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Isobaric vapor–liquid equilibria of the binary system maleic anhydride and dimethyl phthalate at 2.67, 5.33 and 8.00 kPa

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Abstract

Isobaric vapor–liquid equilibrium data for the binary system maleic anhydride + dimethyl phthalate at 2.67, 5.33 and 8.00 kPa were determined using the ebulliometric method. Saturated vapor pressures of pure dimethyl phthalate were also measured and Antoine constants were obtained. The experimental equilibrium temperatures, pressures and feed compositions were used to obtain NRTL parameters and equilibrium liquid and vapor compositions. Moreover, vapor–liquid equilibrium data for the binary system were predicted by use of the UNIFAC model. Predicted results were compared with those from the ebulliometric method, and good agreement was found.

Keywords: Vapor–liquid equilibrium data; Ebulliometric method; Maleic anhydride; Dimethyl phthalate; UNIFAC model

1. Introduction

At present, maleic anhydride (MAN) is usually made by the vapor-phase air oxidation of an appropriate hydrocarbon. The product from such a method is a vapor consisting of inert gas, water and MAN. Traditionally, MAN is recovered from such gas mixtures by first cooling the gas to condense about one-half of the amount of MAN and then, after separating the condensate, scrubbing the gas stream with water. The resulting aqueous mixture of MAN is dehydrated by azeotropic distillation with xylene. However, this type of recovery has a number of drawbacks, among which the following are worthy to note:

(a) the distillation of the water and the dehydration of the maleic acid involve high energy consumption;
(b) a fair amount of MAN is converted into solid fumaric acid, which in turn causes plugging problems in the MAN recovery sections of the plant.

Alternatively, it has been shown that the solvent-based absorption method has a higher recovery of maleic anhydride and a lower energy consumption than that of the aqueous-based system [1], and some organic agents have been used to absorb MAN [2,3], especially, dimethyl phthalate (DMP) has been used as the solvent to absorb MAN [3]. The design and optimization of MAN recovery process using DMP as the solvent requires VLE data of the system MAN + DMP at low pressures. To our knowledge, VLE data for this binary system are not available in the literature. To obtain these VLE data using a direct method [4], one would encounter difficulties in analyzing the equilibrium vapor and liquid compositions because of the high melting point component—MAN. Therefore, in the present work, an indirect method, the ebulliometric method was adopted to determine VLE data for the binary system MAN + DMP at subatmospheric conditions. This method has been employed and verified in our previous studies [5–8] on the determination of VLE data for binary systems.

In this paper, isobaric VLE data for the binary system MAN + DMP at 2.67, 5.33 and 8.00 kPa, by using the ebulliometric method are reported. The data were fitted to the NRTL model. The universal quasi-chemical functional group contribution (UNIFAC) model was used to predict the vapor phase compositions.

2. Experimental section

2.1. Chemicals

Analytical-grade DMP, supplied by the Tianjin Solvent Factory in China, was purified twice by distillation at low

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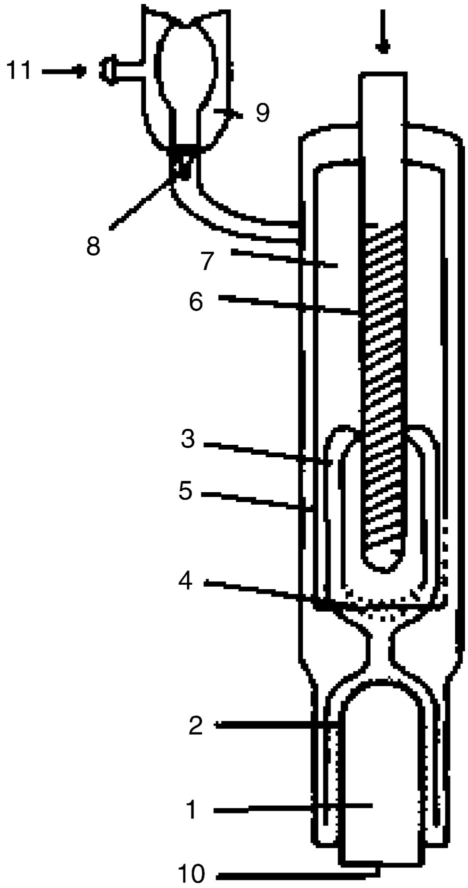

