J. Chem. Eng. Data **2004,** *49,* 333−338

Heat Capacities, Densities, and Speeds of Sound for {(1,5-Dichloropentane or 1,6-Dichlorohexane) + Dodecane}

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Densities and speeds of sound for {(1,5-dichloropentane or 1,6-dichlorohexane) + dodecane} in the temperature interval (278.15 to 328.15) K were determined using a tube vibrating densimeter and sound analyzer (Anton-Paar DSA-48). Isobaric heat capacities per unit volume for the same systems were measured in the temperature interval (283.15 to 323.15) K by means of a micro DSC II calorimeter using the scanning method. In all cases, measurements were made at atmospheric pressure. From these data, the molar volumes, isobaric and isochoric molar heat capacities, isentropic and isothermal compressibilities, and isobaric thermal expansivities as well as their excess quantities were calculated. Some comments related to the influence of the well-known effects of {polar + long alkyl chain linear alkane} on excess properties were included.

Introduction

There have been extensive studies on the thermophysical properties of mixtures containing organic compounds in order to understand their behavior at both the macroscopic and microscopic level.[1−3] Specifically, several excess properties for {α,ω-dichloroalkane + linear alkane} were found to be sensitive to the intramolecular effect denominated *proximity effect*.[4−6] Excess molar Gibbs free energy $G_{\mathrm{m}}^{\mathrm{E}}$, excess molar enthalpy $H_{\mathrm{m}}^{\mathrm{E}}$, and excess molar volume $V_{\mathrm{m}}^{\mathrm{E}}$ have been the most studied properties and to a less extent the excess isobaric molar heat capacity $C_{p,\mathrm{m}}^{\mathrm{E}}$. However, little is known about other second-order excess properties such as the isochoric molar heat capacity $C_{v,\mathrm{m}}^{\mathrm{E}}$, isentropic κ_S^{E} and isothermal κ_T^{E} compressibility, and isobaric thermal expansivity α_p^{E} due mainly to the scarcity of experimental data. In this context, we previously[7] reported all these excess properties for {1,3-dichloropropane + dodecane}.

In this work, second-order excess properties of the binary systems {(1,5-dichloropentane or 1,6-dichlorohexane) + dodecane} are presented. To this end, densities ρ and speeds of sound u from (278.15 to 328.15) K with a step of 1 K and isobaric heat capacities per unit volume C_pV^{-1} from (283.15 to 323.15) K with a step of 0.1 K were measured at atmospheric pressure and covering the whole composition range. These values were used to obtain the molar volumes, isobaric thermal expansivities, isentropic and isothermal compressibilities, and isochoric and isobaric molar heat capacities using a previously reported methodology.[8] The excess properties were calculated using the Benson and Kiyohara criterion.[9] Some comments related to the influence of the well-known effects of {polar + long alkyl chain linear alkane} on excess properties were included.

Experimental Section

Chemicals. Heptane and octane were purchased from Fluka, and dodecane, 1,5-dichloropentane, and 1,6-dichlorohexane from Aldrich. In all cases, the purity was checked by gas chromatography (GC) analysis obtaining heptane (99.60 mol %), octane (99.50 mol %), dodecane (99.20 mol %), 1,5-dichloropentane (99.1 mol %), and 1,6-dichlorohexane (99.50 mol %). Liquids were degassed and passed by molecular sieves of 0.4 nm prior to use. Mole fractions of the mixtures were obtained by weighing in a Mettler Balance AE-240 with a sensitivity of 0.000 01 g.

Apparatus and Procedure. Densities ρ and speeds of sound u were measured using a tube vibrating densimeter and sound analyzer Anton-Paar DSA-48. Densimeter calibration was carried out with MilliQ water and octane using literature values from Riddick[10] and the TRC databases,[11] respectively. Calibration for the sound analyzer was done with MilliQ water using the literature data from Bilaniuk and Wong.[12,13] Uncertainty in the determination of the density and the speed of sound under the above-mentioned considerations was previously[8] estimated as $\pm 1 \times 10^{-4}$ g·cm^{-3} and ± 0.1 m·s^{-1}, respectively.

Isobaric heat capacities per unit volume C_pV^{-1} were measured in a micro DSC II scanning calorimeter from Setaram using the scanning method at the rate of 0.25 K·min^{-1}. Isobaric molar heat capacities $C_{p,\mathrm{m}}$ were calculated from these data, mass molar data, and density values. 1-Butanol and heptane with literature values obtained from Ginnings and Furukawa[14] and Zabransky[15] were used for calibration. More detailed information about the measurement procedure can be found elsewhere.[16] Uncertainty in $C_{p,\mathrm{m}}$ was estimated[8] as ± 0.1 J·K^{-1}·mol^{-1}.

