

Density, Speed of Sound, Isentropic Compressibility, and Excess Volume of (Monoethanolamine + 2-Amino-2-methyl-1-propanol), (Monoethanolamine + Triethanolamine), and (Monoethanolamine + *N*-Methyldiethanolamine) at Temperatures from (293.15 to 323.15) K

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Density and speed of sound of (monoethanolamine + 2-amino-2-methyl-1-propanol), (monoethanolamine + triethanolamine), and (monoethanolamine + *N*-methyldiethanolamine) were measured over the entire composition range and at temperatures from (293.15 to 323.15) K. The experimental values were used to calculate the isentropic compressibilities, excess molar volumes, and isentropic compressibility deviations. Redlich–Kister-type polynomial equations were used to fit the excess molar volumes and isentropic compressibility deviations.

Introduction

Natural, synthesis, and refinery gas streams contain H₂S and CO₂ that cause corrosion and fouling in pipelines and in processing plants. Therefore, to remove these acid gases aqueous solutions of one alkanolamine have traditionally been used. Some of the most important alkanolamines used in industrial processes include monoethanolamine (MEA), diethanolamine (DEA), triethanolamine (TEA), 2-amino-2-methyl-1-propanol (AMP), and *N*-methyldiethanolamine (MDEA).

The use of mixtures of two alkanolamines (mainly aqueous solutions of a tertiary alkanolamine with a primary or secondary alkanolamine) has also been proposed with the aim of substituting at the industrial level the solutions of a single alkanolamine.^{1,2} Aqueous mixtures of alkanolamines combine the advantages of the individual amines to produce formulations of solvents with higher loading capacity, faster reaction rates, and lower energy required for regeneration. On the other hand, recent experimental studies^{3,4} on the solubility of CO₂ and H₂S have shown that selected aqueous solutions of three alkanolamines (MDEA, DEA, and AMP) are more efficient than aqueous solutions of either one or two alkanolamines for the removal of those acid gases from hydrocarbon-rich streams. Other studies⁵ have shown the use of nonaqueous solutions of alkanolamine causes an enhancement in the rate of absorption of CO₂.

It is well-known that to fully characterize the physicochemical behavior of new formulations of solvents it is important to create a reliable body of information on their different thermophysical properties that are relevant for the design, operation, and optimization of sour gas treatment plants. In this sense, we have measured the density, viscosity, and surface tension of binary or ternary aqueous solutions of alkanolamines^{6,7} and, recently,

published several papers on the physical properties of (alkanolamine + ethanol).^{8,9}

This paper reports experimental data of density and ultrasonic velocity of {monoethanolamine (MEA) + 2-amino-2-methyl-1-propanol (AMP)}, {monoethanolamine + triethanolamine (TEA)}, and {monoethanolamine + *N*-methyldiethanolamine (MDEA)}. These data represent the continuation of previous experimental works on binary and ternary solutions of alkanolamines.

Experimental Section

All solutions were prepared by mass using an analytical balance with an uncertainty of ± 0.1 mg. The solutes were Merck reagents of nominal mass fraction purity > 0.95 for AMP (CAS registry No. 124-68-5), > 0.98 for MDEA (CAS registry No. 105-59-9), and > 0.99 for both MEA (CAS registry No. 141-43-5) and TEA (CAS registry No. 102-71-6).

The density, ρ , and speed of sound, u , of the pure alkanolamines and their mixtures were measured at temperature intervals of 5 K at temperatures between (293.15 and 323.15) K with an Anton Paar DSA 5000 densimeter with an uncertainty in density of $\pm 5 \cdot 10^{-5}$ g·cm⁻³ and sound speed of ± 0.05 m·s⁻¹. The apparatus temperature was controlled with a precision of ± 0.01 K. Before each series of measurements, the instrument was calibrated with double-distilled degassed water and dry air at atmospheric pressure. Densities of both water and dry air at the various working temperatures were supplied by the manufacturer in the instruction manual.

