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SOLUBILITY OF SODIUM METHOXIDE IN PURE AND MIXED SOLVENTS

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Abstract

Sodium methoxide is a catalyst for biodiesel production. This study aims to investigate of the solubility of sodium methoxide in methanol and methanol+n-hexane, methanol+dimethyl carbonate mixed solvents. The property of sodium methoxide solubility is important information for crystallization process design. The solubility of sodium methoxide in methanol was studied measured within the temperature range at 10, 20, 30, 40, 50, 60 ˚C respectively. The measurement of concentration of saturated solution at each temperature was used gravimetric method. The solubility of sodium methoxide was measured in 0-100 % methanol with n-hexane varying from 100-0 % and 0-100 % methanol with dimethyl carbonate from 100-0 % at 33 ˚C. The dissolution of the sodium methoxide was carried out in a 1,000 mL jacketed glass vessel. The mixture was stirred vigorously for 72 hours. The results show that the solubility of sodium methoxide in methanol increase as the temperature increase significantly. N-hexane and dimethyl carbonate are antisolvent for sodium methoxide so the solubility of sodium methoxide in methanol+n-hexane mixed solvents is decrease with the increase of n-hexane ratio and the results are the same for methanol+dimethyl carbonate system.

Keywords: Sodium methoxide, Solubility, Methanol, n-Hexane, Dimethyl carbonate

Introduction

Sodium methoxide is an important catalyst because it can use as a catalyst to produce biodiesel by the transesterification of triglyceride with alcohol from vegetable oils and animal fat [1-4]. Sodium methoxide is used as an intermediary in several industrial application such as transesterification [5]. Figure 1 shows the molecular structure of sodium methoxide. Lin et al. used sodium methoxide catalyst to produce palm-biodiesel assisted by a microwave system [2]. Shi et al. used waste chicken fat to produce biodiesel by an integrated catalytic process of composite membrane and sodium methoxide [4]. Nowadays, there are several methods to produce sodium methoxide. For example, electrodialysis in a non-aqueous medium [6], preparing sodium methoxide from sodium hydroxide reaction coupling with separation process [7], manufacture of sodium methoxide from sodium metal and from sodium hydroxide by using reactive distillation [8], and sodium methoxide catalyst prepared by crystallization [1].

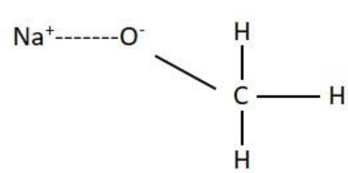


Figure 1 Molecular structure of sodium methoxide

The pure sodium methoxide was produced by many separation techniques, but re-crystallization process is very interesting [6-9]. The quality of the final product of crystallization process depends on the selected process. For determination of the crystallization process and type of solvents, the solubility of a compound in different solvents is the key [9]. The solubility is defined by the quantity of solute dissolve at the saturated solutions point and the saturations at a given temperature can be prepared by dissolved a maximum quantity of solute in a given solvent [10]. Hu et al. reported that the solubility of dimethyl succinyl succinate in tetrahydrofuran, acetic ether, acetone, acetonitrile, 1-propanol, ethanol and methanol pure solvents increased with increasing temperature [9]. There are a lot of studies about solubility such as sodium sulfate solubility in (water + ethanol) mixed solvent in the presence of hydrochloric acid [11], solubility improvement of the anti-cancer drug pazopanib hydrochloride [12], solubility prediction of pharmaceutical compounds in organic and aqueous solvents [13], and solubility parameters of subcritical state and supercritical state of ethanol [14]. Unfortunately, the solubility of sodium methoxide in common solvents was rarely reported in the literature.

In this work, the solubility of sodium methoxide in methanol and mixed organic solvent were investigated. The solubility of sodium methoxide in pure methanol was measured over the temperature range from 10 °C to 60 °C at atmospheric pressure. For mixed organic solvents, there are (methanol+n-hexane) and (methanol+dimethyl carbonate) which varying the ratio from 0 :100 to 100 : 0 at 33 °C. The dissolution of sodium methoxide in various solvents also investigated. Finally, the experimental results were correlated with power law and linear model.

