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Composition of Vapor and Liquid Phases in the Potassium Hydroxide + Methanol Reaction System at 25 °C

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Abstract The composition of the vapor and liquid phases of the KOH + CH_3OH system has been studied by the gas chromatography (GC) method at 25 °C. It has been found that the methanol vapor concentration, and the quantity of potassium methoxide formed as a result of the acid–base reaction of potassium hydroxide with methanol, both depend on the KOH/CH_3OH mole ratio. The maximum mass fraction of potassium methoxide that forms is 2.6% at the mole ratio 0.018.

Keywords Potassium hydroxide · Methanol · Potassium methoxide · Vapor-liquid equilibrium

1 Introduction

It is known that an acid-base reaction according to Eq. 1 can be used for the production of alkali metal alkoxides [1, 2]:

$$\mathrm{ROH} + \mathrm{MOH} \rightleftarrows \mathrm{ROM} + \mathrm{H_2O} \tag{1}$$

where R represents an alkyl group C_nH_{2n+1}, n ranges from 1–4, and M represents an alkali metal (Na, K). This process has some advantages over alcoholysis of alkali metals (Eq. 2):

$$\mathrm{ROH} + \mathrm{M} \rightarrow \mathrm{ROM} + 0.5\mathrm{H_2}\ (\mathrm{g}) \tag{2}$$

because hydroxides of alkali metal elements (alkali) are cheaper raw material than their corresponding alkali metals. The known methods, as a rule, utilize the shift of equilibrium of Eq. 1 according to Le Chatelier's principle, by removing water from the reaction mixture with the use of drying agents, by distillation or other procedures. These processes have

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been appropriately studied and published [1]. On the contrary, composition data for the MOH + ROH reaction system at equilibrium has not been studied in detail.

The systems consisting of an alkali metal hydroxide and alcohol were described for the first time by Engel [3], where it was reported that an ethanol solution of potassium hydroxide at room temperature yielded crystals of $C_2H_5OK\cdot C_2H_5OH$ upon being cooled. This complex decomposed rapidly into potassium ethoxide and alcohol at 60 °C. It was identified by an indicator color change method [4] that showed in KOH (0.1 mol·dm^{-3})+ ethanol solution, 96% of the total base consists of the ethoxide ion. Analysis of the solubility of KOH in water + ethanol mixtures at 30 °C showed that the formation of potassium ethoxide takes place in ethanol when the mass fraction of water is less than 2% [5]. The authors of a later study [6] established that values of the photoelectron emission threshold energy for solutions of KOH in C_1 to C_4 alcohols were the same as those for the corresponding solutions prepared with metallic potassium. It was concluded that alkoxide ions predominate, even if there is about a 50% by mass excess of water with respect to the hydroxide. Using IR-spectroscopy, Williams and Bost [7] found that the yield of sodium ethoxide, after boiling ethanol with NaOH, was 75–100% within one hour.

The constants for the acid-base equilibrium given by Eq. 1 have been determined several times by different methods [4, 8–12]. However data comparing the acidity of lower aliphatic alcohols and water are substantially contradictory. Caldin and Long [4], on the basis of equilibrium constant measurement for Eq. 1 with $R = C_2H_5$ and M = Na at 25 °C, concluded that the acidities of water and ethanol are comparable. By using conductimetric measurements and cryoscopic studies, Unmack [13] found that methanol is about three times more acidic than water, and from potentiometric data [14] is twice as acidic. The authors [15] reached the same conclusion when they determined the relative acidity constants of water and methanol by measuring optical densities. These values at the temperature of 27 °C are 1.2 and 4.0 for water and methanol, respectively. However, calculations based on the autoprotolysis constants of these compounds indicated that water is twice as strong an acid than methanol [16].

