

# Temperature Dependence of Binary Mixing Properties for Acetone, Methanol, and Linear Aliphatic Alkanes (C<sub>6</sub>–C<sub>8</sub>)

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In this work we analyze the temperature dependence of the speed of sound, density, and refractive index of binary mixtures of acetone, methanol, and linear aliphatic alkanes (hexane, heptane, or octane) at atmospheric pressure. From the experimental measurements of these physical properties, the corresponding excess molar volumes, isentropic compressibility deviations, and refractive index deviations were derived. A set of variable-degree polynomials have been fitted to the results. Despite the large excess molar volumes obtained, they were satisfactorily correlated by a cubic equation of state with simple combinatorial mixing rules.

## Introduction

This paper is a continuation of our work concerned with thermodynamic studies of homogeneous and heterogeneous azeotropic liquid mixtures.<sup>1,2</sup> This work presents experimental speeds of sound, densities, and refractive indexes for the binary mixtures acetone + (methanol, hexane, heptane, or octane) and methanol + (hexane, heptane, or octane) at various temperatures and atmospheric pressure, covering the whole composition range. Excess molar volumes, refractive index deviations, and isentropic compressibility deviations were calculated, and polynomials were fitted to the results. The application of equations of state for predicting the excess molar volumes, as well as other mixing properties, demonstrates that a satisfactory prediction can be obtained in polar/self-associative multicomponent or partially miscible systems using simple mixing rules, critical properties, and acentric factors for the pure components and binary interaction parameters.<sup>2</sup>

## Experimental Section

Merck Lichrosolv quality chemicals were used to prepare the samples. The pure components, which had recently been acquired and stored in an inert argon atmosphere (<3 ppmv in water) as soon as the bottles were opened, were degassed with an ultrasound technique and stored over freshly activated molecular sieves type 4 Å or 3 Å, 1.6 mm, for several days before use. The main physical properties were determined for each component, and the results are shown together with literature values in Table 1. Precautions were taken to reduce evaporation errors during sample preparation. The solvents were analyzed by GLC using a HP 6890 GC Series System chromatograph equipped with a flame ionization detector and a HP-INNOWax 19091N-133 column of cross-linked poly(ethylene glycol) (30

**Table 1. Comparison of Data with Literature Values for Pure Liquids at 298.15 K**

component	$\rho/\text{g}\cdot\text{cm}^{-3}$		$n_D$		$u/\text{m}\cdot\text{s}^{-1}$	
	exp	lit. <sup>3</sup>	exp	lit. <sup>3</sup>	exp	lit.
acetone	0.7844	0.785 47	1.355 80	1.355 96	1161.0	1160.6 <sup>4</sup>
methanol	0.7865	0.786 64	1.326 45	1.326 52	1102.1	1102 <sup>5</sup>
hexane	0.6551	0.654 84	1.372 34	1.372 26	1077.0	1076.37 <sup>6</sup>
heptane	0.6794	0.679 46	1.385 12	1.385 11	1130.5	1129.85 <sup>6</sup>
octane	0.6985	0.698 62	1.395 14	1.395 05	1172.1	1172.02 <sup>6</sup>

m  $\times$  2.5  $\times$  10<sup>-4</sup> m  $\times$  2.5  $\times$  10<sup>-7</sup> m film thickness). The injector and detector temperatures were maintained at 448.15 K and 473.15 K, respectively. The column temperature was maintained at 313.15 K, and the flow rate of nitrogen carrier gas was 6  $\times$  10<sup>-7</sup> mL/min. The analysis showed that the major peak area exceeds 99.8 mass % for acetone and methanol and 99.5 mass % for alkanes, with maximum water contents of 6.8  $\times$  10<sup>-3</sup>, 1.5  $\times$  10<sup>-2</sup>, 7.8  $\times$  10<sup>-4</sup>, 8.1  $\times$  10<sup>-4</sup>, and 8.0  $\times$  10<sup>-4</sup> mass % (Metrohm 737 KF coulometer), for acetone, methanol, and alkanes (C<sub>6</sub>–C<sub>8</sub>), respectively. The samples were prepared by mass using a Mettler AE-240 balance with a precision of  $\pm$ 10<sup>-4</sup> g. A PolyScience controller bath model 9510, with a temperature stability of  $\pm$ 10<sup>-2</sup> K, was used to thermostat the samples before experimental measurement, at least 30 min. The densities and speeds of sound of the mixtures and pure components were measured with an Anton Paar DSA-48 densimeter and sound analyzer with an uncertainty of  $\pm$ 10<sup>-4</sup> g $\cdot$ cm<sup>-3</sup> and  $\pm$ 5  $\times$  10<sup>-1</sup> m $\cdot$ s<sup>-1</sup>, respectively. The refractive indices were measured with an automatic refractometer (ABBEMAT-HP Dr. Kernchen) with an uncertainty of  $\pm$ 5  $\times$  10<sup>-5</sup>. Both apparatus calibrations were performed periodically with Millipore quality water and air. The uncertainties were estimated as better than  $\pm$ 10<sup>-2</sup> cm<sup>3</sup> $\cdot$ mol<sup>-1</sup> for excess molar volumes,  $\pm$ 10<sup>-4</sup> for refractive index deviations, and  $\pm$ 1 TPa<sup>-1</sup> for isentropic compressibility deviations.

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**Table 2. Densities,  $\rho$ , Refractive Indices,  $n_D$ , Speeds of Sound,  $u$ , Isentropic Compressibilities,  $\kappa_S$ , and Excess Molar Volumes,  $V^E$ , for Acetone (1) + (Methanol or Hexane or Heptane or Octane) (2) and Methanol (1) + (Hexane or Heptane or Octane) (2) at Different Temperatures**

