

Molar Heat Capacity of Various Aqueous Alkanolamine Solutions from 303.15 K to 353.15 K

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The molar heat capacities of aqueous 2-((2-aminoethyl)amino)ethanol (AEEA), 3-amino-1-propanol (AP), 2-(methylamino)ethanol (MAE), 1-amino-2-propanol (MIPA), and *N,N*-dimethylethanolamine (DMEA) solutions are reported at 11 different temperatures in the range (303.15 to 353.15) K. The percentage average absolute deviation (% AAD) of the measured molar heat capacities of MEA and MDEA is found to be 0.23 % when compared with the literature values. Molar excess heat capacities are calculated from the measurement results and correlated as a function of the mole fractions using the Redlich–Kister equation. The excess partial molar heat capacities ($C_i^o - C_i^*$) are also reported.

Introduction

Alkanolamine solutions have been extensively studied during the last 25 years because of their industrial importance for natural gas processing, synthetic ammonia plants, fossil fuel fired power plants, steel production, and chemical and petrochemical industries. Alkanolamines are mainly used in the removal of acid gas impurities such as carbon dioxide (CO₂), hydrogen sulfide (H₂S), and sulfur dioxide (SO₂) from gas streams.¹

Heat capacities of alkanolamine solutions are required for the calculation of the heat duty in condensers, heat exchangers, and reboilers used in gas-treating processes. In addition, heat capacities (C_p) are directly linked with temperature derivatives to basic thermodynamic functions such as enthalpy (H) and entropy (S). C_p data are necessary in evaluating the effect of temperature on phase and reaction equilibria.

No published data were found for the molar heat capacity of 2-((2-aminoethyl)amino)ethanol (AEEA) (1) + water (2), 3-amino-1-propanol (AP) (1) + water (2), 2-(methylamino)ethanol (MAE) (1) + water (2), 1-amino-2-propanol (MIPA) (1) + water (2), and *N,N*-dimethylethanolamine (DMEA) (1) + water (2) systems, except for pure MAE and DMEA at a few temperatures. Maham et al.² have measured the molar heat capacities of pure MAE (99 %) and pure DMEA (99 %) at (299.1, 322.8, 348.5, 373.2, and 397.8) K. It is the purpose of this study to determine experimentally the molar heat capacities of these alkanolamines at 11 different temperatures in the range (303.15 to 353.15) K. The calculated molar excess heat capacities are then correlated as a function of mole fractions using the Redlich–Kister equation.³ For the sake of completeness, the partial molar quantities $C_i^o - C_i^*$ are calculated by extrapolating the reduced excess heat capacity (C_p^E/x_1x_2) function at $x_1 = 0$ and $x_1 = 1$. The reduced excess heat capacity (C_p^E/x_1x_2) function serves as a sensitive indicator of phase transitions and to understand the changes in the structure of liquid solutions.

Experimental Section

Alkanolamines used in this study were purchased from Sigma-Aldrich with a purity of 99 % for 2-((2-aminoethyl)amino)ethanol, ≥98 % for 3-amino-1-propanol, 98+ % for 2-(meth-

ylamino)ethanol, ≥98 % for 1-amino-2-propanol, and 99.5+ % for *N,N*-dimethylethanolamine and were used without further purification. The purity was based on mass %. A standard reference material, synthetic sapphire (α -Al₂O₃, 99.99 % pure by mass) was purchased from the National Institute of Standards and Technology, Gaithersburg, MD.

Aqueous solutions were prepared on the basis of mole fractions. An analytical Ohaus balance (Model AP250D, Florham Park, NJ) was used to prepare gravimetrically the binary mixtures of alkanolamine and deionized water with a precision of ±0.1 mg. The overall possible uncertainty in the mole fractions is around ±0.0001.

The measurements of the molar heat capacities were carried out in a C80 heat flow calorimeter manufactured by SETARAM (France). The C80 calorimeter works on the Tian-Calvet heat flow principle which is described in detail by Calvet et al.⁴ To obtain a precise measurement of the molar heat capacity of a sample, the sensitivity and the temperature scale of the C80 calorimeter were calibrated. The calibration was performed for the entire temperature range of the C80 calorimeter, i.e., (303 to 573.15) K at a scanning rate of 0.1 K/min, as suggested by SETARAM. Two specially designed Joule effect calibration cells and a calibration unit (EJ3) were used for the sensitivity calibration. A detailed description of the sensitivity calibration is given elsewhere.⁵ The temperature calibration was performed by measuring the temperature of a phase change of the substance (indium or tin); both have well-documented precise transition temperatures. A sample of the pure substance (indium or tin) was encapsulated in an aluminum foil and placed inside the standard cell. The melting point was found by measuring the rate of the heat flow into the sample as a function of temperature. The difference between the observed transition temperature and the actual transition temperature determined the amount of adjustment necessary for the temperature. A detailed description of the temperature calibration is given elsewhere.⁵

For the measurement of the molar heat capacity, a sample weighing about (5.5 to 6) g was placed inside the sample cell. Both the sample cell and the reference cell were allowed to come to an isothermal condition over the period of (3 to 4) h. The scanning rate was set at 0.1 K/min for all runs. After allowing a sufficient period of time to reach the isothermal condition at 298.15 K, the temperature of both cells was increased at a scanning rate of 0.1 K/min. To obtain the most

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Table 1. Comparison of the Molar Heat Capacity (C_p) of MEA and MDEA

