Ag^+/Ag and $\text{Hg}_2^{2+}/\text{Hg}$ couples and predicted free energies of transfer of single ions based on the ferrocene(I/O) assumption. The probable validity of these two (and other) sets of predictions has been discussed by Marcus (ref. 12). Recommended values of transfer energies indicate that, as compared to the virtually isodielectric solvent acetonitrile, nitromethane is a weaker solvator of the smaller alkali metal ions and a comparable solvator of the halide ions. Unfortunately, reliable estimates for hydrogen ion are not yet available owing to the exceptionally strong influence of residual water and other impurities on the activity of this ion in a very weakly basic solvent such as nitromethane.

Potentiometric titrations

Nitromethane is an exceptionally differentiating solvent for the titration of bases. A wide variety of bases have been titrated with perchloric acid (glass electrode) by Streuli (ref. 13). These and other results have been summarized by Charlot and Trémillon (ref. 14).

IMPURITIES IN COMMERCIAL NITROMETHANE

Nitromethane is manufactured by gas-phase nitration of methane, a process which evidently introduces several impurities.

The purification of commercial nitromethane has presented formidable problems in the past; these have been discussed by Cunningham (ref. 15). Apart from water, which is easily removed by distillation down to concentrations near 1×10^{-3} M owing to the formation of a water-nitromethane azeotrope ($t_b = 83^\circ\text{C}$ at 1 atm.), nitromethane contains relatively high concentrations of homologues (ref. 6, 7, 15, 16) which have little effect on the chemical properties of the solvent but which lower its density and raise its viscosity (important in transport property measurements). Different concentrations of the homologues undoubtedly caused the large variations in density ($1.1230 - 1.13124 \text{ kg dm}^{-3}$) and viscosity ($6.08 - 6.275 \text{ mPa s}$) reported by various authors (ref. 7). Furthermore, additional impurities were detected in several studies (ref. 7, 17, 18) but these could not be identified.

In a particularly effective gas chromatographic study of several commercial products, Bardin (ref. 16) identified not only nitroethane and 2-nitropropane at concentrations near 10^{-1} M, but also propionitrile at concentrations near 10^{-1} M. The presence of the nitrile would be objectionable in certain critical applications because it is generally a considerably stronger base than nitromethane and, furthermore, it undergoes specific interactions with such d^{10} ions as copper(I) and silver(I) ions. Bardin investigated the relative efficacies of fractional distillation through a spinning band column and crystallization (as well as other approaches) and recommended a combination of both methods, in agreement with previous conclusions (ref. 6, 7). In this manner, the homologues could be essentially removed and the nitrile content lowered to 5×10^{-3} M. Finally, Parrett and Sun (ref. 18) found that crystallization from ether was particularly effective.

PURIFICATION OF NITROMETHANE

The procedure recommended here is essentially that of Parrett and Sun (ref. 18) with slight modifications.

To a stirred 1:1 (v/v) mixture of commercial nitromethane and diethyl ether in a Dewar flask, add Dry Ice powder slowly until the temperature is well below -60°C . Stir for five more minutes and transfer the mixture to a deep Buchner-type funnel (with coarse fritted disc) jacketed with Dry Ice. Apply a water pump for several seconds to remove most of the ether. Stop pumping and pack the crystals tight in the funnel with a glass rod. Spread some Dry Ice powder over the surface and suck for 20 s. Wash twice with ether precooled at -78°C , each portion half the amount in the original mixture. Pack the crystals and add more Dry Ice as above during each washing. Remove the Dry Ice jacket and allow the solid in the funnel to melt and filter through into a distilling flask. Vacuum distill the liquid through an efficient packed column to the boiling point of nitromethane, discarding the distillate. Clean and dry the condenser thoroughly and continue distilling. Collect the middle 80% cut. Store the solvent in a dark container under dry nitrogen and dispense it through a delivery tube by nitrogen pressure.

DETERMINATION OF RESIDUAL IMPURITIES

The density of the solvent is a useful criterion for the presence of homologues (v.s.). Their presence, as well as that of propionitrile, can be confirmed by gas chromatography; details are given by Bardin (ref. 16). Water can be determined by gas chromatography or by Karl Fischer titration.

ULTRAVIOLET CUTOFF

For a typical commercial reagent grade of nitromethane (intended for spectrophotometry), maximum absorbances (in a 1-cm optical cell) are specified as 1.00 at 380 nm and 0.10 at 400 nm.

TOXICITY AND EXPLOSION HAZARD

Nitromethane acts as a moderate irritant when inhaled (threshold limit in air: 100 ppm). It forms explosive mixtures with air when its concentration exceeds 7.3% (v/v).

Liquid nitromethane is always a potential explosion hazard. Its distillation when even traces of bases are present (especially if heavy metal ions are also present) is especially hazardous owing to formation of nitronate salts (v.s.). Ignition of previously dried nitromethane on adding fresh molecular sieves has also been reported (ref. 19).

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