Thermophysical Properties of Acetone or Methanol + *n*-Alkane (C_9 to C_{12}) Mixtures

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Liquid−liquid equilibria for methanol + *n*-alkanes (C_9 to C_{12}) were determined in the temperature range (278.15 to 308.15 K), using a visual static method. Densities, refractive indices, and speeds of sound were also measured at 288.15, 298.15, and 308.15 K for acetone + *n*-alkane mixtures and at 298.15 and 308.15 K for methanol + *n*-alkane mixtures to study the temperature influence on mixing phenomena. The results were used to model liquid−liquid coexistence and derived properties trend. The calculated values based on the UNIQUAC equation were found to be similar to those based on the NRTL model. The Prigogine−Flory−Paterson theory was applied to estimate the excess molar volumes and the UNIFAC group contribution model for phase equilibria.

Introduction

In current industrial processes involving nonideal mixtures, the design and development of separation units are conditioned by a knowledge of the thermodynamics of mixtures. One of our research activities is the identification and study of alternative separation agents in modified rectification processes.[1,2] As a continuation of previous works[3] related to heterogeneous modified distillation of the azeotrope acetone + methanol, new measurements of speeds of sound, densities, and refractive indices are presented in the range (288.15 to 308.15) K of the binary mixtures acetone + *n*-alkane (nonane, decane, undecane, or dodecane) and at (298.15 and 308.15) K of methanol + *n*-alkane mixtures and the corresponding derived magnitudes (excess molar volumes and refractive index deviations). Liquid−liquid equilibria for the binary mixtures of methanol + *n*-alkane (C_9−C_{12}) has been measured by GLC in the temperature range (278.15 to 308.15) K. The experimental data were correlated with the UNIQUAC[4] and NRTL[5] equations as a function of temperature. The UNIFAC group contribution method[6] was used to predict the experimental values; only qualitative results were obtained.

Experimental Data

Materials, Apparatus, and Procedure. Acetone and methanol were supplied by Merck, nonane by Fluka, and decane, undecane, and dodecane by Sigma. Ultrasonic treatment was used for degassing, and molecular sieves (type 4A or 3A, 1/16 in.) were introduced into the bottles to reduce the water content of the solvents. A Metrohm 737 KF coulometer was used to determine the maximum water content of the solvents (see Table 1). Precautions were taken to avoid evaporation losses during experimental work by cooling the materials and storing them in an inert atmosphere of argon gas (<3 ppmv in water) before sample preparation. Further details of the experimental procedure and mode of operation have previously been provided.[13] The purity of pure components are checked by GLC. The density, refractive index, and speed of sound of the pure components are compared with literature values (see Table 1). Samples were prepared by mass using a Mettler AE-240 Delta Range balance with an accuracy of $\pm 2 \times 10^{-5}$ g, covering the whole composition range of the mixtures. The accuracy of the mole fraction is estimated to be better than 10^{-4}. The densities and speeds of sound were measured with an Anton Paar DSA-48 digital densimeter and sound analyzer with an accuracy of $\pm 10^{-4}$ g·cm^{-3} and $\pm 5 \times 10^{-1}$ m·s^{-1}, respectively. The refractive indices of the pure liquids and mixtures were measured with the automatic refractometer ABBEMAT-HP Dr. Kernchen with an accuracy of $\pm 2 \times 10^{-5}$ and thermostated with a PolyScience controller bath model 9010 with a temperature stability of $\pm 10^{-2}$ K. Calibration of this equipment was performed periodically, in accordance with specifications, using Millipore quality water (resistivity, 18.2 MΩ·cm) and air. Maximum deviation in the calculation of excess molar volumes and refractive index deviations for these mixtures are estimated to be better than $\pm 8 \times 10^{-9}$ m^3·mol^{-1} and $\pm 10^{-4}$, respectively. The apparatus for determining the liquid−liquid equilibria (LLE) consists of a glass cell with a water jacket to maintain a constant temperature. The temperature was controlled within $\pm 5 \times 10^{-2}$ K inside the cell. The cell was connected to a Polyscience 9010 controller bath, with a stability of $\pm 10^{-2}$ K. The temperature in the cell was measured with a Yokogawa 7563 digital thermometer with a precision of $\pm 10^{-2}$ K, calibrated with an Anton Paar MKT-100 digital thermometer (precision $\pm 10^{-3}$ K, temperature scale ITS-90) over the entire range of temperatures. The mixture was prepared by mass, placed in the cell, stirred for 1 h, and left to settle for 12 h. Samples were taken with a syringe from the upper and lower phases, through a needle. A series of liquid−liquid equilibrium measurements was made by changing the temperature. Tie-line phase compositions were analyzed by GLC using a Hewlett-Packard HP-6890 Series GC System chromatograph equipped with a flame ionization detector. Two capillary columns were used, HP-INNOWax 19091N-133 (cross-linked poly(ethylene glycol), 30-m length, 0.25-mm internal diameter) and HP-1 19091Z-215 (methyl siloxane, 50-m length, 0.32-mm internal diameter) for the analysis of methanol + alkane (C_{10}−C_{12}) and methanol + nonane mixtures, respectively. The carrier gas was helium and the injector and detector temperature were both 523.15

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Table 1. GLC Purity, Maximum Water Content, and Comparison of Data with Literature for Pure Liquids at 298.15 K

