

A THERMODYNAMIC STUDY OF SOLUTIONS OF SODIUM DIHYDRIDO-BIS(2-METHOXYETHOXY)ALUMINATE IN AROMATIC HYDROCARBONS*

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With the view of characterizing partially the thermodynamics of solutions of sodium dihydrido-bis(2-methoxyethoxy)aluminate in aromatic hydrocarbons, the activity coefficients, γ_i , of the constituents were determined in relation to temperature and composition of the solutions. The calculations are based on solubility measurements. The solubilities of sodium dihydrido-bis(2-methoxyethoxy)aluminate in toluene, isomeric xylenes and mesitylene have been determined at different temperatures up to the upper critical solution temperature, and the constants A and B of van Laar's equation III for different temperatures have been calculated. The approximate dissolution heats of sodium dihydrido-bis(2-methoxyethoxy)aluminate in the given aromatic hydrocarbons have been determined for 20°C at an infinite dilution, and the logarithms of the activity coefficients of sodium dihydrido-bis(2-methoxyethoxy)aluminate and of the aromatic hydrocarbon in a given system at 20°C have been calculated. The results suggested solvation of hydrides by aromatic solvents, which possibility has been confirmed by DTA and DTG. Moreover, formation of a 2 : 1 solvate with benzene has been determined by conductance measurements.

This paper supplements the previous fundamental physico-chemical data of solutions of sodium dihydrido-bis(methoxyethoxy)aluminate (SDMA) in aromatic hydrocarbons (viscosity¹, density¹, cryoscopic² and ebullioscopic³ data) by a basic thermodynamic characterization.

SDMA dissolves infinitely in benzene, whereas in toluene, isomers of xylene and in mesitylene two conjugated phases are formed at certain concentrations and temperatures¹; the conjugated solutions are formed even with diethyl ether¹. The concentrations of SDMA in the individual phases of such a system depend on temperature. To determine the solubility of a given system, the two phases of this system were equilibrated at a chosen, constant temperature and the concentrations of SDMA in the two phases were determined analytically.

The solvation of SDMA by aromatic hydrocarbons was already mentioned in the paper on its synthesis¹. Cryoscopy showed² that SDMA is solvated by benzene and

* Part X in the series On the Behaviour and Reactivity of Solutions of Complex Hydrides; Part IX: This Journal 38, 2379 (1973).

that the composition of the solvates at 5°C varies when the ratio of the hydride to the donor is changed from 1 : 1 to 2 : 1. These facts and the effect of solvation of complex hydrides on the stereochemistry of reductions⁴⁻⁹ have induced us to study the solvation in more detail. The most usual and simple physico-chemical methods employed for studying solvation are the measurements¹⁰ of viscosity, conductance, volume properties and (in some cases) surface tension. A rewarding approach to our problem was the measurement of DTA and DTG, supplemented by conductance and viscosity data in the case of benzene.

EXPERIMENTAL

Chemicals: Benzene solutions of SDMA of required concentrations were prepared from a 55% stock solution in an inert atmosphere, either by concentrating this solution *in vacuo* or by its dilution with benzene that had been dried by distillation from SDMA. The solutions of SDMA in other aromatic hydrocarbons were prepared from the solution of this hydride in benzene, which was distilled off *in vacuo*. The absence of benzene was checked chromatographically on the addition and removal (by distillation) of a small amount of an aromatic hydrocarbon. The dry residue was dissolved in toluene, *o*-xylene, *m*-xylene, *p*-xylene or mesitylene. The aromatic hydrocarbons had been purified by reported procedures¹¹. Prior to use they were dried with SDMA and distilled *in vacuo*.

Solubility measurements. A cylindrical vessel was charged with a solution of SDMA in a given hydrocarbon and such a quantity of the same hydrocarbon was added that there formed two phases of approximately equal volumes. The two phases were stirred for 2 h (kinetic experiments showed that equilibrium was established in about 1 h). The phases were allowed to separate by 1 h's standing. After measuring the equilibrium the temperature was elevated and the mea-

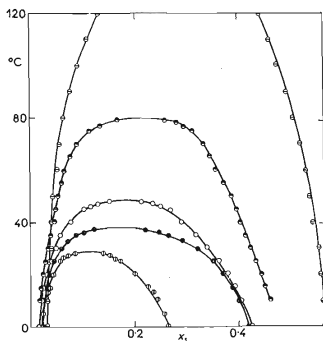


FIG. 1
Solubility of SDMA in Aromatic Hydrocarbons in Relation to Temperature

○ Toluene, ○ *m*-xylene, ● *o*-xylene,
● *p*-xylene, ⊙ mesitylene.

