Thermochimica Acta 487 (2009) 26–32

Contents lists available at ScienceDirect

Thermochimica Acta

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

Heat capacities of the mixed-solvents desiccants (glycols + water + salts)

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ARTICLE INFO

Article history:
Received 1 October 2008
Received in revised form 2 January 2009
Accepted 11 January 2009
Available online 20 January 2009

Keywords:
Heat capacity
Differential scanning calorimeter
Glycol/H_2O/salt systems

ABSTRACT

Heat capacities of glycol/H_2O/salt systems have been measured over the temperature range 303.15–353.15 K with a differential scanning calorimeter. The salts studied were lithium chloride and lithium bromide; the glycols considered were diethylene glycol, triethylene glycol, tetraethylene glycol, propylene glycol and dipropylene glycol. For each ternary system, four systems of which (4–25 mass%) salt mixed with various glycols (50–80 mass%) were studied. An extended Redlich-Kister-type binary system equation was used to correlate the measured heat capacity data. To this end, the heat capacities of pure glycols and aqueous glycol solutions were also measured. The correlations give satisfactory results as shown by an overall AAD for heat capacity calculations of 0.5% for 234 data points. The present measurements are, in general, of sufficient accuracy for most engineering-design calculations for the design of dehumidifier equipments.

1. Introduction

The aqueous–organic with salt systems have been recently considered as potential absorbents for liquid desiccants to absorb moisture from air for they have been shown to yield smaller values of vapor pressure than those of the conventionally used liquid desiccants [1]. The conventional liquid desiccants in absorption dehumidification systems are aqueous solutions of either aqueous salts, such as lithium chloride (LiCl), lithium bromide (LiBr), and calcium chloride ($CaCl_2$), or organic compounds such as diethylene glycol (DEG), triethylene glycol (TEG), tetraethylene glycol (T_4EG), propylene glycol (PG), and dipropylene glycol (DPG) [2–5].

For air dehumidification, TEG and aqueous LiCl solutions are the two most often used systems [1]. The vapor pressure of some aqueous–organic solutions with salts (glycol/water/salt) systems such as TEG/H_2O/LiCl, TEG/H_2O/LiBr, and PG/H_2O/LiCl have been shown to yield smaller values of vapor pressure than those of the conventionally used liquid desiccants [2]. Thus, the aqueous–organic solvents with salt systems may reasonably be considered as the potential absorbents for liquid desiccants.

For the rational design of the dehumidifier process, heat capacities of liquid desiccants are required to estimate the correct heating load of dehumidifier equipments. However, the experimental data such as heat capacity of aqueous organic desiccants are very few in the literature [6,7]. Therefore, it is the purpose of this study to investigate experimentally the heat capacity of some mixed-solvents with salt liquid desiccants for the temperature range of 303.15–353.15 K. The glycols considered in this work were diethylene glycol, triethylene glycol, tetraethylene glycol, propylene glycol and dipropylene glycol and the salts studied were lithium chloride (LiCl) and lithium bromide (LiBr). Ten ternaries, namely: DEG/H_2O/(LiCl or LiBr), TEG/H_2O/(LiCl or LiBr), T_4EG/H_2O/(LiCl or LiBr), PG/H_2O/(LiCl or LiBr), and DPG/H_2O/(LiCl or LiBr), were selected for this study. For each ternary system, four systems of which (4–25 mass%) salt mixed with various glycols (50–80 mass%) were investigated. An extended Redlich-Kister-type binary system equation was used to represent the measured heat capacity data of the investigated ternaries. In this regard, the heat capacity of pure glycols and aqueous glycol solutions were also measured. To validate the present procedures of heat capacity measurements, the heat capacity of pure glycols were then compared to available literature data.

2. Experimental

2.1. Chemicals

Diethylene glycol was Riedel-deHaën reagent grade with a minimum purity of 99%; tripropylene (TEG) was Fulka reagent grade with a minimum purity of 97%; tetraethylene glycol was Aldrich reagent grade with a minimum purity of 99%; propylene glycol was Baker reagent grade with a minimum purity of 99%; dipropylene glycol was Fulka reagent grade with a minimum purity of 99%; lithium chloride (LiCl) was Baker reagent grade with a minimum purity of 99%; and lithium bromide (LiBr) was Riedel-deHaën reagent grade with a minimum purity of 98%. A water purification system from Barnstead (model EASYpure LF) was used to provide Type I reagent-grade water (resistivity $\leq 18.3\ M\Omega\ cm$) with

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doi:10.1016/j.tca.2009.01.008

Table 1
Heat capacity of DEG..

T (K)	Heat capacity, C_p (J mol^{-1} K^{-1})					
	Zaripov [9]	AAD%[a]	Stephens and Tamplin [10]	AAD%[a]	This study	AAD%[a]
293.15			243.0	0.082		
298.15	243.9	0.423				
303.15					248.2	0.466
313.15			251.0	0.080	251.3	0.039
323.15					255.0	0.109
333.15			259.0	0.105	259.2	0.027
343.15					263.8	0.234
353.15			267.0	0.004	266.8	0.079
Overall AAD%		0.42		0.07		0.16

[a] Calculated from C_p (J mol^{-1} K^{-1}) = $a + b(T(\mathrm{K})) + c(T(\mathrm{K}))^2$.

Table 2
Heat capacity of TEG, T_4EG, PG, and DPG.

