J. Chem. Eng. Data **2002,** *47,* 1175−1176

Solubility of Potassium Carbonate and Potassium Hydrocarbonate in Methanol

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The solubility of potassium carbonate in methanol and the acid−base interaction of these compounds with each other have been considered. The reaction results in the formation of methoxide and hydrocarbonate of potassium. The reported values on the solubility of potassium carbonate differ essentially from the data described in the literature. The solubility of potassium hydrocarbonate in methanol has also been determined.

The solubilities of potassium carbonate in alcohols as well as other carbonates have been studied previously.[1−3] However, the authors of the papers did not take into account the possible reaction between carbonate of alkali metal as the base and alcohol as the acid

$$\mathrm{ROH + M_2CO_3 = ROM + MHCO_3} \qquad (1)$$

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

Loder and Lee[4] reported the formation and the recovery of alkoxides according to eq 1 for the first time. They offered the process for the preparation of potassium methoxide wherein 8.6 parts of K_2CO_3 and 94.6 parts of CH_3OH reacted at 20 °C for 6 h. The solid $KHCO_3$ precipitated from a reaction mixture was filtered out. The remaining carbonates were separated by evaporating methanol from the solution, and then the carbonates precipitated were readily filtered from the saturated potassium methoxide solution. This latter solution may be further evaporated to obtain solid potassium methoxide.

Studying the reactions of diethyl phosphite with electrophiles in the K_2CO_3/C_2H_5OH system, we established the formation of potassium ethoxide after stirring of potassium carbonate with ethanol using a titrimetric method.[5]

In the present paper, the solubility of K_2CO_3 in methanol was determined in view of the above interaction. In addition, the distribution of all components in the K_2CO_3/CH_3OH system was investigated under the conditions of phase and chemical equilibrium. The solubility of $KHCO_3$ in anhydrous methanol was also determined.

Experimental Section

Reagents. As far as possible, anhydrous chemicals were used. After dehydration, the methanol obtained from Merck was stored above molecular sieves type 3A. The water content in the methanol was controlled by the GC method and did not exceed 0.02 mass %. Potassium carbonate and potassium hydrocarbonate obtained from Aldrich (ReagentPlusTM) had a purity of 99.99 mass %. Before the experiment, the potassium carbonate was warmed to 120 °C for 1 h.

Procedure. The equilibrium concentrations of the components of K_2CO_3/CH_3OH and $KHCO_3/CH_3OH$ systems were determined using the titrimetric method. For this purpose, a mixture of the appropriate carbonate (a known mass of sample from 2.8 to 6.8 g) and 10 mL of methanol was continuously agitated within 6 h in a temperature-controlled cell at either (25 ± 0.05 °C) or (35 ± 0.05 °C). Then the suspension was passed through a porous glass filter under pressure. The solid and liquid phases were treated with water separately. The concentrations of K_2CO_3, $KHCO_3$, and CH_3OK were determined by hydrochloric acid solution using phenolphthalein and methyl orange solutions as the indicators. Potassium methoxide was titrated as a strong KOH base that was formed from CH_3OK as a result of a hydrolysis (see eq 2).

$$\mathrm{CH_3OK + H_2O = CH_3OH + KOH} \qquad (2)$$

This acid−base titration with recording of two points of equivalence allowed us to determine jointly K_2CO_3 and KOH, as well as K_2CO_3 and $KHCO_3$.

Analogously, the K_2CO_3/CH_3OH system was analyzed at 30, 40, and 45 °C.

Results and Discussion

The mixture of potassium carbonate and methanol is a heterogeneous system at a K_2CO_3/CH_3OH ratio greater than 30 g/100 g. The analysis of the liquid phase of this system showed the presence of K_2CO_3, $KHCO_3$, and CH_3OK, which are formed according to eq 1. The concentrations of these compounds under the conditions of the thermodynamic equilibrium are presented in Table 1.

Only two components, namely potassium carbonate and potassium hydrocarbonate, were found in the solid phase of the heterogeneous K_2CO_3/CH_3OH system. The absence of potassium methoxide in the solid phase was confirmed in a separate trial. After the suspension was filtered, 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 (see Experimental Section). No strong base was discovered.

