INTERNATIONAL UNION OF
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# N-METHYLPROPIONAMIDE AS AN ELECTROLYTIC SOLVENT: PURIFICATION AND PROPERTIES

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N-Methylpropionamide (abbreviated NMP in this report) is a solvent remarkable chiefly for its high dielectric constant. At −40°C, the dielectric constant of the undercooled liquid is 341[1], one of the highest reported for a non-ionic liquid. This property, together with a wide liquid range (normal boiling point, 193°C[2]) and good chemical and thermal stability. make NMP an interesting and valuable solvent for electrochemical research. Its chemical properties resemble those of N-methylacetamide. the subject of an earlier report in this series[3].

## PHYSICAL PROPERTIES OF NMP

Pure NMP is a colorless. odorless liquid at room temperature. Apparently no toxic properties have been reported although. in common with several other N-alkyl aliphatic amides, NMP was teratogenic in rats[4]. In *Table 1* some physical properties are listed according to the source of the data. since there were evident differences in the purity of the NMP samples on which the properties were measured. Some reported values for the boiling point are 103°C/12–13 torr[5], 134°C/60 torr[6], and 146°C/90 torr[7]. (1 torr = 133·32 $N\,m^{-2}$). The vapor pressures measured by Gopal and Rizvi[2] lead to an extrapolated normal boiling point of 193°C. The vapor pressure data correspond to somewhat lower boiling temperatures at reduced pressures than those given by the preceding references.

Estimates of the high-frequency dielectric constant $\varepsilon_\infty$. derived according to Lindenberg's formula[8] from the gas-phase dipole moment of NMP and

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*Table 1.* Physical properties of N-methylpropionamide

| Property | Ref. 1 | Ref. 6 | Ref. 7 | Ref. 9 | Ref. 10 | Ref. 23 | Ref. 24 | Ref. 25 | Ref. 26 | Ref. 31 |
|---|---|---|---|---|---|---|---|---|---|---|
| Freezing point, °C | −39 | | −43 | −30.9 | | | −30.9 | | | |
| Specific conductance $10^6\,\Omega^{-1}\,\mathrm{cm}^{-1}$ | | 1 | | 0.12 | | | 0.22 | 0.1 | 0.6 | |
| Refractive index, $n_D^{25}$ | | 1.4350 | 1.4345 | 1.4350 | | | | | | |
| Density, g cm$^{-3}$ | | | | | | | | | | |
| 25°C | | 0.9306 | 0.9304 | | 0.93050 | | 0.9308 | | 0.9305 | |
| 30 | | | | 0.92647 | 0.92650 | 0.9269 | | | | |
| 40 | | | | 0.91847 | 0.91850 | 0.9188 | | | | |
| Viscosity, cP* | | | | | | | | | | |
| 25°C | | | | | | | 5.25 | 5.22 | 5.21 | 5.215 |
| 30 | | | | | | 4.568 | 4.58 | 4.56 | | 4.554 |
| 40 | | | | | | 3.541 | 3.56 | 3.52 | | 3.533 |
| Dielectric constant, ε | | | | | | | | | | |
| 20°C | 170 | 179.8 | | 185.3 | | | | | | |
| 25 | | 172.2 | | | 175.4 | | 176 | | 176 | |
| 30 | | 164.3 | | 166.7 | | 164.3 | | | | |
| 40 | 139 | | | 150.6 | 150.7 | 148.9 | | | | |
| 60 | 114 | | | | 124.2 | 117.9 | | | | |

* 1 cP = $1.0 \times 10^{-3}$ N s m$^{-2}$

its static dielectric constant, are appreciably higher than estimates derived from the refractive index[1]. Static dielectric constants were measured over the range −40°C to 120°C by Cole and co-workers[1] with a transformer bridge at 100 kHz. The sample they used appears to have been impure, however, on the basis of the low freezing point and reported corrosion of the nickel cell. Malmberg and Hoover[9, 10] also measured static dielectric constants from the freezing point (−30°C) to 150°C. These data were obtained at audio-frequencies both with a transformer bridge and with a Wheatstone conductivity bridge. Several preparations of NMP were measured in guarded and in two-terminal cells. The combined results of Malmberg and Hoover[10] are represented by either of the following equations with a standard deviation less than 0.5 unit in $\varepsilon$.