T (K)	Heat capacity, C_p (J mol^{-1} K^{-1})			
	TEG	T_4EG	PG	DPG
303.15	336.3	428.5	192.8	329.0
313.15	339.5	430.9	197.0	335.3
323.15	343.1	434.7	201.3	341.5
333.15	347.9	438.5	206.0	348.8
343.15	353.7	443.6	210.6	355.8
353.15	359.3	449.1	215.3	363.8

extremely low organic content (≤15 ppb). The studied solutions were prepared by mass, with a weighing accuracy of $\pm 1 \times 10^{-4}$ g. The estimated uncertainty of the mole fraction of aqueous solutions is $\pm 1.5 \times 10^{-4}$. The prepared aqueous solutions have been degassed by using ultrasonic cleaner (Branson, Model 3510).

2.2. *Heat capacity measurements*

The C_p was measured using the differential scanning calorimeter (DSC) consisting of a DSC-2010 and a thermal analysis controller from TA Instruments. The DSC operating range is from the room temperature to 725 °C. Both the temperatures and the heat flow associated with transitions in materials can be easily and rapidly measured with the system. The DSC operates with a temperature repeatability of ±0.1 K. Calorimetric sensitivity is 1 μW (rms). The calorimetric precision is ±1% based on measurements of metal samples. The purge gas was nitrogen with a flow rate of 40 mL min^{-1}. The heating rate was set to be 5 K min^{-1}. To obtain accuracy results, the temperature calibration has been checked periodically. The temperature calibration is obtained from the run in which a calibration material (e.g., indium) is heated through its melting point. The melting point of indium is utilized to calibrate the temperature. By using the sample encapsulating press, the liquid sample was prepared within a hermetic sample pan. The internal volume of the hermetic pan was approximately 10 mm^3. Sample weight is in the range (15–20) mg. Five replicate runs were carried out for each measurement. The apparatus and the experimental procedures were the same as those described by Chiu et al. [8]. On the basis of comparison with literature values for water, the uncertainty of the C_p measurements was estimated to be ±0.015 (kJ kg^{-1} K^{-1}).

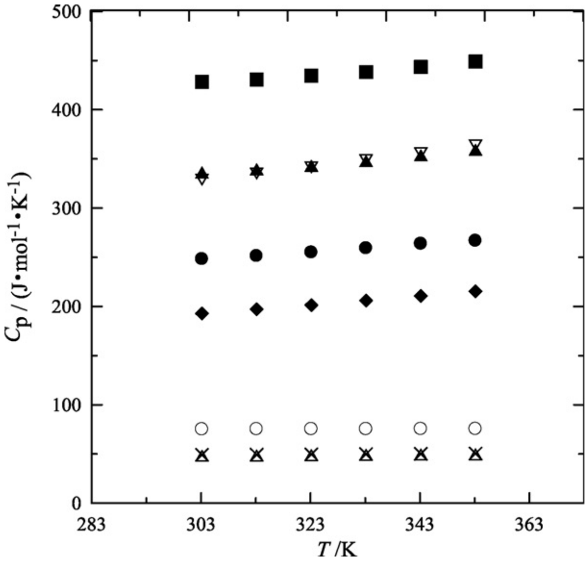

Fig. 1. Heat capacity of glycols, H_2O and salts: (●) DEG; (▲) TEG; (■) T_4EG; (♦) PG; (▽) DPG; (△) LiCl ref. [11], (×) LiBr ref. [11]; (○) H_2O, ref. [12].

3. Results and discussion

The heat capacities were measured for the studied glycols for temperature range of 303.15–353.15 K. The results are presented in Tables 1 and 2. As seen in Table 1, the measured heat capacities of DEG are in good agreement with the literature values [9,10] as shown by a very reasonable average absolute deviation (AAD) percentage, thus, validating the procedures and apparatus for the heat capacity measurement.

In Fig. 1, heat capacities of glycols, salts, [11] and water [12] as a function of temperature are shown. At 303.15 K, the heat

Table 3
Determined parameters of Eq. (1) for glycols.

Parameters	DEG	TEG	T4EG	PG	DPG	H_2O[b]
a_1	127.95	194.05	301.24	56.45	118.6	73.22
a_2	0.3947	0.4648	0.4153	0.4489	0.692	0.0065
AAD%[a]	0.16	0.20	0.17	0.09	0.11	
No of data points	6	6	6	6	6	

[a] $\mathrm{AAD\%} = (100/n) \times \sum_{i=1}^{n} \left| (y_{\mathrm{expt}} - y_{\mathrm{calc}})/y_{\mathrm{expt}} \right|_i$.

[b] Determined from data of Osborne et al. [12].

Table 4
Heat capacity of aqueous glycol solutions.

