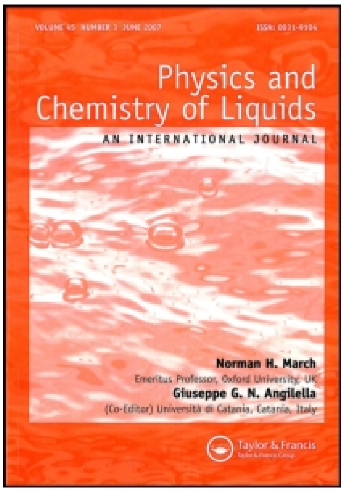

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Excess Dielectric Permittivity and Excess Molar Volumes of Binary Mixtures of *n*-Hexane with 1-Alkanol at the Temperature 298.15 K

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EXCESS DIELECTRIC PERMITTIVITY AND EXCESS MOLAR VOLUMES OF BINARY MIXTURES OF *n*-HEXANE WITH 1-ALKANOL AT THE TEMPERATURE 298.15 K

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Excess dielectric permittivity and excess molar volumes have been measured for the binary liquid mixtures of *n*-hexane with (1-butanol, 1-hexanol, 1-octanol) at the temperature 298.15 K and atmospheric pressure. Dielectric permittivity was determined using the short-circuited line method and the excess molar volume from densities measured by vibrating-tube densimetry.

KEY WORDS: Dielectric permittivity, excess molar volumes, *n*- alkane + 1-alkanol.

INTRODUCTION

As a part of studies on properties of binary mixtures (a 1-alkanol + an *n*-alkanes)[1–4], we report here the excess dielectric permittivity and excess molar volumes of *n*-hexane + (1-butanol, 1-hexanol, 1-octanol) at the temperature 298.15 K and atmospheric pressure. Dielectric permittivity were determined at 1 GHz, using the short-circuited line method and the excess molar volume was calculated from the experimental density values measured by vibrating-tube densimetry. Variable-degree polynomials have been fitted to the results.

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EXPERIMENTAL SECTION

All chemicals used were supplied by Merck, and presented the following commercial characteristics: *n*-hexane (>99%), 1-butanol (>99.5%), 1-hexanol (>99%) and 1-octanol (>99%). These substances were degassed and dried on molecular sieves (Union Carbido, type 4 Å), also by Fluka. The densities values (Table 1) were in close agreement with the values reported in the literature[5,6].

Table 1 Dielectric permittivity, excess dielectric permittivity, densities and excess molar volumes at the temperature 298.15 K