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10.1021/je034177v CCC: $27.50

Table 1. Densities ρ for $\{x$ (1,5-Dichloropentane or 1,6-Dichlorohexane) $+ (1 - x)$ Dodecane$\}$ at the Temperature T

	ρ/g·cm^{-3}										
x	T = 278.15 K	T = 283.15 K	T = 288.15 K	T = 293.15 K	T = 298.15 K	T = 303.15 K	T = 308.15 K	T = 313.15 K	T = 318.15 K	T = 323.15 K	T = 328.15 K
1,5-Dichloropentane + Dodecane											
0	0.759 56	0.755 96	0.752 36	0.748 74	0.745 14	0.741 52	0.737 88	0.734 24	0.730 60	0.726 95	0.723 29
0.052 37	0.769 83	0.766 19	0.762 54	0.758 89	0.755 23	0.751 58	0.747 91	0.744 24	0.740 56	0.736 88	0.733 17
0.101 36	0.780 00	0.776 32	0.772 61	0.768 91	0.765 22	0.761 51	0.757 80	0.754 07	0.750 34	0.746 61	0.742 86
0.200 75	0.802 34	0.798 55	0.794 74	0.790 94	0.787 14	0.783 32	0.779 49	0.775 66	0.771 82	0.767 98	0.764 14
0.303 95	0.827 99	0.824 08	0.820 16	0.816 25	0.812 33	0.808 40	0.804 47	0.800 53	0.796 59	0.792 63	0.788 68
0.394 50	0.852 98	0.848 97	0.844 93	0.840 90	0.836 86	0.832 82	0.828 76	0.824 71	0.820 64	0.816 57	0.812 52
0.498 32	0.884 91	0.880 76	0.876 58	0.872 42	0.868 24	0.864 07	0.859 88	0.855 70	0.851 51	0.847 29	0.843 12
0.601 44	0.920 97	0.916 68	0.912 36	0.908 04	0.903 71	0.899 38	0.895 05	0.890 70	0.886 36	0.882 00	0.877 69
0.698 72	0.959 17	0.954 72	0.950 25	0.945 78	0.941 31	0.936 82	0.932 33	0.927 83	0.923 36	0.918 84	0.914 40
0.797 49	1.003 24	0.998 63	0.993 99	0.989 35	0.984 72	0.980 06	0.975 41	0.970 74	0.966 10	0.961 42	0.956 80
0.902 10	1.056 96	1.052 15	1.047 30	1.042 45	1.037 61	1.032 76	1.027 91	1.023 05	1.018 21	1.013 35	1.008 57
0.949 74	1.084 25	1.079 35	1.074 40	1.069 46	1.064 51	1.059 56	1.054 61	1.049 66	1.044 74	1.039 77	1.034 90
1	1.115 28	1.110 26	1.105 20	1.100 16	1.095 11	1.090 07	1.085 02	1.079 97	1.074 95	1.069 89	1.064 93
1,6-Dichlorohexane + Dodecane											
0	0.759 56	0.755 96	0.752 36	0.748 74	0.745 14	0.741 52	0.737 88	0.734 24	0.730 60	0.726 95	0.723 29
0.049 80	0.769 76	0.766 11	0.762 46	0.758 82	0.755 16	0.751 50	0.747 81	0.744 13	0.740 46	0.736 76	0.733 07
0.100 30	0.780 41	0.776 72	0.773 04	0.769 35	0.765 66	0.761 96	0.758 26	0.754 53	0.750 82	0.747 09	0.743 36
0.149 73	0.791 41	0.787 68	0.783 94	0.780 20	0.776 45	0.772 70	0.768 93	0.765 15	0.761 37	0.757 60	0.753 83
0.252 71	0.815 84	0.812 00	0.808 17	0.804 33	0.800 48	0.796 64	0.792 76	0.788 89	0.785 03	0.781 15	0.777 28
0.401 73	0.855 12	0.851 13	0.847 16	0.843 16	0.839 16	0.835 16	0.831 14	0.827 13	0.823 12	0.819 09	0.815 09
0.501 99	0.884 56	0.880 48	0.876 39	0.872 29	0.868 18	0.864 08	0.859 96	0.855 84	0.851 72	0.847 59	0.843 49
0.599 98	0.916 30	0.912 10	0.907 89	0.903 68	0.899 46	0.895 24	0.891 01	0.886 78	0.882 55	0.878 32	0.874 11
0.701 11	0.952 18	0.947 86	0.943 53	0.939 19	0.934 87	0.930 52	0.926 17	0.921 82	0.917 48	0.913 12	0.908 81
0.798 62	0.990 33	0.985 89	0.981 42	0.976 96	0.972 49	0.968 02	0.963 55	0.959 07	0.954 61	0.950 13	0.945 71
0.899 82	1.034 17	1.029 59	1.024 98	1.020 39	1.015 80	1.011 20	1.006 61	1.002 00	0.997 44	0.992 83	0.988 30
0.949 34	1.057 53	1.052 88	1.048 19	1.043 52	1.038 85	1.034 18	1.029 52	1.024 85	1.020 20	1.015 52	1.010 92
0.969 11	1.067 22	1.062 53	1.057 82	1.053 11	1.048 42	1.043 71	1.039 00	1.034 30	1.029 61	1.024 90	1.020 27
1	1.082 70	1.077 97	1.073 22	1.068 47	1.063 74	1.059 00	1.054 25	1.049 50	1.044 78	1.040 03	1.035 37