T (K)	Heat capacity C_p and excess heat capacity C_p^E (J mol^{-1} K^{-1})									
	$x_1 = 0.2$		$x_1 = 0.4$		$x_1 = 0.5$		$x_1 = 0.6$		$x_1 = 0.8$	
	C_p	C_p^E	C_p	C_p^E	C_p	C_p^E	C_p	C_p^E	C_p	C_p^E
DEG(1) + H_2O(2)										
303.15	111.8	1.62	148.7	3.99	167.6	5.65	184.5	5.31	217.9	4.24
313.15	113.5	2.98	150.7	5.04	169.9	6.56	187.1	6.24	221.2	5.08
323.15	115.3	4.08	153.3	6.10	172.6	7.41	190.3	7.14	225.0	5.90
333.15	117.4	5.21	155.9	7.04	175.5	8.23	193.6	7.95	229.1	6.69
343.15	119.3	6.13	158.7	7.87	178.7	9.05	197.3	8.77	233.6	7.48
353.15	121.7	7.45	161.8	8.89	182.2	9.93	201.2	9.66	238.5	8.28
TEG(1) + H_2O(2)										
303.15	129.3	1.51	184.1	4.15	211.3	5.31	237.8	5.70	288.3	4.14
313.15	131.0	2.89	186.3	5.34	213.6	6.24	240.5	6.68	291.8	5.15
323.15	132.9	3.99	189.0	6.51	216.5	7.22	243.7	7.64	295.7	6.14
333.15	135.1	5.16	192.1	7.67	219.8	8.15	249.7	8.59	300.3	6.94
343.15	137.2	6.08	195.2	8.40	233.4	8.85	251.8	9.36	306.0	7.92
353.15	139.7	7.35	198.7	9.63	227.3	9.85	256.1	10.27	311.3	8.74
T_4EG(1) + H_2O(2)										
303.15	156.0	9.71	230.6	13.75	266.0	13.9	300.5	13.12	366.5	8.50
313.15	157.2	10.8	232.4	14.91	267.9	14.8	302.4	13.79	369.5	9.72
323.15	158.9	11.74	234.9	15.82	270.4	15.4	305.3	14.35	373.5	10.71
333.15	161.0	12.95	237.5	16.82	273.4	16.4	308.6	15.26	377.5	11.56
343.15	163.0	13.90	240.5	17.74	277.1	17.6	312.4	16.07	382.6	12.61
353.15	165.4	15.03	243.7	18.67	280.9	18.5	316.5	16.8	388.0	13.52
PG(1) + H_2O(2)										
303.15	101.9	2.78	127.0	4.44	138.9	4.61	150.3	4.30	172.1	2.65
313.15	103.0	3.35	129.4	5.39	141.9	5.76	153.9	5.57	176.4	3.73
323.15	104.3	3.79	132.1	6.34	145.1	6.83	157.7	6.83	180.9	4.81
333.15	105.8	4.29	134.9	7.21	148.7	7.98	161.8	8.02	185.8	5.92
343.15	107.2	4.73	137.7	8.18	152.1	9.10	165.8	9.25	190.6	7.02
353.15	108.8	5.20	140.7	9.15	155.6	10.16	169.9	10.45	195.5	8.14
DPG(1) + H_2O(2)										
303.15	129.1	2.73	181.8	4.79	207.2	4.86	231.9	4.25	279.7	1.34
313.15	130.8	3.45	184.9	5.57	210.9	5.63	236.2	4.93	285.0	1.71
323.15	132.7	4.17	188.2	6.40	214.7	6.29	240.7	5.65	290.4	2.12
333.15	135.0	4.87	191.9	7.08	219.3	7.15	245.8	6.37	296.6	2.45
343.15	137.1	5.55	195.5	7.85	235.5	7.87	250.8	7.04	302.7	2.89
353.15	139.5	6.27	199.6	8.66	228.3	8.61	256.3	7.80	309.4	3.25

capacity of the studied glycols and water are in the order: T_4EG (428.5 J mol^{-1} K^{-1}, MW = 194.2 g mol^{-1}) > TEG (336.3 J mol^{-1} K^{-1}, MW = 150.2 g mol^{-1}) > DPG (329.0 J mol^{-1} K^{-1}, MW = 134.2 g mol^{-1}) > DEG (248.2 J mol^{-1} K^{-1}, MW = 106.1 g mol^{-1}) > PG (192.8 J mol^{-1} K^{-1}, MW = 76.1 g mol^{-1}) > H_2O (75.3 J mol^{-1} K^{-1}, MW = 18.0 g mol^{-1}). The heat capacity is generally related to the chemical structure; the higher molar mass of a molecule is, the larger molar heat capacity will be observed. The measured heat capacities of glycols follow this trend. As also seen in Fig. 1, the heat capacity of salts, LiCl and LiBr, have lower heat capacity values since they are in the solid state.

The heat capacity of glycols was represented as a function of temperature as follows:

$$C_p\,(\mathrm{J\,mol^{-1}\,K^{-1}}) = a_1 + a_2 T\,(\mathrm{K}) \tag{1}$$

where a_i are empirical parameters. The results of heat capacity calculation for glycols are presented in Table 3. The determined parameters a_i correlated well the present heat capacity for glycols as shown by AAD of less than 0.2%.

To correlate the heat capacity of aqueous glycol solutions, a Redlich-Kister-type equation for the concentration dependence is applied. The excess molar heat capacity C_p^E for an aqueous glycol solution is defined [13] as

$$C_p^E = C_p - (x_1 C_{p,1} - x_2 C_{p,2}) \tag{2}$$

where $C_{p,i}$ is the molar heat capacity of the component i, x_i the mole fraction of ith component. The value of C_p^E can be calculated from the measured C_p and $C_{p,i}$. The measured heat capacity C_p and the calculated C_p^E for five aqueous glycol solutions are presented in Table 4. In the calculation of C_p^E, the $C_{p,i}$ for glycols were from Tables 1 and 2, $C_{p,i}$ for water was from Osborne et al. [12]. As presented in Table 4, the C_p^E of all the studied binary aqueous glycol systems have a positive value.