$$\varepsilon = 231.6 - 2.7207\,t + 0.02123\,t^2 - 1.098 \times 10^{-4}\,t^3 + 2.534 \times 10^{-7}\,t^4$$

$$\log \varepsilon = 2.3649 - 5.0427 \times 10^{-3}\,t + 9.8455 \times 10^{-6}\,t^2 - 1.915 \times 10^{-8}\,t^3$$

The estimated error of the measured values is within two per cent. Densities of the same specimens of NMP were measured over the range −25°C to 150°C in four pyknometers and quartz dilatometers[10]. With a standard deviation of $5 \times 10^{-5}$, the densities ($\mathrm{g\,cm^{-3}}$) were represented by the equation

$$\rho = 0.95069 - 8.136 \times 10^{-4}\,t + 2.921 \times 10^{-7}\,t^2 - 1.79 \times 10^{-9}\,t^3$$

The dipole moment has been reported[11] to be 3.59 Debyes.

From the vapor pressure measurements[2] the calculated heat of vaporization is 54.4 $\mathrm{kJ\,mol^{-1}}$. The cryoscopic constant is 4.7 $\mathrm{K\,kg\,mol^{-1}}$ on the basis of the writer's measurements with cyclohexane and N-methylacetamide as solutes[12]. The corresponding heat of fusion is 9.2 $\mathrm{kJ\,mol^{-1}}$.

## CHEMICAL PROPERTIES OF NMP

NMP is essentially neutral and inert as a solvent but there is almost no quantitative information on its acidity or basicity. Nuclear magnetic resonance studies[13] showed that NMP was 50 per cent protonated in an aqueous sulfuric acid solution having an acidity value $H_A = -0.95$. $H_A$ is a special acidity function of Yates *et al.*[14] that was shown to be applicable to amides. At the value in question it was substantially the same as the Hammett $H_0$. Thermochemical measurements[15] showed a greater exothermic heat of solution for hydrogen chloride in NMP than in water, partly as a result of the difference in dielectric constants. On the basis of precise conductance measurements[16], hydrogen chloride is a strong electrolyte in NMP, having a limiting molar conductance and ionization comparable to those of the alkali halides. The specific conductance of purified NMP suggests that the autoprotolysis constant probably is less than $5 \times 10^{-11}$, estimated as $10^6\,\kappa^2/\Lambda_0^2$. Rapid equilibration of NMP with $D_2O$ indicated that the amide H is labile[17], but not necessarily ionizable. Protolysis of NMP is catalysed by acid and base, and the kinetics have been measured at 34°C in water[18] and in 16 mol-per-cent *tert.*-butyl alcohol[19]. The respective values of the base-catalysed rate constant, $k_{\mathrm{OH}}$, are $3.8 \times 10^6$ and $2.8 \times 10^5\ \mathrm{mol^{-1}\,s^{-1}}$

and of the acid-catalysed constant, $k_H$, $1.1 \times 10^3$ and $6.3 \times 10^2$ mol$^{-1}$ s$^{-1}$. The activation energies for the protolysis in aqueous solution were 46.3 kJ mol$^{-1}$ for the base-catalysed reaction and 35.8 kJ mol$^{-1}$ for the acid-catalysed protolysis. Electrolysis of NMP containing 5–10 per cent sulfuric acid yielded the methane bis-amide (4,6-diaza-3,7-nonadione), among other products[20].

The kinetics of the formation and hydrolysis of NMP in dilute aqueous solution have been measured[21]. Although NMP is thermodynamically unstable with respect to its hydrolysis products, the rate of hydrolysis is slow. The second-order rate constant for the OH$^-$-catalysed hydrolysis in dilute solution, extrapolated to 25°C, is $3.13 \times 10^{-6}$ l mol$^{-1}$ s$^{-1}$[21]. Aqueous NMP has been used successfully as a high-dielectric constant solvent for studying the kinetics of hydrolytic reactions[22]. In a study of the hydrolysis of alkyl halides, Ross and Labes[5] could not determine whether NMP was electrophilic, nucleophilic, or both.