Materials and methods

Chemicals

Sodium methoxide ($NaOCH_3$) with purity of 98 % was supplied by Alfa Aesar company. Methanol (CH_3OH) was used analytical reagent purity of 99.8 % from Ajex Finechem Pty Ltd. Dimethyl carbonate (DMC) purity of 99 % was supplied by Alfa Aesar company and n-hexane (C_6H_{14}) purity of 96 % was supplied by DAEJUNG company. The organic solvents were analytical grade obtained from Ajex Finechem Pty Ltd. They are hexane, cyclohexane, benzyl alcohol, phenol, 1-butanol, 2-butanol, ethyl alcohol, ethyl acetate, acetonitrile, acetone, dimethyl sulfoxide, dimethyl carbonate, dichloromethane.

Apparatus

The solubility of sodium methoxide was measured by using jacket glass vessel reactor of 1,000 mL from IKA®-Werke GmbH & Co.KG. as shown in figure 2 and using syringe filter cellulose acetate from HYUNDAI Micro Co., LTD with a pore size of 0.45 μm and diameter of 25 mm for filtering the solution. The analytical tools for analysis of solid samples are commonly used hot air oven and weighing by four digits balance.

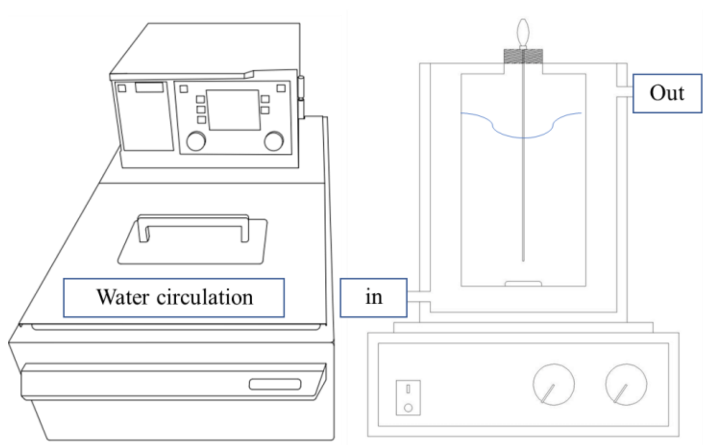


Figure 2 The set-up of solubility measurements

Methods

Solubility of sodium methoxide in pure methanol

Determination of solubility by using jacket glass vessel reactor of sodium methoxide in pure methanol was performed by varying the temperature at 10, 20, 30, 40, 50 and 60 °C respectively. Sodium methoxide 100 g was added into the reactor then added pure methanol 1,000 mL into the reactor. The stirring speed was set at 200 rpm and the solution was maintained at the specific temperature for 72 h. After the solution was saturated the stirring was stopped. The 5 mL of saturated solution was sampling and filtered by syringe. The filtered sample was dried in the oven for 1 h at 105 °C. The weight of dried sample was measured by four digits balance and then calculated the solubility of sodium methoxide.

Dissolution experiment of sodium methoxide in solvents

Determination of dissolution of sodium methoxide in 13 solvents were studied by adding sodium methoxide 0.054 g into 1 mL of each solvent. The solution was shake for 2 h at room temperature. The 0.6 mL of solution was sampling and filtered by syringe. The filtered samples were dried in the oven for 1 h at 105 °C. The weights of dried samples were measured by four digits balance and then the concentration of sodium methoxide was calculated.

Solubility of sodium methoxide in mixed solvents

From the dissolution experiments, n-hexane and dimethyl carbonate were selected as anti-solvent for study the solubility of sodium methoxide in the mixed solvents. The solubility was measured in 0-100 % methanol with n-hexane varying from 100-0 % and 0-100 % methanol with dimethyl carbonate from 100-0 % at 33 ˚C. At each solvent ratio, the saturated solution in methanol was prepared by adding 100 g of sodium methoxide into 1,000 mL of methanol and stirring for 72 h at 33 °C. Then the saturated solution was mixed with the anti-solvent following the specific methanol to anti-solvent ratio. The 10 mL of saturated solution was filtered by syringe. The filtered sample was dried in the oven for 2 h at 105 °C. The weight of dried sample was measured by four digits balance and then the solubility of sodium methoxide was calculated.

