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Dielectric Properties of Methanol Mixtures with Ethanol, Isomers of Propanol, and Butanol

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The relative permittivities of seven binary mixtures of methanol with ethanol, isomers of propanol, and butanol are reported for various mole fractions at (288.15, 293.15, 298.15, 303.15, and 308.15) K. The excess dielectric permittivity, the temperature coefficients, $(\partial \ln \varepsilon_r)/(\partial T)$, and their excess values were calculated. The excess parameters have been fitted to the Redlich−Kister polynomial equation. The results of measurements were used in the analysis of the molecular interactions occurring in the alcoholic solutions.

Introduction

Dielectric studies about binary mixtures are important for the understanding of the intermolecular interactions in the mixture due to the dipole−dipole interactions and hydrogen bonding. The relative permittivity, ε_r, is a macroscopic property, which gives information about association of molecules. The variation of this value with temperature carries knowledge about the dynamics of the microstructures.[1]

In the case of alcohol mixtures, dipole moments of all alcohol molecules result from the value of the dipole moment of the OH group and are approximately the same. Therefore, the changes of relative permittivity as the function of the composition of the mixtures depend mainly on the intermolecular interactions. Many workers have extensively studied dielectric properties of pure alkanols or mixtures of alkanols with water or nonpolar components.[1−11] Although there have been several dielectric studies on binary alcohol mixtures investigated in this manuscript, these were carried out with different measurement methods and concern the frequency-dependent dielectric properties of the solvent system, for example, time domain reflectometry (TDR)[12] or dielectric relaxation spectroscopy.[13−15]

Values of the relative permittivity of the methanol + ethanol system at 298.15 K were determined by Sengwa et al.[16] The relative permittivity of methanol + 1- propanol and methanol + 2-propanol mixtures at different temperatures were measured in ref 17. In the next section of this manuscript, we will make comparisons between the literature and our data.

The aim of this paper is to report a dielectric study on the binary mixtures of methanol (MeOH) with ethanol (EtOH), 1-propanol (1-PrOH), 2-propanol (*i*-PrOH), 1-butanol (1-BuOH), 2-methyl-1-propanol (*i*-BuOH), 2-butanol (*s*-BuOH), and 2-methyl-2-propanol (*t*-BuOH) over the whole composition range and at five different temperatures in the interval of 5 K from (288.15 to 308.15) K.

Experimental Section

Chemicals. Analytical grade reagents purchased from Merck, Fluka, and Aldrich were used. All liquids were stored in dark bottles over molecular sieves (Sigma, (0.3 to 0.4) nm) to reduce water content. Before use, they were double distilled and degassed in an ultrasound bath. The purities of the alcohols were checked by comparison the densities, d, and refractive indices, n_D, at 298.15 K with their corresponding literature values (Table 1). The comparison shows a very reasonable agreement.

Table 1. Experimental and Literature Densities, *d*, and Refractive Indices, n_D, for Pure Alcohols at 298.15 K

	d/g·cm^{-3}		n_D	
alcohol	this work	lit.	this work	lit.
MeOH	0.78667	0.78664[18] 0.78665[19] 0.78657[20] 0.786573[21] 0.78637[22]	1.3266	1.32652[18] 1.32645[19,23] 1.32652[22] 1.3268[2] 1.32715[24]
EtOH	0.78510	0.785095[21] 0.78493[22]	1.3594	1.35941[18] 1.35941[22] 1.35922[23] 1.35931[24]
1-PrOH	0.79960	0.79957[20,21] 0.79960[22] 0.79975[18]	1.3833	1.3831[2] 1.38370[18,22] 1.38283[25]
i-PrOH	0.78101	0.78088[20] 0.78089[26] 0.78126[22]	1.3751	1.3752[18,22] 1.37444[26]
1-BuOH	0.80564	0.805737[21] 0.80575[22] 0.80589[19] 0.8060[18]	1.3974	1.39730[18] 1.39741[22] 1.3975[27] 1.3967[2]
i-BuOH	0.79774	0.7978[22] 0.797874[28]	1.3938	1.39389[22] 1.3938[29]
s-BuOH	0.80214	0.80241[22] 0.802487[28] 0.80237[30]	1.3953	1.39530[22] 1.3949[29] 1.39488[30]
t-BuOH	0.78077[a]	0.7812[22] 0.779479[28b]	1.3848[a]	1.3852[22] 1.3850[29]

[a] Values extrapolated from the dependence $y = f(x_2)$ for $x_2 = 1$, where y are experimental densities or refractive indices data. [b] Value at 299.15 K.