			ρ / g·cm^{-3}		n_D		u / m·s^{-1}	
component	purity / mass %	max. water content / mass %	exp.	lit.[7]	exp.	lit.[7]	exp.	lit.
acetone	>99.8	$<6.8 \times 10^{-3}$	0.7844	0.78429[8]	1.35580	1.35596	1160.96	1160.6[9]
methanol	>99.8	$<1.5 \times 10^{-2}$	0.7866	0.78664	1.32645	1.32652	1102.13	1102.0[10]
nonane	>99.2	$<2.6 \times 10^{-3}$	0.7142	0.71375	1.40336	1.40311	1207.35	1212[11]
decane	>99.6	$<10^{-3}$	0.7261	0.72614	1.40937	1.40967	1234.75	1234[11]
undecane	>99.0	$<10^{-3}$	0.7365	0.7365	1.41473	1.41507	1258.16	1257.95[12]
dodecane	>99.6	$<10^{-3}$	0.7451	0.74518	1.41953	1.41949	1279.61	1277.97[12]

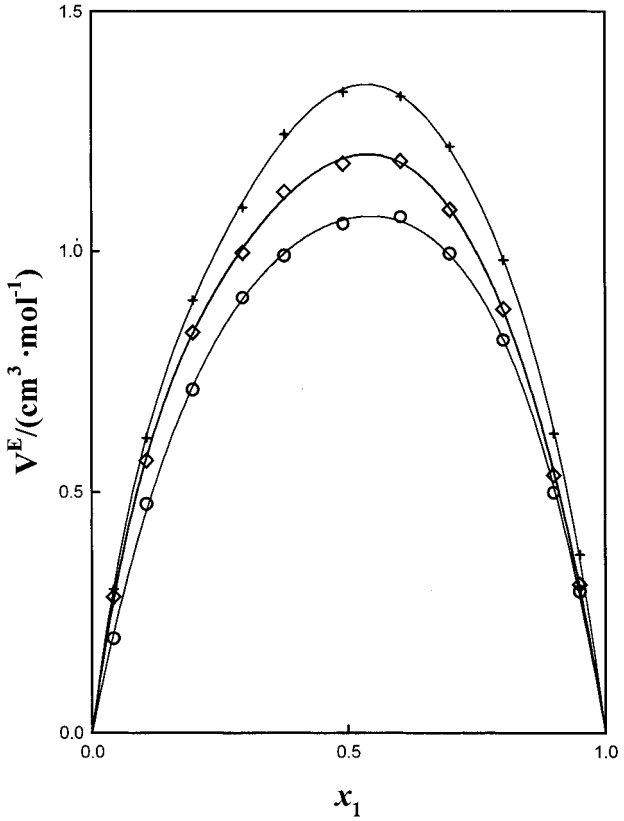

Figure 1. Excess molar volumes (cm^3·mol^{-1}) with mole fraction for acetone + nonane at the temperatures (○) 288.15 K, (◊) 298.15 K, and (+) 308.15 K.

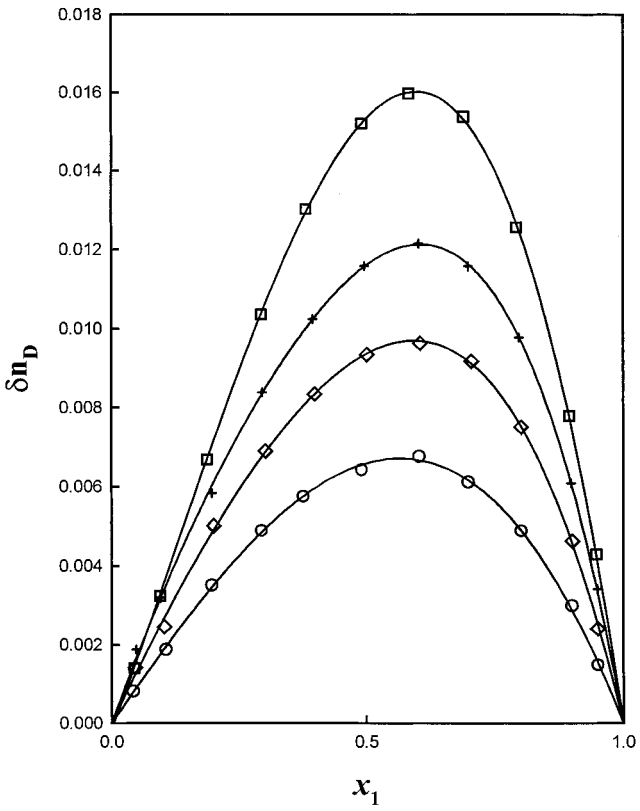

Figure 2. Refractive index deviations with mole fraction for acetone + (○) nonane, (◊) decane, (+) undecane, and (□) dodecane mixtures at 298.15 K.

K. The peak areas were converted to the mole fractions using weight factors determined by the GLC analysis of mixtures of known composition. The estimated uncertainty for mole fractions was determined to be $\pm 2 \times 10^{-3}$ and $\pm 3 \times 10^{-3}$ in the methanol-rich phase and alkane-rich phase, respectively.

Results and Conclusions

Physical Properties. The excess molar volumes and refractive index deviations are presented in Table 2 and were computed from eqs 1 and 2:

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

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

In these equations, ρ is the density and n_D is the refractive index. The ρ_i and n_{Di} are the properties of pure components and N is the number of components in the mixture. The Redlich−Kister[14] equation was used to correlate the derived properties of the binary mixtures, by using the unweighted least-squares method, all experimental points weighing equally. The degree of this equation was optimized by applying the F-test.[15] The fitting parameters are reported in Table 3.