x	ε'	ε''	ρ $g \cdot cm^{-3}$	ε'^E	ε''^E	v^E $cm^3 \cdot mol^{-1}$
x *n*-hexane + $(1 - x)$ 1-butanol						
0.0000	4.880	4.170	0.80580	0.000	0.000	0.0000
0.0791	4.468	3.574	0.79066	−0.175	−0.266	−0.0421
0.1464	4.170	3.109	0.77812	−0.272	−0.450	−0.0577
0.1866	4.040	2.890	0.77084	−0.282	−0.502	−0.0676
0.2333	3.858	2.580	0.76260	−0.325	−0.617	−0.0633
0.2838	3.705	2.298	0.75397	−0.326	−0.689	−0.0545
0.3761	3.447	1.816	0.73890	−0.308	−0.786	−0.0294
0.4782	3.167	1.256	0.72319	−0.282	−0.920	0.0346
0.5484	2.981	0.928	0.71289	−0.258	−0.955	0.0633
0.5484	2.981	0.928	0.71289	−0.258	−0.955	0.0633
0.5641	2.942	0.865	0.71063	−0.251	−0.953	0.0668
0.6244	2.753	0.627	0.70213	−0.255	−0.939	0.0989
0.6738	2.626	0.435	0.69533	−0.239	−0.925	0.1212
0.7106	2.528	0.304	0.69037	−0.227	−0.902	0.1373
0.8088	2.262	0.109	0.67633	−0.199	−0.687	0.1431
0.8626	2.131	0.051	0.67090	−0.160	−0.512	0.1332
1.0000	1.889	0.000	0.65520	0.000	0.000	0.0000
x *n*-hexane + $(1 - x)$ 1-hexanol						
0.0000	3.498	1.846	0.81505	0.000	0.000	0.0000
0.0561	3.424	1.703	0.80644	0.016	−0.040	−0.0633
0.1519	3.302	1.505	0.79136	0.048	−0.061	−0.1782
0.2228	3.209	0.351	0.78005	0.069	−0.083	−0.2336
0.2933	3.113	1.195	0.76877	0.087	−0.110	−0.2575
0.3435	3.041	1.075	0.76074	0.096	−0.137	−0.2673
0.3934	2.972	0.941	0.75276	0.107	−0.178	−0.2587
0.4424	2.899	0.806	0.74491	0.113	−0.223	−0.2502
0.4793	2.845	0.725	0.73899	0.118	−0.236	−0.2371
0.4947	2.822	0.680	0.73652	0.120	−0.253	−0.2315
0.5333	2.758	0.579	0.73031	0.118	−0.282	−0.2199
0.5716	2.672	0.474	0.72414	0.094	−0.317	−0.1994
0.5899	2.641	0.432	0.72118	0.092	−0.325	−0.1912
0.6490	2.527	0.303	0.71160	0.073	−0.345	−0.1665
0.6925	2.431	0.212	0.70453	0.047	−0.355	−0.1378
0.7418	2.327	0.141	0.69649	0.022	−0.336	−0.1101
0.7905	2.232	0.080	0.68356	0.005	−0.306	−0.0743
0.8375	2.150	0.047	0.68092	0.000	−0.253	−0.0440
0.8827	2.061	0.015	0.67363	−0.017	−0.202	−0.0117
0.8959	2.040	0.008	0.67151	−0.016	−0.184	−0.0082
0.9393	1.977	0.003	0.66462	−0.010	−0.112	−0.0123
1.0000	1.889	0.000	0.65520	0.000	0.000	−0.0000

Table 1

x	ε'	ε''	ρ $g\cdot cm^{-3}$	ε'^E	ε''^E	v^E $cm^3\cdot mol^{-1}$
			x n-hexane $+ (1-x)$ 1-octanol			
0.0000	3.096	1.010	0.82176	0.000	0.000	0.0000
0.0644	3.051	1.968	0.81346	0.032	0.023	−0.1117
0.0730	3.038	1.965	0.81232	0.030	0.028	−0.1291
0.1090	3.016	1.905	0.80746	0.052	0.004	−0.1742
0.1999	2.943	1.838	0.79471	0.088	0.029	−0.2775
0.2747	2.879	1.760	0.78377	0.114	0.027	−0.3459
0.3002	2.890	1.739	0.77995	0.156	0.032	−0.3662
0.3365	2.829	0.692	0.77444	0.138	0.022	−0.3868
0.4760	2.711	0.487	0.75239	0.189	−0.042	−0.4265
0.5455	2.622	0.381	0.74082	0.184	−0.078	−0.4254
0.6294	2.486	0.247	0.72630	0.149	−0.128	−0.3836
0.7427	2.296	0.109	0.70565	0.095	−0.151	−0.2883
0.7839	2.225	0.079	0.69785	0.074	−0.139	−0.2368
0.8540	2.103	0.027	0.68492	0.036	−0.120	−0.1530
0.9136	2.004	0.005	0.76350	0.010	−0.082	−0.0775
1.0000	1.889	0.000	0.65520	0.000	0.000	0.0000

The permittivity dielectric was determined using the standing wave technique for a short-circuited termination. The sample is located at the end of a coaxial line where electromagnetic standing waves with fixed wavelength λ are established. Relating the sample impedance as calculated from characteristics of the standing wave, which can be measured, yields the transcendental equation on the complex plane,

$$-j\lambda(1 - jS\tan(2\pi D_m/\lambda))/(2\pi d(S - j\tan(2\pi D_m/\lambda))) = \tanh(\gamma d)/(\gamma d) \qquad (1)$$

The l.h.s. of this equation is known from experiment: S is the voltage standing wave ratio (VSWR); D_m is the distance the surface of the dielectric and first minimum of the standing wave pattern and d is the sample thickness.

