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Volumetric Properties of Highly Nonideal Binary Mixtures Containing Ethanoic Acid and Propanoic Acid with Butan-2-ol, Methyl-2-propanol, and 2-Methyl-2-butanol at Different Temperatures

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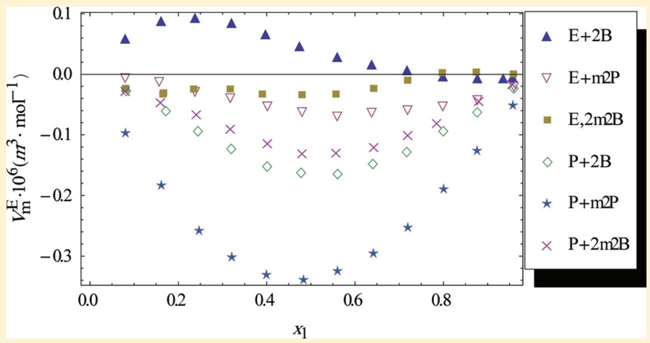
ABSTRACT: Excess molar volumes, V_m^E, of six binary mixtures of ethanoic acid and propanoic acid with butan-2-ol, methyl-2-propanol, and 2-methyl-butan-2-ol were obtained from density measurements over the entire range of compositions at T = (293.15 to 333.15) K. A sigmoidal behavior was observed for the V_m^E values of ethanoic acid with butan-2-ol and 2-methyl-butan-2-ol, and negative V_m^E values were obtained for the binary mixture of ethanoic acid with methyl-2-propanol at T = (293.15 to 303.15 or 313.15) K. But the effect of the rising temperature is not the same for these mixtures. For the mixtures containing propanoic acid with alcohols the V_m^E values were negative and become more negative with increasing temperature over the entire range of compositions and temperatures except for the mixture of propanoic acid with methyl-2-propanol. Totally unregulated behavior was observed by a mixture of carboxylic acids with alcohols at different temperatures.



INTRODUCTION

Highly nonideal systems are of considerable importance due to specific intermolecular interactions. Information about molecular structures and molecular interactions can be useful for the related macroscopic properties. These data and their dependence on temperature and pressure are necessary to design chemical reactors and separation equipment and to test theories of solutions. Excess properties of binary liquid mixtures assist in understanding the nature of molecular interactions between the molecules of the mixtures.[1,2] Binary mixtures of ethanoic acid and propanoic acid with butan-2-ol, methyl-2-propanol, and 2-methyl-butan-2-ol were selected to access the above purposes as well as for their industrial applications.[3,4] Both acids and alcohols are self-associated liquids through hydrogen bonding. The self-associated of alkanols presents a picture of complicated equilibria involving monomer, dimers, trimers, tetramers, and so forth with both linear and cyclic structure. Mainly, alcohols form linear chains. The extent of this association depends on the concentration of the alcohols in the liquid state and on temperature.[5−7] Carboxylic acid molecules associate by the formation of dimers. The extent of the dimerization depends on the temperature and pressure of the system.[4,8−10]

In this work, excess molar volumes, V_m^E, of six binary mixtures of ethanoic acid and propanoic acid with butan-2-ol, methyl-2-propanol, and 2-methyl-butan-2-ol were calculated from density data at T = (293.15 to 333.15) K and atmospheric pressure over the entire range of composition. The V_m^E values of the ethanoic acid + butan-2-ol binary mixture were compared with the reported values at 298.15 K.[10] The differences between the literature data and our results are about the order of uncertainties.

EXPERIMENTAL SECTION

Chemicals. The source and purity of pure substances are collected in Table 1. To clarify the stated purities of the solvents by the manufacturer, density and refractive index measurements were performed and are reported in Table 1 together with the literature values[1,3,11−17] at different temperatures. Prior to the experimental measurements, the liquids were degassed with a bath ultrasonic cleaner.

Apparatus and Procedure. Densities of pure components and binary mixtures were measured with an Anton Paar DMA 4500 oscillating u-tube densimeter, provided with automatic viscosity correction. The temperature in the cell was regulated to ± 0.01 K with a solid state thermostat. The uncertainty in the density measurements was ± $1 \cdot 10^{-2}$ kg·m^{-3}. The calibration of the instrument was performed once a day with bi-distilled water and dry air. The refractive indices measurements were performed with a thermostatted Abbé refractometer (model DR-A1) with an uncertainty of ± 0.0002. The mixtures

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Table 1. Source, Purity Grade, Densities, ρ, and Refractive Indices, n_D^{25}, of the Pure Components with Their Literature Values at Different Temperatures

