*Kirk-Othmer Encyclopedia of Chemical Technology.*

# DIMETHYLACETAMIDE

Dimethylacetamide [127-19-5], DMAC, mol wt 87.12, $CH_3CON(CH_3)_2$, is a colorless, high boiling polar solvent. DMAC is a good solvent for a wide range of organic and inorganic compounds and it is miscible with water, ethers, esters, ketones, and aromatic compounds. Unsaturated aliphatics are highly soluble, but saturated aliphatics have limited solubility in DMAC. The polar nature of DMAC enables it to act as a combined solvent and reaction catalyst, in many instances producing high yields and pure product in short time periods.

The rate of hydrolysis of DMAC is very low, but increases somewhat in the presence of acids or bases. DMAC is a stable compound, but is mildly hygroscopic and desiccation and/or dry nitrogen blanketing of storage vessels are sometimes used to reduce water pick-up. In the absence of water, acids, or bases, DMAC is stable at temperatures up to its boiling point at atmospheric pressure. Its greater stability enables more economical recovery by distillation relative to that of other similar solvents.

## 1. Physical Properties

Selected physical properties of DMAC are boiling point, 166.1°C; melting point, $-20^\circ C$; vapor pressure at 25°C, 0.27 kPa (2 mm Hg); density at 15.6°C, 0.945 g/mL; viscosity at 25°C, 0.92 mPa·s (=cP); surface tension at 30°C, 32.43 mN/m (=dyn/cm); refractive index $n_D^{25}$, 1.4356; heat of vaporization at 166°C, 43.1 kJ/mol (10.3 kcal/mol); heat of combustion, 2544 kJ/mol (608 kcal/mol); thermal conductivity at 22.2°C, 0.1835 W/(m·K) (0.1579 kcal/(m·h·°C)); a flash point (Tag closed cup), 63°C; ignition temperature, 490°C; flammability limits in air, 1.8 vol% LEL (lower explosive limit) (100°C), 8.6 wt% UL (upper limit) (120°C); critical temperature, 385°C; critical pressure, 4.02 MPa (39.7 atm); dielectric constant at 25°C, 10 kHz, 37.8; dipole moment at 20°C, $1.64 \times 10^{-29}$ C·m (4.6 Debye units); solubility parameter, 10.8; hydrogen- bonding index, 6.6; DMAC–acetic acid azeotrope at 170.8°C and 101.3 kPa (1 atm), 84.1 and 15.9 wt% (78.5 and 21.5 mol%), respectively (1).

## 2. Chemical Properties

The chemical reactions of DMAC are typical of those of disubstituted amides. Under suitable conditions, DMAC will react as follows:

*Hydrolysis in the Presence of Strong Acids*

$$CH_3CON(CH_3)_2 + H_2O + HCl \longrightarrow CH_3COOH + (CH_3)_2NH{\cdot}HCl$$

*Saponification in the Presence of Strong Bases*

$$CH_3CON(CH_3)_2 + NaOH \longrightarrow CH_3COONa + (CH_3)_2NH$$

*Alcoholysis in the Presence of Hydrogen Ions*

$$CH_3CON(CH_3)_2 + ROH \longrightarrow CH_3COOR + (CH_3)_2NH$$

## 3. Manufacture

Dimethylacetamide can be produced by the reaction of acetic acid [64-19-7] and dimethylamine [124-40-3]:

$$CH_3COOH + (CH_3)_2NH \longrightarrow CH_3CON(CH_3)_2 + H_2O$$

The product of this reaction can be removed as an azeotrope (84.1% amide, 15.9% acetic acid) that boils at 170.8–170.9°C. Acid present in the azeotrope can be removed by the addition of solid caustic soda [1310-73-2] followed by distillation (2). The reaction can also take place in a solution having a DMAC /acetic acid ratio higher than the azeotropic composition, so that an azeotrope does not form. For this purpose, dimethylamine is added in excess of the stoichiometric proportion (3). If a substantial excess of dimethylamine reacts with acetic acid under conditions of elevated temperature and pressure, a reduced amount of azeotrope is formed. Optimum temperatures are between 250 and 325°C, and pressures in excess of 6200 kPa (900 psi) are required (4).