The acetone + *n*-alkane mixtures show a high expansive trend, as does the whole aliphatic compounds set.[16] The acetone + *n*-hexane mixtures show a high expansive trend but the polar difference is weak enough for phase splitting at ambient temperature, although liquid−liquid equilibria has been experimentally determined at lower temperature values.[17] Only the acetone + *n*-hexane mixture shows an expansive trend clearly lower than those of the other systems. As the temperature is increased, a similar trend with higher expansion is apparent in all mixtures and derived properties. As before, this tendency increases with temperature because of the difficult packing of the polar ketone group among apolar methylene groups (i.e., Figure 1).

All the binary mixtures with methanol show phase splitting because of the high difference of polarity and molecular volume and shape. This effect increases with rising temperature and chain length. The increase of the *n*-alkane chain length for methanol + *n*-alkane mixtures produces a similar expansive tendency.

Table 2. Densities ρ, Refractive Indices n_D, Speeds of Sound U, Excess Molar Volumes V^E, and Refractive Index Deviations δn_D for the Mixtures

x_1	ρ / g·cm^{-3}	n_D	u / m·s^{-1}	V^E / cm^3·mol^{-1}	δn_D	x_1	ρ / g·cm^{-3}	n_D	u / m·s^{-1}	V^E / cm^3·mol^{-1}	δn_D
					Acetone + Nonane						
					T = 288.15 K						
0.0000	0.7216	1.40783	1248.0	0.000	0.0000	0.6036	0.7432	1.38648	1193.8	1.070	0.0065
0.0421	0.7221	1.40687	1242.5	0.196	0.0010	0.6993	0.7507	1.38141	1189.5	0.994	0.0059
0.1064	0.7230	1.40519	1235.1	0.475	0.0023	0.8027	0.7614	1.37526	1187.7	0.814	0.0045
0.1968	0.7251	1.40227	1225.5	0.712	0.0035	0.9002	0.7754	1.36877	1191.4	0.498	0.0025
0.2948	0.7280	1.39932	1216.9	0.902	0.0051	0.9505	0.7845	1.36518	1196.9	0.293	0.0013
0.3763	0.7311	1.39632	1209.6	0.990	0.0059	1.0000	0.7958	1.36161	1205.9	0.000	0.0000
0.4911	0.7365	1.39161	1200.6	1.056	0.0065						
					T = 298.15 K						
0.0000	0.7142	1.40336	1207.4	0.000	0.0000	0.6036	0.7338	1.38141	1150.8	1.187	0.0068
0.0421	0.7143	1.40218	1201.7	0.283	0.0008	0.6993	0.7410	1.37621	1146.2	1.085	0.0061
0.1064	0.7151	1.40018	1194.2	0.565	0.0019	0.8027	0.7512	1.37006	1144.1	0.878	0.0049
0.1968	0.7169	1.39751	1184.2	0.830	0.0035	0.9002	0.7647	1.36354	1147.6	0.534	0.0030
0.2948	0.7197	1.39423	1173.4	0.996	0.0049	0.9505	0.7735	1.35965	1152.8	0.308	0.0015
0.3763	0.7224	1.39121	1167.3	1.122	0.0057	1.0000	0.7844	1.35580	1161.0	0.000	0.0000
0.4911	0.7275	1.38642	1158.0	1.181	0.0064						
					T = 308.15 K						
0.0000	0.7064	1.39839	1167.0	0.000	0.0000	0.6036	0.7241	1.37706	1107.3	1.321	0.0076
0.0421	0.7064	1.39744	1161.4	0.300	0.0011	0.6993	0.7309	1.37161	1102.2	1.216	0.0067
0.1064	0.7070	1.39571	1154.0	0.612	0.0024	0.8027	0.7408	1.36521	1099.7	0.982	0.0052
0.1968	0.7086	1.39299	1143.7	0.897	0.0040	0.9002	0.7537	1.35822	1102.7	0.621	0.0029
0.2948	0.7111	1.38971	1133.2	1.090	0.0054	0.9505	0.7623	1.35452	1107.8	0.371	0.0016
0.3763	0.7135	1.38666	1125.1	1.242	0.0063	1.0000	0.7733	1.35052	1117.5	0.000	0.0000
0.4911	0.7181	1.38213	1115.3	1.330	0.0073						
					Acetone + Decane						
					T = 288.15 K						