				$\rho \cdot 10^{-3}$/kg·m^{-3}		n_D^{25}	
component	source	purity (mass fraction)	T/K	exptl	lit.	exptl	lit.[g]
ethanoic acid	Merck	> 99.8 %	293.15	1.04931	1.04930[a]	1.3687	1.3698
			298.15	1.04365	1.04365[a]		
			303.15	1.03799	1.03800[a]		
			313.15	1.02668	1.0258[b]		
			323.15	1.01536	1.01544[c]		
			333.15	1.00401	1.00409[c]		
propanoic acid	Sigma-Aldrich	> 99.5 %	293.15	0.99356	0.9934[b]	1.3835	1.3843
			298.15	0.98815	0.98823[d]		
			303.15	0.98275	0.9829[b]		
			313.15	0.97196	0.9721[b]		
			323.15	0.96116	0.9613[b]		
			333.15	0.95035			
butan-2-ol	Aldrich	> 99 %	293.15	0.80675	0.80684[e]	1.3943	1.3950
			298.15	0.80262	0.80272[e]		
			303.15	0.79843	0.79851[e]		
			313.15	0.78975	0.78965[f]		
			323.15	0.78065	0.78055[f]		
			333.15	0.77110	0.77099[f]		
methyl-2-propanol	Merck	> 99 %	293.15	0.80199	0.8016[g]	1.3929	1.3939
			298.15	0.79813	0.79803[h]		
			303.15	0.79424	0.79417[h]		
			313.15	0.78628	0.78610[h]		
			323.15	0.77809	0.77793[f]		
			333.15	0.76960	0.76944[f]		
2-methyl-butan-2-ol	Riedel	> 99.5 %	293.15	0.80898	0.80888[i]	1.4016	1.4024
			298.15	0.80439	0.80432[i]		
			303.15	0.79975	0.79968[i]		
			313.15	0.79027	0.79018[i]		
			323.15	0.78046			
			333.15	0.77027			

[a]Reference 11. [b]Reference 1. [c]Reference 12. [d]Reference 13. [e]Reference 14. [f]Reference 3. [g]Reference 15. [h]Reference 16. [i]Reference 17.

Table 2. Densities, ρ, and Excess Molar Volumes, V_m^E, for the Binary Mixtures of Carboxylic Acid (1) + Alkanols (2) at the Temperature Range from (293.15 to 333.15) K

x_1	$\rho \cdot 10^{-3}$ kg·m^{-3}	$V_m^E \cdot 10^6$ m^3·mol^{-1}	x_1	$\rho \cdot 10^{-3}$ kg·m^{-3}	$V_m^E \cdot 10^6$ m^3·mol^{-1}
Ethanoic Acid (1) + Butan-2-ol (2)					
T = 293.15 K					
0.0822	0.81904	0.057	0.6399	0.93404	0.011
0.1628	0.83216	0.083	0.7197	0.95597	0.002
0.2395	0.84565	0.087	0.8003	0.98006	−0.008
0.3210	0.86112	0.076	0.8796	1.00580	−0.012
0.3979	0.8768	0.061	0.9365	1.02567	−0.010
0.4759	0.89389	0.041	0.9586	1.03371	−0.007
0.5611	0.91400	0.022			
T = 298.15 K					
0.0822	0.81482	0.059	0.6399	0.92904	0.017
0.1628	0.82783	0.088	0.7197	0.95084	0.007
0.2395	0.84123	0.093	0.8003	0.97478	−0.004
0.3210	0.85658	0.084	0.8796	1.00035	−0.007
0.3979	0.87217	0.067	0.9365	1.02012	−0.007
0.4759	0.88916	0.047	0.9586	1.02812	−0.005
0.5611	0.90912	0.029			
T = 303.15 K					
0.0822	0.81053	0.063	0.6399	0.92401	0.023
0.1628	0.82344	0.093	0.7197	0.94568	0.013
0.2395	0.83676	0.098	0.8003	0.96949	0.000
0.3210	0.85200	0.091	0.8796	0.99491	−0.004
0.3979	0.86749	0.075	0.9365	1.01458	−0.006
0.4759	0.88437	0.055	0.9586	1.02254	−0.004
0.5611	0.90422	0.035			
T = 313.15 K					
0.0822	0.80169	0.066	0.6399	0.91387	0.030
0.1628	0.81446	0.097	0.7197	0.93530	0.019
0.2395	0.82762	0.103	0.8003	0.95884	0.007
0.3210	0.8427	0.095	0.8796	0.98399	0.001
0.3979	0.85802	0.079	0.9365	1.00346	−0.002
0.4759	0.87469	0.060	0.9586	1.01136	−0.002
0.5611	0.89432	0.041			
T = 323.15 K					
0.0822	0.79250	0.064	0.6399	0.90362	0.027
0.1628	0.80517	0.093	0.7197	0.92481	0.019
0.2395	0.81822	0.097	0.8003	0.94810	0.009
0.3210	0.83316	0.089	0.8796	0.97301	0.004
0.3979	0.84833	0.073	0.9365	0.99231	0.001
0.4759	0.86483	0.055	0.9586	1.00014	0.000
0.5611	0.88426	0.037			