Table 2. Speeds of Sound u for $\{x$ (1,5-Dichloropentane or 1,6-Dichlorohexane) $+ (1-x)$ Dodecane$\}$ at the Temperature T

	u/m·s^{-1}										
x	T = 278.15 K	T = 283.15 K	T = 288.15 K	T = 293.15 K	T = 298.15 K	T = 303.15 K	T = 308.15 K	T = 313.15 K	T = 318.15	T = 323.15 K	T = 328.15 K
1,5-Dichloropentane + Dodecane											
0	1357.05	1337.42	1317.62	1298.04	1278.49	1259.15	1240.00	1221.04	1202.28	1183.64	1165.12
0.052 37	1353.87	1334.36	1314.61	1295.09	1275.61	1256.41	1237.28	1218.44	1199.71	1181.04	1162.67
0.101 36	1351.32	1331.88	1312.23	1292.77	1273.45	1254.20	1235.22	1216.37	1197.70	1179.26	1160.80
0.200 75	1347.06	1327.75	1308.24	1289.03	1269.79	1250.73	1231.85	1213.17	1194.62	1176.21	1157.91
0.303 95	1344.08	1324.93	1305.67	1286.58	1267.47	1248.60	1229.85	1211.36	1192.89	1174.69	1156.50
0.394 50	1342.41	1323.56	1304.40	1285.47	1266.56	1247.80	1229.23	1210.88	1192.55	1174.38	1156.36
0.498 32	1342.09	1323.38	1304.47	1285.73	1266.96	1248.38	1229.96	1211.75	1193.61	1175.58	1157.74
0.601 44	1343.60	1325.12	1306.39	1287.86	1269.30	1250.93	1232.71	1214.61	1196.66	1178.82	1161.16
0.698 72	1347.13	1328.89	1310.33	1291.99	1273.66	1255.43	1237.41	1219.57	1201.74	1184.06	1166.54
0.797 49	1353.39	1335.28	1316.98	1298.83	1280.68	1262.64	1244.75	1227.05	1209.45	1191.88	1174.52
0.902 10	1363.50	1345.63	1327.53	1309.54	1291.60	1273.79	1256.11	1238.55	1221.13	1203.81	1186.58
0.949 74	1369.47	1351.70	1333.66	1315.80	1297.96	1280.26	1262.65	1245.20	1227.88	1210.63	1193.52
1	1376.62	1358.93	1340.96	1323.21	1305.44	1287.86	1270.32	1252.99	1235.76	1218.65	1201.63
1,6-Dichlorohexane + Dodecane											
0	1357.05	1337.42	1317.62	1298.04	1278.49	1259.15	1240.00	1221.04	1202.28	1183.64	1165.12
0.049 80	1355.02	1335.46	1315.74	1296.26	1276.84	1257.60	1238.46	1219.61	1200.91	1182.36	1163.90
0.100 30	1353.35	1333.89	1314.28	1294.86	1275.54	1256.37	1237.39	1218.53	1199.93	1181.37	1163.04
0.149 73	1352.02	1332.68	1313.18	1293.86	1274.58	1255.48	1236.59	1217.90	1199.33	1180.88	1162.62
0.252 71	1350.38	1331.21	1311.85	1292.74	1273.66	1254.74	1235.99	1217.47	1199.03	1180.77	1162.61
0.401 73	1350.41	1331.40	1312.37	1293.53	1274.73	1256.08	1237.61	1219.28	1201.18	1183.13	1165.23
0.501 99	1351.88	1333.30	1314.53	1295.87	1277.29	1258.82	1240.55	1222.40	1204.43	1186.55	1168.83
0.599 98	1355.08	1336.66	1318.07	1299.67	1281.31	1263.08	1244.95	1227.04	1209.23	1191.57	1174.01
0.701 11	1360.12	1341.95	1323.64	1305.41	1287.26	1269.21	1251.27	1233.56	1215.98	1198.46	1181.13
0.798 62	1366.83	1348.88	1330.73	1312.80	1294.81	1276.99	1259.29	1241.77	1224.33	1207.04	1189.91
0.899 82	1376.13	1358.40	1340.43	1322.68	1304.92	1287.34	1269.80	1252.45	1235.31	1218.19	1201.23
0.949 34	1381.55	1363.95	1346.12	1328.42	1310.81	1293.34	1275.96	1258.80	1241.71	1224.72	1207.85
0.969 11	1383.70	1366.18	1348.41	1330.86	1313.25	1295.81	1278.52	1261.33	1244.29	1227.38	1210.55
1	1387.42	1369.99	1352.28	1334.77	1317.28	1299.94	1282.70	1265.65	1248.65	1231.83	1215.11

