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Measurement of thermodynamic properties of ammoniated salts and thermodynamic simulation of resorption cooling system

Rakesh Sharma, E. Anil Kumar *

Discipline of Mechanical Engineering, Indian Institute of Technology Indore, Indore 452020, India

ARTICLE INFO

Article history:
Received 2 December 2015
Received in revised form 10 February 2016
Accepted 11 March 2016
Available online 21 March 2016

Keywords:
Pressure-concentration isotherms
Hysteresis
Ammonia
Metallic salts
Resorption cooling system

ABSTRACT

The adsorption and desorption pressure-concentration isotherms (PCIs) of ammonia on NaBr and $MnCl_2$ salts are measured at different temperatures. Significant hysteresis is observed between adsorption and desorption PCIs. From PCI data, van't Hoff plots are constructed to estimate the enthalpies of formation for different ammonia concentrations. Substantial variation in reaction enthalpy during adsorption and desorption is noticed from beginning to the end of the processes. The average values of ΔH for NaBr and $MnCl_2$ are –28.59 kJ mol^{-1} and –60.17 kJ mol^{-1} respectively for adsorption and 29.16 kJ mol^{-1} and 65.62 kJ mol^{-1} respectively for desorption. The resorption cooling system is thermodynamically analyzed using measured equilibrium data. The coefficient of performance (COP) and specific cooling power (SCP) of resorption system is evaluated to be 0.31 and 52 W kg^{-1} at refrigeration, regeneration and ambient temperatures of –15 °C, 170 °C and 25 °C respectively at a mass ratio of 4. About 49.18% decrease in COP is noticed in comparison with maximum theoretical COP in which 32.78% and 16.36% reductions are due to hysteresis effect and thermal capacity of metallic mass respectively.

Mesure des propriétés thermodynamiques de sels d'ammoniac et simulation thermodynamique de système de refroidissement à résorption

Mots clés : Isothermes pression-concentration ; Hystérésis ; Ammoniac ; Sels métalliques ; Système de refroidissement à résorption

* *Corresponding author.* Discipline of Mechanical Engineering, Indian Institute of Technology Indore, Indore 452020, India. Tel.: +91 7324 240730; Fax: +91 7324 240761.
E-mail address: anil@iiti.ac.in (E. Anil Kumar).
http://dx.doi.org/10.1016/j.ijrefrig.2016.03.006
0140-7007/

Nomenclature

A	slope of van't Hoff lines
B	intercept of van't Hoff lines
C_p	specific heat [kJ kg^{-1} K^{-1}]
COP	coefficient of performance
ΔH	reaction enthalpy [kJ mol^{-1}]
m	mass [g]
m_{salt}	mass of metallic salt [g]
m_T	mass of ammonia adsorbed [g]
n	number of moles of ammonia
P	pressure [Pa]
ΔP	pressure difference between reference volume and supply volume [Pa]
Q	heat load [kJ]
R	universal gas constant [kJ mol^{-1} K^{-1}]
R_{NH_3}	characteristic gas constant of ammonia [kJ kg^{-1} K^{-1}]
ΔS	entropy [kJ mol^{-1} K^{-1}]
SCP	specific cooling power [W kg^{-1}]
t	time [minute]
T	temperature [K]
V_s	supply volume [m^3]
W	amount of ammonia adsorbed/desorbed [wt%]

Subscripts

a	adsorption
aa	after adsorption
ad	after desorption
amb	ambient
ba	before adsorption
bd	before desorption
d	desorption
e	equilibrium
r	reactor
ref	refrigeration
reg	regeneration

Greek letters

δ	uncertainty

1. Introduction

Conventional refrigeration systems are based on vapour compression cycle which utilizes CFCs and HCFCs as refrigerant. But these refrigerants are responsible for ozone layer degradation. Also conventional refrigeration systems require high grade energy for operation and indirectly contribute to the global warming. One of the alternatives to conventional refrigeration systems is a refrigeration system based on chemical reaction between substances, generally termed as chemical heat pump (CHP). The advantage of chemical heat pump over conventional vapour compression refrigeration system is that it can be driven by low grade heat and uses natural refrigerants such as water, methanol, ethanol and ammonia which are eco-friendly. The liquid absorption refrigeration systems are the most ancient chemical heat pumps but they are accompanied with the problem of crystallization and are not compatible at places where vibration occurs. For last three decades, chemical heat pump based on gas-solid reaction have been explored either to reduce or to replace the use of conventional refrigeration systems (Neveu and Castaing, 1993; Spinner, 1993). Among several natural refrigerants available, ammonia is widely used for the development of chemical heat pump because of its capability to react with wide variety of solids within the temperature range of –50 to 300 °C (Spinner, 1993). Ammonia gas is physisorbed by activated carbons, zeolites and MOFs while it chemically reacts with metallic salts. The adsorption and desorption of gas by a solid are characterized by exothermic and endothermic reactions respectively.

Various researchers have utilized the heat interactions during chemical reaction between ammonia and metallic salts to develop prototype of cooling system based on either adsorption cycle or resorption cycle or both (Goetz et al., 1997; Li et al., 2009b; Neveu and Castaing, 1993). In adsorption cycle refrigeration system, cooling effect is obtained by the evaporation of ammonia which is simultaneously adsorbed by the metallic salt and further recycled to the evaporator via condenser. Wang et al. (2004) tested an adsorption refrigeration system to produce ice on fishing boats and study the performances of different samples of $CaCl_2$ and its composites with activated carbon. The composite of $CaCl_2$ and expanded graphite is used to develop refrigeration system based on adsorption cycle and performance of the system has been evaluated (Oliveira and Wang, 2007; Oliveira et al., 2007). The adsorption cooling system based on the composite of $MnCl_2$-expanded graphite has been investigated by Li et al. (2009a) to achieve deep freezing. Kiplagat et al. (2013) examined the performance of an air-conditioner developed using ammonia as refrigerant and composite of NaBr-expanded graphite as adsorbent. Whereas in the resorption cooling system, desorption enthalpy of another reactive salt, which replaces the evaporator/condenser in adsorption cycle, is responsible for cooling production. Resorption system based on the working pair of $BaCl_2$ and $NiCl_2$ has been experimentally investigated for the purpose of refrigeration and air-conditioning by Goetz et al. (1997) and for heating and cooling simultaneously by Vasiliev et al. (2004). A thermochemical transformer, using the pair of $BaCl_2$-$MnCl_2$, working on the principle of resorption cycle is theoritically and experimentally examined by Lepinasse et al. (1994). While using the same pair of $BaCl_2$ and $MnCl_2$, resorption refrigeration system has been experimentally studied and its performance is compared with that of basic adsorption refrigeration system by Wang et al. (2009) and Li et al. (2010). Bao et al. (2011a) experimentally compared the performance of cooling system based on different working pairs of NH_4Cl–$MnCl_2$, NaBr–$MnCl_2$ and $BaCl_2$–$MnCl_2$. The working pair of NH_4Cl–$MnCl_2$ is used to inspect resorption system employed for refrigeration, simultaneous heating and cooling, and cold storage and long-distance refrigeration by Bao et al. (2011b), Xu et al. (2011) and Bao et al. (2012) respectively. Oliveira et al. (2009) performed experimental investigation of NaBr based adsorption refrigeration system for air conditioning and NaBr–$MnCl_2$ based resorption system for simultaneous heating and cooling. A box has been maintained at 5 °C for 3 hours with the help of $PbCl_2$–$MnCl_2$ based resorption cooling system by Lepinasse et al. (2001). In another type of