Multielement NMR and ESR Study of Solutions of the Alkali Metals Na to Cs in N,N-Diethylacetamide, N,N-Dipropylacetamide, N,N-Dimethylpropanamide, and Tetramethylurea

Dolores M. Holton,[†] Peter P. Edwards,*[†] David C. Johnson,[‡] Catherine J. Page,[‡] William McFarlane, and Brian Wood

Contribution from the University Chemical Laboratory, Cambridge, CB2 1EW, United Kingdom, the Baker Laboratory of Chemistry, Cornell University, Ithaca, New York 14853, and the Department of Chemistry, City of London Polytechnic, London ED3N 2EY, United Kingdom. Received November 28, 1984

Abstract: Metal solutions of sodium through cesium in the title amide and urea solvents have been examined by multielement NMR and ESR spectroscopy. Characteristic ^{23}Na NMR spectra of the sodide anion in the solvents N,N-diethylacetamide, N,N-dipropylacetamide, and N,N-dimethylpropanamide are reported. Solutions of the heavier alkali metals K through Cs in these three solvents showed no evidence of genuine alkalide ions. The corresponding ESR spectra of the liquid metal solutions show only a singlet resonance arising from a time-average of the signals from the solvated electron, e_s^-, and the ion-pair species, $M_s^+e_s^-$. In contrast, metal solutions prepared at room temperature and then quenched in liquid nitrogen exhibit signals from both these species: a singlet due to the corresponding trapped electron and resolved hyperfine coupling to the alkali metal due to the presence of the electron–cation encounter species ($M_s^+e_s^-$) in these vitreous solids. Our NMR and ESR data are discussed in terms of the various chemical equilibria occurring in the metal solutions. Finally, we consider how these potential reducing species may be implicated both in dissolving metal reduction (DMR) reactions and also in the mode of decomposition of the metal solutions themselves.
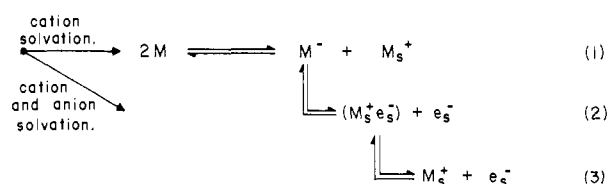
The polar solvents N,N-diethylacetamide (DEA), N,N-dipropylacetamide (DPA), N,N-dimethylpropanmide (DMP), tetramethylurea (TMU), and tetraethylurea (TEU) have recently attracted attention both as media for electrochemical studies[1] and as potential solvent systems for the reaction of organic compounds with dissolving metals (dissolving metal reductions).[2] They have also been proposed as new nonaqueous solvents for the alkali metals.[3-5]

Lüttringhaus and Dirkensen[6] first reported that vigorous shaking of TMU with sodium–potassium alloy (NaK) produced "a dark blue solution within a few seconds" thought to resemble metal ammonia and related systems. Similarly, optical studies on DEA and other tertiary amides[3] found that sodium metal dissolves to give blue solutions containing solvated electrons, e_s^-, and sodium anions, Na⁻.

A representation of the general equilibria present in metal solutions has been given by Dye[7] (Scheme I). Strongly solvating media of relatively high dielectric constant tend to shift all equilibria to the right, to give predominantly e_s^- and M_s^+ with $M_s^+e_s^-$ present only in small concentrations if at all. Ammonia is the classic solvent showing this behavior. Although the dielectric constant of hexamethylphosphoramide (HMPA) is higher than that of ammonia, powerful and preferential solvating power for cations rather than anions leads to the presence of substantial concentrations of M⁻ in solution.[8] Solvents such as methylamine and ethylenediamine give mixtures of M⁻, $M_s^+e_s^-$, and e_s^-, while the less polar amines and ethers give predominantly M⁻ with only small concentrations of $M_s^+e_s^-$ and e_s^-.[9] Note that the precise amount of each of these species in solution is both metal and concentration dependent.

The title solvents resemble HMPA in having exceptional cation solvating powers, a property at least partially responsible for the characterization of stable, long-lived alkalide ions (M⁻) in both metal–HMPA[8,9] and metal–DEA[2,9] solution. There is some evidence, however, that greater solvation of anions occurs in TMU[6] than in HMPA. The established solvated electron optical absorption in the title solvents[3,4] indicates that the excess electron ins only weakly bound or solvated.

Scheme I

$$\text{2 M} \rightleftharpoons \text{M}^- + \text{M}_s^+ \qquad (1)$$

cation solvation. ↗

cation and anion solvation ↘

$$\longmapsto (\text{M}_s^+e_s^-) + e_s^- \qquad (2)$$

$$\longmapsto \text{M}_s^+ + e_s^- \qquad (3)$$

We undertook the present NMR/ESR study to obtain information on the electronic structure of these alkali metal/organic amide solutions. A second objective was to probe the fundamental problem[10] of the solvating power and reactivity of "carbonyl-containing solvents" toward the solvated electron and alkali metal anions. We present here magnetic resonance data which support the inferences drawn from earlier optical measurements,[3] namely that these solutions contain both Na⁻ and e_s^-, as well as the ion-pair species $M_s^+e_s^-$. In addition, our resonance measurements probe the microscopic structure of these diamagnetic and paramagnetic species in solution.

Experimental Section

Solutions of the alkali metals in DEA, DPA, DMP, and TMU were prepared by high-vacuum techniques. Sodium, potassium, rubidium, and cesium were purified initially by melting under vacuum (ca. 10^{-3} torr)

(1) Sawyer, D. T.; Roberts, J. L. "Experimental Electrochemistry for Chemists"; Wiley: New York, 1974; Chapter 4.

