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

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Dynamic viscosities, densities, and speeds of sound of acetic acid with water, methanol, ethanol, methyl acetate, and ethyl acetate at T = (293.15, 298.15, and 303.15) K have been measured over the whole composition range and at atmospheric pressure along with the properties of the pure components. Excess molar volumes and deviations in isentropic compressibility and viscosity for the binary systems at the above-mentioned temperatures were calculated. These results were fit to the Redlich−Kister equation to determine the fitting parameters and the root-mean-square deviations. The UNIQUAC equation was used to correlate the viscosity experimental data.

1. Introduction

In the chemical industry, information on the viscosity and the density of liquid mixtures is necessary in different applications for surface facilities, pipeline systems, mass-transfer operations, and so forth, and in case of the studied mixtures, these physical properties are very important to obtaining esters industrially. As an extension of our work concerning the dynamic viscosity of binary systems,[1−4] in this paper we present measurements on the dynamic viscosity, density, and speed of sound data of acetic acid with water, methanol, ethanol, methyl acetate, and ethyl acetate at T = (293.15, 298.15, and 303.15) K. The Redlich−Kister[5] polynomial was used to fit these results and to determine the fitting parameters and the root-mean-square deviations. Viscosity data were correlated using the UNIQUAC[6] equation.

2. Experimental Section

Chemicals. The pure components were supplied by Fluka and by Merck. The components were degassed ultrasonically, dried over molecular sieves (type 4Å, Aldrich), and kept in inert argon with a maximum water content of 2×10^{-6} mass fraction. The maximum water contents of the liquids was determined using a Metrohm 737 KF coulometer. Their mass fraction purities were >99 mass % for acetic acid, >99.8 mass % for methanol, ethanol, and ethyl acetate, and >99 mass % for methyl acetate. The water was tridistilled.

Apparatus and Procedure. Binary mixtures were prepared by mass using a Mettler AX-205 Delta Range balance with a precision of $\pm 10^{-5}$ g, covering the whole composition range of the mixture.

Kinematic viscosities of liquids and their mixtures were determined using a Lauda PVS1 automatic viscosimeter with two Ubbelhode capillary microviscosimeters of 0.4×10^{-3} and 0.53×10^{-3} m diameter. Gravity fall is the principle of measurement on which this viscosimeter is based. The capillary is maintained in a D20KP Lauda thermostat with a resolution of 0.01 °C. The capillaries are calibrated and certified by the company that supplies us. The uncertainty of the capillary diameter is ±0.005 mm. The equipment has a PVS1 (Processor Viscosity System) control unit that is a PC-controlled instrument for the precise measurement of fall time using standardized glass capillaries with an accuracy of 0.01 s.

The kinematic viscosity is determined from the following relationship

$$\nu = k(t - y) \quad (1)$$

where y is the Hagenbach correction, t is the flow time, and k is the Ubbelhode capillary microviscosimeter constant that is supplied by the company. The dynamic viscosity is determined from

$$\eta = \nu\rho \quad (2)$$

where η is the dynamic viscosity, ν is the kinematic viscosity, and ρ is the density. The uncertainty for the viscosimeter is better than ±0.001 mPa·s.

The densities and the speed of sound of the pure liquids and mixtures were measured using an Anton Paar DSA-5000 digital vibrating tube densimeter. The uncertainty in the density measurement is $\pm 2 \times 10^{-6}$ g·cm^{-3}, and that for the speed of sound is ±0.1 m·s^{-1}. In Table 1, the

Table 1. Comparison of Density, ρ, and Viscosity, η, with Literature Data for Pure Components at T = 298.15 K

	ρ/(g·cm−3)		$10^3\eta$/(Pa·s)		u/(m·s^{-1})	
components	exptl	exptl	lit	lit	exptl	lit
acetic acid	1.04365	1.0439[a]	1.115	1.130[a]	1132	
ethyl acetate	0.89443	0.8945[a]	0.426	0.426[a]	1140	1144[g]
methyl acetate	0.92698	0.9268[b]	0.367	0.367[b]	1151	1161[g]
ethanol	0.78546	0.7854[d]	1.082	1.082[e]	1145	1142[h]
methanol	0.78720	0.7872[f]	0.545	0.545[a]	1104	1102[h]
water	0.99705	0.9971[c]	0.890	0.890[c]	1497	1498[i]

[a] Riddick et al.[7] [b] Lorenzi et al.[8] [c] Kapadi et al.[9] [d] Nikam et al.[10] [e] Das et al.[11] [f] Wei et al.[12] [g] Aminabhavi et al.[13] [h] Orge et al.[14] [i] George et al.[15]

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10.1021/je0342825 CCC: $27.50
Published on Web 09/23/2004

Table 2. Density, ρ, Speed of Sound, u, Dynamic Viscosity, η, Excess Molar Volume, V^E, Isentropic Compressibility, κ_s, Deviation in Isentropic Compressibility, $\Delta\kappa_s$, and Viscosity Deviation, $\Delta\eta$, of Acetic Acid (1) with Ethyl Acetate (2)

acetic acid (1) + ethyl acetate (2)

