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### Refractive Indices and Speeds of Sound of Binary Mixtures of *N*-Octane with 1-Alkanol at the Temperature 298.15 K

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# REFRACTIVE INDICES AND SPEEDS OF SOUND OF BINARY MIXTURES OF *N*-OCTANE WITH 1-ALKANOL AT THE TEMPERATURE 298.15 K

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This paper reports experimental values for the refractive index, speed of sound, and isentropic compressibility of binary mixtures of *n*-octane with (1-butanol, 1-hexanol and 1-octanol) at the temperature of 298.15 K and atmospheric pressure, as a function of mole fraction. From the experimental values, the corresponding derived values were computed (changes of refractive index, changes of speed of sound and changes of isentropic compressibilities) using variable-degree polynomials to fit the data. Also, an attempt was made to correlate the behaviour of these magnitudes to the number of carbon atoms in the 1-alkanol chain.

**Keywords:** Refractive index; speed of sound; isentropic compressibility; *n*-alkane; 1-alkanol

## 1. INTRODUCTION

Continuing a serie of theoretical and experimental works (Iglesias *et al.*, 1993, 1994, 1995; Franjo *et al.*, 1995; Fernández *et al.*, 1990;

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Peleteiro *et al.*, 1992; Romaní *et al.*, 1994; De Cominges *et al.*, 1998) about binary mixtures *n*-alkane + 1-alkanol, this paper reports refractive indices ( $n_D$ ), speeds of sound ( $u$ ) and isentropic compressibilities ( $k_S$ ) and the corresponding increments of mixtures of *n*-octane with (1-butanol, 1-hexanol and 1-octanol), which were measured at the temperature of 298.15 K and atmospheric pressure, over the entire range of composition.

The refractive index was measured with a refractometer ABBE-MAT-HP Dr. Kernchen and the speed of sound with an Anton-Paar DSA-48 sound analyzer. From the experimental values of the pure liquids and their mixtures, the corresponding increments were computed (changes of refractive index on mixing, changes of speed of sound and changes of isentropic compressibility). The results were fitted to a polynomial of the Redlich-Kister type.

The results of the studied mixtures have been compared with other available physical properties. For these systems, have been reported values of densities ( $\rho$ ) and excess volumes ( $V^E$ ) (Iglesias *et al.*, 1995 and Franjo *et al.*, 1995), excess molar enthalpies ( $H^E$ ) (Jiménez *et al.*, 1988 and Amigo *et al.*, 1990), excess Gibbs energies ( $G^E$ ) (Gierycz *et al.*, 1988 and Plesnar *et al.*, 1988), excess heat capacities ( $C_p^E$ ) (Andreolli-Ball *et al.*, 1988), dinamic viscosities ( $\eta$ ) and their increments ( $\Delta\eta$ ) (Franjo *et al.*, 1995) and the complex relative permittivity ( $\epsilon^* = \epsilon' - j\epsilon''$ ) at the frequency 1 GHz and their increments ( $\Delta\epsilon'$  and  $\Delta\epsilon''$ ) (Iglesias *et al.*, 1995). Also, an attempt was made to correlate the behaviour of these magnitudes to the number of carbon atoms in the 1-alkanol chain.

## 2. EXPERIMENTAL SECTION

The 1-alkanols employed were supplied by Merck and the *n*-octane by Fluka. Their mole fraction purities were: *n*-octane (> 0.995), 1-butanol (> 0.995), 1-hexanol (> 0.98) and 1-octanol (> 0.99). The substances were degassed and dried on molecular sieves (Union Carbide, type 0.4 nm). Precautions such as cooling chemicals before sample preparation and minimizing empty space in vessels were taken, in order to avoid evaporation losses during manipulations and then possible errors in calculations.

The refractive index was measured by an automatic refractometer ABBEMAT-HP Dr. Kernchen, with a precision of  $\pm 0.00001$ . In order to keep a constant temperature, the measuring prism was water-jacketed using a PolyScience controller bath model 9510 with a temperature stability of  $\pm 0.01$  K. Triply distilled water (Millipore quality) and ambient air were used for refractometer calibration.

The speed of sound of the mixtures and pure liquids was measured with an Anton Paar DSA-48 sound analyzer with a precision of  $\pm 0.1 \text{ m}\cdot\text{s}^{-1}$ . The apparatus calibration was performed periodically. For calibrating the speed of sound cell, triply distilled water (Millipore quality) is used.

The experimental techniques and mode of operation have been described previously (De Cominges *et al.*, 1998).

The samples were prepared by weight using a Mettler AE-240 balance with a precision of  $\pm 1\cdot 10^{-4}$  in mole fraction, covering the whole composition ranges of the mixture. A digital controller bath with a temperature stability of  $\pm 10^{-2}$  K was used to thermostatize the samples, that remained at the measure temperature at least 30 minutes.

Accuracy in the changes on mixing was estimated to be better than  $\pm 5\cdot 10^{-5}$  for the refractive index,  $\pm 0.5 \text{ m}\cdot\text{s}^{-1}$  for the speed of sound and  $\pm 0.9 \text{ TPa}^{-1}$  for the isentropic compressibilities.

### 3. RESULTS AND DISCUSSION

Refractive indices, speeds of sound, isentropic compressibilities, complex relative permittivity and viscosities of the pure component liquid are listed in Table I together with literature values.

The experimental results of density,  $\rho$ , refractive index,  $n_D$ , speed of sound,  $u$ , and isentropic compressibility,  $k_S$  ( $k_S = \rho^{-1}u^{-2}$ ), at 298.15 K, for all binary mixtures are reported in Table II.

