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DIMETHYLFORMAMIDE: PURIFICATION,
TESTS FOR PURITY AND PHYSICAL
PROPERTIES

Prepared for publication by
JEAN JUILLARD

Laboratoire d'Etude des Interactions Solutés-Solvants,
Université de Clermont—B.P. 45—63170 Aubière, France

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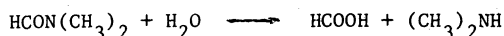
Commission on Electroanalytical Chemistry

DIMETHYLFORMAMIDE: PURIFICATION, TESTS FOR PURITY AND PHYSICAL PROPERTIES[†]

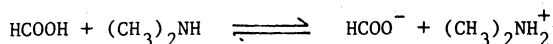
N,N'-Dimethylformamide (DMF) is a good solvent for organic and to a lesser extent inorganic compounds. It is, together with dimethylsulfoxide and acetonitrile, one of the most widely used of the so-called dipolar aprotic solvents. Owing to its fairly high dielectric constant, it is a moderately dissociating solvent for electrolytes. Acid-base reactions as well as thermodynamic properties of electrolyte solutions have been studied by many authors. Contrary to the N-methylamides it is a typically weakly associated solvent, as seen (Ref. 1) from dielectric studies (the Kirkwood g factor is about one at all temperatures).

Owing to its electron-donor character, DMF reacts with many acids. For example, Gutmann's donicity number (Ref. 2) is 27. Its polarographic range is quite large, e.g., 3.5 V at the dropping mercury electrode with 0.1 M Bu_4NClO_4 as supporting electrolyte (Ref. 3). It is therefore widely used as a solvent for electrochemical reactions, especially reductions.

Pure DMF is colorless and, at room temperature, odorless. It is subject to thermal as well as photochemical degradation. In presence of water, DMF is slowly hydrolyzed according to the equation:



Formic acid and dimethylamine are thus predominant impurities in DMF and determine the odor of the impure solvent. They are weakly acidic and weakly basic respectively; therefore, partial ionization does occur:



and results in a buffered solution (pH 11) with an increase in the conductivity of the solvent.

Thermal degradation produces dimethylamine and carbon monoxide. Hydrogen (Ref. 4) and hydrogen cyanide (Ref. 5) have been identified among the products of the photochemical degradation of the solvent.

Strongly basic media are difficult to obtain in DMF; there is, to our knowledge, no substance behaving as a strong base in DMF. If autoprotolysis of the medium actually occurs, the anion of the solvent must be very unstable (Ref. 6). It has been claimed (Ref. 7 and 8) that the autoprotolysis constant is smaller than 10^{-25} but no definite value has yet been proposed.

Attention must be paid to the fact that DMF has toxic effects, particularly on the liver and kidneys; the threshold value for air has been fixed (Ref. 9) at 30 mg/m³.

PURIFICATION OF DIMETHYLFORMAMIDE

Good quality DMF is commercially available. As noted by Vaughn (Ref. 10), spectrograde solvent is not always suitable for all purposes. As a consequence of hydrolysis, the residual water content of commercial DMF is frequently low (0.1%). Many procedures have been proposed and used for the purification of the solvent. Four types of successive operation can be distinguished: treatment with a drying agent, neutralization of basic or acidic impurities, careful distillation, and elimination of gaseous impurities.

[†] Titular Members: R. G. Bates, Chairman (USA); J. F. Coetzee, Secretary, (USA); Members: E. Bishop (UK), T. Fujinaga (Japan), Z. Galus (Poland), J. Jordan (USA), H. W. Nürnberg (FRG), P. Zuman (USA); Associate Members: M. Branica (Yugoslavia), A. K. Covington (UK), L. Gierst (Belgium), K. Izutsu (Japan), L. Meites (USA), E. Pungor (Hungary), O. A. Songina (USSR), B. Trémillon (France); National Representatives: D. D. Perrin (Australia), G. Kraft (FRG), R. C. Kapoor (India), N. Tanaka (Japan), W. Kemula (Poland), P. O. Kane (UK).

1. Preparing water-free solvent. Although the boiling point of water is far from that of DMF it is not possible to obtain a dry solvent by distillation only.

