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Assessment of Autoxidative Resistance for Organic Solvent by Pressure Monitoring Test

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Abstract : In the recycle process of organic solvent, the atmospheric oxygen can cause autoxidation and product peroxide. The time-saving method to evaluate the hazards has been required. In this study, oxygen pressure monitoring experiment was proposed as a new method to evaluate autoxidative resistances of solvents. Some of organic solvents were pressurized by oxygen and kept under isothermal condition. At the same time, the pressure in the vessel tracked. Iodometrical titration, thermal analysis and spectroscopic analysis were performed to measure peroxide concentration, the heat of reaction and chemical bonding change. From the results that THF has larger oxygen consumption rate than CPME, it is considered that autoxidative resistance of THF is lower than that of CPME. This method enables to obtain results in shorter time than other methods. These experimental results were consistent with the previous research with longer test durations [1-2].

Key words : autoxidation, peroxides, tetrahydrofuran, cyclopentylmethylether, dimethylsulfoxide

1. Introduction

For chemical industry, the organic solvent is essential and used in large amount. To reuse of waste solvent by resources-saving concept, the organic solvent is recovered by distillation, and the process takes on a growing importance. In the recycle process of organic solvent, the atmospheric oxygen can cause autoxidation and product peroxide [3]. In the past, peroxide caused some serious accidents by explosion [4]. The production of peroxide should be avoided to prevent similar accidents. Although antioxidants are usually added in a solvent as inhibitor to the autoxidation, the antioxidants cannot be used or do not work depending on a use environment. Therefore, to use an organic solvent safely, the prior experiment to clarify whether impurities are generated by autoxidation should be carried out.

Present examinations of autoxdative resistance for organic solvents have required several months for keeping them under isothermal conditions. The long examination time, however, does not suit for fine chemical industries using a large variety of solvents under time pressure. The time-saving method to evaluate the hazards has been required.

In this study, oxygen pressure monitoring experiment was proposed as a new method to evaluate autoxidative resistances of solvents. Dimethylsulfoxide (DMSO), Tetrahydrofuran (THF) and Cyclopentylmethylether (CPME) were pressurized to 0.99 MPa by O_2 in SUS316 closed vessel, kept under isothermal condition. The pressure in the vessel was measured at the same time.

2. Experiment

2.1 Materials

Fig. 1 and Table 1 show the chemical formula and physical properties of materials used in this study.
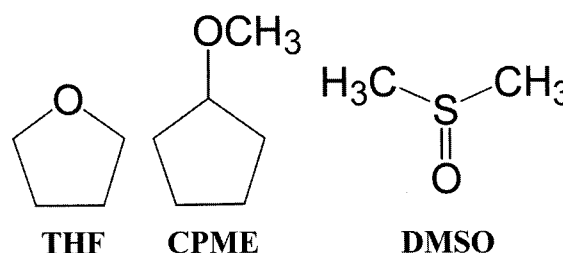

Fig. 1. Chemical formula of materials.

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Table 1. Physical properties of materials

	THF	CPME	DMSO
CAS-No.	109-99-9	5614-37-9	67-68-5
concentration [%]	99.9	99.5	99.0
manufacturer	Wako Pure Chemical Industries	Zeon Corporation	Wako Pure Chemical Industries
b.p. [°C]	65	106	189
m.p. [°C]	-108.5	< -140	18.5
steam pressure [kPa]	19.3	4.5	0.06
dipole moment [D]	1.7	1.27	4.6

2.2 Pressurization And Isothermal Holding

Four mL of the samples were pressurized to 0.99 MPa by oxygen in SUS316 closed vessel (Fauske & Associates), and stored under isothermal condition.

2.3 PRESSURE MONITORING

As the decrement of oxygen is correlated with increment of the peroxide produced by autoxidation, the progress of autoxidation was evaluated by the oxygen pressure monitoring experiment. The oxygen pressure in the vessel was measured by digital manometer PG-200 (COPAL ELECTRONICS).

2.4 Iodometrical Titration

Peroxide concentration of stored samples was measured by iodometrical titration. After the addition of sufficient quantity of 99.9% 2-plopanol, 99.7% acetic acid and potassium iodide powder to sampled materials under reflux, testing liquid was titrated with 0.01 mol/L aqueous solution of sodium thiosulfate. These reagents of this titration experiment were provided by Wako Pure Chemical Industry.

2.5 Spectroscopic Analysis

The infrared spectra of samples were investigated by infrared spectroscopy FT/IR-420 (JASCO) to measure chemical bonding changes before and after the storage.

2.6 Thermal Analysis

Differential scanning calorimetery Q-200 (TA instruments) was used to determine the thermal characteristics of samples. The samples put into the SUS-303 stainless closed crucible and heat up to 300°C at a heating rate of 5 K/min.