$x_1$	$\rho$ g·cm <sup>-3</sup>	$n_D$	$u$ m·s <sup>-1</sup>	$\kappa_S$ TPa <sup>-1</sup>	$V^E$ cm <sup>3</sup> ·mol <sup>-1</sup>	$x_1$	$\rho$ g·cm <sup>-3</sup>	$n_D$	$u$ m·s <sup>-1</sup>	$\kappa_S$ TPa <sup>-1</sup>	$V^E$ cm <sup>3</sup> ·mol <sup>-1</sup>
Acetone (1) + Methanol (2), $T = 278.15$ K											
0.0000	0.8052		1169.2	908.5	0.000	0.5461	0.8111		1236.5	806.4	-0.34
0.0339	0.8066		1177.0	894.9	-0.07	0.6481	0.8105		1241.8	800.1	-0.30
0.0783	0.8078		1186.0	880.1	-0.12	0.7458	0.8098		1246.9	794.3	-0.25
0.1615	0.8095		1199.4	858.7	-0.22	0.8427	0.8089		1250.3	790.9	-0.18
0.2570	0.8106		1211.7	840.2	-0.28	0.8972	0.8082		1250.6	791.2	-0.12
0.3392	0.8112		1220.3	827.8	-0.32	0.9576	0.8074		1250.9	791.6	-0.05
0.4454	0.8113		1229.5	815.4	-0.34	1.0000	0.8069		1250.5	792.5	0.00
$T = 288.15$ K											
0.0000	0.7960	1.33070	1135.3	974.7	0.00	0.5470	0.8004	1.35421	1195.4	874.3	-0.33
0.0357	0.7971	1.33282	1143.0	960.3	-0.06	0.6545	0.7997	1.35666	1200.8	867.3	-0.30
0.0781	0.7981	1.33544	1150.5	946.7	-0.11	0.7414	0.7990	1.35834	1204.0	863.4	-0.26
0.1636	0.7996	1.34024	1163.4	924.0	-0.21	0.8339	0.7979	1.35974	1205.9	861.8	-0.18
0.2673	0.8006	1.34511	1174.9	904.8	-0.29	0.9042	0.7971	1.36066	1206.8	861.5	-0.11
0.3442	0.8009	1.34815	1182.2	893.4	-0.32	0.9232	0.7969	1.36085	1206.7	861.7	-0.10
0.4551	0.8008	1.35178	1190.3	881.4	-0.34	1.0000	0.7958	1.36161	1205.9	864.1	0.00
Acetone (1) + Hexane (2), $T = 278.15$ K											
0.0000	0.6728		1167.8	1089.8	0.00	0.5451	0.7203		1167.4	1018.7	0.88
0.0415	0.6750		1164.6	1092.4	0.18	0.6475	0.7345		1176.2	984.1	0.80
0.0859	0.6775		1162.0	1093.2	0.37	0.7684	0.7545		1192.5	932.1	0.63
0.1781	0.6838		1158.6	1089.4	0.61	0.8779	0.7765		1214.5	873.1	0.39
0.2714	0.6913		1158.0	1078.8	0.77	0.9405	0.7912		1231.1	833.9	0.20
0.3496	0.6985		1158.8	1066.1	0.84	1.0000	0.8069		1250.5	792.5	0.00
0.4586	0.7099		1162.4	1042.5	0.89						
$T = 288.15$ K											
0.0000	0.6646	1.37847	1123.2	1192.7	0.00	0.5481	0.7110	1.36796	1122.4	1116.5	0.95
0.0899	0.6693	1.37648	1116.8	1198.0	0.41	0.6869	0.7305	1.36577	1135.9	1061.0	0.82
0.1745	0.6749	1.37454	1113.7	1194.7	0.65	0.7592	0.7425	1.36461	1146.2	1025.2	0.70
0.2642	0.6817	1.37285	1112.6	1185.1	0.83	0.8793	0.7661	1.36296	1169.8	953.8	0.41
0.3479	0.6891	1.37139	1113.5	1170.5	0.93	0.9355	0.7791	1.36229	1185.3	913.7	0.23
0.4492	0.6994	1.36960	1116.6	1146.8	0.97	1.0000	0.7958	1.36161	1205.9	864.1	0.00
$T = 298.15$ K											
0.0000	0.6551	1.37234	1077.0	1316.1	0.00	0.5551	0.7011	1.36168	1076.7	1230.4	1.04
0.0381	0.6568	1.37156	1074.0	1320.0	0.22	0.6590	0.7154	1.36011	1086.5	1184.0	0.93
0.0761	0.6588	1.37074	1071.4	1322.3	0.39	0.7640	0.7325	1.35867	1101.2	1125.7	0.73
0.1645	0.6647	1.36881	1068.1	1318.8	0.61	0.8842	0.7559	1.35706	1125.9	1043.6	0.44
0.2754	0.6725	1.36670	1066.2	1308.0	0.93	0.9413	0.7692	1.35638	1141.7	997.5	0.23
0.3515	0.6791	1.36519	1067.1	1293.2	1.02	1.0000	0.7844	1.35580	1161.0	945.9	0.00
0.4510	0.6890	1.36341	1070.8	1265.8	1.07						
Acetone (1) + Heptane (2), $T = 278.15$ K											
0.0000	0.6963		1217	970.0	0.00	0.6060	0.7377		1196	947.0	0.91
0.0641	0.6985		1210	977.4	0.29	0.6895	0.7479		1200	928.2	0.83
0.0863	0.6994		1208	979.0	0.37	0.7989	0.7642		1210	894.4	0.64
0.2025	0.7051		1201	983.0	0.67	0.8492	0.7731		1216	874.4	0.52
0.2948	0.7105		1197	981.8	0.85	0.9318	0.7901		1232	834.1	0.26
0.3993	0.7181		1195	975.5	0.93	1.0000	0.8069		1251	792.5	0.00
0.4956	0.7264		1194	964.9	0.95						
$T = 288.15$ K											
0.0000	0.6880	1.38999	1173	1055.9	0.00	0.5952	0.7265	1.37439	1151	1039.0	1.02
0.0530	0.6896	1.38860	1168	1062.7	0.28	0.6900	0.7378	1.37143	1155	1015.7	0.91
0.0901	0.6910	1.38770	1164	1067.4	0.42	0.7875	0.7518	1.36833	1163	982.9	0.74
0.2010	0.6961	1.38503	1157	1073.4	0.75	0.8935	0.7709	1.36489	1179	933.5	0.44
0.2930	0.7014	1.38264	1153	1072.8	0.91	0.9422	0.7813	1.36336	1190	903.2	0.27
0.4058	0.7092	1.37976	1150	1066.1	1.03	1.0000	0.7958	1.36161	1206	864.1	0.00
0.4896	0.7162	1.37748	1150	1056.6	1.04						
$T = 298.15$ K											
0.0000	0.6794	1.38512	1130.5	1151.6	0.00	0.5840	0.7152	1.36944	1106.1	1142.8	1.11
0.0694	0.6815	1.38316	1122.8	1164.0	0.35	0.6627	0.7240	1.36694	1109.2	1122.7	1.03
0.1121	0.6831	1.38211	1119.3	1168.5	0.52	0.7002	0.7286	1.36564	1111.3	1111.4	0.99
0.1703	0.6856	1.38066	1115.1	1173.0	0.71	0.7345	0.7332	1.36457	1113.8	1099.5	0.92
0.2263	0.6884	1.37919	1111.7	1175.4	0.85	0.7697	0.7383	1.36330	1117.0	1085.6	0.85
0.3004	0.6925	1.37728	1108.5	1175.2	1.00	0.7978	0.7426	1.36242	1120.0	1073.6	0.79
0.3645	0.6967	1.37561	1106.6	1172.1	1.07	0.8520	0.7519	1.36050	1127.3	1046.5	0.62
0.4505	0.7031	1.37331	1105.1	1164.6	1.13	0.9014	0.7614	1.35892	1136.1	1017.6	0.45
0.4968	0.7069	1.37201	1105.0	1158.7	1.15	0.9510	0.7721	1.35727	1147.2	984.1	0.25
0.5000	0.7072	1.37191	1105.0	1158.2	1.14	0.9780	0.7787	1.35645	1154.7	963.1	0.12
0.5447	0.7113	1.37060	1105.4	1150.6	1.13	1.0000	0.7844	1.35580	1161.0	945.9	0.00