TABLE I
Equilibrium of the System Sodium Dihydrido-bis(2-methoxyethoxy)aluminate-Aromatic Hydrocarbon

Temperature °C	x_1	\bar{x}_1	A	B
Toluene				
0	0.0235	0.2661	1.58	0.291
5	0.0259	0.2574	1.55	0.298
10	0.0313	0.2444	1.51	0.291
13	0.0331	0.2348	1.49	0.287
15	0.0379	0.2265	1.46	0.289
20	0.0437	0.2010	1.42	0.278
25	0.0614	0.1731	1.39	0.264
26	0.0640	0.1633	1.36	0.276
27	0.0706	0.1518	1.34	0.277
28	0.0857	0.1402	1.32	0.284
<i>o</i> -Xylene				
0	0.0269	0.4206	1.63	0.432
10	0.0285	0.4056	1.57	0.422
15	0.0325	0.3906	1.53	0.418
20	0.0365	0.3713	1.51	0.411
25	0.0464	0.3512	1.44	0.409
30	0.0619	0.3223	1.38	0.395
33	0.0729	0.2932	1.34	0.400
35	0.0914	0.2670	1.30	0.404
36	0.1034	0.2479	1.28	0.398
37	0.1246	0.2219	1.27	0.405
<i>m</i> -Xylene				
0	0.0181	0.4255	1.71	0.414
10	0.0215	0.4008	1.65	0.401
15	0.0247	0.3936	1.61	0.403
20	0.0328	0.3778	1.57	0.407
25	0.0419	0.3612	1.53	0.410
30	0.0505	0.3397	1.47	0.407
35	0.0580	0.3193	1.43	0.401
40	0.0798	0.2907	1.32	0.406
45	0.1028	0.2704	1.28	0.421
46	0.1170	0.2518	1.26	0.415
47	0.1310	0.2370	1.24	0.426
48	0.1532	0.2164	1.20	0.427

TABLE I
(Continued)

Temperature °C	x_1	\bar{x}_1	A	B
<i>p</i> -Xylene				
10	0.0183	0.4617	1.72	0.447
15	0.0212	0.4503	1.67	0.440
20	0.0254	0.4464	1.62	0.457
25	0.0283	0.4353	1.57	0.450
30	0.0367	0.4230	1.61	0.454
35	0.0401	0.4146	1.49	0.453
40	0.0450	0.4043	1.47	0.441
45	0.0490	0.3971	1.43	0.453
50	0.0561	0.3875	1.40	0.460
55	0.0616	0.3730	1.41	0.461
60	0.0661	0.3568	1.37	0.455
65	0.0709	0.3456	1.33	0.447
70	0.0898	0.3359	1.30	0.457
75	0.1139	0.3141	1.25	0.465
76	0.1252	0.3058	1.23	0.467
77	0.1353	0.2975	1.21	0.468
78	0.1498	0.2830	1.20	0.468
79	0.1696	0.2601	1.18	0.473
Mesitylene				
0	0.0326	0.5633	1.57	0.578
10	0.0335	0.5625	1.56	0.585
20	0.0346	0.5577	1.54	0.599
25	0.0351	0.5563	1.54	0.576
30	0.0398	0.5548	1.52	0.582
40	0.0399	0.5417	1.50	0.570
50	0.0448	0.5366	1.47	0.573
60	0.0532	0.5327	1.43	0.583
70	0.0570	0.5181	1.40	0.573
80	0.0651	0.5066	1.37	0.574
90	0.0784	0.4946	1.31	0.599
100	0.0929	0.4746	1.28	0.578
110	0.1098	0.4580	1.24	0.581
120	0.1317	0.4410	1.20	0.587
130	0.1547	0.4209	1.19	0.580
140	0.1839	0.4017	1.14	0.600

surements were repeated in the same way. To be sure that equilibria had been established some measurements were repeated at progressively lowered temperatures. The results agreed within the range of experimental error.

Conductance measurements: The procedure is described in the paper¹ on the synthesis of SDMA. The constant of the cell was $1.0231 \cdot 10^{-2} \text{ cm}^{-1}$.

Measurement of DTA and DTG: Changes of DTA and DTG were measured with a Mettler apparatus. The samples were placed into crucibles in an inert atmosphere and weighed by the difference method. The measurements were performed under a protective nitrogen atmosphere, the pressure of which did not drop under 780 Torr. The values of DTA and DTG were measured in a temperature range from 25 to 350°C. The temperature change was 0.5 and 1°C/min. The reference material was aluminium oxide. The concentration of a solution was calculated from the decrease in its weight.