Table 2. continued

x_1	$\rho\cdot10^{-3}$ / $kg\cdot m^{-3}$	$V_m^E\cdot10^6$ / $m^3\cdot mol^{-1}$	x_1	$\rho\cdot10^{-3}$ / $kg\cdot m^{-3}$	$V_m^E\cdot10^6$ / $m^3\cdot mol^{-1}$
		T = 333.15 K			
0.0822	0.78293	0.055	0.6399	0.89319	0.017
0.1628	0.79554	0.079	0.7197	0.91419	0.012
0.2395	0.80851	0.081	0.8003	0.93726	0.006
0.3210	0.82336	0.070	0.8796	0.96197	0.003
0.3979	0.83839	0.056	0.9365	0.98111	0.001
0.4759	0.85477	0.038	0.9586	0.98887	0.001
0.5611	0.87400	0.025			
		Ethanoic Acid (1) + Methyl-2-propanol (2)			
		T = 293.15 K			
0.0813	0.81494	−0.011	0.5599	0.91199	−0.081
0.1574	0.82782	−0.020	0.6396	0.93248	−0.075
0.2405	0.84293	−0.039	0.7199	0.95487	−0.070
0.3190	0.85814	−0.051	0.7998	0.97904	−0.061
0.4018	0.87536	−0.064	0.8786	1.00498	−0.048
0.4803	0.89290	−0.075	0.9595	1.03393	−0.023
		T = 298.15 K			
0.0813	0.81095	−0.006	0.5599	0.90722	−0.070
0.1574	0.82371	−0.012	0.6396	0.92756	−0.064
0.2405	0.83869	−0.029	0.7199	0.94979	−0.060
0.3190	0.85378	−0.040	0.7998	0.97380	−0.053
0.4018	0.87087	−0.053	0.8786	0.99957	−0.043
0.4803	0.88827	−0.063	0.9595	1.02835	−0.021
		T = 303.15 K			
0.0813	0.80692	0.000	0.5599	0.90244	−0.059
0.1574	0.81956	−0.002	0.6396	0.92263	−0.054
0.2405	0.83442	−0.019	0.7199	0.94471	−0.051
0.3190	0.84939	−0.029	0.7998	0.96856	−0.046
0.4018	0.86635	−0.041	0.8786	0.99416	−0.037
0.4803	0.88363	−0.052	0.9595	1.02277	−0.018
		T = 313.15 K			
0.0813	0.79873	0.007	0.5599	0.89278	−0.037
0.1574	0.81115	0.011	0.6396	0.91270	−0.034
0.2405	0.82576	0.000	0.7199	0.93447	−0.032
0.3190	0.84050	−0.008	0.7998	0.95802	−0.030
0.4018	0.85721	−0.020	0.8786	0.98331	−0.026
0.4803	0.87424	−0.031	0.9595	1.01159	−0.013
		T = 323.15 K			
0.0813	0.79031	0.016	0.5599	0.88300	−0.017
0.1574	0.80254	0.023	0.6396	0.90265	−0.014
0.2405	0.81692	0.016	0.7199	0.92416	−0.016
0.3190	0.83145	0.010	0.7998	0.94740	−0.015
0.4018	0.84792	0.000	0.8786	0.97240	−0.015
0.4803	0.86470	−0.009	0.9595	1.00040	−0.009
		T = 333.15 K			
0.0813	0.78164	0.020	0.5599	0.87307	−0.001
0.1574	0.79368	0.033	0.6396	0.89249	0.001
0.2405	0.80786	0.028	0.7199	0.91372	0.000
0.3190	0.82219	0.024	0.7998	0.93671	−0.003
0.4018	0.83844	0.015	0.8786	0.96143	−0.006
0.4803	0.85501	0.006	0.9595	0.98916	−0.004
		Ethanoic Acid (1) + 2-Methyl-butan-2-ol (2)			
		T = 293.15 K			
0.0794	0.81964	−0.031	0.4798	0.88762	−0.020
0.0827	0.82007	−0.029	0.5577	0.90494	−0.019
0.1664	0.83207	−0.034	0.6427	0.92588	−0.012
0.1672	0.83217	−0.032	0.7195	0.94694	−0.001
0.2361	0.84273	−0.021	0.7999	0.97166	0.008