0.0000	0.7336	1.41435	1274.1	0.000	0.0000	0.5014	0.7443	1.39695	1220.3	1.142	0.0090
0.0460	0.7338	1.41301	1268.0	0.233	0.0011	0.6058	0.7494	1.39172	1211.3	1.126	0.0093
0.1033	0.7343	1.41115	1260.8	0.466	0.0022	0.7055	0.7559	1.38587	1203.6	1.033	0.0087
0.2009	0.7357	1.40801	1250.4	0.755	0.0043	0.8025	0.7645	1.37902	1197.7	0.850	0.0070
0.3025	0.7378	1.40484	1239.8	0.965	0.0064	0.9015	0.7768	1.37115	1196.4	0.547	0.0043
0.3989	0.7405	1.40135	1230.1	1.088	0.0080	0.9507	0.7851	1.36648	1199.3	0.318	0.0023
					T = 298.15 K						
0.0000	0.7261	1.40937	1234.8	0.000	0.0000	0.5014	0.7355	1.39185	1178.2	1.222	0.0093
0.0460	0.7262	1.40832	1229.4	0.251	0.0014	0.6058	0.7402	1.38655	1168.5	1.212	0.0096
0.1033	0.7266	1.40629	1222.3	0.489	0.0025	0.7055	0.7462	1.38075	1160.2	1.113	0.0092
0.2009	0.7278	1.40362	1209.9	0.797	0.0050	0.8025	0.7543	1.37388	1154.1	0.920	0.0075
0.3025	0.7296	1.40006	1198.6	1.027	0.0069	0.9015	0.7662	1.36570	1152.5	0.575	0.0046
0.3989	0.7320	1.39634	1188.3	1.159	0.0083	0.9507	0.7742	1.36085	1155.1	0.327	0.0024
					T = 308.15 K						
0.0000	0.7185	1.40494	1195.8	0.000	0.0000	0.5014	0.7263	1.38812	1136.8	1.377	0.0105
0.0460	0.7186	1.40367	1190.0	0.237	0.0012	0.6058	0.7307	1.38250	1126.3	1.349	0.0105
0.1033	0.7188	1.40206	1182.4	0.514	0.0027	0.7055	0.7364	1.37634	1117.3	1.238	0.0098
0.2009	0.7197	1.39923	1170.8	0.860	0.0052	0.8025	0.7441	1.36912	1110.7	1.020	0.0079
0.3025	0.7211	1.39596	1159.3	1.147	0.0075	0.9015	0.7553	1.36051	1108.3	0.663	0.0046
0.3989	0.7232	1.39237	1147.9	1.302	0.0091	0.9507	0.7630	1.35566	1110.9	0.395	0.0025
					Acetone + Undecane						
					T = 288.15 K						
0.0000	0.7438	1.41950	1297.6	0.000	0.0000	0.4963	0.7509	1.40164	1238.9	1.165	0.0109
0.0479	0.7439	1.41830	1291.3	0.217	0.0016	0.6023	0.7548	1.39643	1227.4	1.170	0.0118
0.0960	0.7441	1.41708	1285.3	0.410	0.0031	0.6990	0.7599	1.39059	1216.9	1.070	0.0116
0.1968	0.7449	1.41414	1273.2	0.732	0.0060	0.7978	0.7671	1.38315	1207.1	0.888	0.0098
0.2963	0.7463	1.41048	1261.4	0.939	0.0081	0.8987	0.7778	1.37336	1200.7	0.587	0.0059
0.3948	0.7482	1.40638	1250.0	1.085	0.0097	0.9499	0.7857	1.36769	1201.1	0.330	0.0032
					T = 298.15 K						
0.0000	0.7365	1.41473	1258.2	0.000	0.0000	0.4963	0.7424	1.39707	1196.9	1.229	0.0116
0.0479	0.7364	1.41379	1252.3	0.259	0.0019	0.6023	0.7459	1.39139	1184.8	1.238	0.0122
0.0960	0.7366	1.41227	1245.9	0.435	0.0032	0.6990	0.7506	1.38512	1173.7	1.131	0.0116
0.1968	0.7372	1.40897	1233.1	0.771	0.0058	0.7978	0.7572	1.37750	1163.8	0.949	0.0098
0.2963	0.7383	1.40566	1220.7	1.006	0.0084	0.8987	0.7673	1.36786	1157.0	0.620	0.0061
0.3948	0.7399	1.40171	1208.9	1.168	0.0102	0.9499	0.7748	1.36217	1157.4	0.346	0.0034
					T = 308.15 K						
0.0000	0.7291	1.41012	1220.4	0.000	0.0000	0.4963	0.7336	1.39292	1156.0	1.355	0.0124
0.0479	0.7290	1.40932	1213.3	0.247	0.0021	0.6023	0.7368	1.38714	1142.8	1.350	0.0129
0.0960	0.7290	1.40808	1206.9	0.465	0.0037	0.6990	0.7410	1.38103	1131.2	1.252	0.0126
0.1968	0.7294	1.40500	1193.8	0.819	0.0066	0.7978	0.7471	1.37281	1120.3	1.057	0.0102
0.2963	0.7302	1.40151	1181.3	1.086	0.0090	0.8987	0.7566	1.36284	1112.7	0.700	0.0063
0.3948	0.7315	1.39770	1168.6	1.269	0.0111	0.9499	0.7639	1.35668	1113.0	0.389	0.0032