Viscosity was measured with an Ubbelohde viscometer and calculated from the Poiseuille equation.

Concentration of SDMA in a solution was calculated from the contents of active hydrogen (determined volumetrically¹²) and aluminium (determined complexometrically¹²).

RESULTS AND DISCUSSION

The concentrations of SDMA in the two phases of the systems of the individual aromatic hydrocarbons at different temperatures are given in Table I. The solubility of SDMA in aromatic hydrocarbons as a function of temperature is shown in Fig. 1.

The solubility of SDMA in aromatic hydrocarbons was measured from 0°C (with the exception of *p*-xylene, where at so low a temperature the solid phase already separated) up to the upper critical solution temperatures. In the case of mesitylene the equilibria were measured up to a limit of 140°C, above which temperature the hydride might partially decompose. As is seen in Fig. 1, the lowest solubility was in mesitylene, whereas in toluene it was very good. The solubility in benzene proved infinite. It is evident that the solubility depends on the number and positions of substituents in the benzene ring, *i.e.* on the possibility of formation of solvates of SDMA with aromatic hydrocarbons. The formation of these solvates in benzene was proved cryoscopically², in the other aromatic hydrocarbons by differential thermal analysis, described below.

Since the components considered form conjugated solutions it was possible to calculate the constants *A* and *B* of van Laar's 3rd order equation¹³ from the compositions of the two conjugated phases (Table I).

With systems described by the van Laar equation the constants *A* and *B* are related to temperature by the simple equations¹³.

$$dA/d(1/T) = L_0^1/2 \cdot 303R,$$

$$dB/d(1/T) = L_0^2/2 \cdot 303R,$$

where L_0^1 and L_0^2 denote the respective dissolution heats of SDMA and the aromatic hydrocarbon at infinite dilution. The courses of these functions for these systems under study are plotted in Fig. 2.

It shows that the constant A was considerably temperature-dependent and decreased with increasing temperature. The constant B was virtually independent of temperature; on raising the temperature to a degree at which the conjugated phases combined the constant B moderately rose with further increasing temperature.

The dissolution heats of SDMA in aromatic hydrocarbons at infinite dilution were calculated from the slopes of the function $A = f(1/T)$ at the individual temperatures. The dissolution heats at 20°C are given in Table II. From the constants A and B in the van Laar equation at 20°C the logarithms of the activity coefficients of SDMA and the aromatic hydrocarbons were calculated according to a reported procedure¹³. The curves relating the activity coefficients of the individual systems to composition of the solutions are shown in Fig. 3.

Table III gives a survey of the solvates determined. These were calculated from weight reductions in the differential thermal analysis. A decrease in weight remained constant until a 1 : 1 solvate had converted into a 3 : 2 one (equation (A)), or until the ratio 3 : 2 had changed to 2 : 1 (equation (B)). These conversions manifested themselves by changes in the weight reductions and these changes were made use

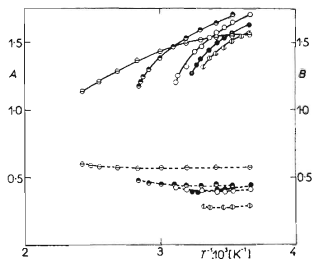


FIG. 2

Constants A and B of the van Laar 3rd Order Equation as Functions of Temperature for Systems SDMA-Aromatic Hydrocarbon

The solid curves refer to the constant A , the dashed ones to the constant B . The individual hydrocarbons are denoted as in Fig. 1.

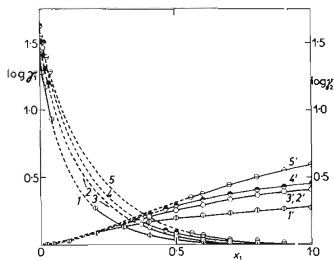
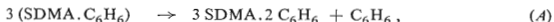


FIG. 3

Logarithms of Activity Coefficients of SDMA and an Aromatic Hydrocarbon in Relation to Composition of the System

The solid curves refer to one-phase regions, the dashed curves to two-phase regions. For designation of the individual systems see Fig. 1.

of for calculating the ratios of the hydride to an aromatic hydrocarbon. Thus for the system SDMA benzene it applies