T/K	MEA		MDEA		
	$C_p/\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$		T/K	$C_p/\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$	
	Chiu et al. ⁸	present study		Chen et al. ⁹	present study
303.15	167	168	303.15	272	273
308.15	169	169	308.15	275	276
313.15	170	169	313.15	278	279
318.15	172	171	318.15	281	282
323.15	173	173	323.15	285	285
328.15	175	174	328.15	288	288
333.15	176	175	333.15	291	290
338.15	178	178	338.15	295	294
343.15	179	179	343.15	298	298
348.15	180	180	348.15	301	301
353.15	182	182	353.15	304	304

precise values of C_p , the three-step method was employed. In this method, two additional runs were performed with (1) both cells empty and (2) with the reference material before running the sample run; i.e., the measurements of the molar heat capacities were conducted with (1) a blank run, (2) a reference run, and (3) a sample run. For the reference run, a standard

sapphire was used as the reference material. All runs were performed under the same experimental conditions. The heat flow values were recorded for all runs at the required temperature. The molar heat capacity values were then calculated using the following equation:⁶

$$C_p(T) (\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}) = \left(\frac{H_{\text{sample}}^F - H_{\text{blank}}^F}{H_{\text{reference}}^F - H_{\text{blank}}^F} \right) \left(\frac{m_{\text{reference}}}{m_{\text{sample}}} \right) C_{p,\text{reference}}(T) \quad (1)$$

where $C_p(T)$ and $C_{p,\text{reference}}(T)$ are the molar heat capacity of the sample and reference substance (sapphire) at the desired temperature T , respectively; H_{sample}^F , $H_{\text{reference}}^F$, and H_{blank}^F are the heat flows of the sample, reference (sapphire), and blank runs, respectively, at temperature T ; and m_{sample} and $m_{\text{reference}}$ are masses of the sample and reference substance (sapphire), respectively. The values of $C_{p,\text{reference}}(T)$ in eq 1 were taken from the National Bureau of Standards.⁷

To verify the accuracy of the C80 calorimeter, the molar heat capacities of pure MEA and pure MDEA were measured at 11 different temperatures in the range (303.15 to 353.15) K and

Table 2. Molar Heat Capacity (C_p) for AEEA (1) + Water (2) Mixtures from (303.15 to 353.15) K

T/K	x_1									
	0.0999	0.1999	0.2995	0.4000	0.5002	0.5997	0.7011	0.8003	0.8979	1.0000
					$C_p/\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$					
303.15	100	121	141	161	181	201	221	240	258	279
308.15	103	125	145	165	185	205	226	245	263	284
313.15	104	127	147	167	187	207	227	247	265	285
318.15	106	129	150	170	190	209	229	249	266	286
323.15	107	131	152	172	192	211	231	250	267	287
328.15	110	134	155	175	195	214	233	252	269	289
333.15	112	137	158	178	197	216	235	254	271	290
338.15	116	141	162	181	201	219	238	257	273	292
343.15	120	146	167	185	204	223	241	260	275	293
348.15	124	152	172	189	208	227	244	262	277	295
353.15	130	158	177	194	213	231	248	265	279	296

Table 3. Molar Heat Capacity (C_p) for AP (1) + Water (2) Mixtures from (303.15 to 353.15) K

T/K	x_1									
	0.0999	0.2001	0.3003	0.4015	0.4996	0.6006	0.7003	0.8003	0.8966	1.0000
					$C_p/\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$					
303.15	94	108	120	131	143	155	168	180	193	204
308.15	96	111	123	135	147	159	171	184	196	207
313.15	97	112	124	136	148	160	172	185	197	208
318.15	98	113	126	138	150	162	173	186	198	208
323.15	99	115	128	140	152	163	175	187	199	209
328.15	101	117	130	142	154	166	177	189	200	210
333.15	103	119	132	145	157	169	179	191	202	211
338.15	106	122	135	148	160	172	182	193	204	213
343.15	110	126	139	151	163	175	185	196	206	214
348.15	114	130	143	155	167	179	188	198	208	216
353.15	119	135	147	160	172	183	192	201	210	217

Table 4. Molar Heat Capacity (C_p) for MAE (1) + Water (2) Mixtures from (303.15 to 353.15) K

T/K	x_1									
	0.1000	0.1998	0.3003	0.3990	0.5002	0.6061	0.6987	0.8003	0.9004	1.0000
					$C_p/\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$					
303.15	96	108	119	129	139	151	160	172	182	194
308.15	98	111	122	132	143	155	165	176	187	199
313.15	99	113	124	135	146	157	167	178	189	200
318.15	100	114	126	137	148	160	170	180	190	202
323.15	101	116	128	139	150	162	172	183	192	203
328.15	103	118	131	142	153	165	175	185	195	205
333.15	105	121	134	145	157	168	178	188	197	206
338.15	107	124	138	149	161	172	182	191	199	207
343.15	110	127	141	153	164	176	185	194	201	208
348.15	114	132	146	158	169	181	190	198	205	210
353.15	119	138	152	163	174	186	195	203	208	212

Table 5. Molar Heat Capacity (C_p) for MIPA (1) + Water (2) Mixtures from (303.15 to 353.15) K

T/K	x_1									
	0.1000	0.2007	0.2996	0.4001	0.4983	0.6013	0.6999	0.7996	0.8959	1.0000
	$C_p/\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$									
303.15	95	110	121	133	145	158	170	183	196	209
308.15	97	113	124	137	149	162	174	187	200	213
313.15	98	114	126	139	151	164	176	188	201	214
318.15	99	116	128	141	154	166	177	190	202	215
323.15	100	117	130	144	156	168	180	192	204	217
328.15	102	119	133	147	159	171	182	194	206	218
333.15	104	121	136	150	162	174	185	197	209	221
338.15	106	125	140	154	166	178	188	200	211	223
343.15	109	128	144	158	170	181	192	203	214	225
348.15	112	133	149	163	175	185	195	206	216	228
353.15	117	138	155	169	180	190	199	209	219	230

Table 6. Molar Heat Capacity (C_p) for DMEA (1) + Water (2) Mixtures from (303.15 to 353.15) K