To date, there is no information for the quantitative composition of the liquid phase of MOH + ROH systems except for the data of Caldin and Long [4] and Murray [17]. This information is not enough to conclusively characterize the efficiency of alkoxide formation in these systems (Table 1). Furthermore, in these earlier studies, nonselective methods such

Table 1 Published data on the liquid phase composition of MOH + ROH systems

No	R	M	Initial solution of MOH/ (g·dm^{-3})	t/°C	$C_{(\mathrm{MOH})}$/ (g·dm^{-3})	$C_{(\mathrm{ROM})}$[a]/ (g·dm^{-3})	Ref.
1	CH_3	Na	saturated solution	28	239.00	–	[17]
2	C_2H_5	Na	saturated solution	28	136.00	–	[17]
			4.00	25	0.32	6.75[b]	[4]
			20.00	25	0.74	32.74[b]	[4]
			40.00	25	2.76	63.31[b]	[4]
3	CH_3	K	saturated solution	28	405.00	–	[17]
4	C_2H_5	K	saturated solution	28	290.00	–	[17]

[a] The author of [17] did not take into account the formation of alkali alkoxide according to Eq. 1

[b] Recalculated based on values for the NaOH/(NaOH + C_2H_5ONa) ratio

as titrimetry and colorimetry were used for hydroxide- and alkoxide-ion determination when both are present.

Much less is known about the vapor phase composition of these systems [18, 19]. In reference [19], vapor pressure data for methanol were measured at 24.9 °C in the NaOH + CH_3OH system at different NaOH concentrations. It was found that the vapor-pressure depression of methanol increased with increasing NaOH concentration.

In the present paper, the vapor and liquid phase compositions of the KOH + CH_3OH system have been studied at 25 °C. The quantitative determination of the concentrations of volatile components, both in the liquid and vapor phases of this system, was accomplished with the GC method.

2 Experimental

2.1 Chemicals

The chemicals used were obtained from Merck and Aldrich. Methanol (CH_3OH, 99.9 mass-%) was stored over 3 Å molecular sieves. The water mass fraction in methanol was determined by the GC method and it did not exceed 0.1%. Potassium hydroxide (KOH, 99.8 mass-%) was previously dried in a vacuum oven at 140 °C for 5 h. Potassium carbonate (K_2CO_3, 99.9 mass%) was previously heated at 120 °C for 1 h.

2.2 Apparatus and Procedure

A Chrom-5 gas chromatograph, with a 1.5 m glass column filled with Separon CHN of (0.125–0.200) mm and a thermal conductivity detector, was used. The temperatures of the column oven and sample chamber were 96 and 220 °C, respectively. Helium (purity 99.9%) was used as a carrier-gas with a flow rate of 0.5 $cm^3 \cdot s^{-1}$. The GC sample from a liquid phase was taken through a gasket of the vial using a Hamilton micro syringe (sample volumes about 0.5×10^{-3} cm^3). Four parallel runs were usually accompanied by sampling at an interval of about 0.5 h. A gas syringe preheated to the same temperature as the sample vial was used for the analysis of a vapor phase. The sampling and analysis of the vapor phase were carried out similarly to that for the liquid phase analysis (sample volume about 3 cm^3). The experimental setup and apparatus for testing are described in detail in our previous work [18].

The mixtures consisting of methanol and potassium hydroxide were prepared gravimetrically. For each experiment, various quantities of methanol from (4 to 11) g and KOH from (0.1 to 3.5) g were charged into the 20 cm^3 sample vial containing a Teflon® stirrer. The vial was hermetically sealed by a silicone rubber gasket and placed in a temperature-controlled cell. The sample was continuously stirred for 1 h at the target temperature.

Liquid sample calibration was performed using water + methanol solutions of known concentrations. The area of the water peak was normalized to that of the methanol peak. Calculation of the quantity of water in a sample was made based on the ratio of the peak areas of water and methanol taking into account the stoichiometry of Eq. 1. The relative standard deviation of the water determination in the liquid phase did not exceed 9% (at the confidence level 0.95).

