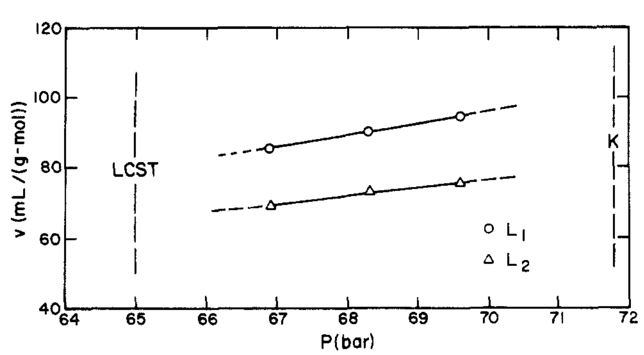

Figure 10. Molar volume as a function of pressure for the L_1 and L_2 phases for the liquid–liquid–vapor region of CO_2 + propane + *n*-nonadecane at 36 °C.

nonadecane resulted in a three-phase region developing to the low-temperature side (and high-pressure) of the binary LLV locus, while the addition of propane causes the three-phase region to extend to the high-temperature side of the LLV locus.

In terms of the CO_2 flooding of petroleum reservoirs, the data presented herein indicate that the addition of nitrogen can reduce or actually eliminate LLV behavior, while the buildup of propane in the gas phase can induce LLV behavior at temperatures where it otherwise would not have existed.

Registry No. CO_2, 124-38-9; N_2, 7727-37-9; propane, 74-98-6; *n*-nonadecane, 629-92-5.

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Excess Molar Volumes of the Mixtures Hexan-2-ol + *n*-Alkane at 298.15 K

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Values of V_m^E were determined at 298.15 K as a function of the alkanol mole fraction for the nine binary mixtures $\{xC_4H_9CH(OH)CH_3 + (1 - x)C_nH_{2n+2}\}$ from $n = 5$ to $n = 13$. V_m^E's were calculated indirectly from the density measurements effected with a vibrating-tube densimeter. Excess molar volumes were positive for the hydrocarbons with $n \geq 8$ in the entire range of compositions and sigmoidal for $5 \leq n \leq 7$.

Introduction

There are several works already done in which we have studied the behavior of hexanol isomers with different compounds (*1* - *3*). Although it is very important to know the distinct effects the presence of the hydroxyl group causes, the analysis of the interactions caused by an alkanol isomeric with another substance must begin by considering an *n*-alkane as the second component. For this reason, there are several works in the literature stating the investigations of the behavior of some mixtures of this type: *n*-alkanol + *n*-alkene (*4*), *n*-alkanol + alkane isomers (*5*), alkanol isomers + *n*-alkane (*6*), and alkanol isomers + alkane isomers (*7*). In this paper, we report the excess molar volumes at 298.15 K of hexan-2-ol + C_nH_{2n+2} (where $5 \leq n \leq 13$) fitting the experimental values by a suitable equation.

Experimental Section

All products used were from Fluka, excepting the *n*-heptane. The characteristics, indicated by Fluka, were >99.5 mol % for C_5, C_6, C_8, and C_{13}, and >98 mol % for C_9, C_{10}, C_{11}, C_{12}, and hexan-2-ol. *n*-Heptane (Riedel-de Haën, AG) was purified before use by washing with 10% Na_2CO_3 solution, drying with anhydrous magnesium sulfate, and rectifying twice in a packed column with a height equivalent to 120 theoretical plates, the final purity being 98.7 mol %. Prior to use, all products were degassed and kept in darkness on a molecular sieve (Union Carbide, Type A4, from Fluka). The properties of all pure compounds used agreed satisfactorily with the values found in the literature (*8*, *9*).

