NN-Diethylacetamide, *NN*-Dipropylacetamide, *NN*-Dimethylpropanamide, Tetramethylurea, and Tetraethylurea: Solvents for Alkali Metals

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Summary Sodium was found to dissolve in *NN*-diethylacetamide, *NN*-dimethylpropanamide, and tetramethylurea while Na–K alloy dissolved in tetraethylurea, *NN*-dipropylacetamide and *NN*-dimethylpropanamide forming metastable blue solutions of varying stability.

We report preliminary observations concerning the dissolution of the alkali metals in *NN*-diethylacetamide (DEA), tetraethylurea (TEU), *NN*-dipropylacetamide (DPA), *NN*-dimethylpropanamide (DMP), and tetramethylurea (TMU). We have found that these structurally related solvents form metastable blue solutions with certain alkali metals or with Na–K alloy. Studies of the unique chemical and physical properties of metal solutions[1] formed by the dissolution of alkali metals in such solvents as ammonia,[1,2] hexamethylphosphoramide[3] (HMPA),[3,4] and various amines[5,6] and ethers[5,7] have been, and are currently, the subject of a great deal of interest.

All solvents and metals used in this study were obtained in the highest purity commercially available. The solvents were further purified by at least two high-vacuum distillations: first from calcium hydride or sodium and then from freshly distilled sodium or Na–K alloy. All metal solutions were prepared in borosilicate glass systems using high vacuum techniques (*ca.* 5×10^{-6} Torr). A Cary 17 recording spectrophotometer was used to record optical spectra using borosilicate cells of 1·0-mm nominal path length.

When DEA was poured on previously distilled sodium metal, a dark blue solution formed immediately upon contact at room temperature. When the blue solution was removed from contact with the Na metal, the blue colour disappeared in *ca.* 10—15 min at room temperature but at dry-ice temperature the blue colour persisted for a day or longer. When the Na–DEA solution was frozen with liquid nitrogen, the resultant solid also exhibited a uniform dark blue colour. The optical absorption spectrum of the blue solution showed the presence of two maxima: one peak located in the visible region at *ca.* 700 ± 20 nm and another very broad band at 1500 ± 200 nm. The former band is characteristic of the metal anion, Na^-,[5] while the latter is consistent with assignment to solvated electrons.[5,8] The optical spectra of the Na–DEA solution is very similar to that observed in the case of Na–HMPA solutions[4] except that the band due to the solvated electron is at shorter wavelengths.

A dark blue solution formed immediately upon contact of TEU with Na–K alloy at room temperature. This solution exhibited only one optical absorption maximum, at *ca.* 735 nm. This band is consistent with metal anions being the absorbing species.[5,8] TEU appeared to be inert when in contact with Na, *i.e.* no reaction or dissolution of the metal was observed. When TEU was in contact with K metal for about a day an extremely faint blue solution was observed.

When DPA was poured over Na–K alloy a blue solution formed, the colour of which disappeared too rapidly at room temperature to obtain a meaningful optical spectrum. Both Na and K did not appear to dissolve or react with DPA at room temperature. Caesium metal did not appear to dissolve in DPA to form a blue solution but some reaction was evident.

Both Na and Na–K alloy dissolved in DMP to yield transient blue solutions the colour of which was too short-lived for optical spectra to be obtained at room temperature.

Sodium dissolved readily in TMU forming a blue solution at room temperature which was too unstable for an optical spectrum to be obtained. A solution of naphthalene in TMU turned dark green when poured momentarily on sodium. The green solution was very stable (no visible discharge of colour after several days) and the solution exhibited an optical spectrum characteristic of the naphthalene radical anion.[9] Prolonged exposure of the green solution to sodium resulted in a dark red solution characteristic of the naphthalene dianion.[9] The red solution, however, was not stable presumably because of protonation by the solvent.[9]

We believe that it will be possible to improve the stability of the various metal solutions reported herein by more rigorous purification of materials and cleanliness of glassware. The use of these metal solutions as reducing media warrants investigation. Moreover, the present study suggests that some of these solvents might replace HMPA (a toxic and carcinogenic compound[10]). Also, these solvents find utility as media for electrochemical studies.[11]

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