The benzene solvation of SDMA was also studied with the aid of a modified¹⁰ conductance function, $\sigma = \kappa \cdot \eta$. The viscosity measurements were evaluated using data from a previous paper¹ for the mole fractions of SDMA up to 0.5, as well as newly obtained data. The viscosity of pure SDMA was determined by extrapolation as 55.7 cP. The dependence of viscosity on the mole fraction of the hydride at $60 \pm 0.1^\circ\text{C}$ is shown in Fig. 4. As the course of the viscosity function is neither monotonous nor convex the solvation could not be determined by Fialkov's method¹⁰, applicable to such functions only. The ascertained S-shaped course is possible in systems¹⁰ where the individual constituents are considerably different in viscosity and where the solvation is incomplete (transition from solvates with a firmly bound solvent to solvates with a very weak linkage).

The course of conductivity was obtained by measuring the conductances of differently concentrated solutions of SDMA, prepared by diluting a 92% stock solution with benzene. The curve for the temperature of $60 \pm 0.1^\circ\text{C}$ is drawn in Fig. 5. In determining the degrees of solvation we employed conductivities corrected for

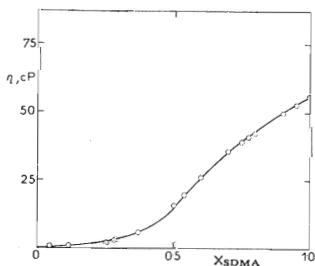


FIG. 4

Viscosity, η , of Benzene Solutions of SDMA as a Function of mole Fraction of SDMA at $60 \pm 0.1^\circ\text{C}$

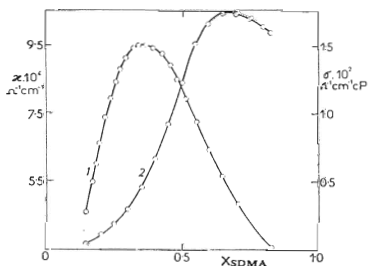


FIG. 5

Conductivity, κ (curve 1) and Quantity σ (curve 2) of Benzene solutions of SDMA as Functions of mol Fraction of SDMA at $60 \pm 0.1^\circ\text{C}$

viscosity. The dependence of σ on concentration of the solution is also shown in Fig. 5. Conductivity, κ , takes a characteristic course with systems considerably differing in viscosity; the maximum conductivity was calculated from the conductance measured with a system containing 36 mol% of SDMA. However, the modified conductivity function exhibits a maximum typical of solvation at 67 mol% of SDMA and 33 mol% of benzene, which corresponds to a hydride: benzene ratio of 2 : 1. The fact that only one solvate (2 : 1) was detected by conductance measurements at 60°C, in contrast to the result obtained by DTA measurements, can be explained by the thermal lability of the other two solvates, as well as by their very small quantities. However, the formation of these two solvates was demonstrated on the curves of DTA and DTG, because the heat introduced into a sample caused evaporation of benzene and gradual decomposition of the solvates 1 : 1 and 3 : 2, according to equations (A) and (B).

TABLE II

Dissolution Heats of Sodium Dihydrido-bis(2-methoxyethoxy)aluminate in Aromatic Hydrocarbons at Infinite Dilution (L_1^0) at 20°C

System	L_1^0 , cal/mol	t crit., °C	x_1 crit.
Hydride-toluene	4 000	28.8	0.114
Hydride- <i>o</i> -xylene	3 800	37.9	0.166
Hydride- <i>m</i> -xylene	3 300	48.4	0.185
Hydride- <i>p</i> -xylene	2 000	79.8	0.220
Hydride-mesitylene	600	—	—

TABLE III

Solvates Found in the System Sodium Dihydro-bis(2-methoxy-ethoxy)aluminate-Aromatic Hydrocarbon

Hydrocarbon	Molar ratio hydride : hydrocarbon
Benzene	2 : 1, 3 : 2, 1 : 1
Toluene	2 : 1, 1 : 1
<i>o</i> -Xylene	2 : 1, 1 : 1
<i>m</i> -Xylene	2 : 1, 1 : 1
<i>p</i> -Xylene	1 : 1

The deviation from ideal behaviour of the systems SDMA–aromatic hydrocarbon increases in the order toluene < *o*-xylene < *m*-xylene < *p*-xylene < mesitylene, whereas solubility and the dissolution heat of the hydride decrease in this order. These facts suggest that in addition to solvation, which evidently is the decisive factor for solubility, there are other interactions in the considered systems influencing their behaviour. The activity coefficients may be substantially affected by the association phenomena, and it is just with weakly solvated systems that the effect of association should be the strongest.

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