
**ON THE BEHAVIOUR AND REACTIVITY
OF SOLUTIONS OF COMPLEX HYDRIDES. IX.*****A CRYOSCOPIC STUDY OF THE ASSOCIATION AND SOLVATION
OF SODIUM (2-METHOXYETHOXY)HYDRIDOALUMINATES**

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Employing the cryoscopic method, the apparent degrees of association of sodium 2-methoxyethoxyhydridoaluminates in relation to their concentrations in benzene have been determined. Sodium bis(2-methoxyethoxy)dihydridoaluminate has been found to form solvates with benzene and tetrahydrofuran, in which the ratio of the hydride to the donor ranges from 2 : 1 to 1 : 1, depending on the starting ratio of these two components. With isomolar series sodium bis(2-methoxyethoxy)dihydridoaluminate-donor-benzene, displacement of benzene did not occur even in the case of strong donors.

The apparent degrees of association (n) of sodium bis(2-methoxyethoxy)dihydridoaluminate, $\text{NaAlH}_2(\text{OCH}_2\text{CH}_2\text{OCH}_3)_2$ in benzene and/or tetrahydrofuran at 25°C were previously determined ebulliometrically¹. The present paper describes a cryoscopic study of the dependence of n on the concentration of sodium dihydrido-bis(2-methoxyethoxy)aluminate (*I*), sodium hydrido-tris(2-methoxyethoxy)aluminate (*II*), $\text{NaAlH}(\text{OCH}_2\text{CH}_2\text{OCH}_3)_3$, sodium hydrido-tris(2-dimethylaminoethoxy)aluminate (*III*), $\text{NaAlH}(\text{OCH}_2\text{CH}_2\text{N}(\text{CH}_3)_2)_3$, and sodium tetrakis(2-methoxyethoxy)aluminate (*IV*), $\text{NaAl}(\text{OCH}_2\text{CH}_2\text{OCH}_3)_4$, in benzene. The measurements with the compounds *III* and *IV* were carried out for the purpose of comparisons. The paper also deals with the solvation of the hydride *I* by various donors. This problem was studied by cryoscopic measurements of ternary systems hydride-donor-benzene, the method of isomolar series² being employed. The same method was applied to studying the solvation of the hydrides *II* and *III* by benzene in cyclohexane, in which either hydride is soluble. The solvation of *I* (*IV*) by benzene has been studied in the systems *I* (*IV*)-benzene-cyclohexane, in which both the non-solvated compound and the possibly formed solvate are insoluble. The interpretation of the data obtained with these pseudoternary systems is based on the assumption that a change in the melting point of cyclohexane is due exclusively to the presence of free benzene.

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EXPERIMENTAL

Chemicals. The hydrides had been prepared in our laboratory^{3,4}. Their purity was tested by analytical determination of the ratio Na : Al : H⁻; within the range of experimental error the found ratios were identical with the calculated ones. The solvents were dried over lithium tetrahydroaluminate or calcium hydride and distilled prior to immediate use.

Procedure. The depression of the melting point, ΔT_m , was measured in a cryoscopic apparatus, adapted for work in an inert medium. The measuring vessel was dried before every experiment by heating to 60°C at 1 Torr. The temperature was read on a Beckmann thermometer with an accuracy of $\pm 0.003^\circ\text{C}$. The melting points, T_m , were determined by the method of warming curves. Besides ΔT_m , in some cases we also determined the depressions of the freezing points, ΔT_f , from cooling curves. There were no appreciable differences between the values of n calculated from ΔT obtained by these two methods. The value of T_m of the solvent was measured before every series of experiments. The n value of the hydrides in benzene solutions was calculated with a cryoscopic constant⁵ of 5.1. The apparatus was tested by determining the molecular weight of tetrahydrofuran in benzene; in the concentration range 0.02 to 0.45 m its value was found to be 74.0 ± 0.3 (the theoretical value is 72.1). The apparent degrees of association, n , were calculated from the relation $n = 1000K_m w_2 / \Delta T_m M w_1$, wherein K_m is the cryoscopic constant, M theoretical molecular weight of the compound, w_1 and w_2 the weights (g) of benzene and the compound, respectively.