The measured densities and ultrasonic velocities of the pure components are listed in Table 1 and are compared with values published by other authors.^{10–18}

Finally, the isentropic compressibility, k_s , was calculated from the density, ρ , and speed of sound, u , values from

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Table 5. Adjustable Parameters K_0 and K_1 (in Equation 2) with the Standard Deviations, σ_{st} , the Densities, and Ultrasonic Velocities^a

x_1	$\rho/\text{kg}\cdot\text{m}^{-3}$			$u/\text{m}\cdot\text{s}^{-1}$			x_1	$\rho/\text{kg}\cdot\text{m}^{-3}$			$u/\text{m}\cdot\text{s}^{-1}$		
	K_1	K_2	$\sigma_{st}\cdot 10^3$	K_1	K_2	σ_{st}		K_1	K_2	$\sigma_{st}\cdot 10^3$	K_1	K_2	σ_{st}
Monoethanolamine (1) + 2-Amino-2-methyl-1-propanol (2)													
0.0000	1184.30	0.8443	0.043	2626.07	3.8376	1.202	0.6869	1230.86	0.8387	0.027	2646.04	3.4141	0.379
0.1410	1194.71	0.8519	0.039	2622.54	3.7419	1.056	0.7724	1237.13	0.8336	0.018	2657.38	3.3737	0.259
0.2691	1202.08	0.8495	0.045	2623.99	3.6635	0.883	0.8532	1243.57	0.8288	0.023	2666.20	3.3261	0.172
0.3862	1209.17	0.8460	0.032	2626.90	3.5917	0.747	0.9268	1249.21	0.8221	0.018	2672.76	3.2750	0.114
0.4939	1216.83	0.8448	0.033	2629.20	3.5191	0.629	1.0000	1250.17	0.7988	0.018	2689.17	3.2531	0.077
0.5933	1224.26	0.8431	0.037	2635.27	3.4592	0.496							
Monoethanolamine (1) + Triethanolamine (2)													
0.0000	1288.55	0.5625	0.028	2075.83	1.5624	1.061	0.6192	1291.06	0.7059	0.026	2317.90	2.1187	0.226
0.1159	1293.20	0.5931	0.027	2083.09	1.5380	1.002	0.7099	1287.00	0.7294	0.030	2382.98	2.3095	1.322
0.2165	1294.40	0.6138	0.028	2109.30	1.5832	0.858	0.7849	1281.84	0.7491	0.021	2443.14	2.4854	0.567
0.3017	1294.80	0.6314	0.031	2146.57	1.6718	0.711	0.8509	1275.31	0.7658	0.021	2496.67	2.6474	0.476
0.3788	1295.00	0.6489	0.030	2184.57	1.7663	0.570	0.9070	1268.27	0.7806	0.015	2548.77	2.8080	0.452
0.4492	1294.44	0.6643	0.024	2219.36	1.8538	0.471	0.9561	1260.13	0.7923	0.014	2607.83	2.9932	0.419
0.5121	1293.49	0.6786	0.022	2252.65	1.9403	0.357	1.0000	1250.17	0.7988	0.016	2689.17	3.2531	0.077
Monoethanolamine (1) + <i>N</i> -Methyldiethanolamine (2)													
0.0000	1273.10	0.7876	0.023	2484.92	3.0681	0.042	0.8197	1267.91	0.8238	0.019	2621.53	3.1474	0.133
0.1789	1274.33	0.7982	0.074	2495.33	3.0414	0.082	0.8540	1267.08	0.8259	0.015	2631.84	3.1596	0.131
0.3286	1274.60	0.8055	0.043	2518.54	3.0570	0.057	0.8865	1265.68	0.8263	0.027	2642.33	3.1729	0.144
0.4560	1273.52	0.8086	0.040	2541.65	3.0754	0.078	0.9461	1261.84	0.8243	0.049	2661.83	3.2012	0.128
0.5658	1272.53	0.8130	0.038	2562.78	3.0916	0.117	0.9738	1258.29	0.8189	0.013	2673.79	3.2211	0.134
0.6614	1271.19	0.8166	0.026	2582.32	3.1062	0.117	1.0000	1250.17	0.7988	0.022	2689.17	3.2531	0.077
0.7449	1269.69	0.8204	0.020	2602.66	3.1264	0.125							

^a $\sigma_{st} = [\sum(Y_{cal} - Y_{exp})^2/(N - n)]^{1/2}$, where Y is the function, N is the number of data, and n is the number of parameters.