Measurements. Measurements of relative permittivity were made using a dielectrometer constructed in the Institute of Chemistry at University of Łódź. For capacity measurement, a self-excited method was used. The measuring cell was from DK- meter GK-68 (VEB MWL-Germany), as in ref 17. The liquids were thermostatted using a Julabo F32-MH refrigerated/heating circulator with a temperature stability of ± 0.01 K and a temperature uncertainty of 0.03 K in the measuring cell. Values of relative permittivity were obtained from the calibration curve received from measurements of about 30 special grade liquids

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Table 2. Experimental Values of Relative Permittivity, ε_r, for Mixtures of Alcohols in the Function of the Composition of the Mixture

	ε_r				
	T/K				
x_2	288.15	293.15	298.15	303.15	308.15
			MeOH + EtOH		
0.0000	34.62	33.60	32.60	31.65	30.72
0.0517	34.02	32.97	31.96	30.97	30.00
0.1023	33.43	32.37	31.32	30.34	29.38
0.1496	32.84	31.78	30.78	29.76	28.80
0.2011	32.25	31.20	30.17	29.20	28.25
0.2490	31.67	30.64	29.66	28.67	27.74
0.2997	31.12	30.11	29.11	28.19	27.27
0.3523	30.53	29.54	28.61	27.67	26.78
0.4021	30.04	29.08	28.13	27.25	26.38
0.4489	29.57	28.63	27.74	26.84	25.99
0.5031	29.10	28.18	27.28	26.44	25.60
0.5487	28.71	27.80	26.95	26.08	25.26
0.5995	28.34	27.45	26.57	25.75	24.94
0.6525	27.95	27.07	26.24	25.39	24.59
0.7017	27.66	26.78	25.91	25.11	24.32
0.7485	27.36	26.49	25.66	24.83	24.04
0.8022	27.07	26.21	25.35	24.56	23.77
0.8497	26.79	25.93	25.12	24.29	23.51
0.9026	26.52	25.68	24.84	24.06	23.29
0.9526	26.21	25.38	24.59	23.80	23.05
1.0000	25.92	25.12	24.35	23.60	22.87
			MeOH + 1-PrOH		
0.0000	34.62	33.60	32.60	31.65	30.72
0.0498	33.41	32.44	31.49	30.57	29.67
0.1003	32.28	31.32	30.41	29.53	28.69
0.1497	31.23	30.35	29.46	28.61	27.76
0.1999	30.29	29.39	28.53	27.70	26.92
0.2501	29.37	28.53	27.70	26.90	26.09
0.3008	28.56	27.70	26.89	26.10	25.36
0.3497	27.79	26.99	26.20	25.42	24.66
0.4004	27.10	26.29	25.50	24.76	24.03
0.4499	26.45	25.68	24.91	24.17	23.44
0.5001	25.87	25.07	24.32	23.59	22.89
0.5503	25.31	24.56	23.80	23.09	22.37
0.6001	24.82	24.04	23.32	22.59	21.90
0.6490	24.36	23.63	22.88	22.17	21.48
0.7004	23.93	23.15	22.44	21.74	21.06
0.7496	23.52	22.80	22.08	21.37	20.69
0.7998	23.17	22.41	21.69	21.01	20.34
0.8503	22.80	22.08	21.37	20.67	20.00
0.8997	22.50	21.74	21.04	20.36	19.70
0.9501	22.16	21.44	20.75	20.06	19.40
1.0000	21.87	21.15	20.45	19.78	19.13
			MeOH + *i*-PrOH		
0.0000	34.62	33.60	32.60	31.65	30.72
0.0501	33.29	32.31	31.37	30.46	29.56
0.1005	32.05	31.13	30.20	29.32	28.48
0.1499	30.98	30.05	29.18	28.32	27.47
0.1990	29.96	29.09	28.21	27.37	26.57
0.2498	29.03	28.14	27.31	26.49	25.67
0.3003	28.14	27.31	26.45	25.64	24.88
0.3490	27.39	26.52	25.72	24.93	24.14
0.3996	26.62	25.80	24.98	24.19	23.46
0.4501	25.94	25.10	24.33	23.56	22.79
0.4997	25.28	24.50	23.70	22.94	22.23
0.5502	24.70	23.89	23.14	22.39	21.65
0.6004	24.13	23.36	22.58	21.85	21.16
0.6502	23.64	22.84	22.11	21.38	20.66
0.6998	23.15	22.40	21.63	20.91	20.23
0.7502	22.74	21.94	21.21	20.49	19.77
0.7999	22.33	21.57	20.79	20.07	19.38
0.8497	22.01	21.19	20.44	19.70	18.96
0.9010	21.68	20.87	20.06	19.29	18.58
0.9502	21.44	20.56	19.75	18.96	18.17
