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Molar heat capacity of several aqueous solutions of *n*-[tris(hydroxymethyl)methyl-3-amino]propanesulfonic acid (TAPS) + glycol

Yu-Chyi Lu [a], Alvin R. Caparanga [b], Rhoda B. Leron [a], Meng-Hui Li [a,*]

[a] *R&D Center for Membrane Technology and Department of Chemical Engineering, Chung Yuan Christian University, Chung Li, Taiwan*
[b] *School of Chemical Engineering and Chemistry, Mapúa Institute of Technology, Intramuros, Manila, Philippines*

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ABSTRACT

The molar heat capacity (C_p) of a potential solvent system for CO_2 absorption, containing water, glycol and *n*-[tris(hydroxymethyl)methyl-3-amino]propanesulfonic acid (TAPS), was measured at 30–80 °C and different concentrations via differential scanning calorimetry. Each of the glycols – diethylene glycol (DEG), triethylene glycol (TEG), tetraethylene glycol (T_4EG), propylene glycol (PG), dipropylene glycol (DPG) and tripropylene glycol (TPG) – was mixed with TAPS + H_2O to form ternary systems consisting of a fixed amount of the glycol (40 mass%) and variable TAPS/H_2O proportions (4–16 mass% TAPS or 56–44% H_2O). An extended *Redlich–Kister*-type equation was used to correlate heat capacity with concentration and temperature; the average absolute deviation (AAD) of the 198 data points from the corresponding values predicted by the correlation was 0.04%. The new set heat capacity data or the correlation, reported for the ternary system considered, can be used with high degree of accuracy in process design calculations for systems that will utilize these solvent systems.

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1. Introduction

Some amino acids have been used to enhance the rate of absorption of CO_2 in carbonate solution [1]. In this vein, several studies have delved on investigating the absorption of CO_2 in amino acid derivatives, such as amino acid salts and aqueous amino acid salts; the studies have reported encouraging observations [2–5]. *n*-[Tris(hydroxymethyl)methyl-3-amino]propanesulfonic acid or TAPS is a derivative of taurine, an amino acid and biological buffer. On the basis of the predicted interaction between a weak acid (*i.e.*, HCOOH) and a zwitterion in one report [6], it is also predicted that CO_2, which usually forms the weak acid H_2CO_3 in aqueous environment may be capable of association with the zwitterionic species of TAPS via strong OH···O hydrogen bonding interaction despite the weak acid not being capable of deprotonating the zwitterionic species.

Glycols are known gas-dehydrating agents; some have been demonstrated to absorb acid gases, such as CO_2 and H_2S [1,7]. When mixed with an aqueous solution of TAPS, a possible candidate solvent for CO_2 absorption, a glycol is expected to lower the vapor pressure of the resulting mixture. Low solvent vapor pressure makes the separation of the absorbed gas during solvent recovery easier, resulting in recovery of high-purity gas [1]. Since the solvent recovery step in the CO_2 absorption process is an energy-consuming step, it is important that heat effects be quantified to come up with a good design of both the process and the equipment associated with the process. One of the important physical properties of the solvent system necessary for solvent-recovery process and equipment design is heat capacity. Thus, we report the molar heat capacity data from our measurements for the following systems: TAPS + DEG + H_2O, TAPS + TEG + H_2O, TAPS + T_4EG + H_2O, TAPS + PG + H_2O, TAPS + DPG + H_2O, and TAPS + TPG + H_2O at 30–80 °C. The glycol concentration in each system is fixed at 40 wt.%, and the TAPS/H_2O ratio varied from 4 wt.%/56 wt.% to 16 wt.%/44 wt.%.

2. Experimental

2.1. Chemicals

The following indicate the assays of the different chemicals used, in mass%: DEG (TEDIA), purity > 99.9%; TEG (TEDIA), purity > 99.9%; T_4EG (ACROS), purity > 99.5%; PG (ECHO), purity > 99.8%; DPG (ACROS), purity > 99%; TPG (Alfa Aesar), purity > 99%; and TAPS (MP Biomedical), purity > 99%. The water used was Type I reagent-grade water (resistivity ≤ 18.3 MΩ cm; total organics ≤ 15 ppb), which was purified using a compact ultrapure water system (Barnsted EASYpure LF). The aqueous solutions were degassed using ultrasonic cleaner (Branson, Model 3510) before their heat capacities were measured.

