New concept for the preparation of potassium sodides: the use of hexane as a non-polar solvent

Zbigniew Grobelny,[a] Andrzej Stolarzewicz,[a,b,*] Barbara Morejko-Buż[a,b] and Antoni Winiarski[c]

[a]Centre of Polymer Chemistry, Polish Academy of Sciences, 41-819 Zabrze, Poland
[b]Institute of Physics and Chemistry of Metals, University of Silesia, 40-007 Katowice, Poland
[c]Institute of Physics, University of Silesia, 40-007 Katowice, Poland

Abstract—NaK alloy in contact with 15-crown-5 hexane solution became potassium sodide $K^+(15$-crown-5$)_2Na^-$. After the evaporation of hexane the crystalline solid product was analyzed by X-ray diffraction and the lattice parameters were calculated. The potassium sodide thus obtained could be easily dissolved in tetrahydrofuran. A deep blue solution containing sodium anions and complexed potassium cations was formed with a very low concentration of solvated electrons, i.e. of the order of 10^{-7} M. Potassium anions were not detected in this case. A new crystalline potassium sodide $K^+(DCH$-24-crown-8$)_2Na^-$ was obtained using NaK alloy and dicyclohexano-24-crown-8 hexane solution. © 2003 Elsevier Science Ltd. All rights reserved.

1. Introduction

It was known that the liquid eutectic NaK alloy is soluble in ethers, e.g. in tetrahydrofuran ($\varepsilon=7.58$, $\mu=1.75$).[1] Addition of crown ether, e.g. 15-crown-5 (15C5),[2] 18-crown-6 (18C6),[2,3] or dicyclohexano-24-crown-8 (DCH24C8)[4] increased markedly the solubility of metals. Sodium anions (Na^-) and complexed potassium cations (K^+C) were the main species in those solutions whereas the concentration of potassium anions (K^-) was low.[2,4] The [K]/[Na] ratio remained constant during dissolution of the alloy and it was equal to about 1.2.[5] The concentration of metals in saturated solutions was two times greater than the concentration of 18C6[3] and equal to the concentration of 15C5[5] or DCH24C8,[4] respectively. Solvated electrons (e_s^-) were observed in these solutions; their concentrations were of the order of 10^{-5} M.[4,5] Sodium cations were not detected in those systems.[2,4] It was also possible to dissolve NaK alloy in liquid crown ethers.[6] The latter operated, in this case, simultaneously as complexing agents and solvents. A similar phenomenon was observed for some solvents, e.g. for tetraglyme in which NaK was soluble very well without crown ether.[1] All solutions possessed a characteristic deep blue color due to the presence of metal anions.[7]

It was also possible to obtain crystalline colored salts containing alkali metal anions and complexed metal cations, called alkalides by Dye.[8] A great number of them were studied by Dye and his co-workers.[8–12] It was suggested that the most stable were potassium sodides and rubidium sodides, especially $K^+(15C5)_2Na^-$ and $Rb^+(15C5)_2Na^-$.[8] However, it was recently reported that alkalides prepared with the use of the fully methylated aza-analog of cryptand [2.2.2], i.e. without oxygen atoms in the molecule, were stable for weeks at ambient temperature.[13] The crystal structure of alkalides was found to be predominantly monoclinic (e.g. $Cs^+(15C5)_2Na^-$) but orthorombic structures (e.g. $Cs^+(18C6)_2Cs^-$) were also observed.[10]

The ability to prepare alkalide films by codeposition of the complexant and metal promised to eliminate many problems connected with the evaporation method of the solvent from the metal solution.[11] However, the procedure still required the use of polar solvents and low temperatures.

In the present work we describe a new method of the formation of potassium sodides. NaK alloy and hexane as a non-polar solvent ($\varepsilon=1.89$, $\mu=0.00$) containing 15C5 or DCH24C8 were used for this purpose.