Table 2. (Continued)

x_1	ρ / g·cm^{-3}	n_D	u / m·s^{-1}	V^E / cm^3·mol^{-1}	δn_D	x_1	ρ / g·cm^{-3}	n_D	u / m·s^{-1}	V^E / cm^3·mol^{-1}	δn_D
Acetone + Dodecane											
T = 288.15 K											
0.0000	0.7524	1.42327	1318.4	0.000	0.0000	0.4916	0.7569	1.40679	1255.9	1.160	0.0138
0.0441	0.7523	1.42272	1312.4	0.222	0.0022	0.5839	0.7595	1.40182	1244.5	1.156	0.0146
0.0953	0.7523	1.42151	1306.0	0.430	0.0041	0.6906	0.7640	1.39448	1229.8	1.034	0.0138
0.1877	0.7527	1.41857	1294.3	0.711	0.0069	0.7935	0.7697	1.38612	1217.5	0.913	0.0118
0.2945	0.7536	1.41498	1280.8	0.949	0.0099	0.8957	0.7787	1.37562	1206.5	0.638	0.0076
0.3819	0.7547	1.41169	1269.9	1.091	0.0120	0.9479	0.7857	1.36901	1203.9	0.390	0.0042
T = 298.15 K											
0.0000	0.7451	1.41953	1279.6	0.000	0.0000	0.4916	0.7482	1.40340	1215.9	1.276	0.0152
0.0441	0.7450	1.41813	1273.2	0.215	0.0014	0.5839	0.7506	1.39829	1202.4	1.243	0.0160
0.0953	0.7449	1.41669	1266.7	0.427	0.0032	0.6906	0.7545	1.39090	1187.5	1.144	0.0154
0.1877	0.7451	1.41426	1255.1	0.735	0.0067	0.7935	0.7599	1.38152	1173.6	0.980	0.0126
0.2945	0.7456	1.41112	1242.0	1.017	0.0104	0.8957	0.7683	1.37024	1162.1	0.664	0.0078
0.3819	0.7466	1.40822	1229.7	1.151	0.0130	0.9479	0.7749	1.36341	1159.3	0.403	0.0043
T = 308.15 K											
0.0000	0.7379	1.41502	1240.9	0.000	0.0000	0.4916	0.7398	1.39853	1174.7	1.363	0.0152
0.0441	0.7377	1.41377	1235.5	0.228	0.0016	0.5839	0.7418	1.39319	1161.4	1.365	0.0158
0.0953	0.7375	1.41248	1228.6	0.453	0.0036	0.6906	0.7452	1.38581	1145.3	1.260	0.0153
0.1877	0.7375	1.41019	1216.5	0.782	0.0073	0.7935	0.7499	1.37694	1131.0	1.095	0.0131
0.2945	0.7379	1.40724	1201.6	1.070	0.0112	0.8957	0.7577	1.36583	1118.6	0.752	0.0086
0.3819	0.7384	1.40376	1189.9	1.248	0.0134	0.9479	0.7639	1.35879	1115.3	0.467	0.0049
Methanol + Nonane											
T = 298.15 K											
0.0164	0.7141	1.40303	1204.6	0.082	0.0009	0.9849	0.7804	1.33065	1100.2	0.087	0.0030
0.0458	0.7143	1.40239	1200.9	0.156	0.0026	0.9895	0.7823	1.32948	1100.8	0.058	0.0022
0.0699	0.7145	1.40167	1199.0	0.211	0.0037	0.9950	0.7846	1.32797	1101.9	0.024	0.0011
0.0941	0.7148	1.40042	1197.2	0.243	0.0043	1.0000	0.7866	1.32645	1102.1	0.000	0.0000
0.9804	0.7786	1.33176	1099.7	0.117	0.0038						
T = 308.15 K											
0.0236	0.7063	1.39824	1163.5	0.123	0.0017	0.9858	0.7713	1.32599	1066.8	0.089	0.0027
0.0454	0.7064	1.39772	1161.0	0.187	0.0028	0.9910	0.7734	1.32464	1068.1	0.054	0.0017
0.0742	0.7067	1.39720	1158.6	0.233	0.0045	0.9952	0.7752	1.32358	1069.1	0.023	0.0010
0.9756	0.7674	1.32857	1065.5	0.156	0.0045	1.0000	0.7771	1.32223	1068.9	0.000	0.0000
0.9805	0.7692	1.32731	1066.1	0.126	0.0036						
Methanol + Decane											
T = 298.15 K											
0.0450	0.7260	1.40835	1229.0	0.172	0.0027	0.9819	0.7800	1.33200	1101.8	0.096	0.0041
0.0678	0.7262	1.40769	1227.0	0.214	0.0039	0.9850	0.7811	1.33104	1101.7	0.076	0.0033
0.0818	0.7262	1.40734	1225.7	0.242	0.0048	0.9946	0.7845	1.32834	1102.6	0.030	0.0014
T = 308.15 K											
0.0454	0.7184	1.40413	1189.7	0.179	0.0029	0.9852	0.7712	1.32704	1068.2	0.110	0.0036
0.0733	0.7185	1.40337	1187.1	0.247	0.0045	0.9901	0.7731	1.32554	1068.5	0.073	0.0025
0.1019	0.7186	1.40264	1183.7	0.305	0.0061	0.9950	0.7750	1.32396	1069.2	0.038	0.0013
0.9800	0.7694	1.32857	1068.0	0.143	0.0047						
Methanol + Undecane											
T = 298.15 K											
0.0306	0.7364	1.41445	1254.3	0.113	0.0024	0.9849	0.7808	1.33214	1102.7	0.116	0.0044
0.0556	0.7364	1.41400	1252.0	0.182	0.0042	0.9902	0.7827	1.33010	1102.3	0.078	0.0028
0.0710	0.7364	1.41324	1251.7	0.224	0.0048	0.9951	0.7846	1.32829	1102.4	0.040	0.0014
T = 308.15 K											
0.0289	0.7290	1.41008	1217.5	0.107	0.0025	0.9952	0.7752	1.32431	1069.7	0.039	0.0017
0.0471	0.7290	1.40983	1215.5	0.156	0.0038	0.9851	0.7715	1.32822	1069.9	0.119	0.0047
0.0622	0.7289	1.41000	1214.0	0.225	0.0053	0.9903	0.7734	1.32623	1069.7	0.076	0.0031
Methanol + Dodecane											
T = 298.15 K											
0.0105	0.7451	1.41939	1278.5	0.024	0.0008	0.9898	0.7830	1.33086	1104.4	0.073	0.0035
0.0202	0.7451	1.41910	1277.1	0.046	0.0015	0.9926	0.7840	1.32967	1104.0	0.051	0.0025
0.0371	0.7450	1.41871	1275.3	0.114	0.0026	0.9943	0.7846	1.32903	1103.7	0.038	0.0020
0.0542	0.7450	1.41845	1273.6	0.152	0.0040						
T = 308.15 K											
0.0236	0.7377	1.41475	1238.8	0.103	0.0019	0.0825	0.7377	1.41361	1233.6	0.242	0.0062
0.0473	0.7376	1.41446	1236.5	0.181	0.0038	0.9909	0.7736	1.32646	1071.2	0.088	0.0034
0.0689	0.7376	1.41399	1234.5	0.227	0.0054	0.9925	0.7745	1.32578	1071.0	0.056	0.0029

The refractive index deviations show positive trend for all the mixtures studied, such behavior being increased by the *n*-alkane chain length (i.e., Figure 2).