x_1	ρ / g·cm^{-3}	u / m·s^{-1}	$10^3\eta$ / Pa·s	V^E / cm^3·mol^{-1}	κ_s / T·Pa^{-1}	$\Delta\kappa_s$ / T·Pa^{-1}	$10^3\Delta\eta$ / Pa·s	x_1	ρ / g·cm^{-3}	u / m·s^{-1}	$10^3\eta$ / Pa·s	V^E / cm^3·mol^{-1}	κ_s / T·Pa^{-1}	$\Delta\kappa_s$ / T·Pa^{-1}	$10^3\Delta\eta$ / Pa·s
							293.15 K								
0.0000	0.90052	1163	0.452	0.000	821	0	0.000	0.5967	0.97128	1162	0.731	−0.132	763	1	−0.174
0.0697	0.90735	1165	0.473	−0.062	812	−3	−0.032	0.7000	0.98779	1159	0.817	−0.100	753	2	−0.166
0.0988	0.91056	1166	0.485	−0.110	808	−3	−0.042	0.7989	1.00547	1157	0.912	−0.061	744	2	−0.146
0.1960	0.92061	1166	0.523	−0.150	799	−2	−0.078	0.8993	1.02580	1153	1.052	−0.025	733	1	−0.083
0.2944	0.93146	1165	0.561	−0.162	791	−1	−0.114	0.9493	1.03709	1152	1.113	−0.014	727	0	−0.060
0.3968	0.94368	1165	0.617	−0.158	781	0	−0.136	1.0000	1.04930	1149	1.211	0.000	722	0	0.000
0.5007	0.95731	1163	0.668	−0.145	772	1	−0.164								
							298.15 K								
0.0000	0.89443	1140	0.426	0.000	860	0	0.000	0.5967	0.96540	1141	0.684	−0.137	795	2	−0.153
0.0697	0.90130	1143	0.446	−0.065	849	−3	−0.028	0.7000	0.98194	1140	0.762	−0.103	784	3	−0.146
0.0988	0.90453	1144	0.458	−0.116	845	−3	−0.036	0.7989	0.99966	1137	0.848	−0.063	773	3	−0.128
0.1960	0.91462	1144	0.493	−0.157	835	−3	−0.068	0.8993	1.02006	1135	0.975	−0.025	761	2	−0.071
0.2944	0.92550	1144	0.528	−0.170	826	−1	−0.101	0.9493	1.03140	1134	1.031	−0.014	754	0	−0.049
0.3968	0.93774	1143	0.577	−0.166	816	0	−0.122	1.0000	1.04365	1132	1.115	0.000	748	0	0.000
0.5007	0.95140	1142	0.627	−0.151	805	2	−0.144								
							303.15 K								
0.0000	0.88830	1118	0.403	0.000	901	0	0.000	0.5967	0.95950	1121	0.642	−0.144	829	3	−0.138
0.0697	0.89520	1121	0.422	−0.068	889	−3	−0.025	0.7000	0.97609	1120	0.714	−0.108	816	3	−0.131
0.0988	0.89844	1122	0.433	−0.121	885	−3	−0.032	0.7989	0.99385	1119	0.792	−0.066	804	3	−0.115
0.1960	0.90859	1123	0.465	−0.166	873	−3	−0.062	0.8993	1.01432	1117	0.910	−0.027	790	2	−0.060
0.2944	0.91949	1123	0.498	−0.179	863	−1	−0.091	0.9493	1.02569	1116	0.958	−0.015	783	1	−0.044
0.3968	0.93177	1123	0.541	−0.175	852	1	−0.112	1.0000	1.03800	1115	1.034	0.000	776	0	0.000
0.5007	0.94546	1122	0.589	−0.160	840	2	−0.130								

Table 3. Density, ρ, Speed of Sound, u, Dynamic Viscosity, η, Excess Molar Volume, V^E, Isentropic Compressibility, κ_s, Deviation in Isentropic Compressibility, $\Delta\kappa_s$, and Viscosity Deviation, $\Delta\eta$, of Acetic Acid (1) with Methyl Acetate (2)

acetic acid (1) + methyl acetate (2)

x_1	ρ / g·cm^{-3}	u / m·s^{-1}	$10^3\eta$ / Pa·s	V^E / cm^3·mol^{-1}	κ_s / T·Pa^{-1}	$\Delta\kappa_s$ / T·Pa^{-1}	$10^3\Delta\eta$ / Pa·s	x_1	ρ / g·cm^{-3}	u / m·s^{-1}	$10^3\eta$ / Pa·s	V^E / cm^3·mol^{-1}	κ_s / T·Pa^{-1}	$\Delta\kappa_s$ / T·Pa^{-1}	$10^3\Delta\eta$ / Pa·s
							293.15 K								
0.0000	0.93356	1174	0.386	0.000	777	0	0.000	0.5953	0.99615	1169	0.691	−0.200	734	−10	−0.186
0.0496	0.93874	1177	0.401	−0.082	770	−4	−0.026	0.6894	1.00751	1166	0.775	−0.172	730	−9	−0.180
0.0956	0.94344	1177	0.417	−0.138	765	−7	−0.048	0.7943	1.02092	1162	0.894	−0.133	726	−7	−0.147
0.1950	0.95314	1177	0.460	−0.187	757	−8	−0.087	0.8987	1.03493	1156	1.037	−0.074	723	−5	−0.090
0.3007	0.96386	1176	0.506	−0.219	751	−9	−0.128	0.9502	1.04219	1153	1.120	−0.042	721	−3	−0.050
0.3902	0.97323	1174	0.552	−0.227	745	−10	−0.156	1.0000	1.04930	1149	1.211	0.000	722	0	0.000
0.4937	0.98452	1172	0.617	−0.220	740	−10	−0.176								
							298.15 K								
0.0000	0.92698	1151	0.367	0.000	814	0	0.000	0.5953	0.99010	1149	0.646	−0.209	765	−10	−0.166
0.0496	0.93223	1154	0.381	−0.087	806	−5	−0.023	0.6894	1.00155	1147	0.725	−0.180	760	−9	−0.158
0.0956	0.93698	1155	0.395	−0.145	800	−8	−0.044	0.7943	1.01505	1143	0.834	−0.138	755	−7	−0.127
0.1950	0.94677	1155	0.436	−0.197	792	−9	−0.077	0.8987	1.02917	1138	0.962	−0.076	750	−5	−0.077
0.3007	0.95758	1154	0.480	−0.231	784	−10	−0.112	0.9502	1.03649	1136	1.037	−0.043	748	−3	−0.041
0.3902	0.96702	1153	0.521	−0.239	778	−10	−0.138	1.0000	1.04365	1132	1.115	0.000	748	0	0.000
0.4937	0.97840	1151	0.580	−0.232	771	−10	−0.156								
							303.15 K								
0.0000	0.92034	1128	0.348	0.000	854	0	0.000	0.5953	0.98403	1129	0.608	−0.219	797	−10	−0.148
0.0496	0.92565	1131	0.362	−0.091	844	−5	−0.020	0.6894	0.99556	1127	0.680	−0.189	791	−9	−0.141
0.0956	0.93046	1133	0.376	−0.152	838	−8	−0.038	0.7943	1.00916	1124	0.782	−0.144	785	−7	−0.111
0.1950	0.94034	1133	0.412	−0.207	828	−10	−0.070	0.8987	1.02339	1120	0.896	−0.079	779	−5	−0.068
0.3007	0.95124	1133	0.453	−0.242	819	−11	−0.101	0.9502	1.03077	1118	0.964	−0.045	776	−3	−0.036
0.3902	0.96077	1132	0.492	−0.251	812	−11	−0.124	1.0000	1.03800	1115	1.034	0.000	776	0	0.000
0.4937	0.97224	1131	0.547	−0.243	804	−11	−0.140								

