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A Comparative Thermodynamic Study of the Liquid-Liquid Equilibrium Systems: Propylene glycol-cyclohexane-water and Tetrachloromethane-ethanol-water

Thermodynamic Study of Equilibrium System

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***Abstract*—A comparative thermodynamic experimental study for liquid-liquid equilibrium of the propylene glycol-cyclohexane-water and tetrachloromethane-ethanol-water systems were studied at 298.15 K. Data for the construction of ties-lines were determined by preparing mixtures of known mole fraction of components in the region of formation of two phases. Solubility and tie-line data were used in order to complete phase diagrams with CALPHAD method. An eco-friendly method without using great portions of solvents was used with construction of the binodal curves for the evaluation of immiscibility region in the systems. The study showed that molar fractions of each component influenced to the behavior of the whole system. Thermodynamic models provided satisfactory description between the predicted and experimental values.**

Keywords— binodal curves, liquid-liquid equilibrium, thermodynamics, ternary system

I. Introduction

Liquid-liquid is a separation process used in different areas and industries such as chemistry and pharmacy. In terms of protecting the environment, the consideration of using safe process is being of high interest especially in processes of purification and extraction [1]. The application of the rule of the phases for 3-compound system, the number of freedom degree can be between 0 (if there are five phases in a balance state) to 4 (in the special case where only one phase is in the system). In many disciplines in chemistry, analytical recovery plays important role to conclude about the reaction, conditions and the use of an appropriate solvent [1, 2]. The liquids can be mixed in each other, dependable on the chemistry behavior of each compound. Pure liquids when are mixed in appropriate proportions at certain temperatures and pressures tend not to form only one homogeneous liquid phase, but to obtain two liquid phases with different compositions. This is a result of stability of the two-phase state rather than the monophasic state. If these phases with different compositions are in equilibrium, the balance state condition is called liquid-liquid equilibrium (LLE). The number of phases which are in the balanced condition is determined with Gibbs’ rule. They are also connected with the behavior of heterogeneous systems, attractive forces, kinetic and potential energy in the molecules. At the same time the number of intensive parameters without changing the phase numbers in the balance can be altered. The equation $s = 3 - f + 2$, where s is the number of degrees of freedom, and f is the number of phases is a rule of the phases for 3-compound systems. As a result from the Gibbs’ rule of phases, the numbers of phases can be calculated and the behavior of the heterogeneous systems can be predicted. The treasonable diagram of Gibbs, Stokes and Roozeboom is one of the most used systems for the graphical presentation of the 3-compound system [3-5]. The complexity of task to study multi component phase systems is required for triangle constructions. It was found that triangle systems are suitable for the representation of the solubility of three liquids at constant pressure and temperature. Moreover, the diagrams give the exactly ratio of the mixed compounds and the quantitative analyzed can be obtained. The advantage of the system which is consisted of two-phase compounds is due to the eco-friendly characteristics. The organic compound is initially used less with more applications in various fields such as medicine, nanoparticles, and drugs [1, 6, 7]. For example, a separation of aromatic compounds sometimes makes difficulties due to the possibility of an azeotropic mixture [8] or equilibrium data for the system CO_2-ethanol-water was depended on the pressure and ethanol loading [9]. In that case, a ternary diagram can be used to overcome the problem where the thermodynamic equilibrium is achieved with a constant temperature and pressure and a minimum of the Gibbs’ free energy [10].

This research is focused on studying the metastable phase relations of the ternary system consisted of propylene glycol-cyclohexane-water, on one hand and on the other, the system included tetrachloromethane-ethanol-water. The survey of the literature showed that the case of studying the liquid-liquid equilibrium (LLE) and the vapor-liquid equilibrium (VLE) of aqueous mixtures of 3-compound system is often discussed, but a comparison between two different types of systems had not been published. Although through the literature, liquid chromatography was studied by [1, 3] with difficulties in experimental approaches and restrictions [9], the CALPHAD methodological approach gave satisfactory results in terms of miscibility of liquids. Liquid-liquid equilibrium was achieved with the use of water and organic solvents [8].

The adjustment of the phases where the one phase is present in the two-phased system is available in the system where two immiscible liquids are present such as chloroform and water or cyclohexane and water. The comparison to different ternary diagrams showed how much of the compound was needed to achieve miscibility of the solvents in the system. In addition, an eco-friendly method was proposed taking into consideration the proper amount of the solvents in the mixture.