The experimental derived properties obtained in the present work have not been reported in the open literature, with the exception of the excess molar volumes for the

Table 3. Parameters of Redlich−Kister Equation and Root-Mean-Square Deviations, σ

	B_0	B_1	B_2	B_3	B_4	σ
			Acetone + Nonane			
			$T = 288.15$ K			
V^E	4.2626	5.0347×10^{-1}	1.5813			9×10^{-3}
δn_D	2.6256×10^{-3}	5.5301×10^{-3}	-7.5074×10^{-4}	-3.7942×10^{-3}		8×10^{-5}
			$T = 298.15$ K			
V^E	4.7788	5.9039×10^{-1}	1.1303	-9.5654×10^{-1}	1.3457	9×10^{-3}
δn_D	2.6329×10^{-2}	7.3960×10^{-3}				7×10^{-5}
			$T = 308.15$ K			
V^E	5.3575	6.9082×10^{-1}	6.5211×10^{-1}	-6.1442×10^{-1}	2.4265×10^{-1}	8×10^{-3}
δn_D	2.9191×10^{-2}	8.9834×10^{-3}	1.2478×10^{-4}	-6.8532×10^{-3}		8×10^{-5}
			Acetone + Decane			
			$T = 288.15$ K			
V^E	4.5789	3.7631×10^{-1}	9.1021×10^{-1}	4.9628×10^{-1}	1.0550	3×10^{-3}
δn_D	3.6057×10^{-2}	1.4458×10^{-2}				8×10^{-5}
			$T = 298.15$ K			
V^E	4.8998	5.7343×10^{-1}	1.0871	2.3856×10^{-1}	7.4696×10^{-1}	3×10^{-3}
δn_D	3.7419×10^{-2}	1.3950×10^{-2}	4.2333×10^{-3}			1×10^{-4}
			T=308.15 K			
V^E	5.5121	4.1524×10^{-1}	6.8237×10^{-1}	1.3171	1.2816	7×10^{-3}
δn_D	4.1191×10^{-2}	1.4213×10^{-2}				6×10^{-5}
			Acetone + Undecane			
			$T = 288.15$ K			
V^E	4.6697	6.1953×10^{-1}	7.3549×10^{-1}	6.3530×10^{-1}	1.0122	8×10^{-3}
δn_D	4.3926×10^{-2}	2.0625×10^{-2}	2.2410×10^{-2}	-4.1223×10^{-3}	-1.8295×10^{-2}	4×10^{-5}
			$T = 298.15$ K			
V^E	4.9666	6.2598×10^{-1}	6.8546×10^{-1}	6.2542×10^{-1}	1.3158	9×10^{-3}
δn_D	4.6375×10^{-2}	1.8975×10^{-2}	8.6483×10^{-3}			1×10^{-4}
			$T = 308.15$ K			
V^E	5.4300	7.6610×10^{-1}	8.0841×10^{-1}	1.0628	1.2552	5×10^{-3}
δn_D	4.9935×10^{-2}	2.0829×10^{-2}	8.4296×10^{-3}	-7.7519×10^{-3}		1×10^{-4}
			Acetone + Dodecane			
			$T = 288.15$ K			
V^E	4.6600	1.9004×10^{-1}	2.3955×10^{-1}	1.6367	2.7241	8×10^{-3}
δn_D	5.5813×10^{-2}	2.2950×10^{-2}	1.7387×10^{-3}	-2.8636×10^{-3}	1.7646×10^{-2}	7×10^{-5}
			$T = 298.15$ K			
V^E	5.0501	4.3279×10^{-1}	2.0108×10^{-1}	1.5545	2.1862	9×10^{-3}
δn_D	6.1393×10^{-2}	2.6584×10^{-2}	-1.1178×10^{-3}	2.8983×10^{-3}		5×10^{-5}
			$T = 308.15$ K			
V^E	5.4612	7.0368×10^{-1}	2.6422×10^{-1}	1.8101	2.6771	6×10^{-3}
δn_D	6.1400×10^{-2}	2.0395×10^{-2}	9.3656×10^{-3}	1.7174×10^{-2}		5×10^{-5}
			Methanol + Nonane			
			$T = 298.15$ K			
V^E	1.1287×10^{1}	1.5796×10^{1}	-6.4693	-1.6168×10^{1}		4×10^{-3}
δn_D	-1.3420×10^{-1}	-1.6642×10^{-1}	2.8416×10^{-1}	2.5683×10^{-1}		4×10^{-5}
			$T = 308.15$ K			
V^E	5.7914	1.1830×10^{1}	1.6402×10^{-1}	-1.2230×10^{1}		3×10^{-3}
δn_D	8.0080×10^{-2}	6.1004×10^{-2}	5.4622×10^{-2}	2.3474×10^{-3}		5×10^{-5}
			Methanol + Decane			
			$T = 298.15$ K			
V^E	-7.1915×10^{-1}	3.9139×10^{-1}	6.0587			3×10^{-3}
δn_D	1.0167×10^{-1}	8.6093×10^{-2}	4.7635×10^{-2}			9×10^{-5}
			$T = 308.15$ K			
V^E	1.4974	1.4980	4.7586			2×10^{-3}
δn_D	1.0372×10^{-1}	9.1004×10^{-2}	5.5962×10^{-2}			6×10^{-5}
			Methanol + Undecane			
			$T = 298.15$ K			
V^E	2.3885	2.0306	3.7044			2×10^{-3}
δn_D	6.5196×10^{-2}	1.0339×10^{-1}	1.3160×10^{-1}			8×10^{-5}
			$T = 308.15$ K			
V^E	5.8172	2.3386				5×10^{-3}
δn_D	2.0122×10^{-1}	1.2508×10^{-1}				9×10^{-5}
			Methanol + Dodecane			
			$T = 298.15$ K			
V^E	4.9241	2.1604				6×10^{-3}
δn_D	1.6034×10^{-1}	1.3944×10^{-1}	5.1245×10^{-2}			5×10^{-5}
			$T = 308.15$ K			
V^E	-2.8604×10^{-1}	1.9834	7.4050			6×10^{-3}
δn_D	1.3947×10^{-1}	1.4843×10^{-1}	9.6519×10^{-2}			4×10^{-5}

