J. Chem. Thermodynamics 41 (2009) 859–863

Contents lists available at ScienceDirect

J. Chem. Thermodynamics

journal homepage: www.elsevier.com/locate/jct

Binodal curve measurements for (water + propionic acid + dichloromethane) ternary system by cloud point method

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ARTICLE INFO

Article history:
Received 17 January 2009
Accepted 4 February 2009
Available online 12 February 2009

Keywords:
Binodal curve
Tie line data
Propionic acid
Dichloromethane
Water
Cloud point method
UNIQUAC activity coefficient model

ABSTRACT

The binodal (solubility) curves and tie line data for ternary systems of (water + propionic acid + dichloromethane) at 91.3 kPa and $T = (277.15, 284.15, \text{and } 294.15)$ K are reported. The binodal curve results were determined by cloud point measurements method. A simple titration method has been used for determining of the concentration of propionic acid in the both liquid phases at equilibrium. The results obtained were successfully correlated with the UNIQUAC activity coefficient model. The deviations between experimental and calculated compositions in both phases for the ternary system using this model are reported. The partition coefficients of propionic acid and the selectivity factor of dichloromethane for extracting of propionic acid from water were calculated and are reported. The phase diagrams for the ternary system studied including both the experimental and correlated tie lines are presented.

1. Introduction

Most of carboxylic acids can be produced by chemical synthetic or fermentation processes. Recovery and removal of the carboxylic acids such as propionic acid from aqueous solutions resulting from fermentation processes is important from the theoretical and industrial viewpoints. Propionic acid is one of the most widely used carboxylic acids, which has many applications in chemical and bio-chemical industries [1–5]. Therefore, investigations to find the separation methods for recovery of propionic acid from aqueous solutions have economic and scientific importance. Although the distillation processes have the general applications in different separation processes but from technical and economical aspects, solvent extraction is the more effective industrial process for removal of propionic acid from aqueous solutions. Considering the important role of solvents used in the effectiveness of the extraction process, many organic solvents have been used for the extraction of propionic acid from aqueous solutions. So, binodal curve and tie line data of ternary systems containing (water + propionic acid + organic solvents) are important for design and optimized operation of the recovery systems. The separation of propionic acids from aqueous solutions with various organic solvents has been investigated by several researchers. Sólimo *et al.* showed the effect of addition of sodium chloride on the (liquid + liquid) equilibrium (LLE) data of the system (water + propionic acid + 1-butanol) [6]. The phase equilibria data of the system (water + propionic acid+ 2-butanol) have been studied by Radwan and Al-Muhtaseb [7]. The LLE data of system (water + propionic acid + oleyl alcohol) have been presented by Bilgin and Arısoy [8]. Özmen have studied the system (water + propionic acid + methyl isoamyl ketone, or diisobutyl ketone, or ethyl isoarnyl ketone) [9]. The LLE data of systems (water + carboxylic acid + cumene) have been presented by Çehreli [10]. Recently, the determination and correlation of LLE data for the system (water + carboxylic acid + dimethyl maleate) have been carried out by Özmen [11]. Ghanadzadeh *et al.* have investigated LLE data of the system (water + propionic acid + 2-ethyl-1-hexanol) [12]. The LLE data of systems (water + propionic acid + diethyl succinate, or diethyl glutarate, or diethyl adipate) and (water + propionic acid + dibasic esters) have been presented by İsmail Kırbaşlar *et al.* [13,14]. The author of this work with co-workers investigated the salting-out effect of NaCl and KCl on the ternary LLE data for the systems (water + propionic acid + isopropyl methyl ketone) and of (water + propionic acid + isobutyl methyl ketone) [15]. In this work, using the cloud point measurement method, the binodal curve and tie-line data for ternary systems of (water + propionic acid + dichloromethane) at $T = (277.15, 284.15, \text{and } 294.15)$ K are reported. The experimental results have been correlated by means of the UNIQUAC activity coefficient model [16]. In the LLE calculations, the chemical potential of component i on both phases is equal and the mole fractions x_i^I, x_i^{II} of the equilibrium phase can be calculated using the following equation:

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0021-9614/$ - see front matter © 2009 Elsevier Ltd. All rights reserved.
doi:10.1016/j.jct.2009.02.004

$$\gamma_i^I x_i^I = \gamma_i^{II} x_i^{II}, \tag{1}$$

where γ_i^I and γ_i^{II} are the corresponding activity coefficients of component *i* in the two phases which are at equilibrium. The interaction parameters between each of the components can be obtained by using the UNIQUAC activity coefficient model for correlating the LLE experimental results. The interaction parameters of the model and the deviations between experimental LLE results and those calculated by the model are reported.

2. Experimental

2.1. Materials

Propionic acid and dichloromethane were supplied by Merck. The purity of propionic acid was checked on the basis of its refractive index at $T = (293.15 \pm 0.20)$ K. The refractive index was measured using a thermostatically controlled Abbe refractometer (Atago 3T, made in Japan) with an accuracy of ±0.0001 n_D. The measured physical properties are listed in table 1 along with values from the literature [17]. A 25 cm^3 calibrated glass pycnometer was used for density measurements. Boiling point measurements were obtained by using a Fischer boiling point measurement. The estimated uncertainties in the density and boiling point measurements were $\pm 0.0001\ \text{g} \cdot \text{cm}^{-3}$ and 0.01 K, respectively. The purity of dichloromethane was checked by gas chromatography, and results confirmed the mass fraction purity higher than 0.99. Before use, dichloromethane was stored in desiccators with a drying agent.

