



Differential scanning calorimetry determination of phase diagrams and water activities of aqueous carboxylic acid solutions

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ABSTRACT

We have investigated the solid-liquid equilibria phase diagrams and water activities of the several carboxylic acid/water binary systems using differential scanning calorimetry (DSC) method. These mixtures were formed by water and low molecular weight carboxylic acids (formic acid, acetic acid, propionic acid and butyric acid). Water activities of the investigated solutions were obtained from the freezing point depression data in the range of the ice melting envelope. The experimental results indicated that all the aqueous carboxylic acid systems present a eutectic point in their respective phase diagrams. The activity coefficients of two components in the liquid phase were used to adjust the parameters of the Wilson and NRTL models. For all of the investigated systems, the best correlations of the solid-liquid equilibrium data have been determined by using the NRTL model. Finally, the phase behaviors of the systems were compared to the ideal state and the influence of the chemical structure of the carboxylic acids on the magnitude of the deviation from the ideal state was discussed.

1. Introduction

During the recent studies on climate change, the presence of organic material in the tropospheric aerosols has attracted more attention [1,2]. The incorporation of organic components into different aerosols can be investigated mainly according to the study of various cloud water properties such as the influence on the acidity of wet deposition, phase transitions, deliquescence, nucleation and aqueous phase reactions [2–6]. Water and solute activities and liquid-solid phase diagrams of atmospheric aerosols containing dissolved organic compounds are currently summarized and modeled at 298 K [4,5]. However, in the beginning, the effect of organic compounds on phase transition of aqueous systems that make up tropospheric aerosols at low temperatures is required. In a type of classify, some of the most abundant identified organic compounds in aerosols can be divided into monocarboxylic acids (such as: formic acid, acetic acid and etc.), dicarboxylic acids (such as oxalic, malonic, succinic, maleic, glutaric, and etc.) and multifunctional acids such as malic. The binary systems of dicarboxylic acids-water have been extensively studied with respect to solubilities of the solute and liquid-solid phase equilibrium [3–6]. However, slight studies have been carried out regarding to the thermodynamic behavior of binary systems of monocarboxylic acids-water at low temperatures [7]. In this study, we present the liquid-solid phase diagrams of the aqueous systems of formic acid, acetic acid, propionic, and butyric acids over the entire range of compositions.

Moreover, low molecular weight carboxylic acids such as formic acid, acetic acid, propionic acid and butyric acid are main intermediates in the process of biochemical and food industries [8,9]. The different processes such as liquid-liquid extraction method for the efficient separation of carboxylic acids from aqueous systems have been studied [10–12]. However, since the crystallization method operates at low temperatures with low energy consumption and product with high purification, it is widely used in the pharmaceutical, process and food industries as a useful separation and purification technique [13–15]. In order to evaluation the possibility of separating a known binary mixture by using the crystallization method or the design and equipment of separation and/or purification processes for the crystallization, having the accurate solid-liquid equilibrium (SLE) data for the system is crucial. Despite the growing of studies on the determination of the solid-liquid phase diagram of organic solutions, as far as we know, there is no any information in the literature about the solid-liquid phase diagram of aqueous formic acid and butyric acid solutions. However, the experimental osmotic coefficient data for aqueous solutions of the volatile carboxylic acids have been reported in the literature [16,17]. Determination of the solid-liquid phase diagram of mixtures can be achieved with different methods such as: DSC and synthetic techniques [7,18,19]. In this work, the solid-liquid phase diagram, water activities, and eutectic temperature of the carboxylic acid/water binary systems containing formic acid, acetic acid, propionic acid, and butyric acid have been investigated using the DSC technique.

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Table 1
Names, provenances, purities, content water and melting point of the chemicals studied at 845 hPa.

Chemical	Source	Purification method	Content water/ppm	Mass fraction purity	Melting point
Formic acid	Merck	None	11573	≥ 0.99	282.85 ^a , 274.45 ⁺ 281.55 ^a
Acetic acid	Merck	None	8854	≥ 0.99	289.95 ^a , 287.15 ⁺ 289.65 ^b , 289.62 ^c
Propionic acid	Merck	None	1078	≥ 0.99	251.95 ^a , 248.65 ⁺ 251.65 ^b , 252.85 ^d , 250.89 ^e
Butyric acid	Merck	None	4266	≥ 0.99	268.65 ^a , 264.85 ⁺ 267.35 ^b , 267.75 ^d

* and + are the peak and onset temperatures, respectively. ^aReference [20] ^bReference [21] ^cReference [22] ^dReference [23] ^eReference [7]. Standard uncertainties for temperature and pressure are 1 K and 10 hPa, respectively.

2. Experimental

2.1. Sample preparation

The specifications of the chemicals used in this work are given in Table 1. Double distilled water was used for the preparation of the solutions. The binary mixtures were prepared gravimetrically by its mass using an analytical balance with a precision of $\pm 1 \times 10^{-5}$ g. The water contents in the acids were measured by Karl Fischer titration with precision of 3 ppm and they were taken into account in the calculation of the compositions of the investigated solutions. The differences between the melting points of pure carboxylic acids obtained in this work with those available in the literature may be attributed to the high water content of the carboxylic acids.