In order to prepare calibration samples for the vapor phase, various mixtures of methanol and water were completely vaporized in a 1000 ± 0.1 cm^3 vessel at 25 ± 0.1 °C, and vapor samples were injected into the chromatograph. The water and methanol peak areas were

Table 2 Liquid phase composition of the $KOH + CH_3OH$ and $CH_3OK + CH_3OH + H_2O$ systems at 25 °C

No	Initial $100\cdot w$[a]				Liquid $100\cdot w$[a]				Yield[b]/%
	KOH	CH_3OH	CH_3OK	H_2O	KOH	CH_3OH	CH_3OK	H_2O	
1.	2.15	97.85	–	–	0.08	96.66	2.60	0.66	96.7
2.	–[c]	94.96	3.64	1.40	1.70	94.95	2.50	0.85	–
3.	16.98	83.02	–	–	8.28	77.98	10.94	2.80	51.2
4.	36.05	63.95	–	–	23.23	56.61	16.02	4.14	35.7

[a] w is the mass fraction

[b] Calculated from the quantity of water formed according to Eq. 1

[c] K_2CO_3 used rather than KOH

normalized to the air peak area to yield calibration factors. The relative standard deviation of the analysis of vapor phase components did not exceed 20% for water and 10% for methanol (at the confidence level 0.95).

The concentration of "background" water was determined both by the calibration and at the performance of the experiments, using blank sample analysis. As a rule, the "background" water mass fraction did not exceed 0.1% and it was taken into account for calculations of the liquid sample's composition.

Potassium methoxide obtained by reaction of methanol and potassium carbonate was used in an experiment (Table 2, experiment 2). Potassium carbonate (5 g) and about 20 cm^3 of dry methanol were placed in the circulation device [20]. The repeated circulation of methanol through a layer of potassium carbonate was performed analogously to hot percolation in the device. Potassium methoxide was obtained as a strong solution in methanol according to Eq. 3:

$$CH_3OH + K_2CO_3 \rightleftarrows CH_3OK + KHCO_3 \tag{3}$$

The concentration of CH_3OK, after treating a corresponding sample with water, was determined by a titrimetric method [21]. The methanol solution of CH_3OK was adjusted to a desired concentration by addition of pure methanol and then used according to a procedure described above for the $KOH + CH_3OH$ system.

3 Results and Discussions

3.1 Liquid Phase Composition

We established that the quantity of water generated in the liquid phase (Eq. 1) regularly increases with increasing concentration of potassium hydroxide (Fig. 1).

Figure 2 illustrates the correlation between reaction yield according to Eq. 1 at 25 °C, as calculated from the quantity of water formed and the mole ratio of KOH/CH_3OH. The curve has a maximum close to 100% at the KOH/CH_3OH ratio of 0.018. This means that a methanol solution of KOH prepared in the KOH/CH_3OH mass proportion of 1:30 contains potassium methoxide, water and only minor quantities of potassium hydroxide (Table 2, item 1). Increasing the KOH/CH_3OH ratio results in a decrease of the yield of potassium methoxide and water. Equilibrium is shifted in the reverse direction, and is accompanied by

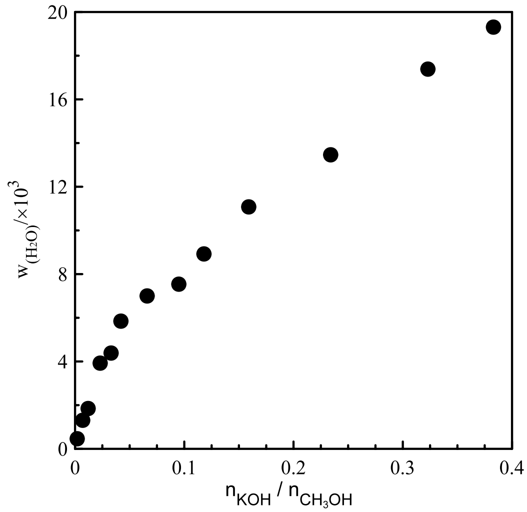

Fig. 1 Variation of the water mass fraction present in the liquid phase (Eq. 1) depending on the KOH/CH_3OH mole ratio

