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Viscosities and Excess Properties of Aqueous Solutions of Mono- and Diethylethanolamines at Temperatures between 298.15 and 353.15 K

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Viscosities of aqueous solutions of monoethylethanolamine and diethylethanolamine have been measured at temperatures from 298.15 to 353.15 K over the entire range of concentrations. The excess activation energies for viscous flow and the excess entropies for viscous flow have been calculated for these aqueous solutions in this temperature range. The viscosities, excess activation energies for viscous flow, and the excess entropies for viscous flow of these solutions have been compared with our earlier values for aqueous solutions of monoethanolamine.

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1. Introduction

The physical properties such as density and viscosity of pure alkanolamines and their mixtures with water are needed by industries for the design of processes for the removal of sour gases from natural gas and petroleum streams.[1−2] The physical properties of pure alkanolamines such as density and viscosity,[3] thermal conductivity,[4] and heat capacity[5] have been studied. The excess properties (V^E, H^E) of the binary aqueous solutions of monoethanolamine (MEA), monomethylethanolamine (MMEA), and dimethylethanolamine (DMEA) have been studied by Touhara et al.[6] The excess volumes of aqueous solutions of monoethanolamine (MEA), diethanolamine (DEA), and triethanolamine (TEA);[7] and of methyldiethanolamine (MDEA) and ethyldiethanolamine (EDEA);[8] of dimethylethanolamine (DMEA) and diethylethanolamine (DEEA);[9] of monomethylethanolamine (MMEA) and dimethylethanolamine (DMEA);[10] and of monoethylethanolamine (MEEA) and diethylethanolamine (DEEA)[11] have been reported.

The excess enthalpies of the binary aqueous solutions of diethanolamine, triethanolamine and methyldiethanolamine have been studied,[12] as well as those of monoethylethanolamine, diethylethanolamine, *n*-propylethanolamine (*n*-PEA), and 2-amino-2-methyl-1-propanol (AMP)[13] and of monoethanolamine, diethanolamine, methyldiethanolamine, ethyldiethanolamine, and *n*-butyldiethanolamine (*n*-BDEA).[14] The transport properties of aqueous solutions of diethanolamine and methyldiethanolamine[15] have been also studied.

In this work, the viscosity of the binary mixtures (monoethylethanolamine + water) and (diethylethanolamine + water) was measured at temperatures from 298.15 to 353.15 K.

2. Experimental Section

Table 1. Viscosities (η/mPa·s) of Monoethylethanolamine(2) + Water(1) Mixtures from 298.15 to 353.15 K

x_2	298.15 K	303.15 K	313.15 K	333.15 K	353.15 K
0.0000	0.890	0.801	0.658	0.475	0.366
0.0100	1.089	0.970	0.785	0.551	0.419
0.0217	1.366	1.198	0.949	0.643	0.469
0.0333	1.692	1.469	1.133	0.747	0.529
0.0467	2.146	1.836	1.384	0.878	0.605
0.0622	2.759	2.315	1.706	1.026	0.695
0.0772	3.465	2.815	2.049	1.188	0.790
0.1167	5.735	4.525	3.075	1.652	1.032
0.1656	9.455	7.046	4.573	2.233	1.343
0.2308	14.59	10.71	6.551	3.024	1.711
0.3169	19.66	14.66	8.805	3.983	2.089
0.3893	21.80	16.85	10.24	4.515	2.331
0.4490	22.25	17.79	10.90	4.801	2.416
0.5356	22.31	17.99	11.21	4.944	2.473
0.6845	21.05	16.24	10.16	4.568	2.350
0.8213	17.45	13.21	8.401	4.002	2.139
0.9202	13.96	11.00	7.227	3.599	1.985
0.9560	12.96	10.26	6.823	3.458	1.921
1.0000	12.00	9.528	6.396	3.290	1.848

Monoethylethanolamine [$(C_2H_5)NHC_2H_4OH$, MEEA] was obtained from Aldrich Chemical Co. with a purity of 99%, and diethylethanolamine [$(C_2H_5)_2NC_2H_4OH$, DEEA] was obtained from Fluka Chemical Company with a purity of >99%. These compounds were used as received after their water contents had been checked. The water was triply distilled water. All of the solutions were prepared by mass.