2. Results and discussion

2.1. 15C5 system

In the main series of experiments, a solution of 15C5 in hexane was mixed with an excess of NaK alloy. In this case no blue colored solution was observed to form but a dark brown product started to precipitate from the colorless hexane. The concentration of 15C5 diminished successively and the complete decay of crown ether followed after
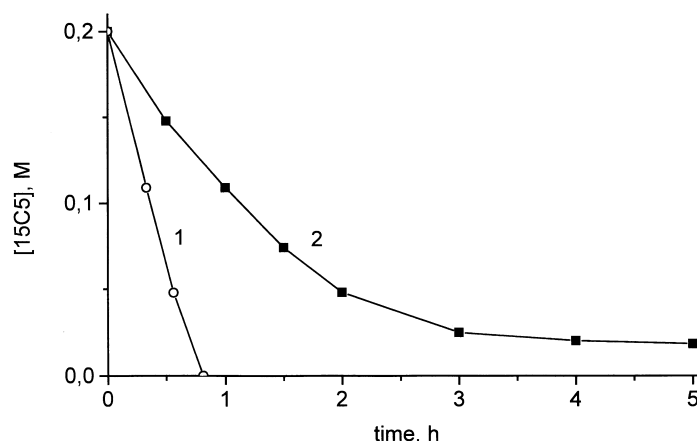
Figure 1. Changes of 15C5 concentration in hexane during its mixing with NaK alloy. Initial amount of NaK: 0.5 g (8 mmol, Na and 8 mmol, K)—curve 1, and 0.062 g (1 mmol, Na and 1 mmol, K)—curve 2. [15C5]$_0$=0.2 M. Temperature 20°C.

50 min (Fig. 1, curve 1). Then, the solvent was distilled off at reduced pressure and at ambient temperature. The solid dark brown substance was observed to form in the reactor.

The X-ray diffraction pattern of the solid substance is displayed in Figure 2(a). The diffraction lines are narrow and the spectrum clearly shows a crystalline structure of the compound. Moreover, the spectrum seemed to be similar to the spectra of known alkalides. Therefore, appropriate crystallographic data placed in the literature[10,14,15] were used as the starting parameters to determine the structure of the measured substance. The calculations pointed to its monoclinic structure with the following lattice parameters: a=12.7 Å, b=14.7 Å, c=18.5 Å and β=95°. It was also found that the unit cell of the product consisted of four molecules.

The solid substance was very well soluble in tetrahydrofuran giving a deep blue solution. Undissolved balls of NaK were observed on its surface. In order to separate unreacted alloy the solution was filtered. The concentration of metals in this solution was equal to the initial concentration of 15C5. The solution contained Na$^-$ and K$^+$(15C5)$_2$ ions; K$^-$ ions were not detected in ^{39}K NMR spectra. The Na/K molar ratio was 1:1. The concentration of e$_s^-$ was unexpectedly 3.7×10^{-7} M, i.e. two orders lower than in the solution

obtained by the direct dissolution of NaK alloy in tetrahydrofuran with 15C5.[7]

In the next experiments, NaK alloy and 15C5 were introduced in (1:1):2 molar ratio into hexane. This resulted in the decay of 90% of crown ether in the organic layer after 4 h (Fig. 1, curve 2). Then, the concentration of 15C5 in hexane did not change over a long period. The solid dark brown substance was observed after evaporation of the solvent. However, small amounts of NaK alloy were still present in the reaction products.

The experiments clearly indicated that NaK alloy did not dissolve in hexane even in the presence of crown ether, however, its complex with 15C5 undoubtedly caused the formation of the solid phase. This was confirmed by the decay of metallic color of the alloy showing that delocalized electrons underwent localization, the transition of the crown molecules from hexane solution into the alloy, the formation of the dark brown product, and the results of its crystallographic analysis.

Consequently, it was assumed that in the studied process, NaK alloy formed potassium sodide K$^+$(15C5)$_2$Na$^-$ **1** with 15C5. This alkalide was well soluble not only in tetrahydrofuran but also in other polar solvents as tetrahydropyran (ε=5.61, μ=1.55) or tetraglyme (ε >7.20, μ=1.97) giving deep blue solutions. The solubility of **1** was poor, below <10^{-3} M in solvents of a low polarity, e.g. diisopropyl ether (ε=3.88, μ=1.22), dibutyl ether (ε=3.06, μ=1.16) or 1,4-dioxane (ε=2.21, μ=0.00).