**Table 2. (Continued)**

$x_1$	$\rho$ g·cm <sup>-3</sup>	$n_D$	$u$ m·s <sup>-1</sup>	$\kappa_S$ TPa <sup>-1</sup>	$V^E$ cm <sup>3</sup> ·mol <sup>-1</sup>	$x_1$	$\rho$ g·cm <sup>-3</sup>	$n_D$	$u$ m·s <sup>-1</sup>	$\kappa_S$ TPa <sup>-1</sup>	$V^E$ cm <sup>3</sup> ·mol <sup>-1</sup>
Acetone (1) + Octane (2), $T = 278.15$ K											
0.0000	0.7146		1256	887.7	0.00	0.6002	0.7451		1218	905.4	0.97
0.0580	0.7159		1249	895.7	0.26	0.6839	0.7534		1217	896.0	0.89
0.1060	0.7172		1244	900.9	0.44	0.7805	0.7652		1220	878.1	0.74
0.1928	0.7203		1237	907.7	0.65	0.8926	0.7831		1229	845.0	0.45
0.3030	0.7250		1229	913.0	0.87	0.9348	0.7916		1236	827.5	0.29
0.3928	0.7299		1224	913.8	0.95	1.0000	0.8069		1251	792.5	0.00
0.4920	0.7364		1220	912.1	0.99						
$T = 288.15$ K											
0.0000	0.7066	1.40006	1214	961.0	0.00	0.5980	0.7351	1.38100	1173	988.3	1.08
0.0530	0.7076	1.39840	1207	970.1	0.27	0.6845	0.7434	1.37722	1174	976.6	1.00
0.1003	0.7088	1.39768	1202	976.4	0.45	0.7971	0.7572	1.37210	1176	955.2	0.77
0.1926	0.7117	1.39495	1194	986.0	0.73	0.8938	0.7726	1.36727	1184	922.7	0.49
0.3024	0.7162	1.39150	1186	992.9	0.94	0.9411	0.7820	1.36470	1192	900.2	0.29
0.3911	0.7207	1.38871	1181	995.5	1.05	1.0000	0.7958	1.36161	1206	864.1	0.00
0.4892	0.7267	1.38520	1176	994.6	1.11						
$T = 298.15$ K											
0.000	0.6985	1.39514	1172.1	1042.2	0.00	0.577	0.7237	1.37629	1130.0	1082.1	1.17
0.043	0.6992	1.39392	1166.9	1050.3	0.23	0.656	0.7306	1.37305	1128.9	1073.9	1.11
0.087	0.7001	1.39250	1162.3	1057.4	0.43	0.726	0.7378	1.36988	1129.3	1062.8	1.00
0.103	0.7005	1.39218	1161.1	1058.9	0.49	0.784	0.7448	1.36703	1131.3	1049.2	0.89
0.184	0.7029	1.38970	1152.4	1071.3	0.74	0.845	0.7534	1.36417	1135.0	1030.3	0.72
0.184	0.7029	1.38975	1152.6	1070.9	0.74	0.895	0.7618	1.36155	1140.4	1009.4	0.53
0.257	0.7055	1.38754	1146.6	1078.2	0.92	0.945	0.7715	1.35879	1148.3	983.1	0.31
0.304	0.7074	1.38594	1143.2	1081.6	1.02	0.987	0.7810	1.35649	1157.4	955.8	0.09
0.375	0.7108	1.38354	1138.8	1084.8	1.11	1.000	0.7844	1.35580	1161.0	945.9	0.00
0.481	0.7170	1.38005	1133.7	1085.2	1.16						
Methanol (1) + Hexane (2), $T = 278.15$ K											
0.0000	0.6728		1167.8	1089.8	0.00	0.8772	0.7592		1136.6	1019.5	0.33
0.0279	0.6737		1163.8	1096.0	0.05	0.9040	0.7670		1140.0	1003.3	0.28
0.0953	0.6761		1158.9	1101.2	0.16	0.9569	0.7857		1151.9	959.2	0.15
0.1175	0.6769		1157.5	1102.6	0.20	1.0000	0.8052		1169.2	908.5	0.00
$T = 288.15$ K											
0.0000	0.6646	1.37847	1123.2	1192.7	0.00	0.8630	0.7466	1.34398	1098.6	1109.7	0.35
0.0787	0.6665	1.37638	1114.5	1208.0	0.28	0.9015	0.7571	1.34062	1102.9	1085.9	0.30
0.1022	0.6673	1.37544	1112.8	1210.1	0.32	0.9463	0.7726	1.33645	1114.4	1042.2	0.18
0.1357	0.6685	1.37425	1111.2	1211.5	0.39	1.0000	0.7960	1.33070	1135.3	974.7	0.00
0.8532	0.7438	1.34474	1096.6	1118.0	0.38						
Methanol (1) + Heptane (2), $T = 278.15$ K											
0.0000	0.6963		1216.8	970.0	0.00	0.9268	0.7771		1154.5	965.5	0.24
0.0383	0.6970		1212.0	976.8	0.10	0.9410	0.7815		1155.7	958.1	0.21
0.0499	0.6973		1210.9	978.0	0.11	0.9712	0.7924		1160.1	937.7	0.12
0.0772	0.6980		1209.1	980.1	0.15	1.0000	0.8052		1169.2	908.5	0.00
$T = 288.15$ K											
0.0000	0.6880	1.38999	1173	1055.9	0.00	0.9169	0.7646	1.34289	1117	1048.6	0.30
0.0446	0.6887	1.38958	1168	1064.8	0.14	0.9412	0.7720	1.33979	1119	1033.8	0.25
0.0744	0.6894	1.38852	1165	1068.5	0.19	0.9702	0.7826	1.33547	1126	1008.6	0.14
0.0901	0.6898	1.38825	1164	1069.6	0.21	1.0000	0.7960	1.33070	1135	974.7	0.00
0.1022	0.6901	1.38788	1163	1071.0	0.23						
Methanol (1) + Octane (2), $T = 278.15$ K											
0.0000	0.7146		1255.5	887.7	0.00	0.9568	0.7880		1162.5	939.0	0.19
0.0164	0.7147		1253.2	890.9	0.06	0.9668	0.7913		1163.1	934.2	0.16
0.0253	0.7148		1252.5	891.8	0.08	0.9817	0.7971		1164.9	924.6	0.09
0.0624	0.7153		1249.0	896.2	0.17	1.0000	0.8052		1169.2	908.5	0.00
$T = 288.15$ K											
0.0000	0.7066	1.40006	1213.5	961.0	0.00	0.9527	0.7772	1.34059	1127.1	1012.9	0.23
0.0287	0.7068	1.39965	1209.6	967.0	0.10	0.9657	0.7816	1.33796	1128.6	1004.6	0.18
0.0568	0.7072	1.39919	1207.1	970.5	0.16	0.9808	0.7875	1.33473	1130.3	993.9	0.11
0.0667	0.7073	1.39876	1206.4	971.4	0.19	1.0000	0.7960	1.33070	1135.3	974.7	0.00