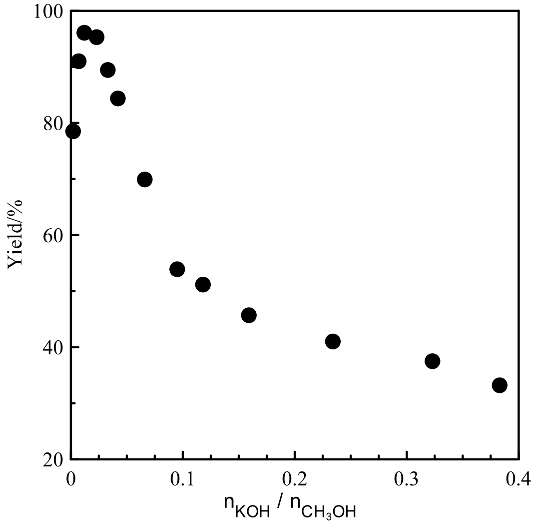

Fig. 2 Relationship between reaction yield and the KOH/CH_3OH mole ratio at 25 °C

a gradual increase of the viscosity until the appearance of a solid phase at an KOH/CH_3OH ratio above 0.4 (Fig. 2).

Thus, the equilibrium of Eq. 1 gives rise to nearly complete formation of potassium methoxide only in dilute solutions. The decreasing yield of Eq. 1 at KOH/CH_3OH mole ratios less than 0.018 is probably due to a small amount of water being present in methanol under the experimental conditions. According to the data from blank runs, the mass fraction of this "background" water is about 0.1% in methanol. This amount is comparable to the quantity of water forming from the reaction at low KOH concentrations. As a result, the equilibrium is shifted to the left and the reaction yield decreases.

In order to clarify the influence of water on the quantity of CH_3OK formed in methanol, a solution of potassium methoxide was prepared from K_2CO_3 and dry methanol at a mole ratio of CH_3OK/CH_3OH close to 0.018 (when converted to the equivalent amount of KOH).

After that, water was added to this solution equivalent to an amount 20% higher than the number of moles of potassium methoxide. Analysis of this mixture shown that water had reacted with only 30% of the potassium methoxide. The mixture compositions calculated on the basis of GC data for the water concentration are presented in Table 2 (item 2). The composition of potassium methoxide and water are close to those obtained from KOH and methanol when the KOH/CH_3OH mole ratio is 0.018 (compare experiments 1 and 2 of Table 2). This means that the widespread use of the term "solution of potassium hydroxide in methanol" or "methanol solution of KOH" is not quite correct. In fact, when preparing a so-called "methanol solution of KOH" at about 17% (or 3 mole·L^{-1}) potassium hydroxide, the mixture will contain approximately equal quantities of CH_3OK and KOH in the presence of $w_{H_2O} = 2.8\%$ in weight per cent (Table 2, experiment 3). Moreover, for certain proportions of KOH and CH_3OH (Table 2, experiment 1), the system consists of a solution of potassium methoxide in methanol having a small water concentration. Thus, the KOH + CH_3OH system is more properly described as a four-component mixture whose component ratios may vary.

The data cited from [5, 17] were based on a titrimetric determination of the total amount of base (KOH + CH_3OK) in this system, but the alkalinity was assigned only to potassium hydroxide. We have mixed KOH and CH_3OH at 25 °C in the proportions according to Table 1, experiment 3, i.e. at a KOH/CH_3OH mole ratio equaled 0.315. As a result, a mixture was obtained that contains 292.6 g·dm^{-3} KOH, 201.8 g·dm^{-3} CH_3OK, and 51.7 g·dm^{-3} H_2O. The liquid phase composition of this mixture is presented in Table 2, experiment 4. The subsequent recalculation of KOH and CH_3OK concentrations to the equivalent amount of potassium hydroxide alone gives the value 410.9 g·dm^{-3}. This value is close to 405 g·dm^{-3} reported by Murray [17].

3.2 Vapor Phase Composition

Analysis of the vapor phase for the equilibrium system described by Eq. 1 has shown that the methanol vapor concentration changes according to the concentration of K^+ present as both hydroxide and methoxide. The concentration of methanol vapors decreases by a factor of 3.5 with increasing K^+ concentration in the solution (Fig. 3). The same correlation for the methanol vapor concentration was also found for the methanolic solution of CH_3OK obtained from K_2CO_3. The authors of [18] observed a decreasing methanol concentration in the vapor phase of the NaOH + CH_3OH system at 24.9 °C, with a slightly greater vapor pressure depression in comparison with the KOH + CH_3OH system. The increasing vapor pressure depression values correlate with the decreasing cationic radii in going from K^+ to Na^+ [19].