(2) Sowinski, A. F.; Whitesides, G. M. *J. Org. Chem.* **1979**, *44*, 2369.

(3) Young, C. A.; Dewald, R. R. *J. Chem. Soc., Chem. Commun.* **1977**, 188.

(4) Guy, S. C.; Edwards, P. P.; Salmon, G. A. *J. Chem. Soc., Chem. Commun.* **1982**, 1257.

(5) Holton, D. M.; Edwards, P. P.; Salmon, G. A. *J. Phys. Chem.* **1984**, *88*, 3855.

(6) Lüttringhaus, A.; Dirksen, H. W. *Angew. Chem., Int. Ed. Engl.*, **1964**, *3*, 260.

(7) Dye, J. L. In "Electrons in Fluids: The Nature of Metal–Ammonia Solutions", Colloque Weyl III; Jortner, J., Kestner, N. R., Eds.; Springer-Verlag: West Berlin, 1973; p 77.

(8) Edwards, P. P.; Guy, S. C.; Holton, D. M.; McFarlane, W. *J. Chem. Soc., Chem. Commun.* **1981**, 1185.

(9) For a recent review, see: Edwards, P. P. *J. Phys. Chem.* **1984**, *88*, 3772.

(10) Symons, M. C. R. In "Specialist Periodical Report, Electron Spin Resonance"; Royal Society of Chemistry: London, 1983; Vol. 8, p 166.

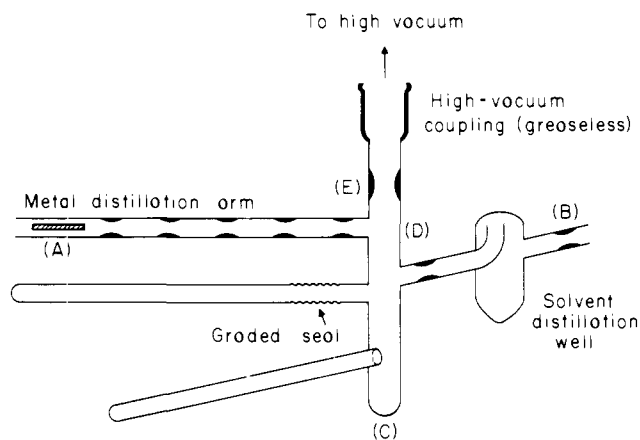† University Chemical Laboratory.
‡ Baker Laboratory of Chemistry.

Figure 1. A typical reaction cell for preparing both NMR and ESR samples of solutions of sodium through cesium in organic amides.

Table I. Metal-Amide Solutions Prepared

metal	solvent			
	DEA	DPA	DMP	TMU
Na	√(Na^-)[a]	√(Na^-)[a]	√(Na^-)[a]	√
K	√	√	×	(AsNa/K)
Rb	√	√	√	×
Cs	√	√	√	×

[a] (Na^-) indicates the detection of the sodium anion by NMR. √ indicates stable solution, see also Table II. × indicates solutions decompose very rapidly.

and forcing the molten metal into 3 mm o.d. capillary tubing; this was carried out with an atmosphere of argon which had been dried previously by passing over baked molecular sieves. In this form, any oxidation of the metal was confined to the open end of the capillary; lengths of metal could then be conveniently cut to prepare metal solutions of (approximately) the desired concentration.

Solvents (DEA, DPA, DMP, and TMU) were initially purified by refluxing over calcium hydride. Freshly prepared NaK was then added, and the solution was refluxed for a further hour, followed by distillation under vacuum (ca. 10^{-3} torr) into ampules of approximately 5 cm^3 capacity—sufficient for the preparation of one metal solution.

A typical sample cell is shown in Figure 1. This design enables both ESR and NMR samples to be obtained from a single metal solution preparation. The glassware was soaked overnight in the alkaline cleansing agent Decon 90 (BDH) and was then rinsed repeatedly with deionized water and oven-dried; acid-cleaning (e.g., with HF/HNO_3 mixtures) was found to promote decomposition of the metal solution. A length of capillary tubing (normally of the order of 3 cm in length) containing the required metal was placed in the distillation arm at A and the sidearm sealed. During this operation, dry argon gas was allowed to flow through the cell prior to the final seal-off to inhibit any metal oxidation. A solvent ampule was then cracked open, and the liquid was pipetted into the distillation well at B, against a gentle counter-current of argon. Freshly-prepared NaK alloy was added, and a blue solution was (generally) immediately formed. The resulting solution was frozen in liquid nitrogen, thereby forming a solid layer of argon above the NaK/solvent mixture, and the sidearm was sealed at B. The argon was allowed to melt and was pumped out of the cell via the high-vacuum connection. The solvent well was refrozen, and the remaining sections of the apparatus were flamed out, first under low (10^{-2} torr) and then under high (10^{-4}–10^{-5} torr) vacuum until no further outgassing of the glass was detectable on a vacuum gauge. The solution was isolated from the main vacuum manifold, and the solvent was thawed to allow degassing and then refrozen before exposure to high vacuum again. This freeze–pump–thaw cycle was repeated at least three times, and the solvent well was then frozen in a liquid nitrogen bath. The metal was melted out of the capillary tubing under vacuum with an oxygen-gas hand torch and evaporated on to the walls of the first section. The initial section was then removed by sealing at the constriction and discarded. Having completely degassed the solvent, it was distilled at (10^{-4} torr) to C, where it was trapped in a liquid nitrogen bath. The solvent well B was subsequently sealed off from the apparatus. The metal was then distilled along the metal arm, sealing off under high vacuum at each constriction behind the metal, to finally give a high-purity film at D. The sequence of metal–solvent–metal distillation ensured a good vacuum throughout sample preparation. The cell was removed from the vacuum line by sealing at E once a vacuum of at least 10^{-5} torr had been attained. Finally, the solvent was thawed slowly to room temperature and shaken vigorously with metal. The resulting blue solution was tipped into the ESR and NMR tubes, the constrictions were heated gently to clear them of residual solvent, and the samples were frozen in liquid nitrogen and sealed with a hand torch. Both ESR and NMR samples prepared in this fashion were then stored at 77 K until required.

