August, 1986] © *1986 The Chemical Society of Japan* **NOTES** *Bull. Chem. Soc. Jpn., 59, 2623—2624 (1986)* 2623

Determination of the Solvation Number of Sodium Anion in Hexamethylphosphoric Triamide

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(Received October 25, 1985)

Synopsis. Electronic absorption spectra for saturated solutions of Na in HMPA-THF mixtures with HMPA mole fractions 0.39—0.061 exhibit only a band for Na^-. A log-log plot of maximum absorbance vs. HMPA concentration has led to a numerical value 3 for the number of HMPA molecules solvating a Na^- ion.

Of stable solvated-electron species existing in solutions of alkali metals in certain amines, amides, or ethers, (free) solvated electron (e_s^-) and metal anion (M^-) have been identified by electronic spectroscopy[1] and investigated on their physicochemical properties. The solvation number of e_s^- has been determined with an interest in the nature of this specific chemical species.[2] No paper has, however, dealt with the solvation number of electron-excess species, M^-. This paper presents an indirect determination of the solvation number of Na^- in hexamethylphosphoric triamide (HMPA) from the known solvation number of Na^+ with the aid of electronic and NMR spectroscopies.

Experimental

HMPA and tetrahydrofuran (THF) were purified by the usual method in which sodium anthracenide was used to remove trace impurities.[3] Commercial sodium tetraphenylborate (NaTPB) was dried in vacuo at 60 °C for 24 h and used as a ^{23}Na source in NMR measurements. The other chemicals were commercially obtained and used without further purification. Mixing HMPA with THF at various HMPA mole fractions (x) and addition of sodium metal to pure HMPA or mixed solvents were carried out under nitrogen atmosphere. The electronic absorption spectrum of a supernatant solution was recorded after stirring the solution with excess sodium metal overnight. After additional one hour stirring of this solution, the absorbance at λ_{max} decreased slowly after stirring was stopped. However, when this absorbance for the solution was reproduced after the additional stirring of the solution, this solution was considered as a saturated solution of sodium. Mixed solvents are denoted by HMPA(x)-THF.

Electronic absorption spectra in the visible and near-IR regions were recorded at 25 °C on a Hitachi 220 and a Shimadzu MPS-50L double-beam spectrophotometers, respectively, by using a cell of 1 *mm* path length and a reference solution of THF. ^{23}Na NMR spectra were recorded at 23 °C on a Bruker CXP-300 spectrometer operating at 83.08 MHz. The chemical shifts reported are relative to external 0.1 M (1M=1 mol dm^{-3}) NaCl in D_2O, with positive sign representing a downfield shift. No signal locks were used because of broad line width.

Results and Discussion

Solvation of Na^- in HMPA-THF. The two bands at 750 and 2250 nm in the absorption spectrum of a solution of Na in HMPA have been assigned to Na^- and e_s^-, respectively.[4] Each of the spectra for the saturated solutions of Na in HMPA(0.039)-THF and HMPA(0.061)-THF exhibits only a band at 750 nm, which indicates that of the two electron-excess species only Na^- should be considered in saturated solutions of Na in HMPA(x)-THF with $0.039<x<0.061$. In view of the facts that the peak wavelengths λ_{max} for Na^- in pure HMPA and these HMPA-THF mixtures agree with one another and not with that in pure THF in the presence of cryptand (680 nm),[5] it may be safe to conclude that Na^- is solvated exclusively by HMPA molecules in solutions with $0.039<x<1$.

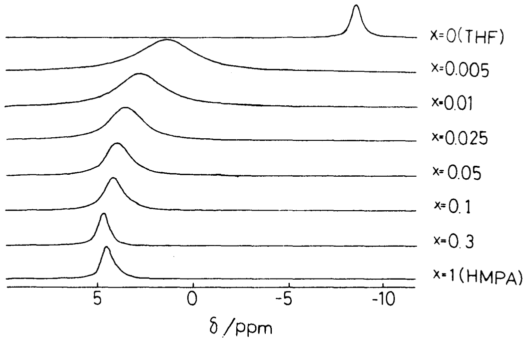

Fig. 1. ^{23}Na NMR spectra of 0.01 M sodium tetraphenylborate in HMPA-THF mixtures with varying HMPA mole fractions (x). Chemical shifts (δ) are referred to an external standard of 0.1 M NaCl in D_2O. Temperature: 23 °C.