T/K	x_1									
	0.0997	0.1962	0.3003	0.3984	0.4983	0.6008	0.6980	0.7981	0.8938	1.0000
	$C_p/\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$									
303.15	103	118	132	144	156	168	179	191	202	213
308.15	104	119	134	146	158	170	181	193	205	215
313.15	105	121	136	149	161	173	185	196	208	217
318.15	105	123	139	152	164	177	188	199	210	219
323.15	107	125	141	155	168	180	191	203	213	221
328.15	108	127	144	158	171	184	195	206	215	222
333.15	109	129	147	161	175	187	199	209	217	223
338.15	112	132	150	165	179	192	203	213	220	223
343.15	114	136	155	170	184	196	208	218	223	223
348.15	118	140	160	176	190	203	214	223	225	224
353.15	123	146	166	184	198	210	221	229	228	226

Table 7. Extrapolated Excess Partial Molar Quantities for Alkanolamines ($C_1^o - C_1^*$) and Water ($C_2^o - C_2^*$)

T/K	AEEA + H ₂ O		AP + H ₂ O		MAE + H ₂ O		MIPA + H ₂ O		DMEA + H ₂ O	
	$C_1^o - C_1^*$	$C_2^o - C_2^*$	$C_1^o - C_1^*$	$C_2^o - C_2^*$	$C_1^o - C_1^*$	$C_2^o - C_2^*$	$C_1^o - C_1^*$	$C_2^o - C_2^*$	$C_1^o - C_1^*$	$C_2^o - C_2^*$
303.15	64	-13	87	28	162	-8	110	-1	273	57
308.15	104	-11	124	38	187	0	143	13	271	73
313.15	122	-7	137	46	196	5	159	23	277	83
318.15	1412	-8	157	53	208	95	174	29	286	89
323.15	166	-6	178	59	223	17	186	42	300	88
328.15	199	3	219	71	249	29	214	47	315	93
333.15	241	7	260	75	278	46	247	39	335	97
338.15	295	9	315	81	316	51	282	41	374	108
343.15	359	16	383	95	371	83	328	38	436	119
348.15	439	20	469	101	443	120	407	30	518	100
353.15	546	36	583	112	524	127	484	34	626	44

Table 8. Molar Excess Heat Capacity (C_p^E) for AEEA (1) + Water (2) Mixtures from (303.15 to 353.15) K

T/K	x_1									
	0.0999	0.1999	0.2995	0.4000	0.5002	0.5997	0.7011	0.8003	0.8979	
	$C_p^E/\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$									
303.15	4	5	5	4	4	3	3	2	0	
308.15	6	8	7	7	6	5	4	3	1	
313.15	8	9	9	8	7	6	5	4	1	
318.15	9	11	11	10	9	7	6	5	1	
323.15	11	13	13	12	10	8	7	5	2	
328.15	13	16	16	14	12	10	8	6	2	
333.15	15	19	19	16	14	12	9	7	3	
338.15	19	23	22	19	17	14	11	8	3	
343.15	22	27	26	22	20	17	13	10	4	
348.15	27	32	30	26	23	20	15	11	4	
353.15	33	38	36	30	27	23	18	13	5	

compared with the literature values. As shown in Table 1, the molar heat capacities of MEA and MDEA measured in the C80 calorimeter are in excellent agreement with those measured in a differential scanning calorimeter (DSC) by Chiu et al.⁸ and Chen et al.⁹ The percentage average absolute deviation of the measured molar heat capacity values of MEA and MDEA was found to be 0.23 %.

Results and Discussion

The experimental molar heat capacities of aqueous 2-((2-aminoethyl)amino)ethanol (AEEA), 3-amino-1-propanol (AP), 2-(methylamino)ethanol (MAE), 1-amino-2-propanol (MIPA), and *N,N*-dimethylethanolamine (DMEA) solutions at (303.15, 308.15, 313.15, 318.15, 323.15, 328.15, 333.15, 338.15, 343.15, 348.15, and 353.15) K for the entire range of mole fractions

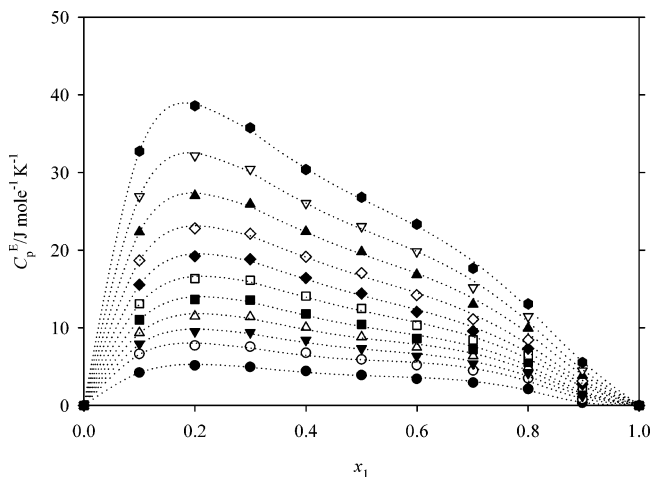


Figure 1. Molar excess heat capacity of aqueous AEEA solutions: ●, 303.15 K; ○, 308.15 K; ▼, 313.15 K; △, 318.15 K; ■, 323.15 K; □, 328.15 K; ◆, 333.15 K; ◇, 338.15 K; ▲, 343.15 K; ▽, 348.15 K; ●, 353.15 K; ⋯, Redlich–Kister.

Table 9. Redlich–Kister Equation Fitting Coefficients for the Molar Excess Heat Capacity (C_p^E) (Equation 4), for AEEA (1) + Water (2) Mixtures from (303.15 to 353.15) K

T/K	a_0	a_1	a_2	a_3	a_4	$\sigma/J \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$
303.15	15.4	-5.61	25.7	-33.0	-15.6	0.15
308.15	23.5	-7.51	36.5	-50.3	-13.6	0.31
313.15	29.1	-13.0	42.6	-51.6	-14.1	0.31
318.15	34.7	-17.5	52.7	-57.3	-20.5	0.34
323.15	40.7	-24.0	61.0	-62.1	-22.2	0.38
328.15	48.7	-31.3	66.0	-66.8	-13.1	0.36
333.15	56.7	-37.8	73.9	-79.1	-6.5	0.38
338.15	66.7	-44.1	82.9	-98.9	3.1	0.45
343.15	78.0	-50.9	97.4	-120	12.1	0.47
348.15	91.0	-59.0	115	-151	24.1	0.52
353.15	106	-70.7	131	-185	54.2	0.68

are listed in Tables 2 to 6, respectively. The extrapolated excess partial molar quantities for alkanolamines ($C_1^o - C_1^*$) and water ($C_2^o - C_2^*$) are listed in Table 7.