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* Corresponding author. Tel.: +886 3 265 4109; fax: +886 3 265 4199.
E-mail address: mhli@cycu.edu.tw (M.-H. Li).

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Table 1
Heat capacity, C_p, and heat capacity difference, $C_p - C_{p,a}$, of TAPS (1) + DEG (2) + H_2O (3).

T °C	mass% TAPS/mass% DEG/mass% H_2O (m_{TAPS}, molality in mol kg^{-1})					
	4/40/56 (0.1713)		9/40/51 (0.4065)		16/40/44 (0.7829)	
	C_p	$C_p - C_{p,a}$	C_p	$C_p - C_{p,a}$	C_p	$C_p - C_{p,a}$
30	230.4	135.7	260.5	164.0	295.9	196.5
35	231.8	136.4	262.3	165.0	298.2	197.9
40	232.9	136.9	264.1	166.2	300.7	199.6
45	233.6	136.9	265.4	166.8	302.5	200.7
50	235.0	137.7	267.3	168.0	304.1	201.6
55	235.9	137.9	268.2	168.2	305.8	202.5
60	237.5	138.7	270.2	169.4	308.2	204.1
65	238.5	139.1	271.6	170.1	310.0	205.1
70	239.7	139.5	273.2	170.9	311.9	206.1
75	241.3	140.4	275.2	172.1	314.5	207.9
80	242.8	141.1	276.9	172.9	316.9	209.3

Table 2
Heat capacity, C_p, and heat capacity difference, $C_p - C_{p,a}$, of TAPS (1) + TEG (2) + H_2O (3).

T °C	mass% TAPS/mass% TEG/mass% H_2O (m_{TAPS}, molality in mol kg^{-1})					
	4/40/56 (0.1713)		9/40/51 (0.4065)		16/40/44 (0.7829)	
	C_p	$C_p - C_{p,a}$	C_p	$C_p - C_{p,a}$	C_p	$C_p - C_{p,a}$
30	294.7	198.5	319.3	221.2	347.5	246.1
35	296.6	199.9	321.3	222.6	349.8	247.8
40	298.1	200.8	323.3	224.1	352.7	250.1
45	299.3	201.5	324.5	224.7	355.0	251.8
50	300.8	202.4	326.6	226.2	357.2	253.4
55	302.1	203.2	328.0	227.1	359.5	255.1
60	304.0	204.5	330.2	228.6	362.0	256.9
65	305.4	205.3	331.4	229.2	364.5	285.6
70	307.2	206.5	333.4	230.5	366.9	260.3
75	308.8	207.5	335.2	231.6	369.1	261.8
80	310.7	208.6	337.2	232.9	372.0	263.9

2.2. Heat capacity measurements

The apparatus (including equipment models and measurement uncertainties), calibration method, and experimental procedures used were the same as those of our previous works [8,9].

The C_p values were measured using a differential calorimeter or DSC (Model: DSC-2010), equipped with a thermal analysis controller (TA Instruments). The DSC operates within room temperature and 725 °C with uncertainty equal to ±0.10 °C. Calorimetric sensitivity is 1 μW (rms), while calorimetric precision is ±1%, based on metal samples.

The equipment was purged with nitrogen, flowing at 40 cm^3 min^{-1}. The heating rate was set to 5 K min^{-1}. To ensure accuracy, calibration of temperature was performed periodically (i.e., indium heated to melting point). Each sample, 5–20 mg, was contained in a hermetically sealed pan (volume ~ 10 mm^3). At least five replicate measurements were performed for a particular sample.

Based on comparison between the C_p of water measured using the setup described in the preceding paragraphs and those values reported (for the corresponding temperatures) in literature, the uncertainty of C_p measurements was estimated to be ±0.15 kJ kg^{-1} K^{-1}.