Solvation of Na^+ in HMPA-THF. Figure 1 shows ^{23}Na NMR spectra for 0.01 M NaTPB in HMPA-THF of varying HMPA contents. An Addition of even a small amount of HMPA to THF, e.g., to $x=0.005$, is enough to cause a drastic change in ^{23}Na chemical shift δ, while this is not the case with the addition of THF to HMPA. These features may indicate that HMPA molecules solvate Na^+ much more strongly than THF molecules. The change in ^{23}Na chemical shift caused by a change in x may be attributed to the replacement of the THF molecules solvating Na^+ by HMPA molecules, since the observed chemical shift δ is related to the intrinsic shifts of each species i by[10]

$$\delta = \sum x_i \delta_i,$$

where x_i is the molar fraction of species i. The following discussion is based on the approximation that Na^+ is solvated selectively by HMPA molecules in HMPA(x)-THF mixtures with $0.039<x<1$.

The Sovation Number of Na^+ and Na^-. In view of the bulk dielectric constants of THF (7.4) and HMPA (30), bulk dielectric constants of HMPA(x)-THF mixtures ($0.039<x<0.061$) are expected to be 8.5—9.7 based on the volume average. A calculation with the Fuoss equation[6] for ion pair formation for a closest approach distance of about 12 Å (center to center distance) has led to an ion pair formation constant of 2×10^{2} M^{-1} at concentration 2.5×10^{-4} M for both Na^+ and Na^-, where the closest approach distance was estimated by assuming that both Na^+ and Na^- are solvated only by HMPA. The degree of ion pairing is expected to be less than 0.07, so small that ion pairing may be negligible. The following equilibrium is established in an HMPA-THF mixture saturated by Na:

$$2\mathrm{Na(solid)} + n\mathrm{L} \overset{K}{\rightleftharpoons} \mathrm{Na^+L}_k + \mathrm{Na^-L}_{n-k}, \quad (1)$$

where K is the equilibrium constant, k the solvation number of Na^+, and L stands for HMPA. The equilibrium constant is written as

$$K = [\mathrm{Na^+}][\mathrm{Na^-}]/[L]^n = c^2/[L]^n, \quad (2)$$

where brackets mean the concentration in molarity and $c=[Na^+]=[Na^-]$. The absorbance at λ_{max} for Na^-, A, can then be expressed by the following equation in terms of the molar absorptivity ε, the optical path length l, n, $[L]$, and K:

$$\ln A = (n/2)\ln[L] + \ln(\varepsilon l K^{1/2}). \quad (3)$$

When the total HMPA concentration $[HMPA]_0$ is much higher than c, the plot of $\ln A$ vs. $\ln[HMPA]_0$ should give a straight line whose slope and intercept on the $\ln A$ axis are $n/2$ and $\ln(\varepsilon l K^{1/2})$, respectively.[7]

Figure 2 shows that the experimental points within the concentration range of $[HMPA]_0=0.46$—0.71 M or $x=0.039$—0.061 are well fit to the following straight line obtained by the least-squares method:

$$\ln A = [(5.8\pm0.3)/2]\ln[\mathrm{HMPA}]_0 + 2.0. \quad (4)$$

The slope of this straight line gives a round number of 6 as n, i.e., the sum of the solvation numbers for Na^+ and Na^-. This n value combined with the literature k value[8-10] of 3 leads to a numerical value of 3 for the number of HMPA molecules solvated to a Na^- ion in HMPA-THF mixtures with HMPA mole fractions ranging from 0.039 to 0.061. It is very likely that this solvation number is also valid for Na^- in pure HMPA, since the λ_{max} value for Na^- and solvation number of HMPA to a Na^+ in the HMPA-THF mixtures of the above composition are, respectively, equal and nearly equal to those in pure HMPA.

We are grateful to Mr. Yoshiharu Toida, Bruker Japan Co. for furnishing NMR spectra and to Professor Makoto Okamoto of our Institute and his group for optical providing spectra. Facilities for preliminary NMR experiments were offered by Professor Hiroshi Fukutomi of our Institute and his group.

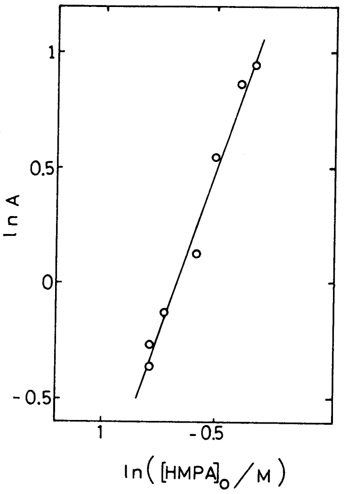

Fig. 2. A plot of the logarithmus of the absorbance at λ_{max} for Na^- (A) against the logarithmus of the total concentration of HMPA in HMPA-THF ($[HMPA]_0$). Temperature: 25 °C.

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