Results and discussion

1. **Solubility of $NaOCH_3$ in CH_3OH**

The solubility behavior mostly depends on the temperature. The solubility data of sodium methoxide in pure methanol at temperature 10, 20, 30, 40, 50, and 60 °C were determined using the gravimetric method. Figure 3 shows the solubility of sodium methoxide in pure methanol. Table 1 shows the experimental condition and the solubility of sodium methoxide in pure methanol as well. From figure 3 and table 1, we can see that the solubilities of sodium methoxide in pure methanol was temperature-dependent, increased with increasing the temperature [9]. The reason that the solubility increased with the temperature is when the temperature increased the space between the molecules in the solutions is also increase so the molecule of solute dissolved more in the solvent [13].

Table 1 The solubility of sodium methoxide and experimental conditions

Set number	Temperature, (°C)	Solubility of $NaOCH_3$, (g solute/100 g solvent)
Set I	10	20
Set II	20	20
Set III	30	22
Set IV	40	26
Set V	50	29
Set VI	60	45

Additional data: Mass of sodium methoxide in the solution is 100 g
Time for the experiment is 72 h
Stirring speed is 200 rpm

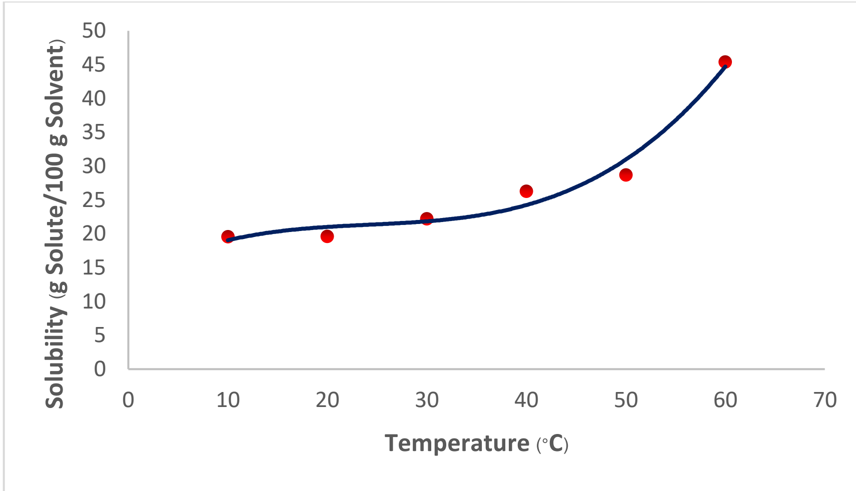


Figure 3 The solubility curves of sodium methoxide in methanol at difference temperature

The solubility of sodium methoxide in pure methanol can calculate from equation 1. As you can see in the equation 1, when the temperature increases the solubility of sodium methoxide is also increase as a function of Polynomial law. R-squared value of equation 1 is 0.9743

$$Solubility = 0.0005T^3 - 0.0331T^2 + 0.871T + 13.182 \quad (1)$$

2. **Dissolution of sodium methoxide in solvents**

The important of dissolution in anti-solvent crystallization is how to select the type of suitable anti-solvent. From experiment of dissolution of sodium methoxide in solvents, table 2 reports the measured dissolution of sodium methoxide in various solvent at room temperature. There are 13 solvents in the experiment. They are n-hexane, cyclohexane, benzyl alcohol, phenol, 1-butanol, 2-butanol, ethyl alcohol, ethyl acetate, acetonitrile, acetone, dimethyl sulfoxide, dimethyl carbonate and dichloromethane respectively. Figure 4 shows the relationship between concentration and weight of sodium methoxide with type of solvent at room temperature. From figure 4 and table 2, they were found that n-hexane, 2-butanol, dimethyl carbonate, and dichloromethane cannot dissolved sodium methoxide. Figure 5 shows the color of the solution that changed after mixing of sodium methoxide and solvent. There are 2 solvents which changed the solution color. They are acetone and 2-butanol. This happened because of the chemical reaction between sodium methoxide and solvent. The ionic solute was dissolved by polar solvent [15]. Sodium methoxide is an ionic solvent, so it can dissolve in the polar solvent. Therefore, n-hexane and dimethyl carbonate are the suitable solvent for anti-solvent crystallization of sodium methoxide because the sodium methoxide is insoluble these solvents.