3. Results and discussion

The measurement method we used was validated by comparing our measurement of molar heat capacity of DPG at different temperatures with those published in literature [9–12] for the same system. The combined data from the literature and from our measurement were fit in the correlation

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

where a_1 and a_2 are empirical parameters, whose values for the DPG system were regressed from the combined data. It was found out the average absolute deviation of the data from those calculated from the model (Eq. (1)) was less than 1%. This suggested that the method by which we measured molar heat capacity would give reliable data. The details of the validation test were reported in our previous study [9].

Tables 1–6 present the molar heat capacity of the different (TAPS + glycol + H_2O) systems at temperatures 30–80 °C and different TAPS and H_2O proportions at fixed glycol wt.%. Such data suggest that the molar heat capacity increases with increase in temperature and TAPS concentration. However, the change in molar heat capacity with respect to change in concentration is steeper than the corresponding change with respect to change in temperature. Same behavior applies to concentration- and temperature-dependence of $C_p - C_{p,a}$. Such behaviors are graphically described, in terms of representative systems, in Figs. 1 and 2.

Table 3
Heat capacity, C_p, and heat capacity difference, $C_p - C_{p,a}$, of TAPS (1) + T_4EG (2) + H_2O (3).

T °C	mass% TAPS/mass% T_4EG/mass% H_2O (m_{TAPS}, molality in mol kg^{-1})					
	4/40/56 (0.1713)		9/40/51 (0.4065)		16/40/44 (0.7829)	
	C_p	$C_p - C_{p,a}$	C_p	$C_p - C_{p,a}$	C_p	$C_p - C_{p,a}$
30	355.6	254.8	370.2	267.1	407.6	300.3
35	357.4	256.2	372.5	268.8	410.8	302.9
40	359.2	257.4	375.0	270.5	414.5	306.1
45	360.6	258.5	376.4	271.8	417.9	309.0
50	362.2	259.6	378.7	273.6	422.0	312.6
55	363.7	260.7	380.7	275.1	425.0	315.1
60	365.5	262.2	382.8	277.0	428.0	317.5
65	367.3	263.2	385.3	278.6	431.7	320.6
70	369.2	264.6	387.4	280.2	435.4	323.6
75	371.0	265.9	389.7	281.9	438.0	325.6
80	373.0	267.0	391.9	283.3	441.2	328.1

The temperature- and concentration-dependence of molar heat capacity for the system was described in terms of a model based on the correlation proposed by Sohnel and Novotny [13]:

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

where m is the molality of salt (in mol of salt/kg of water + glycol), $C_{p,a}$ is the heat capacity of (TAPS-free) water + glycol solution. B_i is assumed temperature-dependent, *i.e.*,

$$B_i = b_{i,0} + b_{i,1}(T\quad \text{K}) \tag{3}$$

Table 4
Heat capacity, C_p, and heat capacity difference, $C_p - C_{p,a}$, of TAPS (1) + PG (2) + H_2O (3).

T °C	mass% TAPS/mass% PG/mass% H_2O (m_{TAPS}, molality in mol kg^{-1})					
	4/40/56 (0.1713)		9/40/51 (0.4065)		16/40/44 (0.7829)	
	C_p	$C_p - C_{p,a}$	C_p	$C_p - C_{p,a}$	C_p	$C_p - C_{p,a}$
30	180.4	86.0	211.3	115.4	254.3	155.8
35	181.3	86.4	212.7	116.2	256.1	157.0
40	182.2	86.7	213.9	116.9	258.0	158.2
45	182.9	87.0	214.8	117.2	259.2	158.8
50	183.8	87.4	216.1	117.9	261.0	160.0
55	184.4	87.4	217.1	118.4	262.4	160.7
60	185.5	87.9	218.5	119.1	264.4	162.0
65	186.3	88.2	219.7	119.7	266.0	162.9
70	187.1	88.5	220.8	120.3	267.7	164.0
75	188.2	89.0	222.3	121.1	269.3	164.9
80	189.3	89.4	223.5	121.7	271.4	166.3

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