To investigate the frozen metal solutions by ESR, samples prepared at room temperature were rapidly frozen by immersion in liquid nitrogen. Vitreous blue solid solutions were formed by this method for a wide range of metal/solvent systems.

NMR spectra were recorded on a Jeol FX90Q pulsed Fourier transform multinuclear spectrometer. Samples were homogenized in CO_2/ acetone baths (–78 °C) prior to spectroscopic examination and allowed to come to thermal equilibrium before spectra were recorded. Each spectrum was monitored continuously until no further change in chemical shift position with time could be detected. The magnetic field was stabilized by the deuterium signal from an external D_2O sample built into the probe. Resonance shifts, which are uncorrected for bulk susceptibility, were measured by substitution relative to NaCl, KCl, RbCl, or CsCl in D_2O at infinite dilution (^{23}Na, ^{39}K, ^{85}Rb and ^{87}Rb, and ^{133}Cs, respectively) or Me_4Si (^{1}H and ^{13}C), all reference samples being at room temperature. The reproducibility of measurement (unless otherwise indicated) was ±0.1 ppm for ^{1}H, ^{13}C, and ^{23}Na resonances. In reporting NMR shifts (δ/ppm) we adopt the following convention: a negative δ corresponds to a low frequency shift and hence an increase in nuclear shielding.

Results and Discussion

A. Stability Considerations. Young and Dewald[3] have previously reported that elemental sodium dissolves in DEA, DMP, and TMU, while NaK alloy dissolves in DMP, DPA, and TEU to form metastable blue solutions of varying stability. They found that the remaining metal/solvent systems decomposed too rapidly to obtain meaningful optical data. With the cleaning procedures and purification techniques for metal solutions adopted in the present work, we have found that a wide range of metal/substituted amide systems can be prepared. As Table I indicates, except with TMU (for which only sodium solutions are stable), we have been able to prepare relatively stable blue solutions of the alkali metals Na through to Cs. Tetraethylurea (TEU) solutions were not examined in the present work. We have not carried out controlled experiments to establish the relative stabilities of the various metal solutions formed by the title solvents, but we can offer some qualitative observations. In particular, we have found that the multielement NMR spectra offer at least an empirical guide to selective solution stabilities. For example, freshly prepared Na–DMP solutions exhibit a strong ^{23}Na NMR absorption from the sodide ion species, Na^-, discussed in detail later in this report. No Na_s^+ resonance is observed in these solutions for reasons similarly discussed below. In contrast, the decomposed metal solution shows *only* a broad ^{23}Na resonance from the sodium cation in various decomposition products. Hence by monitoring the time decay of the Na^- absorption, coupled with visual observation of the sample, an approximate guide to the stability of the various sodium solutions could be obtained.

The approximate lifetimes of the four sodium solutions are listed in Table II, together with the corresponding observation temperatures and the freezing points of the neat solvents. Pure DEA, DPA, and DMP form excellent glasses at low temperature. Therefore, the freezing points listed are the temperatures at which the solvents soldify, as evidenced by the disappearance of the ^{1}H NMR resonance. The observed stabilities for sodium solutions may at least be helpful in formulating future strategies for the use of these solutions as dissolving metal reduction (DMR) media at low temperatures. Note that these stability considerations closely parallel the results of our recent pulse radiolytic studies of e_s^- in the neat solvents.[4]

Solutions of the heavier metals K through Cs in DEA and DPA are intrinsically less stable than their Na counterparts. However, in all cases they were sufficiently stable for multinuclear NMR spectra to be recorded over a reasonable time interval. Solutions of Rb in DEA, for example, were stable for at least 1.5 h at 218 K. We have been unable to detect the characteristic alkalide ion resonances[11] of any of the heavier metals. Thus, for these solutions,

Table II. Stabilities of Sodium–Amide Solutions[a]

	solvent			
	DEA	DPA	DMP	TMU
structure	CH₃CN(=O)(CH₂CH₃)(CH₂CH₃)	CH₃CN(=O)(CH₂CH₂CH₃)(CH₂CH₂CH₃)	CH₃CH₂CN(=O)(CH₃)(CH₃)	(H₃C)(H₃C)NCN(=O)(CH₃)(CH₃)
stability	2 h/183–233 K	1 h/218 K	4 h/231 K	<5 min/273 K
freezing point[b]	180	188	196	222

[a] Numbering system for carbon atoms refers to Table III. [b] As deduced from NMR studies.