3. Results and Discussion

3.1 Pressure Monitoring

Fig. 2 shows the pressure in the vessel of materials as a function of storing time at 70°C. The pressure in the
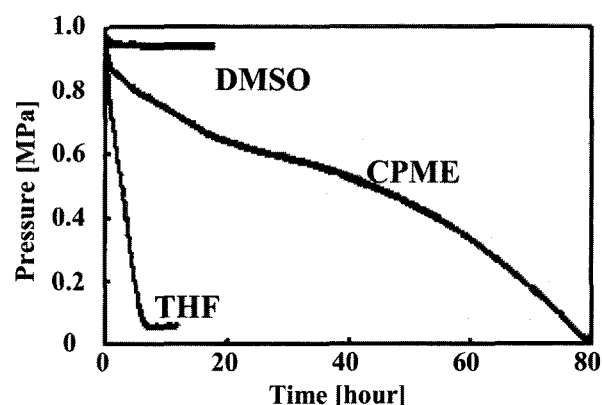

Fig. 2. Pressure change in vessel with time at 70°C.

vessel decreases by two reasons, dissolution or consumption of oxygen. According to the past report, the autoxidation occurs chiefly liquid phase. So it is would appear that dissolution is caused first, and oxygen is consumed by liquid phase next. If only dissolution of oxygen is caused, the pressure curve gradually decreases slope and reaches a constant value eventually.

As the results of pressure monitoring test, The pressure curve of DMSO remained at 0.94 MPa just after the start of storage, while the pressure of THF and CPME decreased up to their vapor pressure.

So the amount of oxygen decrement and oxygen consumption rate was calculated from equation (1-2).

$$OD = \frac{\Delta P \cdot V}{R \cdot T} \qquad (1)$$

$$^k OC = \frac{OD}{t \cdot n} \qquad (2)$$

OD: the amount of Oxygen Decrement [mol],
ΔP: the amount of Pressure decrement [Pa],
V: Volume of Vessel [m^3], R: gas constant [J/(K·mol)],
T: holding Temperature [K],
k_{OC}: oxygen consumption rate [h^{-1}],
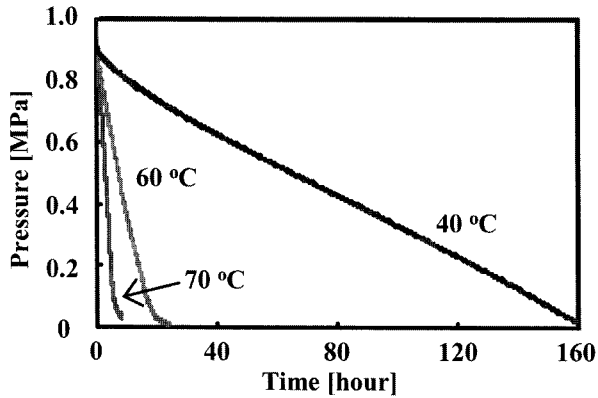t: time taken for oxygen consumption [h],
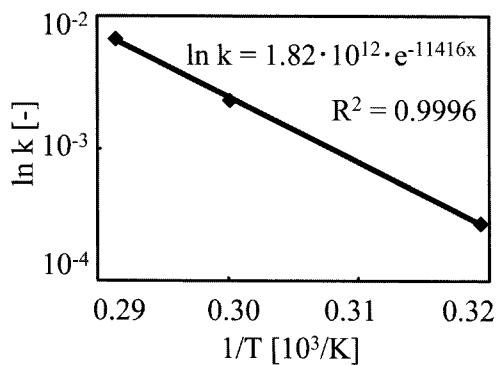
Fig. 3. Pressure change in vessel of THF with time.

Fig. 4. Oxygen consumption rate with temperature.

Fig. 5. FT-IR spectrum peaks of THF.

Fig. 6. FT-IR spectrum peaks of CPME.

n: the amount of material [mol]