2-((2-Aminoethyl)amino)ethanol (AEEA). As shown in Table 2, the molar heat capacity increases with increasing temperature. The molar heat capacity increases with increasing mole fractions of AEEA. The molar heat capacities of pure AEEA are represented as a linear function of the temperature in the range from (303.15 to 353.15) K by

$$C_{p,\text{AEEA}}/J \cdot \text{mol}^{-1} \cdot \text{K}^{-1} = 0.31T(\text{K}) + 187 \quad (2)$$

In eq 2, $C_{p,\text{AEEA}}$ represents the molar heat capacity of pure AEEA. The average absolute deviation for eq 2 is found to be 0.0018. The maximum value of $C_{p,\text{AEEA}}$ is found at 353.15 K.

Table 10. Molar Excess Heat Capacity (C_p^E) for AP (1) + Water (2) Mixtures from (303.15 to 353.15) K

T/K	x_1								
	0.0999	0.2001	0.3003	0.4015	0.4996	0.6006	0.7003	0.8003	0.8966
	$C_p^E/J \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$								
303.15	5	7	6	4	3	2	2	2	1
308.15	7	9	8	6	5	4	3	3	2
313.15	8	10	9	7	7	5	4	3	2
318.15	9	11	10	9	8	6	5	4	3
323.15	10	13	12	11	9	8	6	5	3
328.15	12	15	14	13	12	10	7	6	4
333.15	14	17	16	15	13	11	9	7	4
338.15	17	19	19	17	16	14	10	8	5
343.15	20	22	21	20	18	17	12	9	6
348.15	24	26	25	23	22	19	14	11	7
353.15	29	31	29	27	25	23	17	12	8

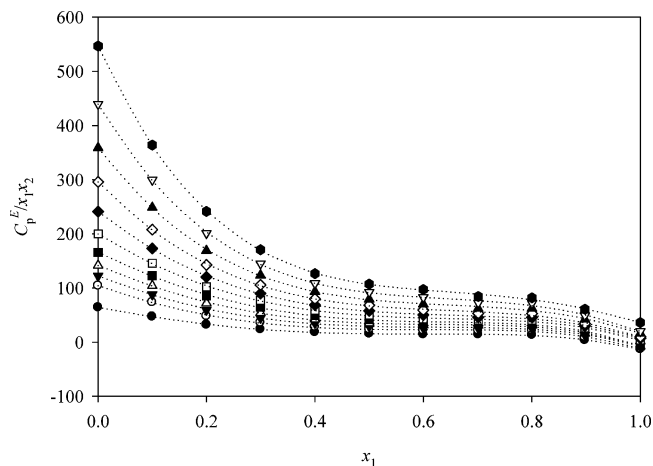


Figure 2. Reduced molar excess heat capacity (C_p^E/x_1x_2) of aqueous AEEA solutions: ●, 303.15 K; ○, 308.15 K; ▼, 313.15 K; △, 318.15 K; ◆, 323.15 K; ◇, 328.15 K; ▲, 333.15 K; ◇, 338.15 K; ▲, 343.15 K; ▽, 348.15 K; ●, 353.15 K; ⋯, Redlich–Kister.

The molar excess heat capacities (C_p^E) are calculated from the experimental molar heat capacity values by

$$C_p^E/J \cdot \text{mol}^{-1} \cdot \text{K}^{-1} = C_p - (x_1 C_{p,1} + x_2 C_{p,2}) \quad (3)$$

where C_p is the molar heat capacity of the solution, $C_{p,1}$ and $C_{p,2}$ are the molar heat capacities of pure alkanolamine and water, respectively, and x_1 and x_2 are the mole fractions of the alkanolamine and water, respectively. The molar heat capacity ($C_{p,2}$) values of water are taken from Osborne et al.¹⁰ The calculated values of the molar excess heat capacity of the AEEA (1) + water (2) system are listed in Table 8. Figure 1 shows the concentration dependency of the molar excess heat capacities at various temperatures. At all temperatures, the molar excess heat capacity curves are positive with a maximum at around $x_1 = 0.3$. The C_p^E value increases with increasing temperature for the entire range of mole fractions of AEEA. Figure 1 shows the sharp changes in molar excess heat capacity values in the water-rich region.

A Redlich–Kister relation is employed to correlate the molar excess heat capacity values:

$$C_p^E/J \cdot \text{mol}^{-1} \cdot \text{K}^{-1} = x_1 x_2 \sum_{i=0}^n a_i (x_1 - x_2)^i \quad (4)$$

The coefficients and the standard deviations for the AEEA (1) + water (2) system are presented in Table 9. All the fitting polynomials are examined by the F-test (Shoemaker et al.¹¹ and Harris¹²). Figure 2 shows the concentration dependency of the

Table 11. Redlich–Kister Equation Fitting Coefficients for the Molar Excess Heat Capacity (C_p^E) (Equation 4), for AP (1) + Water (2) Mixtures from (303.15 to 353.15) K