Table III. Solvent Chemical Shifts in Alkali Metal–Amide Solutions

solvent	metal	temp, K	δ[a](¹H)					δ[a](¹³C)				
			1	2	3	4	5	1	2	3	4	5
DEA		273	2.26		3.57	1.29		21.72	169.02	40.12	13.72	
					3.61[b]	1.40				43.18	14.83	
DEA		203	2.25		3.54	1.32		NM[c]	NM[c]	NM[c]	NM[c]	NM[c]
DEA	NaBPh₄	203	2.11		3.40	1.18		21.72	168.81	39.66	13.49	
										42.69	14.46	
DEA	Na	203	2.11		3.43	1.20		21.83	168.81	39.76	13.54	
						1.12				42.74	14.57	
DEA	K	213	NM[c]	NM[c]	NM[c]	NM[c]	NM[c]	21.2	168.2	39.1	12.9	
										42.2	14.0	
DEA	Rb	223	1.87		3.18	0.86		21.56	168.59	39.55	13.38	
						0.97				42.53	14.35	
DPA		213	1.50		2.75	1.04	0.35	21.3	168.4	46.8	22.3	11.0
										49.6	20.8	11.2
DPA	Na	213	1.56		2.8	1.10	0.39	21.3	168.4	46.8	22.3	11.0
										49.8	20.8	11.2
DPA	K	213	1.56		2.8	1.1	0.39	21.3	168.4	46.8	22.3	11.0
										49.8	20.8	11.2
DMP		231	1.12	2.48	3.00			9.8	26.5	172.9	36.8	
					3.16						34.9	
DMP	Na	231	1.14	2.51	3.02			9.8	26.5	172.9	34.9	
			±0.01		3.18			±0.2			36.8	

[a] In ppm relative to Me₄Si; numbering of ¹H and ¹³C resonances as in Table II. [b] Inequivalence of ethyls due to restricted rotation about C–N bond owing to double bond character; line widths too broad to resolve this inequivalence at lower temperatures. [c] Not measured.

more accurate estimates of stability would have to rely on the rate of appearance of either the M_s^+ resonance or a solvent decomposition product (formed in very low concentration).

B. Multielement NMR. The multielement (²³Na, ¹³C, ¹H) NMR spectra (220 K) from a solution of sodium in DPA are shown in Figure 2. The ¹H and ¹³C chemical shifts in this system are very similar to those for the pure solvent, changes in δ with respect to the pure solvent being less than 0.1 ppm for ¹H and ¹³C resonances. The ¹H and ¹³C NMR data for all alkali metal–amide solutions examined are summarized in Table III. In each case, the chemical shifts are very similar to those for the pure solvent, a phenomenon also observed in M–MeNH₂ solutions (except where M = Li). For Na–DMP and Na– and K–DPA solutions, the shifts are virtually indistinguishable from those of the solvent within experimental error (±0.1 ppm). Larger deviations are observed when DEA is the solvent. The changes in chemical shifts are negative, corresponding to an increase in shielding in the metal solutions over the pure solvent. They are larger for Rb (typically 0.4 ppm) than for Na solutions (−0.2 ppm) in the ¹H spectrum, whereas ¹³C shifts become increasingly negative in the order Na > Rb > K (values range from −0.4 to −1.0 ppm along the series for the ¹³CH₂ resonance of the ethyl group, for instance). Note that the chemical shifts of the DEA metal solutions (with respect to pure DEA) are of the same sign and magnitude as for solutions of NaBPh₄ in DEA, despite the paramagnetic nature of the former samples.
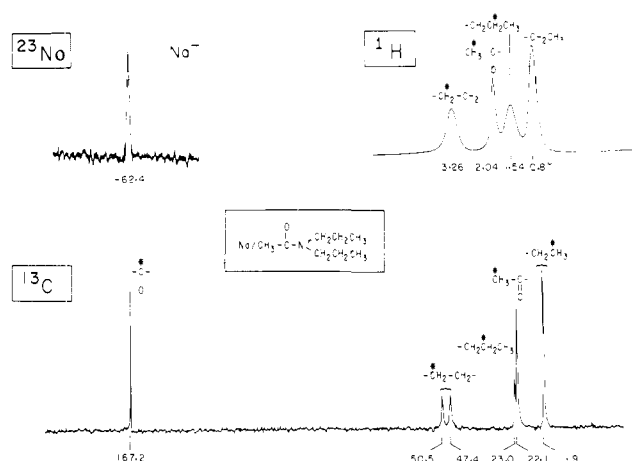

Figure 2. Multielement NMR (¹H, ¹³C, and ²³Na) spectra of a solution of sodium in *N,N*-dipropylacetamide at 220 K. Resonance shifts for ²³Na are relative to Na⁺ in D₂O (for ¹³C and ¹H relative to Me₄S; see text).

The assignment of the ²³Na NMR in Na–DPA solutions (Figure 2) to the sodide ion, Na⁻, is unambiguous. In particular the combination of both the characteristic chemical shift and the NMR peak width at half-height ($\Delta\nu_{1/2}$) have been used previously[11,12] as fingerprint magnetic parameters for the Na⁻ species

(11) Dye, J. L.; Andrews, C. W.; Ceraso, J. M. *J. Phys. Chem.* **1975**, *79*, 3076.

(12) Edwards, P. P.; Guy, S. C.; Holton, D. M.; Johnson, D. C.; Sienko, M. J.; McFarlane, W.; Wood, B. *J. Phys. Chem.* **1983**, *87*, 4362.

Table IV. NMR Parameters for Sodide (Na⁻) and Sodium Ions (Na⁺) in Amide Solutions

ion	solvent	temp, K	δ, ppm	$\Delta\nu_{1/2}$, Hz
Na⁺ (NaCl, at ∞ dilution)	D₂O	301	reference	14
Na⁺ (NaBPh₄, 0.1 mol dm⁻³)	DEA	250	-2.8 ± 0.2	310
		273	-2.4	130
		279	-2.2	110
Na⁻	DEA	185	-62.3 ± 0.1	45
		188	-62.3	25
		200	-62.1	13
		203	-62.4	8
		233	-62.3	≤ 10
Na⁻	DPA	213	-62.4	20
Na⁻	DMP	231	-62.0	14
Na⁻	HMPA	263	-62.0	13
Na⁻	gas		-61.8^a (calcd)	

^{a} This value calculated with respect to Na⁺ at infinite dilution.