Table 6. Adjustable Parameters a_i (in Equation 5) with the Standard Deviations, σ_{st} , for Excess Molar Volumes, V^E , and Isentropic Compressibility Deviations, Δk_s^a

Y	T/K	a_0	a_1	a_2	a_3	a_4	$\sigma_{st}\cdot 10$	
Monoethanolamine (1) + 2-Amino-2-methyl-1-propanol (2)								
$V^E/\text{cm}^3\cdot\text{mol}^{-1}$	293.15	-0.7093	0.1561	0.2934	0.0489	-0.5833	0.004	
	298.15	-0.6793	0.1644	0.2682	-0.0164	-0.4160	0.005	
	303.15	-0.6677	0.1380	0.2760	0.0294	-0.3372	0.005	
	308.15	-0.6435	0.1328	0.2554	0.0432	-0.2380	0.009	
	313.15	-0.6233	0.1297	0.2834	0.0471	-0.1995	0.010	
	318.15	-0.6029	0.1208	0.2883	0.0568	-0.1021	0.015	
	323.15	-0.5794	0.1089	0.2863	0.0875	-0.0070	0.023	
	Δk_s	293.15	12.7968	2.5183	-6.4082	0.9768	7.1881	0.180
		298.15	11.5959	2.5001	-5.3970	1.8477	6.3992	0.155
		303.15	10.3394	2.4609	-5.6381	2.1352	6.5737	0.115
308.15		8.8726	2.9372	-4.7855	1.8678	5.7523	0.133	
313.15		7.7646	3.0491	-3.3685	1.3230	2.9677	0.141	
318.15		6.7120	2.9894	-1.8802	1.0280	0.8594	0.117	
323.15		5.8026	3.0186	-1.0977	0.3768	-0.8707	0.176	
Monoethanolamine (1) + Triethanolamine (2)								
$V^E/\text{cm}^3\cdot\text{mol}^{-1}$	298.15	-1.8782	0.6638	-0.1686	-0.2771	-0.6052	0.012	
	303.15	-1.8291	0.6666	-0.1871	-0.2449	-0.4818	0.011	
	308.15	-1.7855	0.6679	-0.1492	-0.1602	-0.3763	0.008	
	313.15	-1.7401	0.6982	-0.0993	-0.2424	-0.4886	0.010	
	318.15	-1.6803	0.6575	-0.1528	-0.1528	-0.2740	0.016	
	323.15	-1.6403	0.6828	-0.1950	-0.1950	-0.5203	0.015	
	Δk_s	298.15	-47.7473	22.5168	-7.9950	-4.3149	2.8542	0.348
		303.15	-53.3747	22.6085	-2.8054	-3.3497	-1.9190	0.225
		308.15	-57.5201	22.0778	0.6306	1.2711	-15.4807	0.622
		313.15	-62.9707	25.4661	-11.9916	-2.0121	2.2606	0.183
318.15		-68.2449	26.8349	-15.3160	0.8567	-2.5979	0.792	
323.15		-74.8239	28.2280	-2.9019	3.8982	-30.5849	1.165	
Monoethanolamine (1) + <i>N</i> -Methyldiethanolamine (2)								
$V^E/\text{cm}^3\cdot\text{mol}^{-1}$	293.15	-0.6773	-0.3844	0.2154	-0.0491	-0.3027	0.494	
	298.15	-0.7073	-0.3862	0.3014	-0.0767	-0.5361	0.329	
	303.15	-0.7836	-0.3995	0.2713	-0.2351	-0.7389	0.132	
	308.15	-0.7611	-0.3872	0.2967	-0.1884	-0.6708	0.018	
	313.15	-0.7370	-0.3887	0.3560	-0.1314	-0.6940	0.016	
	318.15	-0.7073	-0.3862	0.3014	-0.0767	-0.5361	0.014	
	323.15	-0.6773	-0.3844	0.2154	-0.0491	-0.3027	0.018	
	Δk_s	293.15	9.6727	1.9708	5.8331	4.6791	-6.2219	0.029
		298.15	9.3223	2.2773	5.7058	3.8476	-6.8400	0.098
		303.15	9.0376	2.3532	5.4485	3.3283	-7.7849	0.095
308.15		8.7739	2.4479	4.9892	3.2297	-7.8018	0.108	
313.15		8.4920	2.4675	5.0723	3.0294	-8.7950	0.135	
318.15		8.2499	2.4476	4.4599	3.0103	-8.3061	0.133	
323.15		7.9867	2.3454	3.7360	3.1088	-7.4530	0.140	

^a $\sigma_{st} = [\sum(Y_{cal} - Y_{exp})^2/(N - n)]^{1/2}$, where N is the number of data and n is the number of parameters.

