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Heat Capacity of Aqueous Mixtures of Monoethanolamine with 2-Amino-2-methyl-l-propanol

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Heat capacities of aqueous mixtures of monoethanolamine with 2-amino-2-methyl-l-propanol were measured from 30 °C to 80 °C with a differential scanning calorimeter (DSC). The heat capacities of 2-amino-2-methyl-l-propanol, 2-amino-2-methyl-l-propanol + water, and monoethanolamine + 2-amino-2-methyl-l-propanol were also studied. Eight binary systems and sixteen ternary systems were studied. The estimated uncertainty of the measured heat capacities is ±2%. An excess molar heat capacity expression using the Redlich−Kister equation for the composition dependence is used to represent the measured C_p of aqueous alkanolamine solutions. The results (AAD %, the average absolute percentage deviation) for the calculation of the excess molar heat capacities are 3.6% and 13.2% for the binary and ternary systems, respectively. The heat capacities of aqueous mixtures of monoethanolamine with 2-amino-2-methyl-l-propanol presented in this study are, in general, of sufficient accuracy for most engineering-design calculations.

Introduction

Aqueous alkanolamine solutions have been extensively studied during the last 20 years because of their industrial importance for the natural gas, petroleum chemical plant, and ammonia industries for removal of CO_2 and H_2S from gas streams. Alkanolamines such as monoethanolamine (MEA), diglycolamine (DGA), diethanolamine (DEA), diisopropanolamine (DIPA), triethanolamine (TEA), and *N*-methyldiethanolamine (MDEA), 2-amino-2-methyl-l-propanol (AMP), and 2-piperidineethanol (2-PE) can be used as an absorbent for the acid gas removal processes.[1]

Heat capacity data for alkanolamine solutions are required for the design of the heat exchanger equipment used in gas-treating processes. The heat capacities of pure alkanolamines have been reported in the literature.[2−6] Some heat capacities of aqueous alkanolamine solutions are also available in the literature: MEA + H_2O;[7] DEA + H_2O;[7] DGA + H_2O;[8] and MDEA + H_2O.[9] Chiu and Li[10] have reported the heat capacities of eight aqueous alkanolamine solutions (MEA, DGA, DEA, DIPA, TEA, MDEA, AMP, 2-PE) at temperatures ranging from 30 °C to 80 °C. At 25 °C, heat capacities of CO_2-loaded, aqueous solutions of MEA, DEA, MDEA, aqueous MDEA + MEA, and MDEA + DEA were also studied.[11] The heat capacity of aqueous mixtures of MEA + AMP has not yet appeared in the literature. It is the purpose of this study to determine experimentally the heat capacities of MEA + AMP + H_2O by using a differential scanning calorimeter (DSC). An excess molar heat capacity expression, using the Redlich−Kister equation for the concentration dependence, will be applied to represent the measured C_p data.

Experimental Section

MEA is Riedel−de Haën reagent grade with the minimum purity 99% (water max. 0.5%), and AMP is Acros Organics reagent grade with the minimum purity 99%. The water is liquid chromatography grade from Alps Chemical Co.

Table 1. Heat Capacities of AMP

t/°C	C_P/(J·mol^{-1}·K^{-1})	t/°C	C_P/(J·mol^{-1}·K^{-1})
30	241	60	257
35	244	65	259
40	246	70	262
45	249	75	264
50	252	80	267
55	254		

The differential scanning calorimeter used for this study consists of a DSC-2010 and a thermal analysis controller from TA Instruments. The DSC operating range is from room temperature to 725 °C. The DSC operates with a temperature repeatability of ±0.1 °C. The purge gas is nitrogen with a flow rate of 40 mL·min^{-1}. The calorimetric sensitivity is 1 μW (rms). The calorimetric precision is ±1%, on the basis of measurements of metal samples. By using the sample-encapsulating press, the liquid sample was prepared within a hermetic sample pan. The internal volume of the hermetic pan is approximately 10 mm^3. The sample mass is in the range 15 to 20 mg. The accuracy of the C_p measurements is estimated to be ±2% on the basis of the measurement of the C_p of liquid water.[6] The apparatus and the experimental procedure are the same as those described by Chiu et al.[6]