The complex relative permittivity $\varepsilon^* = \varepsilon' - j\varepsilon''$ can be written as a function of the complex propagation coefficient, γ, for electromagnetic waves inside a non-magnetic sample.

$$\varepsilon^* = -(\gamma\lambda/2\pi)^2 \qquad (2)$$

Figure 1 shows the experimental set-up. This is calibrated by using a variable attenuator to ensure the detector is operating in the square-law region and that the output of the amplifier is linear. The frequency is maintained constant within precision ±10 Hz and D_m with ±0.002 cm. Corrections were made for losses in the coaxial line walls between minimum and the sample boundary.

Figure 2 shows a scheme of the coaxial cell. This was done in special steel, Nilo 36, of low dilatation coefficient ($2.6\cdot 10^{-6}$/°C) and possesses a thermal shirt which allows free circulation of the thermostatization fluid. The transition between the type

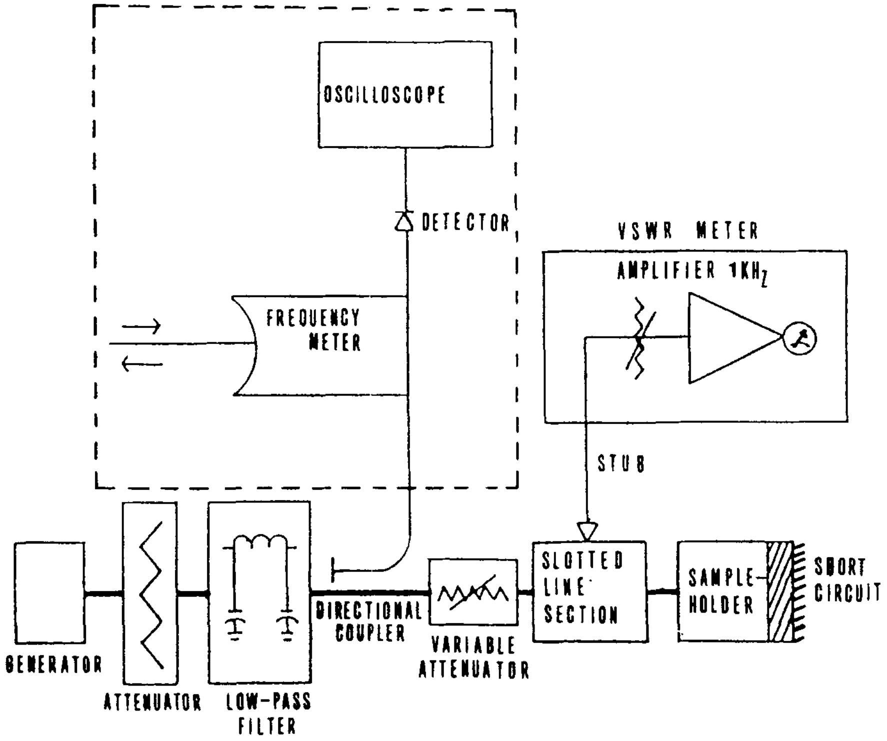

Figure 1 Block diagram of the coaxial line experimental bench.

GR 900-BT connector of the slotted line and the sample holder was implemented with a flange adaptor built with an air line of the GR 900-L3 series, 3 cm long. The thickness of the sample is determined by a piston which is fitted with a slot allowing the liquid conduction to flow into the cavity where it is kept between the short circuit and a sheet of silica which prevents the liquid from pouring on the line. The corrections due to this sheet are taken into account in the program which enables the resolution of the transcendental Eq. (1)[7]. In order to increase sensitivity in the measurement of losses, both the inner surface of the sample-holder and the piston are coated with a layer of silver 50 μm thick.