**Results and Discussion**

The experimental data of speed of sound, density, and refractive index for the binary systems as a function of

temperature are reported in Table 2. The isentropic compressibility deviations, refractive index deviations, and excess molar volumes were evaluated for each composition

**Table 3. Parameters of Eq 4 and Root Mean Square Deviations,  $\sigma$** 

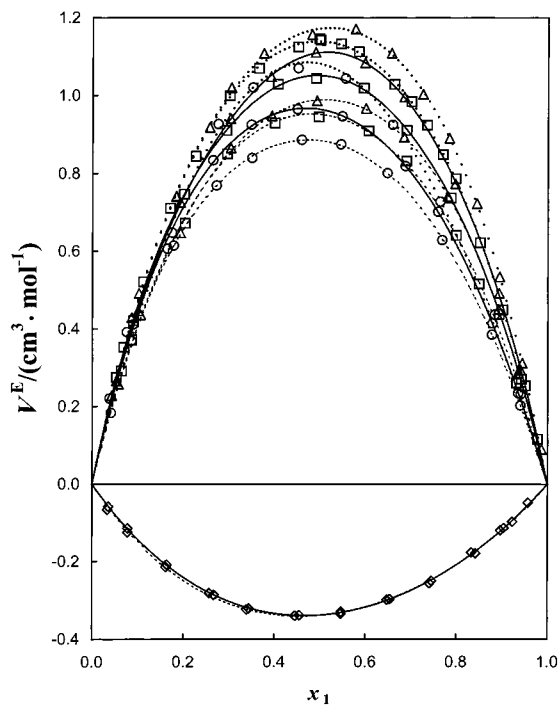
	$A_0$	$A_1$	$A_2$	$A_3$	$A_4$	$A_5$	$A_6$	$\sigma$
Acetone (1) + Methanol (2), $T = 278.15$ K								
$V^E/\text{cm}^3\cdot\text{mol}^{-1}$	-1.3555	$2.0011 \times 10^{-1}$	$-2.1241 \times 10^{-1}$					0.005 $\text{cm}^3\cdot\text{mol}^{-1}$
$\delta\kappa_S/\text{TPa}^{-1}$	$-1.5966 \times 10^2$	$5.3779 \times 10^1$	$-6.4076 \times 10^1$		$2.1494 \times 10^1$			0.4 $\text{TPa}^{-1}$
$T = 288.15$ K								
$V^E/\text{cm}^3\cdot\text{mol}^{-1}$	-1.3526	$1.6393 \times 10^{-1}$	$-1.4618 \times 10^{-1}$					0.003 $\text{cm}^3\cdot\text{mol}^{-1}$
$\delta n_D$	$2.7763 \times 10^{-2}$	$-6.7887 \times 10^{-3}$						0.0001
$\delta\kappa_S/\text{TPa}^{-1}$	$-1.6653 \times 10^2$	$5.4609 \times 10^1$	$-6.2231 \times 10^1$		$2.2749 \times 10^1$			0.3 $\text{TPa}^{-1}$
Acetone (1) + Hexane (2), $T = 278.15$ K								
$V^E/\text{cm}^3\cdot\text{mol}^{-1}$	3.5369	$-2.9013 \times 10^{-1}$	$8.2738 \times 10^{-1}$	$-4.6809 \times 10^{-1}$				0.004 $\text{cm}^3\cdot\text{mol}^{-1}$
$\delta\kappa_S/\text{TPa}^{-1}$	$3.6227 \times 10^2$	$4.7966 \times 10^1$	$4.6228 \times 10^1$	$-2.5762 \times 10^1$				0.1 $\text{TPa}^{-1}$
$T = 288.15$ K								
$V^E/\text{cm}^3\cdot\text{mol}^{-1}$	3.8577	$-3.9330 \times 10^{-1}$	$8.4494 \times 10^{-1}$	$-3.5548 \times 10^{-1}$				0.005 $\text{cm}^3\cdot\text{mol}^{-1}$
$\delta n_D$	$-5.1469 \times 10^{-3}$	$3.0847 \times 10^{-4}$	$-2.4752 \times 10^{-3}$					0.0001
$\delta\kappa_S/\text{TPa}^{-1}$	$4.1480 \times 10^2$	$4.5556 \times 10^1$	$5.0952 \times 10^1$	$-2.4236 \times 10^1$				0.2 $\text{TPa}^{-1}$
$T = 298.15$ K								
$V^E/\text{cm}^3\cdot\text{mol}^{-1}$	4.3252	$-5.2555 \times 10^{-1}$						0.028 $\text{cm}^3\cdot\text{mol}^{-1}$
$\delta n_D$	$-5.8591 \times 10^{-3}$	$-4.0765 \times 10^{-4}$						0.0001
$\delta\kappa_S/\text{TPa}^{-1}$	$4.7828 \times 10^2$	$4.1930 \times 10^1$	$4.4742 \times 10^1$					0.6 $\text{TPa}^{-1}$
Acetone (1) + Heptane (2), $T = 278.15$ K								
$V^E/\text{cm}^3\cdot\text{mol}^{-1}$	3.8066	$-2.3625 \times 10^{-1}$	$8.8276 \times 10^{-1}$					0.009 $\text{cm}^3\cdot\text{mol}^{-1}$
$\delta\kappa_S/\text{TPa}^{-1}$	$3.3240 \times 10^2$	$8.9282 \times 10^1$	$7.2486 \times 10^1$					0.1 $\text{TPa}^{-1}$
$T = 288.15$ K								
$V^E/\text{cm}^3\cdot\text{mol}^{-1}$	4.2062	$-9.6491 \times 10^{-2}$	$6.7911 \times 10^{-1}$	$-2.6622 \times 10^{-1}$	$6.4815 \times 10^{-1}$			0.005 $\text{cm}^3\cdot\text{mol}^{-1}$
$\delta n_D$	$5.5606 \times 10^{-3}$	$4.3910 \times 10^{-4}$	$-6.9283 \times 10^{-3}$	$-3.9123 \times 10^{-3}$	$1.4007 \times 10^{-2}$	$3.7578 \times 10^{-3}$	$-1.3920 \times 10^{-2}$	0.0001
$\delta\kappa_S/\text{TPa}^{-1}$	$3.8159 \times 10^2$	$1.0169 \times 10^2$	$7.6072 \times 10^1$					0.4 $\text{TPa}^{-1}$
$T = 298.15$ K								
$V^E/\text{cm}^3\cdot\text{mol}^{-1}$	4.5550	$-7.3191 \times 10^{-2}$	$9.6669 \times 10^{-1}$					0.005 $\text{cm}^3\cdot\text{mol}^{-1}$
$\delta n_D$	$5.8150 \times 10^{-3}$	$9.6104 \times 10^{-4}$	$-5.3967 \times 10^{-3}$	$-1.8635 \times 10^{-3}$				0.0001