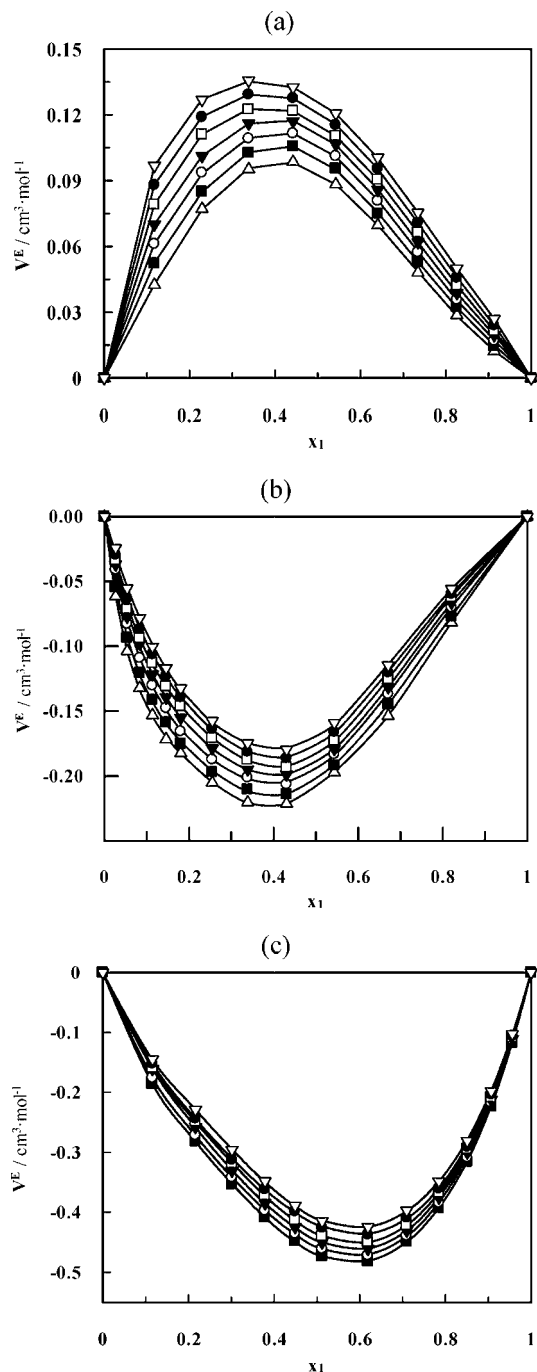


Figure 1. Excess molar volumes, V^E , for (a) 1-amino-2-propanol (1) + 2-amino-1-methyl-1-propanol (2), (b) monoethanolamine (1) + triethanolamine (2), and (c) monoethanolamine (1) + *N*-methyldiethanolamine (2): Δ , 293.15 K; \blacksquare , 298.15 K; \circ , 303.15 K; \blacktriangledown , 308.15 K; \square , 313.15 K; \bullet , 318.15 K; ∇ , 323.15 K; —, Redlich–Kister fit curves.

With regard to the influence of the composition, it is observed that the ultrasonic velocity decreases as the mixture is enriched in monoethanolamine and that, for the mixtures of monoethanolamine with triethanolamine or *N*-methyldiethanolamine, the density decreases with the mole fraction of MEA. However, for the mixtures of monoethanolamine with 2-amino-2-methyl-1-propanol, the density increases with the concentration of MEA.

The excess molar volumes of mixtures V^E were calculated from density measurements by applying the following equation¹⁹

$$V^E = \sum_{i=1}^2 x_i M_i \left(\frac{1}{\rho_m} - \frac{1}{\rho_i} \right) \quad (3)$$

where x_i represent the molar fraction of the component i in the mixture; ρ_i represents the density of the i th pure component; and ρ_m is the measured mixture density.

