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Electronic Supplementary Information

Is Formamide a Geochemically Plausible Prebiotic Solvent?

Electronic Supplementary Information (ESI)

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Materials and Methods

All glassware was washed with Sparkleen detergent (Fisher), then rinsed with water (Fisher W5-4 HPLC grade) and then baked at 500°C under air overnight. All conductivity measurements were made with a NISTapproved Fisher digital conductivity meter. Density measurements were conducted using Chase USA #370526 ASTM 127H а hydrometer for heavy liquids. The hydrometer has a range of 1.100 to 1.150 g/ml (calibrated at 15.6°C).

The possible presence of purines and pyrimidines in samples was determined by HPLC using a 4.6 x 150 mm YMC ODS-AQ S5 120 A column eluted isocratically with 0.1 M pH 4.8 sodium phosphate. Products were identified by comparison with the retention time of known standards and by co-injection. Detection was with a Kratos 757UV/Visible absorbance detector at 260 nm.

Commercially available formamide is generally stated to be >99.5 % pure. Formamide (BP227-500, molecular biology

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grade) was purchased from Fisher. We have found that formamide available from various vendors has a measurable electrical of conductivity (a measure dissolved electrolytes, in this case formate and ammonium). The conductivities we measured in our commercial formamide were usually around ~1-10 µmho whereas rigorously purified formamide^{SM1} has a specific conductivity of 0.1 to 0.5 µmho. The 0.5 % impurities in commercial formamide consist mainly of water and the electrolytes formate and ammonium. The water concentration of commercial formamide is estimated to be 0.04 M and the ammonium formate concentration ~0.03 M^{S1}. Using 3 Å molecular sieves followed by a mixed bed of ion-exchange resins^{S1} very high purity formamide can be made that has a water content of <0.01 M and a specific conductivity of 0.2 µmho, corresponding to an electrolyte concentration of $\sim 10^{-5}$ M.

With resin-based purification it has been emphasized that only dry resin with no bound water should be utilized because the release of bound water decreases the final formamide purity^{S2}. We found that treatment of our >99.5 % commercial formamide with Amberlite IRN 150 resin of unknown water content from FLUKA lowered the conductivity of our commercial formamide by over a factor of 10.

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As far as we could ascertain, all prebiotic chemistry studies in which formamide was the solvent used what was obtained from the supplier without further purification. Thus we decided not to attempt any purification of the commercial formamide we used in our experiments.

Table S1 shows various properties of formamide in comparison to water.

Table S1: Properties of formamide: taken from (except where indicated) Höhn, A. p. 678 in: Glenn D. Considine. *Van Nostrand Reinhold Encyclopaedia of Chemistry*. Van Nostrand Reinhold, Fifth edition, 2005: Höhn, A. updated by Staff. 2014. Formamide. *Kirk-Othmer Encyclopedia of Chemical Technology*. 1–10.

Property	Formamide	Water
Molecular weight	45.04	18.01
Melting point (°C)	2.55	0
Boiling point (°C)	210.5	100
Density of liquid (g/cm ³) at 10°C	1.141	0.9997
Density of liquid (g/cm³) at 20°C	1.133	0.9982
Density of liquid (g/cm ³) at 50°C	1.108	0.9880
^{S3} Autoprotolysis constant (pK _a) at 25°C	16.8	14
Vapor Pressure (mm Hg) at 20°C	0.06	17.5
^{S4} Density of solid (g/cm ³)	>1.147	0.9162
Dielectric constant at 20°C	109±1.5	80.1
Electrical conductivity (µmho)	0.1-0.5	0
^{S5}Viscosity (η, mPa·s) at 25°C	3.23	1.002
^{S5} Viscosity (η, mPa·s) at 50°C	1.49	0.547
Heat of vaporization (kJ/mol)	64.98	40.68
Heat of fusion (kj/mol)	6.694	6.02
Specific heat (kJ/kg K)	2.30	4.18
^{S6} Solubility NaCl (g/100g) at 25°C	9.9	38
Solubility KCl (g/100g)	8.1 (at 25°C)	34.2 (at 20°C)
Solubility CaCO ₃ (g/100g) at 25°C	0.07	6.2×10 ⁻⁴ (calcite)
^{s7} Solubility ZnCl₂ (g/100g) at 25°C	43.1	432
^{\$8} Solubility glycine (g/100g) at 25°C	6.29	21.6
^{S8} Solubility DL-Norleucine (g/100g) at	0.23	9.0
25°C		
^{S9} Propionic acid pK _a at 25°C	7.06	4.87
^{\$9} Succinic acid pK _a at25°C	5.90	4.20

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Figure S1: The density of formamide-water mixtures at various temperatures (taken from refs. 6-9 in main text). **Top**: Density at 25°C from 0 to 100 % (w/w) formamide; **Bottom**: In order to show the density differences at high formamide concentrations, the densities of 60 to 100 % formamide are emphasized: Red line, 15°C; Red dotted line, 20°C; Black dotted line, 25°C; and Black line, 30°C.



Figure S2: Formamide ice forming at the bottom of a beaker of formamide.



Figure S3: The formamide-water phase diagram showing the eutectic at ~46 wt. % formamide and ~54 wt. % water^{S10, S11}.

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