Results and Discussion

The values of C_p of AMP have been measured for temperatures from 30 °C to 80 °C and are presented in Table 1. In Figure 1, comparisons between our measurement and the literature values[5,6] are shown. Probably due to higher AMP purity (with 99%), while only 95% AMP purity for Chiu et al.,[6] the values of C_p obtained in this study are slightly higher that those of Chiu et al.[6] As shown in Figure 1, an excellent agreement between our measure-

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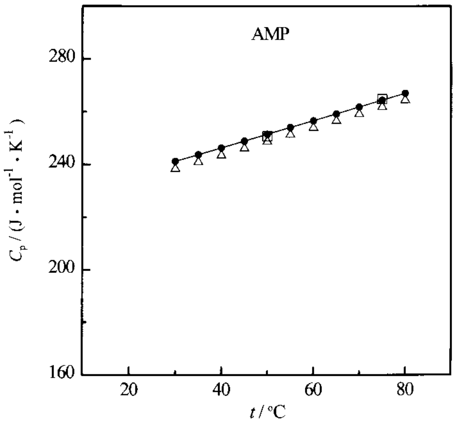

Figure 1. Molar heat capacity of AMP: ●, this study; □, Maham et al.;[5] △, Chiu et al.;[6] line, calculated using eq 1.

Table 2. Heat Capacities (J·mol^{-1}·K^{-1}) of AMP (1) + H$_2$O (2)

	$x_1 = 0.20$		$x_1 = 0.40$		$x_1 = 0.60$		$x_1 = 0.80$	
t/°C	C_p	C_p^E	C_p	C_p^E	C_p	C_p^E	C_p	C_p^E
30	112	3.1	146	4.4	179	4.3	210	2.3
35	112	3.4	148	5.2	182	5.1	213	2.7
40	113	3.7	150	5.9	184	5.9	215	3.2
45	114	4.1	151	6.6	186	6.6	218	3.7
50	115	4.4	153	7.4	188	7.4	220	4.1
55	116	4.7	155	8.1	191	8.1	223	4.6
60	117	5.0	157	8.8	193	8.9	226	5.1
65	118	5.3	158	9.5	195	9.6	228	5.5
70	118	5.6	160	10.	198	10.	231	6.0
75	119	5.9	162	11.	200	11.	233	6.4
80	120	6.2	164	12.	202	12	236	6.9

Table 3. Heat Capacities (J·mol^{-1}·K^{-1}) of MEA (1) + AMP (2)

	$x_1 = 0.20$		$x_1 = 0.40$		$x_1 = 0.60$		$x_1 = 0.80$	
t/°C	C_p	C_p^E	C_p	C_p^E	C_p	C_p^E	C_p	C_p^E
30	226	−0.3	211	−0.4	197	−0.3	182	−0.2
35	228	−0.4	213	−0.6	198	−0.5	183	−0.3
40	231	−0.5	215	−0.8	200	−0.7	185	−0.4
45	233	−0.6	217	−1.0	202	−0.8	187	−0.5
50	235	−0.8	219	−1.1	203	−1.1	188	−0.6
55	237	−0.9	221	−1.3	205	−1.2	190	−0.7
60	240	−1.0	223	−1.5	207	−1.5	191	−0.8
65	242	−1.2	225	−1.7	209	−1.7	193	−0.9
70	244	−1.3	227	−1.8	210	−1.8	195	−1.0
75	246	−1.4	229	−2.0	212	−2.1	196	−1.2
80	248	−1.6	231	−2.2	214	−2.3	198	−1.3

ments and those of Maham et al.[5] is shown. The obtained values of C_p of AMP are expressed as a function of temperature as

$$C_p/(\mathrm{J{\cdot}mol^{-1}{\cdot}K^{-1}}) = 85.68 + 0.513(T/\mathrm{K}) \qquad (1)$$

The solid line in Figure 1 is calculated from eq 1.

The values of C_p for the binary systems AMP (1) + H$_2$O (2) and MEA (1) + AMP (2) were also measured for temperatures from 30 °C to 80 °C and are presented in Tables 2 and 3.