Similarly, like other alkalides, **1** underwent decomposition at ambient temperature. Its dark brown color turned into a light gray in several days. However, **1** could be kept for a long time in an inert atmosphere at temperatures below −20°C. Then, after its dissolution in tetrahydrofuran it was possible to use it as a strong reducing agent. Its solution was applied for example in reactions with methyloxirane and oxetane. The reaction products were the same as by the use of K$^+$(15C5)$_2$K$^-$ solution obtained after potassium dissolution in tetrahydrofuran containing 15C5.[16,17] In the case of methyloxirane they involved benzyl isopropyl ether and tetraethylene glycol benzyl vinyl ether after quenching with benzyl bromide. Ethylene, benzyl methyl ether, benzyl
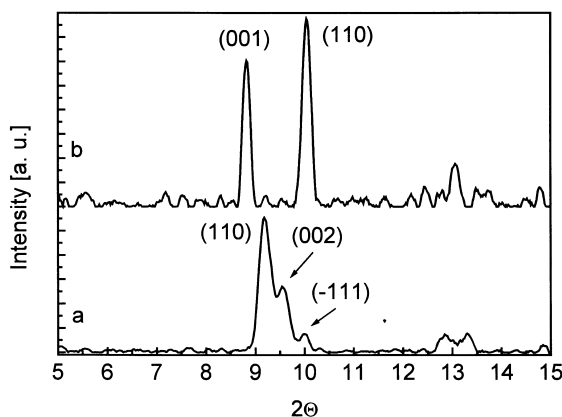

Figure 2. X-Ray diffraction spectra taken from K$^+$(15C5)$_2$Na$^-$ (a) and K$^+$(DCH24C8)$_2$Na$^-$ (b). The most intense lines are indicated with the Miller indices.

propyl ether and tetraethylene glycol benzyl vinyl ether were formed in the reaction with oxetane.

On the other hand, an application of the suspension of **1** in hexane can also be helpful. It is known that the solvent polarity possesses in some cases a large influence on the regioselectivity of the ether bond cleavage. For example in the reaction of NaK alloy with anisole in tetrahydrofuran solution the alkyl–oxygen bond was cleaved (in 96% yield) whereas, in heptane the scission of the aryl–oxygen bond was observed (in 98%).[18]

As mentioned, the enhanced stability of **1** was already described in the literature,[8] however, it seems that its other properties are presented for the first time in this work.

2.2. DCH24C8 system

The dependence of the concentration of DCH24C8 in hexane in contact with NaK alloy had a similar character to that presented in Figure 1. The dark brown product was also precipitated in this case during mixing of the reagents. The X-ray spectrum of this solid product, obtained after the evaporation of hexane, is displayed in Figure 2(b). The spectrum points to a monoclinic structure. The calculated lattice parameters are as follows: $a=11.5$ Å, $b=13.4$ Å, $c=10.0$ Å and $\beta=91°$. The unit cell of this product seems to contain only one molecule. The calculations also indicate that the potassium cation presented in the solid product formed with DCH24C8, a sandwich 1:2 complex. Such a complex was already suggested to exist in NaK tetra-hydrofuran solution prepared in the presence of DCH24C8.[4] The results show that a new crystalline potassium sodide was obtained, i.e. $K^+(DCH24C8)_2Na^-$ **2**. According to our best knowledge such an alkalide has not previously been described in the literature.

Solid compound **2** was dissolved in tetrahydrofuran to confirm the proposed structure of the potassium complex. The concentration of metals in this solution reached a value equal to the initial crown concentration. The concentration of e_s^- was equal to 10^{-5} M. This was the same result as found by the preparation of the blue alkalide solution from NaK alloy and tetrahydrofuran containing DCH24C8.[4]

Thus, a structure for the potassium complex with two DCH24C8 molecules seems to be very probable. On the other hand, this statement might be rather unexpected because dibenzo-24-crown-8 (DB24C8) possessing the same number of oxygen atoms is ever known to form a complex with two potassium cations.[19] However, the ability of DCH24C8 to form sandwich complexes in some strong polar solvents was earlier confirmed for the cesium cation.[20] In that instance such complexes were also unexpected because the intramolecular cavity of the ligand was greater than the ionic diameter of Cs^+. It is worth noting that in the same conditions DB24C8 formed exclusively a flat 1:1 complex with cesium. That phenomenon was explained by the fact that the DCH24C8 ring is much more flexible than its dibenzo-analog. The cation diameter—ligand hole size relationship probably plays the greatest role when the ligand molecule is a rigid one.[21] Moreover, molecular models clearly demonstrate that more puckered conformations, i.e.