Table 5
Parameters of Eq. (4) for the studied binary systems.

Systems	i	Parameters		No. of data points	AAD%	
		$a_{i,0}$	$a_{i,1}$		C_p^E	C_p
DEG(1) + H_2O(2)	1	−85.09	0.3478	30	1.1	0.2
	2	67.95	−0.1801			
	3	−236.97	0.7633			
TEG(1) + H_2O(2)	1	−94.44	0.3812	30	1.3	0.8
	2	54.51	−0.1341			
	3	−242.83	0.7721			
T_4EG(1) + H_2O(2)	1	−47.38	0.3391	30	1.4	0.2
	2	12.50	−0.0611			
	3	−249.50	0.8393			
PG(1) + H_2O(2)	1	−116.81	0.4462	30	0.4	0.1
	2	−95.83	0.3132			
	3	−43.49	0.1305			
DPG(1) + H_2O(2)	1	−72.04	0.3023	30	1.7	0.8
	2	43.11	−0.1658			
	3	−48.96	0.0983			

The Redlich-Kister equation representing the compositional dependence of the excess molar heat capacity has the following form:

$$C_p^E\,(\mathrm{J\,mol^{-1}\,K^{-1}}) = x_1x_2\sum_{i=1}^{n} A_i(x_1-x_2)^{i-1} \qquad (3)$$

where A_i's are pair-parameters and assumed to have the following temperature-dependent function

$$A_i = a_{i,0} + a_{i,1}T\,(\mathrm{K}) \qquad (4)$$

where $a_{i,0}$ and $a_{i,1}$ are determined from C_p^E calculated from Eq. (2).

In Table 5, the parameters in Eq. (4) for aqueous glycol solutions are presented. For a total of 150 data points for aqueous glycol solutions, the overall AAD% of the calculations are 1.2 and 0.4% for the excess molar heat capacity and the molar heat capacity, respectively. In Fig. 2, the excess molar heat capacities of PG(1) + H_2O(2) were shown. As seen from this figure, the value of C_p^E increases as the temperature increases. A comparison of the C_p^E of aqueous glycol solutions at 333.15 K is shown in Fig. 3. Among the five studied aqueous glycol solutions, C_p^E of T_4EG + H_2O has the highest values while that of DPG + H_2O has the lowest values. The systems of DEG + H_2O, TEG + H_2O, and PG + H_2O have a similar trend. As also shown in Fig. 3, the Redlich-Kister equation can satisfactory represents the composition dependence of aqueous glycol solutions.

The heat capacities glycol/H_2O/LiCl and glycol/H_2O/LiBr were listed in Tables 6 and 7, respectively. For each ternary system, four

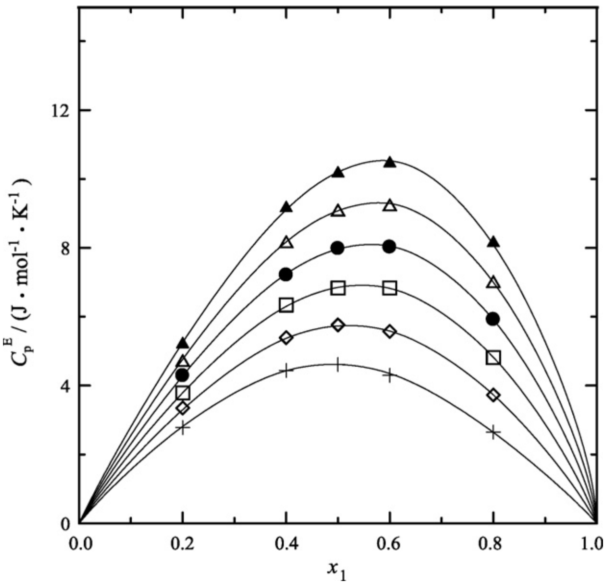

Fig. 2. Excess molar heat capacity of PG(1) + H_2O(2): (+) 303.15 K; (◊) 313.15 K; (□) 323.15 K; (●) 333.15 K; (△) 343.15 K; (▲) 353.15 K; lines, calculated using Eq. (3).

Table 6
Heat capacity C_p and heat capacity difference $C_p - C_{p,a}$ of glycols/H_2O/LiCl.

