racemization, they can, in principle, be isolated as free ligands at room temperature.

Two isomeric forms I and II of the $|18|aneP_4O_2$ ligand have been isolated and their nickel(II) tetrafluoborate derivatives have been synthesized and characterized. Conductometric, magnetic and spectroscopic measurements indicate that the latter compounds contain square planar $\{Ni(|18|aneP_4O_2)\}^{2+}$ cations, the nickel(II) ion being coordinated to the four phosphorus atoms. The ^{31}P NMR spectrum of isomer I is reported in Fig. 2 and shows a pattern of resonances which indicates the presence of four nonequivalent phosphorus atoms. The (d) configuration, therefore, is proposed for this stereoisomer. Both ^1H and ^{31}P NMR spectra indicate a symmetric configuration for isomer II. Since from ^1H NMR trace it appears that the ethylenic chains spanning the phosphorus atoms adopt the *gauche* conformation, only configurations (b) and (e) can be proposed for this stereoisomer. Preliminary X-ray diffractometric data indicate that the configuration (b) is to be assigned to the isomer II. Attempts to isolate and characterize all the possible isomers are actually in progress.

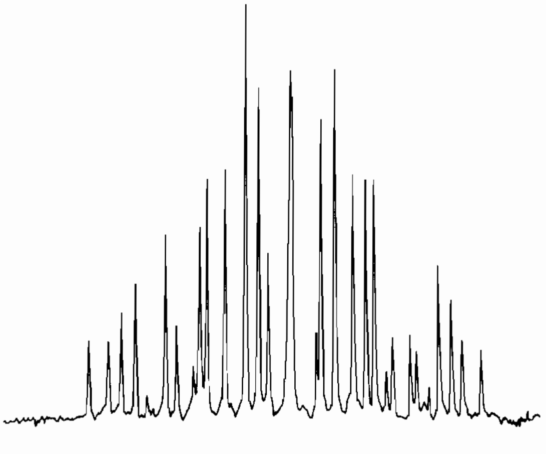

Fig. 2. ^{31}P NMR spectrum at 30 °C of d_6-DMSO solution of $\{Ni(|18|aneP_4O_2\text{-}I)\}^{2+}$.

NMR Studies on Ion Pairing in Solution

ELENA BORGHI

Laboratorio per lo Studio dei Composti di Coordinazione del CNR, and Istituto di Chimica Generale della Facoltà di Farmacia, Università di Firenze, Florence, Italy

A series of compounds of general formula (ZR_4)-$(MPPh_3X_3)$ Z = N, P; R = butyl, propyl, ethyl; M = Co, Ni, Zn; X = Br, I, has been prepared, and their chloroform or dichloromethane solutions have been investigated by means of T_1, T_2, and chemical shift measurements on ^1H, ^{13}C, and ^{31}P nuclei. Earlier proton NMR data on a limited number of the above compounds were interpreted on the ground of purely dipolar interactions between the cations and the paramagnetic complexes [1, 2], although later reports on ^{14}N and ^{31}P shifts [3, 4] suggested the existence of some contact contributions. The thorough investigation of the above systems allows to generalize their NMR behavior as follows:

1) all of the R protons undergo upfield shifts in the cobalt(II) and downfield shifts in the nickel(II) compounds, with respect to the zinc analogues; their absolute values decrease with increasing distance from the Z hetero atom along the alkyl chain;

2) all of the R carbons experience downfield isotropic shifts in both cobalt(II) and nickel(II) compounds, again decreasing in magnitude from C_1 to C_n;

3) the ^{31}P nucleus of the cation, analogously to the nitrogen atom in the corresponding compounds [3], always experiences downfield shifts like the attached carbon atoms;

4) the longitudinal and transverse relaxation enhancements (T_1^{-1} and T_2^{-1}), measured with respect to the zinc analogues, are generally small but are only slightly attenuated passing from the central atom to the outer atoms of the cation, even taking into account the difference in gyromagnetic ratios. The T_2^{-1} values are always larger than the T_1^{-1} values of the same nucleus.

Systems of the type $(C_4H_9)_4Z_2(MX_4)$ and $(C_4H_9)_4Z(MquinX_3)$ have also been considered for comparison purposes. The data on these systems are in agreement with the above results, showing that they do not depend on any particular geometry of the paramagnetic anion considered.

While the absolute magnitude of the observed paramagnetic effects is rather small, thus confirming that only weak interactions are operative, a qualitative analysis shows that even in such weakly coupled systems the true “through space’ dipolar coupling is very small; most of the measured effect is due to some unpaired spin delocalization, since the ratios between proton and carbon isotropic shifts are different in sign in cobalt and nickel compounds. The occurrence of such spin delocalization is confirmed by the difference in T_1 and T_2 values. Since the R_4Z^+ cations experience relevant contact contributions, point-dipole equations for shifts and relaxation times [5–7] cannot be used to perform structural analysis. Furthermore, ^1H and ^{13}C measurements at decreasing sample concentrations show that, besides the expected general decrease of the paramagnetic effects due to progressive uncoupling of the ions, there is also a sizeable change in the isotropic shift *ratios* suggesting the existence of more than one geometric arrangement of the ionic couples.