Results and Discussion

Derived Properties: Calculation and Correlation. Densities ρ and speeds of sound u for (278.15 to 328.15) K are given in Tables 1 and 2, whereas isobaric molar heat capacities $C_{p,\mathrm{m}}$ for (283.15 to 323.15) K are displayed in Table 3. Experimental data for the rest of the temperatures are available from the authors. These data were fitted to the expression

$$Y = \sum_{i=1}^{n}\sum_{j=1}^{m} A_{ij} 10^{1-j} (T/\mathrm{K} - T_0/\mathrm{K})^{j-1} x^{i-1} \qquad (1)$$

where Y can be the density ρ/g·cm^{-3}, speed of sound u/m·s^{-1}, and isobaric molar heat capacity $C_{p,\mathrm{m}}$/J·mol^{-1}·K^{-1}, x

Table 3. Isobaric Molar Heat Capacities $C_{p,\mathrm{m}}$ for {x (1,5-Dichloropentane or 1,6-Dichlorohexane) + (1 − x) Dodecane} at the Temperature T

	$C_{p,\mathrm{m}}/\mathrm{J{\cdot}mol^{-1}{\cdot}K^{-1}}$								
x	T = 283.15 K	T = 288.15 K	T = 293.15 K	T = 298.15 K	T = 303.15 K	T = 308.15 K	T = 313.15 K	T = 318.15	T = 323.15 K
				1,5-Dichloropentane + Dodecane					
0	368.47	370.48	372.74	375.04	377.43	380.02	382.73	385.48	388.29
0.052 37	359.49	361.46	363.60	365.89	368.28	370.79	373.41	376.07	378.83
0.101 36	351.13	353.16	355.31	357.53	359.81	362.28	364.84	367.48	370.16
0.200 75	334.84	336.79	338.81	340.93	343.08	345.47	347.87	350.35	352.88
0.303 95	318.47	320.33	322.17	324.17	326.18	328.38	330.63	332.93	335.27
0.394 50	304.32	305.98	307.85	309.60	311.52	313.55	315.68	317.86	320.07
0.498 32	288.13	289.64	291.34	293.02	294.78	296.69	298.58	300.38	302.59
0.601 44	271.74	273.20	274.79	276.35	277.97	279.71	281.49	283.32	285.18
0.698 72	256.40	257.78	259.23	260.76	262.21	263.83	265.47	267.13	268.85
0.797 49	240.83	242.08	243.45	244.78	246.18	247.69	249.17	250.73	252.27
0.902 10	224.47	225.70	226.92	228.16	229.39	230.74	232.08	233.47	234.85
0.949 74	217.25	218.41	219.54	220.73	221.90	223.14	224.40	225.70	227.02
1	209.65	210.73	211.89	212.94	214.06	215.21	216.38	217.56	218.76
				1,6-Dichlorohexane + Dodecane					
0	368.47	370.48	372.74	375.04	377.43	380.02	382.73	385.48	388.29
0.049 80	361.24	363.25	365.49	367.75	370.17	372.73	375.36	378.07	380.85
0.100 30	354.21	356.20	358.37	360.64	363.07	365.53	368.13	370.69	373.37
0.149 73	347.40	349.35	351.58	353.74	356.06	358.52	361.02	363.62	366.28
0.252 71	333.57	335.52	337.63	339.74	341.93	344.27	346.63	349.13	351.62
0.401 73	314.16	315.92	317.89	319.79	321.84	323.95	326.16	328.40	330.71
0.501 99	301.12	302.83	304.61	306.46	308.39	310.38	312.43	314.57	316.72
0.599 98	288.34	289.93	291.62	293.38	295.19	297.07	299.01	300.97	303.01
0.701 11	275.07	276.60	278.22	279.86	281.55	283.34	285.15	287.00	288.89
0.798 62	262.36	263.83	265.40	266.90	268.50	270.16	271.87	273.60	275.38
0.899 82	249.37	250.76	252.22	253.67	255.12	256.63	258.18	259.77	261.42
0.949 34	242.86	244.24	245.67	247.09	248.51	249.99	251.50	253.03	254.57
0.969 11	240.39	241.75	243.14	244.52	245.90	247.38	248.85	250.37	251.90
1	236.59	237.90	239.26	240.60	241.94	243.37	244.81	246.28	247.76