T/K	a_0	A_1	a_2	a_3	a_4	a_5	$\sigma/\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$
303.15	12.9	-22.2	35.7	-7.19	9.26	--	0.19
308.15	20.4	-24.7	35.8	-18.4	25.2	--	0.14
313.15	25.6	-27.3	34.5	-18.6	31.7	--	0.16
318.15	31.6	-29.2	32.8	-22.7	40.7	--	0.18
323.15	37.6	-31.0	31.0	-29.5	50.6	--	0.24
328.15	46.5	-33.1	23.5	-32.9	75.2	-7.57	0.17
333.15	54.2	-35.5	20.7	-39.3	93.1	-17.8	0.18
338.15	63.8	-38.6	20.1	-49.7	114	-28.4	0.20
343.15	75.1	-40.1	15.8	-66.7	148	-37.0	0.26
348.15	87.7	-45.3	12.2	-84.2	185	-54.1	0.32
353.15	103	-50.4	8.2	-108	237	-77.4	0.44

Table 12. Comparison of C_p Values for Pure MAE

Maham et al. ²		this study	
T/K	$C_p/\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$	T/K	$C_p/\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$
299.1	191.6	299.11	193
322.8	198.1	322.80	200
348.5	209.4	348.50	210

reduced molar excess heat capacity (C_p^E/x_1x_2) function of the AEEA + water system at various temperatures. The reduced molar excess heat capacity function gives a better picture of the origin of nonideality in the mixtures.¹³ Because of the limitations of the calorimeter, the heat capacity of mole fractions below 0.1 are difficult to measure accurately for this system. Figure 1 shows the sharp change in the reduced molar heat capacity function in the water-rich region. The trend is similar for all other remaining alkanolamine + water systems. The partial molar excess quantities for alkanolamines ($C_1^o - C_1^*$) and water ($C_2^o - C_2^*$) are calculated by extrapolating C_p^E/x_1x_2 at $x_1 = 0$ and $x_1 = 1$, respectively, and are listed in Table 7. The Table shows that the value of $C_1^o - C_1^*$ increases with temperatures for all the studied alkanolamines. Table 7 also shows that the value of $C_2^o - C_2^*$ increases with temperatures for AEEA, AP, and MAE, but for the remaining two systems MIPA and DMEA, their values decrease at higher temperatures.

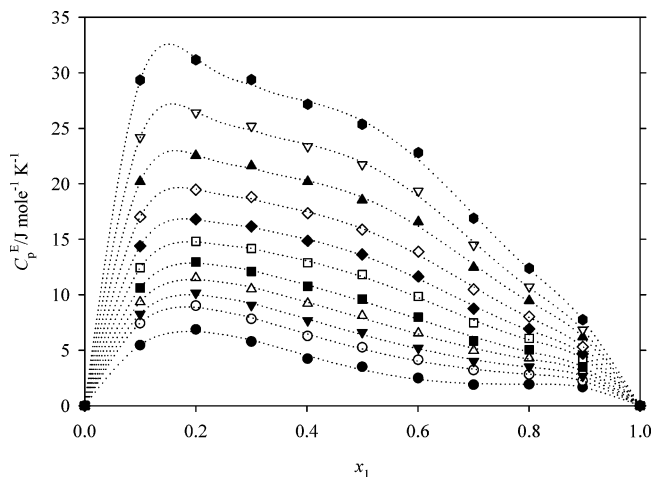
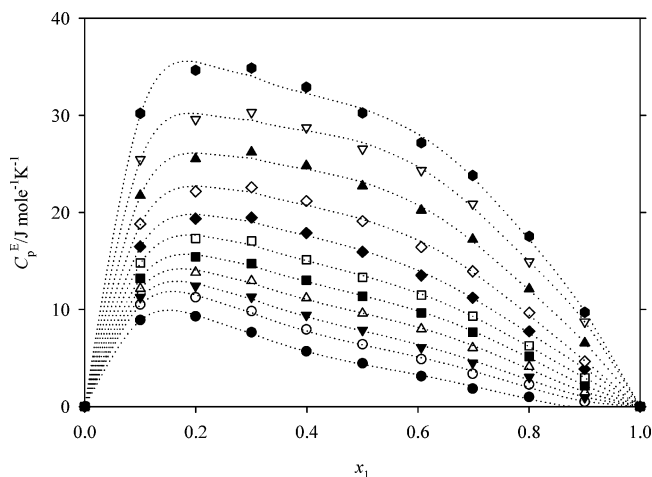
3-Amino-1-propanol (AP). As shown in Table 3, the molar heat capacity increases with increasing temperature for the entire range of mole fractions of AP as well as for pure AP. The molar heat capacity values of pure AP are represented as a linear function of temperature in the range from (303.15 to 353.15) K by

$$C_{p,AP}/\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1} = 0.23T(\text{K}) + 134 \quad (5)$$

In eq 5, $C_{p,AP}$ represents the molar heat capacity of pure AP. The average absolute deviation (AAD) for eq 5 is 0.0026. The molar excess heat capacity (C_p^E) values are calculated from the

Table 13. Molar Excess Heat Capacity (C_p^E) for MAE (1) + Water (2) Mixtures from (303.15 to 353.15) K

T/K	x_1									
	0.1000	0.1998	0.3003	0.3990	0.5002	0.6061	0.6987	0.8003	0.9004	
					$C_p^E/\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$					
303.15	9	9	7	6	4	3	2	1	-0.2	
308.15	10	11	10	8	6	5	3	2	0.5	
313.15	11	12	11	9	8	6	4	3	1	
318.15	12	14	13	11	9	8	6	4	1	
323.15	13	15	145	13	11	9	8	5	2	
328.15	15	17	17	15	13	11	9	6	3	
333.15	16	19	19	18	16	13	11	8	4	
338.15	19	22	23	21	19	16	14	9	4	
343.15	22	25	26	25	23	20	17	12	6	
348.15	25	30	30	29	26	24	21	15	9	
353.15	30	35	35	33	30	27	24	17	10	