Figure 3. ESR spectra of a frozen solution of sodium in DPA (145 K) at (a) low (0.05 mW) and (b) high (10 mW) incident (microwave) power. The very narrow resonance of spectra a and b possibly arises from small particles of sodium metal—this is a tentative assignment. The broader resonance originates from the trapped electron. Spectrum b illustrates the hyperfine coupling to ²³Na in the association complex, Na$_s^+$e$_s^-$, formed in the frozen solid.

both in solution and in the solid state.[13] In Na–DPA solutions at 220 K, the Na⁻ signal is shifted 62.4 ppm to low frequency of the external reference (Na⁺ in D₂O at infinite dilution) and has $\Delta\nu_{1/2} = 20.6$ Hz at this temperature. Note that the error in $\Delta\nu_{1/2}$ is greater than that in spectra from Na–DEA and Na–HMPA[8] solutions, reflecting the reduced signal-to-noise ratio of the DPA sample. The chemical shift of Na⁻ in DPA is virtually identical with that of the gaseous free anion, Na⁻(g).[14] The narrow line width characteristic of the Na⁻ absorption is once again indicative of a highly symmetric (probably spherically symmetric) metal anion species; this effectively rules out any assignment to a metal-based diagmagnetic state, e.g., the triple-ion species, e$_s^-$M$_s^+$e$_s^-$.

We have also observed the characteristic ²³Na NMR of Na⁻ in Na–DEA[12] and DMP solutions; the magnetic data for the sodide ion in these amide solutions are assembled in Table IV. We have so far been unable to detect the Na⁻ resonance in Na–TMU solutions.

We include in Table IV the corresponding NMR data for the sodium cation absorption in NaBPh₄–DEA solutions. The extreme broadness of the Na⁺ ion NMR compared with that of the anion suggests a low symmetry arrangement of solvent molecules in the first coordination sphere surrounding the cation. The observed chemical shift of –2.4 ppm at 273 K is in contrast to that of Na⁺ in HMPA at the same temperature, which has a shift of +3.9 ppm. Relative to gaseous sodium atoms, the chemical shifts of Na⁺ in DEA and HMPA are, respectively, +58.1 and +64.6 ppm. The reduced shift for DEA reflects a reduced ability to donate electron density from the oxygen lone pair to the metal cation,[15] as measured by the Gutman donor numbers[16] for DEA (32.2) and HMPA (38.8.)

The chemical shift of the sodide ion is both solvent and temperature independent. Contrast the variation in chemical shift for Na⁺/DEA over a 20 deg rise in temperature with the constancy of the Na⁻ resonance position from 185 to 233 K. The line width of the Na⁻ NMR signal is very narrow (8–13 Hz) from 233 down to 200 K, below which the resonance broadens as the sample starts to freeze. This is again in contrast to the behavior of Na⁺; here the cation line width effectively trebles on going from 279 to 250 K. The broader lines observed for the cation are again indicative of a much greater degree of solvation of the cationic rather than the anionic sodium species, and this is entirely consistent with the
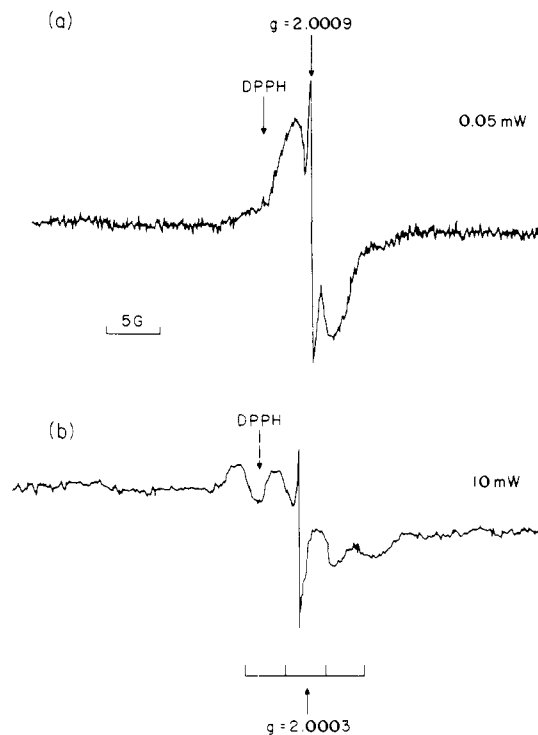
classification of DEA as a good electron pair donor molecule and hence a powerful cation solvator.[6]

In all of the simple, two-component systems which we have so far examined, we have never observed the NMR resonance of Na$_s^+$ in the metal solution.[8,12,17] To investigate the lack of a characteristic Na$_s^+$ NMR resonance in these systems, we have examined the same samples by ESR spectroscopy; the experimental configuration of the preparation cell (Figure 1) means that this dual sample preparation is relatively straightforward. In particular, we wished to examine the possible influence of the known ion-pairing or electron–cation association process on the NMR characteristics of the metal (cation) nucleus in these solutions.

$$M_s^+ + e_s^- \rightleftharpoons M_s^+e_s^-$$
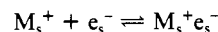
C. ESR Spectra of Vitreous and Fluid Solutions. The ESR spectra of fluid solutions of sodium in DPA and potassium in DEA consist of a singlet resonance centered at $g = 2.0007 \pm 0.0004$, with peak-to-peak (first derivative) line widths (ΔH_{pp}) of 0.6 and 0.5 G, respectively. These singlet resonances reach a maximum signal amplitude at microwave power levels of between 0.1 and 0.2 mW. Both the observed g-values and microwave saturation behavior of the singlet resonances are similar to those observed from solvated electron species in metal–NH₃ and metal–HMPA solutions.[9,18] In these solutions, high rate constants for the forward and reverse rate processes in equilibrium 3 give rise to a time-averaged signal from e$_s^-$ and the corresponding electron–cation encounter species M$_s^+$e$_s^-$. We suggest that a similar situation occurs in the title systems; supportive evidence for this assignment comes from our ESR studies of the quenched metal solutions.