Table 4. Coefficients A_{ij} and Standard Deviations σ

		i						
	j	1	2	3	4	5	6	7
				1,5-Dichloropentane + Dodecane				
$\rho/\mathrm{g{\cdot}cm^{-3}}$	1	0.75952	0.19297	0.08603	0.07297	−0.03777	0.04157	
	2	−0.00718	−0.00150	−0.00290	0.00467	−0.00473	0.00153	
$\sigma = 0.00005$	3	−0.00001	0.00000	0.00000	0.00007	−0.00015	0.00010	
$C_{p,\mathrm{m}}/\mathrm{J{\cdot}mol^{-1}{\cdot}K^{-1}}$	1	368.47	−176.63	61.11	−79.45	36.19		
	2	4.05	−0.50	−6.33	9.05	−4.15		
	3	0.23	−0.23	0.10	−0.03	−0.04		
$u/\mathrm{m{\cdot}s^{-1}}$	1	1357.20	−64.06	74.49	−6.35	−68.26	143.14	−59.38
	2	−39.97	3.36	0.76	−0.22	0.18	0.67	−0.86
$\sigma = 0.09$	3	0.31	−0.14	0.14	−1.15	3.31		1.59
				1,6-Dichlorohexane + Dodecane				
$\rho/\mathrm{g{\cdot}cm^{-3}}$	1	0.75958	0.19873	0.09101	0.00405	0.02932		
	2	−0.00718	−0.00173	−0.00048	−0.00003	−0.00008		
$\sigma = 0.00005$	3	−0.00001	0.00002	−0.00006	0.00012	−0.00006		
$C_{p,\mathrm{m}}/\mathrm{J{\cdot}mol^{-1}{\cdot}K^{-1}}$	1	368.42	−146.59	47.99	−59.09	25.85		
	2	4.06	0.78	−8.71	11.24	−4.76		
	3	0.23	−0.48	1.16	−1.50	0.63		
$u/\mathrm{m{\cdot}s^{-1}}$	1	1357.22	−46.00	95.50	−100.40	126.92	−45.62	
	2	−39.99	5.12	−12.42	39.18	−46.00	18.53	
$\sigma = 0.09$	3	0.31	−0.29	1.59	−4.67	5.38	−2.12	

is the mole fraction of the α,ω-dichloroalkane, T is the absolute temperature, and T_0 is 278.15 for ρ and u and 283.15 for $C_{p,\mathrm{m}}$. The fitting coefficients A_{ij} were obtained using the least-squares method, and they are given in Table 4 together with their respective standard deviations σ. The method for the determination of the number of coefficients was previously reported.[7]

Molar volumes V_m were derived from density and mass molar data. Isentropic compressibilities κ_S were calculated using the Laplace equation $\kappa_S = 1/(\rho u^2)$ from density and speed of sound values. Isobaric thermal expansivities α_p at the temperature T were obtained using the expression

$$\alpha_p(T) = \frac{-1}{\rho_T}\left(\frac{\rho_{T+\Delta T/2} - \rho_{T-\Delta T/2}}{\Delta T}\right) \tag{2}$$

where ΔT was chosen as 10 K. The validity of this treatment was checked using the methodology reported in previous work.[8] Finally, isothermal compressibilities κ_T and isochoric molar heat capacities $C_{v,\mathrm{m}}$ were calculated from the following thermodynamic relations:

$$\kappa_T = \kappa_S + \frac{T V_\mathrm{m} {\alpha_p}^2}{C_{p,\mathrm{m}}} \tag{3}$$

$$C_{v,\mathrm{m}} = C_{p,\mathrm{m}}\frac{\kappa_S}{\kappa_T}. \tag{4}$$

Excess properties were calculated by using $Y^\mathrm{E} = Y - Y^\mathrm{id}$ where Y^E is the excess quantity of the property Y and Y^id is its ideal value. Y^id values were calculated using the