Kinematic viscosities were measured using Ubbelohde-type viscometers (Schott Geräte type 24 501 capillary viscometers) of various sizes with an automatic reading timer.[15,16] The accuracy of the flow time measurement was ±0.01 s. The temperature of the water bath was controlled to within ±0.05 °C. The details of measurements are given in our earlier work.[15,16] The densities of these solutions have been reported earlier.[10] The estimated relative uncertainty in the absolute viscosity is ±0.1%.

3. Results and Discussion

The viscosities of the binary mixtures (MEEA + water) and (DEEA + water) are given in Tables 1 and 2, respectively, from 298.15 to 353.15 K. The viscosity of the (MEEA + water), (DEEA + water), and (MEA + water)[16] mixtures at 298.15 K are shown in Figure 1. The viscosity

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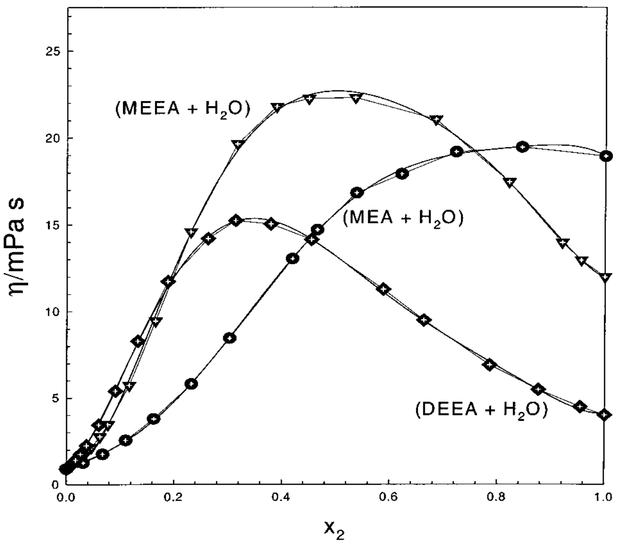

Figure 1. Viscosity of aqueous solutions of MEA, MEEA, and DEEA at 298.15 K.

Table 2. Viscosities (η/mPa·s) of Diethylethanolamine (2) + Water (1) Mixtures from 298.15 to 353.15 K

x_{DEEA}	298.15 K	303.15 K	313.15 K	333.15 K	353.15 K
0.0000	0.890	0.801	0.658	0.475	0.366
0.0039	0.991	0.885	0.723	0.512	0.387
0.0080	1.104	0.980	0.791	0.551	0.412
0.0121	1.233	1.085	0.866	0.591	0.439
0.0169	1.400	1.219	0.958	0.643	0.466
0.0261	1.7520	1.495	1.149	0.760	0.527
0.0372	2.242	1.887	1.412	0.896	0.605
0.0602	3.439	2.820	2.016	1.166	0.800
0.0909	5.404	4.364	2.912	1.658	1.010
0.1326	8.287	6.361	4.179	2.067	1.233
0.1883	11.72	8.984	5.497	2.547	1.450
0.2629	14.21	10.81	6.627	2.919	1.607
0.3136	15.25	11.52	7.004	3.019	1.614
0.3789	15.04	11.36	7.054	3.026	1.608
0.4547	14.14	10.78	6.685	2.894	1.555
0.5883	11.28	8.745	5.516	2.510	1.394
0.6638	9.491	7.615	4.668	2.266	1.294
0.7580	6.903	5.577	3.694	1.822	1.152
0.8765	5.478	4.459	3.059	1.673	1.036
0.9544	4.484	3.650	2.639	1.510	0.970
1.0000	4.022	3.308	2.414	1.435	0.925