One of the first methods proposed for preliminary drying (Ref. 11) was azeotropic distillation with about 10% by volume of dry benzene; the benzene-water azeotrope is removed by distillation at atmospheric pressure. To prevent decomposition the temperature is maintained below 80°C. Alternatively, molecular sieves can be used. The solvent is kept in contact for periods ranging from 1 to 4 days with 4 Å (Ref. 12-15) or 5 Å (Ref. 16) sieves which are removed and replaced from time to time. Ritchie (Ref. 17) recommends the use of Linde AW-500 molecular sieves in 1/16-inch pellets. Studying drying efficiency, he finds that the water content is less than 18 ppm after 27 hours. Molecular sieves can be dried before use by heating in a quartz tube under a stream of argon at 375°C for 24 h (Ref. 18). Finally, a procedure which uses chromatographic purification through alumina has been described by Moe (Ref. 13) in some detail. "A column approximately 100 cm long and 5 cm wide will contain 1 kg of alumina, sufficient for the purification of about 10 l of DMF". After bubbling of pure nitrogen for several hours the DMF thus obtained is thought to be convenient for polarographic use.

In our opinion these three types of operation can be considered only as a first step in drying the solvent, and mild chemical drying agents must also be used. These range from anhydrous BaO (Ref. 11 and 19) to MgSO₄ (Ref. 20), Na₂CO₃ (Ref. 6 and 20), or CuSO₄ (Ref. 21). Surprisingly good samples of DMF can be obtained using storage of solvent over these chemicals for at least 24 h. It has been recommended that the drying agent be changed at least twice and the container shaken, if not continuously, at least from time to time. It also has been recommended that such an operation is performed in a cold, dark room. As far as Na₂SO₄ or Na₂CO₃ are concerned, the resulting solvents are of about the same quality (Ref. 20). Little or no degradation of the solvent (as estimated through the concentration of dimethylamine) results from such treatment (Ref. 11).

Some of the more common drying agents react with the solvent itself to produce significant amounts of acidic or basic impurities. BaO, cited previously, belongs to this category if it is used at temperatures above 30°C (Ref. 11). Other reagents are potassium hydroxide, calcium hydride (Ref. 5 and 22) and phosphorus pentoxide (Ref. 17, 23 and 24). P₂O₅ is the most frequently used, CaH₂ is probably the most efficient. Prue and Sherrington (Ref. 23) have shaken DMF for three days with P₂O₅, adding each morning about 10 g of fresh reagent. Recently, drying of amides using Vitrid, sodium bis(methoxy-2-ethoxy)aluminumhydride, has been recommended (Ref. 25). In DMF it allows attainment of very basic media (pH 30). However, distillation of the solvent from the mixture obtained has not been attempted and is probably very hazardous. Whatever the method used, it is important to proceed with these operations in a dark room or apparatus to prevent any photochemical degradation.

2. Neutralization. Depending on the drying agent used, it has been recommended that the basic or acidic impurities produced are neutralised, either by shaking with picric acid (Ref. 20) or KOH pellets (Ref. 24). This last treatment is particularly recommended after drying over P₂O₅ which generates formic acid. Such neutralization can be done either before or after a first distillation.

3. Distillation. The drying process can be further carried out during this operation. The DMF is refluxed and distilled from P₂O₅ or CaH₂. However, owing to a degradation process increased by heating, it is preferable first to decant the solvent and transfer it under dry nitrogen, and then to distil it at reduced pressure.

The quality of the final product is greatly affected by the care with which the distillation is carried out. It seems to be important to work under vacuum, with a darkened column, or in a pure nitrogen or argon atmosphere. As a rule, the temperature must be kept under 60°C; heating must be gentle and overheating avoided. Distillation in daylight results in the production of hydrogen cyanide (Ref. 5), particularly in the presence of CaH₂. No traces of HCN are detected if the operations are conducted in the dark.