II. Experimental methods

A. *Solvents*

Tetrachloromethane, cyclohexane, propylene glycol and ethanol were with analytical purity, purchased from Sigma-Aldrich (Germany). Double-distilled water was used in the analysis was prepared in the laboratory.

B. *Apparatus and analysis*

An analytical balance (VWR, Austria) is applied for sample weighting with 0.1 mg accuracy. Microburets were with 10 cm^3 with accuracy ± 0.02 cm^3. A water bath with thermostat and thermometers were used for temperature regulation.

C. *Procedure*

The binodal curve for the tetrachloromethane-water-ethanol and propylene glycol-cyclohexane-water was determined with the solubility method. The mixture of known composition was shaken in glass conical flasks equipped with microburet. A portion of equilibrium solution was analyzed using standard titration method. For the determination of the binodal curve 2 burettes of 50 mL, one microburet, 9 glass conical flasks of 50 mL and 3 backers (250 mL) were required. One of the burette was filled with the solvent A, the second with the solvent B, where homogeneous mixtures were prepared in the glass conical flasks, where total volume of 10 mL was reached. The microburet was filled with the third compound in the liquid state and the titration was being done. The mixtures were titrated with the solvent, accompanied by vigorous shaking of the conical flasks. The titration was considered in completed state when the first visual turbulence was noticed in the mixture of the analyzed samples. The volume which was consumed for the titration was recorded. The procedure was repeated with the analyzed sample with all conical flasks. The procedure was repeated three times and the average value of volume of used titrant was calculated.

During the experiment, two parallel series of samples were ready to be analyzed. The importance of the second series was due to the determination which of the solvent is miscible with the third solvent and the order of the titration was done in accordance of how the solvents were mixed.

After the titration procedure, the volume part of each component was calculated for the obtained mixture. The values were plotted on a graph with triangular axes to produce a triple phase diagram, known as CALPHAD method. The obtained data were presented in the triangular system and the binodal curve was drawn.

III. Results and discussion

The visual alteration of the mixture could be a good indicator for the end point of the standard titration method where the mixture from homogeneous transforms to heterogeneous state to the first drop of stable turbidity. A monophasic system can be obtained at the moment when the third component was added to the mixture of two-phased components. On the other hand, if a homogenous mixture has already been determined at the beginning, the addition of the third compound can lead to a heterogeneous mixture where monophasic system will be altered to a two-phase-system. In both cases, the composition can be determined and can be obtained one spot from the phase line.

One of the key roles in the representation of the phase diagram is the binodal curve, in the literature known as isothermal curve of solubility for determined temperature and pressure [10]. The curve itself connected more spots obtained with the necessary amount of the third compound for obtaining the heterogeneous system. The part above of the binodal curve is determined as monophasic-homogenous system, where the part under the binodal curve is connected with the two-phase system. The change in the degree of the temperature influences directly to the appearance of the binodal curve and the parts assigned as above and under the curve. The solubility is expected to be decreased at lower temperatures and the two-phased part to be increased and vice versa.

A. *The solubility of cyclohexane in water*

The polarity of the compound plays crucial role in solubility, surface tension, melting and boiling points. For example, cyclohexane is a cyclic compound categorized as non-polar solvent [11]. The solubility of cyclohexane in water is slightly higher at liquid-liquid equilibrium (LLE) than the solubility of cyclohexane at vapor-liquid equilibrium (VLLE) at 295 K. One of the main modules to increase the solubility is to increase the temperature.

Table 1 shows the results of the titration method including propylene glycol, cyclohexane and water. In the system, at first propylene glycol and cyclohexane were mixed, and water was added additionally. It is important to be noticed that in this step, the solvents were checked for their miscibility in each other. The volume fraction was also calculated showing that as far the solvents were closed to the same structure; the probability of miscibility was more present.