The water vapor concentration varies with the mole ratio of KOH/CH_3OH (Fig. 4). The maximum water vapor concentration occurs in the interval where the KOH/CH_3OH mole ratio ranges from 0.14 to 0.18 and exceeds the concentration level of the "background" water by approximately three fold, as determined by the air humidity over the liquid phase. It is necessary to note that the amount of water in the vapor phase is insignificant and does not exceed 0.07% of the amount of water formed according to Eq. 1. The shape of a curve presented in Fig. 4 can, apparently, be explained by the changes of relative quantities of CH_3OK and KOH upon increasing the KOH/CH_3OH mole ratio. It seems that increasing the potassium hydroxide concentration leads to a greater retention of water in the solution phase and thus to a lower water vapor concentration.

In our previous work [18] we measured the mole fractions of methanol in the vapor phase at different initial KOH/CH_3OH mole ratios. In the present paper, the fluid phase component

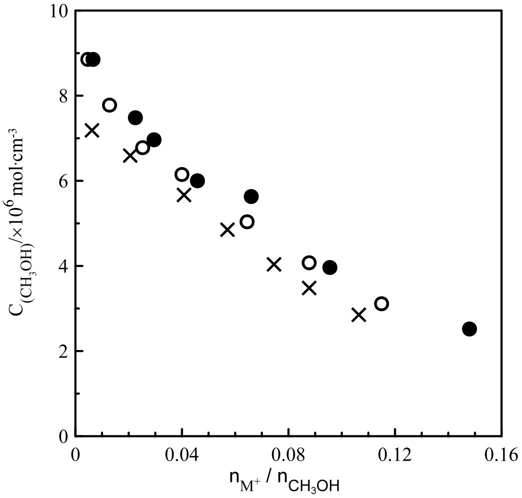

Fig. 3 Methanol vapor concentration dependence on the M^+/CH_3OH mole ratio at 25 °C: ● in the $KOH + CH_3OH$ system (M = K); ○ over a solution of CH_3OK in methanol (M = K); × in the $NaOH+CH_3OH$ system [19] (M = Na)

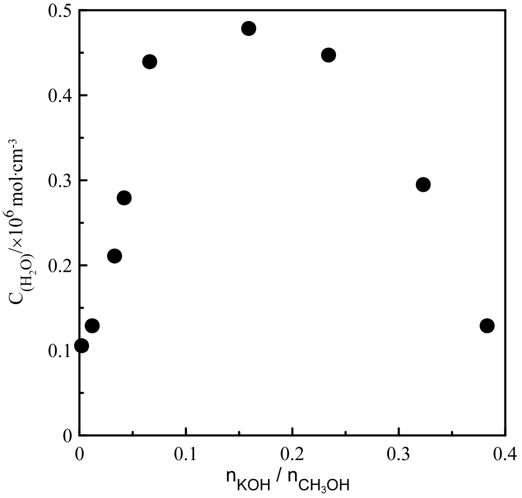

Fig. 4 The dependence of the water concentration in the vapor phase on the initial KOH/CH_3OH mole ratio at 25 °C

concentrations are presented in molar concentration units. This information clearly shows where a maximum of the reaction yield occurs.

4 Conclusion

It has been demonstrated that when KOH is dissolved in dry methanol at 25 °C, equilibrium among all components of the reaction mixture is established as a result of acid-base interaction. The equilibrium composition and amount of potassium methoxide formed depend on the KOH/CH_3OH mole ratio. At the mole ratio 0.018 and 25 °C, the liquid phase at equilibrium contains the follow mass fractions: 2.6% CH_3OK, 0.66% H_2O and 0.08% KOH. In the vapor phase, the methanol vapor concentration decreases by a factor of 3.5 when the KOH/CH_3OH mole ratio is changed from 0.01 to 0.20.