DMAC can also be made by the reaction of acetic anhydride [108-24-7] and dimethylamine:

$$(CH_3CO)_2O + 2\ (CH_3)_2NH \longrightarrow 2\ CH_3CON(CH_3)_2 + H_2O$$

Dimethylamine is added somewhat in excess of the stoichiometric proportion in this synthesis. Another method employs the reaction of methyl acetate [79-20-9] and dimethylamine:

$$CH_3CO_2CH_3 + (CH_3)_2NH \xrightarrow{NaOCH_3} CH_3CON(CH_3)_2 + CH_3OH$$

Dimethylamine also reacts with the azeotrope of methyl acetate and methanol to give DMAC in 45% yield (5).

## 4. Shipping and Storage

Dimethylacetamide is available in drums with a capacity of 0.208 $m^3$ (55 gal), 186 kg net, and in tank cars or trucks. Although the DOT classifies DMAC as a combustible liquid, no DOT label is required.

Mild steel is a suitable material of construction for storage and handling of DMAC at ambient temperatures. Aluminum or stainless steel is recommended for cases involving very stringent color or iron contamination requirements. Mild steel is not recommended for high temperature service or handling aqueous solutions of $<50$ mol% (82.86 wt%) DMAC.

DMAC is a good solvent for many resins; therefore, flange gaskets and pump and valve packing should be limited to Teflon fluorocarbon resins.

## 5. Analytical Methods

### 5.1. Determination of Water in DMAC

DMAC is hygroscopic and precautions must be taken to minimize exposure to the atmosphere. Trace amounts of water can be determined by the Karl-Fischer method.

### 5.2. Determination of DMAC in Air

DMAC can be measured in air by passing a known amount of sample through water in a gas-scrubbing vessel and then analyzing the solution either chemically or by gas chromatography.

## 6. Health and Safety Factors

DMAC is capable of producing systemic injury when repeatedly inhaled or absorbed through the skin. Symptoms of overexposure are nausea, headache, and weakness. The principal effect is cumulative damage to the liver and kidney. DMAC has a low order of acute toxicity when swallowed or upon brief contact of the liquid vapor with the eyes or skin. Although DMAC is not a skin sensitizer, it is irritating to the skin and eyes. The $LD_{50}$ (oral, rats) for DMAC is $> 2250$ mg/kg (6).

In laboratory tests, application of DMAC to the skin of pregnant rats has caused fetal deaths when the dosages were close to the lethal dose level for the mother. Embryonal malformations have been observed at dose levels 20% of the lethal dose and higher. However, when male and female rats were exposed to mean DMAC concentrations of 31,101, and 291 ppm for 6 h/ day over several weeks, no reproductive effects were observed (6).

It is important to note that DMAC can rapidly penetrate the skin, leading to overexposure. Contact of DMAC liquid or mixtures containing DMAC with the eyes, skin, and clothing should be avoided. If contact is unavoidable, appropriate personal protective equipment, including chemical splash goggles, butyl rubber gloves, or an impervious butyl chemical suit having breathing air supply should be worn.

The U.S. Department of Labor (OSHA) has ruled that an employee's exposure to dimethylacetamide in any 8-h work shift of a 40-h work week shall not exceed a time-weighted average of 10 ppm DMAC vapor in air by volume or 35 $mg/m^3$ in air by weight (7) ACGIH TLV is also 10 ppm (8). If there is significant potential for skin contact with DMAC, biological monitoring should be carried out to measure the level of DMAC metabolites in urine specimens collected at the end of the shift. One industrial limit is 40 ppm DMAC metabolites, expressed as *N*-methylacetamide [79-16-3], for individuals, and 20 ppm metabolite average for workers on the job (9).

## 7. Environmental Considerations

DMAC may be released to the environment as a fugitive emission during production, formulation, and use. If released to soil, DMAC displays very high mobility. DMAC is stable to hydrolysis except under strongly acidic or basic conditions, and it is not expected to hydrolyze in soil. If released to water, it does not bioconcentrate in fish and aquatic organisms nor does it adsorb to sediment and suspended organic matter or volatilize from water. The estimated half-life for volatilization from a model river is 2800 days. DMAC will be partially dissociated in basic waters. If released to the atmosphere, the chemical may undergo a rapid gas-phase reaction with photochemically produced hydroxyl radicals. An estimated half-life for this process is 6.1 h. DMAC may undergo atmosphere removal by wet deposition processes (8).