0.3176	0.85635	−0.017	0.8769	0.99852	0.007
0.3914	0.86987	−0.021	0.9600	1.03162	0.001
		T = 298.15 K			
0.0794	0.81495	−0.025	0.4798	0.88280	−0.033
0.0827	0.81538	−0.023	0.5577	0.90005	−0.032
0.1664	0.82735	−0.032	0.6427	0.92088	−0.023
0.1672	0.82745	−0.030	0.7195	0.94183	−0.010
0.2361	0.83801	−0.025	0.7999	0.96642	0.002
0.3176	0.85161	−0.025	0.8769	0.99312	0.004
0.3914	0.86510	−0.032	0.9600	1.02604	0.001
		T = 303.15 K			
0.0794	0.81022	−0.020	0.4798	0.87794	−0.046
0.0827	0.81064	−0.016	0.5577	0.89512	−0.044
0.1664	0.82259	−0.030	0.6427	0.91586	−0.034
0.1672	0.82269	−0.028	0.7195	0.93671	−0.020
0.2361	0.83324	−0.028	0.7999	0.96116	−0.005
0.3176	0.84684	−0.035	0.8769	0.98772	0.000
0.3914	0.86030	−0.044	0.9600	1.02047	0.000
		T = 313.15 K			
0.0794	0.80060	−0.013	0.4798	0.86811	−0.077
0.0827	0.80102	−0.010	0.5577	0.88516	−0.073
0.1664	0.81292	−0.031	0.6427	0.90572	−0.060
0.1672	0.81302	−0.029	0.7195	0.92637	−0.040
0.2361	0.82357	−0.039	0.7999	0.95058	−0.018
0.3176	0.83715	−0.057	0.8769	0.97688	−0.008
0.3914	0.85057	−0.072	0.9600	1.00932	−0.003
		T = 323.15 K			
0.0794	0.79072	−0.015	0.4798	0.85810	−0.115
0.0827	0.79114	−0.012	0.5577	0.87504	−0.110
0.1664	0.80302	−0.043	0.6427	0.89544	−0.091
0.1672	0.80312	−0.041	0.7195	0.91592	−0.065
0.2361	0.81368	−0.061	0.7999	0.93991	−0.036
0.3176	0.82725	−0.088	0.8769	0.96596	−0.018
0.3914	0.84064	−0.110	0.9600	0.99813	−0.005
		T = 333.15 K			
0.0794	0.78053	−0.025	0.4798	0.84789	−0.166
0.0827	0.78094	−0.021	0.5577	0.86474	−0.157
0.1664	0.79286	−0.067	0.6427	0.88501	−0.132
0.1672	0.79296	−0.065	0.7195	0.90533	−0.098
0.2361	0.80354	−0.096	0.7999	0.92913	−0.059
0.3176	0.81714	−0.135	0.8769	0.95498	−0.032
0.3914	0.83051	−0.161	0.9600	0.98689	−0.009
		Propanoic Acid (1) + Butan-2-ol (2)			
		T = 293.15 K			
0.0820	0.81964	−0.029	0.5609	0.90361	−0.161
0.1717	0.83426	−0.065	0.6404	0.91881	−0.145
0.2442	0.84652	−0.100	0.7186	0.93419	−0.122
0.3200	0.85963	−0.126	0.8009	0.95085	−0.090
0.4004	0.87399	−0.154	0.8776	0.96689	−0.058
0.4773	0.88798	−0.162	0.9593	0.98454	−0.020
		T = 298.15 K			
0.0820	0.81541	−0.027	0.5609	0.89885	−0.164
0.1717	0.82991	−0.061	0.6404	0.91396	−0.148
0.2442	0.84208	−0.095	0.7186	0.92925	−0.127
0.3200	0.85512	−0.123	0.8009	0.94579	−0.094
0.4004	0.86939	−0.152	0.8776	0.96172	−0.062
0.4773	0.88330	−0.162	0.9593	0.97923	−0.023
		T = 303.15 K			
0.0820	0.81110	−0.023	0.5609	0.89407	−0.167
0.1717	0.82551	−0.057	0.6404	0.90909	−0.152
0.2442	0.83760	−0.091	0.7186	0.92429	−0.131
0.3200	0.85056	−0.120	0.8009	0.94074	−0.100

