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Determination and correlation of molar excess enthalpies of binary systems 2,4-pentanedione + (1-butanol, + 2-methyl-1-propanol, + 1-pentanol, + 1-heptane, + ethyl acetate, and + water)

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Abstract

A high pressure flow-mixing isothermal microcalorimeter was used to determine molar excess enthalpies of six binary systems for 2,4-pentanedione + (1-butanol, + 2-methyl-1-propanol, + 1-pentanol, + 1-heptane, + ethyl acetate, and + water) at T = 298.15, 313.15, and 328.15 K and p = 0.1 and 10.0 MPa. The molar excess enthalpies increased with an increase of the temperature and the molecular size of alcohols and decreased slightly with an increase of pressure. The experimental data were correlated by the Redlich–Kister equation and three local composition models (Wilson, NRTL, and UNIQUAC).

Keywords: 2,4-Pentanedione; Molar excess enthalpy; Redlich–Kister equation; Wilson; NRTL; UNIQUAC

1. Introduction

As an important industrial chemical, 2,4-pentanedione (acetylacetone) is widely used as a solvent for acetyl cellulose, additives of gasoline, a desiccant of paint, and medical intermediate to synthesize antiviral agent and so on. 2,4-Pentanedione can form coordination complexes with almost all metals. This property has made it been extensively used as catalysts [1,2] and selective extractant [3].

Different types of phase equilibria and excess properties are widely used for simultaneous fitting and validating of the interaction parameters of the prediction models [4]. Excess enthalpy data are of particular importance as supporting data at different temperatures. 2,4-Pentanedione is just a meaningful chemical due to its strong intramolecular O–H···O hydrogen bond. The possible structures of 2,4-pentanedione in the liquid state has been studied with the help of experiment [5] and theoretical analysis [6]. Just because of its special structure, the thermodynamic properties of a pure component and its mixtures with other solvents are helpful to better understand and explain molecular interaction, as well as to test and develop new models and theories that are able to describe the thermodynamic behavior of liquids. Else the phase equilibria for the systems containing 2,4-pentanedione have been studied [7].

Until now, very few data of molar excess enthalpies of mixtures containing 2,4-pentanedione have been reported. De Torre et al. [8] has determined the excess molar enthalpies of 2,4-pentanedione + alkanes at T = 303.15 K. In this work, the excess molar enthalpies of six binary systems for 2,4-pentanedione + (1-butanol, + 2-methyl-1-propanol, + 1-pentanol, + 1-heptane, + ethyl acetate, and + water) were determined using a high pressure flow-mixing isothermal microcalorimeter at T = 298.15, 313.15 and 328.15 K and p = 0.1 and 10.0 MPa. The experimental data were fitted by Redlich–Kister equation and three local composition models (Wilson, NRTL, and UNIQUAC).

2. Experimental

2.1. Materials

2,4-Pentanedione (guaranteed grade, better than 99.5 mass%) was provided by Huzhou Haipu Pharmaceutical & Chemical Co., Ltd. 1-Butanol, 2-methyl-1-propanol, 1-pentanol (HPLC grade, better than 99.7 mass%) were purchased from Tianjin

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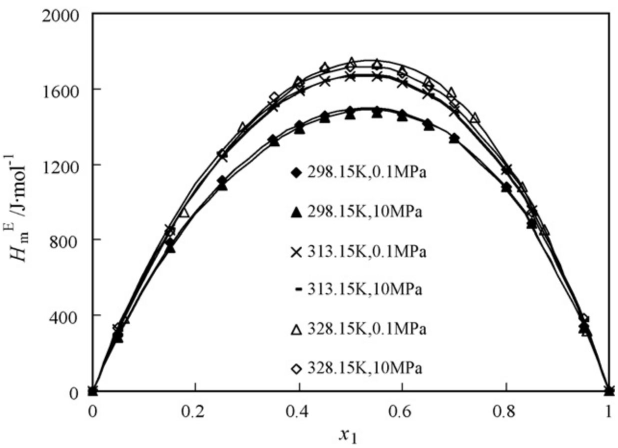

Fig. 1. Molar excess enthalpies of the system 2,4-pentanedione (1) + 1-butanol (2) as a function of mole fraction x_1. The curves were calculated by Redlich–Kister equation (parameters taken from Table 7).

Saifu Technologies Co., Ltd. 1-Heptane (analytical grade, better than 99.5 mass%) and ethyl acetate (analytical grade, better than 99.5 mass%) were provided by Yixing Second Chemical Reagent Plant and Sinopharm Chemical Reagent Co., Ltd., respectively. Deionized water was distilled by using a quartz sub-boiling purifier. All the chemicals were dried with molecular sieves 3–4 Å and filtrated through Millipore filter (0.45 μm). The purities of these compounds were determined by gas chromatography and were found to be between 99.5 and 99.9 mass%. Before use, all chemicals were degassed by evacuation.

