Activity Coefficients of Methanol and Water in the Reaction of Potassium Hydroxide Methanolysis

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The activity coefficients of methanol and water in the methanol + KOH reaction system were determined with the help of gas chromatography at 298 K, 303 K, and 308 K. The optimal parameters of the extended UNIQUAC model were used to correlate the activity coefficients of methanol and water.

Introduction

Water−solvent solutions of electrolytes have received attention in recent years with interest in solutions of salts in solvent + water mixtures. Metal hydroxides + water + alcohols systems have not been studied in detail. Such systems are of practical interest in industrial alkoxides' production.

Popular reference books and databases on vapor−liquid equlibrium in electrolyte + solvents systems (refs 1 and 2 and the Dortmund Data Bank) have no information about MOH + H_2O + ROH systems. Special cases are ROH + MOH systems (in initial anhydrous alcohol), in which water is produced during the reaction. Engel[3] reported for the first time that the mixing of potassium hydroxide with ethanol is accompanied by the reaction of these components according to eq 1

$$\mathrm{ROH} + \mathrm{MOH} = \mathrm{ROM} + \mathrm{H_2O} \qquad (1)$$

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

Unmack[4] has studied the equilibria between alkaline metal hydroxides and their alkoxides in aqueous−methanol solutions. It is important to have further measurements on alcohol + water + metal hydroxide and alcohol + metal hydroxide systems both for practical needs as well as for the development of models. Predictive models for vapor−liquid equilibrium in electrolyte-containing systems (for example, the electrolyte NRTL model of Mock et al.,[5] the modified UNIFAC group-contribution model of Kikic et al.,[6] the extended UNIQUAC model of Sander et al.,[7] and the LIQUAC model of Li et al.[8]) have not been used to describe ROH + H_2O + MOH and ROH + MOH systems.

The aims of this work is to determine the activity coefficients of methanol and water in the methanol + KOH reaction system with the help of gas chromatography at 298 K, 303 K, and 308 K. The experimental data presented in this work were correlated using the extended UNIQUAC model of Sander et al.[7] Several new interaction parameters for the model were obtained and are presented in this work.

Experimental Section

Materials. As far as possible, anhydrous chemicals were used. The methanol (99.9 mass %) from Merck was dehydrated and stored above 3 Å molecular sieves. The water content in the methanol was determined by a GC method and did not exceed 0.02 mass %. Potassium hydroxide was obtained from Aldrich (semiconductor grade), had a purity of 99.99 mass %, and was previously dried at 140 °C in a vacuum oven for 5 h.

Procedure. Mixtures consisting of methanol and potassium hydroxide were prepared gravimetrically using an analytical balance with an accuracy of ±0.1 mg. For each experiment ≈10 g of methanol and a corresponding amount of KOH were charged into the 20 cm^3 heated sample vial. After the vial was closed by means of a special lid, with a silastic (silicone rubber) washer, it was brought to the required temperature in the thermostatic cell controlled to within ±0.05 K. The mixture was continuously agitated for 6 h at the given temperature (298 K, 303 K, or 308 K).

Analysis Method. Initial concentrations of potassium hydroxide and solvent in the liquid phase were determined by means of weighing KOH and methanol. Potassium hydroxide and alkoxide were regarded as nonvolatile components.

Methanol and water mole fractions (on a potassium compound free basis) in the liquid (x_i) and vapor (y_i) phases can be analyzed by gas chromatography. To analyze the vapor and liquid phases, a gas syringe (1 mL) and Hamilton microsyringe are used, respectively. A gas chromatograph (Chrom-5, Laboratorny Pristroje, Praha, Czech Republic) with a thermal conductivity detector (electric current was 80 mA) and a 1.5 m glass column (Separon CHN 0.125−0.200 mm) and an intergrator was used. The injector and chamber were 220 °C and 90 °C, respectively. The carrier gas was helium (purity = 99.9%) flowing at 0.5 $cm^3 \cdot s^{-1}$. The uncertainty of the GC analysis was ±0.5 mass %.