## 8. Uses

The uses of dimethylacetamide are very similar to those for dimethylformamide [68-12-2] (see Formic acid). DMAC is employed most often where higher temperatures are needed for solution of resins or activation of chemical reactions.

### 8.1. Resin and Polymer Solvent

Dimethylacetamide is an excellent solvent for synthetic and natural resins. It readily dissolves vinyl polymers, acrylates, cellulose derivatives, styrene polymers, and linear polyesters. Because of its high polarity, DMAC has been found particularly useful as a solvent for polyacrylonitrile, its copolymers, and interpolymers. Copolymers containing at least 85% acrylonitrile dissolve in DMAC to form solutions suitable for the production of films and yarns (10). DMAC is reportedly an excellent solvent for the copolymers of acrylonitrile and vinyl formate (11), vinylpyridine (12), or allyl glycidyl ether (13).

Polyimides for use in molded products and high temperature films can be produced by the reaction of pyromellitic dianhydride [89-32-7] and 4,4′-diaminodiphenyl ether [101-80-4] in DMAC to form a polyamide that can be converted into a polyimide (14). DMAC can also be used as a spinning solvent for polyimides. Additionally, polymers containing $> 50\%$ vinylidene chloride are soluble up to 20% at elevated temperatures in DMAC. Such solutions are useful in preparing fibers (15).

DMAC and nonpolar solvents form synergistic mixtures that dissolve high molecular weight vinyl chloride homopolymers. For example, a mixture of DMAC with an equal volume of carbon disulfide [75-15-0], a nonsolvent, dissolves 14 wt% of Geon 101 vinyl chloride homopolymer at room temperature, whereas the solubility of Geon 101 in DMAC alone is $\sim 5$ wt% (16).

### 8.2. Crystallization and Purification Solvent

Dimethylacetamide is useful in the purification by crystallization of aromatic dicarboxylic acids such as terephthalic acid [100-21-0] and *p*-carboxyphenylacetic acid [501-89-3]. These acids are not soluble in the more common solvents. DMAC and dibasic acids form crystalline complexes containing 2 mol of the solvent for each mole of acid (17). Microcrystalline hydrocortisone acetate [50-03-3] having low settling rate is prepared by crystallization from an aqueous DMAC solution (18).

### 8.3. Electrolytic Solvent

The use of DMAC as a nonaqueous electrolytic solvent is promising because salts are modestly soluble in DMAC and appear to be completely dissociated in dilute solutions (19).

### 8.4. Complexes

In common with other dialkylamides, highly polar DMAC forms numerous crystalline solvates and complexes. The HCN–DMAC complex has been cited as an advantage in using DMAC as a reaction medium for hydrocyanations. The complexes have vapor pressures lower than predicted and permit lower reaction pressures (20).

Complexes of DMAC and many inorganic halides have been reported (21). These complexes are of interest because they catalyze a number of organic reactions. Complexes of DMAC and such heavy metal salts as $NiBr_2$ exert a greater catalytic activity than the simple salts (22). The crystalline complex of $SO_3$ and dimethylacetamide has been suggested for moderating the reaction conditions in sulfation of leuco vat dyestuffs (23).

### 8.5. Chemical Reaction Medium and Catalyst

DMAC, as well as other alkyl carboxylic amides, has the ability to serve as a reaction catalyst, often increasing yields, improving product quality and reducing reaction time. DMAC is a highly polar solvent of high dielectric properties and is capable of converting many organic and inorganic molecules into reactive forms by solvation. Types of reactions improved by the use of DMAC are elimination reactions (24), halogenation (25), cyclization (26), alkylations (27), nitrile formation (28), formation of organic isocyanates (29), interesterification (30), phthaloylation (31), and formation of sulfonyl chlorides (32). A method of stripping a photoresist from semiconductor substrate dimethylacetamide or a combination of monoethanalamine and dimethylsulfide has been patented (33,34).

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