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Influence of a microwave irradiation field on vapor–liquid equilibrium

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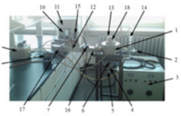
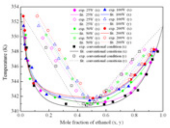
HIGHLIGHTS

- We developed an instrument for Vapor Liquid Equilibrium (VLE) measurement in the microwave field.
- We found that the vapor–liquid equilibrium can be changed by microwave irradiation field.
- The influence factors of the microwave irradiation on VLE are systematically investigated.
- The study of this paper is very important for the evolution in the Chemical Engineering field.

GRAPHICAL ABSTRACT





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ABSTRACT

Based on the modified Othmer still, an instrument is developed for vapor–liquid equilibrium (VLE) measurements in a microwave field. The isobaric conventional binary VLE experimental data compare favorably with the literature data and the results predicted from the universal quasi-chemical (UNIQUAC) model, which also verifies the reliability of the new instrument. A systematic experimental study of the effects of a microwave field on the VLE for the binary mixtures is reported herein for the first time to the best of the author's knowledge. Isobaric VLE data for two binary systems, benzene/ethanol and DOP/iso-octanol, at 101.33 kPa are determined under conventional conditions and various microwave fields. The results clearly demonstrate that the VLE of benzene/ethanol in a microwave field is shifted compared to the conventional condition; no change is observed in the DOP/iso-octanol binary system. It is concluded that the ethanol can be vaporized selectively because the rate of microwave energy absorption of ethanol is higher than the rate of heat transfer from ethanol to benzene. Furthermore, various microwave irradiation powers and the dielectric constants of the binary mixture are chosen to investigate the influence of the microwave irradiation on the VLE. The results indicate that microwave field strengths from 25 W to 200 W have varying effects on the VLE. The results also show that the effect of the microwave field on VLE is more prominent in the binary system with a larger dielectric constant difference between the two substances.

1. Introduction

Process intensification (PI) is commonly considered one of the most promising development paths for the chemical process industry and one of the most important progress areas for chemical engineering research (Gerven and Stankiewicz, 2009; Harmsen, 2010; Krtschil et al., 2011). External energy field PI technology is a useful tool for achieving drastic improvements in the efficiency of chemical processes. The PI potential of many external energy fields, such as high-gravity fields (Zhao et al., 2010), electric fields (Coppens and Ommen, 2003; Maerzke and Siepmann, 2010), magnetic fields (Munteanu et al., 2005), ultrasonic fields (Neis, 2002) and electromagnetic radiation fields

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(i.e., light fields and microwave fields) (Zhang, 2011; Bahnemann, 2004) has already been proven.

Microwave field PI technology, based on molecular-level heating, has gained a great deal of attention in academia and industry. The effect of a microwave field on chemical processes is an important area of study in fields as diverse as reaction intensification and separation technology. Many studies have investigated the effects of microwave fields on chemical reactions (Kappe, 2004, 2008; Dallinger and Kappe, 2007; Komorowska et al., 2009); however, relatively few studies discuss the effect of microwave fields on the processes of physical separation, such as extraction (Sridhar et al., 2011), desorption (Meier et al., 2009) and drying (Therdthai and Zhou, 2009). These studies show that microwave radiation has a different effect than conventional heating.

In recent years, several studies (Roussy et al., 1986; Chemat and Esveld, 2001; Navarrete et al., 2012) have focused on understanding the behavior of liquids in microwave fields. Experimental studies of the effects of a microwave field on the boiling point of pure chemicals show that the application of a microwave field may drastically improve the performance of distillation separation, which depends on the boiling point difference between the components of the target mixture. Several microwave distillation concepts have been developed based on the idea that microwave fields enhance evaporation (Deng et al., 2007; Sahraoui et al., 2008). Despite the extensive literature about the intensification effects of microwave fields on distillation, no successful industry-scale application has been reported. One of the major challenges of the large-scale application is the scale up the microwave field and the mechanism of microwave-intensified distillation separation. Recently, Gao (2011) developed a pilot plant scale microwave reactive distillation column for the synthesis of bis(2-ethylhexyl)phthalate (DOP). The experimental results show that the application of a microwave field enhances the performance of reactive distillation due to the promotion of the water separated from the reagent. The promotion also revealed that the microwave field could improve the distillation separation efficiency of certain mixtures. The same conclusion is obtained by Altman et al. (2010), who studied the effects of a microwave field on distillation at the vapor–liquid interface of a binary system and found that a microwave field improves the separation of binary mixtures only when they interact directly with the vapor–liquid interface. However, the intensification mechanism for this distillation separation process remains unclear. Because microwave fields have such complex interactions with materials, two benefits of these fields in distillation separation are suspected: the effects on the rate of vapor–liquid mass transfer and the vapor–liquid equilibrium. Altman attributed this phenomenon to the microwave field changing the phase equilibria and/or the microwave accelerating the rate of vapor–liquid mass transfer Because there is no equipment for accurately measuring the VLE data in a microwave field, a clear answer has not been found. Therefore, a more complete understanding of VLE behavior under the influence of an applied microwave field is important.

