J. Chem. Thermodynamics 70 (2014) 81–87

Contents lists available at ScienceDirect

J. Chem. Thermodynamics

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

Isobaric specific heat capacity of typical lithium chloride liquid desiccants using scanning calorimetry

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ARTICLE INFO

Article history:
Received 28 February 2013
Received in revised form 20 May 2013
Accepted 23 October 2013
Available online 31 October 2013

Keywords:
Heat capacity
Calorimeter
Liquid desiccant

ABSTRACT

Three kinds of lithium chloride desiccants were selected, which are considered to be potential and interesting working fluids for a desiccant/dehumidification or absorption refrigeration system, and their isobaric specific heat capacities were determined in this context. Experiments were conducted at a high accuracy twin-cell scanning calorimeter. The temperature accuracy and heat flux resolution of the calorimeter are ±0.05 K and 0.1 μW respectively. The data of lithium chloride + water and lithium chloride + triethylene glycol (TEG)/propylene glycol (PG) + water systems were achieved at temperatures from 308.15 K to 343.15 K and atmospheric pressure. The mass fraction of LiCl ranged from 15% to 45% in the LiCl + H_2O system, and the mass fraction of LiCl and glycol ranged from 10% to 23.3% and 20% to 46.7% in the ternary systems respectively. Based on the experimental heat capacity data, a universal empirical formula was correlated as a function of temperature and solute mass fraction. In the experimental mass fractions and temperatures range, the average absolute deviation (AAD) between experiment results and calculated values is no more than 0.15%, and maximum absolute deviation (MAD) is within 0.38%. These thermodynamic data of lithium chloride solutions can be effectively used for analysis and design of desiccant/dehumidification systems and absorption refrigeration systems in both refrigeration and chemical industry.

1. Introduction

The increasing global warming and energy shortage inspire researchers to search for sustainable desiccant/dehumidification and refrigeration technology, as alternatives to currently dominative refrigeration technologies which rely mostly on electricity. One of the most potential methods is the adhibition of liquid desiccant /dehumidification systems and absorption refrigeration systems, because both of the two kinds of systems can be driven by ‘low grade’ energy sources, like solar energy, exhausted heat and geothermal energy [1,2].

The performance of a dehumidification or an absorption refrigeration system is basically determined by the property of the working fluids. Since the systems were proposed, a lot of different liquid solutions have been chosen to be used in those systems, the lithium chloride aqueous solution is one of the most widely used because of its excellent thermodynamic properties [3]. To get better access to analyzing or designing liquid dehumidification or absorption refrigeration systems in engineering, high accurate thermodynamic property data of the working fluids are essentially required, including viscosity, density, vapor pressure and heat capacity. Heat capacity is directly linked with temperature derivatives of basic thermodynamic functions and therefore irreplaceable for the calculations of properties changes between different temperatures. Besides, heat capacity also reflects the information of interaction between molecules or ions, so the variation of heat capacity is an important way for understanding the changes in the structure of solutions. Measurements for heat capacity of lithium chloride solutions have been reported by Jauch [4], Richards and Rowe [5], Lange and Durr [6], Gucker and Schminke [7] Bennewitz and Kratz [8], Kapustinskii *et al.* [9] and Fortier *et al.* [10] at around room temperatures. Tucker [11], Uemura *et al.* [12] and Ruterjans *et al.* [13] reported their heat capacity data at extended temperature ranges. The distribution of the available literature data is shown in table 1 and figure 1.

In 2004, Conde [14] presented a review of some typical thermodynamic property data of the LiCl aqueous solution. For heat capacity, he proposed an empirical formula to calculate the value at different temperatures and mass fractions based on the literature data. The formula fitted well with the literature data he referred at low solute concentrations but not so well when compared with data at relatively higher temperatures and higher mass fractions. This might because the data points are adequate at lower temperatures and concentrations while limited at higher temperatures and concentrations. Even more, the two sources of

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http://dx.doi.org/10.1016/j.jct.2013.10.028

Nomenclature

Cp	isobaric specific heat capacity ($kJ \cdot kg^{-1} \cdot K^{-1}$)
P	pressure (MPa)
HF	heat flow (kW)
T	temperature (K)
t	time (s)
w	mass fraction
AAD	average absolute deviation
MAD	maximum absolute deviation
wt	weight
a	parameters
b	parameters

Subscripts

p	isobaric
a	binary system
b	TEG/PG in ternary system
sample	vessel filled with sample
blank	vessel remained empty
i	integer
j	integer

data at higher temperatures and concentrations that were obtained by Tucker [11] and Uemura *et al.* [12] respectively did not agree with each other. Pátek and Klomfar [15] in 2008 presented a formulation for Gibbs free energy equation for the LiCl + H_2O system at (vapor + liquid) equilibrium and derived the equations for the thermophysical properties, including heat capacity. During the correlation, they referred to the literature data at around room temperatures (291 K to 299 K) and rejected the experimental heat capacity data obtained at wider temperature ranges for their relatively high deviations.