Excess complex permittivity dielectric were calculated from the expression:

$$\varepsilon^{*E} = \varepsilon^* - (x\varepsilon^*_{\mathrm{al}} + (1 - x)\varepsilon^*_{\mathrm{ol}}) \qquad (3)$$

where ε^* denotes the complex permittivity dielectric of mixture, $\varepsilon^*_{\mathrm{al}}$ of the *n*-hexane, $\varepsilon^*_{\mathrm{ol}}$ of the 1-alkanol, and x is the mole fraction of *n*-hexane.

Excess molar volumes (V^E) were determined from densities of the pure liquids and mixtures measured with a Kyoto Electronics DA-210 densimeter. The experimental technique has been described previously[8].

Mixtures were prepared by weighing with an estimated precision of $1 \cdot 10^{-4}$ in

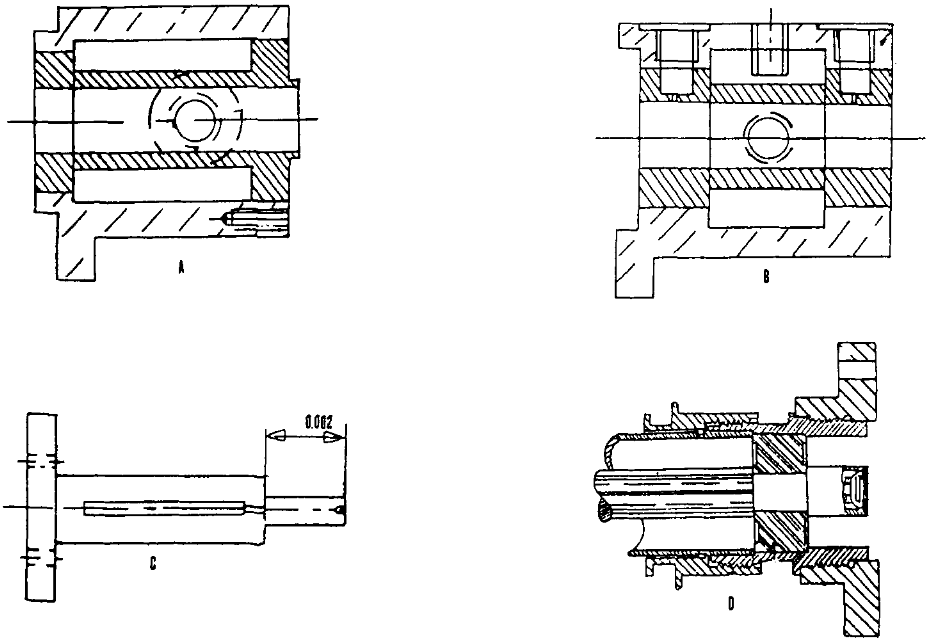

Figure 2 Scheme of the sample holder. (a) Section for the window of Silica. (b) Cavity for the liquid, between the short circuit and a sheet of silica. (c) Short circuit. (d) Flange adaptor on type GR900-BT.

mole fraction; The densimeter was thermostatted by a Hetotherm PF-CBIIe circulating-water bath to ±0.01 K. The precision of the excess molar dielectric permittivity was estimated better than ±0.002 and excess molar volumes $\pm 0.001\ \mathrm{cm^3 \cdot mol^{-1}}$.

RESULTS AND DISCUSSION

Table 1 reports the ε' and ε'' of the measurements in terms of mole fractions for the systems investigated. In Figure 3 the ε' and ε'' are plotted against volume fraction ϕ defined by

$$\phi = xv_{\mathrm{al}}/(xv_{\mathrm{al}} + (1 - x)v_{\mathrm{ol}}) \tag{4}$$

where v_{al} denotes the molar volume of the n-hexane, and v_{ol} of the 1-alkanol, observing a quasi-lineal behaviour in the ε' whilst the ε'' presents a quasi-exponential behaviour.