experimental density and viscosity of the pure components are compared with literature data.

3. Results and Discussion

The dynamic viscosity, density, speed of sound, excess molar volume, isentropic compressibility (determined by means of the Laplace equation, eq 3), and deviation in isentropic compressibility for the systems acetic acid with water, methanol, ethanol, ethyl acetate, and methyl acetate at T = (293.15, 298.15, and 303.15) K and atmospheric pressure are reported in Tables 2 to 6. The isentropic compressibility, the excess molar volume, the deviation in isentropic compressibility, and viscosity are calculated by the following equations:

$$k_s = \rho^{-1}u^{-2} \tag{3}$$

$$V^E = \sum_{i=1}^{N} x_i M_i(\rho^{-1} - \rho_i^{-1}) \tag{4}$$

$$\Delta\kappa_s = \kappa_s - \sum_{i=1}^{N} x_i \kappa_{s,i} \tag{5}$$

$$\Delta\eta = \eta - \sum_{i}^{N} x_i \eta_i \tag{6}$$

Table 4. Density, ρ, Speed of Sound, u, Dynamic Viscosity, η, Excess Molar Volume, V^E, Isentropic Compressibility, κ_s, Deviation in Isentropic Compressibility, $\Delta\kappa_s$, and Viscosity Deviation, $\Delta\eta$, of Acetic Acid (1) with Ethanol (2)

acetic acid (1) + ethanol (2)															
x_1	ρ / $g \cdot cm^{-3}$	u / $m \cdot s^{-1}$	$10^3\eta$ / Pa·s	V^E / $cm^3 \cdot mol^{-1}$	κ_s / $T \cdot Pa^{-1}$	$\Delta\kappa_s$ / $T \cdot Pa^{-1}$	$10^3\Delta\eta$ / Pa·s	x_1	ρ / $g \cdot cm^{-3}$	u / $m \cdot s^{-1}$	$10^3\eta$ / Pa·s	V^E / $cm^3 \cdot mol^{-1}$	κ_s / $T \cdot Pa^{-1}$	$\Delta\kappa_s$ / $T \cdot Pa^{-1}$	$10^3\Delta\eta$ / Pa·s
293.15 K															
0.0000	0.78975	1162	1.187	0.000	938	0	0.000	0.5981	0.95175	1196	1.432	−0.482	735	−74	0.231
0.0493	0.80350	1168	1.190	−0.086	913	−15	0.002	0.7031	0.97885	1192	1.444	−0.450	719	−67	0.240
0.1004	0.81730	1173	1.195	−0.138	889	−27	0.006	0.7973	1.00217	1184	1.419	−0.360	712	−53	0.213
0.1992	0.84480	1182	1.230	−0.284	847	−48	0.038	0.8979	1.02640	1171	1.338	−0.228	711	−33	0.129
0.2971	0.87159	1190	1.276	−0.382	810	−64	0.082	0.9515	1.03872	1161	1.275	−0.124	715	−17	0.065
0.3962	0.89837	1195	1.336	−0.449	780	−72	0.139	1.0000	1.04930	1149	1.211	0.000	722	0	0.000
0.4961	0.92497	1197	1.383	−0.481	755	−76	0.184								
298.15 K															
0.0000	0.78546	1145	1.082	0.000	972	0	0.000	0.5981	0.94659	1178	1.297	−0.483	761	−77	0.195
0.0493	0.79915	1151	1.083	−0.088	945	−15	−0.001	0.7031	0.97355	1175	1.310	−0.451	744	−70	0.205
0.1004	0.81287	1156	1.089	−0.138	921	−28	0.004	0.7973	0.99674	1166	1.291	−0.361	738	−56	0.183
0.1992	0.84020	1165	1.120	−0.285	877	−50	0.031	0.8979	1.02084	1153	1.225	−0.227	736	−34	0.113
0.2971	0.86686	1172	1.162	−0.384	839	−66	0.070	0.9515	1.03311	1143	1.172	−0.123	741	−18	0.059
0.3962	0.89350	1177	1.215	−0.450	808	−75	0.120	1.0000	1.04365	1132	1.115	0.000	748	0	0.000
0.4961	0.91996	1179	1.258	−0.483	781	−79	0.160								
303.15 K															
0.0000	0.78115	1128	0.987	0.000	1007	0	0.000	0.5981	0.94142	1160	1.183	−0.485	789	−80	0.168
0.0493	0.79478	1133	0.989	−0.089	979	−16	0.000	0.7031	0.96823	1157	1.198	−0.452	771	−73	0.178
0.1004	0.80839	1139	0.994	−0.138	954	−29	0.002	0.7973	0.99129	1149	1.181	−0.361	764	−58	0.157
0.1992	0.83558	1148	1.023	−0.285	908	−52	0.027	0.8979	1.01528	1136	1.126	−0.227	764	−36	0.097
0.2971	0.86209	1155	1.060	−0.384	869	−69	0.059	0.9515	1.02750	1126	1.084	−0.123	768	−19	0.052
0.3962	0.88860	1160	1.108	−0.452	837	−79	0.102	1.0000	1.03800	1115	1.034	0.000	776	0	0.000
0.4961	0.91493	1162	1.152	−0.485	809	−83	0.142								