An excess molar heat capacity C_p^E for a mixture defined by Lide and Kehiaian[12] is as follows

$$C_p^E = C_p - \sum_i x_i C_{p,i} \qquad (2)$$

where $C_{p,i}$ is the molar heat capacity of the pure component i. In this study, the molar heat capacities of water, MEA, and AMP are from Osborne et al.,[13] Chiu et al.,[10] and eq 1 of this study, respectively. The obtained excess molar heat capacities, C_p^E, from eq 2 are also presented in Tables 2 and 3. The values of C_p^E for AMP (1) + H$_2$O (2) appear to be all positive values for temperatures 30 to 80 °C, as shown in Figure 2. The values of C_p^E for AMP (1) + H$_2$O (2) increase as the temperature increases at a constant x_1. As shown in Figure 3, values of C_p^E for MEA (1) + AMP (2) appear to be all negative values for the entire concentration range, and the more negative values are observed at higher temperatures for a constant x_1.

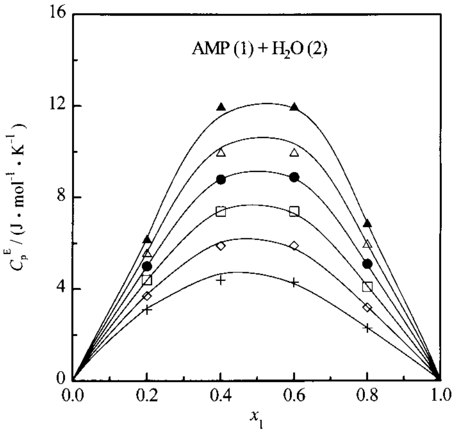

Figure 2. Excess molar heat capacity of AMP (1) + H$_2$O (2): ▲, 80 °C; △, 70 °C; ●, 60 °C; □, 50 °C; ◇, 40 °C; +, 30 °C; lines, calculated using eq 3.

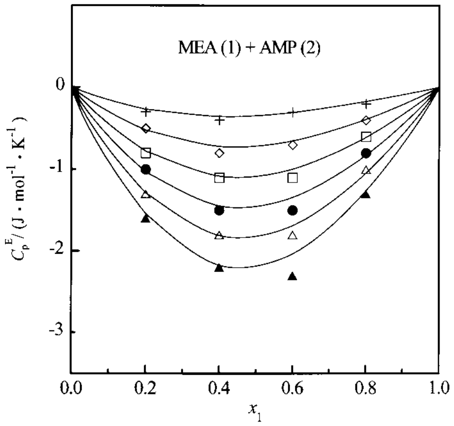

Figure 3. Excess molar heat capacity of MEA (1) + AMP (2): ▲, 80 °C; △, 70 °C; ●, 60 °C; □, 50 °C; ◇, 40 °C; +, 30 °C; lines, calculated using eq 3.

A Redlich−Kister equation was applied to represent the compositional dependence of the excess molar heat capacity for a binary mixture as follows,

$$C_{p,12}^E/(\mathrm{J{\cdot}mol^{-1}{\cdot}K^{-1}}) = x_1 x_2 \sum_{i=1}^{n} A_i (x_1 - x_2)^{i-1} \qquad (3)$$

The temperature dependence of A_i is assumed to follow the relation

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

The number of terms (A_i), in eq 3, which should be used to represent the excess molar heat capacity depends on the degree of complexity of the binary systems. Plotting the values of $C_p^E/(x_i x_i)$ versus x_1 for three binary systems for temperatures 30 to 80 °C, it was found that the straight lines were observed for MEA (1) + AMP (2) while curves were observed for both MEA (1) + H$_2$O (2) and AMP (1) +

Table 4. Parameters of Excess Molar Heat Capacity for Binary and Ternary Systems

binary system	i	parameters $a_{i,0}$	 $a_{i,1}$	no. of data points	AAD %[b] C_p^E	 C_p
MEA (1) + H_2O (2)[a]	1	−146.65	0.4898			
	2	22.60	−0.0790			
	3	10.876	−0.0532	44	4.6	0.2
AMP (1) + H_2O (2)	1	−170.32	0.6236			
	2	−52.19	0.1575			
	3	119.23	−0.4081	44	1.2	0.2
MEA (1) + AMP (2)	1	43.50	−0.148			
	2	−5.19	0.0188	44	5.1	0.1
			Overall	132	3.6	0.2

ternary system	i	$b_{i,0}$	$b_{i,1}$			
MEA (1) + AMP (2) + H_2O (3)	1	31.94	−0.3788			
	2	6.058	−0.1932			
	3	−730.5	2.713	176	13.2	0.2

[a] Data of Chiu and Li.[10] [b] AAD %: average absolute percentage deviation.