In this work, the vapor–liquid equilibria of the binary benzene/ethanol and DOP/iso-octanol systems are investigated under microwave fields ranging from 0 W to 200 W. One of the aims of this work is to develop an instrument that can accurately measure the VLE data in the microwave field. The instrument used for the measurement and relevant experimental procedures is described in Section 2. The validation of the instrument for the measurement of vapor–liquid equilibrium in microwave fields is discussed in Section 3.1. In Section 3.2, the thermodynamics are investigated to confirm whether the experimental VLE data generated by this study are consistent with the Gibbs–Duhem equation. The changes in the VLE properties caused by microwave irradiation are reported in Section 3.3. The effects of the power of the microwave field on the VLE of the binary system of benzene/ethanol are presented in Section 3.4. In Section 3.5, the effects of the differences in dielectric properties on the changes of VLE in the microwave field are discussed.

2. Experimental section

2.1. Chemicals

The chemicals following analytical-grade chemicals were supplied by Shen-yang Sinopharm Chemical Reagent Co. Ltd. in China: benzene with a stated minimum purity of 99.5 mass%, ethanol with a stated minimum purity of 99.9 mass%, DOP with a stated minimum purity of 99.0 mass%, and iso-octanol with a stated minimum purity of 99.5 mass%.

2.2. Apparatus

The experimental apparatus consisted of a modified dual circulation vapor–liquid equilibrium still (a modified Othmer still) (Zhao et al., 2006; Li et al., 2008) and a microwave generator. The instrument shown in Fig. 1, was designed and built to determine the effects of microwave irradiation on the VLE of the binary system. The primary energy was applied to the still through a heating rod controlled by a variac, and the secondary energy was applied to the interface of the vapor–liquid equilibrium by microwave irradiation. The VLE chamber was placed in a customized cylindrical microwave cavity, and the vapor–liquid equilibrium interface was placed in the VLE chamber. The configuration of the cavity and the VLE chamber is shown in Fig. 2. The modified VLE still consists of a VLE chamber in the microwave cavity, a vapor condenser and a boiling chamber outside of the microwave cavity. In this still, both equilibrium liquid and condensed vapor are continuously recirculated to provide intimate contact between the two phases and ensure that equilibrium can be established quickly. The equilibrium vapor sampling port is set in the vapor condensation system and the equilibrium liquid sampling port is connected to the VLE chamber by a thin tube. The total volume of the boiling chamber is approximately 130 cm^3, of which approximately 90 cm^3 is occupied by the liquid solution. The temperature outside the microwave cavity was measured with an accuracy of ± 0.1 K by a thermometer placed

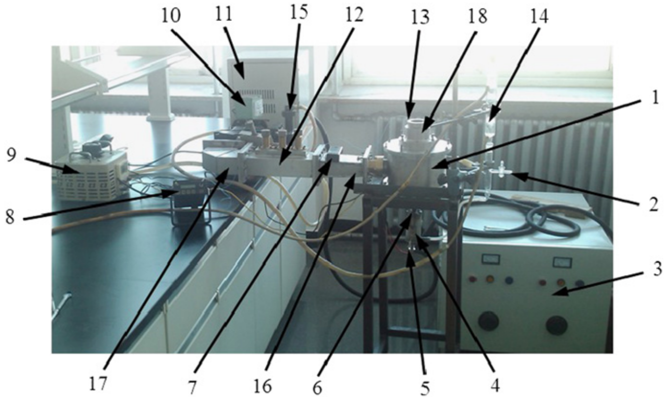

Fig. 1. Experimental instrument for VLE measurement under microwave field. 1—cylindrical microwave cavity, 2—vapor phase sampling port, 3—power of microwave source, 4—boiling chamber, 5—heating rod, 6—liquid phase sampling port, 7—microwave leakage detector, 8—FTI-10 single-channel signal conditioner, 9—variac, 10—microwave reflection indicator, 11—microwave generator, 12—microwave reflection modulator (three stub tuner), 13—fiber optic temperature probe, 14—condensor, 15—water dummy load, 16—modified section of rectangular waveguide, 17—rectangular waveguide and 18—microwave chokes.