Table 5. Density, ρ, Speed of Sound, u, Dynamic Viscosity, η, Excess Molar Volume, V^E, Isentropic Compressibility, κ_s, Deviation in Isentropic Compressibility, $\Delta\kappa_s$, and Viscosity Deviation, $\Delta\eta$, of Acetic Acid (1) with Methanol (2)

acetic acid (1) + methanol (2)															
x_1	ρ / $g \cdot cm^{-3}$	u / $m \cdot s^{-1}$	$10^3\eta$ / Pa·s	V^E / $cm^3 \cdot mol^{-1}$	κ_s / $T \cdot Pa^{-1}$	$\Delta\kappa_s$ / $T \cdot Pa^{-1}$	$10^3\Delta\eta$ / Pa·s	x_1	ρ / $g \cdot cm^{-3}$	u / $m \cdot s^{-1}$	$10^3\eta$ / Pa·s	V^E / $cm^3 \cdot mol^{-1}$	κ_s / $T \cdot Pa^{-1}$	$\Delta\kappa_s$ / $T \cdot Pa^{-1}$	$10^3\Delta\eta$ / Pa·s
293.15 K															
0.0000	0.79190	1121	0.585	0.000	1005	0	0.000	0.4992	0.95637	1196	1.161	−0.709	731	−132	0.264
0.0498	0.81192	1133	0.626	−0.115	960	−31	0.010	0.5996	0.98068	1198	1.274	−0.718	711	−125	0.314
0.1006	0.83139	1143	0.676	−0.220	920	−57	0.028	0.6998	1.00188	1195	1.352	−0.651	699	−108	0.329
0.2016	0.86761	1162	0.784	−0.403	853	−95	0.073	0.7969	1.02024	1187	1.380	−0.541	695	−84	0.296
0.2995	0.89977	1178	0.899	−0.549	801	−119	0.126	0.9555	1.04382	1162	1.283	−0.148	709	−25	0.100
0.4010	0.92999	1189	1.038	−0.654	761	−131	0.202	1.0000	1.04930	1149	1.211	0.000	722	0	0.000
298.15 K															
0.0000	0.78720	1104	0.545	0.000	1042	0	0.000	0.5996	0.97536	1181	1.162	−0.728	735	−131	0.275
0.0498	0.80717	1116	0.583	−0.118	994	−33	0.010	0.6998	0.99646	1178	1.229	−0.659	723	−113	0.285
0.1006	0.82660	1127	0.628	−0.225	952	−60	0.026	0.7969	1.01472	1170	1.260	−0.547	720	−88	0.261
0.2016	0.86271	1146	0.729	−0.412	883	−100	0.069	0.9000	1.03106	1156	1.224	−0.330	726	−51	0.166
0.2995	0.89477	1161	0.825	−0.560	829	−125	0.109	0.9555	1.03820	1145	1.177	−0.149	735	−26	0.087
0.4010	0.92488	1172	0.954	−0.666	787	−137	0.180	1.0000	1.04365	1132	1.115	0.000	748	0	0.000
0.4992	0.95116	1179	1.062	−0.721	756	−139	0.232								
303.15 K															
0.0000	0.78248	1088	0.508	0.000	1080	0	0.000	0.5996	0.97001	1164	1.062	−0.739	761	−137	0.239
0.0498	0.80241	1100	0.543	−0.121	1030	−35	0.009	0.6998	0.99101	1161	1.124	−0.668	748	−119	0.248
0.1006	0.82179	1111	0.585	−0.230	986	−63	0.024	0.7969	1.00919	1153	1.151	−0.553	745	−92	0.224
0.2016	0.85779	1130	0.678	−0.420	914	−105	0.064	0.9000	1.02545	1138	1.126	−0.333	752	−54	0.145
0.2995	0.88974	1145	0.765	−0.570	858	−131	0.099	0.9555	1.03256	1128	1.088	−0.150	762	−28	0.077
0.4010	0.91975	1156	0.879	−0.678	814	−144	0.160	1.0000	1.03800	1115	1.034	0.000	776	0	0.000
0.4992	0.94592	1162	0.975	−0.732	783	−145	0.204								

where ρ and ρ_i are the density of the mixture and the density of the pure components, respectively; M_i is the molar mass of the pure components; k_s is the isentropic compressibility of the mixture; $k_{s,i}$ is the isentropic compressibility of the pure components; x represents the mole fraction; and η and η_i are the dynamic viscosity of the mixture and the pure component, respectively.