Table 1. Standard titration method for the miscibility of propylene glycol, cyclohexane and water

Sample	V_A (cm^3)	V_B (cm^3)	V_C (cm^3)	φ_{A*}	φ_{B*}	φ_{C*}
1	1	9	8	0.056	0.500	0.444
2	2	8	4.5	0.138	0.552	0.311
3	3	7	2	0.250	0.583	0.167
4	4	6	1.4	0.351	0.526	0.123
5	5	5	1.85	0.422	0.422	0.156
6	6	4	2.5	0.480	0.320	0.200
7	7	3	2	0.583	0.250	0.167
8	8	2	4.75	0.542	0.136	0.322
9	9	1	4	0.643	0.071	0.286

*A-propylene glycol, B-cyclohexane, C-water (A+B)+C (the experiment was triple repeated)

The determination of the miscibility of the solvents was achieved using the droplet method, mixing each component with each other. Cyclohexane was chosen as a solvent with different characteristics from water and the fractions were determined again using standard titration method with narrower range (Table 2).

Table 2. Solubility of propylene glycol, water and cyclohexane with standard titration method

Sample	V_A (cm^3)	V_B (cm^3)	V_C (cm^3)	φ_A	φ_B	φ_c
1	1	9	1.4	0,088	0.500	0.444
2	2	8	1.2	0,179	0.552	0.311
3	3	7	1.3	0,265	0.583	0.167
4	4	6	1.5	0,348	0.526	0.123
5	5	5	1.4	0,439	0.422	0.156
6	6	4	1.5	0,522	0.320	0.200
7	7	3	8.4	0.381	0.250	0.167
8	8	2	1.8	0.678	0.136	0.322
9	9	1	3.1	0.643	0.071	0.286

A-propylene glycol, B-water, C- cyclohexane (A+B)+C (the experiment was triple repeated)

B. *The solubility of tetrachloromethane in water*

Tetrachloromethane is an organic solvent which is approximately 793 mg/L soluble in water. The solvent is rather hydrophobic which means that the solubility in water is less than in the organic solvents [12]. In contrast, the prediction and the experimental observations of less quantities of tetrachloromethane were not in good correlation. Thus it was reflected in the behavior of the binodal curve where the determination of miscibility at lower amount was problematic. The main idea was to increase association forces for accurate determination the border of the miscibility of the liquids in the system. The results of the standard titration method including water, ethanol and tetrachloromethane are presented in Table 3.

Table 3. Solubility of water, ethanol and tetrachloromethane with standard titration method

Sample	V_A (cm^3)	V_B (cm^3)	V_C (cm^3)	φ_A	φ_B	φ_C
1	1	9	3	0.076	0.692	0.231
2	2	8	2.1	0.165	0.661	0.174
3	3	7	1.8	0.254	0.593	0.153
4	4	6	1.7	0.342	0.513	0.145
5	5	5	1.5	0.435	0.435	0.130
6	6	4	1.1	0.540	0.360	0.099
7	7	3	0.7	0.654	0.281	0.065
8	8	2	0.4	0.769	0.192	0.038
9	9	1	0.2	0.882	0.098	0.019

A-water, B-ethanol, C-tetrachloromethane (A+B)+C

C. *Binodal curves for propylene glycol-cyclohexane-water and tetrachloromethane-ethanol-water*

The binodal curves for water-chloroform on one hand, and propylene glycol, cyclohexane and water on the other were determined using solubility method. The phase behavior with the changes in the volume fractions is presented with the Gibbs' phase triangle (Figure 1). The curves present the part that lies inside the solubility region curve where three components from the system are completely miscible. The phases represent microstructures which were enriched either with cyclohexane or with tetrachloromethane. In the systems can be noticed that microstructures can exist as one phase in determined conditions, completely miscible in each of them in any proportion.

Ternary diagrams for propylene glycol-cyclohexane-water and tetrachloromethane-ethanol-water are shown in Figure 1a and b, respectively. The observed ternary diagram showed partially miscibility in the binary water-cyclohexane system. Increasing the concentration of propylene glycol tend to raise the solubility of cyclohexane due to the polarity of the solvent in the comparison to cyclohexane.