with smaller ring cavities can be assumed by various *cis*-isomers in which four proximal oxygen atoms are situated above the ring whereas, the remaining ones are below it. Such a conformation would readily permit the formation of sandwich complexes by DCH24C8 with Cs^+ as well as with K^+.

3. Conclusions

The formation of potassium sodides described in the present work occurs during the direct contact of NaK alloy with crown ether dissolved in the non-polar solvent. A dis-advantage of this method has been till now the presence of an admixture of free NaK in the reaction product. However, the blue solutions obtained after the dissolution of solid potassium sodides in tetrahydrofuran are characterized by well-defined concentrations of sodium anions and com-plexed potassium cations. They do not contain potassium anions. The extremely low concentration of solvated electrons was observed for the use of 15C5.

4. Experimental

4.1. Materials

NaK alloy was prepared by mixing of 3.91 g (0.1 mol) of potassium (Aldrich) with 2.3 g (0.1 mol) of sodium (Aldrich). Hexane (Aldrich) was dried over CaH_2 and distilled. Tetrahydrofuran, tetrahydropyran, tetraglyme, diisopropyl ether, dibutyl ether and 1,4-dioxane (all Aldrich) were purified as in the literature.[7] 15C5 and DCH24C8 (both Aldrich) were also used as in the literature.[22]

4.2. Preparation of solid potassium sodides and their solutions

10 cm^3 of 0.2 M 15C5 (0.44 g, 2 mmol) or DCH24C8 (0.92 g, 2 mmol) in hexane was introduced into a 50 cm^3 reactor filled with dry argon and containing 0.5 g of NaK alloy (8 mmol Na and 8 mmol K) or 0.062 g of NaK alloy (1 mmol Na and 1 mmol K). The reactor was placed in an ultrasonic bath thermostatted at 20°C. Hexane was evapo-rated under vacuum giving the solid potassium sodide. Then, 10 cm^3 of tetrahydrofuran was added into the reactor. After mixing during 15 min the blue solution was filtered through a glass frit. A 0.1 M solution of potassium sodide was obtained in this way.

In the case of X-ray diffraction analysis the samples were prepared as follows. The suspension of **1** or **2** obtained in the reactor was thickened by evaporation of a part of hexane (about 7 cm^3). Then, 1 cm^3 of paraffin oil was poured into the system and mixed together. After the evaporation of the remaining hexane the mixture was then placed on a copper plate and put in the diffractometer.

4.3. Measurements

^{39}K and ^{23}Na NMR measurements were performed on a Varian VXR-300 multinuclear pulsed spectrometer operating

at the ^{39}K resonance frequency of 14 MHz and ^{23}Na resonance frequency of 79.3 MHz. Chemical shifts in ^{39}K NMR spectra were measured relative to the K$^+$ signal from the potassium fluoride solution in D$_2$O. ^{23}Na NMR spectra were referenced to the Na$^+$ signal from a sodium chloride solution in D$_2$O.

Electron spin resonance (ESR) measurements were carried out with an ESR 300 Bruker X-band spectrometer employing 100 kHz field modulation and a microwave frequency of ca. 9.6 GHz. In order to determine the concentration of paramagnetic species a double rectangular cavity was used. A solution of 2,2-bis(4-*tert*-octylphenyl)-1-picrylhydrazyl (DPPH) served as a reference.