Types of distillation apparatus currently described in the literature do not seem to be very efficient. It is not surprising to note that the best quality DMF, if conductivity is accepted as a test of purity, has been obtained by Brummer (Ref. 12), who used only molecular sieves as drying agents, but carried out the distillation in a slow current of dry nitrogen at low pressure (2 torr) and an efficient column (1 meter packed with Fenske helices). The use of a long column (60 cm at least) with good packing and reflux is recommended. For example, Tanaka (Ref. 21) distilled DMF which had been dried over anhydrous CuSO₄ at a pressure of 5 torr through an adiabatic fractional distillation column which was 1.3 cm in diameter, 120 cm in length and packed with helipack coils. Dry nitrogen was passed through the apparatus during the distillation; 60% of the distillate was collected. The conductivity was lower than $1 \times 10^{-7} \Omega^{-1} \text{ cm}^{-1}$ (25°C). Boiling temperatures at various pressures are given in Table 1.

TABLE 1. Recommended values for physical constants of DMF at 25°C and 1 atm (except where noted otherwise)

Boiling temperature	T_B	152.3°C (Ref. 47) 79°C at 61-62 torr (Ref. 37) 55-56°C at 25-26 torr (Ref. 40) 34°C at 2-3 torr (Ref. 15)
Melting temperature	T_M	-61°C
Refractive index (Ref. 44)	n_D^{25}	1.42689
Dielectric constant	D	37.0
Surface tension (Ref. 45)	σ	37.1 dyne/cm
Viscosity (Ref. 23)	η	0.00796 poise
Density	ρ	0.9440 g cm ⁻³
Molal volume	V	77.39 cm ³
Heat capacity at constant pressure (Ref. 44)	C_p	37.4 cal/mol
Cubic expansion coefficient	α_p	1.00 x 10 ⁻³ K ⁻¹ *
Adiabatic compressibility coefficient (Ref. 44)	β_s	6.1 x 10 ⁻⁵ atm ⁻¹
Isothermal compressibility coefficient	β_T	6.3 x 10 ⁻⁵ atm ⁻¹ *

* Calculated from data in Ref. (12)

4. Elimination of gaseous impurities. A flow of pure dry nitrogen or argon is passed through the solvent for several hours, in order to eliminate oxygen, carbon monoxide and carbon dioxide. Such a solvent can then be used for polarographic purposes. A more complete deaeration can be achieved using a vacuum line.

5. Conclusions and recommendations. As various authors used different starting materials, it is difficult to compare the efficiency of the various methods of purification. Comparison between different papers of treating the same batch of solvent can be found to our knowledge in only two papers (Ref. 11 and 20). Thomas and Rochow (Ref. 11) always used first azeotropic distillation with benzene and compared subsequent treatment with MgSO₄, BaO, alumina and triphenylchlorosilane, followed in each case by distillation. Comparisons were made in terms of specific conductance and water content. Barium oxide as well as alumina treatment meet rather well these two criteria and do not have any side effects, such as producing dimethylamine or HCN. Juillard (Ref. 20) compared drying with Na₂CO₃, Na₂SO₄ or molecular sieves with azeotropic distillation with benzene and distillation over P₂O₅. As far as conductivity and water content are concerned, the different batches of solvent thus obtained were of about the same quality, except that P₂O₅ has the disadvantage of promoting degradation of the solvent and thus of decreasing the efficiency of the distillation; therefore the use of P₂O₅ is not recommended. As a confirmation it can be noted that authors using P₂O₅ or CaH₂ as drying agents did not obtain purer solvents than those who employed BaO or Na₂CO₃ or even only molecular sieves.

It is therefore recommended that use is made first either of azeotropic distillation with benzene, as suggested by Thomas (Ref. 11), or of treatment with molecular sieves, as suggested by Ritchie (Ref. 17), and that the resulting DMF is then shaken with Na₂CO₃ or, better, with BaO for 1 or 2 days. After decantation the DMF is distilled twice under nitrogen (pressure <15 torr) using a 1-m column. All these operations must be carried out in the dark. After deaeration the solvent is stored under nitrogen and used as soon as possible.

TESTS FOR PURITY

Owing to its various modes of degradation (hydrolysis, thermal and photochemical decomposition) the principal impurities found in DMF are: dimethylamine, formic acid, hydrogen cyanide, carbon dioxide and carbon monoxide. To this list must be added: water, oxygen, which is quite soluble, and impurities resulting from the purification process.

Conductivity. As stressed earlier, hydrolysis as well as decomposition results in ionic impurities: dimethylammonium formate, carbonate or cyanide. Thus, the conductivity of the solvent is a very good test of its purity.

