ON THE BEHAVIOUR AND THE REACTIVITY OF SOLUTIONS OF COMPLEX HYDRIDES. V.*

DETERMINATION OF THE ASSOCIATION OF SODIUM BIS(2-METHOXYETHOXY)DIHYDRIDOALUMINATE IN BENZENE AND TETRAHYDROFURAN

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Using the method of inverse ebulioscopy and dynamic tensimetry the colligative properties of sodium bis(2-methoxyethoxy)dihydridoaluminate in benzene and tetrahydrofuran were determined and apparent association degrees in both solvents were calculated.

In our previous paper[1] we described an apparatus for the ebuliometry of moisture and oxygen sensitive substances. The apparatus functions on the principle of inverse ebuliometry and dynamic tensimetry. The measurements were carried out by a comparative method at a constant boiling temperature of the solution (25°C). Temperature and pressure data also enable the calculation of the empirical relations $p–T$ for the given range of temperatures and pressures. At the equilibrium state of the system and while simultaneously measuring the temperature and the pressure, samples for analysis were withdrawn from the temperature sensor space.

In this paper the determination of the association of sodium bis(2-methoxyethoxy)-dihydridoaluminate in benzene and tetrahydrofuran is described. In view of the relatively considerable difficulties connected with the work with dilute solutions of this hydride, and the errors inherent in the analytical determination of its concentration, the measurements were carried out in the range of higher concentrations. Experimentally obtained dependences of Δt on concentration were then approximated to the region of dilute solutions.

EXPERIMENTAL

When "apparent" molecular weights were calculated Antoine's equation was made use of

$$\log p = [-A/(C' - \Delta t)] + B . \qquad (1)$$

A and B values were computed from experimental data by the method of least squares on a Gier

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computer; $C' = 298.15$. In the region of dilute solutions equation (1) may be inserted into the logarithmic form of Raoult's law, and under the supposition that for $p_0 \Delta t$ is equal to zero the following equation may be obtained

$$\log x_1 = - A \Delta t / C'(C' - \Delta t) \qquad (2)$$

from which the apparent molecular weight of the measured substance may be calculated by means of analytical data. The correct functioning of the apparatus[1] was checked by the system azobenzene–benzene and phenanthrene–benzene. For the first system it was established that the deviation of the calculated molecular weights is 3·5% (from the average value 182·22) within a relatively broad concentration range, up to 12 w % (i.e. the mole fraction $x_2 = 0.0557$) (Fig. 1). In the case of the system phenanthrene–benzene the deviations of the molecular weights exceed 10% for concentrations $x_2 = 0.0126$. The following substances were used: benzene was dried with sodium bis(2-methoxyethoxy)dihydridoaluminate and rectified on a 60 TP column filled with cantal spirals.
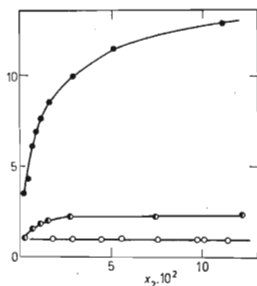

Fig. 1

Dependence of Degrees of Association (α) on Mole Fractions x_2 for Systems Benzene–Azobenzene ($\circ$), Benzene–Sodium Bis(2-methoxyethoxy)dihydridoaluminate ($\bullet$) and Tetrahydrofuran–Sodium Bis (2-methoxyethoxy)dihydridoaluminate ($\circledcirc$)

TABLE I

Extrapolated (Determined) Values of Mole Fractions x_2 of Sodium Bis-(2-methoxyethoxy)-dihydridoaluminate, Apparent Molecular Weights and the Degrees of Association α

$x_2 . 10^3$	Benzene		$(x_2 . 10^2)$	Tetrahydrofuran	
	m.w.	α		m.w.	α
3	713·1	3·5		202·2	1
4	874·1	4·3		239·4	1·2
5	1 011·0	5·0		269·1	1·3
7	1 231·5	6·1		313·5	1·5
9	1 401·2	6·9		345·1	1·7
(1.1)	(1 535·9)	(7·6)	(1·1)	(368·8)	(1·8)
(1·51)	(1 736)	(8·5)	(1·5)	(401·6)	(2·0)
(2·9)	(2 009·4)	(9·9)	(2·7)	(480·4)	(2·2)
(5·1)	(2 331·4)	(11·5)	(7·4)	(483·9)	(2·2)
(11·1)	(2 626·1)	(12·9)	(12·2)	(505·9)	(2·3)

Tetrahydrofuran (analytical grade) was boiled with 0·4 weight % of CuCl for 2 hours, distilled, dried over solid KOH, and redistilled. Drying was carried out over calcium hydride. Rectification was carried out on a 20TP column. Azobenzene and phenanthrene were purified by zonal melting (Lachema, Brno). Sodium bis(2-methoxyethoxy)dihydridoaluminate was prepared[2] in this Institute. The determination of azobenzene was carried out reductometrically with $TiCl_3$ in acidic medium. Phenanthrene was determined chromatographically on a Chrom-3 apparatus, the column was filled with 3% of silicon oil F 60 on Chromosorb W, column length 1 200 mm, carrier gas nitrogen, temperature 225°C, FID. The concentration of hydrides was determined iodometrically by determining the hydride hydrogen with a iodine solution in benzene. The content of hydride hydrogen found was recalculated to the content of the whole substance. All manipulations with hydride solutions were carried out under argon or nitrogen.

RESULTS

By the above mentioned method the systems bis(2-methoxyethoxy)-dihydridoaluminate-benzene, or tetrahydrofuran, were measured. The calculated constants A and B of the equation (*1*) were 1963·34; 8·55 for benzene and 1933·86; 8·69 for tetrahydrofuran. Relative errors of the calculated constants were $3·3 \cdot 10^{-2}$; $2·5 \cdot 10^{-2}$, or $5·54 \cdot 10^{-2}$; $4·14 \cdot 10^{-2}$. The extrapolated and determined values of the "apparent" molecular weights are listed in Table I. It is evident that the benzene solution of the hydride displays a substantially larger change of the apparent molecular weight (as a function of concentration) than the tetrahydrofuran solution (Fig. 1). The difference may evidently be assigned to the easier solvation of the hydride by tetrahydrofuran than by benzene[3], which decreases simultaneously the tendency of the hydride to associate. The association of the substances containing an Al—O bond is quite common[4]. A similar increase of association with concentration as in our case was observed in the case of lithium trimethoxyhydridoaluminate in tetrahydrofuran by other authors[5] as well.

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