References

1 G. N. La Mar, *J. Chem. Phys., 41,* 2992 (1964).
2 G. N. La Mar, *J. Chem. Phys., 43,* 235 (1965).
3 D. G. Brown and R. S. Drago, *J. Am. Chem. Soc., 92,* 1871 (1970).
4 H. P. Fritz, W. Gretner, H. J. Keller and K. E. Schwarzhans, *Z. Naturforsch., 25b,* 174 (1970).
5 H. M. McConnell and R. E. Robertson, *J. Chem. Phys., 29,* 1361 (1958).
6 I. Solomon, *Phys. Rev., 99,* 559 (1955).
7 N. Bloembergen, *J. Chem. Phys., 27,* 572, 595 (1957).

The Temperature Dependence of the Dielectric Properties of Unassociated Organic Solvents at Polarizable Interfaces

Z. BORKOWSKA

Institute of Physical Chemistry, Polish Academy of Sciences, 01-229 Warsaw, Poland

R. M. DE NOBRIGA and W. R. FAWCETT

Guelph-Waterloo Centre for Graduate Work in Chemistry, Guelph Campus, Department of Chemistry, University of Guelph, Guelph, Ont., N1G 2W1, Canada

As it was shown previously [1, 2], the three state model for solvent dipoles can be used successfully to describe the differential capacity at Hg/nonaqueous interface in the case of unassociated or weakly associated organic solvents.

The model may be tested further by examining the temperature dependence of the surface potential and the adsorption entropy as was done previously for Hg/aqueous interface [3, 4]. The temperature coefficient of the surface potential for a number of organic solvents with the exception for methanol is positive [5]. However the interpretation of this quantity in terms of solvent dipole orientation and the sign of the surface potential depends on the molecular model used to describe the dielectric properties of the solvent monolayer. Another quantity which is accessible experimentally is the solvent adsorption entropy. The only data available for nonaqueous solvents are those for Hg/propylene carbonate interface [6]. It is evident that the accepted interpretation based on a two state model is not valid in this case. The molar adsorption entropy has a maximum at a negative charge density which would suggest a preferred orientation at the uncharged mercury with the negative end of the propylene carbonate dipole pointing towards the metal and consequently, a negative surface potential. However the occurrence of the solvent capacity 'hump' at a high positive charge density would imply just the opposite.

The purpose of this paper is to discuss the temperature dependence of the dielectric properties of the Hg/solution interface in the case of N,N-dimethylformamide, methanol and acetone including also the literature data for propylene carbonate [5]. The adsorption entropy has been calculated on the basis of the temperature dependence of the double layer differential capacity following the thermodynamic arguments of Harrison *et al.* [7]. The results have been compared with the prediction of three state model.

References

1 W. R. Fawcett, *Israel J. Chem., 18,* 3 (1979).
2 Z. Borkowska and W. R. Fawcett, *Electrokhimiya,* accepted.
3 R. M. Reeves, *Mod. Aspects Electrochem., 2,* 239 (1974).
4 R. Parsons, *Electrochim. Acta, 21,* 681 (1976).
5 Z. Borkowska, W. R. Fawcett and S. Anatawan, *J. Phys. Chem.,* submitted.
6 Nguyen Huu Chong, A. Jenard and H. D. Hurwitz, *J. Electroanal. Chem.,* in press.
7 J. A. Harrison, J. E. B. Randles and D. J. Shiffrin, *J. Electroanal. Chem., 48,* 359 (1973).

Solvent Effect on N-Methylthiourea. A ^{1}H-NMR Study

G. GONZALEZ, S. ALEGRIA

Facultad de Ciencias, Universidad de Chile, Chile

and A. M. LEIVA

Instituto de Ciencias Químicas, Pontificia Universidad Católica de Chile, Chile

The solvent influence on the spectroscopic properties of the solute can be used to obtain information about its configuration in solution. With this objective the influence of the temperature on the ^{1}H-nmr spectra of N-methylthiourea was studied in the following solvents 1,2-propanodiolcarbonate, trimethylphosphate, tributylphosphate and dimethylsulfoxide mixed with CCl_4 in a ratio 1:1 in volume. At low temperature the methyl group signals of thiourea split showing the signals corresponding to *cis* and *trans* positions of methyl protons. These results agree with the behaviour reported for other solvents.

However, the low field spectra corresponding to N–H and N–H_2 protons show a higher complexity as is shown in Fig. 1.

The splitting of the N–H_2 signal in two signals with different intensities, **A** and B, indicates the presence of two non equivalent configurations of