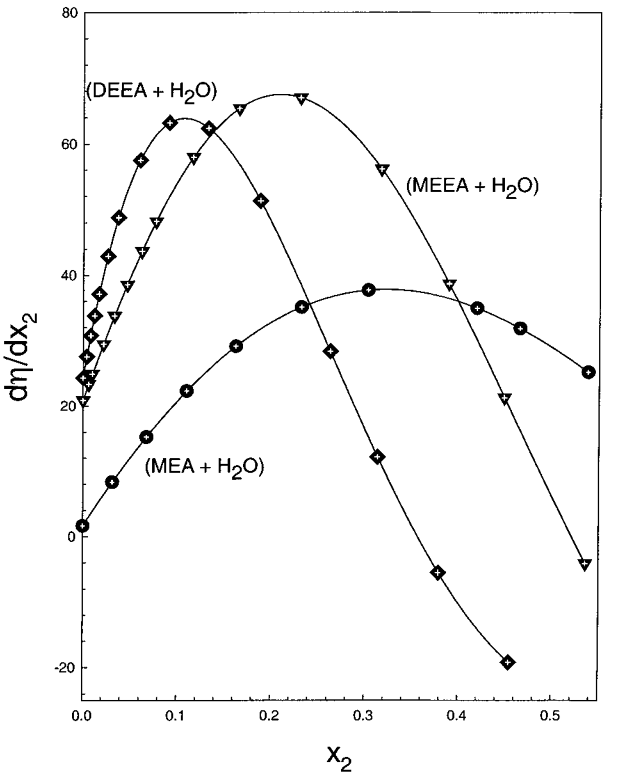

Figure 2. Variations of the composition derivative of the viscosity for aqueous solutions of MEA, MEEA, and DEEA at 298.15 K.

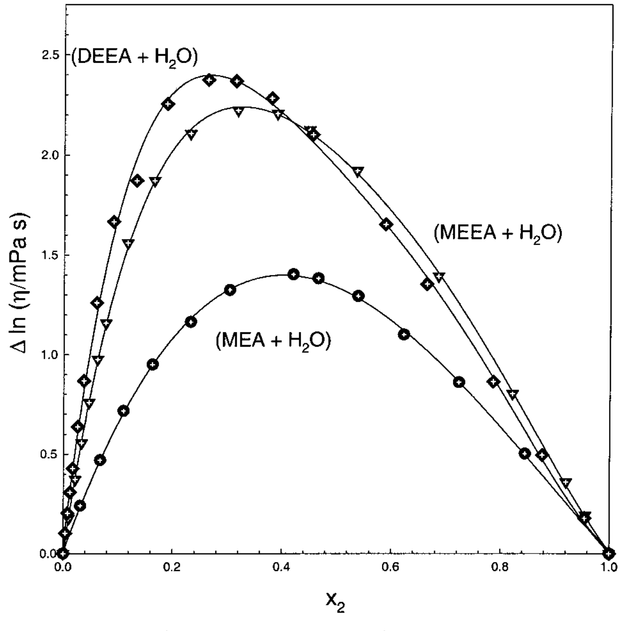

Figure 3. Δ ln η for aqueous solutions of MEA, MEEA, and DEEA at 298.15.

values for (MEEA + water) and (DEEA + water) show a maximum at $x_{MEEA} = 0.54$ and at $x_{DEEA} = 0.34$, whereas there is no clear maximum for (MEA + water) mixtures. The structural differences among these three ethanolamines are the presence of one or two ethyl groups on the nitrogen atom. This is comparable with the excess molar volumes[7,10,11] and excess molar enthalpies[6,13] of these mixtures, where the position of minimum moves to higher water concentration with increasing size of the alkyl group attached to the nitrogen atom. The viscosities of the pure compounds are in the following order: $\eta_{MEA} > \eta_{MMEA} > \eta_{DEEA}$. Another way to show this effect is in Figure 2where ($\partial\eta/\partial x_2$) is plotted against the mole fraction of ethanolamine. We have shown the region $0.00 < x_2 < 0.55$. This plot shows that the viscosity change with addition of ethanolamine increases to a composition of $x_{MEA} \approx 0.30$, $x_{MEEA} = 0.20$, and $x_{DEEA} = 0.10$. This shows that the presence of one or two ethyl groups on the nitrogen atom of ethanolamine has a major effect on the viscosity change of these solutions. One can think about two factors in this case: one is the packing of water and ethanolamine molecules, which changes with the size of the ethanolamine molecules, and the other is the breakdown of the hydrogen bonds due to the presence of large ethyl groups on the nitrogen atom. Figure 2 presents the combination of these factors.