The ESR spectra of frozen solutions of metals in DEA and DPA reveal the presence of at least two localized electron species. Figure 3 shows spectra obtained from a Na–DPA solution at 145 K at

(13) Ellaboudy, A.; Dye, J. L. *Chem. Br.* **1984**, *20*, 210. This is a short review on solid-state NMR of Na⁻; see also: Ellaboudy, A.; Tinkham, M. L.; Van Eck, B.; Dye, J. L.; Smith, P. B. *J. Phys. Chem.* **1984**, *88*, 3852.

(14) Pyper, N. C.; Edwards, P. P. *J. Am. Chem. Soc.*, in press.

(15) Herlem, M.; Popov, A. I. *J. Am. Chem. Soc.* **1972**, *94*, 1431.

(16) Guttmann, V. "Coordination Chemistry in Nonaqueous Solvents"; Springer-Verlag: New York, 1968.

(17) Holton, D. M.; Edwards, P. P.; Johnson, D. C.; Page, C. J.; McFarlane, W.; Wood, B. *J. Chem. Soc., Chem. Commun.* **1984**, 740.

(18) Page, C. J.; Millhauser, G. L.; Edwards, P. P.; Freed, J. H.; Sienko, M. J. *J. Phys. Chem.* **1984**, *88*, 3785.

two microwave power levels, ca. 0.05 mW (a) and 10 mW (b). At very low power levels the spectra consist of a very narrow signal ($\Delta H_{pp} \simeq 0.4$ G) centered on $g = 2.0009$ and a somewhat broader resonance with $\Delta H_{pp} = 3.5$ G, again centered close to the free spin value at $g = 2.0009$.

The precise identification of the very narrow resonance is uncertain at the present time. One possibility is that it originates from small metallic particles of sodium precipitated from the solution during the freezing process. These small metallic particles have recently been observed in other quenched metal solutions,[19,20] but a definitive assignment is not yet possible in this case and further studies are in progress.

The broader resonance (Figure 3a) observed at low power levels is assigned to trapped or solvated electrons in the low-temperature solid. This assignment is based upon two important experimental characteristics of the resonance. The first is its microwave power saturation characteristics. The broad singlet (Figure 3a) saturates at the very low microwave power level of ca. 0.05 mW, and this is consistent with the known saturation behavior of trapped electrons in other polar systems. Secondly, the ESR data for this species in the quenched metal solutions are very similar to those observed for trapped electrons in the γ-irradiated neat solvents at liquid nitrogen temperature.[5] Once again, the power saturation characteristics of e_s^- are identical in both situations, viz, the frozen metal solution and the γ-irradiated pure solvents.

A third paramagnetic species in these frozen metal solutions is detectable at the higher power levels (Figure 3b). The ESR spectrum of a frozen solution of sodium in DPA signifies, by virtue of the resolved hyperfine coupling to ^{23}Na ($I = {}^3/_2$), the direct electron $-$Na$^+$ interaction for the association complex Na$_s^+$e$_s^-$. The quartet resonance is centered around $g = 2.0003$ and has a hyperfine coupling constant $A_M(^{23}$Na$) = 3.8$ G. The percent atomic character of this association complex is approximately 1% compared to the gaseous (free) sodium atom. Similarly, we have also observed resolved metal-hyperfine coupling in quenched Rb–DEA solutions, and the percent atomic character for the Rb$_s^+$e$_s^-$ species ($I = {}^5/_2$; ^{85}Rb) is also in the region of 1%.

The microwave power saturation characteristics of the trapped electron and the association complex, Na$_s^+$e$_s^-$, yield electron spin–lattice (T_{1e}) relaxation times for these species. Complete details of the experimental procedures are outlined elsewhere.[21] Briefly, a plot of ESR signal amplitude against the square root of the incident microwave power, P, gives a maximum when the following condition is satisfied,

$$H_1 \gamma (T_{1e} T_{2e}) = 1/2^{1/2} \tag{4}$$

where H_1 is the amplitude of the circularly polarized component of the microwave magnetic field at frequency ω, γ is the electron gyromagnetic ratio, and T_{2e} is the electron spin–spin relaxation time, calculated from ΔH_{pp} at low power. Equation 4 is strictly applicable only for homogeneously broadened ESR signals; in the present instance some degree of inhomogeneity is evident from the power saturation data. In this situation, the exact determination of T_{1e} and T_{2e} proceeds via a more elaborate approach.[21] For our purposes, an order of magnitude estimate of T_{1e} is called for, and using eq 4, we estimate $T_{1e} \simeq 3 \times 10^{-4}$ s for the trapped electron, and $T_{1e} \simeq 3 \times 10^{-5}$ for the association complex Na$_s^+$e$_s^-$ in frozen solutions of sodium in DPA at 145 K.