2.2. Apparatus

A commercial isothermal microcalorimeter (model IMC 4400, Calorimetry Sciences Corporation, USA) with a refrigerating/heating circulator (model 9000, PolyScience Inc., USA) was used in this work. The flow-mixing system composed of a sample cell and a reference cell (model CSC 4442), two syringe pumps (model 260D, ISCO Inc., USA) and a back pressure regulator (model CSC 4448). The uncertainties of composition on mole fraction basis, temperature and pressure were 0.0005, 0.1 K and 0.1 KPa, respectively. The uncertainty of H_m^E value was less than 1.0%. The experiment procedure and the reliability of the apparatus have been described in detail elsewhere [9].

3. Results and discussion

In this work, the molar excess enthalpies of six binary systems for 2,4-pentanedione + (1-butanol, + 2-methyl-1-propanol, + 1-pentanol, + 1-heptane, + ethyl acetate, and + water) have been measured at T = 298.15, 313.15, and 328.15 K and p = 0.1 and 10.0 MPa. The experimental data are listed in Tables 1–6. As examples, molar excess enthalpies of 2,4-pentanedione (1) + 1-butanol (2) in Table 1 and 2,4-pentanedione (1) + solvents (2) at 298.15 K and 0.1 MPa are plotted in Figs. 1 and 2, respectively.

The experimental data of excess molar enthalpies are correlated by Redlich–Kister equation and three local composition models (Wilson, NRTL, and UNIQUAC). The expressions

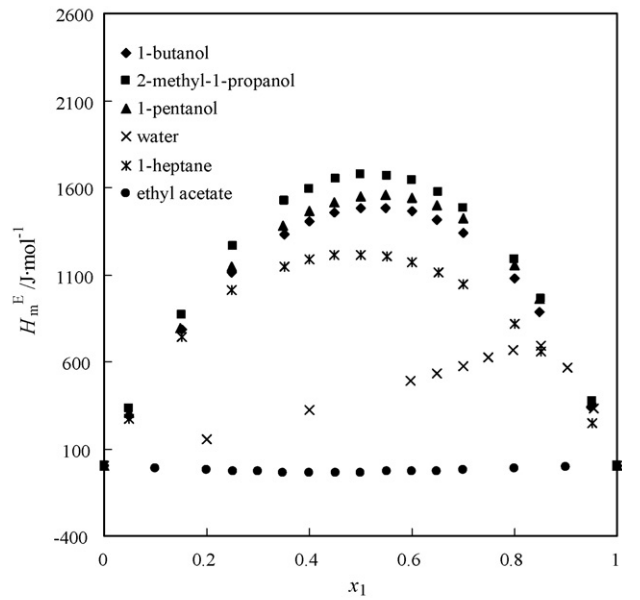

Fig. 2. Molar excess enthalpies for the system 2,4-pentanedione (1) + solvents (2) as a function of mole fraction x_1 at 298.15 K and 0.1 MPa.

of H_m^E derived from the G^E model can be got through the Gibbs–Helmholtz equation:

$$\left[\frac{\partial(G_m^E/T)}{\partial T}\right]_{P,x} = -\frac{H_m^E}{T^2} \tag{1}$$

3.1. Redlich–Kister equation

Redlich–Kister equation [10] is widely used to correlate the H_m^E data:

$$H_m^E\,(\mathrm{J\,mol^{-1}}) = x_1(1-x_1)\sum\nolimits_{i=0}^{n} A_i(2x_1-1)^i \tag{2}$$

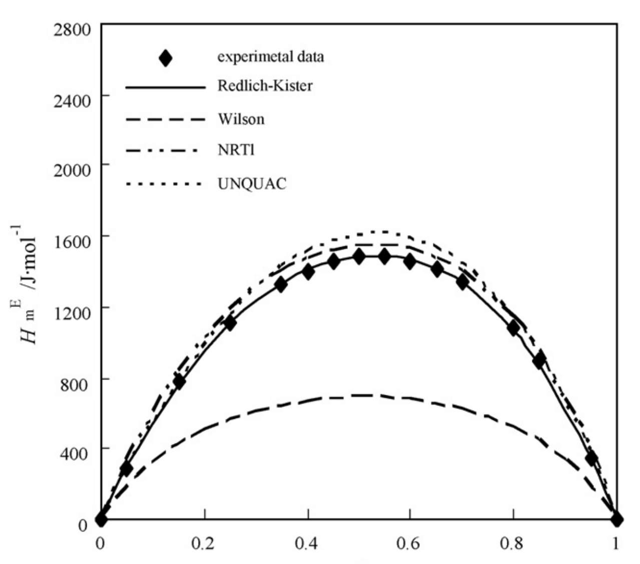

Fig. 3. Correlation of molar excess enthalpies of the system 2,4-pentanedione (1) + 1-butanol (2) at T = 298.15 K and p = 0.1 MPa as a function of mole fraction x_1.