$\delta\kappa_S/\text{TPa}^{-1}$	$4.3712 \times 10^2$	$1.1046 \times 10^2$	$8.3709 \times 10^1$					0.2 $\text{TPa}^{-1}$
Acetone (1) + Octane (2), $T = 278.15$ K								
$V^E/\text{cm}^3\cdot\text{mol}^{-1}$	3.9562	$1.1340 \times 10^{-1}$	$9.9776 \times 10^{-1}$					0.007 $\text{cm}^3\cdot\text{mol}^{-1}$
$\delta\kappa_S/\text{TPa}^{-1}$	$2.8665 \times 10^2$	$1.0776 \times 10^2$	$7.7247 \times 10^1$	$2.6745 \times 10^1$	$2.3530 \times 10^1$			0.1 $\text{TPa}^{-1}$
$T = 288.15$ K								
$V^E/\text{cm}^3\cdot\text{mol}^{-1}$	4.4433	$2.4089 \times 10^{-1}$	$5.1088 \times 10^{-1}$	$-2.1948 \times 10^{-1}$	$7.4434 \times 10^{-1}$			0.004 $\text{cm}^3\cdot\text{mol}^{-1}$
$\delta n_D$	$1.5682 \times 10^{-2}$	$1.6221 \times 10^{-3}$						0.0001
$\delta\kappa_S/\text{TPa}^{-1}$	$3.2640 \times 10^2$	$1.1628 \times 10^2$	$7.4858 \times 10^1$	$4.7627 \times 10^1$	$5.4595 \times 10^1$			0.4 $\text{TPa}^{-1}$
$T = 298.15$ K								
$V^E/\text{cm}^3\cdot\text{mol}^{-1}$	4.6888	$2.8812 \times 10^{-1}$	1.2647					0.008 $\text{cm}^3\cdot\text{mol}^{-1}$
$\delta n_D$	$1.5168 \times 10^{-2}$	$3.8216 \times 10^{-3}$	$-2.0230 \times 10^{-3}$					0.0001
$\delta\kappa_S/\text{TPa}^{-1}$	$3.6506 \times 10^2$	$1.3875 \times 10^2$	$1.0940 \times 10^2$	$4.9706 \times 10^1$				0.4 $\text{TPa}^{-1}$
Methanol (1) + Hexane (2), $T = 278.15$ K								
$V^E/\text{cm}^3\cdot\text{mol}^{-1}$	1.8956	$6.3408 \times 10^{-2}$	1.0156	1.1721				0.003 $\text{cm}^3\cdot\text{mol}^{-1}$
$\delta\kappa_S/\text{TPa}^{-1}$	$2.6621 \times 10^2$	$3.3957 \times 10^2$	$5.3588 \times 10^2$					0.6 $\text{TPa}^{-1}$
$T = 288.15$ K								
$V^E/\text{cm}^3\cdot\text{mol}^{-1}$	1.9338	$-1.6456 \times 10^{-1}$	2.3533					0.008 $\text{cm}^3\cdot\text{mol}^{-1}$
$\delta n_D$	$3.9147 \times 10^{-2}$	$2.4402 \times 10^{-2}$						0.0001
$\delta\kappa_S/\text{TPa}^{-1}$	$3.8431 \times 10^2$	$3.4429 \times 10^2$	$5.1422 \times 10^2$					1 $\text{TPa}^{-1}$
Methanol (1) + Heptane (2), $T = 278.15$ K								
$V^E/\text{cm}^3\cdot\text{mol}^{-1}$	$-3.5959 \times 10^{-1}$	$8.3112 \times 10^{-1}$	4.3653					0.002 $\text{cm}^3\cdot\text{mol}^{-1}$
$\delta\kappa_S/\text{TPa}^{-1}$	$-6.6318 \times 10^1$	$9.1228 \times 10^1$	$7.6546 \times 10^2$	$3.2531 \times 10^2$				0.2 $\text{TPa}^{-1}$
$T = 288.15$ K								
$V^E/\text{cm}^3\cdot\text{mol}^{-1}$	$4.9051 \times 10^{-1}$	$7.8444 \times 10^{-1}$	4.1352					0.004 $\text{cm}^3\cdot\text{mol}^{-1}$
$\delta n_D$	$3.6856 \times 10^{-2}$	$3.0418 \times 10^{-2}$	$4.7358 \times 10^{-2}$					0.0001
$\delta\kappa_S/\text{TPa}^{-1}$	$1.1762 \times 10^2$	$1.7353 \times 10^2$	$6.5656 \times 10^2$	$2.8302 \times 10^2$				0.3 $\text{TPa}^{-1}$
Methanol (1) + Octane (2), $T = 278.15$ K								
$V^E/\text{cm}^3\cdot\text{mol}^{-1}$	$-7.9270 \times 10^{-1}$	$8.1062 \times 10^{-1}$	5.6302					0.003 $\text{cm}^3\cdot\text{mol}^{-1}$
$\delta\kappa_S/\text{TPa}^{-1}$	$-3.2633 \times 10^2$	$-1.3589 \times 10^2$	$9.2830 \times 10^2$	$5.7002 \times 10^2$				0.2 $\text{TPa}^{-1}$
$T = 288.15$ K								
$V^E/\text{cm}^3\cdot\text{mol}^{-1}$	$1.9558 \times 10^{-1}$	1.0930	4.9047					0.004 $\text{cm}^3\cdot\text{mol}^{-1}$
$\delta n_D$	$-5.0574 \times 10^{-1}$	$5.7022 \times 10^{-2}$	1.4438	$-1.0558 \times 10^{-2}$	$-8.5566 \times 10^{-1}$			0.0001
$\delta\kappa_S/\text{TPa}^{-1}$	$-2.3778 \times 10^2$	$4.3506 \times 10^1$	$9.2084 \times 10^2$	$4.0638 \times 10^2$				0.3 $\text{TPa}^{-1}$