The experimental values of excess permittivity dielectric and excess molar volumes at 298.15 K are listed in Table 1. A function of the form:

$$Q^{\mathrm{E}} = x(1 - x) \sum_{i=0}^{m} A_i(2x - 1)^i \tag{5}$$

were fitted to the experimental values of the excess quantities where either $Q^E = \varepsilon^{*E}$

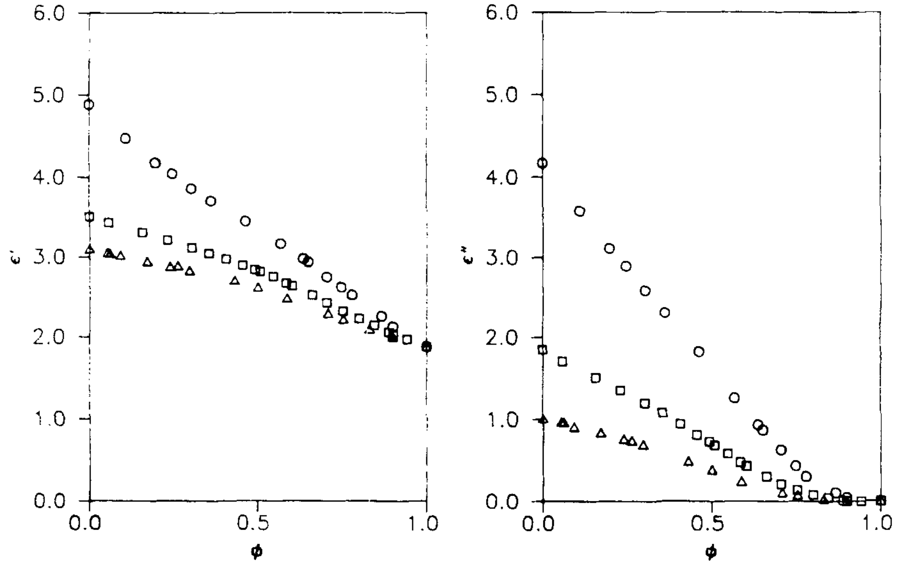

Figure 3 Experimental (a) ε'; (b) ε'' at 298.15 K of $xC_6H_{14} + (1 - x)C_nH_{2n+1}OH$ plotted against the volume fraction φ; ○, $n = 4$; □, $n = 6$; △, $n = 8$.

or $Q^E = V^E_m/(\text{cm}^3 \cdot \text{mol}^{-1})$. The coefficients A_i and the corresponding standard deviations $s(Q^E)$ given in Table 2 were calculated by the unweighted least-squares method, the degree of the polynomial having been optimized by applying the F-test.[9]

Figures 4 and 5 show the experimental points of ε'^E and ε''^E plotted against x together with the curve fitted to them. The ε'^E and ε''^E increase when the length of the 1-alkanol grows, being negative ε'^E for the mixture with 1-butanol and positive for the 1-hexanol and 1-octanol, the values of ε''^E are all negative except for some fractions of the system n-hexane + 1-octanol.

Table 2 Coefficients A_i of Eq. (5) and standard deviations s.

	A_0	A_1	A_2	A_3	A_4	s
			x *n*-hexane + $(1 - x)$ 1-butanol			
ε'^E	−1.104	0.538	−1.291	—	—	0.007
ε''^E	−3.719	−1.421	−0.558	1.507	—	0.013
V^E	0.1364	1.1064	0.3265	—	—	0.0023
			x *n*-hexane + $(1 - x)$ 1-hexanol			
ε'^E	0.445	−0.275	−0.648	—	—	0.006
ε''^E	−1.105	−1.566	−0.328	1.117	—	0.005
V^E	−0.9180	0.7422	−0.3797	0.0863	1.1854	0.0021
			x *n-hexane* + $(1 - x)$ 1-octanol			
ε'^E	0.722	−0.137	−0.635	—	—	0.010
ε''^E	−0.229	−1.086	−0.282	0.476	—	0.009
V^E	−1.7202	0.0961	0.4428	0.6158	—	0.0026