Calibrations were necessary before the peak areas could be used to determine the composition of each phase. The gas chromatograph was calibrated using mixtures of methanol and pure water that were prepared gravimetrically by using an analytical balance with an accuracy of ±0.1 mg. To prepare the calibration samples for the liquid phase, various methanol and water mixtures (summary volume 15 cm^3 in a 20 cm^3 vial) were prepared and injected. Because of negligible amounts in the vapor phase (small vapor volume, moderate pressure), it was reasonable to assume that the liquid-phase composition is the same as the feed composition. To prepare the calibration samples for the vapor phase, various methanol and water mixtures were completely vaporized in a 1000 ± 0.1 cm^3 vessel at 298 K and injected. To obtain the calibration equation, the requied mass fractions and area fractions were correlated

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Table 1. Experimental Reaction Conditions (Initial Mole Ratio of Potassium Hydroxide/Methanol, Temperature), Mole Fractions of Methanol (1) in the Liquid Phase (x'_1) and the Vapor Phase (y'_1) in Equilibrium, and Experimental Activity Coefficients (γ_i) for Methanol (1) and Water (2)

init ratio	T/K	x'_1[a]	y'_1	γ_1	γ_2
0.05	298	0.983	0.998	0.864	0.899
0.10	298	0.967	0.989	0.881	0.870
0.15	298	0.953	0.981	0.898	0.852
0.20	298	0.941	0.979	0.910	0.840
0.25	298	0.932	0.972	0.937	0.829
0.30	298	0.925	0.969	0.951	0.820
0.05	303	0.983	0.996	0.959	0.890
0.10	303	0.967	0.991	0.972	0.879
0.15	303	0.952	0.983	0.994	0.868
0.20	303	0.940	0.980	1.015	0.859
0.25	303	0.931	0.974	1.036	0.847
0.30	303	0.924	0.969	1.050	0.833
0.05	308	0.982	0.997	1.054	0.944
0.10	308	0.966	0.989	1.073	0.876
0.15	308	0.951	0.982	1.088	0.867
0.20	308	0.938	0.978	1.102	0.859
0.25	308	0.930	0.973	1.114	0.846
0.30	308	0.923	0.968	1.128	0.840

[a] Liquid-phase mole fraction on a salt-free basis.

Table 2. UNIQUAC Reference Interaction Parameters (a^*_{ij}/K), Concentration-Dependent Parameters ($\delta_{ij,m}$), Volume Parameters (r_i), and Surface Area Parameters (q_i) for the Extended UNIQUAC Model of Sander

	CH_3OH	H_2O	K^+	OH^-	OCH_3^-
		a^*_{ij}			
CH_3OH	0.0	−164.8	945.3	249.0(f)[a]	−195.0(f)
H_2O	256.6	0.0	458.4	−230.2(f)	−544.0(f)
K^+	334.0	−220.6	0.0	−53.0(f)	−470.0(f)
OH^-	−138.0(f)	353.0(f)	397.2(f)	0.0	0.0
OCH_3^-	−350.0(f)	−420.6(f)	−90.1(f)	0.0	0.0
		r_i and q_i			
r_i	1.4311	0.92	3.0	1.0	1.13
q_i	1.4322	1.40	3.0	1.2	1.26
		$\delta_{ij,m}$			
K^+OH^-	32705(f)	5715(f)			
$K^+OCH_3^-$	830(f)	1508(f)			

[a] (f) means that these interaction parameters have been fitted in this work.

using a third-order polynomial with the least-squares method (mean deviation = 0.1%).

Results and Discussion

The yield of potassium methoxide was determined from the total water amount by eq 1. It is difficult to determine the liquid-phase composition when the initial mole ratio KOH/CH_3OH is more than 0.3. The experimental data are given in Table 1.

To describe the observed VLE behavior, the experimental data are correlated using the extended UNIQUAC model.

Sander et al. presented a model for the calculation of salt effects on the vapor−liquid equilibrium. The model combines a Debye−Hückel term with a modified UNIQUAC term. To ensure a rigorous expression for a Debye−Hückel term, Macedo et al.[9] modified the Debye−Hückel term of Sander's model according to the McMillan−Mayer solution theory.[10] The activity coeffcients (γ_n) of methanol and water in the $KOH + CH_3OH + H_2O + CH_3OK$ system are calculated as

$$\ln \gamma_n = \ln \gamma_n^{\mathrm{UNIQUAC}} + \ln \gamma_n^{\mathrm{DH}} \tag{2}$$

$$\ln \gamma_n^{\mathrm{UNIQUAC}} = \ln \gamma_n^{\mathrm{C}} + \ln \gamma_n^{\mathrm{R}} \tag{3}$$

where γ_n^{DH} is the Debye−Hückel term and γ_n^{C} and γ_n^{R} represent the UNIQUAC combinatorial and residual contributions. In this work the expressions for γ_n^{C} and γ_n^{R} are unchanged.

