Solubility of Sodium Sulfide in Alcohols

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The solubility of sodium sulfide in methanol, ethanol, 2-propanol, 2-methyl-1-propanol, and benzyl alcohol and the acid−base interaction of these compounds have been determined at (20 and 35) °C. The reactions result in the formation of sodium alkoxide and hydrosulfide. The reported values on the solubility of sodium sulfide in alcohols differ essentially from the data described in the literature.

Introduction

Sodium sulfide is used in different branches of chemical technology, for example, pulp and paper, textile, tanning industry, and metallurgy, and as a strong reducing agent in organic synthesis.[1,2] Therefore, physical and chemical properties of solutions of this salt are important, especially solubility data in alcohols which are used in the process of pure anhydrous sodium sulfide production.[1−3] No data on solubility of alkali metal sulfides in methanol as well as in other alcohols were found in the most popular reference books and databases. Both vapor−liquid equilibrium and solubility data for the ternary systems containing alkali metal sulfides and mixed solvents are also absent in the literature. Beyer[3] presented the information about the solubility of anhydrous sodium sulfide and $Na_2S \cdot 9H_2O$ in alcohols. These published data on solubility of sodium sulfide at 20 °C in methanol, ethanol, isobutanol, benzyl alcohol, and ethylene glycol are listed in Table 1.

However, the author[3] did not take into account the possible reaction between sulfide of alkali metal as the base and alcohol as the acid (eq 1)

$$M_2S + ROH = MHS + ROM \qquad (1)$$

where M is an alkali metal and R is an alkyl group.

It is known[4−6] that alcoholysis of some alkali metal compounds: salts (carbonates, cyanides, sulfides, orthophosphates), amides, azides, nitrides, alkali, hydrides, and acetylenides, can be considered as a method for alkoxide production (eqs 2, 3, and 4)

$$MX + ROH = HX + ROM \qquad (2)$$

$$M_2X + ROH = MHX + ROM \qquad (3)$$

$$M_3X + ROH = M_2HX + ROM \qquad (4)$$

where M is an alkali metal; R is an alkyl group; X = OH, NH_2, H, N_3, CN, C≡C (eq 2), S, CO_3 (eq 3), and PO_4 (eq 4).

Moreover, an acid−base interaction according to eq 1 may be used for the production of anhydrous sodium and potassium hydrosulfides which are applied for the synthesis of thiols (mercaptans). Loder and Lee[5] reported the formation and the recovery of alkoxides according to eq 1 at the temperature range (60 to 70) °C for the first time. They offered the process for the preparation of sodium methoxide wherein 21.7 parts of anhydrous Na_2S and 78.3 parts of CH_3OH reacted at 62 °C.

The resulting solution contained 4.2 parts of sodium methoxide, 1.9 parts of sodium hydrosulfide, 15.6 parts of sodium sulfide, and 78.3 parts of CH_3OH. The solid NaHS (2.5 parts) precipitated from a reaction mixture was filtered out. The remaining sodium hydrosulfide and sulfide were separated by evaporating methanol from the solution and then were readily filtered from the sodium methoxide solution.[5]

In the present paper, the solubility of anhydrous Na_2S in methanol, ethanol, 2-propanol, 2-methyl-1-propanol, and benzyl alcohol has been determined at (20 and 35) °C in view of the above interaction. In addition, the distribution of all components in the Na_2S + ROH reaction systems was investigated under the conditions of phase and chemical equilibrium.

Experimental Section

Reagents. Anhydrous chemicals were used as much as possible. All alcohols ($w \geq 99.9$ %, Merck, Sigma-Aldrich, and Vekton) were dehydrated and stored over molecular sieves of type 3A. The water mass fraction in alcohols was determined by the Karl Fischer coulometric method, and it did not exceed 0.01 %. Sodium sulfide was dehydrated, dried in a vacuum oven, and purified from $Na_2S \cdot 9H_2O$ ($w \geq 34.5$ %, Reaktiv-SP) as described by Beyer.[3]

Procedure. The equilibrium concentrations of the components of Na_2S + ROH reaction systems were determined using the titrimetric method.[7] For this purpose, the mixtures of known masses of sulfide and alcohol were prepared gravimetrically using an analytical balance with an uncertainty of 0.1 mg and continuously agitated within 10 h in a temperature-controlled cell at either (20 or 35) °C. The uncertainty of the measured temperature by a mercury-in-glass thermometer was 0.1 °C. Then the suspension was passed through a porous glass filter under pressure. The filter was held at the target temperature. The solid and liquid phases were analyzed separately. The

Table 1. Published Data[a] on Solubility *s* of Anhydrous Sodium Sulfide in Alcohols and Ethylene Glycol at 20 °C

solvent	$\dfrac{s}{\text{g} \cdot \text{L}^{-1}}$
methanol	160
ethanol	90
isobutanol	31
benzyl alcohol	>40
ethylene glycol	>200

[a] Ref 3.