Table 2 The experimental result of $NaOCH_3$ dissolution in solvents

Solvents	Physical property		Weight of $NaOCH_3$, (g)	Concentration of $NaOCH_3$, (g/mL)
	Color	Smell		
n-hexane	-	-	0.0000	0.0
Cyclohexane	-	-	0.0392	0.1
Benzyl alcohol	-	-	0.7217	1.2
Phenol	-	-	0.5371	0.9
1-Butanol	-	-	0.0472	0.1
2-Butanol	Yellow	-	0.0000	0.0
Ethyl alcohol	-	-	0.0309	0.1
Ethyl acetate	-	-	0.4950	0.8
Acetonitrile	-	-	0.0160	0.0
Acetone	Orange	-	0.0574	0.1
Dimethyl sulfoxide	-	-	0.7675	1.3
Dimethyl carbonate	-	-	0.0000	0.0
Dichloromethane	-	Strong	0.0000	0.0

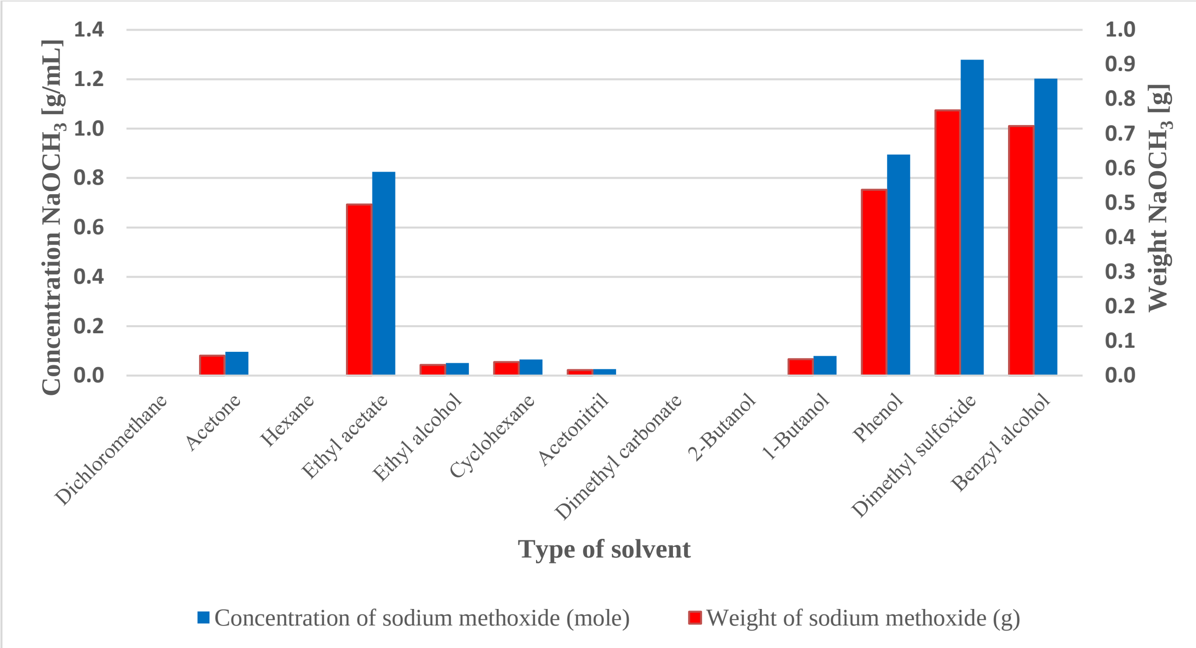
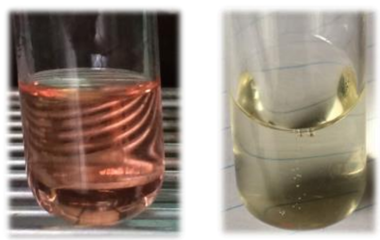


Figure 4 The relationship between concentration and weight of sodium methoxide with type of solvent at room temperature



(a.) (b.)