2.2. Apparatus and procedure

The binodal curve values were determined by means of the cloud point method [18]. The measurements were made in a glass equilibrium thermostated cell equipped with a magnetic stirrer. The cell temperature was controlled with a temperature-controlled bath with an accuracy of ±0.01 K [Lauda ecoline re 206, thermostat]. A known composition, homogeneous and transparent (propionic acid + water) was prepared in a glass equilibrium cell at constant temperature. The mixture was made by mass using a Sartorius analytical balance (Model A200S, accurate to 0.0001 g). Then dichloromethane was progressively added to the mixture using a micro-burette.

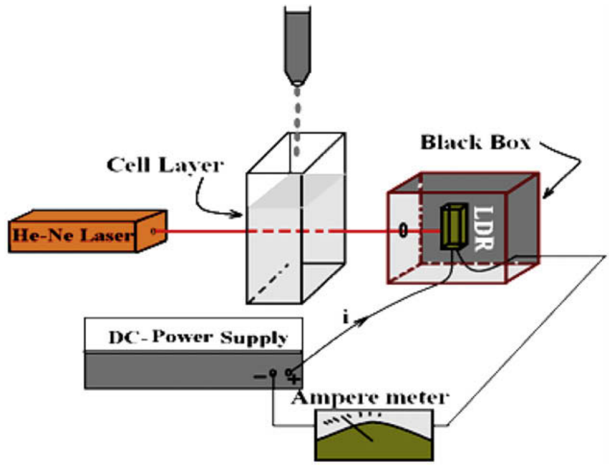

FIGURE 1. Schematic diagram of experimental setup.

The cloud point was determined by observing the transition from a homogeneous to a heterogeneous mixture as indicated by the mixture turbidity. The schematic diagram of experimental setup is shown in figure 1. According to this figure, a He–Ne Laser beam has been used for detection of the change in turbidity of the homogeneous and transparent mixture. The He–Ne Laser beam was passed through the glass cell containing the studied mixture. The transmitted beam will be incident on a LDR (Light Depend Resistor) located in a black box. It is well-known that the electrical resistance of a LDR decreases by increasing the intensity of the laser beam. Therefore, the variation of LDR-resistor, which is dependent on the intensity of the laser beam, can be detected by a simple circuit. This circuit includes a DC-power supply, an ampere meter and the LDR. The ampere meter shows a maximum electrical current (($I_{\max}$) for the transparent (propionic acid + water). After adding dichloromethane to the (propionic acid + water), a sharp decrease in the electrical current indicates the cloud point of {water (1) + propionic acid (2) + dichloromethane (3)} ternary systems. The cloud point was observed to coincide with the measured cloud points by visual inspection. The differences between the measured mass fractions of dichloromethane in the ternary mixtures at cloud point W_3, using this method and those by visual inspection was up to 0.02. This procedure was repeated at least three times. The average of the dichloromethane added was taken for the binodal curve measurements. The maximum deviations from the average value were less than 0.1%.

The tie line for experimental results was determined by using a glass cell, volume about 150 cm^3, with a water jacket. The mixtures were prepared inside the cell and were vigorously agitated with a magnetic stirrer for 10 min at least and left to rest for 4 h. After several experiments and taking samples at different time intervals, it was found that increasing the agitation time (minimum time 10 min) and rest time (minimum time 4 h) had no considerable effect on equilibrium phase compositions. After the necessary rest time, the mixture split into two clear and transparent liquid phases with a well defined interface. The samples of both phases were collected and the tie line values were obtained by titration of the samples with a known concentration NaOH aqueous solution. The titration end point was indicated by turbidity of the solution which was rechecked by measuring pH of the solution using Metrohm pH Meter Ω 691.

TABLE 1
Density and refractive index at $T = 293.15$ K and boiling temperature of propionic acid [17].

Component	$\rho/\text{g} \cdot \text{cm}^3$		n_D		T_b/K	
	Exp.	Lit.	Exp.	Lit.	Lit.	Exp.
Propionic acid	0.9936	0.9930	1.3863	1.3809	141.1	141.0

3. Results and discussion

The compositions of mixtures on the binodal curve of mixtures on the binodal curve of ternary systems of {water (1) + propionic acid (2) + dichloromethane (3)} at $T = (277.15, 284.15,$ and $294.15)$ K are reported in table 2, in which w_i denotes the mass fraction of the *i*th component. Table 3 shows the experimental tie-line compositions of the equilibrium phases, for which w_{i1} and w_{i3} refer to the component *i* in the water (1) rich-phase and dichloromethane (3) rich-phase, respectively. The UNIQUAC activity coefficient model was used to correlate the experimental results. The UNIQUAC activity coefficient model for component *i* are expressed as follows:

$$\ln \gamma_i = \ln\left(\frac{\Phi_i}{x_i}\right) + 0.5 Z q_i \ln\left(\frac{\theta_i}{\Phi_i}\right) + L_i - \left(\frac{\Phi_i}{x_i}\right)\sum_{j=1}^{n} L_j x_j + q_i\left(1.0 - \ln\sum_{j=1}^{n}\theta_j\tau_{ji}\right) - q_i\sum_{j=1}^{n}\left(\frac{\theta_j\tau_{ij}}{\sum_{k=1}^{n}\theta_k\tau_{kj}}\right), \tag{2}$$