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Table 2. continued

x_1	$\rho\cdot10^{-3}$ / $kg\cdot m^{-3}$	$V_m^E\cdot10^6$ / $m^3\cdot mol^{-1}$	x_1	$\rho\cdot10^{-3}$ / $kg\cdot m^{-3}$	$V_m^E\cdot10^6$ / $m^3\cdot mol^{-1}$
		T = 303.15 K			
0.4004	0.86476	−0.152	0.8776	0.95655	−0.066
0.4773	0.87859	−0.162	0.9593	0.97390	−0.024
		T = 313.15 K			
0.0820	0.80226	−0.022	0.5609	0.88441	−0.179
0.1717	0.81650	−0.055	0.6404	0.89928	−0.166
0.2442	0.82846	−0.091	0.7186	0.91432	−0.146
0.3200	0.84130	−0.123	0.8009	0.93057	−0.113
0.4004	0.85537	−0.158	0.8776	0.94617	−0.076
0.4773	0.86908	−0.172	0.9593	0.96326	−0.028
		T = 323.15 K			
0.0820	0.79305	−0.023	0.5609	0.87461	−0.201
0.1717	0.80720	−0.063	0.6404	0.88936	−0.189
0.2442	0.81908	−0.102	0.7186	0.90427	−0.168
0.3200	0.83182	−0.137	0.8009	0.92034	−0.132
0.4004	0.84579	−0.175	0.8776	0.93575	−0.090
0.4773	0.85940	−0.192	0.9593	0.95261	−0.034
		T = 333.15 K			
0.0820	0.78348	−0.033	0.5609	0.86465	−0.233
0.1717	0.79757	−0.079	0.6404	0.87930	−0.220
0.2442	0.80941	−0.124	0.7186	0.89407	−0.194
0.3200	0.82211	−0.165	0.8009	0.91002	−0.155
0.4004	0.83600	−0.205	0.8776	0.92526	−0.105
0.4773	0.84954	−0.224	0.9593	0.94192	−0.040
		Propanoic Acid (1) + Methyl-2-propanol (2)			
		T = 293.15 K			
0.0803	0.81548	−0.099	0.5602	0.90263	−0.324
0.1616	0.82950	−0.187	0.6413	0.91847	−0.295
0.2482	0.84479	−0.261	0.7201	0.93421	−0.250
0.3212	0.85793	−0.305	0.8016	0.95086	−0.187
0.4008	0.87254	−0.333	0.8777	0.96686	−0.120
0.4828	0.88790	−0.341	0.9586	0.98447	−0.049
		T = 298.15 K			
0.0803	0.81149	−0.096	0.5602	0.89796	−0.323
0.1616	0.82539	−0.183	0.6413	0.91369	−0.295
0.2482	0.84055	−0.256	0.7201	0.92932	−0.252
0.3212	0.85359	−0.300	0.8016	0.94584	−0.189
0.4008	0.86809	−0.329	0.8777	0.96172	−0.124
0.4828	0.88334	−0.339	0.9586	0.97916	−0.051
		T = 303.15 K			
0.0803	0.80747	−0.092	0.5602	0.89327	−0.320
0.1616	0.82125	−0.178	0.6413	0.90890	−0.295
0.2482	0.83628	−0.250	0.7201	0.92442	−0.253
0.3212	0.84922	−0.294	0.8016	0.94081	−0.191
0.4008	0.86361	−0.324	0.8777	0.95656	−0.125
0.4828	0.87876	−0.336	0.9586	0.97384	−0.051
		T = 313.15 K			
0.0803	0.79927	−0.087	0.5602	0.88383	−0.319
0.1616	0.81283	−0.170	0.6413	0.89925	−0.296
0.2482	0.82763	−0.242	0.7201	0.91455	−0.256
0.3212	0.84038	−0.286	0.8016	0.93072	−0.195
0.4008	0.85456	−0.317	0.8777	0.94623	−0.130
0.4828	0.86950	−0.330	0.9586	0.96322	−0.054
		T = 323.15 K			
0.0803	0.79086	−0.082	0.5602	0.87427	−0.318
0.1616	0.80420	−0.162	0.6413	0.88949	−0.297
0.2482	0.81879	−0.234	0.7201	0.90462	−0.261
0.3212	0.83137	−0.279	0.8016	0.92057	−0.201
0.4008	0.84537	−0.312	0.8777	0.93586	−0.135
0.4828	0.86012	−0.328	0.9586	0.95258	−0.057
		T = 333.15 K			
0.0803	0.78219	−0.080	0.5602	0.86457	−0.320
0.1616	0.79534	−0.158	0.6413	0.87962	−0.301
0.2482	0.80974	−0.230	0.7201	0.89459	−0.268
0.3212	0.82215	−0.275	0.8016	0.91032	−0.206
0.4008	0.83600	−0.310	0.8777	0.92544	−0.142
0.4828	0.85057	−0.327	0.9586	0.94192	−0.061
		Propanoic Acid (1) + 2-Methyl-butan-2-ol (2)			
		T = 293.15 K			
0.0822	0.81984	−0.026	0.5588	0.89571	−0.103
0.1600	0.83058	−0.039	0.6429	0.91185	−0.094
0.2419	0.84249	−0.051	0.7218	0.92793	−0.079
0.3189	0.85439	−0.071	0.7850	0.94150	−0.061
0.4024	0.86802	−0.090	0.8812	0.96357	−0.032
0.4806	0.88153	−0.104	0.9561	0.98210	−0.011
		T = 298.15 K			
0.0822	0.81521	−0.028	0.5588	0.89097	−0.129
0.1600	0.82594	−0.046	0.6429	0.90705	−0.120
0.2419	0.83785	−0.065	0.7218	0.92303	−0.101
0.3189	0.84975	−0.090	0.7850	0.93652	−0.08
0.4024	0.86337	−0.114	0.8812	0.95843	−0.044
0.4806	0.87685	−0.130	0.9561	0.97680	−0.016
		T = 303.15 K			
0.0822	0.81053	−0.029	0.5588	0.88621	−0.156
0.1600	0.82126	−0.053	0.6429	0.90223	−0.146
0.2419	0.83318	−0.079	0.7218	0.91813	−0.124
0.3189	0.84508	−0.111	0.7850	0.93153	−0.099
0.4024	0.85868	−0.138	0.8812	0.95330	−0.057
0.4806	0.87213	−0.156	0.9561	0.97151	−0.022
		T = 313.15 K			
0.0822	0.80101	−0.036	0.5588	0.87660	−0.213
0.1600	0.81174	−0.071	0.6429	0.8925	−0.200
0.2419	0.82369	−0.112	0.7218	0.90825	−0.172
0.3189	0.83562	−0.157	0.7850	0.92151	−0.140
0.4024	0.84919	−0.191	0.8812	0.94298	−0.082
0.4806	0.86260	−0.214	0.9561	0.96092	−0.032
		T = 323.15 K			
0.0822	0.79120	−0.046	0.5588	0.86684	−0.279
0.1600	0.80199	−0.099	0.6429	0.88264	−0.261
0.2419	0.81400	−0.157	0.7218	0.89828	−0.227
0.3189	0.82596	−0.214	0.7850	0.91141	−0.186
0.4024	0.83953	−0.256	0.8812	0.93262	−0.111
0.4806	0.85291	−0.282	0.9561	0.95030	−0.044
		T = 333.15 K			
0.0822	0.78109	−0.066	0.5588	0.85693	−0.357
0.1600	0.79196	−0.138	0.6429	0.87264	−0.331
0.2419	0.80406	−0.215	0.7218	0.88818	−0.288
0.3189	0.81607	−0.284	0.7850	0.90120	−0.237
0.4024	0.82968	−0.335	0.8812	0.92220	−0.143
0.4806	0.84303	−0.361	0.9561	0.93964	−0.056