RESULTS AND DISCUSSION

Binary systems. The relations between n and the concentrations of the studied hydrides in benzene are shown in Fig. 1. The curves show that the hydride *I* forms oligomers, the value of n being strongly concentration-dependent. Comparison of our cryoscopic data with the ebulliometric ones in the overlapping concentration range reveals that the agreement is very good at low concentrations (0.2 to 0.4 m), where $n < 10$, whereas in more concentrated solutions the values of n determined ebulliometrically are significantly lower. These differences in n , determined at temperatures 5°C and 25°C, suggest depolymerization of the higher oligomers ($n > 10$) with increasing temperature. The plot of n vs concentration at 5°C was linear throughout the concentration range measured. Extrapolation of the graph to zero concentration gave the limit value of n , equalling approx. 4. The hydride *II*, in contrast to *I*, exhibited a constant $n \approx 2.8$ in the same solvent (benzene). For the sake of comparison the values of n were measured in the system *IV*-benzene, and were found to increase moderately with concentration. The limit values for zero concentration was ≈ 2 .

In the series $\text{NaAlH}_4 - n(\text{OCH}_2\text{CH}_2\text{OCH}_3)_n$ the association has been found to increase with n in the order $2 \gg 3 > 4$, so that it is dependent on the number of hydride anions in the molecule. However, the nature of the association phenomena cannot be interpreted unequivocally from these results alone. It should be borne in mind that the compound *IV* can associate through the oxygen atom only, whereas the hydrides can associate by means of hydrogen bonds as well. If there is only one hydridic

atom in a molecule (*II* and *III*) the interlinking can occur through this one atom only, with the formation of chains, whereas compounds with more hydridic atoms (*I*) can give rise to more complex, multibridged particles of higher n values.

The effect of replacement of the donor oxygen at position 2 of the ethoxy group by nitrogen was investigated by comparing the apparent association of the hydride *III* with the results obtained for the analogous hydride *II*. It has been found that association of the two compounds in benzene is comparably concentration-independent, the apparent degree of association being about $n \approx 2.3$ in either case. It seems possible that, the character and extent of the apparent association of the alkoxyhydridoaluminates studied are given mainly by the number of hydride atoms in a molecule, and not by the nature of the donor atom at position 2 of the ethoxy group.

Ternary systems. Solvation is frequently studied cryoscopically by the method of isomolar series². This method was employed in the present study of the above-

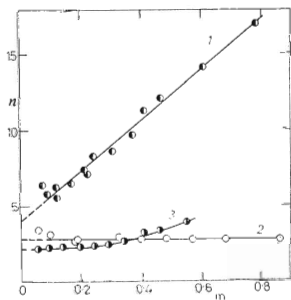


FIG. 1

The Apparent Degree of Association, n , in Benzene as a Function of Concentration
 1 $\text{NaAlH}_2(\text{OCH}_2\text{CH}_2\text{OCH}_3)_2$, 2 $\text{NaAlH}(\text{OCH}_2\text{CH}_2\text{OCH}_2)_3$, 3 $\text{NaAl}(\text{OCH}_2\text{CH}_2\text{OCH}_3)_4$.

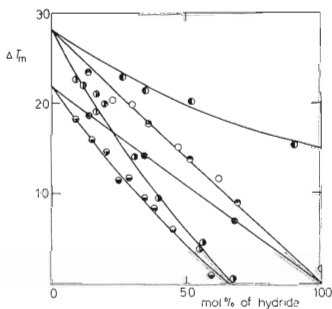


FIG. 2

Depression of the Melting Point, ΔT_m , Plotted vs the Molar Ratio of the Donor to the Hydride