Fig. 1. Diagrammatic sketch of the improved ebulliometer: (1) heating cased tube; (2) boiling room; (3) rectifying tube; (4) liquid storing cell; (5) glass cover; (6) thermometer well; (7) vaporizing tube; (8) drop counter; (9) part condenser; (10) inside heater; (11) connecting to the cooling water.

pressure (about 1.333 kPa). Analysis by gas chromatography confirmed that the sample has a purity greater than 99.8%. The refractive index of the sample was found to be 1.516 at 293.2 K, equal to the value in the literature [9]. Analytical grade MAN was further purified by recrystallizing twice. The melting point of the purified sample of MAN was 325.6 K in close agreement with the literature [10] value of 325.9 K.

2.2. Experimental apparatus

VLE data was determined using a small ebulliometer, shown in Fig. 1, which was used before in similar experiments [5]. This ebulliometer is a modification of an earlier apparatus [11]. In comparison with the earlier apparatus, a glass cover is added to this ebulliometer to provide a more stable VLE state inside the ebulliometer. A vacuum Hg manometer was used to measure the equilibrium pressure in the system with a precision of 1.33 Pa. The mercury level in the manometer was read by a cathetometer (Mahr Co., Germany). A standard Hg thermometer with a reading precision of 0.03 °C was employed to measure the equilibrium temperature of the system.

Table 1
Vapor pressures of dimethyl phthalate (DMP)

T (K)	p_{exp} (kPa)	p_{calc} (kPa)	$\lvert p_{\mathrm{exp}}-p_{\mathrm{calc}}\rvert/p_{\mathrm{exp}}$ (%)
417.59	0.934	0.956	2.35
425.40	1.466	1.414	3.52
435.12	2.210	2.230	0.92
444.50	3.356	3.361	0.13
454.90	5.164	5.133	0.59
466.01	7.823	7.815	0.10
475.82	11.132	11.053	0.70
486.11	15.421	15.539	0.76
496.11	20.928	21.204	1.32
506.87	28.703	29.030	1.14
516.84	38.156	38.183	0.07
525.54	48.709	47.900	1.66

2.3. Experimental procedure

About 20 cm^3 of a liquid mixture of known composition obtained by weighing (on a balance with a resolution of 10^{-4} g) was put into the small ebulliometer. The ebulliometer was connected to a vacuum system and was sealed. After the apparatus was washed with nitrogen gas for several times, the pressure was reduced to the desired point with the help of a vacuum pump. Then the pressure was kept constant and the sample in the ebulliometer was heated slowly with an external heater controlled by a small voltage adjuster. When the temperature and the amount of reflux drops (60–80 drops/min) reached a stable value for more than 5 min, the corresponding temperature and pressure were recorded. Saturated vapor pressure data for the pure DMP sample used in this investigation were also measured using the same ebulliometer and the procedure described.

3. Results and discussion

3.1. Vapor pressure of dimethyl phthalate

Saturated vapor pressures data for pure DMP, measured in the temperature range of 417–525 K, were fitted to the Antoine equation in the form:

$$\ln(p/\mathrm{kPa}) = A - \frac{B}{C + T/\mathrm{K}} \tag{1}$$

Both the measured data and the fitted curve are shown in Table 1 and Fig. 2. As it was evident from Fig. 2, that the saturated vapor pressure values calculated from the regressed values of the Antoine constants are in good agreement with the measured saturated vapor pressures, the regressed Antoine constants were used in the correlation of the VLE data for the MAN + DMP binary system. The Antoine constants for maleic anhydride and dimethyl phthalate's are listed in Table 2.

3.2. Determination of the mean evaporation coefficient

The method of determining the mean evaporation coefficient, $\bar{f}$, of the ebulliometer was described at length in the literature [5]. The system ethanol + benzene, for which vapor–liquid