T (K)	Heat capacity C_p and heat capacity difference $C_p - C_{p,a}$ (J mol^{-1} K^{-1}) mass% glycol/mass% H_2O/mass% salt (m_{salt}, molality in mol kg^{-1})							
	80/16/4 (0.983)		70/21/9 (2.333)		60/24/16 (4.493)		50/25/25 (7.863)	
	C_p	$C_p - C_{p,a}$	C_p	$C_p - C_{p,a}$	C_p	$C_p - C_{p,a}$	C_p	$C_p - C_{p,a}$
DEG(1)/H_2O(2)/LiCl(3)								
303.15	152.5	−6.65	126.2	−15.06	106.0	−23.56	96.4	−24.87
313.15	154.8	−7.12	127.9	−15.91	107.3	−24.55	97.6	−25.92
323.15	157.1	−7.53	129.5	−16.78	108.8	−25.41	98.8	−26.92
333.15	159.6	−7.79	131.4	−17.41	110.5	−26.10	100.2	−27.73
343.15	162.1	−8.11	133.3	−18.09	112.2	−26.76	101.7	−28.48
353.15	164.5	−8.40	135.3	−18.59	114.1	−27.26	103.3	−29.06
TEG(1)/H_2O(2)/LiCl(3)								
303.15	170.3	−4.31	144.6	−7.62	124.5	−12.58	109.9	−17.01
313.15	174.1	−5.41	146.4	−8.35	126.1	−13.29	111.2	−17.81
323.15	176.2	−6.14	148.1	−9.21	127.8	−13.96	112.6	−18.58
333.15	178.7	−6.53	150.0	−9.86	129.6	−14.50	114.1	−19.20
343.15	181.3	−6.78	152.1	−10.26	131.5	−14.94	115.9	−19.56
353.15	184.0	−7.00	154.6	−10.42	133.7	−15.06	117.7	−19.91
T_4EG(1)/H_2O(2)/LiCl(3)								
303.15	182.6	−16.76	137.3	−31.89	114.5	−36.34		
313.15	184.2	−17.55	138.9	−32.40	116.0	−36.73		
323.15	185.5	−18.61	140.5	−32.92	117.5	−37.09		
333.15	187.5	−19.00	142.4	−33.13	119.2	−37.30		
343.15	189.6	−19.31	144.3	−33.34	120.8	−37.64		
353.15	191.9	−19.36	146.3	−33.50	122.5	−37.86		
PG(1)/H_2O(2)/LiCl(3)								
303.15	136.7	−6.67	119.9	−11.59	104.5	−18.64	96.6	−20.25
313.15	139.8	−7.22	122.1	−12.44	106.3	−19.45	98.1	−21.04
323.15	142.8	−7.82	124.3	−13.25	108.0	−20.28	99.6	−21.84
333.15	146.0	−8.26	126.6	−14.01	109.8	−21.08	101.2	−22.50
343.15	149.2	−8.78	128.9	−14.74	111.7	−21.80	102.8	−23.11
353.15	152.3	−9.28	131.2	−15.33	113.6	−22.44	104.6	−23.61
DPG(1)/H_2O(2)/LiCl(3)								
303.15	172.8	−8.98	140.9	−16.75	119.7	−22.57	106.5	−25.19
313.15	175.6	−9.87	143.0	−17.65	121.4	−23.50	107.8	−26.12
323.15	178.5	−10.55	145.2	−18.50	123.2	−24.22	109.1	−27.07
333.15	181.7	−11.04	147.6	−19.08	125.3	−24.67	110.5	−27.87
343.15	184.7	−11.61	149.8	−19.84	127.3	−25.22	112.1	−28.57
353.15	188.0	−11.96	152.6	−20.07	129.5	−25.64	113.7	−29.22

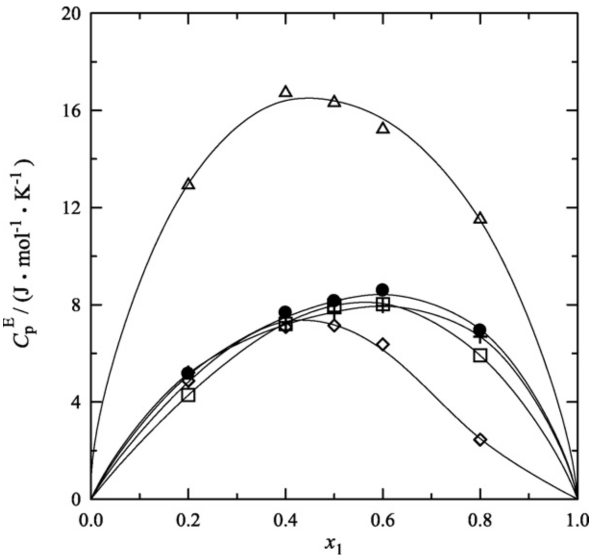

Fig. 3. Excess molar heat capacity of aqueous glycol solutions at 333.15 K: (+) DEG + H_2O; (●) TEG + H_2O; (△) T_4EG + H_2O; (□) PG + H_2O; (◊) DPG + H_2O; lines, calculated using Eq. (3).

solutions of which (4–25 mass%) salt (LiCl or LiBr) mixed with aqueous glycols (50–80 mass% of DEG, TEG, T_4EG, PG, or DPG) were studied. In Tables 6 and 7, the molality m_{salt} of salt was also listed for each concentration. The values of $C_p - C_{p,a}$ are also listed in Tables 6 and 7. As presented in Tables 6 and 7, the $C_p - C_{p,a}$ of all the studied ternaries have negative values. In Table 6, in the investigated concentration range, all the solutions were homogeneous except for the ternary $T_4EG(1)/H_2O(2)/LiCl(3)$ at 50/25/25 (mass% T_4EG/mass% H_2O/mass% LiCl). At this concentration, the salt was not dissolved completely and a supersaturated solution was formed; and with this, the C_p of the solution was not able to measure.

