

Sodium Ion Pairs Aggregates in Amine Solutions

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Multinuclear NMR, and particularly metal ion NMR, has been shown to be very useful in the study of solvation phenomena [1, 2]. However, very few studies have dealt with a conjugate approach of the chemical shift and the relaxation time measurements [3, 4]. We report here Na-23 NMR measurements concerning the nature of solutions of sodium salts (iodide, perchlorate and tetraphenylborate mainly) in solutions of isopropylamine (IPA) and propylamine (PA). In those systems chemical shifts** and relaxation times T_2^{**} depend markedly on the nature of the counter-ions, and we show the necessity of their combination.

Figure 1 shows the variation of the chemical shift with the concentration of the salt. In the case of the iodide, chemical shifts are equal to 16.3 ppm (in IPA) and 14.2 ppm (in PA), in the whole range of concentration ($5 \cdot 10^{-3}$ – 1.0 M). This behaviour suggests the presence of only one ponderable species. The observation of the Na-23 resonance of the iodide salt downfield to those of perchlorate or tetraphenylborate anions is a general trend for most of the solvents [5–7]. We verify this trend here: Na-23 chemical shift is almost constant in the case of the perchlorate anion, around 6 ppm (like hexafluorophosphate or hexacyanocobaltate anions); the tetraphenylborate salt occupies an intermediate position (10–13 ppm).

Variation of chemical shift with temperature (in the range 270–350 K) indicates a perfect invariance in the case of iodide, a linear relationship in the case of perchlorate (0.056 ppm/K) and tetraphenylborate (0.090 ppm/K). Those chemical shifts results suggest the presence of one major species for iodide and perchlorate (respectively contact ion pair and solvent

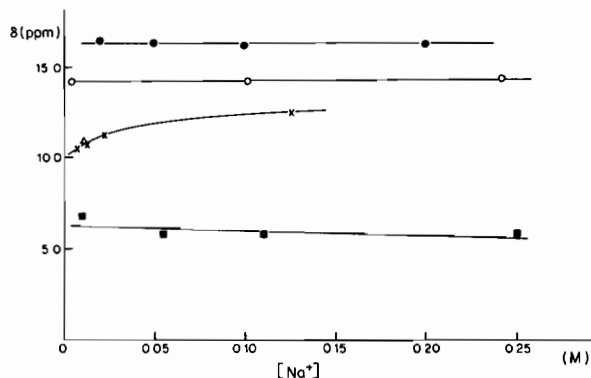


Fig. 1. Variation of the Na-23 chemical shifts with the concentration of Na^+A^- at 303 K: ● NaI in isopropylamine (IPA) ($\delta = 16.3$ ppm for $[\text{NaI}] = 0.499$ and 0.999 M); ○ NaI in propylamine (PA) ($\delta = 14.4$ ppm for $[\text{NaI}] = 0.946$ M); × NaBPh_4 in IPA; △ NaBPh_4 in PA; ■ NaClO_4 in IPA. Moreover, $\delta = 6.6$ ppm for $[\text{NaClO}_4] = 0.458$ M in PA, $\delta = 6.2$ ppm for $[\text{NaPF}_6] = 0.495$ M in PA and $\delta = 5.3$ ppm for $[\text{Na}_3\text{Co}(\text{CN})_6] = 0.120$ M in IPA.