Systems: benzene-cyclohexane (●), tetrahydrofuran-cyclohexane (●), $\text{NaAlH}_2(\text{OCH}_2\text{CH}_2\text{OCH}_3)_2$ -benzene-cyclohexane (○), $\text{NaAlH}_2(\text{OCH}_2\text{CH}_2\text{OCH}_3)_2$ -tetrahydrofuran-cyclohexane (◐), $\text{NaAlH}(\text{OCH}_2\text{CH}_2\text{OCH}_3)_3$ -benzene-cyclohexane (●), $\text{NaAl}(\text{OCH}_2\text{CH}_2\text{OCH}_3)_4$ -benzene-cyclohexane (○).

specified sodium alkoxyhydridoaluminates. Its applicability was verified on the system aluminium chloride–tetrahydrofuran–nitrobenzene; the results were identical with the reported ones⁶, the break occurring at a molar ratio of aluminium chloride to tetrahydrofuran = 1 : 2. The studied systems were *I*-donor–benzene, the donors being mesitylene, diethyl ether, dimethyl ether diethylene glycol, tetrahydrofuran, pyridine and cineol. Not even in one case was there found a break on the plot of ΔT_m vs the molar ratio of the donor to the hydride. This fact suggests that in benzene solutions benzene is not replaced from the solvates even by strong electron-donating agents such as cineol, pyridine and tetrahydrofuran. The systems II (III)–benzene–cyclohexane were studied in the same way (the hydrides *II* and *III* are soluble in cyclohexane). The break on the curve was found with neither hydride (the curve for *II* is plotted in Fig. 2), so that solvation by benzene is improbable in these cases.

Pseudoternary systems. Cryoscopic measurements of “ternary” systems compound–donor–solvent in which both the compound and its solvate are insoluble (pseudoternary systems) were used to investigate the solvation of the hydride *I* by benzene and tetrahydrofuran and of the compound *IV* by benzene (Fig. 2) in cyclohexane. In these systems the measured value of ΔT_m corresponded to the concentration of the free donor. Subtraction of the number of mol of the free donor from the total number of mol of the donor (n_d) gives the number of mol of the bound donor (n_d^*). The solvation number s is then calculated from the equation $s = n_d^*/n_h$, wherein n_h is the number of mol of the hydride. The plot of s vs n_d/n_h for the hydride *I* (Fig. 3) shows that at low values of the ratio n_d/n_h the molar ratio of the hydride to benzene is 2 : 1, at higher values it becomes 1 : 1. The stepwise formation of solvates is consistent with the results obtained by other methods⁷.

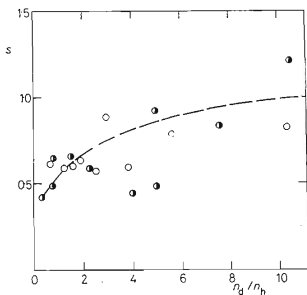


FIG. 3

The Solvation Number s in Relation to the Ratio n_d/n_h

Systems: $\text{NaAlH}_2(\text{OCH}_2\text{CH}_2\text{OCH}_3)_2$ –benzene–cyclohexane (●), $\text{NaAlH}_2(\text{OCH}_2\text{CH}_2\text{OCH}_3)_2$ –tetrahydrofuran–cyclohexane (○).

Like in the case of association, solvation can evidently be correlated with the number of hydridic atoms in the molecule of a hydride, and is independent of the nature of the donor atom at position 2 of the ethoxy group. This means that association and solvation are interdependent phenomena. With the hydride *I*, which is solvated by benzene, the value of *n* is strongly concentration dependent. By contrast, the hydrides *II* and *III* are not solvated and *n* is independent of concentration. The compound *IV* is probably not solvated either.

To conclude it can be said that the structure of the studied alkoxyhydridoaluminates in various solvents at different concentrations and temperatures is a result of complex association and solvation phenomena, dependent chiefly on the number of hydridic atoms in the molecule of a hydride. These phenomena influence their physical properties (solubility, crystallibility) and, to a lesser extent, their chemical properties as well (*e.g.* selectivity⁸ and stereospecificity⁹ in reductions).

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