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References

1. Turova, N.Ya., Novoselova, A.V.: Alcohol derivatives of the alkali and alkaline earth metals magnesium, and thallium(I). Russ. Chem. Rev. **34**, 161–185 (1965)
2. Bradley, D.C.: Metal alkoxides. Prog. Inorg. Chem. **2**, 303–361 (1960)
3. Engel, M.: About potassium crystal-alcoholate. C.R. Séances Acad. Sci. (France) **103**, 155–157 (1886)
4. Caldin, E.F., Long, G.: The equilibrium between ethoxide and hydroxide ions in ethanol–water mixtures. J. Chem. Soc. 3737–3742 (1954)
5. De Wall, A.J.C.: Solid-Liquid Equilibrium in KOH–C_2H_5OH–H_2O System. University of Leyden, Leyden (1910)
6. Sakai, K., Watanabe, I., Yokoyama, Y.: Vertical ionization potentials of alkoxides in solution. Bull. Chem. Soc. Jpn. **67**, 360–362 (1994)
7. Williams, D., Bost, R.W.: Reaction products of ethyl alcohol and sodium hydroxide. J. Chem. Phys. **4**, 251–253 (1936)
8. Slonim, I.Ya., Lyubomilov, V.I.: Nuclear magnetic resonance in butanol–sodium butylate–water system. Zh. Fiz. Khim. **48**, 842–844 (1974)
9. Murto, J.: Kinetics of the reactions of 2,4-dinitrofluorobenzene with hydroxide and alkoxide ions in alkanol–water mixtures. Acta Chem. Scand. **18**, 1029–1043 (1964)
10. Rochester, C.H.: The ionic products of water and methanol in methanol–water mixtures. J. Chem. Soc., Dalton Trans. 5–8 (1972)
11. Mollin, J., Karaskova, E.: Alkoxide-to-hydroxide ion activity ratios in water–ethylene glycol and water–1-propanol systems. Collect. Czech. Chem. Commun. **56**, 269–276 (1991)
12. Komers, K., Machek, J., Stloukal, R.: Biodiesel from rapeseed oil, methanol and KOH. 2. Composition of solution of KOH in methanol as reaction partner of oil. Eur. J. Lipid Sci. Technol. **103**, 359–362 (2001)
13. Unmack, A.: The equilibrium between methylate and hydroxyl ions in mixtures of methanol and water. I. Communication. Z. Phys. Chem. **129**, 349–369 (1927)
14. Unmack, A.: The equilibrium between methylate and hydroxyl ions in mixtures of methanol and water. II. Investigations by means of electrometric hydrogen-ion measurements. Z. Phys. Chem. **131**, 371–388 (1928)
15. Hine, J., Hine, M.: The relative acidity of water, methanol and other weak acids in isopropyl alcohol solution. J. Am. Chem. Soc. **74**, 5266–5271 (1952)
16. Unmack, A.: The equilibrium between methylate and hydroxyl ions in mixtures of methanol and water. III. Calculation of the equilibrium constant from dissociation constant for methyl alcohol and water. Z. Phys. Chem. **133**, 45–50 (1928)
17. Murray, A.G.: Solubility of sodium and potassium hydroxides in methanol and ethanol. J. Assoc. Off. Agric. Chem. **12**, 309–311 (1929)
18. Kurzin, A.V., Evdokimov, A.N., Platonov, A.Yu., Maiyorova, H.D.: Activity coefficients of methanol and water in the reaction of potassium hydroxide methanolysis. J. Chem. Eng. Data **48**, 344–346 (2003)
19. Bixon, E., Guerry, R., Tassios, D.: Salt effect on the vapor pressure of pure solvents: methanol with seven salts at 24.9 °C. J. Chem. Eng. Data **24**, 9–11 (1979)
20. Loder, D.J., Lee, D.D.: Preparation of alkali metal alkoxides. US Patent 2,278,550 (1942)
21. Platonov, A.Yu., Evdokimov, A.N., Kurzin, A.V., Maiyorova, H.D.: Solubility of potassium carbonate and potassium hydrocarbonate in methanol. J. Chem. Eng. Data **47**, 1175–1176 (2002)