Table 5. Properties for the Pure Liquids at the Temperature T

		dodecane		1,5-dichloropentane		1,6-dichlorohexane	
property	T/K	this work	lit. (ref)	this work	lit. (ref)	this work	lit. (ref)
ρ/g·cm^{-3}	283.15	0.75596	0.7559 (11)				
	293.15	0.74874	0.74875 (11)				
	298.15	0.74514	0.74518 (11)	1.09511	1.09508 (17) 1.09527 (18)	1.06374	1.06392 (17) 1.06465 (18)
	303.15	0.74152	0.74160 (11)				
	313.15	0.73424	0.7344 (11)				
	323.15	0.72695	0.7272 (11)				
$C_{p,\mathrm{m}}$/J·mol^{-1}·K^{-1}	298.15	375.04	375.9 (15)	211.89	213.39 (15)	240.60	239.57 (15)
κ_T/TPa^{-1}	298.15	991.7	988 (10)				
α_p/kK^{-1}	298.15	0.969	0.974 (10)				

criterion of Benson and Kiyohara,[9] from which each of them are defined as follows:

$$V_{\mathrm{m}}^{\mathrm{id}} = xV_{\mathrm{m},1}^{*} + (1-x)V_{\mathrm{m},2}^{*} \tag{5}$$

$$\mathrm{C}_{p,\mathrm{m}}^{\mathrm{id}} = x\mathrm{C}_{p,\mathrm{m},1}^{*} + (1-x)\mathrm{C}_{p,\mathrm{m},2}^{*} \tag{6}$$

$$\alpha_{p}^{\mathrm{id}} = \phi\alpha_{p,1}^{*} + (1-\phi)\alpha_{p,2}^{*} \tag{7}$$

$$\kappa_{T}^{\mathrm{id}} = \phi\kappa_{T,1}^{*} + (1-\phi)\kappa_{T,2}^{*} \tag{8}$$

$$\kappa_{S}^{\mathrm{id}} = \kappa_{T}^{\mathrm{id}} - \frac{TV_{\mathrm{m}}^{\mathrm{id}}(\alpha_{p}^{\mathrm{id}})^{2}}{C_{p,\mathrm{m}}^{\mathrm{id}}} \tag{9}$$

$$C_{v,\mathrm{m}}^{\mathrm{id}} = C_{p,\mathrm{m}}^{\mathrm{id}}\frac{\kappa_{S}^{\mathrm{id}}}{\kappa_{T}^{\mathrm{id}}} \tag{10}$$

$$\phi = xV_{\mathrm{m},1}^{*}/V_{\mathrm{m}}^{\mathrm{id}} \tag{11}$$

where ϕ and x are the volume and mole fractions, respectively, of component 1 (1,5-dichloropentane or 1,6-dichlorohexane) and superscript * denotes properties of the pure liquids.

Discussion for Pure Liquids. A comparison between pure liquid values of this work and selected ones from the literature is displayed in Table 5 to show the reliability of the experimental measurements. As can be seen, the densities of dodecane are in good agreement with literature values, specially at low temperatures. The isobaric molar heat capacity agrees with literature data, and the derived properties (isothermal compressibility and isobaric thermal expansivity) are reasonably well reproduced. For both dichloroalkanes, the densities were found to be close to literature data from ref 17. This result was also observed in ref 7 for the 1,3-dichloropropane. Agreement is good for the heat capacity of the 1,6-dichlorohexane, the deviation being less than 2% for 1,5-dichloropentane.

Discussion for Mixtures. Excess molar volumes $V_{\mathrm{m}}^{\mathrm{E}}$ are positive for the whole composition range for both systems, taking higher values for the 1,5-dichloropentane system (at $x = 0.5$ and 298.15 K, the $V_{\mathrm{m}}^{\mathrm{E}}$ values are 0.804 and 0.602 cm^3·mol^{-1}, respectively). This result, which was also obtained for similar {polar + long alkyl chain linear alkane} systems,[19,20] is the result of the predominance of the positive contributions (destruction of dispersive interactions, dipolar order of the pure liquid, and orientational order of the long alkyl chain linear alkane) with respect to the negative ones (packing effects).