The binary deviations at several temperatures were fit to a Redlich−Kister[5]-type equation

$$\Delta Q_{ij} = x_i x_j \sum_{p=0}^{M} B_p (x_i - x_j)^p \tag{7}$$

where ΔQ_{ij} is the excess property, x is the mole fraction, B_P is the fitting parameter, and M is the degree of the polynomic expansion, which was optimized using the F test.[16] The fitting parameters are given in Table 7 with the root-mean-square deviations. These are calculated from the values of the experimental and calculated properties and the number of experimental data and are represented by z_{exptl}, z_{calcd}, and n_{dat}, respectively.

$$\sigma = \left\{ \sum_{i}^{n_{dat}} \frac{(z_{exptl} - z_{calcd})^2}{n_{dat}} \right\}^{1/2} \tag{8}$$

Figures 1 and 2 show the fitted curves as well as excess

Table 6. Density, ρ, Speed of Sound, u, Dynamic Viscosity, η, Excess Molar Volume, V^E, Isentropic Compressibility, κ_s, Deviation in Isentropic Compressibility, $\Delta\kappa_s$, and Viscosity Deviation, $\Delta\eta$, of Acetic Acid (1) with Water (2)

acetic acid (1) + water (2)															
	ρ	u	$10^3\eta$	V^E	κ_s	$\Delta\kappa_s$	$10^3\Delta\eta$		ρ	u	$10^3\eta$	V^E	κ_s	$\Delta\kappa_s$	$10^3\Delta\eta$
x_1	g·cm^{-3}	m·s^{-1}	Pa·s	cm^3·mol^{-1}	T·Pa^{-1}	T·Pa^{-1}	Pa·s	x_1	g·cm^{-3}	m·s^{-1}	Pa·s	cm^3·mol^{-1}	T·Pa^{-1}	T·Pa^{-1}	Pa·s
293.15 K															
0.0000	0.99820	1483	1.003	0.000	456	0	0.000	0.6005	1.06880	1329	2.627	−1.103	530	−86	1.499
0.0503	1.01937	1528	1.304	−0.272	420	−49	0.291	0.7004	1.06655	1286	2.417	−0.995	567	−75	1.268
0.1009	1.03495	1537	1.578	−0.496	409	−74	0.554	0.8017	1.06278	1243	2.077	−0.799	609	−59	0.907
0.2018	1.05388	1509	2.031	−0.811	417	−93	0.986	0.8996	1.05735	1199	1.666	−0.493	657	−38	0.476
0.3006	1.06342	1465	2.355	−1.003	438	−97	1.289	0.9523	1.05356	1175	1.416	−0.266	688	−21	0.215
0.4015	1.06815	1418	2.559	−1.113	466	−97	1.472	1.0000	1.04930	1149	1.211	0.000	722	0	0.000
0.5012	1.06968	1373	2.652	−1.148	496	−93	1.545								
298.15 K															
0.0000	0.99705	1497	0.890	0.000	448	0	0.000	0.6005	1.06348	1314	2.300	−1.095	545	−83	1.275
0.0503	1.01724	1533	1.151	−0.266	418	−45	0.250	0.7004	1.06122	1270	2.129	−0.994	584	−74	1.081
0.1009	1.03204	1536	1.385	−0.486	410	−68	0.472	0.8017	1.05734	1226	1.850	−0.802	629	−59	0.780
0.2018	1.05000	1502	1.777	−0.798	422	−86	0.842	0.8996	1.05180	1183	1.503	−0.496	680	−38	0.411
0.3006	1.05883	1454	2.053	−0.985	447	−91	1.095	0.9523	1.04796	1157	1.294	−0.267	712	−21	0.190
0.4015	1.06342	1405	2.232	−1.105	477	−92	1.252	1.0000	1.04365	1132	1.115	0.000	748	0	0.000
0.5012	1.06477	1359	2.316	−1.145	509	−89	1.313								
303.15 K															
0.0000	0.99565	1509	0.797	0.000	441	0	0.000	0.6005	1.05824	1299	2.029	−1.092	560	−82	1.090
0.0503	1.01494	1537	1.023	−0.261	417	−41	0.214	0.7004	1.05591	1254	1.890	−0.997	602	−74	0.927
0.1009	1.02902	1535	1.226	−0.477	412	−62	0.405	0.8017	1.05190	1210	1.656	−0.805	650	−60	0.669
0.2018	1.04607	1494	1.571	−0.786	428	−80	0.726	0.8996	1.04625	1166	1.367	−0.498	703	−39	0.357
0.3006	1.05420	1443	1.809	−0.970	456	−86	0.941	0.9523	1.04235	1140	1.190	−0.269	738	−22	0.167
0.4015	1.05866	1392	1.965	−1.098	488	−88	1.073	1.0000	1.03800	1115	1.034	0.000	776	0	0.000
0.5012	1.05978	1344	2.046	−1.142	522	−86	1.130								

and deviation values for binary mixtures: acetic acid with ethyl acetate, methyl acetate, ethanol, methanol, and water at three temperatures (T = 293.15, 298.15, and 303.15 K). In Figure 1, we can observe how the excess molar volumes are negative over the entire composition range with over a minimum equimolar for all systems except for acetic acid (1) with ethyl acetate (2) and with methyl acetate (2), which present a minimum around x_1 = 0.3 and 0.4 mole fractions, respectively. The minimum of acid (1) with ethyl acetate (2) is more deviated from the equimolar composition than that of acid (1) with methyl acetate (2). In this system, the excess molar volume decreases as the temperature increases; however, for the other systems, this magnitude does show significant variation over the temperatures range. It can be also observed that the excess molar volume suffers little variations for the interaction of acetic acid with esters; however, these variations increases with the possibility of the formation of hydrogen bonds, being larger with water. In Figure 2, for deviations in isentropic compressibility, the behavior is similar to that for excess molar volumes with negative values observed over the entire composition range except for acetic acid with ethyl acetate, which presents negative and positive values. The acetic acid (1) with ethanol (2) and with methanol (2) systems present over a minimum equimolar, and for the acetic acid (1) with methyl acetate (2) and with water (2) systems, they present other minimum around x_1= 0.4 molar composition; however, the acetic acid (1) with ethyl acetate (2) system presents a minimum around x_1= 0.15 molar composition and a maximum around x_1= 0.7 molar composition.