The measuring equipment and technique used were the same indicated in previous papers (*1*, *2*); however, the calibration of the densimeter was done using water and *n*-nonane

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Table I. Experimental Excess Molar Volumes V_m^E at 298.15 K

x	$\rho/g\cdot cm^{-3}$	$V_m^E/cm^3\cdot mol^{-1}$
$xC_4H_9CH(OH)CH_3 + (1-x)C_5H_{12}$		
0.000 00	0.621 24	0.0000
0.018 77	0.624 91	0.0126
0.042 90	0.629 81	0.0165
0.061 02	0.633 52	0.0106
0.134 54	0.648 66	−0.0493
0.222 76	0.666 70	−0.1405
0.288 65	0.679 98	−0.2015
0.356 08	0.693 38	−0.2550
0.411 81	0.704 26	−0.2840
0.477 29	0.716 87	−0.3093
0.544 87	0.729 69	−0.3261
0.616 07	0.743 02	−0.3394
0.670 94	0.753 15	−0.3434
0.741 04	0.765 90	−0.3386
0.799 30	0.796 35	−0.3289
0.894 68	0.792 85	−0.2514
0.916 96	0.796 61	−0.2242
0.962 75	0.804 04	−0.1305
1.000 00	0.809 69	0.0000
$xC_4H_9CH(OH)CH_3 + (1-x)C_6H_{14}$		
0.000 00	0.654 90	0.0000
0.037 93	0.660 44	0.0810
0.122 19	0.672 65	0.1498
0.170 85	0.679 88	0.1611
0.250 46	0.691 82	0.1696
0.318 51	0.702 12	0.1708
0.367 73	0.709 64	0.1654
0.455 94	0.723 23	0.1494
0.540 91	0.736 46	0.1267
0.613 58	0.747 88	0.1025
0.667 33	0.756 43	0.0752
0.756 72	0.770 77	0.0251
0.834 36	0.783 36	−0.0246
0.897 41	0.793 51	−0.0423
0.936 24	0.799 74	−0.0455
0.967 54	0.804 71	−0.0381
0.983 57	0.807 19	−0.0218
1.000 00	0.809 69	0.0000
$xC_4H_9CH(OH)CH_3 + (1-x)C_7H_{16}$		
0.000 00	0.679 62	0.0000
0.105 91	0.695 91	0.1926
0.167 67	0.699 57	0.2373
0.281 76	0.712 60	0.2966
0.346 93	0.720 37	0.3043
0.432 77	0.730 85	0.3118
0.512 04	0.740 84	0.3058
0.584 40	0.750 29	0.2800
0.662 71	0.760 82	0.2403
0.723 92	0.769 24	0.2086
0.807 90	0.781 26	0.1331
0.862 90	0.789 40	0.0703
0.925 59	0.789 40	−0.0087
0.941 46	0.801 24	−0.0118
0.986 40	0.807 85	−0.0093
1.000 00	0.809 69	0.0000
$xC_4H_9CH(OH)CH_3 + (1-x)C_8H_{18}$		
0.000 00	0.698 50	0.0000
0.049 40	0.702 17	0.1532
0.119 36	0.707 88	0.2702
0.197 59	0.714 74	0.3433
0.236 33	0.718 24	0.3775
0.314 29	0.725 64	0.4132
0.382 67	0.732 39	0.4385
0.463 53	0.740 82	0.4396
0.554 36	0.750 80	0.4244
0.613 97	0.757 69	0.3998
0.694 62	0.767 47	0.3486
0.760 48	0.775 90	0.2866
0.843 66	0.787 14	0.1869
0.901 94	0.795 38	0.1097
0.949 22	0.802 27	0.0497
1.000 00	0.809 69	0.0000
$xC_4H_9CH(OH)CH_3 + (1-x)C_9H_{20}$		
0.000 00	0.713 85	0.0000
0.049 16	0.716 51	0.1739
0.140 55	0.722 38	0.3221
0.193 32	0.726 06	0.3778
0.330 18	0.736 45	0.4573
0.340 68	0.737 28	0.4647
0.425 90	0.744 40	0.4894
0.477 98	0.749 01	0.4937
0.552 55	0.755 96	0.4889
0.634 48	0.764 14	0.4640
0.688 23	0.769 90	0.4245
0.754 03	0.777 35	0.3639
0.783 90	0.780 88	0.3325
0.897 76	0.795 52	0.1503
0.958 93	0.804 02	0.0452
1.000 00	0.809 69	0.0000
$xC_4H_9CH(OH)CH_3 + (1-x)C_{10}H_{22}$		
0.000 00	0.726 34	0.0000
0.054 28	0.728 91	0.1839
0.148 62	0.733 62	0.3610
0.232 92	0.738 45	0.4374
0.304 58	0.742 84	0.4945
0.387 99	0.748 41	0.5308
0.445 43	0.452 46	0.5567
0.511 63	0.757 52	0.5571
0.565 82	0.761 94	0.5457
0.645 83	0.768 96	0.5112
0.738 05	0.777 97	0.4259
0.803 74	0.785 09	0.3315
0.863 74	0.792 00	0.2217
0.911 36	0.798 11	0.1300
0.953 80	0.803 64	0.0557
1.000 00	0.809 69	0.0000
$xC_4H_9CH(OH)CH_3 + (1-x)C_{11}H_{24}$		
0.000 00	0.736 65	0.0000
0.055 82	0.738 01	0.2033
0.115 35	0.740 34	0.3270
0.203 90	0.744 28	0.4394
0.291 24	0.748 61	0.5216
0.364 42	0.752 60	0.5598
0.444 27	0.757 37	0.5868
0.532 59	0.763 17	0.6010
0.613 24	0.769 10	0.5820
0.674 30	0.774 06	0.5451
0.741 35	0.780 15	0.4581
0.811 27	0.787 18	0.3415
0.864 36	0.792 98	0.2451
0.924 62	0.800 09	0.1303
0.958 93	0.804 37	0.0694
1.000 00	0.809 69	0.0000
$xC_4H_9CH(OH)CH_3 + (1-x)C_{12}H_{26}$		
0.000 00	0.745 41	0.0000
0.064 32	0.746 95	0.2413
0.122 02	0.748 76	0.3561
0.192 76	0.751 25	0.4601
0.322 58	0.756 55	0.5819
0.367 51	0.758 62	0.6076
0.476 20	0.764 16	0.6465
0.550 05	0.768 43	0.6503
0.622 02	0.773 10	0.6253
0.689 90	0.778 03	0.5761
0.760 02	0.783 83	0.4811
0.824 73	0.789 77	0.3806
0.877 51	0.795 20	0.2704
0.927 97	0.800 89	0.1523
0.965 81	0.805 42	0.0707
1.000 00	0.809 69	0.0000
0.000 00	0.752 65	0.0000
0.087 53	0.754 35	0.3068
0.143 42	0.755 74	0.4310
0.204 11	0.757 50	0.5256
0.319 19	0.761 43	0.6294
0.433 36	0.766 13	0.6665
0.541 21	0.771 29	0.6835
0.646 11	0.777 33	0.6410
0.699 37	0.780 85	0.5991
0.825 31	0.790 96	0.4295
0.922 98	0.800 57	0.1960
1.000 00	0.809 69	0.0000