Based on the density equation proposed by Söhnel and Novotný [14,15] for solvent/salt solutions, a simple model extended the Redlich-Kister equation for binary system to ternary system was proposed to represent the heat capacity of glycol/H_2O/salt solutions. The proposed equation has the following form:

$$C_p\,(\mathrm{J\,mol^{-1}\,K^{-1}}) = C_{p,a} + B_1(m) + B_2(m)^2 + B_3(m)^3 \tag{5}$$

where m is the molality of salt (in mol of salt/kg of mixed-solvent), $C_{p,a}$ is the heat capacity of salt-free solution, i.e., aqueous glycol solution. The values of $C_{p,a}$ can be calculated from Eq. (3). The B_i is assumed as temperature-dependent as follows:

$$B_i = b_{i,0} + b_{i,1}(T\,(\mathrm{K})) \tag{6}$$

where $b_{i,0}$ and $b_{i,1}$ are empirical constants. In Table 8, the determined parameters in Eq. (6) and the results of heat capacity calculations using Eq. (5) are presented. For the heat capacity of

Table 7
Heat capacity C_p and heat capacity difference $C_p - C_{p,a}$ of glycols/H_2O/LiBr.

T (K)	Heat capacity C_p and heat capacity difference $C_p - C_{p,a}$ (J mol^{-1} K^{-1}) mass% glycol/mass% H_2O/mass% salt (m_{salt}, molality in mol kg^{-1})							
	80/16/4 (0.480)		70/21/9 (1.139)		60/24/16 (2.193)		50/25/25 (3.838)	
	C_p	$C_p - C_{p,a}$	C_p	$C_p - C_{p,a}$	C_p	$C_p - C_{p,a}$	C_p	$C_p - C_{p,a}$
$DEG(1)/H_2O(2)/LiBr(3)$								
303.15	150.2	−8.89	125.3	−15.92	110.5	−19.01	100.5	−20.78
313.15	152.3	−9.58	127.4	−16.43	112.3	−19.60	101.6	−21.87
323.15	154.6	−10.06	129.4	−16.90	113.9	−20.36	102.8	−22.91
333.15	157.2	−10.20	131.5	−17.32	115.7	−20.89	104.2	−23.72
343.15	159.6	−10.55	133.6	−17.73	117.6	−21.41	105.5	−24.64
353.15	162.1	−10.81	135.7	−18.14	119.6	−21.78	107.1	−25.31
$TEG(1)/H_2O(2)/LiBr(3)$								
303.15	174.4	−2.27	148.8	−3.45	133.0	−4.16	116.7	−10.21
313.15	176.8	−2.67	150.8	−3.99	134.6	−4.83	118.1	−10.99
323.15	179.2	−3.14	152.8	−4.47	136.2	−5.53	119.4	−11.74
333.15	181.8	−3.46	155.1	−4.79	137.9	−6.15	121.1	−12.15
343.15	184.3	−3.79	157.3	−5.15	139.8	−6.66	122.7	−12.76
353.15	186.8	−4.17	159.6	−5.39	141.9	−6.84	124.4	−13.14
$T_4EG(1)/H_2O(2)/LiBr(3)$								
303.15	187.9	−11.48	148.8	−20.36	122.7	−28.05	109.5	−28.91
313.15	190.0	−11.69	150.6	−20.69	124.2	−28.48	110.7	−29.48
323.15	192.3	−11.84	152.4	−21.03	125.7	−28.93	111.8	−30.08
333.15	194.5	−11.98	154.3	−21.24	127.2	−29.35	113.2	−30.42
343.15	196.7	−12.14	156.2	−21.40	128.7	−29.72	114.6	−30.78
353.15	198.9	−12.36	158.3	−21.47	130.4	−29.99	116.0	−31.10
$PG(1)/H_2O(2)/LiBr(3)$								
303.15	139.7	−3.71	125.2	−6.32	115.5	−7.61	104.5	−12.45
313.15	142.8	−4.24	127.5	−7.10	117.2	−8.57	105.8	−13.39
323.15	145.9	−4.71	129.7	−7.90	118.9	−9.45	107.0	−14.40
333.15	149.2	−5.07	132.0	−8.66	120.7	−10.19	108.6	−15.06
343.15	152.4	−5.57	134.2	−9.48	122.5	−11.01	110.0	−15.89
353.15	155.5	−6.06	136.4	−10.26	124.5	−11.58	111.8	−16.35
$DPG(1)/H_2O(2)/LiBr(3)$								
303.15	170.0	−11.78	137.4	−20.22	121.3	−20.97	104.3	−27.44
313.15	173.1	−12.36	139.7	−20.99	122.8	−22.09	105.4	−28.52
323.15	176.2	−12.87	141.8	−21.91	124.3	−23.11	106.7	−29.51
333.15	179.3	−13.36	144.4	−22.23	126.0	−24.02	108.0	−30.43
343.15	182.7	−13.63	147.0	−22.70	127.7	−24.89	109.3	−31.30
353.15	186.1	−13.85	149.7	−22.94	129.4	−25.75	110.9	−32.03

Table 8
Determined parameters of Eq. (6) for the studied ternary systems.

