

**Parker A J.** The effects of solvation on the properties of anions in dipolar aprotic solvents. *Quart. Rev. Chem. Soc.* **16**:163-87, 1962.  
[Chemical Inst., Univ. Bergen, Norway and  
William Ramsay and Ralph Forster Labs., University College, London, England]

Small, but not large, anions are less solvated in dipolar aprotic solvents like dimethylsulfoxide than in water or methanol, which donate hydrogen bonds to anions. The review showed the relevance to solubilities, electrochemistry, conductance, stability constants, spectroscopic shifts, acidities, reaction rates, mechanisms, and organic synthesis in such solvents. [The SCI® indicates that this paper has been cited over 780 times since 1962.]

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"In 1956, I was studying the rates and mechanism of the substitution reactions of azide ion with the four p-nitrohalobenzenes in methanol as solvent. The reactions were slow at 100°C. The Stauffer Chemical Company, in a move which still may be unique, sent to the world's universities 500 ml samples of dimethylsulfoxide. Very little was known about this solvent and they were looking for some way of using it. Expecting nothing significant, I ran one of my reactions in DMSO and to my astonishment, found that substitution by azide ion was complete in a few minutes at room temperature.

"By 1961, I had noted several isolated reports from the synthetic organic chemists, always without explanation, of the 'catalytic' effects of DMF and DMSO, and the vastly improved yields when certain substitutions, eliminations, additions, and rearrangements were carried out in these solvents. The physical chemists were also beginning to look at electrolyte solutions in such solvents and notice that solubilities, redox potentials, conductance, acidities, basicities, spectroscopic shifts, and stability constants involving anions were vastly different in dipolar aprotic solvents than they were in water. No explanations were given.

"I was spending the winter as a postdoctoral fellow in Bergen, Norway. The

nights were very long and cold, especially for an Australian, although just married. Thus I undertook to write a review for *Chemical Society*, explaining how all these phenomena were the result of the very different anion solvating properties of dipolar aprotic solvents. Like so many young Englishspeaking chemists of the period, I received tremendous support and advice from R.S. Cahn, the *Chemical Society* editor. The manuscript was completed at University College, London, with help from those great chemists, C.K. Ingold and E.D. Hughes.

"The review was built around the idea that small anions are much better solvated by hydroxylic solvents than by dipolar aprotic solvents, because hydrogen-bonding interactions with anions do not take place in dipolar aprotic solvents. Large anions are often better solvated by dipolar aprotic solvents than by water because of structural and polarizability effects.

"This simple concept was presented for the first time in 1961-1962<sup>1</sup> and explained observations from many fields of chemistry, but especially from organic synthesis. All chemists could understand such a simple idea. The solvents were proving of great value in laboratories all over the world and subsequent reviews<sup>23</sup> kept alive the subject of anion solvation in dipolar aprotic solvents. It is no surprise that the review tended to be widely referenced, despite the naive approach to several of the topics.

"I have continued to grind away at the same principles discovered in 1956. The principles now find application in my patented ideas using DMSO and other solvents for zinc-bromine batteries, copper and silver refining and extraction, lithium batteries, CdS/Cu<sub>2</sub>S solar cells, stripping gold from carbon, and extracting and refining precious metals.<sup>4</sup> I feel that this story has a message for the politicians who are advocating mission oriented research with short-term objectives. My 1956 work was as pure and without objectives as chemical research can be; my 1981 work is totally applied and hopefully of value in solving national energy problems. Both are essential."

1. **Miller J & Parker A J.** Dipolar aprotic solvents in bimolecular aromatic nucleophilic substitution reactions. *J. Amer. Chem. Soc.* **83**:117-23, 1961.
2. **Parker A J.** Dipolar aprotic solvents in organic chemistry. (Raphael R A, Taylor E C & Wynberg H, eds.) *Advances in organic chemistry*. New York: Wiley, 1965. Vol. 5, p. 1-46.
3. ...., Rates of reaction in protic and dipolar aprotic solvents. *Chem. Rev.* **69**:1-32, 1969.
4. ...., Solvation of ions. Applications to minerals and energy. *Rev. Pure Appl. Chem.* In press, 1981.