V^E/(cm^3·mol^{-1})

Table 4. Energy Interaction Parameters (χ_{ij}) for the Prigogine−Flory−Paterson Theory of the Binary Mixtures (J·cm^{-3}) and Root-Mean-Square Deviations (in Brackets)

acetone + nonane	acetone + decane	acetone + undecane	acetone + dodecane
	288.15 K		
88.08 (0.12)	103.45 (0.14)	107.45 (0.14)	108.77 (0.15)
	298.15 K		
98.59 (0.16)	95.72 (0.15)	105.73 (0.15)	111.02 (0.16)
	308.15 K		
108.20 (0.16)	112.99 (0.15)	115.47 (0.15)	120.66 (0.16)
methanol + nonane	**methanol + decane**	**methanol + undecane**	**methanol + dodecane**
	298.15 K		
127.97 (0.02)	141.17 (0.03)	161.75 (0.02)	138.34 (0.01)
	308.15 K		
138.46 (0.03)	151.56 (0.02)	168.11 (0.02)	145.69 (0.01)

Table 5. Experimental Liquid−Liquid Equilibrium Data

	T = 278.15 K		T = 288.15 K		T = 298.15 K		T = 308.15 K	
mixture	x_1^{I}	x_1^{II}	x_1^{I}	x_1^{II}	x_1^{I}	x_1^{II}	x_1^{I}	x_1^{II}
methanol(1) + nonane(2)	0.063	0.974	0.082	0.968	0.098	0.963	0.115	0.955
methanol(1) + decane(2)	0.060	0.984	0.075	0.980	0.091	0.974	0.109	0.972
methanol(1) + undecane(2)	0.054	0.989	0.063	0.987	0.084	0.984	0.104	0.983
methanol(1) + dodecane(2)	0.053	0.992	0.062	0.992	0.084	0.990	0.094	0.987

Table 6. Correlation Parameters of UNIQUAC and NRTL Models and Root-Mean-Square Deviation (σ)

	a_{12}	a_{21}	b_{12}	b_{21}		
	J·mol^{-1}	J·mol^{-1}	J·mol^{-1}·K^{-1}	J·mol^{-1}·K^{-1}	$\sigma(x_1^{I})$	$\sigma(x_1^{II})$
			Methanol + Nonane			
UNIQUAC	6611.7188	13148.3481	−2.0444	−3.9532	0.0007	0.001
NRTL	10641.9052	7757.4579	−21.656	−4.0511	0.0007	0.001
			Methanol + Decane			
UNIQUAC	6586.3911	1333.8341	−1.5257	−3.8807	0.0004	0.004
NRTL	11007.4434	8649.4327	−22.6954	−4.1562	0.0004	0.004
			Methanol + Undecane			
UNIQUAC	8366.3635	945.4004	−6.9861	−2.4099	0.001	0.002
NRTL	13133.3560	7344.2986	−29.3081	3.3741	0.001	0.002
			Methanol + Dodecane			
UNIQUAC	77983.3619	9249.8177	−4.7269	3.3741	0.001	0.006
NRTL	12556.2819	7852.2589	−27.0739	4.2709	0.001	0.006

mixture methanol + decane.[18] These values show deviations around 15% from those measured in this work.

For many practical purposes it is necessary to predict the physicochemical properties of a multicomponent liquid mixture from the properties of pure chemicals or data of binary systems. The excess molar volume measurements obtained in this work have been compared with those calculated by means of the Prigogine−Flory−Paterson (PFP) theory.[19] In Table 4, the energy interaction parameters (χ_{ij}) of the PFP model and the root-mean-square deviations from experimental data are reported. All the binary mixtures show deviations close to the measurement accuracy.