The presence of (at least) two paramagnetic species in the frozen metal solutions suggests that the single line observed in the fluid samples represents a time-average of the signals from e_s^- and M$_s^+$e$_s^-$. Note that the Fuoss equation predicts[7] (from the dielectric constant of DEA and an estimate of the encounter radii for e_s^- and M$_s^+$) a residence time, τ_M, for the electron in the encounter complex Na$_s^+$e$_s^-$ of the order of 10^{-10} to 10^{-11} s in DEA at room

temperature. The observation of only a single line in the ESR of these fluid solutions requires $\tau_M^{-1} \gg A_M$, where A_M is expressed in frequency units (Hz). If we assume that the sodium hyperfine coupling constant observed (Figure 3b) in the low-temperature solids ($A_M \sim 1 \times 10^7$ Hz) is characteristic of the liquid-phase species Na$_s^+$e$_s^-$ then we do indeed find this condition to be satisfied. In fact, we estimate $\tau_M A_M \simeq 10^{-3}$–$10^{-4}$ for the Na/DEA solution at room temperature.

With this ESR information, we can comment on the noticeable absence of an NMR signal from the species Na$_s^+$ or Na$_s^+$e$_s^-$ in the liquid solution, while the metal anion species is readily observed (Figure 2). Any ^{23}Na NMR resonance from the complex Na$_s^+$e$_s^-$ would have a natural width determined by an exchange component of the form $\pi^{-1} \langle A_M^2 \rangle \tau_M$ where $\langle A_M^2 \rangle$ is now the mean square (rigid lattice) hyperfine coupling constant for the encounter species Na$_s^+$e$_s^-$. This yields an NMR line width of ca. 10^4 Hz if we take A_M from the frozen solution data, with $\tau_M = 10^{-10}$ s. This exchange width must be augmented by the (already large) quadrupolar width of ca. 100–300 Hz for Na$^+$ in the neat DEA solution (Table IV). Therefore, a combined width of at least 10^5 Hz is anticipated for the encounter species Na$_s^+$e$_s^-$ in this system. Changing our estimate of τ_M to ca. 10^{-11} s still predicts an NMR line width of some 10^3 Hz in the fluid metal solution. The absence of any NMR from "uncomplexed" sodium cations (i.e., Na$_s^+$) in the metal solution is similarly due to the very rapid formation/dissociation of the constitutive members (Na$_s^+$, e_s^-) of the association complex.

In summary, then, the ESR data are helpful in the present context since, first, they provide independent evidence for the presence of at least two paramagnetic species—one metal based—in the sodium DPA and DEA systems (taken as representative). Secondly, the electronic structure and dynamics of Na$_s^+$e$_s^-$ in these systems as revealed by the ESR data provide an explanation for the lack of any cationic-based NMR resonance in fluid solutions containing high, detectable concentrations of Na$^-$.

D. Chemical Equilibria. By combining the ESR and NMR data for the metal solutions we are able to comment briefly on the relative rates of possible electron exchange processes occurring in these solutions. Clearly, in the sodium solutions, the exchange process

$$*\text{M}_s^+\text{e}_s^- + \text{M}_s^+ \rightleftharpoons *\text{M}_s^+ + \text{M}_s^+\text{e}_s^-$$
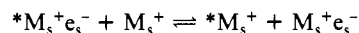
occurs on a considerably faster time scale than the corresponding process limiting the lifetime of Na$^-$ by a one-electron exchange, viz:

$$\text{M}_s^+\text{e}_s^- + *\text{M}^- \rightleftharpoons \text{M}^- + *\text{M}_s^+\text{e}_s^-$$
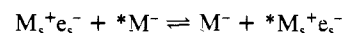
Stable solutions of K, Rb, and Cs in DEA and Rb and Cs in DMP (Table I) gave *no* NMR signals, either from M$_s^+$ or M$^-$. (For the heavier elements, M$^-$ could react very rapidly with the solvent resulting in steady-state concentrations too low for detection.) However, we also point out that all solutions of the heavier elements certainly remained blue for periods well in excess of the required accumulated pulse sequences. Furthermore, ^{1}H and ^{13}C spectra were readily obtained (Table III) from these blue solutions. As with other systems,[9] these results suggest that *for the heavier alkali metals* exchange processes are sufficiently fast to cause signals from M$^-$ to be both paramagnetically shifted and broadened beyond detection. Indeed Dye et al. note difficulties[11,22] even in the three-component (metal + solvent + crown/cryptand) systems, in routinely observing NMR resonances from the heavier alkalide ions. Certainly NMR observations on the higher anions are sparse. In certain systems in which Rb$^-$ and Cs$^-$ are detected, for example, in the three-component system[11] Rb/EtNH$_2$/C222, the line width of the anion is sometimes (but not always) comparable to that of the solvated cations[11,17] in the neat solvent. Thus the lines due to Rb$^-$ and Cs$^-$ may have been broadened either

(19) Edmonds, R. N.; Edwards, P. P.; Guy, S. C.; Johnson, D. C. *J. Phys. Chem.* **1984**, *88*, 3764.

(20) Edmonds, R. N.; Edwards, P. P. *Proc. R. Soc. London*, A **1984**, *395*, 341.

(21) Details of the methods to derive T_{1e} and T_{2e} from power saturation data are given in the following: Poole, C. P. "Electron Spin Resonance", 2nd ed.; Wiley: New York, 1983.

(22) Dye, J. L. *Prog. Macrocyclic Chem.* **1979**, *1*, 63.

(23) Holz, M.; Zeidler, M. D. In "Specialist Periodical Report, Nuclear Magnetic Resonance"; The Chemical Society, London: 1977; Vol. 6, p 92.