point, using the following equations:

$$\delta\kappa_S = \frac{1}{\rho u^2} - \sum_{i=1}^2 \frac{x_i}{\rho_i u_i^2} \quad (1)$$

$$\delta n_D = n_D - \sum_{i=1}^2 x_i n_{D,i} \quad (2)$$

$$V_m^E = \sum_{i=1}^2 x_i M_i (\rho_i^{-1} - \rho^{-1}) \quad (3)$$

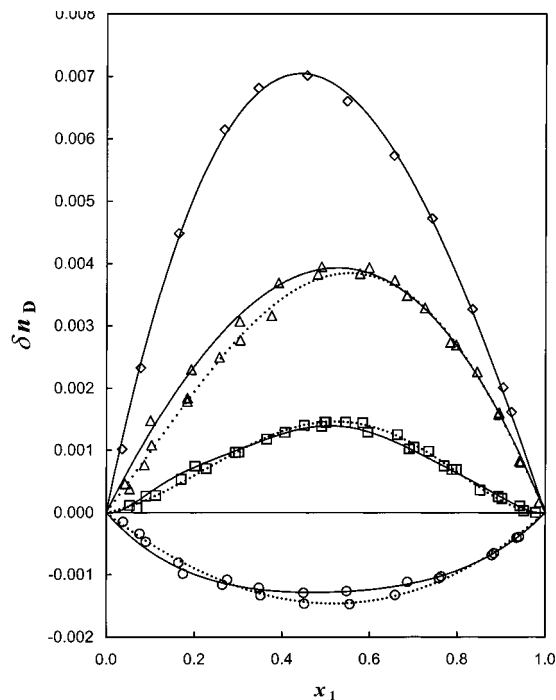


**Figure 1.** Excess molar volumes of acetone + (hexane (○), heptane (□), or octane (△)) at the temperatures (---) 278.15, (—) 288.15, and (···) 298.15 K and of acetone + methanol (◇) at (---) 278.15 and (—) 288.15 K.

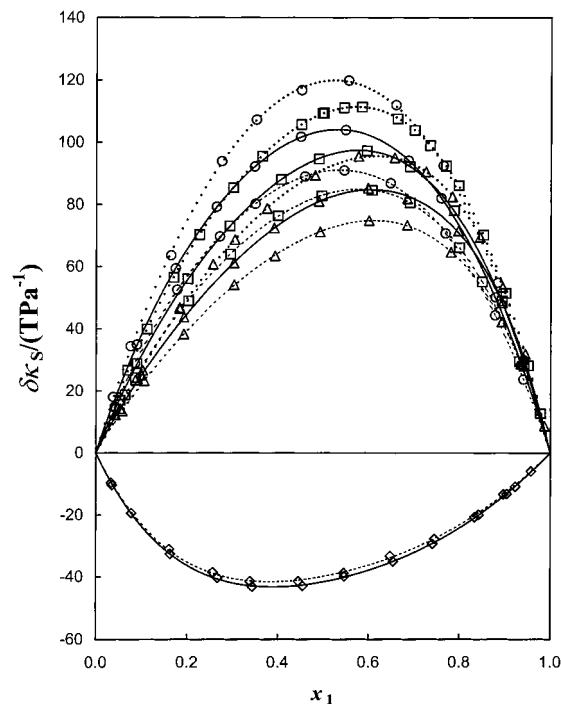
where  $\kappa_S$  is the isentropic compressibility ( $\kappa_S = \rho^{-1}u^{-2}$ ),  $n_D$  is the refractive index,  $\rho$  is the density of the mixture, and the corresponding quantities with subscript  $i$  refer to pure chemicals. Excess and derived values were correlated by means of the Redlich–Kister<sup>7</sup> expression for every binary mixture.

$$\delta Q = x_i x_j \sum_{p=0}^m A_p (x_i - x_j)^p \quad (4)$$

In this equation  $\delta Q$  is the excess or derived property,  $x_i$  is the mole fraction of component  $i$ ,  $A_p$  are the correlation parameters, and  $m$  is the degree of the polynomial expansion. The unweighted least-squares method was used to fit the polynomials to the data. The degree of each equation was optimized by applying the F-test.<sup>8</sup> The parameters calculated using eq 4 are listed in Table 3. Methanol with hexane, heptane, or octane shows a heterogeneous region at every temperature due to disruption of hydrogen bonds by the inert alkane presence. The limiting mixture points (liquid–liquid equilibria) have been previously published.<sup>9</sup> The curves fitted, as well as excess and derived property values, are shown in Figures 1–6. The excess molar volumes of these mixtures show considerable positive trends, such behavior being increased by the chain length or temperature factors. In what is referred to as acetone mixtures, an analogous trend should be observed by the effect of an inert aliphatic alkane, breaking polar interactions among carbonyl molecular groups. In all cases, the acetone + alkane mixtures show a positive tendency with almost equimolar maxima. In a similar way, a longer chain produces a higher expansive effect. Approximately, a temperature change of 20 deg (278.15 to 298.15 K) produces a 10% variation in the excess molar volume for the