Table II. Coefficients of Eq 1 and Standard Deviations $\sigma(V_m^E)$

$xC_4H_9CH(OH)CH_3$ +	R	A_0	A_1	A_2	A_3	$\sigma(V_m^E)/cm^3\cdot mol^{-1}$
$(1-x)C_5H_{12}$	0.9630	0.7455	−10.7084	20.6784	−14.5376	0.0040
$(1-x)C_6H_{14}$	0.9228	2.2922	−8.6004	15.6355	−10.5537	0.0048
$(1-x)C_7H_{16}$	1.8766	2.2964	−7.0211	15.2037	−11.7270	0.0065
$(1-x)C_8H_{18}$	0.7176	3.6802	−8.9372	14.5012	−8.2713	0.0047
$(1-x)C_9H_{20}$	0.9040	4.0012	−11.0587	19.8481	−11.6111	0.0070
$(1-x)C_{10}H_{22}$	1.0302	3.9942	−10.6373	20.7856	−13.1385	0.0055
$(1-x)C_{11}H_{24}$	0.8790	4.4157	−11.7061	22.0234	−13.3060	0.0050
$(1-x)C_{12}H_{26}$	0.8342	4.5847	−10.9506	19.3911	−10.9125	0.0053
$(1-x)C_{13}H_{28}$	1.3670	4.4125	−10.1382	19.0751	−10.9011	0.0048

as reference samples for calibration, as proposed by the author in ref *3*. Density measurements were observed with a precision of ±3 × 10^{-2} kg·m^{-3}, and V_m^E results were estimated with an accuracy better than ±0.002 cm^3·mol^{-1}.