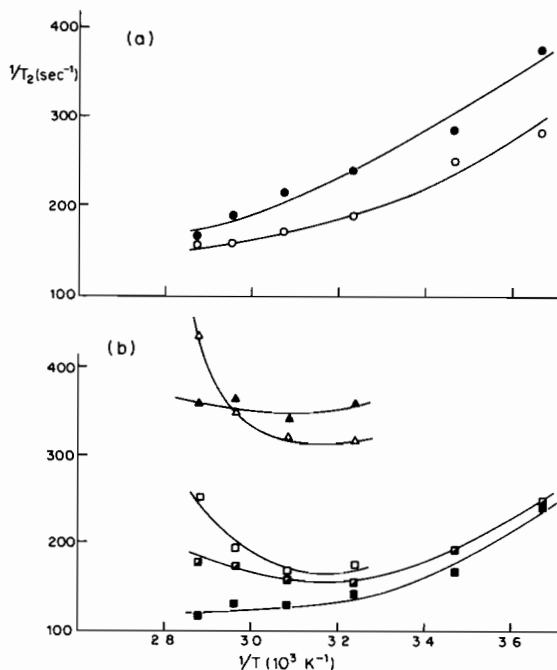


Fig. 2. Variation of the Na-23 relaxation rates with temperature. (a) ● $[\text{NaClO}_4] = 0.255$ M; ○ $[\text{NaClO}_4] = 0.046$ M. (b) ▲ $[\text{NaBPh}_4] = 0.254$ M; △ $[\text{NaBPh}_4] = 0.052$ M; ■ $[\text{NaI}] = 0.250$ M; ▣ $[\text{NaI}] = 0.049$ M; □ $[\text{NaI}] = 0.011$ M.

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**Chemical shifts reference is sodium chloride in water at infinite dilution. Transverse relaxation times are determined from the measurement of the signal line width. Experimental conditions are the same as in ref. [4].

separated ion pair, on the basis of the chemical shifts values [5, 6]) and an equilibrium in the case of tetraphenylborate.

Consider the relaxation times. In the case of the perchlorate the expected relationship between $1/T_2$ and $1/T$ is observed: the line width of the Na-23 signal decreases when the temperature increases (Fig. 2a), and Arrhenius activation energies for the relaxation process can be derived. 6.8 kJ/M ($[\text{NaClO}_4] = 0.046 \text{ M}$, $\rho = 0.984$ for 6 points) or 7.9 kJ/M ($[\text{NaClO}_4] = 0.255 \text{ M}$, $\rho = 0.987$ for 6 points). The conclusion derived from chemical shifts analysis is corroborated: one species exists in solution of sodium perchlorate in IPA or PA: a solvent separated ion pair, $\text{Na}^+_{\text{s}}//(\text{ClO}_4^-)_{\text{s}}$, which is very plausible in the case of the perchlorate anion, good acceptor of hydrogen bonds and capable of being stabilized by solvent molecules, not necessarily by the sodium counter-ion. 7 kJ/M is a likely value for the activation energy of reorientation of a solvated cation in a medium of low viscosity.

A more intriguing behaviour is observed in the case of the tetraphenylborate and iodide salts. The relaxation rates show a pronounced minimum: they decrease with increasing temperatures (270–300 K) and increase with increasing temperatures (300–350 K), mainly in the case of diluted solutions, in such a manner that, above 335 K for $\text{NaB}\phi_4$ and in the whole range for NaI, the Na-23 line width decreases with increasing concentrations: an almost unique situation [8].

The minimum of the $(1/T_2 - 1/T)$ plot could be predicted from the Valiev's theory of anharmonic vibrations [10]. In the case of our study, the Valiev's theory cannot explain why more diluted solutions show the more pronounced effect or why this effect is so dependent on the anions nature. Clearly, a chemical equilibrium must be associated with the observed relaxation behaviour. At higher temperatures, an aggregate of solvated contact ion pairs or solvent bridged ion pairs (for those two anions, iodide and tetraphenylborate poorly stabilized by hydrogen bonds) is equilibrated with a chemical species characterized by a large electric field gradient, such as true contact ion pairs, favoured by a gain of trans-

lational entropy (from solvent molecules or number of species). The presence of such a very dissymmetric solvation shell is readily shown by the relaxation, even if chemical shifts fail to detect it because of too low concentration of this species or/and accidentally nearly identical characteristic chemical shifts. We cannot yet give a precise estimate of the aggregates size. The Arrhenius activation energy for the relaxation process in the case of the iodide (at lower temperatures) is 12 kJ/M, twice as large as the perchlorate case. This is a possible indication for a dimeric ion pair aggregate.

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