The quantities of potassium hydrocarbonate found in the solid phase were 6.87 g/100 g methanol and 6.18 g/100 g

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10.1021/je020012v CCC: $22.00 © 2002 American Chemical Society
Published on Web 06/29/2002

Table 1. Concentrations of the Components in the K_2CO_3/CH_3OH System (grams per 100 g of methanol)

t/°C	[K_2CO_3]	[$KHCO_3$]	[CH_3OK]
25	1.61 ± 0.09[a]	0.0121 ± 0.0009[a]	4.82 ± 0.12[a]
35	2.01 ± 0.15[a]	0.0341 ± 0.0015[a]	4.37 ± 0.18[a]

[a] ±3 std dev.

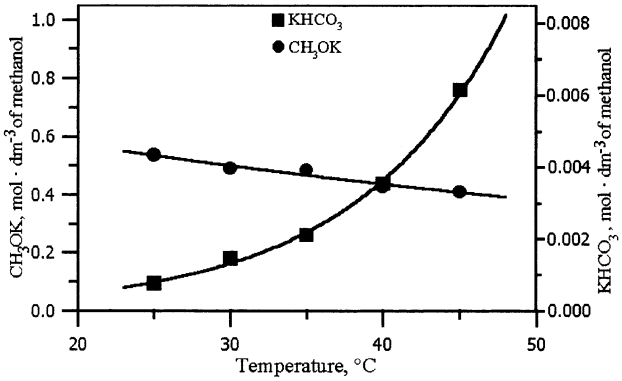

Figure 1. Temperature effect on the concentrations of potassium methoxide and potassium hydrocarbonate in methanol.

methanol at 25 and 35 °C, respectively. This is more than 99% of the total $KHCO_3$ quantity generated according to eq 1. The $KHCO_3$ quantities found both in the liquid and the solid phases corresponded to the CH_3OK quantity revealed in the liquid phase.

Such a distribution of potassium hydrocarbonate between the solid and liquid phases promotes the shifting of equilibrium 1 toward the formation of reaction products according to Le Chatelier's principle. This is confirmed by the temperature dependence of the component composition of the K_2CO_3/CH_3OH system as presented in Figure 1. Obviously, the concentration of the dissolved potassium hydrocarbonate will increase with rising temperature so that the rate of the reverse reaction increases and the concentration of potassium methoxide decreases, accordingly.

When the values of the solubility of K_2CO_3 in methanol are compared with those known from the literature, it is apparent that neglecting the interaction of K_2CO_3 with CH_3OH will result in too high values. In fact, the solubility of potassium carbonate reported[2] is more than 6 g/100 g of methanol at 25 °C; we measured a value approximately four times lower (see Table 1). It is necessary to note that the sum concentration of the dissolved potassium carbonate and potassium methoxide averages 6.4 g/100 g of methanol. The authors of the cited papers used the gravimetric method. These earlier values represent the alkaline equivalents of the three reaction participants, expressed as potassium carbonate.[2,3]

The authors[4] investigated the composition of the K_2CO_3/CH_3OH system. The values of solubility reported in their paper equal 3.11, 3.11, and 0.96 g/100 g of methanol at 20 °C for K_2CO_3, CH_3OK, and $KHCO_3$, respectively. These data are compared to those obtained in the present study except for the solubility of $KHCO_3$, which is more than 100 times higher. Unfortunately, the authors[4] failed to report on the analytical procedure used. Moreover, it is doubtful that the solid phase of the K_2CO_3/CH_3OH system consists of $KHCO_3$ alone.[4]

Since methanol is both the solvent and the reactant in the K_2CO_3/CH_3OH system, the term "solubility of potassium carbonate in methanol" is not precise. Probably, the composition of the K_2CO_3/CH_3OH system is mainly determined by the thermodynamics of the potassium carbonate alcoholysis.

In contrast, the mixing of potassium hydrocarbonate with methanol (up to the temperature 35 °C) is not accompanied by the reaction of these components according to eq 3.

$$KHCO_3 + CH_3OH = CH_3OK + CO_2 + H_2O \quad (3)$$

Only $KHCO_3$ was found both in the liquid and in the solid phases. The solubility of $KHCO_3$ is 0.018 g/100 g of methanol and 0.038 g/100 g of methanol (at 25 °C and 35 °C), respectively.

Acknowledgment

We are grateful to Dr. Gunter Fuhrmann for helpful discussions.

Received for review January 14, 2002. Accepted May 27, 2002. This work was supported by grants for young scientists obtained from the government of Saint Petersburg (M-00-2.5K-436) and the government of Russian Federation.

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JE020012V