Changes of refractive index on mixing  $\Delta n_D$ , changes of speed of sound on mixing  $\Delta u$ , and changes of isentropic compressibility on mixing  $\Delta k_S$ , were evaluated for each composition point, using the following equation:

$$\Delta Q = Q - \sum_{i=1}^2 x_i Q_i \quad (1)$$

TABLE I Comparison of the density  $\rho$ , the refractive index  $n_D$ , the speed of sound  $u$ , the isentropic compressibility  $k_S$ , the complex relative permittivity  $\epsilon^* = \epsilon' - j\epsilon''$  and the viscosity of the pure liquids with the available literature data at  $T = 298.15\text{ K}$

component	$\rho(\text{g}\cdot\text{cm}^{-3})$ literature	$n_D$ expt. literature	$u(\text{m}\cdot\text{s}^{-1})$ expt. literature	$k_S(\text{TPa}^{-1})$ expt. literature	$\epsilon''$ literature	$\eta(\text{mPa}\cdot\text{s})$ literature
<i>n</i> -pentane	0.6213 <sup>[19]</sup>	0.6211 <sup>[20]</sup>	1.35444 <sup>[20]</sup>	1004.6 <sup>[20]</sup>	1595 <sup>[19]</sup>	0.237 <sup>[20]</sup>
<i>n</i> -hexane	0.65520 <sup>[1]</sup>	0.65505 <sup>[5]</sup>	1.37207	1.37226 <sup>[19]</sup>	1315	0.286 <sup>[5]</sup>
<i>n</i> -heptane	0.6794 <sup>[24]</sup>	0.6794 <sup>[20]</sup>	1.38512 <sup>[20]</sup>	1130.5 <sup>[20]</sup>	1.880 <sup>[1]</sup>	0.296 <sup>[23]</sup>
<i>n</i> -octane	0.69847 <sup>[2]</sup>	0.69846 <sup>[2]</sup>	1.39510	1.39514 <sup>[20]</sup>	1151 <sup>[19]</sup>	0.404 <sup>[25]</sup>
<i>n</i> -nonane	0.71369 <sup>[25]</sup>	0.71381 <sup>[19]</sup>	1.40311 <sup>[19]</sup>	1.40311 <sup>[19]</sup>	1.9135 <sup>[23]</sup>	0.506 <sup>[6]</sup>
<i>n</i> -decane	0.72606 <sup>[25]</sup>	0.72605 <sup>[19]</sup>	1.40967 <sup>[19]</sup>	1.40967 <sup>[19]</sup>	1.9422 <sup>[2]</sup>	0.508 <sup>[26]</sup>
Methanol	0.7865 <sup>[20]</sup>	0.78654 <sup>[21]</sup>	1.32652 <sup>[21]</sup>	1102. <sup>[20]</sup>	1046.7 <sup>[20]</sup>	0.686 <sup>[25]</sup>
Ethanol	0.7852 <sup>[20]</sup>	0.78509 <sup>[26]</sup>	1.35941 <sup>[26]</sup>	1142.6 <sup>[20]</sup>	975.5 <sup>[20]</sup>	0.553 <sup>[20]</sup>
1-propanol	0.7995 <sup>[20]</sup>	0.79975 <sup>[26]</sup>	1.38307 <sup>[20]</sup>	1205.4 <sup>[20]</sup>	860.8 <sup>[20]</sup>	1.105 <sup>[20]</sup>
1-butanol	0.80580 <sup>[1]</sup>	0.80581 <sup>[5]</sup>	1.39719	1.39716 <sup>[26]</sup>	806	1.970 <sup>[20]</sup>
1-pentanol	0.8107 <sup>[21]</sup>	0.81115 <sup>[19]</sup>	1.4079 <sup>[19]</sup>	1240	4.170 <sup>[11]</sup>	1.9425 <sup>[23]</sup>
1-hexanol	0.81507 <sup>[1]</sup>	0.81532 <sup>[5]</sup>	1.41571 <sup>[19]</sup>	1276	758 <sup>[27]</sup>	2.550 <sup>[5]</sup>
1-heptanol	0.8189 <sup>[24]</sup>	0.8189 <sup>[24]</sup>	1.42222 <sup>[24]</sup>	1303	4.170 <sup>[11]</sup>	2.571 <sup>[26]</sup>
1-octanol	0.82162 <sup>[1]</sup>	0.82162 <sup>[5]</sup>	1.42747	1327	694	7.363 <sup>[19]</sup>
1-nonanol	0.8244 <sup>[28]</sup>	0.8244 <sup>[28]</sup>	1348	1348	3.096 <sup>[11]</sup>	5.770 <sup>[21]</sup>
1-decanol	0.82671 <sup>[25]</sup>	0.82659 <sup>[21]</sup>			7.596 <sup>[5]</sup>	11.790 <sup>[25]</sup>
					11.790 <sup>[25]</sup>	11.798 <sup>[21]</sup>

TABLE II Densities,  $\rho$ , refractive indices,  $n_D$ , speeds of sound,  $u$ , isentropic compressibilities,  $k_S$ , changes of refractive index on mixing,  $\Delta n_D$ , changes of speed of sound,  $\Delta u$ , and changes of isentropic compressibility,  $\Delta k_S$ , at 298.15 K