The deviation of the experimental heat capacities of lithium chloride aqueous solutions at higher temperatures (other than room temperature) and higher mass fractions may mainly come from the limitation of the experiment method and apparatus. To maintain the calculation accuracy for engineering application, data of higher quality are needed. In this study, taking consideration of the actual working conditions of dehumidification or absorption refrigeration systems, the heat capacity data of LiCl aqueous solution over temperature range of 308.15 K to 343.15 K and mass fraction range of 15% to 45% were investigated using scanning calorimetry. In addition, on the basis of the experimental data, an empirical formula was achieved for the isobaric heat capacity of LiCl aqueous solution as a function of temperature and mass fraction of the solute.

Besides the LiCl aqueous solution, some ternary solutions composed of LiCl aqueous solution and organic additives like triethylene glycol (TEG) or propylene glycol (PG) may play important roles in prospective liquid desiccant/dehumidification systems with better performance. Tsai *et al.* [16] showed that ternary solutions consisting of salts, glycols and water have relatively lower vapor pressures than glycols or salt solutions alone. In this way, the heat capacity data of LiCl + TEG + H_2O and LiCl + PG + H_2O solutions are also investigated at different mass fractions and temperaturesin this study. The mass fraction of LiCl ranged from 10% to 23.3%, and that of the glycol ranged from 20% to 46.7%. A total of five different compositions of each ternary system were selected. As a result, an empirical formula of the isobaric specific heat capacity was obtained from the experimental data for the ternary systems.

2. Materials and experimental apparatus

2.1. Materials

Anhydrous lithium chloride, triethylene glycol and propylene glycol were obtained from Aladdin Chemistry Co. Ltd. (China). The lithium chloride was analytical reagent grade with a minimum mass fraction purity of 99.9%. The triethylene glycol and propylene glycol were both guaranteed reagent grade. Deionized and distilled

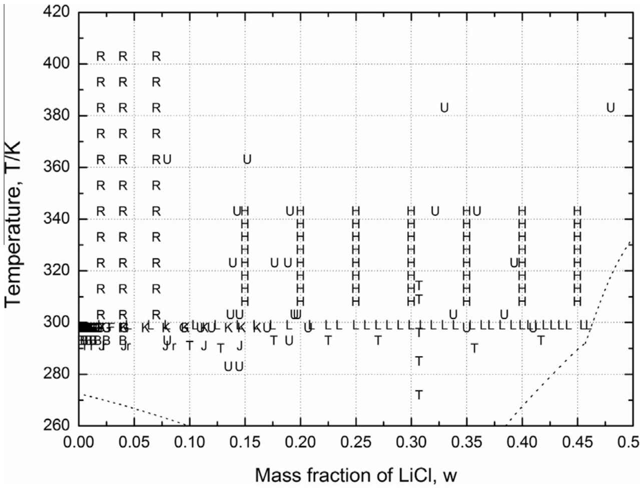

FIGURE 1. Existing experimental data points of the heat capacities of LiCl aqueous solutions (identified by the first letter of the first author name of the study).

TABLE 1
Available data sources for heat capacities of LiCl aqueous solutions.

Author and year	Temperatures range (K)	Mass fractions range (%)	Number of data
Tucker (1915)	272–314	10–41	12
Jauch (1921)	291	2–14.5	5
Richards and Rowe (1921)	293	0.6–8.5	5
Lange and Durr (1926)	299	2–46	36
Gucker and Schminke (1932)	298	0.2–9.5	17
Bennewitz and Kratz (1936)	293	0.2–4	6
Kapustinskii *et al.* (1960)	298	2–16	9
Uemra *et al.* (1965)	283–383	8–48	28
Ruterjans *et al.* (1969)	303–403	2–7	33
Fortier *et al.* (1974)	298	0.2–4	11