2.2. Instruments and methods

The solid-liquid equilibrium data of pure carboxylic acids and binary carboxylic acid/water mixtures were characterized by DSC, using a NETZSCH DSC 204 F1 Phoenix. Industrial grade nitrogen gas was used as a purge gas with a flow rate of 40.0 mL per minute and as a protective gas with a flow rate of 70.0 mL per minute. Samples were weighted and sealed in a 25 μ L aluminum pan and typically had a mass of approximately 8–15 mg. An empty aluminum pan was used as reference during the measurements. Before analyzing, the heat flow was calibrated by using the standards of indium (melting point: 156.60 °C) and bismuth (271.40 °C) and by onset temperatures at three different heating rates, 1, 5, and 10 K min⁻¹. The temperature reproducibility of this instrument is better than ± 0.05 K. Thermal transition was determined by using the following thermal program with the heating/cooling process rate 5 K min⁻¹: Sample was; i) cooled to a temperature at least 50 K below the melting point of the component with smaller melting temperature, ii) held at that temperature for 5 min, iii) warmed until 25 K above the melting point of the component with higher melting temperature, vi) again cooled up to the desired temperature, v) held at that temperature for 5 min, vi) warmed until 298 K. By using this thermal program, measurements have carried out for each concentration. Fig. 1 illustrates the DSC thermograms for all the water + carboxylic acid systems. A single peak is observed in the case of both a sample with composition close to the eutectic point and a pure component. Nevertheless, there are two endotherm peaks for all the other samples. The first one is relating to the eutectic point and the latter one to the melting point of the mixture. In Table 1, the peak and onset temperatures of the pure compounds as well as their melting points reported in the literature have been given. As can be seen, the peak temperatures are in good agreement with the literature data. Therefore, as suggested by Htira et al. [7], in this work the peak temperatures were used as melting points of the samples.

In fact, DSC is a dynamic procedure while a phase diagram indicates an equilibrium state. In order to overcome this fact and to more precisely determination of equilibrium temperatures, a theory was proposed by Kouksou et al. [24]. Fig. 2 shows the application of this theory for the 0.5923 mol fraction of acetic acid in aqueous solution at three different heating rates, 1, 5, and 10 K min⁻¹. As Fig. 2 shows,

there are two endotherm peaks for each thermogram.

The first equilibrium temperature is extrapolated to $T_{eq} = 269.65$ K and the second

one to $T_{eu} = 244.95$ K. We found that there is a linear relationship between the peak temperatures and the heating rates. Liquidus temperatures, T , and eutectic temperatures, (T_{eu}) for different carboxylic acids + water systems are located at the intersection of these lines and the abscissa.

3. Correlation of the solid-liquid equilibrium data

The solid-liquid equilibrium data of the investigated aqueous carboxylic acid systems, which are completely miscible and immiscible, respectively in the liquid and solid phases and therefore these systems show a simple eutectic phase diagrams, can be described according to the following equation [25]:

$$\ln \left(\frac{x_i^s \gamma_i^s}{x_i^l \gamma_i^l} \right) = \frac{\Delta_{fus} H_{m,i}}{RT_{fus,i}} \left(\frac{T_{fus,i}}{T} - 1 \right) - \frac{\Delta C_{p,i}}{R} \left(\frac{T_{fus,i}}{T} - 1 \right) + \frac{\Delta C_{p,i}}{R} \ln \frac{T_{fus,i}}{T} \quad (1)$$

where x_i and γ_i respectively are the mole fraction and activity coefficient of component i and superscripts s and l stand for the solid and liquid phases, respectively. $\Delta_{fus} H_{m,i}$ is molar enthalpy of fusion of component i , $T_{fus,i}$ is the melting temperature of component i , T is the equilibrium temperature, $\Delta C_{p,i}$ is the difference in the heat capacities of component i in the liquid and solid phases, and R is the universal gas constant. Because of the slight difference between the heat capacities of liquid and solid phases, in many cases the terms containing $\Delta C_{p,i}$ can be neglected.

By assuming the immiscibility of water and carboxylic acids in the solid phase ($x_i^s \gamma_i^s = 1$) and no any solid–solid transitions, Eq. (1) can be simplified as:

$$\ln(x_i^l \gamma_i^l) = \ln(a_i^l) = \frac{\Delta_{fus} H_{m,i}}{RT_{fus,i}} \left(1 - \frac{T_{fus,i}}{T} \right) \quad (2)$$

Where $a_i^l (=x_i^l \gamma_i^l)$ is the activity of component i in the liquid phase. Then temperature T , at which the two coexisting phases at a constant pressure are in equilibrium, is then related to the activity according to the following equation:

$$T = \frac{1}{\frac{1}{T_{fus,i}} - \frac{R}{\Delta_{fus} H_{m,i}} \ln(a_i^l)} \quad (3)$$

4. Results and discussion

Fig. 3 shows the solid–liquid equilibria phase diagrams and comparison between the melting temperatures measured in this work and those reported in the literature according to the predictive calculations based on the water activity data determined from the another techniques for the systems: water + (formic acid, acetic acid, propionic acid and butyric acid). The experimental results obtained for the investigated binary systems are presented in Tables 2 and 3. As can be seen from Fig. 3, all the studied binary mixtures present a simple

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