$x$	$\rho^{(a)}$ $g \cdot cm^{-3}$	$n_D$	$u$ $m \cdot s^{-1}$	$k_S$ $TPa^{-1}$	$\Delta n_D$	$\Delta u$ $m \cdot s^{-1}$	$\Delta k_S$ $TPa^{-1}$
$x$ <i>n</i> -octane + (1 - $x$ ) 1-butanol							
0.0268	0.80060	1.39688	1235.2	818.6	-0.00025	-3.3	5.7
0.0561	0.79516	1.39662	1229.8	831.4	-0.00045	-6.7	11.7
0.0901	0.78917	1.39650	1223.9	845.9	-0.00050	-10.3	18.1
0.1173	0.78460	1.39634	1219.8	856.6	-0.00060	-12.6	22.5
0.1571	0.77824	1.39616	1214.0	871.8	-0.00070	-15.7	28.4
0.1951	0.77249	1.39595	1208.7	886.0	-0.00083	-18.4	33.7
0.2352	0.76673	1.39577	1203.7	900.1	-0.00093	-20.7	38.3
0.2979	0.75832	1.39545	1195.9	921.9	-0.00112	-24.2	45.5
0.3151	0.75613	1.39539	1194.6	926.7	-0.00114	-24.4	46.2
0.3602	0.75061	1.39520	1190.3	940.2	-0.00124	-25.6	49.1
0.4116	0.74471	1.39507	1186.2	954.3	-0.00126	-26.2	51.1
0.4608	0.73943	1.39488	1182.4	967.3	-0.00135	-26.7	52.6
0.5099	0.73447	1.39465	1179.2	979.0	-0.00147	-26.5	52.8
0.5714	0.72869	1.39454	1175.9	992.3	-0.00145	-26.5	51.6
0.6289	0.72366	1.39448	1173.3	1003.7	-0.00139	-24.3	49.5
0.6921	0.71850	1.39430	1171.1	1014.8	-0.00144	-22.4	45.8
0.7649	0.71300	1.39433	1169.7	1025.2	-0.00126	-18.8	39.0
0.8388	0.70787	1.39428	1168.6	1033.8	-0.00116	-14.5	30.3
0.9199	0.70279	1.39462	1168.9	1041.2	-0.00065	-9.0	18.7
$x$ <i>n</i> -octane + (1 - $x$ ) 1-hexanol							
0.0402	0.80915	1.41503	1294.6	737.4	-0.00008	-3.4	2.2
0.0776	0.80370	1.41356	1286.7	751.5	-0.00076	-6.4	4.4
0.1184	0.79785	1.41274	1278.5	766.7	-0.00073	-9.3	6.6
0.1624	0.79165	1.41159	1269.8	783.4	-0.00096	-12.2	9.2
0.2004	0.78641	1.41060	1262.4	797.9	-0.00115	-14.7	11.6
0.2476	0.78000	1.40932	1253.8	815.5	-0.00143	-17.0	14.1
0.2906	0.77437	1.40823	1246.2	831.5	-0.00163	-19.0	16.4
0.3360	0.76854	1.40731	1238.5	848.2	-0.00160	-20.8	18.6
0.3841	0.76252	1.40626	1230.9	865.6	-0.00164	-22.1	20.6
0.4295	0.75699	1.40519	1224.0	881.7	-0.00176	-23.0	22.2
0.4771	0.75134	1.40428	1217.2	898.3	-0.00167	-23.6	23.7
0.5235	0.74597	1.40323	1211.0	914.0	-0.00175	-23.7	24.6
0.5817	0.73942	1.40235	1203.9	933.0	-0.00141	-23.2	25.0
0.6351	0.73358	1.40109	1198.0	949.8	-0.00155	-22.2	24.7
0.6886	0.72790	1.39990	1192.6	965.9	-0.00162	-20.6	23.8
0.7420	0.72240	1.39892	1187.5	981.7	-0.00148	-18.7	22.5
0.8045	0.71617	1.39772	1182.3	998.8	-0.00137	-15.7	19.7
0.8627	0.71060	1.39704	1177.9	1014.1	-0.00083	-12.4	16.4
0.9296	0.70449	1.39596	1173.9	1029.9	-0.00051	-7.7	10.9
$x$ <i>n</i> -octane + (1 - $x$ ) 1-octanol							
0.0637	0.81369	1.42531	1334.0	690.6	-0.00010	-2.6	-3.1
0.0979	0.80942	1.42431	1326.5	702.1	-	-4.0	-4.3
0.1549	0.80230	1.42201	1314.4	721.4	-	-6.2	-6.1
0.2013	0.97651	1.42090	1304.6	737.7	-0.00005	-7.9	-7.1
0.2511	0.79031	1.41907	1294.0	755.6	-0.00027	-9.7	-7.7

TABLE II (Continued)

$x$	$\rho$ $g \cdot cm^{-3}$	$n_D$	$u$ $m \cdot s^{-1}$	$k_S$ $TPa^{-1}$	$\Delta n_D$	$\Delta u$ $m \cdot s^{-1}$	$\Delta k_S$ $TPa^{-1}$
0.2873	0.78581	1.41785	1286.6	768.8	-0.00032	-10.8	-8.0
0.3295	0.78056	1.41645	1278.7	784.7	-0.00035	-12.2	-7.7
0.3883	0.77326	1.41446	1265.9	806.9	-0.00044	-13.7	-7.3
0.4480	0.76585	1.41251	1254.5	829.6	-0.00046	-14.7	-6.8
0.4887	0.76080	1.40133	1246.9	845.3		-15.1	-6.3
0.5431	0.75404	1.40978	1237.1	866.5		-15.4	-5.3
0.5872	0.74855	1.40845	1229.3	883.9		-15.5	-4.2
0.6334	0.74281	1.40676	1221.2	902.7		-15.5	-2.6
0.6850	0.73639	1.40503	1213.1	922.8		-14.6	-1.7
0.7305	0.73075	1.40347	1205.9	941.0	-0.00035	-13.8	-0.4
0.7829	0.72428	1.40216	1198.2	961.7		-12.3	0.8
0.8274	0.71881	1.40052	1191.8	979.4	-0.00017	-10.8	1.9
0.8952	0.71065	1.39790	1182.7	1005.9		-8.0	3.3
0.9328	0.70619	1.39682	1178.0	1020.3		-6.1	3.8

(a) Iglesias *et al.*, 1993, 1995.

In this equation,  $Q = n_D$ ,  $u$  or  $k_S$  and  $\Delta Q$  is the excess property ( $\Delta n_D$ ,  $\Delta u$  or  $\Delta k_S$ ), and the corresponding quantities with subscript  $i$  refer to pure chemicals. The excess values are given in Table II. As shown this table, for the mixture including 1-octanol, there are few data of  $\Delta n_D$ . This is due to the fact that the values are within the accuracy of the refractometer.

Excess values were correlated by means of the Redlich-Kister expression (Redlich and Kister, 1948) for every binary mixture:

$$\Delta Q = x(1-x) \sum_{p=0}^M A_p (2x-1)^p, \quad (2)$$

where  $x$  is the molar fraction of *n*-octane,  $A_p$  a parameter and  $M$  the degree of the polynomial expansion. An unweighted least-squares method was used to fit the data. The degree of the polynomials was optimized by applying the Test-F (Bevington, 1969). The parameters calculated using Eq. 2 are listed in Table III.