H_2O (2). Thus, only two terms are required in eq 3 for MEA (1) + AMP (2); however, the three terms have to be used for both MEA (1) + H_2O (2) and AMP (1) + H_2O (2). The determined parameters $a_{i,0}$ and $a_{i,1}$ from the values of $C_{p,12}^E$ for the MEA (1) + H_2O (2), AMP (1) + H_2O (2), and MEA (1) + AMP (2) systems are presented in Table 4. The data of C_p for MEA (1) + H_2O (2) were taken from Chiu and Li.[10] The results (AAD %, average absolute percentage deviation) of the calculations for the excess molar heat capacity are 4.6%, 1.2%, and 5.1% for MEA (1) + H_2O (2), AMP (1) + H_2O (2), and MEA (1) + AMP (2), respectively. The comparisons between the calculated $C_{p,12}^E$ values from eq 3 and the $C_{p,12}^E$ data are also shown in Figures 2 and 3.

The values of C_p of MEA (1) + AMP (2) + H_2O (3) were also measured for temperatures ranging from 30 to 80 °C and for x_3 from 0.2 to 0.8. The results are presented in Tables 5−8. The values of C_p^E derived from eq 2 for MEA (1) + AMP (2) + H_2O (3) are also presented in Tables 5−8.

For a ternary system, the compositional dependence of the excess molar heat capacity is assumed as the following empirical relation

$$C_p^E/(\mathrm{J\cdot mol^{-1}\cdot K^{-1}}) = C_{p,12}^E + C_{p,13}^E + C_{p,23}^E + x_1x_2x_3\sum_{i=1}^{n} B_i(x_1 - x_3)^{i-1} \qquad (5)$$

The temperature dependence of B_i is assumed to be as

Table 5. Heat Capacities ($J\cdot mol^{-1}\cdot K^{-1}$) of MEA (1) + AMP (2) + H_2O (3) for x_3 = 0.80

	x_1/x_2 = 0.04/0.16		x_1/x_2 = 0.08/0.12		x_1/x_2 = 0.12/0.08		x_1/x_2 = 0.16/0.04	
t/°C	C_p	C_p^E	C_p	C_p^E	C_p	C_p^E	C_p	C_p^E
30	109	3.3	105	2.5	101	1.7	97.1	0.5
35	110	3.5	106	2.7	102	2.0	97.9	0.9
40	110	3.8	106	3.0	103	2.3	98.6	1.4
45	111	4.0	107	3.2	103	2.7	99.4	1.8
50	112	4.2	108	3.5	104	3.0	100	2.2
55	112	4.4	108	3.7	105	3.3	101	2.6
60	113	4.6	109	3.9	106	3.6	102	3.0
65	114	4.9	110	4.1	106	3.9	103	3.5
70	115	5.0	110	4.3	107	4.2	103	3.9
75	115	5.3	111	4.5	108	4.5	104	4.3
80	116	5.4	112	4.7	108	4.8	105	4.7

Table 6. Heat Capacities ($J\cdot mol^{-1}\cdot K^{-1}$) of MEA (1) + AMP (2) + H_2O (3) for x_3 = 0.60

	x_1/x_2 = 0.08/0.32		x_1/x_2 = 0.16/0.24		x_1/x_2 = 0.24/0.16		x_1/x_2 = 0.32/0.08	
t/°C	C_p	C_p^E	C_p	C_p^E	C_p	C_p^E	C_p	C_p^E
30	139	2.9	131	1.6	125	0.9	118	0.4
35	140	3.6	133	2.2	126	1.5	120	1.0
40	142	4.3	134	2.9	128	2.1	121	1.6
45	144	5.0	136	3.6	129	2.7	122	2.2
50	145	5.7	138	4.3	130	3.3	124	2.8
55	147	6.3	139	4.9	132	3.9	125	3.4
60	148	7.0	141	5.6	133	4.5	126	4.0
65	150	7.6	142	6.2	134	5.0	127	4.6
70	152	8.3	144	6.9	136	5.6	129	5.2
75	153	8.9	145	7.5	137	6.2	130	5.8
80	155	9.6	147	8.2	138	6.7	131	6.4