The viscosity deviations of these binary mixtures were calculated with the logarithmic additivity rule

$$\Delta\ln\eta = \ln(\eta_{12}) - (x_1 \ln \eta_1 + x_2 \ln \eta_2) \qquad (1)$$

where η_{12} is the viscosity of the mixture and η_1 and η_2 are the viscosities of water and the ethanolamine, respectively. The viscosity deviations of the (MEEA + H_2O), (DEEA + H_2O), and (MEA + H_2O)[16] mixtures at 298.15 K are shown

Table 3. Excess Activation Energies for Viscous Flow ($\Delta_a G^{*E}$/kJ·mol^{-1}) of Monoethylethanolamine (2) + Water (1) Mixtures from 298.15 to 353.15 K

x_2	298.15 K	303.15 K	313.15 K	333.15 K	353.15 K
0.0000	0.00	0.00	0.00	0.00	0.00
0.0100	0.49	0.48	0.46	0.43	0.38
0.0217	1.04	1.00	0.95	0.86	0.77
0.0333	1.55	1.50	1.40	1.28	1.15
0.0467	2.11	2.04	1.91	1.73	1.55
0.0622	2.70	2.59	2.43	2.15	1.96
0.0772	3.22	3.04	2.87	2.54	2.34
0.1167	4.33	4.12	3.83	3.36	3.09
0.1656	5.37	5.05	4.69	4.08	3.77
0.2308	6.14	5.80	5.36	4.70	4.30
0.3169	6.39	6.13	5.69	5.04	4.56
0.3893	6.20	6.05	5.67	5.05	4.52
0.4490	5.85	5.80	5.47	4.88	4.35
0.5356	5.25	5.23	4.97	4.44	3.94
0.6845	3.98	3.88	3.66	3.23	2.88
0.8213	2.42	2.29	2.13	1.89	1.70
0.9202	1.05	1.02	0.96	0.86	0.79
0.9560	0.57	0.55	0.52	0.48	0.43
1.0000	0.00	0.00	0.00	0.00	0.00

Table 4. Excess Activation Energies for Viscous Flow ($\Delta_a G^{*E}$/kJ·mol^{-1}) of Diethylethanolamine (2) + Water (1) Mixtures from 298.15 to 353.15 K

x_2	298.15 K	303.15 K	313.15 K	333.15 K	353.15 K
0.0000	0.00	0.00	0.00	0.00	0.00
0.0039	0.29	0.27	0.27	0.24	0.20
0.0080	0.57	0.55	0.53	0.47	0.42
0.0121	0.87	0.83	0.79	0.69	0.63
0.0169	1.20	1.15	1.07	0.96	0.85
0.0261	1.80	1.70	1.59	1.48	1.27
0.0372	2.44	2.33	2.18	1.99	1.75
0.0602	3.56	3.40	3.18	2.82	2.59
0.0909	4.73	4.56	4.21	3.89	3.45
0.1326	5.80	5.57	5.19	4.57	4.27
0.2883	6.61	6.37	5.88	5.15	4.83
0.2629	6.93	6.69	6.24	5.44	5.00
0.3136	6.95	6.70	6.25	5.41	4.89
0.3789	6.68	6.44	6.05	5.23	4.62
0.4547	6.21	6.01	5.62	4.83	4.22
0.5883	5.00	4.84	4.50	3.85	3.38
0.6638	4.16	4.10	3.68	3.19	2.86
0.7580	2.67	2.62	2.40	1.92	1.88
0.8765	1.55	1.52	1.37	1.17	1.10
0.9544	0.56	0.54	0.50	0.42	0.41
1.0000	0.00	0.00	0.00	0.00	0.00

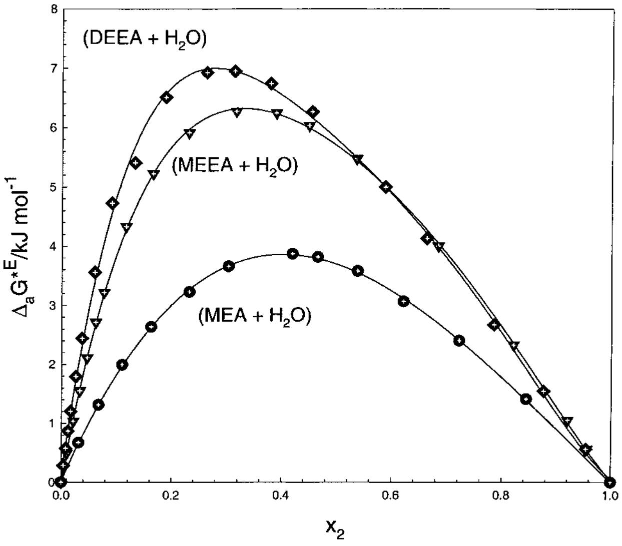

Figure 4. Excess activation energies for viscous flow for aqueous solutions of MEA, MEEA, and DEEA at 298.15 K.

in Figure 3. There is a large difference between the values for the solutions of MEA (without an ethyl group) and those for the solutions of MEEA and DEEA. Here again, the addition of a larger alkyl group makes the plot more symmetric, as shown in Figure 1.