Figure 1 shows the experimental  $\Delta n_D$ ,  $\Delta u$  and  $\Delta k_S$  plotted against  $x$  as well as the smoothed curve for *n*-octane + 1-butanol. The results were compared with other physical properties of the same mixture at 298.15 K: excess volumes  $V^E$  and increments in complex relative permittivity  $\Delta\epsilon'$  and  $\Delta\epsilon''$  (Iglesias *et al.*, 1993), increments in dinamic viscosities  $\Delta\eta$  (Franjo *et al.*, 1995), and excess molar enthalpies  $H^E$

TABLE III Parameters  $A_p$  of Eq. (2) and standard deviations  $s$ 

	$A_0$	$A_1$	$A_2$	$A_3$	$s$
$x$ <i>n</i> -octane + (1 - $x$ ) 1-butanol					
$\Delta n_D$	-0.00556	-0.00190	-0.00279		0.00004
$\Delta u/(m \cdot s^{-1})$	-106.3	9.0	-17.7		0.3
$\Delta k_S/(TPa^{-1})$	211.0	5.4	23.4		0.6
$x$ <i>n</i> -octane + (1 - $x$ ) 1-hexanol					
$\Delta n_D$	-0.00701	-0.00013	-0.00085		0.00006
$\Delta u/(m \cdot s^{-1})$	-944.0	-7.6	-4.3		0.3
$\Delta k_S/(TPa^{-1})$	95.5	35.5	12.4	28.7	0.3
$x$ <i>n</i> -octane + (1 - $x$ ) 1-octanol					
$\Delta n_D$	-0.00162	-0.00031			0.00007
$\Delta u/(m \cdot s^{-1})$	-60.6	-15.4	-5.6	-1.7	0.2
$\Delta k_S/(TPa^{-1})$	-24.8	34.0	24.2	32.2	0.4

(Jiménez *et al.*, 1988). Excess Gibbs energies were measured but at the temperature of 373.15 and 383.15 K (Gierycz *et al.*, 1988).  $\Delta n_D$ ,  $\Delta u$ ,  $\Delta \varepsilon'$ ,  $\Delta \varepsilon''$  and  $\Delta \eta$  are negative and  $\Delta k_S$ ,  $V^E$  and  $H^E$  are positive. With the exception of  $\Delta u$ ,  $\Delta k_S$  and  $\Delta \varepsilon''$ , which are symmetric with respect to  $x = 0.5$ , all the other properties present an asymmetry.  $\Delta n_D$  and  $V^E$  present the shift to the right (high *n*-octane content) and  $\Delta \varepsilon'$ ,  $\Delta \eta$  and  $H^E$  to the left (low *n*-octane content).

Figure 2 shows the experimental  $\Delta n_D$ ,  $\Delta u$  and  $\Delta k_S$  plotted against  $x$  as well as the smoothed curve for *n*-octane + 1-hexanol. The results have been compared with other physical properties of the same mixture at the temperature of 298.15 K. The excess magnitudes are the same that in the previous case, with the exception of  $H^E$  for which available data were not found (excess molar enthalpies were measured but at temperature of 288.15 and 328.15 K (Nguyen and Ratcliff, 1975). However, heat capacity is available for this mixture but not for *n*-octane + 1-butanol). Excess volumes and increments in complex relative permittivity (Iglesias *et al.*, 1995), increments in dinamic viscosities (Franjo *et al.*, 1995), and excess heat capacity  $C_p^E$  (Andreolli-Ball *et al.*, 1988), are available.  $\Delta n_D$ ,  $\Delta u$ ,  $\Delta \varepsilon'$ ,  $\Delta \varepsilon''$  and  $\Delta \eta$  are negative and  $\Delta k_S$  and  $C_p^E$  are positive.  $V^E$  show a small negative region at high alcohol mole fraction. With the exception of  $\Delta u$  and  $\Delta n_D$ , which are symmetric to  $x = 0.5$ , all the other properties present an asymmetry, moving to the right (high *n*-octane content) for  $\Delta k_S$ ,  $\Delta \varepsilon''$ , and  $C_p^E$  and moving to the left (high 1-hexanol content) for  $\Delta \eta$ .