**Figure 3. Molar excess heat capacity of aqueous AP solutions: ●, 303.15 K; ○, 308.15 K; ▼, 313.15 K; △, 318.15 K; ■, 323.15 K; □, 328.15 K; ◆, 333.15 K; ◇, 338.15 K; ▲, 343.15 K; ▽, 348.15 K; ●, 353.15 K; ⋯, Redlich–Kister.****Figure 4. Molar excess heat capacity of aqueous MAE solutions: ●, 303.15 K; ○, 308.15 K; ▼, 313.15 K; △, 318.15 K; ■, 323.15 K; □, 328.15 K; ◆, 333.15 K; ◇, 338.15 K; ▲, 343.15 K; ▽, 348.15 K; ●, 353.15 K; ⋯, Redlich–Kister.**

measured molar heat capacity values using eq 3 and correlated as a function of the mole fractions using the Redlich–Kister eq 4. The molar excess heat capacity values and the coefficients with the standard deviations for the AP (1) + water (2) system are presented in Table 10 and Table 11, respectively. Figure 3 shows the concentration dependency of the molar excess heat capacities at various temperatures. At all temperatures, the molar excess heat capacity curves are positive with a maximum at

Table 14. Redlich–Kister Equation Fitting Coefficients for the Molar Excess Heat Capacity (C_p^E) (Equation 4), for MAE (1) + Water (2) Mixtures from (303.15 to 353.15) K

T/K	a_0	a_1	a_2	a_3	a_4	$\sigma/J\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$
303.15	17.4	-22.5	29.4	-62.7	30.3	0.16
308.15	25.4	-25.0	33.5	-68.5	34.7	0.23
313.15	31.2	-27.1	34.7	-68.4	35.1	0.23
318.15	38.5	-27.0	36.7	-72.8	33.5	0.21
323.15	45.7	-28.5	40.0	-74.8	34.3	0.16
328.15	54.0	-31.6	40.9	-78.2	44.3	0.24
333.15	64.4	-34.1	37.2	-82.1	60.4	0.32
338.15	77.2	-33.5	41.2	-99.4	65.2	0.44
343.15	92.5	-33.9	40.0	-110	94.9	0.45
348.15	109	-33.5	43.2	-128	130	0.53
353.15	123	-37.0	68.9	-162	133	0.66

around $x_1 = 0.2$. These C_p^E values increase with increasing temperature for the entire range of mole fractions.

2-(Methylamino)ethanol (MAE). As shown in Table 4, the molar heat capacities increase with increasing temperature and increasing mole fractions. The molar heat capacities of pure MAE are represented as a linear function of temperature in the range from (303.15 to 353.15) K by

$$C_{p,\text{MAE}}/J\cdot\text{mol}^{-1}\cdot\text{K}^{-1} = 0.31T(\text{K}) + 102 \quad (6)$$

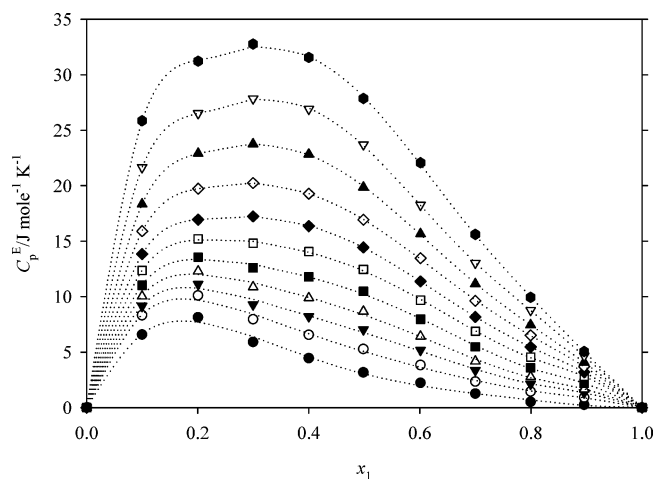
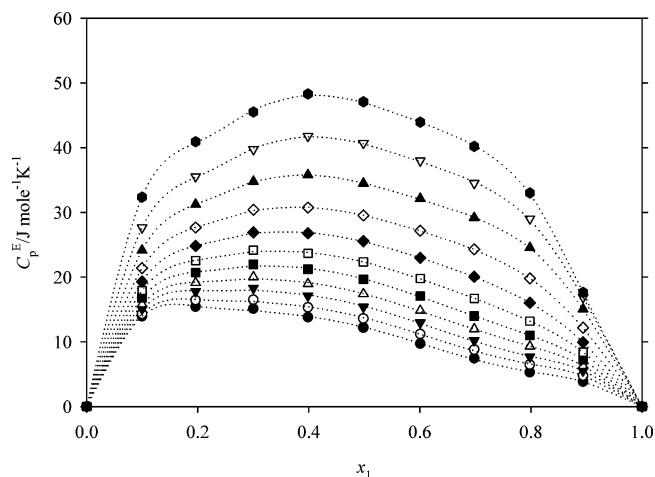
In eq 6, $C_{p,\text{MAE}}$ represents the molar heat capacity of pure MAE. The average absolute deviation (AAD) for eq 6 is 0.0030. Maham et al.² have measured the molar heat capacities of pure MAE (99 % pure) at (299.1, 322.8, 348.5, 373.2, and 397.8) K. The C_p values measured in the present study at (299.11, 322.80, and 348.50) K are compared with the values measured by Maham et al.² in Table 12 and are found to be in good agreement (within 0.6 %).

The molar excess heat capacity (C_p^E) values are calculated from the experimental molar heat capacity values using eq 3 and correlated as a function of the mole fractions employing the Redlich–Kister eq 4. The molar excess heat capacity values, the coefficients, and the standard deviations for MAE (1) + water (2) are presented in Table 13 and Table 14, respectively. Figure 4 shows the concentration dependency of the molar excess heat capacities at various temperatures. At all temperatures, the molar excess heat capacity curves are positive except for 303.15 K at $x_1 = 0.9$, where it becomes a little bit negative. The maximum values of the molar excess heat capacity occur at $x_1 = 0.1$ for 303.15 K and at $x_1 = 0.3$ for 353.15 K. The C_p^E values increase with increasing temperature.