Figure 5 The solution color of the dissolution experiment after mixing of sodium methoxide and solvent

a. Sodium methoxide in pure acetone solution, b. Sodium methoxide in pure 2-butanol solution

3. Solubility of $NaOCH_3$ in mixed solvents

From the previous section, sodium methoxide was insoluble in hexane and dimethyl carbonate, but it was soluble in methanol. So that methanol is the good solvent for sodium methoxide and anti-solvent crystallization of sodium methoxide needs the information of the solubility of sodium methoxide in mixed solvent. The solubility data of sodium methoxide in methanol + n-hexane mixtures with the solvent ratio ranging from 0:100 to 100:0 are presented in figure 6. For comparison with each of the experimental points, experimental solubility data of sodium methoxide in methanol + n-hexane mixtures are presented in figure 6. The solubility of sodium methoxide decreased with solvent ratio because when the amount of n-hexane in the mixture increase the solubility of sodium methoxide decrease. It can be found that the solubility of sodium methoxide in methanol + n-hexane mixtures is a function of solvent composition. More specifically, the solubility of sodium methoxide in methanol + n-hexane mixtures decrease with the rise of solvent ratio, decreases with increasing n-hexane content of the mixed solvent, by these properties, n-hexane could be used as effective anti-solvent in the crystallization process [16].

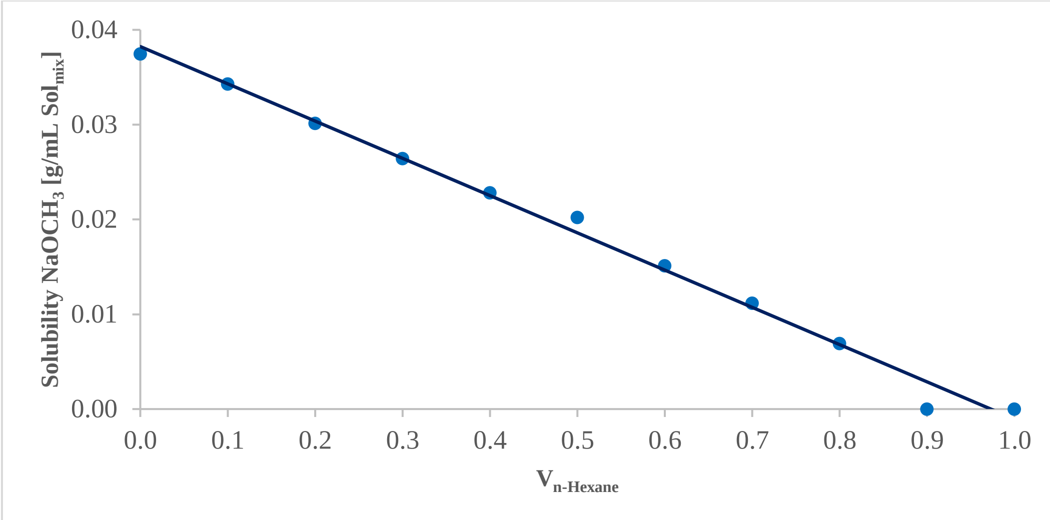


Figure 6 Solubility of $NaOCH_3$ in mixed solvent (methanol + n-hexane) at 33 °C

The solubility of sodium methoxide in mixed solvent (methanol+n-hexane) can calculate from equation 2. As you can see in the figure 6, when the volume fraction of hexane increases the solubility of sodium methoxide decreases in mixed solvent as a linear function in equation 2. R-squared value of equation 2 is 0.9923