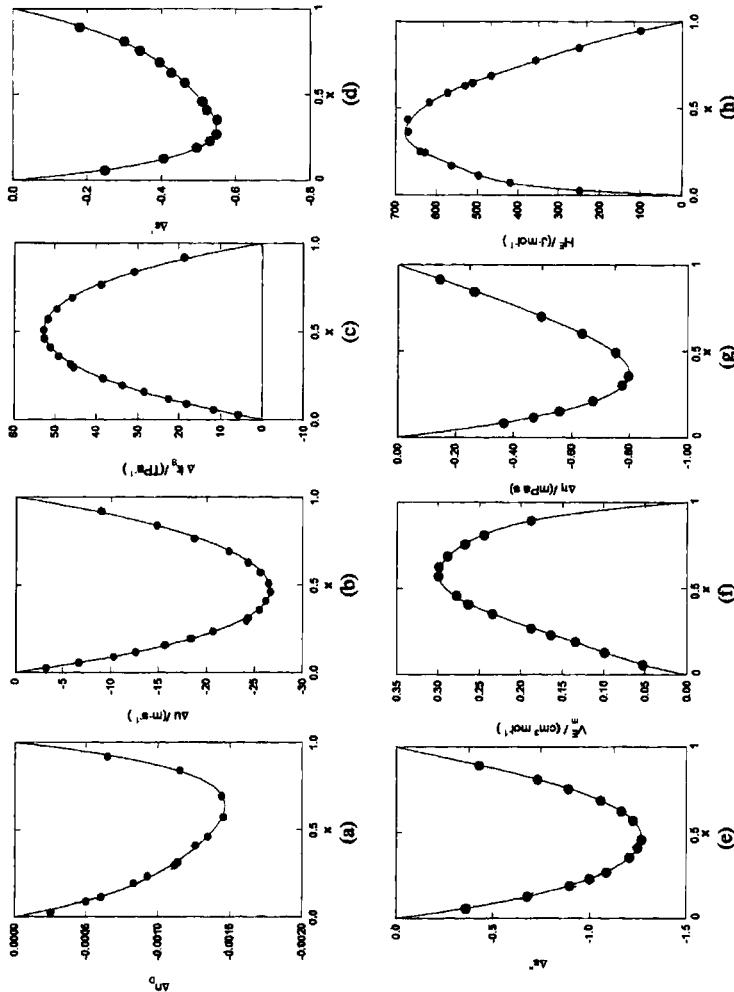


FIGURE 1 Variation of: (a) changes of refractive index,  $\Delta n_D$ , (b) changes of speed of sound,  $\Delta u$ , (c) excess molar volumes,  $V_{\text{Ex}}$ , (e) and (f) relative-permittivity increments<sup>[2]</sup>,  $\Delta \epsilon'$  and  $\Delta \epsilon''$ , respectively, (g) viscosity increments<sup>[6]</sup>,  $\Delta \eta$ , and (h) excess molar enthalpy<sup>[11]</sup>,  $H_{\text{Ex}}$ , on mixing with mole fraction for  $\{x\text{ }n\text{-octane} + (1-x)\text{ 1-butanol}\}$  at 298.15 K.

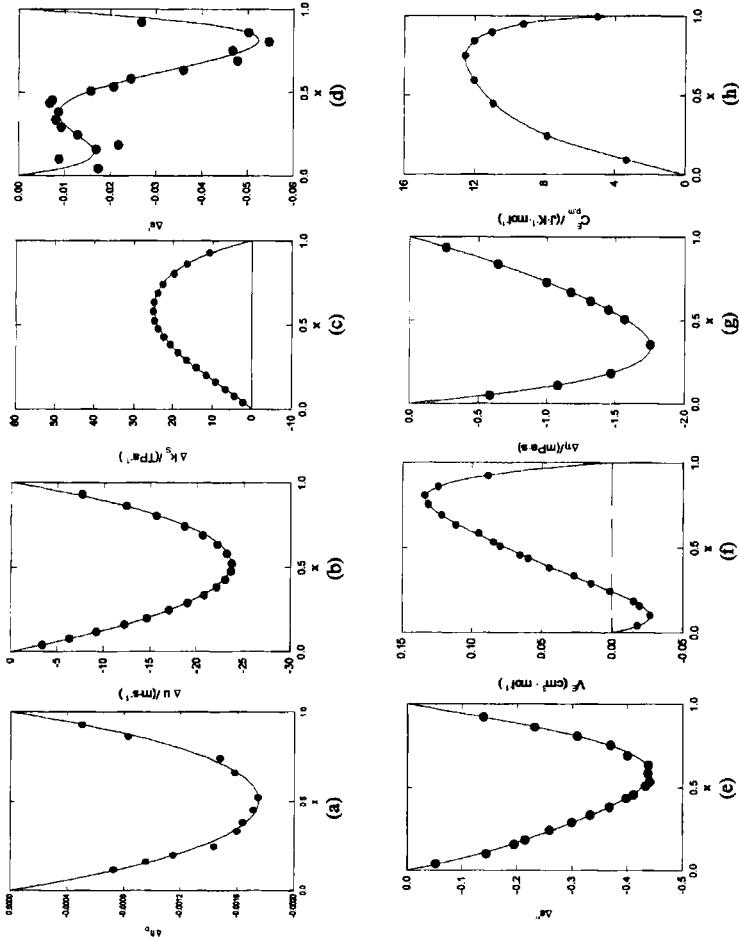


FIGURE 2 Variation of: (a) changes in refractive index,  $\Delta n_D$ , (b) changes in speed of sound,  $\Delta u$ , (c) changes in isentropic compressibility,  $\Delta k_S$ , (d) excess molar volumes<sup>[4]</sup>,  $V_p^E$ , (e) and (f) relative-permittivity increments<sup>[5]</sup>,  $\Delta \epsilon'$  and  $\Delta \epsilon''$ , respectively, (g) viscosity increments<sup>[6]</sup>,  $\Delta \eta$  and (h) excess heat capacities<sup>[15]</sup>,  $C_{p,m}^E$ , on mixing with mole fraction for {*x*-*n*-octane + (1-*x*) 1-hexanol} at 298.15 K.

Figure 3 shows the experimental  $\Delta n_D$ ,  $\Delta u$  and  $\Delta k_S$  plotted against  $x$  as well as the curve fitted of the mixture of *n*-octane + 1-octanol. Again, the results were compared with the physical properties mentioned before of the same mixture at 298.15 K: excess volumes and increments in complex relative permittivity (Iglesias *et al.*, 1995), increments in dinamic viscosities (Franjo *et al.*, 1995), and excess molar enthalpies (Amigo *et al.*, 1990).  $\Delta n_D$ ,  $\Delta u$ ,  $\Delta \epsilon''$  and  $\Delta \eta$  are negative and  $\Delta \epsilon'$  and  $H^E$  are positive.  $\Delta k_S$  and  $V^E$  show a small positive region at low alcohol mole fraction. All properties present an asymmetry.  $\Delta u$ ,  $\Delta \epsilon''$  and  $H^E$  present the shift to the right (high *n*-octane content) and  $\Delta \epsilon'$  and  $\Delta \eta$  on to the left (low *n*-octane content).

Figures 4 to 6 present every previous mentioned properties at equimolar mole fraction against 1-alkanol carbon atom number,  $n$ , at the temperature of 298.15 K.

Figure 4a shows the experimental values of  $\Delta n_D$ . This property seem to have a reversed parabolic behaviour, with a minimum in the same area for all the chains. This minimum seems to move with the length of the 1-alkanol and be independent from the alkane's chain (although more measured data are necessary to affirm this hypothesis).

