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Measurement and correlation of solid–liquid equilibria for three binaries, ethanol–antipyrine, chloroform–antipyrine, and dimethyl ether–antipyrine

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ABSTRACT

Solid–liquid equilibrium (SLE) was measured for three binaries systems, ethanol–antipyrine, chloroform–antipyrine, and dimethyl ether–antipyrine by use of two apparatus based on a direct temperature measuring method. For dimethyl ether–antipyrine, a high pressure variable volume cell was employed, and the pressure was held constant at 5 MPa. Other measurements were carried out by use of a pressure resistance glass tube at the bubble point pressure. Prior to the measurements, SLE was measured for cyclohexane–naphthalene to ensure the reliability of the method. Comparing the three binary systems containing antipyrine, the molar solubility of antipyrine in chloroform was 1.5 times larger than that in ethanol, and 13.5 times larger than that in dimethyl ether at 313 K. The data were correlated with Schroder-van Laar and NRTL equations under the assumption that the binary system had a simple eutectic temperature. The data could be correlated within 0.168%, 0.775%, and 0.102% in temperature for the ethanol–antipyrine, chloroform–antipyrine, and dimethyl ether–antipyrine binary systems, respectively.

1. Introduction

Melting points of pharmacologically active compounds, and their solubility in various solvents have been available in many publications, such as handbooks. Generally the solubility is defined as the required volume of a solvent to dissolve one gram of the pharmacologically active compound at the room temperature, and is a widely tabulated for liquid solvents, such as water, chloroform, ethanol, diethyl ether, and benzene. However, there are few compounds that have perfect solid – liquid equilibrium (SLE) data with the liquid solvents. In our previous study, SLE was measured for some binaries containing caffeine [1]. In this study, SLE is reported for three binaries: chloroform–1,2-dihydro-1,5-dimethyl-2-phenyl-3H-pyrazol-3-one (antipyrine), and ethanol–antipyrine, and dimethyl ether–antipyrine.

Antipyrine (Fig. 1) is a model compound for analgesic antipyretics. Chloroform, and ethanol were chosen as common organic solvents. Dimethyl ether was chosen as a potential for use in nanoparticle processing.

2. Experimental

2.1. Materials

Table 1 lists the all details of Chemical reagent used in this study. Dimethyl ether was distilled before use although the final purity was not checked in this study. Other reagents were used as received without further purification.

2.2. Apparatus and procedure

SLE was measured in the temperature range from 255 to 365 K. Two experimental apparatus were employed in the measurements: (i) glass tube device, and (ii) a variable volume cell. The glass tube

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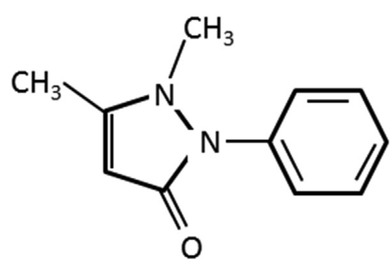

Fig. 1. Chemical structure of antipyrine.

located in a Dewar flask that had an inner volume of 4.5 L. A magnetic stirrer tip, made of rare-earth, was placed in the tube, and was driven by a powerful motor, Asone HS-4SP, Osaka, Japan. The Dewar flask was filled with two types heat transfer medium. One was silicone oil (Shin-etsu Chemical KF-96, Tokyo) for case of temperatures higher than 313 K, and the other was methanol, (chemical grade reagent, Kanto Chemicals, Tokyo). These heat transfer media were vigorously agitated by an agitator (Asone SM-103, Tokyo) with a rotational speed of 720 rpm. To check the safe working pressure of the glass tube device, the inner pressure of the tube was measured by a diaphragm type pressure gauge (Kyowa PG-100KU, Tokyo) that had a maximum capacity of 10 MPa with the resolution of 0.003 MPa. The sample was prepared in the tube, and the composition was determined by mass. After the tube was set in the flask, the sample was heated by a PID controller (Shimaden SR82, Tokyo) connected with a 500 W heater. After ensuring the solid sample was perfectly dissolved in the solvent, the sample was cooled at a cooling rate of 1.93 K/min by use of a handy cooler (Thomas TRL-107NL, Tokyo). The temperature was digitally recorded by computer at intervals of 2 s. A Pt resistance thermometer with an estimated precision of 0.03 K, and a program controller (Shimaden SR253, Tokyo) were employed for the recording temperature. Otherwise, the pressure were not recorded in the glass tube apparatus. The pressure was containing a partial pressure of air, because the sample was not evacuated at the preparation. So, in this measurement, the experimental data were regarded as those

Table 1
Chemical reagent used in this study.