The excess isobaric thermal expansivity α_{p}^{E} is plotted against composition at 303.15 K for both systems in Figure 1. Values only at a unique temperature are shown as the variation of this property in the working temperature interval is less than the uncertainty of this property. As can be seen, α_{p}^{E} is positive over the entire range of composition for both systems showing that the $V_{\mathrm{m}}^{\mathrm{E}}$ values increase with T. On the other hand, the excess isentropic κ_{S}^{E} and isothermal κ_{T}^{E} compressibilities are plotted against composition and at several temperatures for both systems in Figures 2 and 3. κ_{T}^{E} values only at a unique temperature are shown for the 1,5-dichloropentane system for the same reason that it was done for α_{p}^{E}. An S-shaped composition dependence was found for all the curves. Positive values, which were usually found at low mole fractions, suggest that $V_{\mathrm{m}}^{\mathrm{E}}$ values decrease with pressure, showing the contrary behavior at high mole fractions.

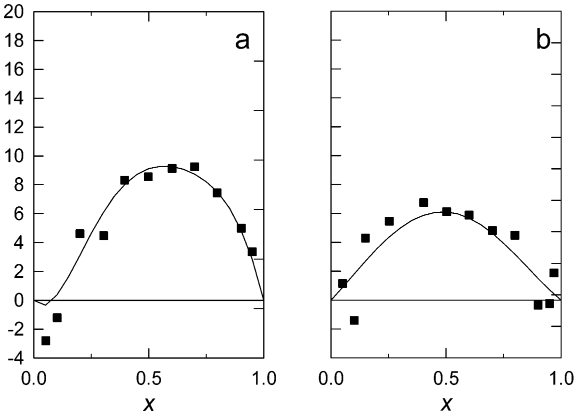

Figure 1. Excess isobaric thermal expansivities α_{p}^{E} for (a) {x 1,5-dichloropentane + $(1 - x)$ n-dodecane} and (b) {x 1,6-dichlorohexane + $(1 - x)$ n-dodecane} at (■) 303.15 K. (—) Calculated values from eq 1.

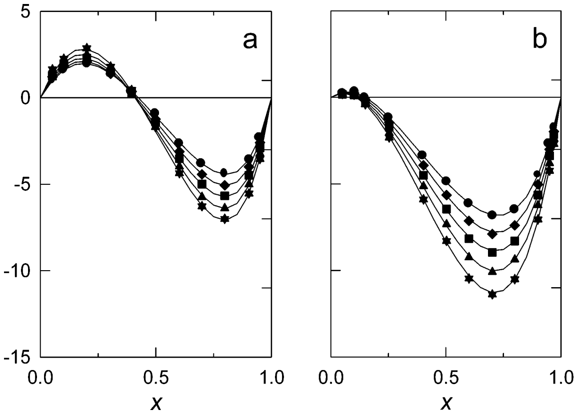

Figure 2. Excess isentropic compressibilities κ_{S}^{E} for (a) {x 1,5-dichloropentane + $(1 - x)$ n-dodecane} and (b) {x 1,6-dichlorohexane + $(1 - x)$ n-dodecane} at (●) 283.15 K, (◆) 293.15 K, (■) 303.15 K, (▲) 313.15 K, and (∗) 323.15 K. (—) Calculated values from eq 1.

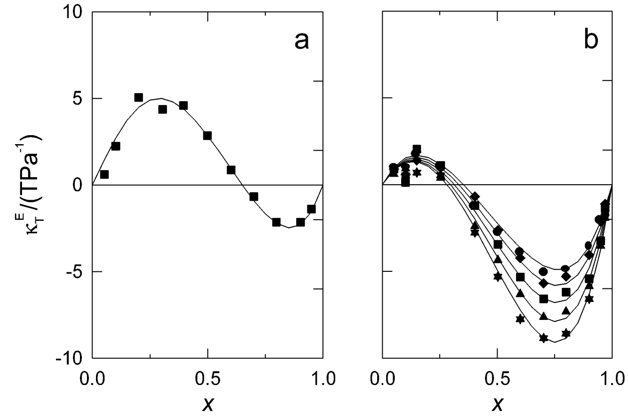

Figure 3. Excess isothermal compressibilities κ_T^E for (a) {x 1,5-dichloropentane + (1 − x) n-dodecane} and (b) {x 1,6-dichlorohexane + (1 − x) n-dodecane} at (●) 283.15 K, (◆) 293.15 K, (■) 303.15 K, (▲) 313.15 K, and (∗) 323.15 K. (−) Calculated values from eq 1.