were prepared by mass using a Mettler AB 204-N balance accurate to ± 0.1 mg. Conversion to molar quantities was based on the relative atomic mass table of 1995 issued by the International Union of Pure and Applied Chemistry (IUPAC).[18] The average uncertainty of the mole fraction was estimated to ± $1\cdot10^{-4}$.

■ RESULTS AND DISCUSSIONS

Density data were applied to calculate the excess molar volume, V_m^E, of six binary mixtures of ethanoic acid and propanoic acid with alcohols (butan-2-ol, methyl-2-propanol, and 2-methyl-butan-2-ol) at T = (293.15 to 333.15) K using eq 1. The V_m^E values are listed in Table 2 and illustrated as a function of the mole fraction of component 1 (ethanoic acid or propanoic acid) in Figure 1(a to f). The excess molar volumes of ethanoic acid with butan-2-ol were compared with reported data at 298.15 K previously[10] in Figure 1a. The average uncertainty in the excess molar volume was estimated to be $\pm\ 2\cdot10^{-9}$ m^3·mol^{-1}.

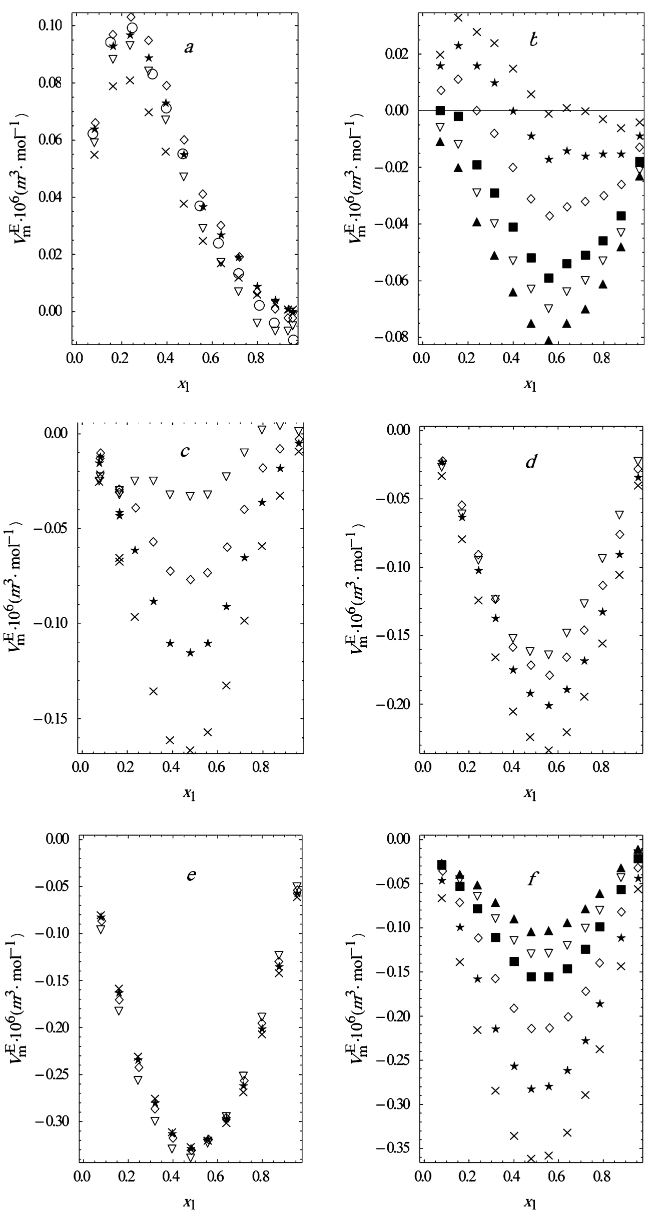

Figure 1. Excess molar volumes of {carboxylic acid (1) + alcohols (2)} mixtures at different temperatures: ▲, 293.15 K; ▽, 298.15 K; ■, 303.15 K; ◊, 313.15 K; ★, 323.15 K; ×, 333.15 K; ○, 298.15 K, ref 10 for: acetic acid with: (a) 2-butanol; (b) isobutanol; (c) 2-methyl-2-butanol and propionic acid with: (d) 2-butanol; (e) isobutanol; (f) 2-methyl-2-butanol.

$$V_m^E = \sum_{i=1}^{2} x_i M_i(\rho^{-1} - \rho_i^{-1}) \quad (1)$$

where ρ and ρ_i are density of the mixture and component i, respectively; x_i and M_i are the mole fraction and molecular mass, respectively.