Potassium sodides were analyzed by X-ray diffraction using a Siemens X-ray Powder Diffractometer D5000. The measurements were conducted under vacuum at ambient temperature. Cu K$_\alpha$ radiation was applied in the 2Θ range of 2.5–50° with the 2Θ step equal to 0.02°. The background was cut using the DIFFRACT AT program with parabolic approximation. The lattice and positional parameters of Cs$^+$(15C5)$_2$K$^-$, Rb$^+$(15C5)$_2$Rb$^-$ and Rb$^+$(15C5)$_2$Na$^-$ taken from the literature[10,14,15] were modified with the PowderCell for Windows v.1 program to generate X-ray diffraction patterns of the measured compounds. The generated pattern was then matched to the measured X-ray diffraction pattern. The lattice parameters and the Miller indexes were found as the result of the program calculation.

The total concentration of metals (both cations and anions) was estimated by titration of their solution with 0.02 M aqueous solution of HCl using bromothymol blue as an indicator. Flame spectrophotometry was used to determine [Na]/[K] ratio. The analysis was performed on a Flapho 4 Carl Zeiss Jena photometer as described in the literature.[23]

References

1. Down, J. L.; Lewis, J.; Moore, B.; Wilkinson, G. *J. Chem. Soc.* **1959**, 3767–3773.
2. Jedliński, Z.; Sokół, M.; Grobelny, J. *J. Phys. IV* **1991**, *1*, 291–296.
3. Grobelny, Z.; Stolarzewicz, A. *Pol. J. Chem.* **1981**, *55*, 1933–1936.
4. Sokół, M.; Grobelny, Z.; Stolarzewicz, A. *J. Phys. Chem.* **1995**, *99*, 12670–12676.
5. Grobelny Z, personal communication.
6. Holton, D. M.; Ellaboudy, A. S.; Edmonds, R. N.; Edwards, P. P. *Proc. R. Soc. Lond. A* **1988**, *415*, 121–140.
7. Stolarzewicz, A.; Grobelny, Z.; Grobelny, J. *Spectrochim. Acta A* **2000**, *56*, 1257–1265.
8. Dye, J. L. *J. Phys. Chem.* **1984**, *88*, 3842–3846.
9. Dye, J. L. *Pure Appl. Chem.* **1989**, *61*, 1555–1562.
10. Dye, J. L. *J. Phys. IV* **1991**, *1*, 259–282.
11. Le, L. D.; Issa, D.; Van Eck, B.; Dye, J. L. *J. Phys. Chem.* **1982**, *86*, 7–9.
12. Ellaboudy, A.; Tinkham, M. L.; Van Eck, B.; Dye, J. L. *J. Phys. Chem.* **1984**, *88*, 3852–3855.
13. Kim, J.; Ichimura, A. S.; Huang, R. H.; Redko, M.; Phillips, R. C.; Jackson, J. E.; Dye, J. L. *J. Am. Chem. Soc.* **1999**, *121*, 10666–10667.
14. Ward, D. L.; Huang, R. H.; Dye, J. L. *Acta Crystallogr. Sect. C* **1990**, *46*, 1838–1841.
15. Daves, S. B.; Ward, D. L.; Fussa-Rydel, O.; Huang, R. H.; Dye, J. L. *Inorg. Chem.* **1989**, *28*, 2132–2136.
16. Grobelny, Z.; Stolarzewicz, A.; Czaja, M.; Demuth, W.; Maercker, A. *J. Org. Chem.* **1999**, *64*, 8990–8994.
17. Grobelny, Z.; Stolarzewicz, A.; Maercker, A. *J. Organomet. Chem.* **2000**, *604*, 283–286.
18. Maercker, A. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 972–989.
19. Poonia, N. S. *Progress in Macrocyclic Chemistry*, Izatt, R. M., Christensen, J. J., Eds.; Wiley: New York, 1979; Vol. 1, pp 115–155.
20. Soong, L.-L.; Leroi, G. E.; Popov, A. I. *Inorg. Chem.* **1990**, *29*, 1366–1372.
21. Gokel, G. W.; Goli, D. M.; Minganti, C.; Echegoyen, L. *J. Am. Chem. Soc.* **1983**, *105*, 6786–6788.
22. Grobelny, Z.; Stolarzewicz, A.; Sokół, M.; Grobelny, J.; Janeczek, H. *J. Phys. Chem.* **1992**, *96*, 5193–5196.
23. Grobelny, Z.; Stolarzewicz, A. *Pol. J. Chem.* **1981**, *55*, 2517–2521.