$\Delta k_S$  (Fig. 4b) decreases with the 1-alkanol carbon number, being positive for all the mixtures except for *n*-hexane + 1-hexanol and 1-octanol and *n*-octane + 1-octanol. By opposition, the dependence with the alkane length is not so regular.

Exces molar volumes  $V^E$  (Fig. 4c) changes from positive to negative values with the length of the 1-alkanol. This behaviour could be considered linear with different slopes but the same value when 1-alkanol carbon atom number approaches to zero.

Figures 5a and 5b show the same representation type, in this case for  $H^E$  and  $G^E$ , respectively. The  $H^E$  could present a maximum for 1-propanol for all the available mixtures (from *n*-pentane to *n*-undecane), although, to affirm this hypothesis, data with ethanol and 1-propanol will be necessary.

In what it is referred to  $G^E$ , the number of available data does not permit to guess a determined behaviour, but seems to decrease with the length of 1-alkanol and increase with the length of *n*-alkane.

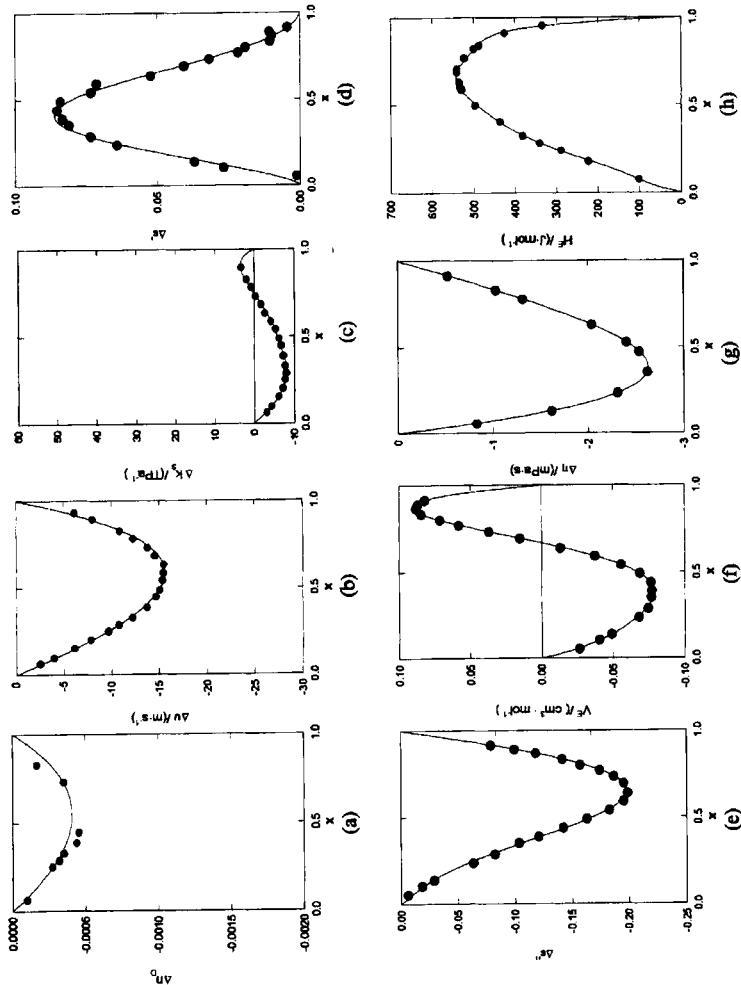


FIGURE 3 Variation of: (a) changes in refractive index,  $\Delta n_D$ , (b) changes in speed of sound,  $\Delta u$ , (c) changes in isentropic compressibility,  $\Delta k_S$ , (d) excess molar volumes<sup>[4]</sup>,  $V^E$ , (e) and (f) relative-permittivity increments<sup>[4]</sup>,  $\Delta\epsilon'$  and  $\Delta\epsilon''$ , respectively, (g) viscosity increments<sup>[6]</sup>,  $\Delta\eta$ , and (h) excess molar enthalpy<sup>[12]</sup>,  $H^E$ , on mixing with mole fraction for  $\{x\text{-}n\text{-octane} + (1-x)\text{1-octanol}\}$  at 298.15 K.