Table 5. Least-Squares Redlich−Kister Coefficients, A_n, for Δ ln η/mPa·s and $\Delta_a G^{*E}$/kJ·mol^{-1}

T (K)	Y^E	A_0	A_1	A_2	A_3	A_4	A_5	s
				MEEA + H$_2$O				
298.15 K	Δ ln η	7.7438	5.5162	4.7512	7.6452	2.9700	−1.9292	0.015
	$\Delta_a G^{*E}$	23.274	15.934	12.598	18.487	8.3447	−3.2526	0.032
303.15 K	Δ ln η	7.2863	5.1245	4.7592	6.8174	2.2109	−1.3677	0.012
	$\Delta_a G^{*E}$	22.527	15.201	12.873	16.871	6.5517	−2.0310	0.026
313.15 K	Δ ln η	6.4460	5.3433	3.1295	2.7479	3.3488	1.7347	0.015
	$\Delta_a G^{*E}$	21.117	16.242	9.1189	7.2084	9.6809	5.6415	0.011
333.15 K	Δ ln η	4.8422	3.8694	2.5564	4.7444	3.1329	−0.6138	0.015
	$\Delta_a G^{*E}$	18.084	13.198	8.3153	13.607	9.5639	−0.8839	0.042
353.15 K	Δ ln η	3.6530	3.0421	3.9914	4.8991	0.6484	−1.8145	0.004
	$\Delta_a G^{*E}$	15.751	11.660	13.074	14.764	2.8743	−4.3223	0.008
				DEEA + H$_2$O				
298.15 K	Δ ln η	7.7438	5.5162	4.7512	7.6452	2.9700	−1.9292	0.015
	$\Delta_a G^{*E}$	23.274	15.934	12.598	18.487	8.3447	−3.2526	0.032
303.15 K	Δ ln η	7.2863	5.1245	4.7592	6.8174	2.2109	−1.3677	0.012
	$\Delta_a G^{*E}$	22.527	15.201	12.873	16.871	6.5517	−2.0310	0.026
313.15 K	Δ ln η	6.4460	5.3433	3.1295	2.7479	3.3488	1.7347	0.015
	$\Delta_a G^{*E}$	21.117	16.242	9.1189	7.2084	9.6809	5.6415	0.011
333.15 K	Δ ln η	4.8422	3.8694	2.5564	4.7444	3.1329	−0.6138	0.015
	$\Delta_a G^{*E}$	18.084	13.198	8.3153	13.607	9.5639	−0.8839	0.042
353.15 K	Δ ln η	3.6530	3.0421	3.9914	4.8991	0.6484	−1.8145	0.004
	$\Delta_a G^{*E}$	15.751	11.660	13.074	14.764	2.8743	−4.3223	0.008

Table 6. Excess Entropies of Activation for Viscous Flow (ΔS^{*E}/J·mol^{-1}·K^{-1}) of Monoethylethanolamine + Water (1) and Diethylethanolamine (2) + Water (1) Mixtures in the Temperature Range from 298.15 to 353.15 K

x_{MEEA}	ΔS^{*E}	x_{DEEA}	ΔS^{*E}
0.0000	0.0	0.0000	0.0
0.0100	1.9	0.0080	2.7
0.0217	4.8	0.0121	4.3
0.0333	7.1	0.0169	6.2
0.0467	10.0	0.0261	8.9
0.0622	13.4	0.0372	12.0
0.0772	15.6	0.0602	17.4
0.1167	22.3	0.0909	22.4
0.1656	28.5	0.1326	28.0
0.2308	32.8	0.2629	35.6
0.3169	33.0	0.2883	36.6
0.4490	28.2	0.3136	37.9
0.5356	24.7	0.3789	37.7
0.6845	20.3	0.4547	36.6
0.8213	12.7	0.5883	29.9
0.9202	4.8	0.6638	24.6
0.9560	2.4	0.7858	15.9
1.0000	0.0	0.8765	8.7
		0.9544	2.9
		1.0000	0.0