Table 7. Heat Capacities ($J\cdot mol^{-1}\cdot K^{-1}$) of MEA (1) + AMP (2) + H_2O (3) for x_3 = 0.40

	x_1/x_2 = 0.12/0.48		x_1/x_2 = 0.24/0.36		x_1/x_2 = 0.36/0.24		x_1/x_2 = 0.48/0.12	
t/°C	C_p	C_p^E	C_p	C_p^E	C_p	C_p^E	C_p	C_p^E
30	168	1.9	157	0.18	148	−0.7	138	−1.0
35	170	2.6	159	0.75	149	−0.1	140	−0.5
40	172	3.2	161	1.3	151	0.5	141	0.1
45	174	3.9	163	1.9	153	1.0	143	0.6
50	176	4.5	165	2.5	154	1.5	145	1.1
55	178	5.2	167	3.1	156	2.1	146	1.7
60	180	5.8	168	3.6	158	2.6	148	2.2
65	182	6.4	170	4.2	159	3.1	149	2.7
70	184	7.1	172	4.8	161	3.7	151	3.2
75	187	7.7	174	5.4	163	4.2	152	3.7
80	189	8.4	176	5.9	165	4.7	154	4.2

Table 8. Heat Capacities (J·mol^{-1}·K^{-1}) of MEA (1) + AMP (2) + H_2O (3) for x_3 = 0.20

	x_1/x_2 = 0.16/0.64		x_1/x_2 = 0.32/0.48		x_1/x_2 = 0.48/0.32		x_1/x_2 = 0.64/0.16	
t/°C	C_p	C_p^E	C_p	C_p^E	C_p	C_p^E	C_p	C_p^E
30	197	0.3	183	−1.3	171	−1.7	160	−1.1
35	199	0.7	185	−1.0	173	−1.4	161	−0.9
40	201	1.0	187	−0.7	174	−1.1	163	−0.6
45	203	1.4	189	−0.4	176	−0.8	164	−0.4
50	205	1.7	191	−0.1	178	−0.6	166	−0.1
55	208	2.1	193	0.2	180	−0.3	168	0.1
60	210	2.4	195	0.5	182	−0.0	169	0.3
65	212	2.7	197	0.8	184	0.3	171	0.6
70	214	3.1	199	1.1	185	0.5	172	0.8
75	217	3.4	201	1.4	187	0.8	174	1.0
80	219	3.8	203	1.7	189	1.0	176	1.3

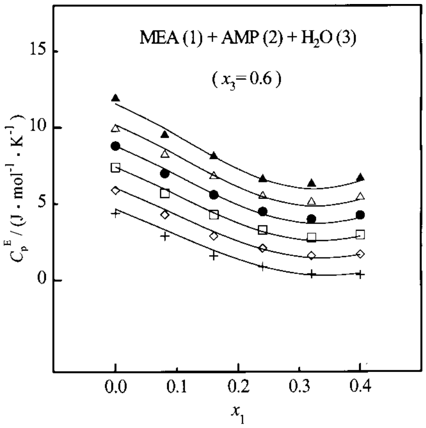

Figure 4. Excess molar heat capacity of MEA (1) + AMP (2) + H_2O (3) as a function of x_1 at x_3 = 0.6: ▲, 80 °C; △, 70 °C; ●, 60 °C; □, 50 °C; ◇, 40 °C; +, 30 °C; lines, calculated using eq 5.