$$Solubility = -0.0393T + 0.0382 \qquad (2)$$

Figure 7 reports the measured solubility of sodium methoxide in (methanol + dimethyl carbonate) mixed solvent, at different volume fraction ranging from 0:100 to 100:0. Figure 7 shows experimental solubility data of sodium methoxide in methanol + dimethyl carbonate mixtures for comparison with each of the experimental points. Similar result of solubility in mixed solvent of methanol and dimethyl carbonate were obtained as found in mixed solvent of methanol and hexane. It can be found that the solubility of sodium methoxide in methanol + dimethyl carbonate mixtures is a function of solvent composition. By the property of dimethyl carbonate, it can be used as anti-solvent in the anti-solvent crystallization of sodium methoxide by using methanol as the solvent [11].

The solubility of sodium methoxide in mixed solvent (methanol+dimethyl carbonate) can calculate from equation 3. As you can see in the figure 7, when the volume fraction of dimethyl carbonate increases the solubility of sodium methoxide decreases in mixed solvent as a linear function as follow:

$$Solubility = -0.0371T + 0.0367 \qquad (3)$$

R-squared value of equation 3 is 0.9982

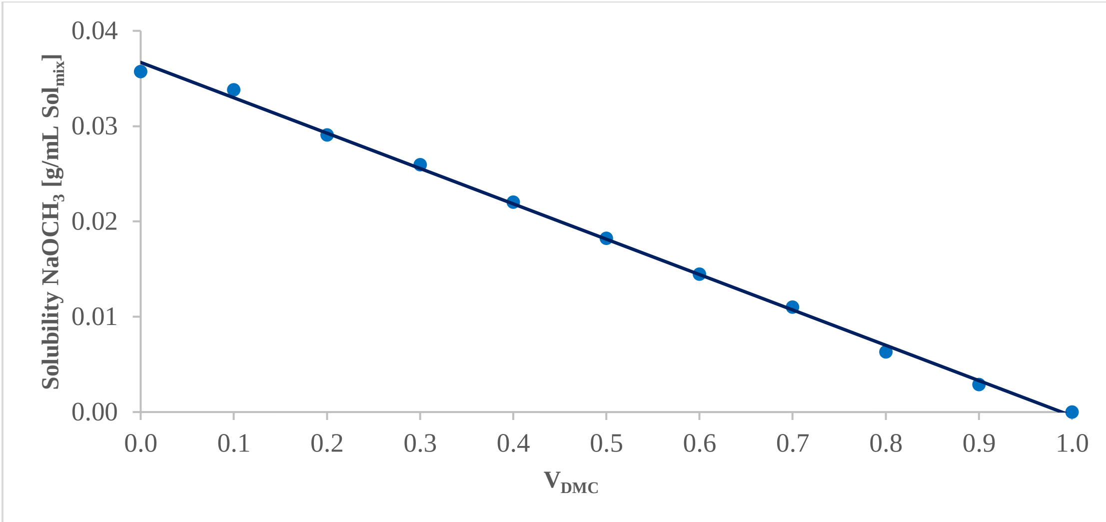


Figure 7 Solubility of $NaOCH_3$ in mixed solvent (methanol + dimethyl carbonate) at 33 °C

Conclusion

Using the gravimetric method, the solubility of sodium methoxide in pure methanol as a function of the temperature from 10 to 60 °C, the dissolution of sodium methoxide in 13 solvents at room temperature, the solubility of sodium methoxide in mixed solvent (methanol+n-hexane and methanol+dimethyl carbonate) as a function of volume fraction were determine in this work. It was found that the solubility of sodium methoxide in pure methanol proportional with the temperature. Hexane, 2-butanol, dimethyl carbonate, and dichloromethane are the solvent that cannot dissolved the sodium methoxide and the suitable solvents for study the solubility of mixed solvent are hexane and dimethyl carbonate. For the solubility of sodium methoxide in mixed solvent, the solubility of sodium methoxide decreases with increased volume fraction of anti-solvent. From this representation, important information needed to anti-solvent crystallization process can be obtained. Moreover, a great impact of hexane and dimethyl carbonate on the solubility of sodium methoxide in the mixed solvent was investigated.

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