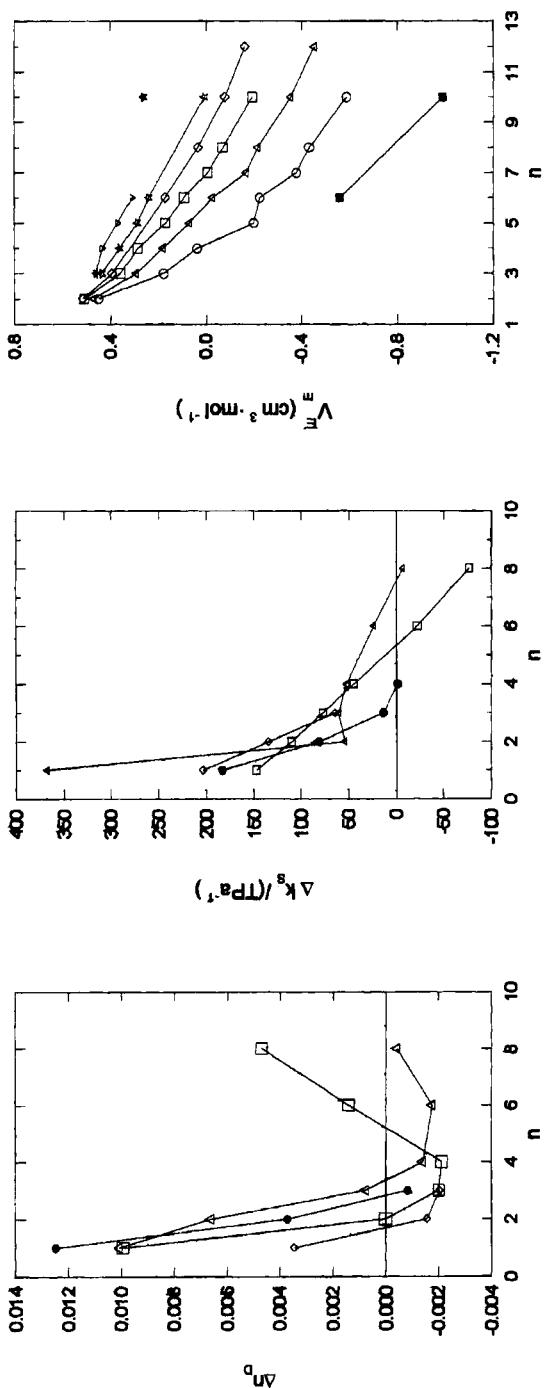


FIGURE 4.  $\Delta n_D$ ,  $\Delta k_S$ , and  $\nu^E$  at 298.15 K of  $\{0.5 \text{C}_m\text{H}_{2m+2} + 0.5 \text{C}_n\text{H}_{2n+1} + \text{OH}\}$  against  $n$ .

a)  $\Delta n_D$ : ( $\diamond$ )  $m = 5^{[20]}$ , ( $\square$ )  $m = 6^{[10, 20]}$ , ( $\bullet$ )  $m = 7^{[20]}$ , ( $\triangle$ )  $m = 8^{[20, \text{this work}]}$ .  
 b)  $\Delta k_S$ : ( $\diamond$ )  $m = 5^{[20]}$ , ( $\square$ )  $m = 6^{[10, 20]}$ , ( $\bullet$ )  $m = 7^{[20, 23, 24]}$ , ( $\triangle$ )  $m = 8^{[20]}$ , this work].  
 c)  $\nu^E$ : ( $\blacksquare$ )  $m = 5^{[29, 30]}$ , ( $\circ$ )  $m = 6^{[31, 32, 5, 33]}$ , ( $\square$ )  $m = 7^{[31, 40, 42]}$ , ( $\triangle$ )  $m = 8^{[31]}$ , ( $\diamond$ )  $m = 9^{[38, 36, 37, 39]}$ , ( $\star$ )  $m = 10^{[40, 37]}$ , ( $\blacklozenge$ )  $m = 11^{[41]}$ , ( $\triangledown$ )  $m = 12^{[31, 40, 42]}$ , ( $\star$ )  $m = 16^{[37]}$ .

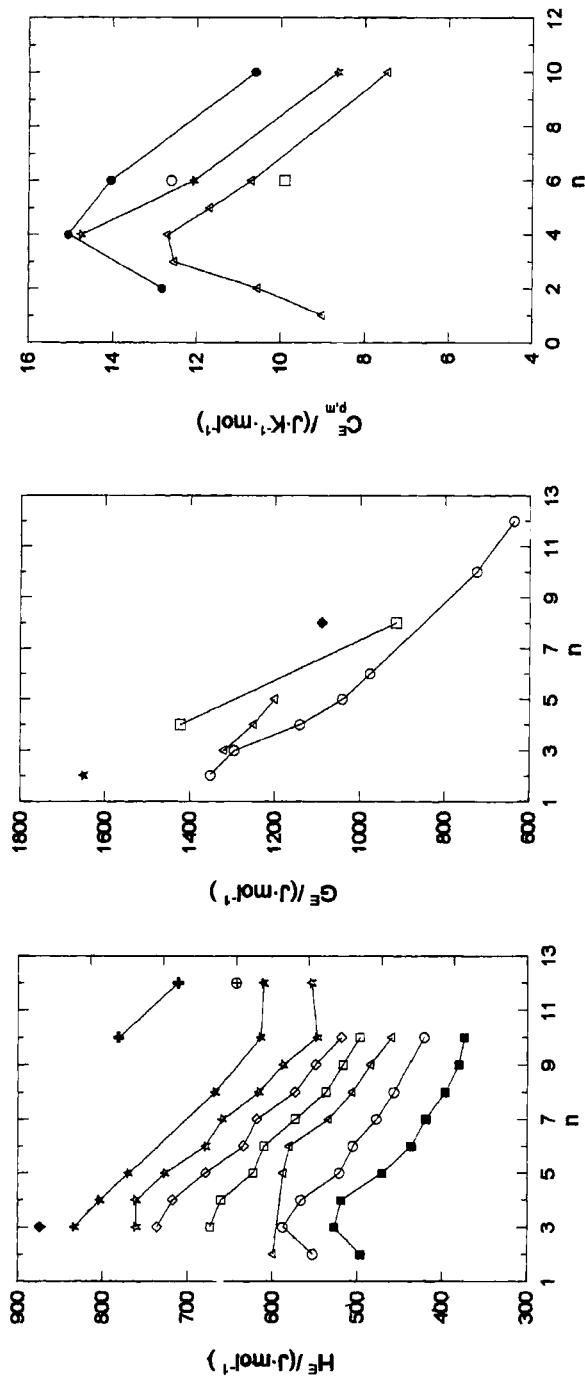


FIGURE 5  $H^E$ ,  $G^E$ , and  $C_p^E$  at 298.15 K of  $\{0.5\text{C}_m\text{H}_{2m+2} + 0.5\text{C}_n\text{H}_{2n+1}\text{OH}\}$  against  $n$ .

a)  $H^E$ : (●)  $m = 5^{[30,43,44]}$ , (○)  $m = 6^{[44,45,46]}$ , (Δ)  $m = 7^{[30,44,47,48]}$ , (□)  $m = 8^{[30,1]}$ , (◇)  $m = 9^{[46,49,12,50,51]}$ , (⊗)  $m = 10^{[46,49,12,50-53]}$ , (★)  $m = 11^{[54,46]}$ , (⊕)  $m = 12^{[53]}$ , (◆)  $m = 13^{[53]}$ , (▲)  $m = 14^{[53]}$ , (▲)  $m = 15^{[53]}$

b)  $G^E$ : (○)  $m = 6^{[57,63]}$ , (Δ)  $m = 7^{[64,36,53]}$ , (□)  $m = 8^{[14,13]}$ , (★)  $m = 9^{[46,66]}$ , (◆)  $m = 10^{[47,15]}$ , (◇)  $m = 11^{[67]}$ , (●)  $m = 12^{[71,5]}$ , (○)  $m = 13^{[67]}$

c)  $C_p^E$ : (□)  $m = 6^{[68]}$ , (Δ)  $m = 7^{[15,69,70]}$ , (○)  $m = 8^{[15]}$ , (★)  $m = 9^{[46,49,12,50-53]}$ , (●)  $m = 10^{[46,49,12,50-53]}$ , (○)  $m = 11^{[54,46]}$ , (□)  $m = 12^{[71,5]}$ , (●)  $m = 13^{[53]}$