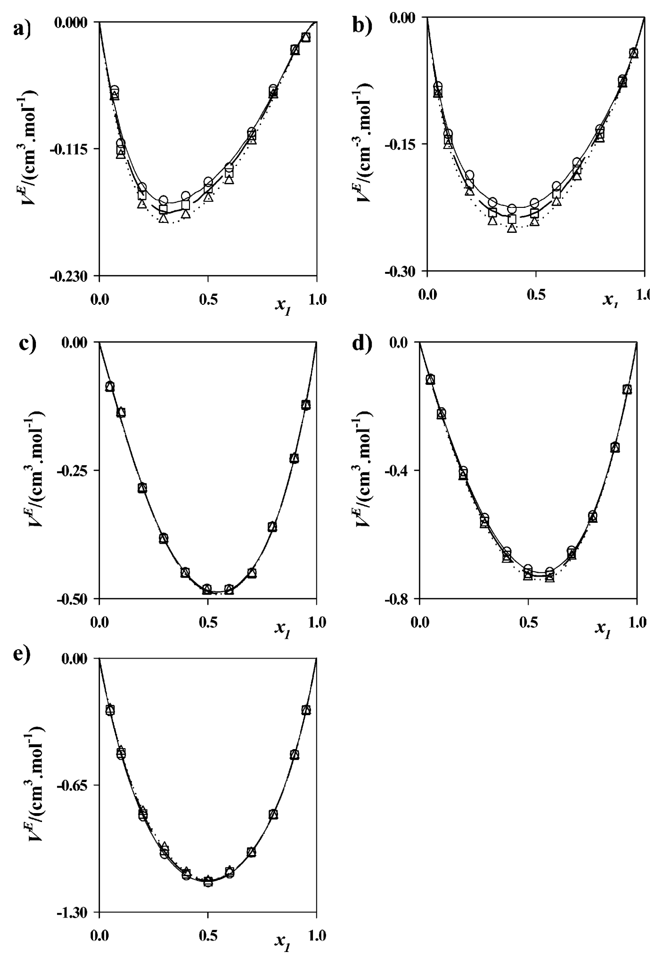

Figure 1. Excess molar volume, V^E, from the Redlich−Kister equation plotted against mole fraction at T = 293.15 K (○, −), T = 298.15 K (□, − −) and T = 303.15 K (△, ···) for the binary mixtures (a) acetic acid (1) + ethyl acetate (2), (b) acetic acid (1) + methyl acetate (2), (c) acetic acid (1) + ethanol (2), (d) acetic acid (1) + methanol (2), and (e) acetic acid (1) + water (2).

4. Correlation

The UNIQUAC equation is used to calculate the excess molar free energy of activation for flow, ΔG^E (eq 9), which it is related to the viscosity, ν, by

$$\ln(\nu M) = \sum_i x_i \ln(\nu_i M_i) + \frac{\Delta G^E}{RT} \qquad (9)$$

Table 7. Fitting Parameters and Root-Mean-Square Deviation, σ, for Binary Mixtures at T = (293.15, 298.15, and 303.15) K

property	T/K	B_0	B_1	B_2	B_3	B_4	σ
			Acetic Acid (1) + Ethyl Acetate(2)				
V^E/(cm^3·mol^{-1})	293.15	−0.5918	0.4414	−0.1821			0.007
	298.15	−0.6180	0.4723	−0.1900			0.007
	303.15	−0.6508	0.4998	−0.1983			0.007
$\Delta\kappa_s$/(T·Pa^{-1})	293.15	2.46	14.50	−0.85	20.81	−33.49	0.09
	298.15	5.77	19.02	−5.74	20.12	−28.62	0.11
	303.15	8.13	22.44	−7.82	23.78	−27.46	0.11
$10^3\Delta\eta$/(Pa·s)	293.15	−0.6478	−0.3272	−0.1420			0.004
	298.15	−0.5745	−0.2806	−0.0968			0.003
	303.15	−0.5202	−0.2426	−0.0669			0.003
			Acetic Acid (1) + Methyl Acetate (2)				
V^E/(cm^3·mol^{-1})	293.15	−0.8633	0.3481	−0.4563			0.006
	298.15	−0.9056	0.3782	−0.4774			0.006
	303.15	−0.9506	0.4022	−0.4902			0.007
$\Delta\kappa_s$/(T·Pa^{1-})	293.15	−39.46	1.38	−7.54	20.20	−46.96	0.16
	298.15	−41.46	4.21	−8.67	26.36	−54.61	0.17
	303.15	−43.02	7.10	−9.82	27.18	−56.66	0.19
$10^3\Delta\eta$/(Pa·s)	293.15	−0.7245	−0.2885	-			0.003
	298.15	−0.6381	−0.2422	-			0.002
	303.15	−0.5698	−0.2076	-			0.002
			Acetic Acid (1) + Ethanol (2)				
V^E/(cm^3·mol^{-1})	293.15	−1.9370	−0.4290	−0.2115			0.007
	298.15	−1.9448	−0.4248	−0.2054			0.007
	303.15	−1.9511	−0.4249	−0.1949			0.007
$\Delta\kappa_s$/(T·Pa^{1-})	293.15	−303.80	−24.95	−44.47			0.58
	298.15	−316.29	−263.39	−45.52			0.60
	303.15	−329.61	−27.75	−46.37			0.63
$10^3\Delta\eta$/ (Pa·s)	293.15	0.7671	0.8923	-			0.004
	298.15	0.6567	0.7724	-			0.002
	303.15	0.5672	0.6712	-			0.002
			Acetic Acid (1) + Methanol (2)				
V^E/(cm^3·mol^{-1})	293.15	−2.8372	−0.6736	−0.2417			0.005
	298.15	−2.8835	−0.6595	−0.2393			0.005
	303.15	−2.9290	−0.6465	−0.2376			0.005
$\Delta\kappa_s$/(T·Pa^{-1})	293.15	−527.20	57.62	−89.61			0.69
	298.15	−553.11	63.76	−95.89			0.72
	303.15	−579.84	68.75	−100.38			0.76
$10^3\Delta\eta$/(Pa·s)	293.15	1.0569	1.1673	0.2397			0.002
	298.15	0.9293	1.0060	0.2169			0.003
	303.15	0.8150	0.8495	0.1913			0.002
			Acetic Acid (1) + Water (2)				
V^E/(cm^3·mol^{-1})	293.15	−4.5608	−0.0194	−1.3672			0.004
	298.15	−4.5328	−0.0615	−1.3326			0.006
	303.15	−4.5134	−0.1433	−1.3074			0.007
$\Delta\kappa_s$/(T·Pa^{-1})	293.15	−372.84	88.48	−165.74	253.17	343.77	0.66
	298.15	−358.39	64.88	−156.74	219.93	−313.82	0.57
	303.15	−346.92	42.35	−150.52	191.66	−288.30	0.47
$10^3\Delta\eta$/(Pa·s)	293.15	6.2117	0.1118	−0.8343	−1.0852		0.006
	298.15	5.2772	0.1078	−0.6164	−0.8845		0.005
	303.15	4.5239	0.0525	−0.4856	−0.6571		0.004