1.0000	21.22	20.31	19.43	18.59	17.79
			MeOH + 1-BuOH		
0.0000	34.62	33.60	32.60	31.65	30.72
0.0504	32.77	31.82	30.88	29.97	29.08
0.0999	31.18	30.24	29.34	28.47	27.65
0.1503	29.72	28.85	27.99	27.16	26.33
0.1990	28.50	27.62	26.80	25.99	25.24
0.2491	27.34	26.53	25.74	24.96	24.19
0.2993	26.34	25.52	24.75	24.00	23.29
0.3502	25.40	24.64	23.89	23.16	22.43
0.3999	24.61	23.83	23.10	22.38	21.71
0.4506	23.84	23.12	22.40	21.70	21.01
0.4969	23.23	22.49	21.78	21.10	20.46
0.5503	22.55	21.86	21.16	20.50	19.83
0.5993	22.01	21.29	20.61	19.95	19.33
0.6505	21.45	20.78	20.11	19.46	18.81
0.6993	20.99	20.29	19.63	18.98	18.38
0.7498	20.52	19.86	19.20	18.57	17.93
0.7975	20.16	19.45	18.80	18.16	17.57
0.8513	19.75	19.08	18.42	17.79	17.15
0.8991	19.47	18.76	18.09	17.45	16.85
0.9477	19.20	18.51	17.84	17.18	16.53
1.0000	19.01	18.28	17.58	16.91	16.26
			MeOH + *i*-BuOH		
0.0000	34.62	33.60	32.60	31.65	30.72
0.0503	32.70	31.75	30.82	29.91	29.03
0.1000	31.00	30.11	29.22	28.36	27.55
0.1502	29.54	28.68	27.83	27.01	26.19
0.1999	28.23	27.39	26.58	25.79	25.04
0.2499	27.11	26.29	25.50	24.73	23.97
0.2998	26.08	25.27	24.50	23.76	23.06
0.3502	25.19	24.40	23.65	22.93	22.20
0.3995	24.38	23.61	22.87	22.16	21.49
0.4502	23.68	22.92	22.20	21.50	20.80
0.4996	23.02	22.28	21.57	20.88	20.23
0.5502	22.46	21.73	21.03	20.34	19.66
0.5992	21.93	21.22	20.52	19.84	19.20
0.6501	21.47	20.77	20.07	19.40	18.73
0.6991	21.05	20.34	19.65	18.97	18.35
0.7490	20.70	19.99	19.29	18.62	17.95
0.7997	20.36	19.63	18.93	18.25	17.62
0.8501	20.10	19.35	18.64	17.96	17.29
0.8998	19.85	19.08	18.36	17.67	17.02
0.9500	19.67	18.89	18.15	17.45	16.75
1.0000	19.51	18.71	17.96	17.23	16.53
			MeOH + *s*-BuOH		
0.0000	34.62	33.60	32.60	31.65	30.72
0.0500	32.65	31.69	30.78	29.88	29.00
0.1001	30.89	30.02	29.13	28.29	27.49
0.1503	29.39	28.52	27.72	26.91	26.11
0.1999	28.06	27.26	26.45	25.67	24.94
0.2503	26.91	26.09	25.34	24.59	23.84
0.2990	25.89	25.13	24.35	23.62	22.93
0.3502	24.98	24.19	23.47	22.74	22.02
0.3997	24.16	23.41	22.66	21.94	21.27
0.4501	23.43	22.66	21.94	21.23	20.53
0.4991	22.76	22.02	21.27	20.56	19.90
0.5489	22.16	21.38	20.67	19.97	19.27
0.6001	21.56	20.82	20.06	19.36	18.70
0.6492	21.05	20.27	19.55	18.84	18.14
0.7004	20.52	19.77	19.01	18.29	17.62
0.7500	20.09	19.28	18.55	17.83	17.11
0.8004	19.64	18.86	18.07	17.33	16.65
0.8487	19.29	18.45	17.68	16.92	16.18
0.9002	18.93	18.09	17.26	16.48	15.75
0.9502	18.68	17.76	16.92	16.11	15.32
1.0000	18.47	17.51	16.60	15.75	14.94
			MeOH + *t*-BuOH		
0.0000	34.62	33.60	32.60	31.65	30.72
0.0503	32.62	31.63	30.68	29.75	28.85
0.0989	30.90	29.94	29.01	28.10	27.23
0.1505	29.28	28.34	27.45	26.56	25.70
0.2010	27.86	26.95	26.06	25.21	24.38
0.2490	26.66	25.76	24.91	24.06	23.25
0.3012	25.49	24.60	23.76	22.93	22.14
0.3488	24.52	23.65	22.84	22.00	21.22
0.3999	23.58	22.72	21.90	21.09	20.32
0.4505	22.73	21.87	21.09	20.26	19.49
0.4998	21.96	21.10	20.30	19.49	18.73
0.5503	21.21	20.36	19.57	18.74	17.98
0.5977	20.55	19.68	18.88	18.05	17.29
0.6478	19.86	18.98	18.19	17.33	16.56
0.7014	19.14	18.23	17.40	16.55	15.77
0.7508	18.47	17.54	16.70	15.81	15.01
0.7980	17.82	16.85	15.98	15.07	14.25
0.8487	17.10	16.09	15.19	14.23	13.39
0.9011	16.32	15.25	14.29	13.31	12.44
0.9511	15.42[a]	14.39	13.37	12.35	11.44
1.0000	14.49[a]	13.38[a]	12.49[a]	11.34	10.40