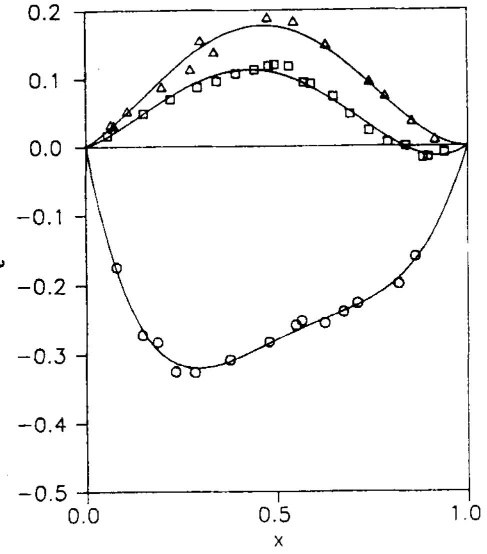

Figure 4 Experimental ε'^E at 298.15 K of $xC_6H_{14} + (1 - x)C_nH_{2n+1}OH$; ○, $n = 4$; □, $n = 6$; △, $n = 8$. The curves have been calculated from Eq. (5).

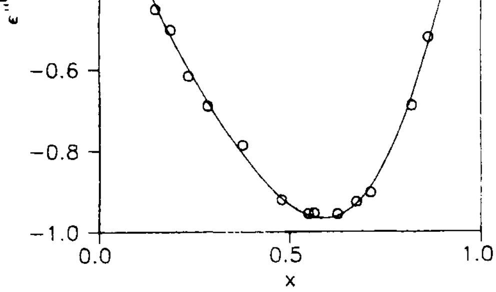

Figure 5 Experimental ε''^E at 298.15 K of $xC_6H_{14} + (1 - x)C_nH_{2n+1}OH$; ○, $n = 4$; □, $n = 6$; △, $n = 8$. The curves have been calculated from Eq. (5).

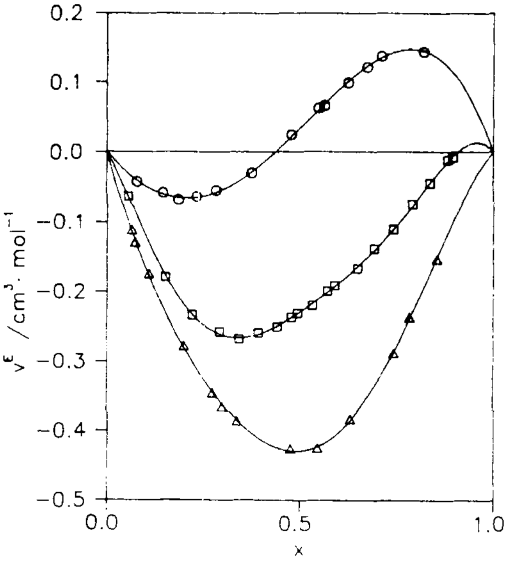

Figure 6 Experimental v^E at 298.15 K of $xC_6H_{14} + (1-x)C_nH_{2n+1}OH$; ○, $n = 4$; □, $n = 6$; △, $n = 8$. The curves have been calculated from Eq. (5).

Figure 6 shows the experimental v^E plotted against x together with the curve fitted. The excess molar volume decreases when the 1-alkanol carbon-atom number increases, finding values close to zero for the 1-butanol + *n*-hexane system and negative values for the systems which contain 1-hexanol and 1-octanol.

The differences between the experimental excess molar volumes of the literature[10] and our results fitted with Eq. (5) where about a 10% for the 1-butanol + *n*-hexane; 3% for the 1-hexanol + *n*-hexane and 1% for the 1-octanol + *n*-hexane.

In these mixtures the behaviour of ε'^E is contrary to that of v^E. This is due to the fact that when v^E decreases the number of dipoles per volume unit increases, which makes the ε'^E go up. There is a similar opposition between the behaviour of ε''^E on the one hand and those of h^E[11-13] and g^E[14,15] on the other: Increasing of the former and decreasing of the latter are both correlated with an increase in the number of atoms of the carbon chain of the 1-alkanol. This behaviour indicates that the delay between the applied field and the response of the mixture decreases with the length of the chain of the 1-alkanol.

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