Liquid−Liquid Equilibria. The equilibrium compositions for the mutual solubilities of methanol + *n*-alkane mixtures are given in Table 5. The UNIQUAC and NRTL equations were used to correlate the experimental data for the binary mixtures discussed here. The corresponding sets of binary interaction parameters were determined by minimizing the differences between the experimental and calculated concentrations using the Newton−Raphson method. The objective function used is

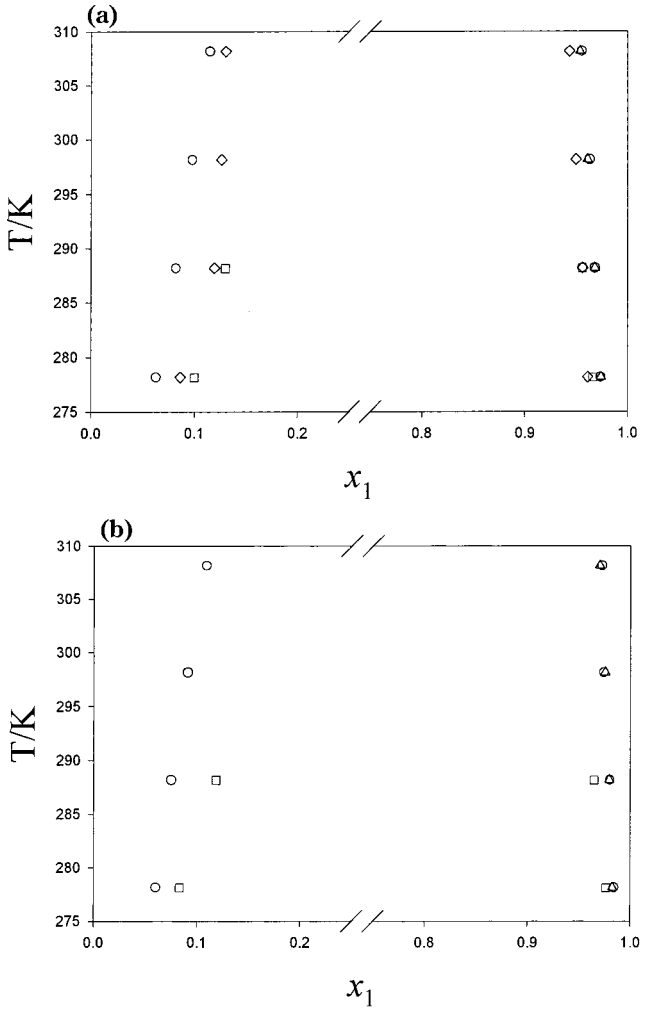

Figure 3. Experimental and literature data for the mixture (a) methanol + nonane and (b) methanol + decane. (○) experimental values, (△) Kiser et al., (□) Higashiuchi et al., and (◊) Kogan et al.

$$F = \min \sum_i \sum_j \sum_k (x_{ijk} - x_{ijk}^{C})^2 \quad (3)$$

where x and x^{C} are respectively the experimental and calculated mole fractions and the subscripts i, j, and k denote respectively the number of components, phases, and tie-lines as a function of temperature. Good correlation has been achieved for all cases using temperature-dependent parameters

$$\tau_{ij} = \exp\left(a_{ij} + \frac{b_{ij}}{T}\right) \quad (4)$$

$$\tau_{ij} = \frac{a_{ij} + b_{ij}T}{RT} \quad (5)$$

for UNIQUAC and NRTL, respectively. The estimated parameters (a_{ij} and b_{ij}) are included in Table 6, together with the root-mean-square values. The nonrandom parameter (α) of the NRTL model has been fixed to 0.3 for all

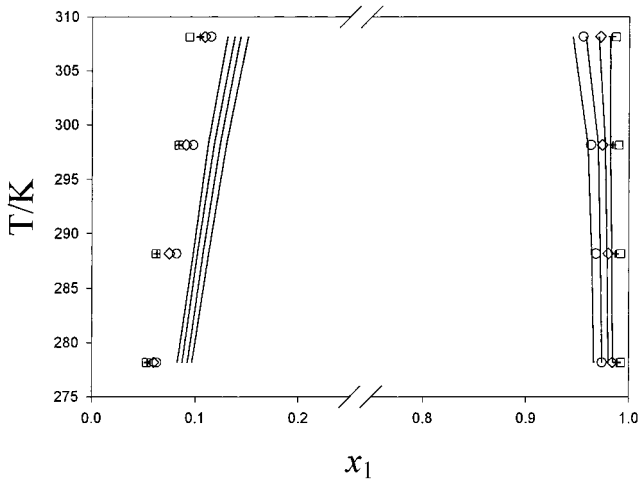

Figure 4. Liquid−liquid experimental data for the methanol + (○) nonane, (◊) decane, (+) undecane, and (□) dodecane mixtures and (—) UNIFAC prediction.

binaries. The liquid−liquid equilibria data of the mixtures methanol + nonane and methanol + decane were compared with previously published data,[20−22] and the results are presented in Figure 3a,b. These sets of data show similar results for phase equilibria compared to those measured in this work, except the data from Kogan et al.[22] The present data seem more reliable considering the accuracy of the analytical methods used and better temperature control.

The functional group contribution method UNIFAC[6,23] and its modifications—UNIFAC−LLE,[24] UNIFAC−Lyngby,[25] and UNIFAC−Dortmund[26,27]—are a way to predict liquid-phase activity coefficients, for which the avaliability of interaction parameters as a function of temperature is necessary. In the present case, these methods were applied to test their prediction capability, but only a poor description was obtained. As a result, we are only presenting the estimation of liquid−liquid equilibria obtained through the UNIFAC method, which showed a similar shape for the binodal curve (Figure 4). Because of several limitations, these methods are not accurate for predicting the liquid−liquid equilibria: that is, strong interactions among polar components in the mixture, the scarcity of experimental heterogeneous mixtures data with different functional groups at wide operational conditions, inadequate thermodynamic consistency tests for experimental equilibrium data quality control, and so forth.

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