Experimental conductivities recorded in DMF are always higher than those reported for other aprotic solvents such as ketones or nitriles. According to a rough estimate, the theoretical conductivity of the solvent should be below $10^{-13} \Omega^{-1}\text{cm}^{-1}$. In fact, conductivities obtained by the most careful workers are scarcely ever less than 10^{-7} . The best values have been reported, to our knowledge, by Brummer (Ref. 12) who used for conductometric studies a solvent having conductivities varying from 2×10^{-8} to $5 \times 10^{-8} \Omega^{-1} \text{cm}^{-1}$. Values below 5×10^{-7} have been reported by numerous authors and any batch of DMF which is more conducting can be considered to be impure.

Water. Water can be titrated by the Karl Fischer (K-F) reagent. Kanatharan (Ref. 22) recommends that the titration is conducted slowly, since K-F reagent reacts only slowly with small amounts of water.

Usual procedures do not allow the determination of less than 10 ppm of water. According to Muroi (Ref. 26) it is possible to titrate as little as 0.2 ppm by increasing the sharpness of the end point, using the following procedure: "Add a 10-30 ml sample to 25 ml MeOH containing 8% of a pyridine-SO₂ solution (320 g SO₂/1 pyridine) and titrate potentiometrically with K-F reagent having a titre of 0.1-0.5 mg H₂O/ml". The use of DMF as a solvent for K-F reagent also has been advocated (Ref. 27).

Prue (Ref. 23) has titrated water in DMF using triphenylsilyl chloride, from which, according to Thomas (Ref. 11), hydrogen chloride is liberated quantitatively by water (amines or acids are thought to interfere); the HCl content is then estimated from the conductivity of the solution.

It is quite easy to prepare a solvent which contains less than 50 ppm of water. Very low concentrations (< 5ppm) are more difficult to attain. The best value, less than 3 ppm, has been reported by Libbey and Stock (Ref. 28).

Dimethylamine. Colorimetric methods have been used by some authors. In our opinion, as long as the autoprotolysis constant of the solvent is not known, it is not possible to say exactly what is basic and what is acidic in DMF. Kolthoff (Ref. 24) has used p-nitrophenol in the colorimetric determination of total basicity, but specific determinations would be preferable.

Thomas and Rochow (Ref. 11) have based the determination of the amine content on the fact that dimethylamine forms with 1-fluoro-2,4-dinitrobenzene a complex which absorbs in the visible spectrum at 3812 Å. Solvent prepared by Chang and Criss (Ref. 29) was found to contain less than 1 ppm of dimethylamine using this method.

Another spectrophotometric method which allows the determination of the dimethylamine content down to 2 ppm with an error of $\pm 10\%$ has been proposed by Pribyl (Ref. 30); dimethyldithiocarbamate, which absorbs at 445 nm, is formed by adding CS₂ and Cu(AcO)₂ to an EtOH-pyridine mixture.

Chromatography was thought by Butler (Ref. 18) not to be a reliable means of establishing the organic impurity content of the solvent since DMF can decompose or hydrolyze at high temperatures. Nevertheless, careful studies of the proper experimental conditions have been undertaken (Ref. 31 and 32). In the paper by Filippov (Ref. 32) it is shown that dimethylamine can be determined in DMF at levels as low as 1 ppm using tetrahydroxyethylenediamine as a stationary phase, polysorb-1 as a solid support and a column temperature of 75°C.

Dimethylamine is not electroactive with mercury but can give coordination compounds with cations which will affect the course of electrochemical reductions.

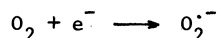
Formic Acid. In contrast to dimethylamine, formic acid is electroactive. Kanatharan and Spritzer (Ref. 22) have attributed to formic acid two peaks, one cathodic, the other anodic, which appear in cyclic voltammograms of aqueous dimethylformamide. Alternating current polarography (Ref. 33), and, better, pulse polarography, can be used to estimate the formic acid content.

Formic acid can also be determined by titration with a base. Potentiometric titration is preferred since it allows determination of the dimethylammonium formate content as well. Megliskii (Ref. 34) has titrated potentiometrically formic acid, dimethylamine and dimethylammonium formate in DMF using two solutions: 0.1 M HClO₄ and 0.1 M KOH, both in alcohol. Such a method is suitable only for concentrations of the order of at least 100 ppm.