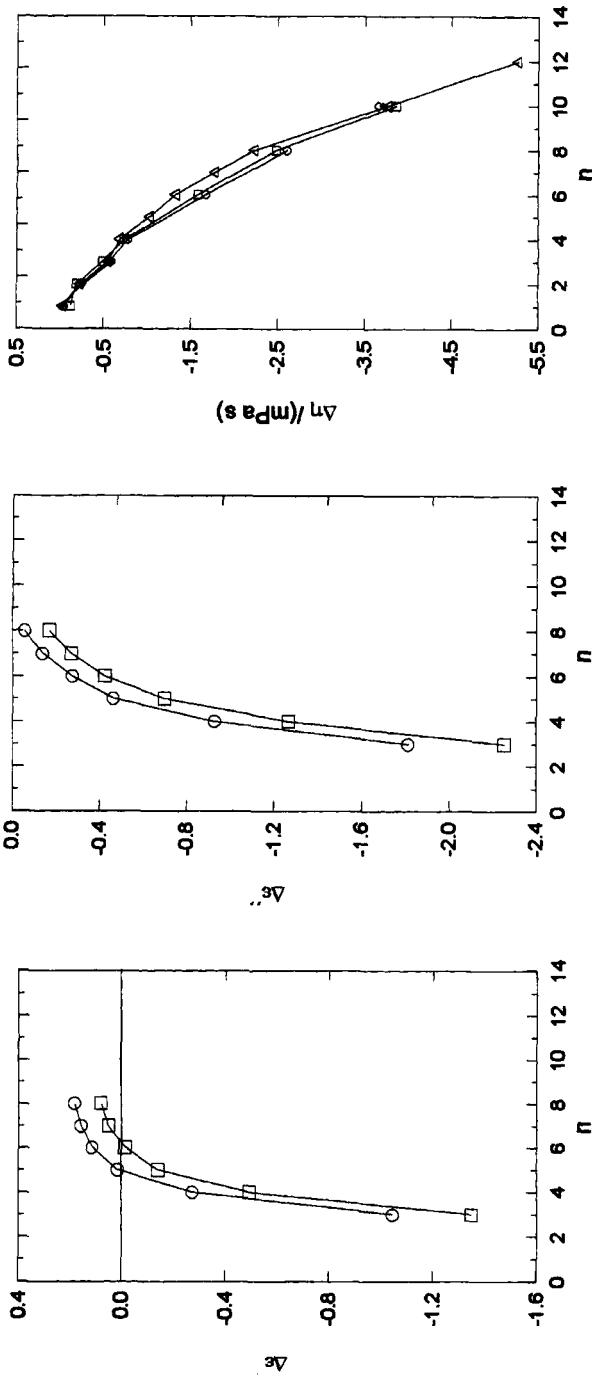


FIGURE 6  $\Delta\eta$ ;  $\Delta\varepsilon'$ ;  $\Delta\varepsilon''$  and  $\Delta\eta$  at 298.15 K of  $\{0.5C_mH_{2m+2} + 0.5C_nH_{2n+1}OH\}$  against  $n$ .

a)  $\Delta\varepsilon'$  (b)  $\Delta\varepsilon''$ : (○)  $m = 6^{[1,3]}$ ; (□)  $m = 8^{[2,4]}$   
 b)  $\Delta\eta$ : (●)  $m = 5^{[20]}$ ; (○)  $m = 6^{[3,20]}$ ; (Δ)  $m = 7^{[20,23,24]}$ ; (□)  $m = 9^{[25]}$ ; (◆)  $m = 9^{[25]}$ ; (◇)  $m = 10^{[25]}$ .

Figure 5c shows the values of  $C_p^E$  for systems for which experimental data are available. The  $C_p^E$  value is positive. The dependence with the alkanol length is not regular:  $C_p^E$  increases from methanol to butanol and decreases for longer chains of 1-alkanol.

At the frequency 1 GHz, as shown in Figures 6a and 6b, the  $\Delta\epsilon'$  and  $\Delta\epsilon''$  behaviour could be compared to a parabolic function. In the same case that previously, more data for large 1-alkanol chains will be necessary to affirm this supposition.  $\Delta\epsilon''$  is negative for all the systems.  $\Delta\epsilon'$  and  $\Delta\epsilon''$  increases with the length of the 1-alkanol and decrease with the length of the *n*-alkane. Note that the studied mixtures the behaviour of  $\Delta\epsilon'$  is contrary to that of  $V^E$ . This can be due to the fact that when  $V^E$  decreases, the number of dipoles per unit volume increases, this producing the  $\Delta\epsilon'$  increasing.  $\Delta\epsilon'$  increases when the length of the 1-alkanol increases and decreases when the *n*-alkane carbon atom number increases. This behaviour is opposite to those of  $H^E$  and  $G^E$ ; that means a minor delay of the response of the mixture to the applied field.

In what it is referred to  $\Delta\eta$  (Fig. 6c), for the available systems from *n*-pentane to *n*-decane with 1-alkanol at 298.15 K, is negative and decreases with the length of the 1-alkanol. As shown,  $\Delta\eta$ , is strongly dependent of the 1-alkanol and weakly of the *n*-alkane. It could be said that although  $\Delta\eta$  is neatly dependent of the length 1-alkanol chain, is not influence by the *n*-alkane chain.

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