	Supplier	Grade	Stated mass contents Mass %
Naphthalene	Wako Pure Chemical Industries, Osaka, Japan	Special	99.0
Ethanol	Wako Pure Chemical Industries, Osaka, Japan	Special	99.5
Antipyrine	Tokyo Chemical Industry, Tokyo	Chemical	99.0
Cyclohexane	Kanto Chemical, Tokyo	Special	99.5
Chloroform	Kanto Chemical, Tokyo	Special	99.0
Dimethyl ether	Koike Kagaku, Tokyo	Industrial use for propellant gas	97.0

device apparatus was used for the cyclohexane–naphthalene, chloroform–antipyrine, and ethanol–antipyrine systems. A pressure resistant glass tube (Ace Glass 8648-09, Vineland, U. S.) had a volume of 35 cm^3. The maximum safe working pressure was 0.79 MPa at 473 K. SLE data from this device was assumed to be at the saturated vapour pressure of the sample solution. For dimethyl ether–antipyrine system, a variable volume cell (max. 49 cm^3) was used, and that was constructed stainless steel 316. The variable volume cell was a specially design reported in our previous study [2]. The maximum safe working pressure was 70 MPa at 298 K. Then, SLE data was obtained under a constant pressure, 5 MPa, and it is higher than the vapour pressure of dimethyl ether in the experimental temperature range.

Fig. 2 shows a schematic diagram of the glass tube apparatus. The apparatus was based on that of Tsuji et al. [1,3]. The tube was

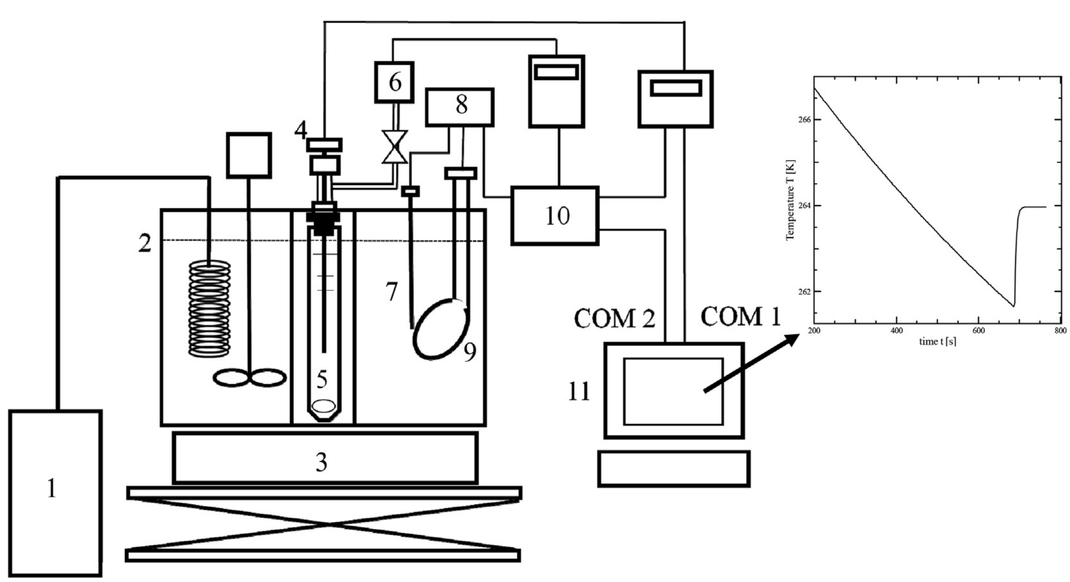

Fig. 2. Schematic diagram of apparatus with glass tube. 1: Chiller unit 2: View type Dewar flask 3: Rare-earth magnetic stirrer 4: Pt resistance thermometer 5: High pressure cell 6: Pressure sensor 7: K-type thermocouple 8: PID controller 9: Heater 10:Data logger 11: Computer.