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Table 2. Composition of the Components in the Na_2S + ROH Reaction Systems in the Liquid Phase

t	Na_2S	NaHS	RONa
°C		(g per 100 g ROH)	
Methanol			
20	5.13 ± 0.12^a	0.901 ± 0.006^a	14.74 ± 0.51^a
35	5.96 ± 0.14^a	1.078 ± 0.009^a	14.11 ± 0.75^a
Ethanol			
20	3.12 ± 0.07^a	0.494 ± 0.007^a	8.04 ± 0.11^a
35	3.65 ± 0.09^a	0.542 ± 0.006^a	7.75 ± 0.11^a
2-Propanol			
20	1.79 ± 0.04^a	0.411 ± 0.006^a	2.14 ± 0.04^a
35	2.16 ± 0.03^a	0.497 ± 0.005^a	1.95 ± 0.05^a
2-Methyl-1-propanol (Isobutanol)			
20	1.14 ± 0.02^a	0.354 ± 0.007^a	2.48 ± 0.07^a
35	1.55 ± 0.03^a	0.510 ± 0.005^a	2.27 ± 0.07^a
Benzyl Alcohol			
20	1.24 ± 0.03^a	0.263 ± 0.003^a	2.69 ± 0.06^a
35	1.63 ± 0.04^a	0.422 ± 0.002^a	2.44 ± 0.07^a

^{a} ± 3 std dev.

concentrations of Na_2S and NaHS were determined by iodometric titration as described by Treadwell.[7] After evaporation of methanol and extraction by benzene, the sodium alkoxide was titrated as a strong NaOH base that was formed from RONa as a result of a hydrolysis with water (after evaporation of benzene).

The average relative uncertainty in the measurement of the solubility is 0.03.

Results and Discussion

The analysis of the liquid phase of all studied systems showed the presence of Na_2S, NaHS, and RONa, which are formed according to eq 1. The concentrations of these compounds under the conditions of the thermodynamic equilibrium are presented in Table 2.

Only two components, namely, sodium sulfide and sodium hydrosulfide, were found in the solid phase of the heterogeneous Na_2S + ROH reaction systems. The absence of sodium alkoxide in the solid phase was confirmed in a separate trial. After filtering the suspension, the precipitate was extracted by dry benzene, the solvent was removed in a vacuum, and the residue was treated with water and analyzed by titrimetry. No strong base was discovered.

More than 98 % of the total NaHS quantity generated according to eq 1 is in the solid phase. The NaHS quantities found both in the liquid and the solid phases corresponded to the RONa quantity revealed in the liquid phase.

Such a distribution of sodium hydrosulfide between the solid and the liquid phases promotes the shifting of eq 1 toward the formation of reaction products according to Le Chatelier's principle. The concentration of the dissolved sodium hydrosulfide will increase at a rising temperature so that the rate of reverse reaction increases and the concentration of sodium alkoxide decreases, accordingly.

Comparing the value of the solubility of Na_2S in methanol with those known from literature,[3] it is apparent that neglecting the interaction of Na_2S with CH_3OH will result in too high values. In fact, the solubility of sodium sulfide reported[3] is 20.21 g per 100 g methanol at 20 °C; we measured approximately four times less (Table 2). It is necessary to note that the sum concentration of the dissolved sodium sulfide and sodium methoxide averages 19.87 g per 100 g methanol. The author of the cited patent[3] used the gravimetric method. This earlier value represents the alkaline equivalents of the three reaction participants, expressed as sodium sulfide.[3] The authors[5] investigated the composition of the Na_2S + CH_3OH reaction system. The values on solubility reported in their paper are equal to 19.92, 5.36, and 2.42 g per 100 g of methanol at 62 °C for Na_2S, CH_3ONa, and NaHS, respectively. Unfortunately, the authors[5] failed to report on the analytical procedure used. Moreover, it is doubtful that the solid phase of the Na_2S + CH_3OH reaction system consists of NaHS alone.[5]

The published[3] solubilities of sodium sulfide in ethanol, 2-methyl-1-propanol, and benzyl alcohol are also less than we have measured (Table 2). Since alcohol is both the solvent and the reactant in the Na_2S + ROH reaction system the term of "solubility of sodium sulfide in alcohol" is not precise. Probably, the composition of the Na_2S + ROH reaction systems is mainly determined by the thermodynamics of the sodium sulfide alcoholysis.

Conclusion

The solubility of sodium sulfide in methanol, ethanol, 2-propanol, 2-methyl-1-propanol, and benzyl alcohol at (20 and 35) °C has been determined in view of the acid−base interaction of the components.

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