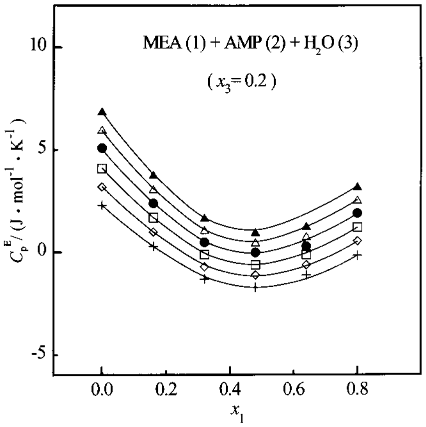

Figure 5. Excess molar heat capacity of MEA (1) + AMP (2) + H_2O (3) as a function of x_1 at x_3 = 0.2: ▲, 80 °C; △, 70 °C; ●, 60 °C; □, 50 °C; ◇, 40 °C; +, 30 °C; lines, calculated using eq 5.

follows

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

For a binary system, any x_i equals zero, eq 5 reduces to eq 3. The three terms B_1, B_2, and B_3 are found to be required for accurately representing the excess molar heat capacities of MEA (1) + AMP (2) + H_2O (3). The parameters $b_{i,j}$ determined from C_p^E values of MEA (1) + AMP (2) + H_2O (3) are also presented in Table 4. Using eq 5 and the parameters in Table 4, the results for C_p^E calculation (AAD %) for a total of 176 data points of MEA (1) + AMP (2) + H_2O (3) for C_p^E and C_p are 13.2% and 0.2%, respectively. Some higher values of deviations in calculation of C_p^E may be due to the smaller values of C_p^E, that is, around 0.1.

Plots of C_p^E for MEA (1) + AMP (2) + H_2O (3) for x_3 = 0.6 and 0.2 for temperatures from 30 °C to 80 °C are shown in Figures 4 and 5, respectively. The solid lines in Figures 4 and 5 are calculated values from eq 5. As shown in Figure 4, the value of C_p^E for MEA (1) + AMP (2) + H_2O (3) increases as the temperature increases at a constant x_1; the value of C_p^E decreases as x_1 increases up to x_1 = 0.32 and then increases as x_1 increases for temperatures beyond 40 °C. As shown in Figure 5 for x_3 = 0.2, the value of C_p^E for MEA (1) + AMP (2) + H_2O (3) decreases as x_1 increases up to x_1 = 0.5 and then increases as x_1 increases for a constant temperature.

The isotherms for C_p^E with a constant value of 4.0 (J·mol^{-1}·K^{-1}) for the MEA (1) + AMP (2) + H_2O (3) system were calculated from eq 5 and are shown in Figure 6. As shown in Figure 6, the calculated (predicted) isotherms distribute systematically along the paths of the various concentrations; the lowest isotherm appears in the region with a small concentration of MEA.

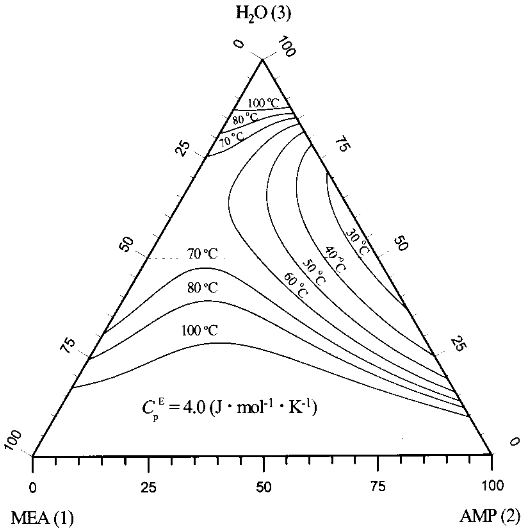

Figure 6. Excess molar heat capacity of MEA + AMP + H_2O at constant C_p^E = 4.0 (J·mol^{-1}·K^{-1}) for temperatures from 30 to 100 °C: lines are calculated using eq 5.

Conclusions

Heat capacities of aqueous mixtures of MEA with AMP were measured from 30 °C to 80 °C with a differential scanning calorimeter. The heat capacities of AMP, AMP (1) + H_2O (2), and MEA (1) + AMP (2) were also studied. An excess molar heat capacity expression using the Redlich–Kister equation for the composition dependence is used to represent the measured C_p of aqueous alkanolamine solutions. The overall average absolute percentage deviations for the calculations of the excess molar heat capacities are 3.6% and 13.2% for the binary and ternary systems, respectively. The heat capacities of aqueous mixtures of monoethanolamine with 2-amino-2-methyl-l-propanol presented in this study are, in general, of sufficient accuracy for most engineering-design calculations.

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