1-Amino-2-propanol (MIPA). As shown in Table 5, the molar heat capacities increase with increasing temperature. Also, the molar heat capacity increases with mole fractions. The molar heat capacity values of pure MIPA are represented as a linear function of temperature in the range from (303.15 to 353.15) K

Table 15. Molar Excess Heat Capacity (C_p^E) for MIPA (1) + Water (2) Mixtures from (303.15 to 353.15) K

T/K	x_1									
	0.1000	0.2007	0.2996	0.4001	0.4983	0.6013	0.6999	0.7996	0.8959	
	$C_p^E/J\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$									
303.15	6	8	6	4	3	2	1	0.5	0.2	
308.15	8	10	8	6	5	4	2	1	1	
313.15	9	11	9	8	7	5	3	2	1	
318.15	10	12	11	10	8	6	4	3	2	
323.15	11	13	13	12	10	8	5	3	2	
328.15	12	15	15	14	12	10	7	4	3	
333.15	14	17	17	16	14	11	8	5	3	
338.15	16	20	20	1	17	13	9	6	4	
343.15	18	23	24	23	20	16	11	7	4	
348.15	22	26	28	27	24	18	13	9	5	
353.15	26	31	33	32	28	22	16	10	5	

**Figure 5.** Molar excess heat capacity of aqueous MIPA solutions: ●, 303.15 K; ○, 308.15 K; ▼, 313.15 K; △, 318.15 K; ■, 323.15 K; □, 328.15 K; ◆, 333.15 K; ◇, 338.15 K; ▲, 343.15 K; ▽, 348.15 K; ●, 353.15 K; ⋯, Redlich–Kister.**Figure 6.** Molar excess heat capacity of aqueous DMEA solutions: ●, 303.15 K; ○, 308.15 K; ▼, 313.15 K; △, 318.15 K; ■, 323.15 K; □, 328.15 K; ◆, 333.15 K; ◇, 338.15 K; ▲, 343.15 K; ▽, 348.15 K; ●, 353.15 K; ⋯, Redlich–Kister.

by

$$C_{p,\text{MIPA}}/J\cdot\text{mol}^{-1}\cdot\text{K}^{-1} = 0.39T(\text{K}) + 90.4 \quad (7)$$

In eq 7, $C_{p,\text{MIPA}}$ represents the molar heat capacity of pure MIPA. The average absolute deviation (AAD) for eq 7 is 0.0027. The molar excess heat capacity (C_p^E) values are calculated from the measured molar heat capacity values using eq 3 and correlated as a function of the mole fractions employing the Redlich–

Table 16. Redlich–Kister Equation Fitting Coefficients for the Molar Excess Heat Capacity (C_p^E) (Equation 4), for MIPA (1) + Water (2) Mixtures from (303.15 to 353.15) K

T/K	a_0	a_1	a_2	a_3	a_4	a_5	$\sigma/\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$
303.15	12.1	-25.8	37.4	-29.8	4.65		0.31
308.15	20.2	-30.1	31.6	-34.8	26.6		0.30
313.15	26.9	-31.7	21.6	-36.4	43.1		0.29
318.15	33.3	-35.3	16.3	-36.7	52.0		0.25
323.15	40.8	-35.8	10.4	-48.8	63.2	12.6	0.21
328.15	49.2	-42.6	6.7	-32.0	74.5	-9.0	0.11
333.15	57.5	-51.5	5.5	-7.1	80.5	-45.5	0.01
338.15	67.6	-60.9	8.8	-1.3	85.0	-57.7	0.06
343.15	79.6	-75.1	7.5	15.6	96.1	-85.5	0.07
348.15	94.2	-92.3	-1.1	52.4	126	-148	0.06
353.15	112	-101	-8.3	25.9	156	-150	0.17

Table 17. Comparison of C_p Values for Pure DMEA

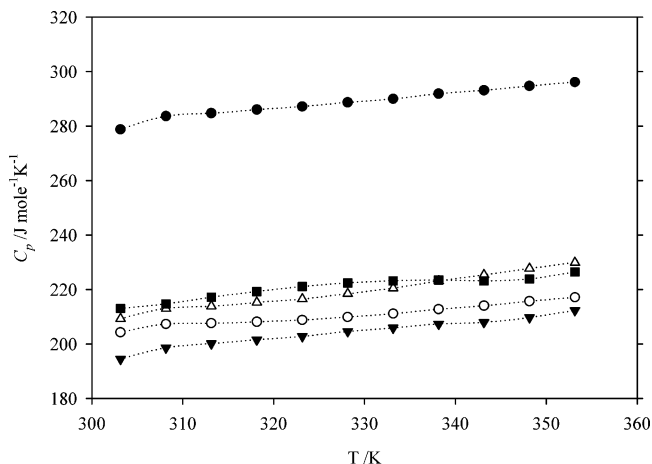
Maham et al. ²		this study	
T/K	$C_p/\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$	T/K	$C_p/\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$
299.1	205.1	299.11	204
322.8	218.0	322.80	220
348.5	228.8	348.50	225

Kister eq 4. The molar excess heat capacity values and the coefficients plus the standard deviations for MIPA (1) + water (2) are presented in Table 15 and Table 16, respectively. Figure 5 shows the concentration dependency of the molar excess heat capacities at various temperatures. The molar excess heat capacity curves are positive with a maximum at around $x_1 = 0.1$ for 303.15 K and at $x_1 = 0.3$ for 353.15 K. These C_p^E values increase with increasing temperature. Figure 5 shows sharp changes in the molar excess heat capacities in the water-rich region.