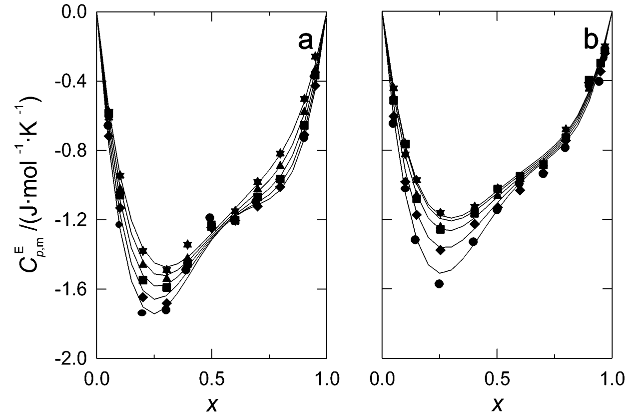

Figure 4. Excess isobaric molar heat capacities $C_{p,m}^E$ for (a) {x 1,5-dichloropentane + (1 − x) n-dodecane} and (b) {x 1,6-dichlorohexane + (1 − x) n-dodecane} at (●) 283.15 K, (◆) 293.15 K, (■) 303.15 K, (▲) 313.15 K and (∗) 323.15 K. (−) Calculated values from eq 1.

Figure 4 shows the excess isobaric molar heat capacity $C_{p,m}^E$ for both systems plotted against composition at several temperatures. The values were found to be negative over the whole composition range with slightly lower values for the 1,5-dichloropentane system. Little pronounced W-shaped composition dependence was found for all the curves. Temperature acts to increase $C_{p,m}^E$ values at the composition intervals (0 to 0.4) and (0.8 to 1), and the values remain approximately invariant at the rest of the compositions. The microscopic description associated with this result can be exposed using the interpretation proposed by Saint-Victor and Patterson[21] where $C_{p,m}^E$ is understood as a sum of two opposite contributions. Randomness during the mixing process contributes negatively to $C_{p,m}^E$, whereas its absence contributes positively. In these systems, at the extreme of the composition range, molecules of the diluted component remain separated and randomly distributed in the bosom of the liquid of higher composition. This fact favors the randomness contribution making $C_{p,m}^E$ negative. At intermediate compositions, this last conclusion could not be absolutely established. In that case, the mean separation between molecules decreases toward distances where interactions between like molecules can act. This fact tends to modify the randomness in the mixture increasing the positive contribution to $C_{p,m}^E$. This last effect is favored at low temperatures tending, in some cases, toward phase separation.[22]

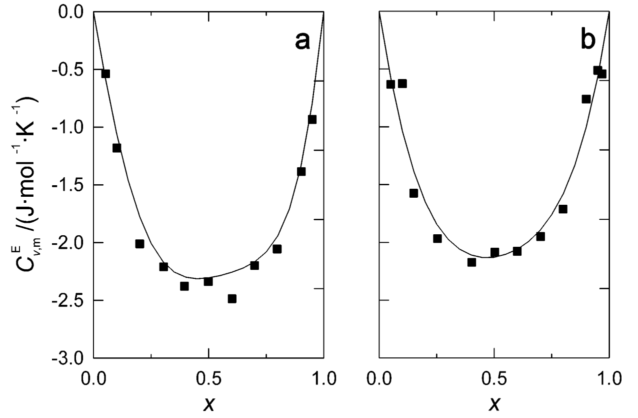

Figure 5. Excess isochoric molar heat capacities $C_{v,m}^E$ for (a) {x 1,5-dichloropentane + (1 − x) n-dodecane} and (b) {x 1,6-dichlorohexane + (1 − x) n-dodecane} at (■) 303.15 K. (−) Calculated values from eq 1.

Figure 5 shows the $C_{v,m}^E$ values plotted against composition for both systems. Values only at 303.15 K are shown for the same reason that it was done for α_p^E. As can be seen, negative values were found for both cases, being lower than those of $C_{p,m}^E$. The $C_{v,m}^E$ curves take a different shape than those of $C_{p,m}^E$.

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Received for review September 12, 2003. Accepted December 15, 2003. This work is part of Research Projects PGIDT00PXI38305PR and PGIDT01PXI38304PN. The authors are indebted to the Secretaría Xeral de Investigación e Desenvolvemento (Xunta de Galicia) for financial support.

JE034177V