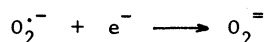
Hydrogen Cyanide. Trisler *et al.* (Ref. 5) reported the presence of HCN in DMF distilled over CaH₂ in natural light. Concentrations ranged from 10⁻⁵ to 10⁻³ M. Spectrophotometric titration can be carried out with 4-nitrobenzil, which reacts with cyanide ion to form a deep violet ion.

Oxygen. Oxygen is rather soluble in DMF. A study of oxygen solubility in relation to the oxygen content of the gas phase has been made by James (Ref. 35). When the gas phase was air and pure oxygen, the solubility was 2.2 x 10⁻³ and 3.1 x 10⁻³ M, respectively.

Oxygen is an electroactive impurity which interferes in polarography and other electrochemical processes. Two waves are observed (Ref. 36) with E_{1/2} = -0.8 and -2.8 V vs. SCE; the first corresponds to the reduction of oxygen to superoxide:



and the second one to the reduction of superoxide to peroxide ion:



James (Ref. 35) has proposed two methods for the determination of the oxygen concentration; polarography and the Winkler method. Polarographic measurements are made at -1.2 V vs. SCE, in order to ensure that the measured diffusion current is not influenced by a polarographic maximum. A modified Winkler method allows concentrations as low as 10 ppm to be determined. It depends upon quantitative oxidation of iodide ion to iodine. Such a process is described in some detail (Ref. 35).

PHYSICAL PROPERTIES OF DIMETHYLFORMAMIDE

Numerical values of physical constants are highly dependent on the purity of the solvent. Consequently, important discrepancies are found in the literature. The present recommended values result from a careful examination of three aspects: accuracy of the measurements, consistency of the data of various authors at different temperatures, and purification of the solvent. Such a choice is subject to personal evaluation and it seems prudent to give also the other references.

Density. The density is probably a good criterion of the purity of the solvent. Contamination with water increases the density (Ref. 23). The following values of the density at 25°C have been found (Ref. 23,8,37,12): 0.9439, 0.9440₂, 0.9441₅ and 0.9442 g cm⁻³, respectively. Old values greater than 0.9443 frequently found in tables are probably too high. New work by Kawaizumi and Zana (Ref. 38) seems to indicate that the density of the pure solvent is lower. These authors obtain values ranging from 0.94360 to 0.94368. It is our feeling that these data are more accurate than previous ones but such a low value (ρ = 0.94364 ± 0.00004) must be confirmed by others before being accepted.

Values at various temperatures other than those appearing in Table 2 have been given by Gopal and Rizvi (Ref. 39). At 20°C Saphon (Ref. 40) has obtained ρ = 0.94878 g cm⁻³, in good agreement with the value in Table 2.

TABLE 2. Recommended values for physical constants of DMF at various temperatures

		ρ g cm ⁻³	η poise	D
Temperature	20°C	0.9488	0.00845	38
	30°C	0.9394	0.00746	36.1
	40°C	0.9298	0.00664	34.4
	50°C	0.9202	0.00598	32.8
Reference		12	49	1

Viscosity. Other values can be found in References (29) and (41). Prue's data at 25°C are confirmed by measurements reported by Ames and Sears (Ref. 42).

Dielectric constant. Data given by Bass and Cole (Ref. 1) are preferred to previous results (Ref. 43) of Leader and Gormley (36.71 at 25°C). The value reported at 25°C is interpolated from measurements at various temperatures. Data of Saphon (Ref. 40) are in good agreement with the value reported in Table 2 at 20°C (D = 38.13).

Miscellaneous. Data at various temperatures concerning refractive index, surface tension and isothermal compressibility can be found in Refs. (44), (45) and (12), respectively. Other data concerning thermodynamic properties are reported in Refs. (39) and (44). Plots of vapor pressure, heat of vaporization, heat capacity, density, viscosity, surface tension and thermal conductivity for a large range of temperature have been drawn up by Gallant (Ref. 46). The solubilities of some sixty substances in DMF have been tabulated (Ref. 50). Organic reactions in or with DMF have been summarized (Ref. 51).

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