The excess activation energies for viscous flow were obtained by using the equation[16−18]

$$\Delta_a G^{*E} = RT\{\ln(\eta_{12}V/hN_A) - [x_1 \ln(\eta_1 V_1/hN_A) + x_2 \ln(\eta_2 V_2/hN_A)]\} \quad (2)$$

where R is the gas constant; T is the absolute temperature; h is Planck's constant; N_A is Avogadro's number; and η_1, η_2 and V_1, V_2 are the viscosities and molar volumes of pure water and pure ethanolamine, respectively. The molar volumes of the mixtures were calculated by $V = (x_1M_1 + x_2M_2)/d_{12}$, and the molar volumes of the pure compounds were obtained from $V = M/d$. M is the molar mass and d is the density of the pure compounds, and d_{12} is the density of the mixture. The excess volumes of aqueous solutions of MEEA and DEEA were given earlier.[11] The excess energies of activation for viscous flow at different temperatures for (MEEA + water) and (DEEA + water) mixtures are given in Tables 3 and 4, respectively. The excess activation energies for viscous flow for (MEA + water),[16] (MEEA + water), and (DEEA + water) mixtures at 298.15 K are shown in Figure 4. The values for MEEA solutions are practically twice as large as the values for MEA, and the

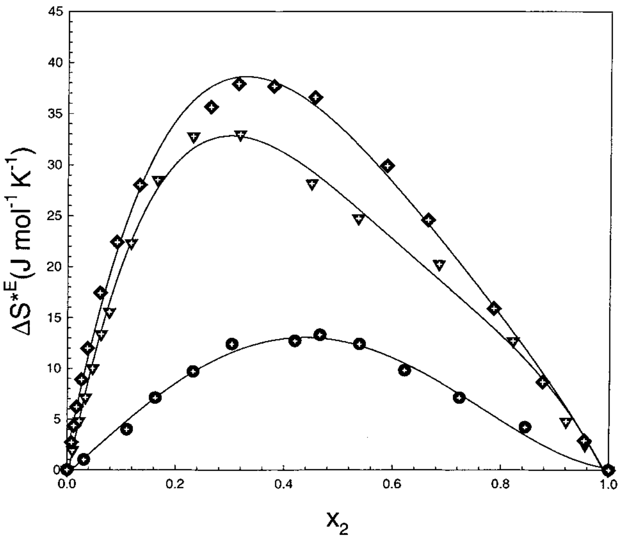

Figure 5. Excess entropies for viscous flow for aqueous solutions of MEA, MEEA, and DEEA in the temperature range of 298.15–353.15 K

values for DEEA solutions are slightly higher than those for MEEA solutions. The excess volumes[11] and excess enthalpies[13] of these mixtures were studied earlier.

The viscosity deviation values and the excess activation energies for viscous flow were fitted to the Redlich–Kister equation

$$Y^{\mathrm{E}} = x_2(1 - x_2)\sum A_n(1 - 2x_2)^n \tag{3}$$

where Y^{E} represents the viscosity deviation and excess activation energy for viscous flow, x_2 is the mole fraction of the ethanolamine, and A_n represents the coefficients of the fitting polynomials. The fitting coefficients and the standard deviation values are given in Table 5 for aqueous solutions of MEEA and DEEA at temperatures from 298.15 to 353.15 K.

The excess entropy of activation for viscous flow is calculated by[16,17]

$$\Delta S^{*\mathrm{E}} = -\left[\frac{\partial(\Delta_{\mathrm{a}}G^{*\mathrm{E}})}{\partial T}\right] \tag{4}$$

The plot of the $\Delta_{\mathrm{a}}G^{*\mathrm{E}}$ versus temperature was linear in the temperature range of 298.15–353.15 K for the ethanolamines studied. The slope is equal to $-\Delta S^{*\mathrm{E}}$. The entropy values for (MEEA + water), (DEEA + water), and (MEA + water)[16] are given in Table 6. A comparison among these (ethanolamine + water) mixtures is shown in Figure 5.

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