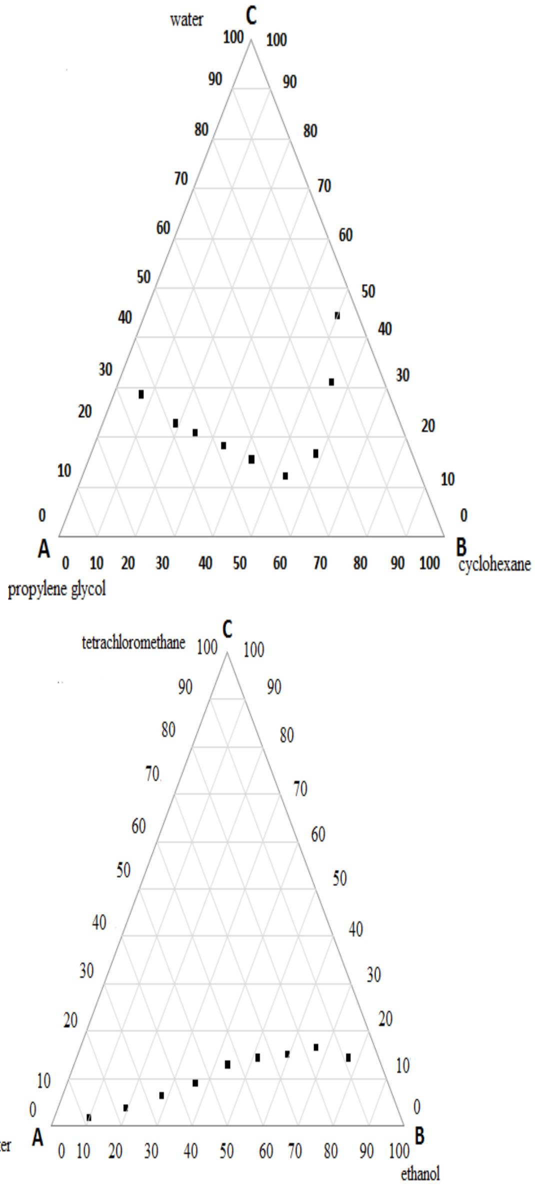

Figure 1. Ternary diagrams for propylene glycol-cyclohexane-water (a) and tetrachloromethane-ethanol-water (b)

On the other hand, the miscibility boundaries in the ternary diagram (Figure 1b) made difficulties in the representation in the region of low tetrachloromethane content. The partial diagram of the ternary diagram was depicted in the graph where the fraction tends to zero. The region where the single phase exists could be shown as macroscopically homogenous part. The formation of only one phase was not always present when two liquids were present in the system. An appropriate amount of pure liquids at certain temperature and pressure leads to formation of two liquid phases with different compositions. A minimum of the Gibbs free energy was achieved at constant temperature and pressure.

The region of the graph that was not bounded by the binodal curve represents the one-phase region. The mixture with composition that falls into this region was clear and the phases were homogenous (Figure 1). The points that lie at both ends of the curve were the limits of solubility of solvents in each other.

The solvents A and C on one hand and the solvents B and C, on the other, presented in Figure 1 are completely miscible, while the solvents A and B are partly miscible. The homogeneous mixtures then are presented with the points of the sides AC of the triangle and the points of the sides BC of the triangle corresponded with the homogenous mixtures of liquids B and C. The diagrams show lower critical solution temperature (LCST) and upper critical solution temperature (UCST) for propylene glycol-cyclohexane-water (a) and tetrachloromethane-ethanol-water (b), respectively (Figure 1). Binodal curves represented the coexistence of two phases. The solvents could be separated as a result of conditions suitable to achieve the thermodynamically favorable state [11-14]. A constant was consisted of three variables was a sum obtained in the ternary graph. From the equilateral triangle could be read the information about the ratios of three variables. Reducing of experimental trials of the equilibrium condition was done using the CALPHAD method. A two-phased system was formed when two liquids are partly soluble in each other. A monophasic system was formed if enough amount of the third solvent was present in the system when it was gradually added to the mixture of the liquids where the added one was miscible with the others in any proportion.

IV. CONCLUSION

The liquid-liquid equilibrium of two systems consisted of propylene glycol-cyclohexane-water and tetrachloromethane-ethanol-water was achieved at 298.15 K. The comparison between two ternary systems showed that there were partly and completely miscible liquids in certain ratios of the solvents. The addition of sufficient amount of the solvent would be produced a single liquid phase in which all three components are miscible and the mixture is homogeneous. The presented parameters can be employed for studying phase equilibrium of the considered system where the further investigations will be in direction to compare with both a mathematical method and a chromatography.

Conflict of Interest Statement

The author declares no conflict of interest.

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