As can be seen in Figure 1(a to f), a different and complex trend was observed for the V_m^E values of ethanoic acid and propanoic acid with butan-2-ol, methyl-2-propanol, and 2-methyl-butan-2-ol at T = (293.15 to 333.15) K. For greater clarity in these figures, some of them were not represented at (293.15 and 303.15) K so their trend is similar to 298.15 K at the temperatures.

The binary mixture of ethanoic acid with butan-2-ol (Figure 1a) exhibits a positive V_m^E trend, and an inversion of sign is observed at ethanoic acid rich regions at T = (293.15 to 313.15) K. A maximum around $x_1 \approx 0.2$ and a minimum around $x_1 \approx 0.87$ are observed. This trend becomes more positive with increasing temperature. At higher temperatures, (323.15 and 333.15 K), the V_m^E values will be decreased with rising temperature. The experimental data at (323.15 and 333.15) K do not follow the trend of the other temperatures. To confirm the trend, an experimental point between x_1 = 0.88 and x_1 = 0.96 (x_1 = 0.94) was measured, and the same trend was obtained. In an ethanoic acid + methyl-2-propanol mixture (Figure 1b), the V_m^E values are negative over the entire range of composition and become less negative with increasing temperature, and at high temperatures of (313.15 to 333.15) K, a sigmoidal behavior was observed. For the ethanoic acid + 2-methyl-butan-2-ol mixture (Figure 1c), the trend is more complicated. It is interesting to note that two local minima and one maximum were observed for the V_m^E dependence on composition at lower temperatures. To confirm the trend, the x = 0.16 mol fraction was repeated, and the same result was obtained exactly. With increasing temperature, the maximum at the rich regions of ethanoic acid will disappear, and one of the minima ($x_1 \approx 0.5$) becomes more negative. The other minimum (at ethanoic acid poor-region) becomes less negative until it disappears with rising temperature.

In the case of binary mixture of propanoic acid with alcohols, the V_m^E values are negative over the whole mole fraction range. With increasing temperature, the V_m^E trend of the binary mixture of propanoic acid with butan-2-ol and 2-methyl-2-butanol become more negative. For the mixture of propanoic acid with methyl-2-propanol, the changes of V_m^E values with temperature are small and become less negative up to x_1 = 0.56, and then the trend is vice versa. The observed complex behaviors can be explained as follows.

Both acids and alkanols are self-associated through hydrogen-bonding because of the presence of electron donor and electron acceptor sites. They can be associated through hydrogen bonding in the pure state, and cross-association can happen in the mixing process. Alkanols can form dimers, trimers, tetramers, and so forth in the pure state, and carboxylic acid molecules associate by the formation of dimers.[9,19] During mixing, the disruption of self-association of alkanols and carboxylic acids occurs which makes a positive contribution to V_m^E, and the formation of a new H-bond between them provides a negative contribution to V_m^E. On the other hand, interstitial accommodation of alkanol in hydrogen-bonded carboxylic acid aggregates (packing effect) makes a negative contribution to V_m^E. The actual V_m^E values are resultant of the balance between the two positive and negative effects. It seems that the small V_m^E values of the mentioned systems are very sensitive to the presence of a branch on the alcohol chain and also on the position of −OH group in the alkyl chain of alkanol. The complexity of the behavior pattern for the interactions between the molecules in the mixtures with increasing temperature can be related to the sensitivity of the extent of association of

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alkanols (dimers, trimers, tetramers, and so forth) and carboxylic acids (dimerization) to temperature. In other hand, the esterification reaction may happen at higher temperatures.

■ CONCLUSION

The excess molar volume, V_m^E, of six binary mixtures containing ethanoic acid and propanoic acid with butan-2-ol, methyl-2-propanol, and 2-methyl-butan-2-ol were obtained from density measurements over the whole range of composition and from T = (293.15 to 333.15) K. A sigmoidal behavior was observed for the V_m^E values of ethanoic acid with butan-2-ol and 2-methyl-butan-2-ol, and negative values were obtained for the binary mixture of ethanoic acid with methyl-2-propanol in the (293.15 to 313.15) K temperature range. With rising temperature, different behaviors were observed for the mixtures. The V_m^E values of propanoic acid with alcohols were negative over the entire range of composition and temperatures and become more negative with increasing temperature over the entire range of compositions and temperatures except for the mixture of propanoic acid with methyl-2-propanol. The current work shows that the temperature dependence of propanoic acid with methyl-2-propanol mixture is smaller than the other systems.

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) Vong, W. T.; Tsai, F. N. Densities, molar volumes, thermal expansion coefficients, and isothermal compressibilities of organic acids from 293.15 to 323.15 K and at pressures up to 25 MPa. *J. Chem. Eng. Data* **1997**, *42*, 1116−1120.

(2) Letcher, T. M.; Redhi, G. G. Thermodynamic excess properties for binary mixtures of (benzonitrile plus a carboxylic acid) at T = 298.15 K. *Fluid Phase Equilib.* **2002**, *198*, 257−266.