N,N-Dimethylethanolamine (DMEA). As shown in Table 6, the molar heat capacity values increase with increasing temperature and mole fractions. The molar heat capacity values of pure DMEA are represented as a function of temperature in the range from (303.15 to 353.15) K by

$$C_{p,\text{DMEA}}/\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1} = 627 - 0.745T(\text{K}) - 17261814/T^2(\text{K}) \quad (8)$$

In eq 8, $C_{p,\text{DMEA}}$ represents the molar heat capacity of pure DMEA. The average absolute deviation (AAD) for eq 8 is 0.0025. Maham et al.² have measured the molar heat capacity of pure DMEA (99 % pure) at (299.1, 322.8, 348.5, 373.2, and 397.8) K. The C_p values measured in this study at (299.11, 322.80, and 348.50) K are compared with the values measured by Maham et al.² in Table 17. Values measured in this study are in good agreement with those measured by Maham et al.² (within 1 %). The molar excess heat capacity (C_p^E) values are calculated from the measured molar heat capacity values using

**Figure 7. Comparison of C_p values for the five alkanolamines: ●, AEEA; ○, AP; ▼, MAE; △, MIPA; ■, DMEA.**

eq 3 and correlated as a function of the mole fractions employing the Redlich–Kister eq 4. The molar excess heat capacity values and coefficients with the standard deviations for DMEA (1) + water (2) are presented in Table 18 and Table 19, respectively. Figure 6 shows the concentration dependency of the molar excess heat capacities at various temperatures. The maximum values of the molar excess heat capacity vary between $x_1 = 0.2$ at 303.15 K and $x_1 = 0.4$ at 353.15 K.

Comparison of the C_p Values of Alkanolamines. As shown in Figure 7, among the five studied alkanolamines, the aqueous AEEA solution has the highest values of molar heat capacity. Maham et al.² have studied the molar heat capacities of 14 pure alkanolamines and concluded that the values of the molar heat capacity of alkanolamines are dominated by $-\text{CH}_2$ and $-\text{OH}$ group contributions, and these contributions increase with increasing temperature. They also concluded that the $-\text{NH}$ group has exhibited its contribution on the molar heat capacity in terms of largest temperature dependency, whereas the contribution of the $-\text{N}$ group is almost zero. In this study, AEEA has the highest molar heat capacity because of the higher number of $-\text{CH}_2$ groups present in the AEEA molecule and also because of the contributions of the $-\text{NH}$ and $-\text{NH}_2$ groups. If we compare the values of the molar heat capacity of MAE and DMEA, we find that the additional methyl group present in DMEA contributes toward a higher value of the molar heat capacity for DMEA. This is also confirmed by comparing the molar heat capacities of two primary alkanolamines AP and MIPA. MIPA has higher values of the molar heat capacities compared to AP because of the presence of one methyl ($-\text{CH}_3$) group in the MIPA molecule. Figure 7 shows that, at 338 K and higher, the molar heat capacity MIPA becomes very near to and then exceeds the values of DMEA. The shape of the

Table 18. Molar Excess Heat Capacity (C_p^E , $\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$), for DMEA (1) + Water (2) Mixtures from (303.15 to 353.15) K

T/K	x_1								
	0.0997	0.1962	0.3003	0.3984	0.4983	0.6008	0.6980	0.7981	0.8938
	$C_p^E/\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$								
303.15	14	15	15	14	12	10	7	5	4
308.15	14	16	16	15	14	11	9	6	5
313.15	15	18	18	17	15	13	10	8	6
318.15	16	19	20	19	17	15	12	9	6
323.15	17	21	22	21	20	17	14	11	7
328.15	18	22	24	24	22	20	17	13	8
333.15	19	25	27	27	26	23	20	16	10
338.15	21	28	30	31	29	27	24	20	12
343.15	24	31	35	36	34	32	29	24	15
348.15	28	35	40	42	41	38	34	29	17
353.15	32	41	45	48	47	44	40	33	18

Table 19. Redlich–Kister Equation Fitting Coefficients for the Molar Excess Heat Capacity (C_p^E) (Equation 4), for DMEA (1) + Water (2) Mixtures from (303.15 to 353.15) K

T/K	a_0	A_1	a_2	a_3	a_4	a_5	$\sigma/\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$
303.15	48.9	-42.7	5.4	-8.1	111	-57.2	0.16
308.15	54.8	-43.5	9.6	-6.6	108	-49.0	0.17
313.15	62.1	-45.0	12.8	-6.8	106	-45.2	0.18
318.15	69.7	-45.9	20.7	4.9	93.9	-61.4	0.17
323.15	78.8	-45.8	24.2	8.4	91.4	-68.8	0.14
328.15	89.2	-42.6	33.9	6.8	81.2	-74.9	0.13
333.15	102	-41.0	48.6	18.2	65.6	-96.5	0.08
338.15	118	-39.2	62.9	39.0	60.3	-133	0.06
343.15	138	-42.2	78.9	89.7	61.1	-206	0.07
348.15	162	-44.4	86.0	129	60.4	-294	0.17
353.15	188	-48.7	101	160	46.8	-402	0.23

excess and reduced molar excess heat capacity plots suggest that, in the water-rich region, the alkanolamine molecules associate in water. The shape of the plots also reflect the difference in size between water and the alkanolamines.¹³

Conclusions

The molar heat capacities of the aqueous AEEA, AP, MAE, MIPA, and DMEA solutions were measured over a range of temperatures from (303.15 to 353.15) K. The molar excess heat capacity (C_p^E) values for the aqueous AEEA, AP, MIPA, and DMEA solutions were positive at all temperatures and mole fractions. Only at 303.15 K and for $x_1 = 0.9$, an aqueous MAE solution exhibited a negative value of the molar excess heat capacity. The molar excess heat capacities are correlated as a function of the mole fractions employing the Redlich–Kister equation. The values of $C_1^o - C_1^*$ increase with the temperature for all the studied alkanolamines, and the values of $C_2^o - C_2^*$ increase with temperature for AEEA, AP, and MAE. However, for the remaining two systems MIPA and DMEA, the values decrease with an increase in temperature.

Among the five alkanolamines studied, AEEA had the highest values of the molar heat capacity and MAE had the lowest values. This study confirms the observations made by Maham et al.² that the values of molar heat capacity of alkanolamines

are dominated by $-\text{CH}_2$ and $-\text{OH}$ group contributions, and these contributions increase with increasing temperature.

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