System	i	Parameters		No. of data points	AAD%	
		$b_{i,0}$	$b_{i,1}$		$C_p - C_{p,a}$	C_p
DEG(1)/H_2O(2)/LiCl(3)	1	2.30	−0.0331	24	1.7	0.2
	2	−0.81	0.0043			
	3	0.07	−0.0002			
TEG(1)/H_2O(2)/LiCl(3)	1	7.59	−0.0541	24	5.7	0.6
	2	−2.24	0.0140			
	3	0.16	0.0010			
T_4EG(1)/H_2O(2)/LiCl(3)	1	23.78	−0.0799	18	1.5	0.1
	2	−18.66	−0.0507			
	3	2.77	−0.0069			
PG(1)/H_2O(2)/LiCl(3)	1	15.93	0.0722	24	4.1	0.1
	2	−5.64	0.0200			
	3	0. 46	0.0015			
DPG(1)/H_2O(2)/LiCl(3)	1	10.12	−0.0684	24	1.6	0.2
	2	−4.08	0.0188			
	3	0.35	−0.0015			
DEG(1)/H_2O(2)/LiBr(3)	1	7.57	−0.0678	24	1.3	0.1
	2	−6.23	0.0410			
	3	1.25	−0.0068			
TEG(1)/H_2O(2)/LiBr(3)	1	13.18	−0.0636	24	4.6	0.1
	2	−3.99	0.0239			
	3	0.27	−0.0029			
T_4EG(1)/H_2O(2)/LiBr(3)	1	2.53	−0.0501	24	2.9	0.2
	2	−4.66	0.0288			
	3	0.94	−0.0042			
PG(1)/H_2O(2)/LiBr(3)	1	29.08	−0.1284	24	0.9	0.1
	2	−13.90	0.0609			
	3	1.85	0.0086			
DPG(1)/H_2O(2)/LiBr(3)	1	−12.30	−0.0665	24	0.7	0.1
	2	12.50	0.0100			
	3	−2.41	0.0003			

glycol/H_2O/salt systems, the overall AAD% of the heat capacity calculations was 0.5% for 234 data points. Thus, the heat capacities of glycol/H_2O/salt systems can be represented satisfactorily by Eq. (5).

Fig. 4 shows the heat capacity of glycol/H_2O/LiBr as a function of molality of LiBr. Since the heat capacity of LiBr is smaller than those of glycols and H_2O (as shown in Fig. 1), the heat capacity of glycol/H_2O/LiBr decreases as the molality of salt increases as seen in Fig. 4. The heat capacity of DEG/H_2O/LiCl as function of temperature is shown in Fig. 5. Since heat capacity of DEG is larger than those of H_2O and LiCl, The higher mass fraction of DEG exhibits higher values of the heat capacity, i.e., DEG (80 mass%)/H_2O/LiCl (4 mass%) > DEG

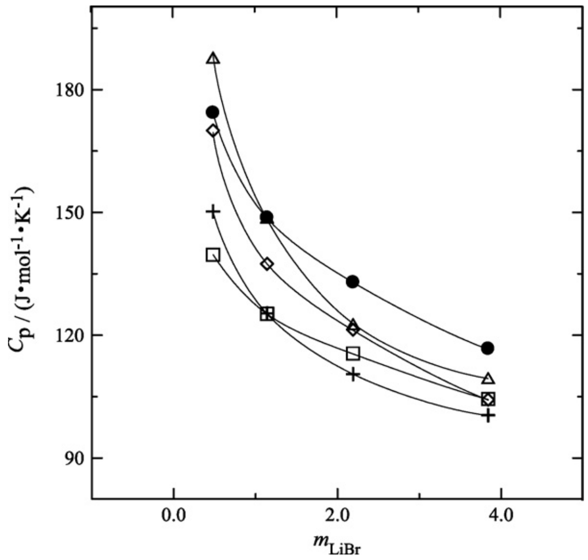

Fig. 4. Heat capacity of glycols(1)/H_2O(2)/LiBr(3): (+) DEG + H_2O + LiBr; (●) TEG + H_2O + LiBr; (△) T_4EG + H_2O + LiBr; (□) PG + H_2O + LiBr; (◊) DPG + H_2O + LiBr; lines, calculated using Eq. (5).

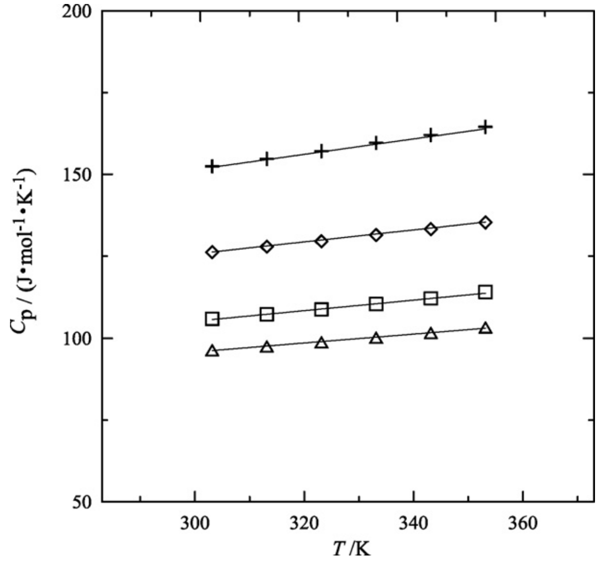

Fig. 5. Heat capacity of DEG(1)/H_2O(2)/LiCl(3): (+) DEG (80 mass%) + H_2O + LiCl (4 mass%); (◊) DEG (70 mass%) + H_2O + LiCl (9 mass%); (□) DEG (60 mass%) + H_2O + LiCl (16 mass%); (△) DEG (50 mass%) + H_2O + LiCl (25 mass%); lines, calculated using Eq. (5).