Results and Discussion

Experimental values for V_m^E at 298.15 K for mixtures of $\{xC_4H_9CH(OH)CH_3+(1-x)C_nH_{2n+2}\}$ with n = 1, 2, ..., 12, 13

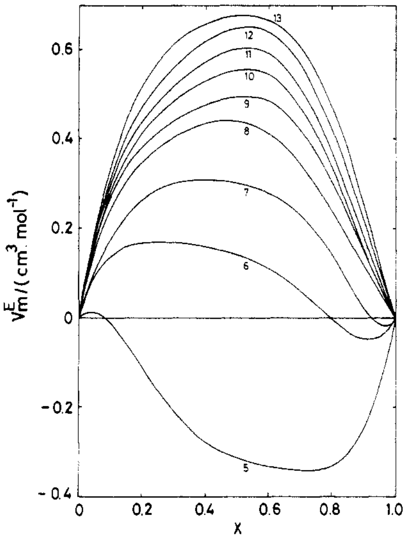

Figure 1. Excess molar volumes at 298.15 K for $\{xC_4H_9CH(OH)CH_3 + (1-x)C_nH_{2n+2}\}$. The curves were calculated from the coefficients given in Table II; numbers indicate n.

are listed in Table I. In order to correlate experimental data whose distribution has a sigmoidal form, one of the authors recommended in ref *10* the use of a polynomial equation of type

$$V_m^E(\mathrm{cm^3 \cdot mol^{-1}}) = x(1-x)\sum_i A_{i-1}Z^{i-1} \qquad i = 1, 2, \ldots \qquad (1)$$

where

$$Z = x/[x + R(1-x)] \qquad (2)$$

The coefficients A_{i-1} were obtained by a method of least squares while R was found by optimization in order to achieve the best fitting possible. The values used for the parameters in eq 1 are given in Table II together with the standard deviations obtained, $\sigma(V_m^E)$. The smooth representations of our results are presented in Figure 1. Contrarily to the mixtures studied in other works (*1*–*3*), the curves for the present mixtures of hexan-2-ol + C_nH_{2n+2} are sigmoidal when n = 5, 6, 7, causing expansions occurring at mole fractions low in alkanol and contractions at higher alkanol mole fractions.

In previous works where hexanol isomers were used with different types of compounds, it can be observed that V_m^E's are greater when the said compounds are mixed with secondary or tertiary alkanols than when mixed with primary alkanols. This fact is also observed in works such as that of Treszczanowicz et al. (*11*) where results for mixtures $\{xC_6H_{13}(OH) + (1-x)C_nH_{2n+2}\}$ (from n = 5 to 10), or with those obtained by Bravo et al. (*6*) for $\{xC_3H_7CH(CH_3)CH_2(OH) + (1-x)C_nH_{2n+2}\}$ (for n = 6, 7, 10, 14), it being evident from our results that branched alkanols produce a less negative contribution for V_m^E on mixing them with n-alkanes. This is due to the typical contributions appearing in these type of systems such as, on the one hand, that caused by the dipole–dipole interaction, and on the other, that caused by the effect of the alkanol's self-association. This self-association effect seems to predominate over the former when the alkanol is not primary, thus confirming the asymmetries of the curves at low x, which disappear with the increase of the n-alkane chain. The variation of V_m^E for these mixtures, at a determined concentration, was correlated with the number of carbon atoms in the n-alkane by means of a quadratic equation of the form $V_m^E = -2.0217 + 0.4626n - 0.0199n^2$, giving, for $x = 0.5$, a correlating coefficient $r = 0.98$.

Registry No. $C_4H_9CH(OH)CH_3$, 626-93-7; C_5H_{12}, 109-66-0; C_6H_{14}, 110-54-3; C_7H_{16}, 142-82-5; C_8H_{18}, 111-65-9; C_9H_{20}, 111-84-2; $C_{10}H_{22}$, 124-18-5; $C_{11}H_{24}$, 1120-21-4; $C_{12}H_{26}$, 112-40-3; $C_{13}H_{28}$, 629-50-5.

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