These systems were correlated using the UNIQUAC equation and good results were obtained for acetic acid (1) with ethyl acetate (2) and with methyl acetate (2) systems, but because the other systems present a high interaction, it is necessary to use the modified UNIQUAC equation, which introduces a new temperature-dependent energy parameter.

$$\tau_{ij} = \exp -\left[\frac{a_{ij} + b_{ij}T}{RT}\right] \qquad (10)$$

The correlation has been performed with experimental data to minimize the following objective function

$$\mathrm{OF} = \sum \left|\frac{G^E_{calcd}/RT - G^E_{exptl}/RT}{G^E_{exptl}/RT}\right| \qquad (11)$$

where G^E_{calcd} is the calculated excess molar free energy and G^E_{exptl} is the experimental excess molar free energy. The fitting parameters with the root-mean-square deviations are reported in Table 8.

Figure 3 shows the viscosity deviation correlated by the UNIQUAC equation and by the modified UNIQUAC equation. The UNIQUAC equation fit the experimental data fairly well at several temperatures for the acetic acid (1) with ethyl acetate (2) system and the acetic acid (1) with methyl acetate (2) system. However, for the other systems with a high interaction, it is necessary to use the modified UNIQUAC equation; nevertheless, for the acetic acid (1) with ethanol (2) system, none of these equations show a good fit to the experimental data. For the viscosity deviation, positive values are observed over the entire composition range except for the acetic acid (1) with ethyl acetate (2) and methylacete (2) systems, which present negative values. The acetic acid (1) with methanol (2) and with ethanol (2) systems present a maximum around $x_1 = 0.7$ molar composition. However, for the acetic acid (1) with