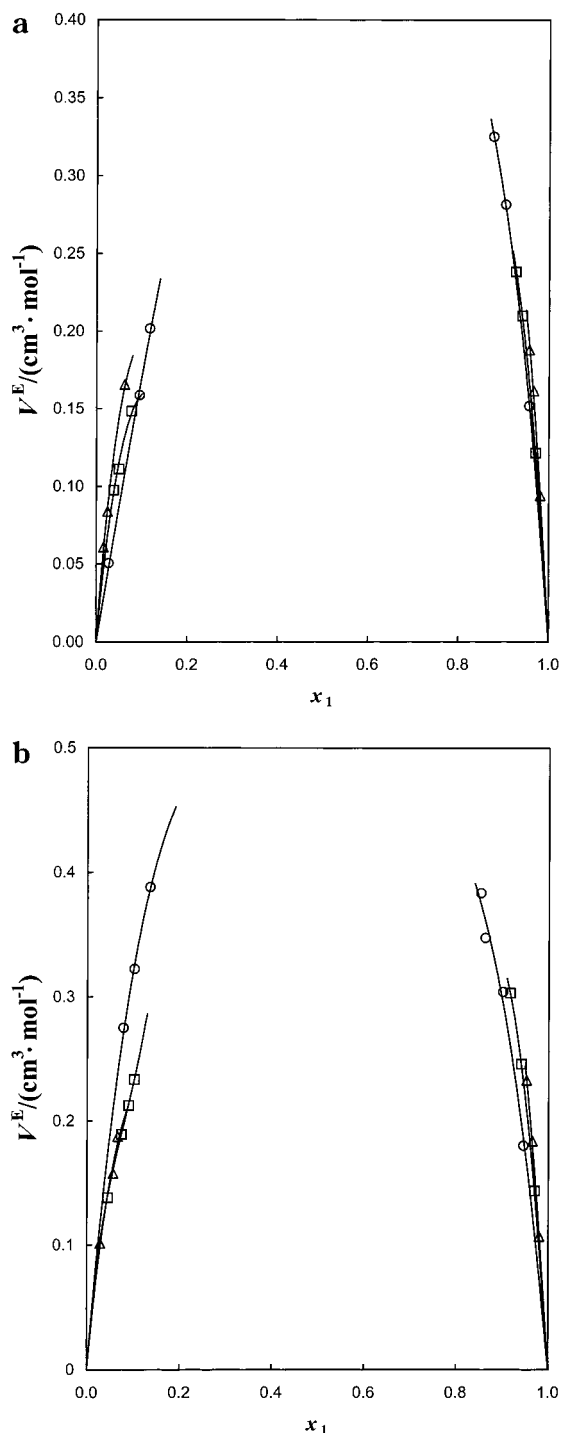
**Figure 2.** Refractive index deviations of acetone + (hexane (○), heptane (□), or octane (△)) at the temperatures (---) 278.15, (—) 288.15, and (···) 298.15 K and of acetone + methanol (◇) at (---) 278.15 and (—) 288.15 K.



**Figure 3.** Isentropic compressibility deviations of acetone + (hexane (○), heptane (□), or octane (△)) at the temperatures (---) 278.15, (—) 288.15, and (···) 298.15 K and of acetone + methanol (◇) at (---) 278.15 and (—) 288.15 K.

mixtures studied. Only the acetone + methanol mixture presents a contractive tendency with negligible temperature dependence due to polar and hydrogen bond interactions, as suggested in a previous work.<sup>1</sup> The refractive index deviations are positive for all the binary mixtures except for the acetone + hexane, in agreement with the excess molar volume behavior. The increasing of the alkane



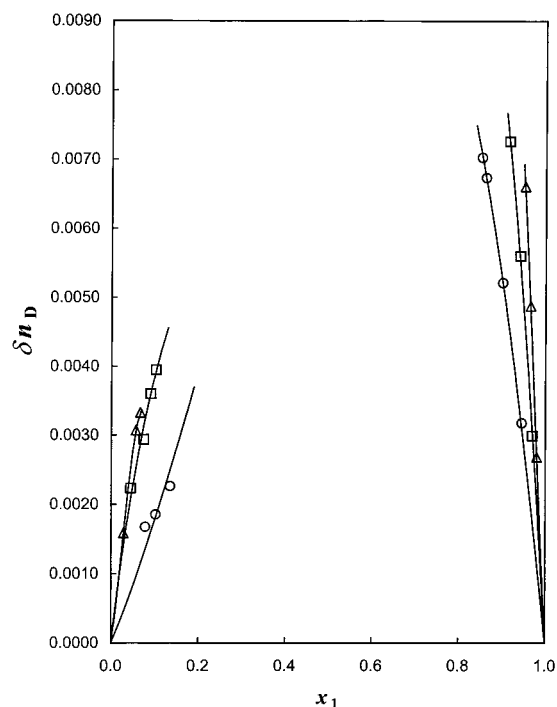


**Figure 4.** Excess molar volumes of methanol + (hexane (○), heptane (□), or octane (△)) at the temperatures (a) 278.15 and (b) 288.15 K.

chain length produces lower positive isentropic compressibility deviations. This effect is also produced with the decreasing of the temperature. The acetone + methanol mixture presents a different behavior, due to the hydrogen bonds and molecular packing.

#### Equations of State

The interest related to theoretical and semiempirical work based on equations of state for prediction of thermodynamic quantities or phase equilibria has increased in the past few years. This fact is due to their high simplicity, accuracy, low information requirements, and versatility in

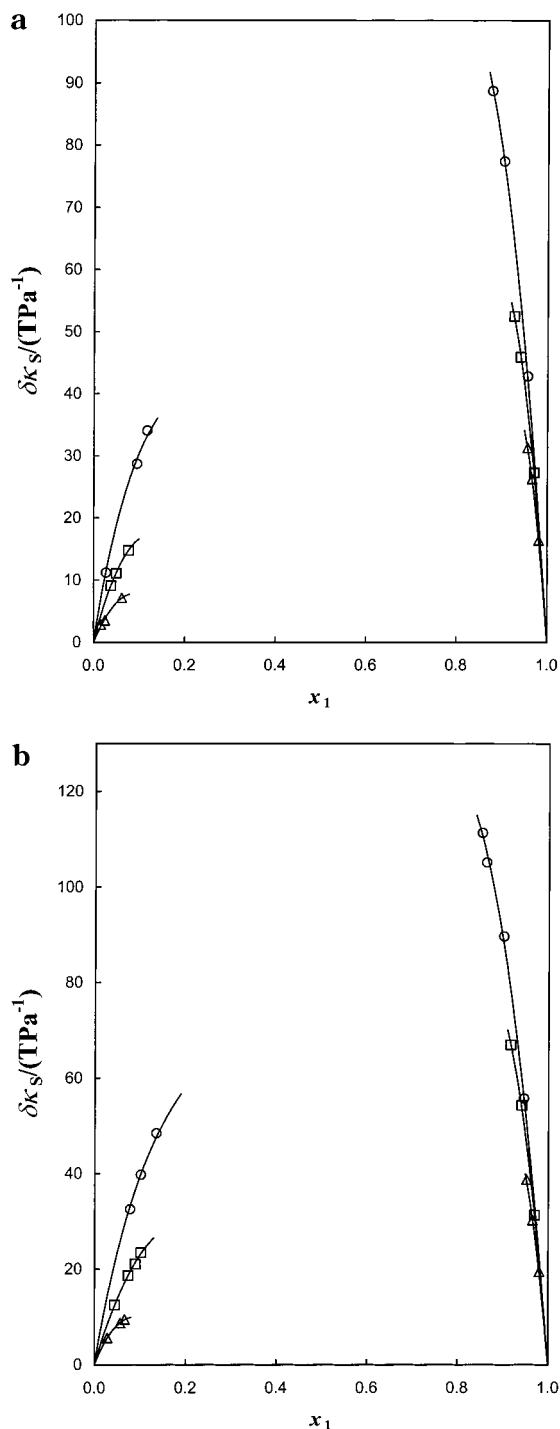


**Figure 5.** Refractive index deviations of methanol + (hexane (○), heptane (□), or octane (△)) at the temperature 288.15 K.