Scheme II
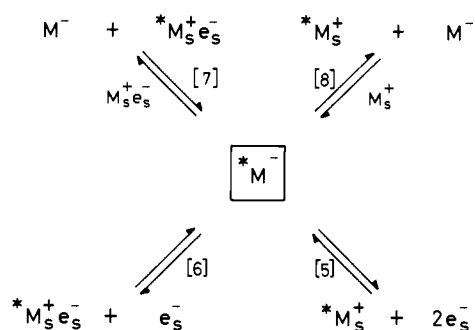
paramagnetically (e.g., by e_s^-) or by exchange.

The exchange processes which effectively limit the lifetime of M^- in solutions, and hence may cause NMR broadening, are equilibria 5–8 given in Scheme II. We have already ruled out (7) as a contender for fast exchange in sodium solutions. Our ESR spectra show the concentration of e_s^- in Na–DPA solutions to be relatively low, suggesting equilibria 5 and 6 lie to the left as found previously for Na^- in other systems.[24] Equilibrium 8 involves a M_s^+–M^- exchange process, perhaps in a binuclear complex M_s^+–M^-, and this is likely to be the rate-limiting step which results in lifetime broadening of the NMR.[25,26] A detailed analysis of nuclear spin relaxation in Na^- is currently under way.

Results on Rb^- and Cs^- in other systems (e.g., 12-crown-4[17] and three-component systems[11]) indicate a greater solvent involvement in the ground-state wave function of these larger alkalide ions.[14] This appears to result in more efficient nuclear relaxation, giving rise to extremely broad NMR resonances. Clearly, in the present system, a substantial "solvation" of the heavier anions may be occurring, resulting in rapid electron/cation exchange (eq 2, 3, 5, and 6).

E. Reduction Mechanisms. In an elegant study of the reduction of N,N-dimethylacetamide (DMA) by sodium in liquid ammonia Young and Dewald[27] found a fourth-order rate law to be obeyed:

$$-d(e_s^-)/dt = [e_s^-][Na_s^+][e_s^-][amide]$$

Within the overall context of Scheme I, this could implicate the triple-ion, $e_s^-Na_s^+e_s^-$, as one of the reducing species in Na–NH₃ solutions. However, this might imply that the rates of all Na–NH₃ reductions are sodium ion dependent, which does not seem to be the case. Young and Dewald[27] suggest that the reaction sequence envisaged for the M–NH₃ reduction of the amide may also be responsible for the decomposition of the metal–amide solutions. In the amide-like solvents the corresponding reducing species may now be the sodium anion, Na^-. Clearly in TMU the decomposition reaction is facile; in certain of the other tertiary amides the identification of Na^- as a stable, long-lived entity suggests a relative inertness of the solvents toward concerted electron/anion attack at the carbonyl group. This is also demonstrated from the pulse radiolysis studies in these systems.[4,5]

Attempts to reduce DEA in Na–NH₃ solutions and to study Na/DMA and Na/DEA systems have shown DEA to be more resistant to reduction than the dimethyl analogue.[27] Whether the relative inertness of DEA results from steric[28] or electronic[29] effects is not clearly understood at present. The inertness of DEA to Na–NH₃ solutions is reminiscent of the behavior of HMPA which is not readily cleaved by e_s^-, either in Na–NH₃ or in HMPA itself.[30] The stability of HMPA solutions increases by a factor of 3–4 when the temperature is lowered from 298 to 283 K. Likewise, certain metal–amide solutions are stable at reduced temperatures but decompose more rapidly at room temperature. It is interesting to note the corresponding changes in behavior of e_s^- via pulse radiolysis studies.[5] Lowering the temperature increases both the lifetime and the radiolytic yield of solvated electrons in neat DEA.

(24) Dye, J. L. *Prog. Inorg. Chem.* **1984**, *32*, 327.
(25) Phillips, R. C.; Khazaeli, S.; Dye, J. L. *J. Phys. Chem.* **1985**, *89*, 606.
(26) Edwards, P. P. *Adv. Inorg. Chem. Radiochem.* **1982**, *25*, 135.
(27) Young, C. A.; Dewald, R. R. *J. Am. Chem. Soc.* **1979**, *101*, 2884.
(28) Young, C. A., private communication.
(29) Jones, R. L.; Dewald, R. R. *J. Am. Chem. Soc.* **1974**, *96*, 2315.
(30) Dewald, R. R. *J. Phys. Chem.* **1975**, *79*, 3044.

Structural Differentiation of CO and O₂ Binding to Iron Porphyrins: Polar Pocket Effects

T. G. Traylor,* Noboru Koga, and Larrie A. Deardurff

Contribution from the Department of Chemistry, D-006, University of California, San Diego, La Jolla, California 92093. Received March 18, 1985

Abstract: A new iron porphyrin, 3,5-pyridine-5,5-hemecyclophane, has been prepared, and its dioxygen and carbon monoxide binding studied. In contrast to other "strapped" pyridines with larger cyclophane links, this compound shows no tendency to bind its attached pyridine. With use of 1,5-dicyclohexylimidazole as proximal base, a five-coordinated heme is obtained. This heme shows severe steric hindrance toward both dioxygen and carbon monoxide binding. It displays a ratio of carbon monoxide to dioxygen affinities as low as 5, a much lower binding ratio than those shown by any other model systems, by hemoglobin, or by myoglobin. This suggests ways of preparing artificial dioxygen-binding materials which preferentially bind dioxygen.

The relative affinities of carbon monoxide and dioxygen to hemes and hemoproteins is of great current interest, both with

respect to the understanding of those factors which govern these affinities in biological systems[1–12] and in regard to the preparation