The isentropic compressibility listed in Tables 2 to 4 was used to obtain the isentropic compressibility deviations, Δk_s , defined by

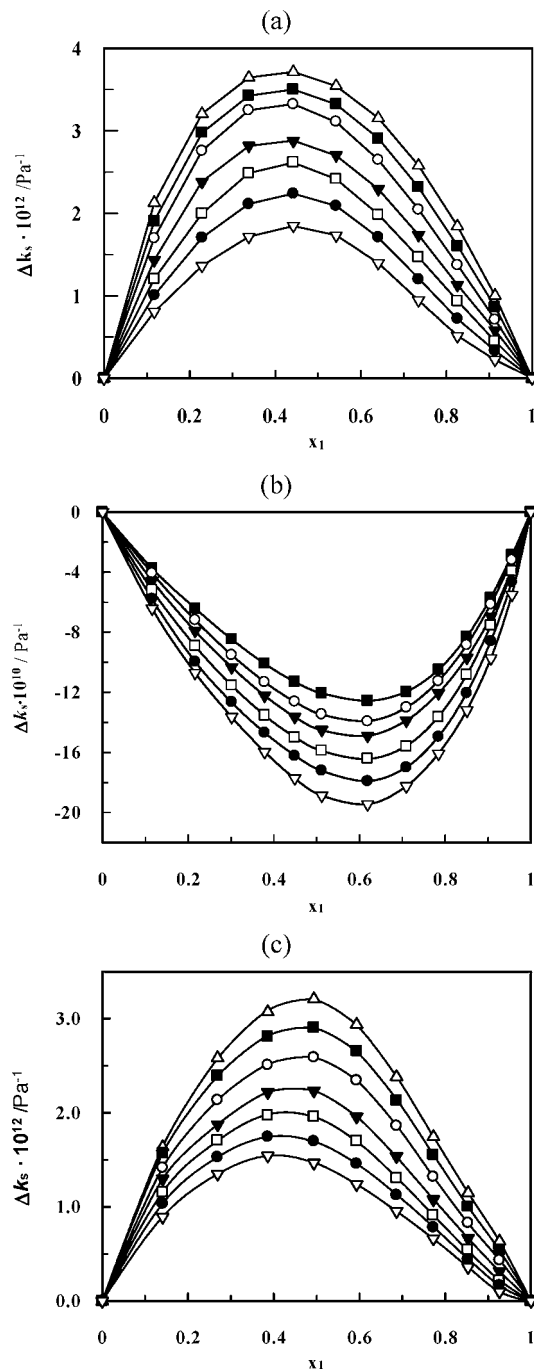


Figure 2. Isentropic compressibility deviations, Δk_s , for (a) 1-amino-2-propanol (1) + 2-amino-1-methyl-1-propanol (2), (b) monoethanolamine (1) + triethanolamine (2), and (c) monoethanolamine (1) + *N*-methyldiethanolamine (2): Δ , 293.15 K; \blacksquare , 298.15 K; \circ , 303.15 K; \blacktriangledown , 308.15 K; \square , 313.15 K; \bullet , 318.15 K; ∇ , 323.15 K; —, Redlich–Kister fit curves.

$$\Delta k_s = k_{s,m} - \sum_{i=1}^2 x_i k_{s,i} \quad (4)$$

where x_i and $k_{s,i}$ represent the mole fraction and isentropic compressibility of the i th pure component, respectively, and $k_{s,m}$ is the isentropic compressibility of the mixture.

A Redlich–Kister type equation was used to correlate the excess molar volume and the isentropic compressibility deviation. For a binary system, this equation has the following expression

$$Y = x_1 x_2 \sum_{i=0}^4 a_i (1 - 2x_1)^i \quad (5)$$

where Y represents the isentropic compressibility deviation or the excess molar volume and x_1 and x_2 are the mole fraction of the monoethanolamine and (AMP, TEA, or MDEA), respectively. The coefficients a_i for the two functions, V^E and Δk_s , are listed in Table 6, with the standard deviation σ_{st} between the experimental and calculated values.

The excess molar volumes and the deviations in isentropic compressibility are shown in Figures 1 and 2.

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