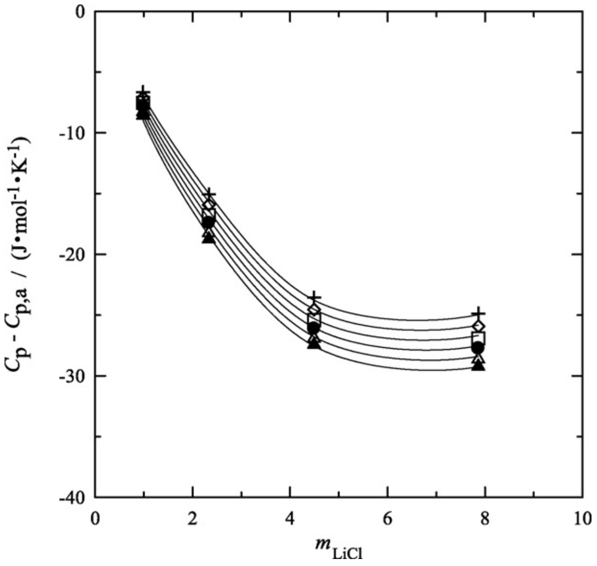

Fig. 6. Heat capacity difference $C_p - C_{p,a}$ of DEG(1)/H_2O(2)/LiCl(3): (+) 303.15 K; (◇) 313.15 K; (□) 323.15 K; (●) 333.15 K; (△) 343.15 K; (▲) 353.15 K; lines, calculated using Eq. (5).

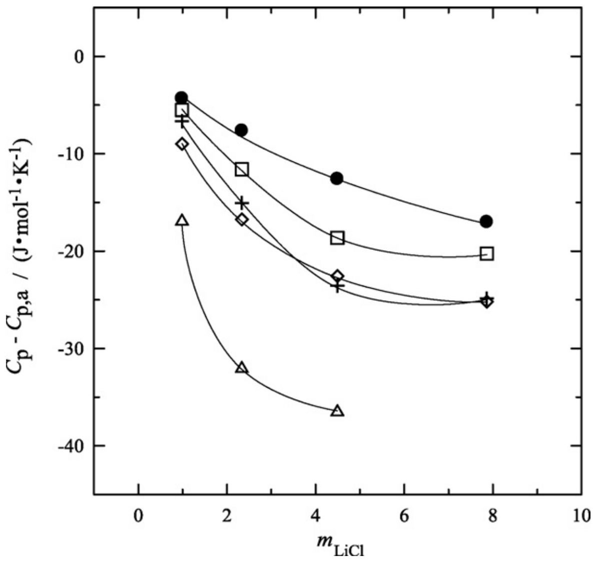

Fig. 7. Heat capacity difference $C_p - C_{p,a}$ of glycols(1)/H_2O(2)/LiCl(3) at 303.15 K: (+) DEG/H_2O/LiCl; (●) TEG/H_2O/LiCl; (△) T_4EG/H_2O/LiCl; (□) PG/H_2O/LiCl; (◇) DPG/H_2O/LiCl; lines, calculated using Eq. (5).

(70 mass%)/H_2O/LiCl (9 mass%) > DEG (60 mass%)/H_2O/LiCl (16 mass%) > DEG (50 mass%)/H_2O/LiCl (25 mass%), as shown in Fig. 5.

Fig. 6 plotted the values of $C_p - C_{p,a}$ of DEG/H_2O/LiCl versus the molality of LiCl at different temperatures. As shown in this figure, the values of $C_p - C_{p,a}$ of DEG/H_2O/LiCl systematically decrease as the salt concentration (in molality) and temperature increases. This figure also showed that $C_p - C_{p,a}$ as a function m_{salt} was not represented well by a simple linear fit nor by a second degree function but instead can be well correlated by a third degree function as in Eq. (5). Fig. 7 shows the values of $C_p - C_{p,a}$ as function of the molality of LiCl for glycols/H_2O/LiCl systems at 303.15 K. As shown in Fig. 7, the ternary T_4EG/H_2O/LiCl has the strongest dependence of the value of $C_p - C_{p,a}$ on LiCl concentration as shown by its sharp decreased on the value of $C_p - C_{p,a}$ while the ternary TEG/H_2O/LiCl has the weakest dependence on LiCl concentration.

4. Conclusions

Heat capacities of glycol/H_2O/salt systems have been measured in this study over the temperature range (303.15–353.15 K) with a DSC. Ten ternaries, namely: DEG/H_2O/(LiCl or LiBr), TEG/H_2O/(LiCl or LiBr), T_4EG/H_2O/(LiCl or LiBr), PG/H_2O/(LiCl or LiBr), and DPG/H_2O/(LiCl or LiBr), were selected for this study. For each ternary system, four systems of which (4–25 mass%) salt mixed with various glycols (50–80 mass%) were investigated. In addition to ternary systems, the heat capacities of glycols and aqueous glycol solutions were also measured. A simple equation extended the Redlich-Kister-type equation to represent the molar heat capacity was applied to correlate the C_p of glycol/H_2O/salt solutions. The heat capacities of glycol/H_2O/salt systems can be represented satisfactorily by the equation. The molar heat capacities of glycol/H_2O/salt systems presented in this study are, in general, of sufficient accuracy for most engineering-design calculations for design dehumidifier equipments.

Acknowledgement

This research was supported by a Grant, NSC 97-2221-E-033-015, of the National Science Council of the Republic of China.

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