**Table 4. Binary Interaction Parameters Calculated for the Described Mixing Rules, Applied in Combination with the SRK Equation of State, and, in Parentheses, Root Mean Square Deviations of  $V^E$  ( $\text{cm}^3 \cdot \text{mol}^{-1}$ ) Obtained**

	R1	R2	R3
Acetone (1) + Methanol (2)			
$k_{12} = -5.202 \times 10^{-2}$ (0.02)	$k_{12} = 1.107 \times 10^{-2}$ $m_{12} = 1.016 \times 10^{-2}$ (0.007)	$k_{12} = 1.428 \times 10^{-2}$ $l_{12} = -6.670 \times 10^{-4}$ $m_{12} = 1.069 \times 10^{-2}$ (0.007)	
Acetone (1) + Hexane (2)			
$k_{12} = 4.841 \times 10^{-2}$ (0.05)	$k_{12} = 2.447 \times 10^{-2}$ $m_{12} = -4.583 \times 10^{-3}$ (0.05)	$k_{12} = 2.598 \times 10^{-2}$ $l_{12} = -9.059 \times 10^{-3}$ $m_{12} = -4.258 \times 10^{-3}$ (0.03)	
Acetone (1) + Heptane (2)			
$k_{12} = 2.612 \times 10^{-2}$ (0.06)	$k_{12} = -2.361 \times 10^{-2}$ $m_{12} = -8.580 \times 10^{-3}$ (0.05)	$k_{12} = 1.243 \times 10^{-2}$ $l_{12} = -1.115 \times 10^{-2}$ $m_{12} = -2.563 \times 10^{-3}$ (0.04)	
Acetone (1) + Octane (2)			
$k_{12} = 4.487 \times 10^{-3}$ (0.06)	$k_{12} = -3.724 \times 10^{-2}$ $m_{12} = -6.416 \times 10^{-3}$ (0.05)	$k_{12} = 3.076 \times 10^{-3}$ $l_{12} = -1.368 \times 10^{-2}$ $m_{12} = -4.429 \cdot 10^{-4}$ (0.04)	
Methanol (1) + Hexane (2)			
$k_{12} = 1.186 \times 10^{-2}$ (0.09)	$k_{12} = -1.535 \times 10^{-1}$ $m_{12} = -2.564 \times 10^{-2}$ (0.05)	$k_{12} = 1.305 \times 10^{-2}$ $l_{12} = 2.727 \times 10^{-2}$ $m_{12} = -2.347 \cdot 10^{-4}$ (0.05)	
Methanol (1) + Heptane (2)			
$k_{12} = -6.697 \times 10^{-2}$ (0.05)	$k_{12} = -4.760 \times 10^{-1}$ $m_{12} = -5.243 \times 10^{-2}$ (0.04)	$k_{12} = -6.580 \times 10^{-2}$ $l_{12} = 2.829 \times 10^{-2}$ $m_{12} = -7.564 \times 10^{-4}$ (0.02)	
Methanol (1) + Octane (2)			
$k_{12} = -1.175 \times 10^{-1}$ (0.03)	$k_{12} = 8.851 \times 10^{-2}$ $m_{12} = 2.2442 \times 10^{-2}$ (0.02)	$k_{12} = -1.671 \times 10^{-1}$ $l_{12} = 2.982 \times 10^{-2}$ $m_{12} = -6.023 \times 10^{-3}$ (0.01)	

operation conditions. A considerable number of equations of state are currently available in the open literature, most



**Figure 6.** Isentropic compressibility deviations of methanol + (hexane (○), heptane (□), or octane (△)) at the temperatures (a) 278.15 and (b) 288.15 K.

of them being adequate to compute acceptable results in combination with simple mixing rules if interaction parameters are obtained from enclosed binary mixtures in the multicomponent system. In this case the Soave-Redlich-Kwong<sup>10</sup> (SRK) equation was applied. Three different simple combining rules for  $a$  and  $b$  were incorporated to this EOS, according to the general expression

$$a = \sum_{i=1}^n \sum_{j=1}^n x_i x_j (1 - k_{ij} - l_{ij}(x_i - x_j))(a_i a_j)^{0.5} \quad (5)$$

$$b = \sum_{i=1}^n \sum_{j=1}^n x_i x_j (1 - m_{ij}) \frac{(b_i + b_j)}{2} \quad (6)$$

where  $k_{ij} = l_{ij} = m_{ij} = 0$  for  $i = j$ , and  $l_{ij} = m_{ij} = 0$  for the first mixing rule (R1),  $l_{ij} = 0$  for the second one (R2), and, finally,  $k_{ij}$ ,  $l_{ij}$ ,  $m_{ij} \neq 0$  for the third one (R3). These parameters are constant values over the whole composition and temperature ranges for every mixture.

To compute the binary interaction parameters for each mixing rule, the fitting procedure consisted of the minimization of the following objective function:

$$\text{OF} = \sum_{i=1}^n \frac{(V_{\text{exp},i}^E - V_{\text{pred},i}^E)^2}{V_{\text{exp},i}^E} \quad (7)$$

A Marquardt<sup>11</sup> routine was applied, in combination with a Newton-Raphson method, and the fitting parameters obtained are gathered in Table 4. Similar values for deviations were obtained in acetone or methanol + alkane mixtures, the R3 mixing rule (three fitting parameters) yielding the best results with root square deviations lower than  $0.05 \text{ cm}^3 \cdot \text{mol}^{-1}$ . In addition, the mixture acetone + methanol shows, for the same rule, similar deviations comparatively from usual correlation equations. Highly accurate results are obtained by application of such parameters for multicomponent prediction.<sup>12</sup>

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