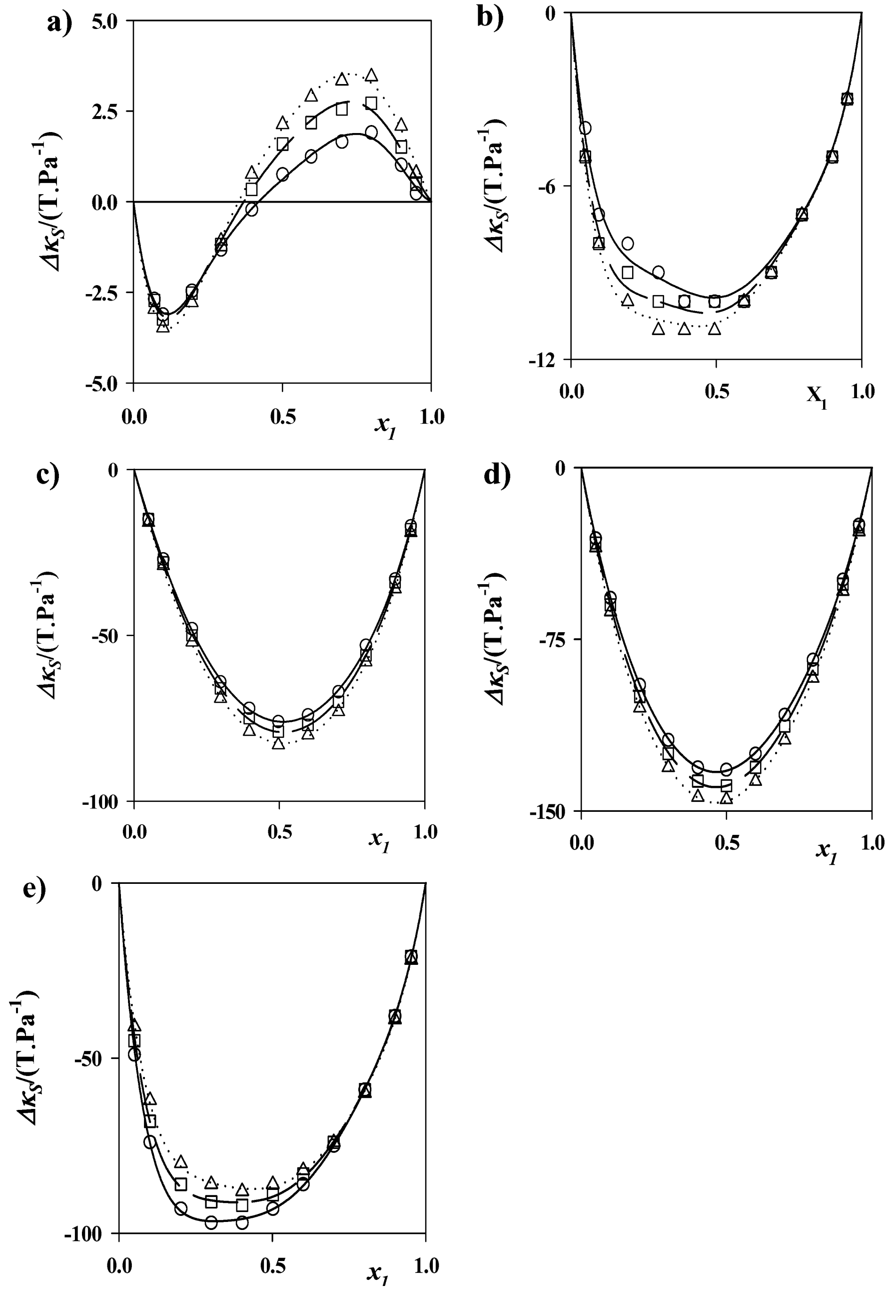

Figure 2. Deviation in isentropic compressibility, $\Delta\kappa_s$, from the Redlich−Kister equation plotted against mole fraction at T = 293.15 K (○, —), T = 298.15 K (□, − −) and T = 303.15 K (△, ···) for the binary mixtures (a) acetic acid (1) + ethyl acetate (2), (b) acetic acid (1) + methyl acetate (2), (c) acetic acid (1) + ethanol (2), (d) acetic acid (1) + methanol (2), and (e) acetic acid (1) + water (2).

Table 8. UNIQUAC Parameters and Root-Mean-Square Deviations, σ

binary system	UNIQUAC equation			modified UNIQUAC equation				
acetic acid (1) +	a_{12} / J·mol^{-1}	a_{21} / J·mol^{-1}	σ	a_{12} / J·mol^{-1}	a_{21} / J·mol^{-1}	b_{12} / J·mol^{-1}	b_{21} / J·mol^{-1}	σ
ethyl acetate (2)	−255.6	242.6	0.181					
methyl acetate (2)	−78.8	145.2	0.117					
ethanol (2)	−874.8	385.1	0.510	470.0	500.0	2.287	−3.154	0.436
methanol (2)	−1317.8	270.4	0.295	870.0	860.0	1.307	−3.720	0.225
water (2)	−1019.9	−870.2	0.623	4150.0	4100.0	−10.264	−11.100	0.472

water (2) system, the maximum is an equimolar composition, and for the acetic acid (1) with ethyl acetate (2) and with methyl acetate (2) systems, a minimum is present around x_1= 0.6 molar composition. We can observe in Figure 3 how the formation of hydrogen blends between different molecules provokes a decrease in the flow of mixtures.

5. Conclusions

In this work, the dynamic viscosities, densities, and speeds of sound of the binary systems acetic acid (1) with water (2), methanol (3), ethanol (4), ethyl acetate (5), and methyl acetate (6) at T = (273.15, 298.15, and 303.15) K and atmospheric pressure over the whole composition range have been determined.

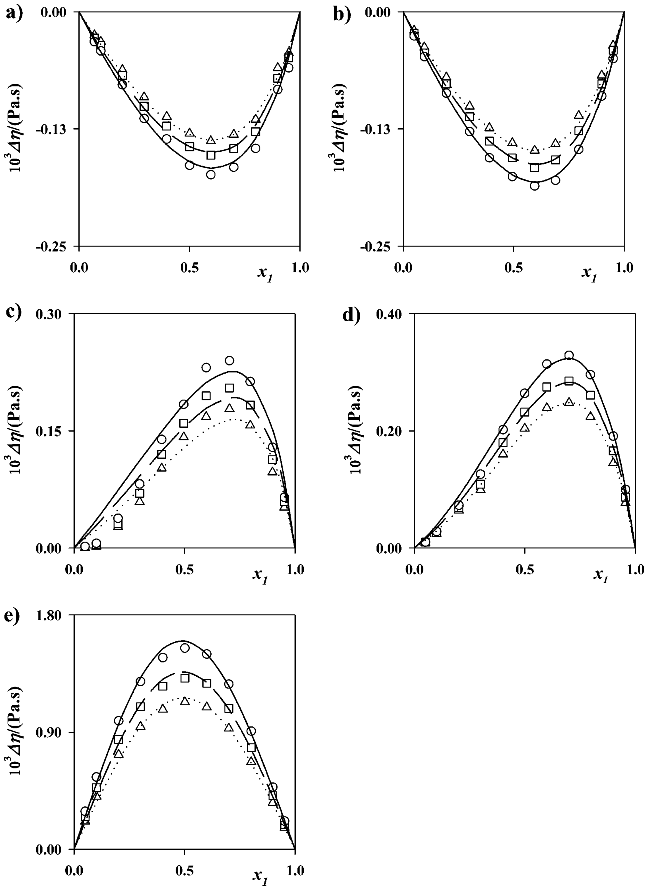

Figure 3. Viscosity deviation, $\Delta\eta$, from (a, b) the UNIQUAC equation and from (c−e) the modified UNIQUAC equation at T = 293.15 K (○, −), T = 298.15 K (□, − −), and T = 303.15 K (△, ···) for the binary mixtures (a) acetic acid (1) + ethyl acetate (2), (b) acetic acid (1) + methyl acetate (2), (c) acetic acid (1) + ethanol (2), (d) acetic acid (1) + methanol (2), and (e) acetic acid (1) + water (2).

The excess molar volumes, deviations in isentropic compresibility, and viscosity deviations were determined, and these data were fit to a Redlich−Kister equation to test the quality of the experimental values.

The correlation of the experimental data had been determined using the UNIQUAC equation and modified UNIQUAC equation. For those systems with a high interaction, it was necessary to use the modified UNIQUAC equation. These equations fit the experimental data of these binary systems fairly well, except for the acetic acid with ethanol system.

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Received for review December 23, 2003. Accepted August 15, 2004.

JE0342825