As is to be expected from its dielectric constant. NMP is a good electrolytic solvent. Conductivity measurements have shown that most electrolytes are highly ionized at much greater concentrations than in water[23–26]. Nevertheless. distinct evidence of ion-pair formation has been found[16, 24]. Apparently NMP has not been used as a polarographic solvent, but the double-layer capacity at the mercury drop was measured for 0.1 *M* $KPF_6$ in NMP[27]. The point of zero charge was −0.342 V versus the normal calomel electrode. Two capacity maxima[27], on either side of the zero charge potential, probably represent different orientations of the solvent dipoles in the double layer. The platinum–hydrogen electrode and the silver–silver chloride electrode behave reversibly in NMP[28, 29].

## PREPARATION AND PURIFICATION OF NMP

NMP is available commercially (e.g., in USA, from Eastman Organic Chemicals). One fractional vacuum distillation of Eastman NMP yielded a product of high quality. Synthesis from inexpensive starting materials is easy but purification of the product is quite laborious. NMP has been made by the reaction of methylamine with propionyl chloride[7, 26, 30] but, for kilogram quantities, it is probably preferable to start with propionic acid[1, 6, 23]. The following procedure is recommended.

Pass anhydrous methylamine rapidly into well-stirred, 50 per cent excess propionic acid (or add an aqueous solution of methylamine to the theoretical quantity of acid[1]). Heat the mixture rapidly to 120–140°C, taking off water through a simple distilling head. Since hydrolysis occurs during this operation the more rapidly the water can be removed the better the yield. Distillation of the xylene azeotrope has also been used to remove water[23]. Purify the crude NMP by fractional distillation at 5–15 torr. Although the expected impurities are more volatile than NMP, removal is difficult and the distillation often must be repeated several times in order to obtain a product of high quality[1, 2, 24, 27]. Although several workers have treated the crude NMP with calcium oxide before or during the distillation[1, 2, 5]. there appears to be little benefit from this procedure[27]. If there are no chemical additives in the pot. it appears that no volatile impurities are present or generated that have higher boiling points than NMP. Consequently, the quality of the distillate, as judged by its specific conductance[24], increases during the distillation. Several pot residues can be combined and re-distilled to yield good distillate NMP until the final residue becomes quite dark colored.

Although NMP does not seem to be subject to oxidation by the air, it can pick up appreciable moisture from the atmosphere and is best stored for extended periods over barium oxide or Molecular Sieves[15]. It is much easier to redistill solvent that has been used in conductivity measurements (and. presumably, other experiments) than to repeat the synthesis and purification.

## TESTS FOR PURITY

Few specific tests for impurities in NMP have been developed or evaluated. The Karl Fischer titration of water can be performed directly in NMP solvent without dilution and has been used to detect water concentrations at the parts per million level[5,9]. Gas chromatography has been used to characterize NMP[1,24,25] but only water and propionic acid have been reported as identified impurities.

The purity of NMP is usually judged by the values of its physical constants. specific conductance being one of the more sensitive tests. As *Table 1* shows, a specific conductance at 25°C less than $1 \times 10^{-6}\ \Omega^{-1}\ \mathrm{cm}^{-1}$ can be obtained routinely: the lowest value that has been reported[25] is $0.8 \times 10^{-7}\ \Omega^{-1}\ \mathrm{cm}^{-1}$. This property is indicative only of total ionic impurities. It should also be borne in mind that limiting molar conductivities in NMP are about one-fifth as great as in water because of the greater viscosity of NMP. Freezing point lowering is a more general measure of impurity but is inconvenient to determine because of the low temperature, high viscosity of the liquid, and the great tendency of NMP to undercool. The dielectric constant is quite sensitive to water[9], 0.1 per cent water reducing the dielectric constant of NMP about one per cent, but the effect of other likely impurities is not known. The viscosity of NMP is increased appreciably by the addition of small amounts of water[25] and most electrolytes[25,26,31,32], but is lowered by some organic solutes[31].