One mol of THF comsumed 7.0 mmol of oxygen per hour. One mol of CPME comsumed 0.87 mmol of oxygen per hour. If the autoxidation were caused, the oxygen decreased by oxygen consumption not only dissolution. From the results that THF has larger oxygen consumption rate than CPME, it is considered that autoxidative resistance of THF is lower than that of CPME. DMSO exhibited high autoxidative resistance.
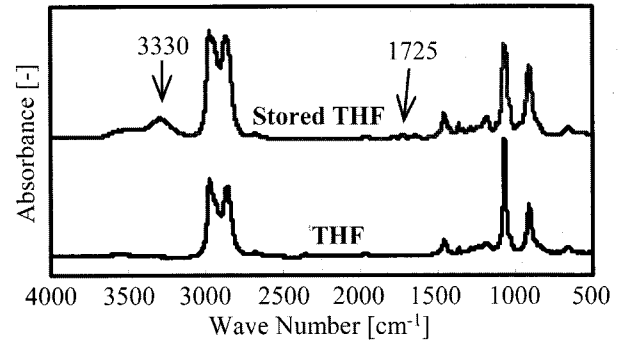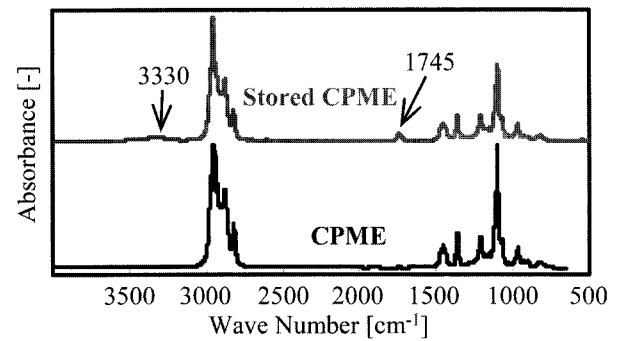
Fig. 3 shows the pressure in the vessel of THF as a function of storing time at 40, 60, 70°C. At each holding temperature, pressure in the vessel decreased up to their vapor pressure. The time taken for oxygen consumption became shortened with a rise in holding temperature. Fig. 4 shows oxygen consumption rate as a function of holding temperature. The temperature dependence at the oxygen consumption rate was confirmed from these results.

3.2 Spectroscopic Analysis

Fig. 5 shows the FT/IR spectrum peaks of THF. After storage of THF, these peaks were identified as OO-H

Table 2. Results of iodometric titration and thermala analysis

	Holding temp. [°C]	OD [mmol]	PO [mmol]	ΔPO [mmol]	C_{PO} [mol%]	Q_{DSC} [J/g]	T_O [°C]	k_{OC} [$10^{-3}h^{-1}$]
THF	-	0	0.16	-	0.32	80	101	-
	40	2.6	2.69	2.53	5.45	325	117	0.27
	60	1.8	2.10	1.94	4.25	179	120	2.3
	70	1.8	1.97	1.81	4.10	204	119	7.0
CPME	-	0	0.01	-	0.04	52	147	-
	70	2.4	1.30	1.29	3.78	152	122	0.87
DMSO	-	0	0.01	-	0.01	61	214	-
	70	0.14	0.01	0.00	0.01	61	215	-

stretch of peroxide at 3330 cm^{-1}, C = O stretch of carboxylic acid at 1725 cm^{-1} [6-7].

Fig. 6 shows the FT/IR spectrum peaks of CPME. These peaks were identified as OO-H stretch of peroxide at 3330 cm^{-1} and C = O stretch of carboxylic acid or cyclic ketone at 1745 cm^{-1} [6-7].

Carboxylic acid, lactone and ketone were considered as the product of the decomposition of the peroxide.

For DMSO, the spectrum peaks did not appear.

3.3 Iodometrical Titration And Thermal Analysis

As the results of iodometrical titration and thermal analysis, Table 2 shows the oxygen decrement (OD), the quantity of peroxides (PO), concentration of peroxide (C_{PO}), the heat of reaction (Q_{DSC}), exothermic onset temperature (T_O) and oxygen consumption rate (k_{OC}) for samples. Following equations show apparent relationship oxygen to peroxides at the early phase of autoxidation [5].

$$RH + O_2 \rightarrow ROOH \tag{1}$$

$$\Delta n_{ROOH} = \Delta n_{o_2} \tag{2}$$

According to the equations, the oxygen consumption is equimolecular to the amount of peroxide. Peroxide has high calorific value, accordingly, the heat of reaction increases with increasing oxygen consumption for organic solvents.

From experimental results, peroxide accumulation was caused by autoxidation for THF and CPME. However, since amount of peroxide was different from oxygen consumption, peroxide decomposed with peroxide production by autoxidation, and the overall molar ratio obtained in the experiments did not follow to one expressed in eq. 1. For CPME in particular, decomposition of peroxide was remarkable in comparison with THF.

For DMSO, the quantity of peroxide and the heat of reaction did not increase during experiments, and the oxygen decrement was fairly-low. Therefore, DMSO does not cause peroxide production by autoxidation.

4. Conclusions

Assessment of autoxidative resistance for organic solvent was performed by pressure monitoring test. The following conclusions were derived from the results and discussion.

(1) In THF and CPME at 70°C, the peroxide decomposed along with peroxide production by autoxidation.

Autoxidative resistance of THF is lower than that of CPME. DMSO exhibited high autoxidative resistance.

(2) This pressure monitoring method got the results by shorter time than other method. Correlation between oxygen decrement, the quantity of peroxides and the heat of reaction was confirmed. This pressure monitoring test was considered reasonable and suitable for examination to evaluate autoxidative resistances.

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