(3) Iglesias-Silva, G. A.; Bravo-Sanchez, M. G.; Estrada-Baltazar, A.; Hall, K. R. Densities and Viscosities of Binary Mixtures of n-Butanol with 2-Butanol, Isobutanol, and tert-Butanol from (303.15 to 343.15) K. *J. Chem. Eng. Data* **2010**, *55*, 2310−2315.

(4) Gonzalez, J. A.; Delafuente, I. G.; Cobos, J. C.; Casanova, C. Thermodynamics of Mixtures Containing Linear Monocarboxylic Acids. 1. Disquac Predictions on Molar Excess Gibbs Energies, Molar Excess-Enthalpies and Solid-Liquid Equilibria for Mixtures of Linear Monocarboxylic Acids with Organic-Solvents. *Fluid Phase Equilib.* **1994**, *99*, 19−33.

(5) Dubey, G. P.; Sharma, M. Thermophysical properties of binary mixtures of 2-methyl-1-propanol with hexane, octane, and decane at 298.15 K. *J. Chem. Eng. Data* **2007**, *52*, 449−453.

(6) Dubey, G. P.; Sharma, M.; Oswal, S. Volumetric, transport, and acoustic properties of binary mixtures of 2-methyl-1-propanol with hexadecane and squalane at T = (298.15, 303.15, and 308.15) K: Experimental results, correlation, and prediction by the ERAS model. *J. Chem. Thermodyn.* **2009**, *41*, 849−858.

(7) Motin, M. A.; Kabir, M. H.; Huque, E. M. Densities and excess molar volumes of formic acid, acetic acid and propionic acid in pure water and in water plus Surf Excel solutions at different temperatures. *Phys. Chem. Liq.* **2005**, *43*, 277−288.

(8) Arai, Y.; Miyamoto, S.; Nakamura, S.; Iwai, Y. Measurement of vapor-phase compressibility factors of monocarboxylic acids using a flow-type apparatus and their association constants. *J. Chem. Eng. Data* **1999**, *44*, 48−51.

(9) Zhao, J. Y.; Hu, Y. Thermodynamics of Associated Solutions - Excess Properties of Alcohol Alkane and Alcohol Carboxylic-Acid Mixtures. *Fluid Phase Equilib.* **1990**, *57*, 89−104.

(10) Zarei, H. A. Densities, excess molar volumes and partial molar volumes of the binary mixtures of acetic acid + alkanol (C_1-C_4) at 298.15 K. *J. Mol. Liq.* **2007**, *130*, 74−78.

(11) Tojo, J.; Gonzalez, B.; Dominguez, A. Dynamic viscosities, densities, and speed of sound and derived properties of the binary systems acetic acid with water, methanol, ethanol, ethyl acetate and methyl acetate at T = (293.15, 298.15, and 303.15) K at atmospheric pressure. *J. Chem. Eng. Data* **2004**, *49*, 1590−1596.

(12) Dai, L. Y.; He, D.; Lei, M.; Chen, Y. Q. Densities and Viscosities of Binary Mixtures of Acetic Acid with Acetic Anhydride and Methenamine at Different Temperatures. *J. Chem. Eng. Data* **2008**, *53*, 2892−2896.

(13) Hnedkovsky, L.; Cibulka, I.; Malijevska, I. Excess Molar Volumes of (Trifluoroethanoic Acid + Propanoic Acid) at 298.15 K and 318.15 K - an Unusual Composition Dependence. *J. Chem. Thermodyn.* **1990**, *22*, 135−141.

(14) Dominguez, A.; Gonzalez, B.; Tojo, J. Viscosity, density, and speed of sound of methylcyclopentane with primary and secondary alcohols at T = (293.15, 298.15, and 303.15) K. *J. Chem. Thermodyn.* **2006**, *38*, 1172−1185.

(15) Riddick, J.; Bunger, W. B. *Organic Solvents*, 3rd ed.; Wiley-Interscience: New York, 1970.

(16) Pardo, J. I.; Langa, E.; Mainar, A. M.; Urieta, J. S. Excess enthalpy, density, and speed of sound for the mixtures 8-pinene + 2-methyl-1-propanol or 2-methyl-2-propanol at several temperatures. *J. Chem. Eng. Data* **2007**, *52*, 2182−2187.

(17) Dzida, M. Study of the Effects of Temperature and Pressure on the Thermodynamic and Acoustic Properties of Pentan-1-ol, 2-Methyl-2-butanol, and Cyclopentanol in the Pressure Range from (0.1 to 100) MPa and Temperature from (293 to 318) K. *J. Chem. Eng. Data* **2009**, *54*, 1034−1040.

(18) Coplen, T. B. Atomic weights of the elements 1995. *Pure Appl. Chem.* **1996**, *68*, 2339−2359.

(19) Nagata, I.; Gotoh, K.; Tamura, K. Association model of fluids. Phase equilibria and excess enthalpies in acid mixtures. *Fluid Phase Equilib.* **1996**, *124*, 31−54.