## STRUCTURAL INTERPRETATION OF THE PROPERTIES OF NMP AND ITS SOLUTIONS

Infra-red spectra[30,33] and proton magnetic resonance studies[34,35] of the structure of N-alkyl aliphatic amides show conclusively that the high dielectric constants result from chainwise hydrogen-bonded association of *trans* isomers that have parallel orientation of the individual dipole moments. Only the formamides contain a significant proportion of the *cis* form[34], which can associate in dimers with antiparallel moments. For substituents bulkier than methyl on both the carbonyl carbon and the nitrogen, steric requirements favor the *trans* form but reduce the extent of association. NMP, which exists almost exclusively in the *trans* form[30,33,34,35] has a lower dielectric constant at 30°C than N-methylacetamide[36] but a higher value of the Kirkwood correlation factor[1], $g$, which is a measure of the number of unit dipoles that act cooperatively. The effects of solutes upon this hydrogen-bonded structure are reflected in changes in the physical properties of the solutions.

At all concentrations water is a net structure-breaking agent in NMP, i.e. more NMP–NMP bonds are broken than NMP–$H_2O$ bonds formed. This conclusion was inferred from the effects of water on the density of the solutions[9, 37], and confirmed by nuclear magnetic resonance studies[35]. Nevertheless, the increased viscosity produced by traces of water in NMP suggests that there must be some crosslinking of the NMP chains by water although the mean chain length is shortened.

From the temperature coefficients of the Walden product[38–40] and of the viscosity *B* coefficient[32] Gopal has classified several ions as structure-reinforcing or structure-breaking. $Li^+$ and $K^+$ increased the structure of the solvent while $Cl^-$, $I^-$, and the tetraalkylammonium ions were structure breakers. The viscosity effects of a series of tetraalkylammonium ions agreed closely with the predictions of the Einstein equation, based on their crystallographic radii. This result indicates that these ions have a purely geometrical effect on NMP, in contrast to the situation in aqueous solutions. It is interesting that the limiting ionic mobility of $K^+$ in NMP is greater than that of $Na^+$ and the same as that of tetrapropylammonium[41] and that the limiting mobilities of $Cl^-$, $Br^-$ and $I^-$ increase in that order. Infra-red spectroscopy[42] has indicated that $Li^+$ is complexed to the carbonyl O of NMP but it is doubtful whether larger ions are specifically solvated. The structural effects of ions upon NMP seem to be mainly electrostatic in nature[43].

## REFERENCES

[1] S. J. Bass, W. I. Nathan, R. M. Meighan and R. H. Cole, *J. Phys. Chem.* **68**, 509 (1964).

[2] R. Gopal and S. A. Rizvi, *J. Indian Chem. Soc.* **45**, 13 (1968).

[3] L. A. Knecht, *Pure Appl. Chem.* **27**, 283 (1971).

[4] T. von Kreybig, R. Preussman and W. Schmidt, *Arzneim.-Forsch.* **18**, 645 (1968); *Chem. Abstr.* **69**, 42521a (1968).

[5] S. D. Ross and M. M. Labes, *J. Amer. Chem. Soc.* **79**, 4155 (1957).

[6] G. R. Leader and J. F. Gormley, *J. Amer. Chem. Soc.* **73**, 5731 (1951).

[7] G. F. D'Alelio and E. E. Reid, *J. Amer. Chem. Soc.* **59**, 109 (1937).

[8] A. B. Lindenberg, *C.R. Acad. Sci., Paris, Ser. C.* **262**, 1504 (1966).

[9] T. B. Hoover, *J. Phys. Chem.* **73**, 57 (1969).

[10] *Electrochemical Analysis Section: Summary of Activities, July 1966 to June 1967* (R. G. Bates, Ed.) *NBS Tech. Note No. 423* (October 1967).