The interaction parameters between an ion i and a solvent m (a_{im} and a_{mi}) are considered to be dependent on concentration in the same way as that proposed by Sander[7]

$$a_{im} = a^*_{im} + \theta_i \sum_{j \neq i} \delta_{ij,m} \theta_j \tag{4}$$

$$a_{mi} = a^*_{mi} + \theta_i \sum_{j \neq i} \delta_{ij,m} \theta_j \tag{5}$$

where a^*_{im} and a^*_{mi} represent reference interaction parameters, $\delta_{ij,m}$ is a parameter, the summation is over all ionic species except i, and θ_i represents the surface fraction of ion i. The volume and surface area parameters, r_i and q_i, are given in Table 2. For the anions, r_i and q_i values are based on the molecular sizes of the ions.

For this system 22 parameters are needed: 2 solvent−solvent interaction parameters, 4 ion−ion interaction parameters, 12 ion−solvent interaction parameters, and 4 electrolyte−solvent interaction parameters. A few a^*_{ij} interaction parameters (K^+/CH_3OH, K^+/H_2O, CH_3OH/K^+, H_2O/K^+) were available in the literature.[7,9] On the other hand, the binary solvent−solvent interaction parameters have been obtained directly from Gmehling et al.[11] The remaining model parameters were fitted to the experimental data by minimization of the following objective function F using the Simplex−Nelder−Mead method[12]

$$F(a_{ij}, a_{ji}, \delta_{ij,m}) = \sum_{nt} \sum_{np} (y_{i,1(\mathrm{exptl})} - y_{i,1(\mathrm{calcd})})^2 = \min \tag{6}$$

where y represents the vapor-phase mole fraction and nt and np are the number of data sets and the number of data points for each data set, respectively. The subscripts exptl and calcd denote experimental data and calculated values, respectively. The vapor-phase composition can be calculated by solving iteratively the equilibrium condition

$$y_i P = x_i \gamma_i P_i^{\mathrm{s}} \Phi_i \tag{7}$$

where

$$P = x_1 \gamma_1 P_1^{\mathrm{s}} \Phi_1 + x_2 \gamma_2 P_2^{\mathrm{s}} \Phi_2 \tag{8}$$

$$\Phi = \varphi_i^{\mathrm{s}} PF_i / \varphi_i^{\mathrm{v}} \tag{9}$$

The saturation vapor pressure of pure solvent i, P_i^{s}, at the system temperature was calculated with the Antoine constants from the literature.[11] φ_i^{v} is the fugacity coefficient of solvent i in the phase vapor. φ_i^{s} is the fugacity coeffcient of pure solvent i at saturation pressure, and PF_i is the Poynting factor. x_i is the liquid-phase mole fraction of solvent i based on the assumption of total dissociation of KOH and CH_3OK. φ_i^{s} is approximately equal to φ_i^{v}, and PF_i is approximately equal to one at atmosphere pressure, so Φ_i is equal to one, respectively.

All UNIQUAC parameters are given in Table 2.

Activity coefficients for the ions are not necessary for calculation of the salt effect on the vapor−liquid equlibrium, and the expressions will not be presented here.

Conclusion

The activity coefficients of the reaction system methanol + KOH have been investigated at 298 K, 303 K, and 308

K at six different initial mole ratios of KOH/CH_3OH. The extended UNIQUAC model was used for the correlation of properties of KOH + CH_3OH + H_2O + CH_3OK reaction systems. New interaction parameters have been fitted between ions (CH_3O^- and OH^-) and solvents (CH_3OH and H_2O). The model represents the experimental data with the required accuracy. The mean absolute deviation of the mole fraction of methanol in the vapor phase (y_1) is 0.009.

Obtained activity coefficients may be used for calculations of equlibria constants of hydroxide alcoholysis reactions.

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