[11] R. M. Meighan and R. H. Cole, *J. Phys. Chem.* **68**, 503 (1964).

[12] *Electrochemical Analysis Section: Summary of Activities, July 1967 to June 1968* (R. G. Bates, Ed.) *NBS Tech. Note No. 453* (July 1968).

[13] M. Liler, *J. Chem. Soc.* **1969B**, 385.

[14] K. Yates, J. B. Stevens and A. R. Katritsky, *Canad. J. Chem.* **42**, 1957 (1964).

[15] J. L. Curnutt, *Dissert. Abstr. (B)*, **29**, 4608 (1969).

[16] W. C. Duer, R. A. Robinson and R. G. Bates, Abstracts—163rd American Chemical Society National Meeting: Boston, Mass., 10–14 April 1972.

[17] K. V. Ramiah, V. V. Chalapathi and C. A. I. Chary, *Current Sci. (India)*, **35**, 350 (1966).

[18] L. C. Martinelli, C. D. Blanton and J. F. Whidby, *J. Phys. Chem.* **75**, 1895 (1971).

[19] L. C. Martinelli, C. D. Blanton and J. F. Whidby, *J. Amer. Chem. Soc.* **93**, 5111 (1971).

[20] D. E. Couch, *Electrochim. Acta*, **9**, 327 (1964).

[21] H. Morawetz and P. S. Otaki, *J. Amer. Chem. Soc.* **85**, 463 (1963).

[22] R. K. Wolford and R. G. Bates, *J. Phys. Chem.* **66**, 1496 (1962).

[23] L. R. Dawson, R. H. Graves and P. G. Sears, *J. Amer. Chem. Soc.* **79**, 298 (1957).
[24] T. B. Hoover, *J. Phys. Chem.* **68**, 876 (1964).
[25] T. B. Hoover, *J. Phys. Chem.* **68**, 3003 (1964).
[26] J. Sandeaux, B. Brun and J. Molenat, *J. Chim. Phys.* **68**, 480 (1971).
[27] R. Payne, *J. Phys. Chem.* **73**, 3598 (1969).
[28] E. S. Etz, R. A. Robinson and R. G. Bates, *J. Solution Chem.* **1**, 507 (1972).
[29] E. S. Etz, R. A. Robinson and R. G. Bates, *J. Solution Chem.* **2**, 405 (1973).
[30] R. L. Jones, *Spectrochim. Acta*, **22**, 1555 (1966).
[31] F. J. Millero, *J. Phys. Chem.* **72**, 3209 (1968).
[32] R. Gopal and P. P. Rastogi, *Z. Phys. Chem. (Frankfurt am Main)*, **69**, 1 (1970).
[33] R. L. Jones, *Spectrochim. Acta*, **23A**, 1745 (1967).
[34] L. A. LaPlanche and M. T. Rogers, *J. Amer. Chem. Soc.* **86**, 337 (1964).
[35] J. F. Hinton and C. E. Westerman, *Spectrochim. Acta*, **26A**, 1387 (1970).
[36] J. W. Vaughn and P. G. Sears, *J. Phys. Chem.* **62**, 183 (1958).
[37] P. Rohdewald and M. Moeldner, *J. Phys. Chem.* **77**, 373 (1973).
[38] R. D. Singh, P. P. Rastogi and R. Gopal, *Canad. J. Chem.* **46**, 3525 (1968).
[39] R. D. Singh and R. Gopal, *Bull. Chem. Soc. Japan*, **45**, 2088 (1972).
[40] R. D. Singh, *Bull. Chem. Soc. Japan*, **46**, 14 (1973).
[41] R. Gopal and O. N. Bhatnagar, *Proc. Symp. Electrode Processes* **1966**, 120: *Chem. Abstr.* **70**, 50525r (1969).
[42] A. F. Diorio, E. Lippincott and L. Mandelkern, *Nature, London*, **195**, 1296 (1962).
[43] P. P. Rastogi, *Z. Phys. Chem. (Frankfurt am Main)*, **75**, 202 (1971).