[a] Values extrapolated from the dependence $\varepsilon_r = f(x_2)$ for $x_2 = 1$, where ε_r are experimental relative permittivity data.

Table 3. Coefficients of the Redlich−Kister Equation and Their Standard Errors for Excess Relative Permittivity, ε_r^E, at 298.15 K

	a_i			
mixture	a_o	a_1	a_2	$\sigma(\varepsilon_r^E)$
MeOH + EtOH	−4.6619 ± 0.0261	0.6452 ± 0.0317	0.9106 ± 0.0649	0.01
MeOH + 1-PrOH	−8.8068 ± 0.0296	2.3617 ± 0.0359	0.1428 ± 0.0736	0.01
MeOH + *i*-PrOH	−9.2682 ± 0.0319	2.6773 ± 0.0388	−0.4896 ± 0.0795	0.01
MeOH + 1-BuOH	−0.1338 ± 0.0389	5.2971 ± 0.0472	−2.7038 ± 0.0971	0.01
MeOH + *i*-BuOH	−0.1485 ± 0.0337	5.8842 ± 0.0410	−2.4237 ± 0.0841	0.01
MeOH + *s*-BuOH	−0.1337 ± 0.0357	6.3958 ± 0.0434	−3.1925 ± 0.0890	0.01
MeOH + *t*-BuOH	−8.8929 ± 0.0716	9.7882 ± 0.0870	−1.9183 ± 0.1780	0.02

and known values of relative permittivity at a temperature range of (288.15 to 318.15) K. Most of these liquids were well-examined water + dioxane mixtures.[31,32] All the solutions were prepared by mass using an analytical balance (Sartorius RC 210D) with an uncertainty of ± $1 \cdot 10^{-5}$ g. The uncertainty of composition of mixtures was 0.0001 on the mole fraction. The solutions were degassed and warmed tentatively to a temperature higher than the one used in the measurements. Measurements were made at a temperature defined for a given mixture for all the compositions and then conducted at incrementally increasing temperatures. The uncertainty of the relative permittivity was estimated at about ± 0.03.

Results and Discussion

The experimental values of relative permittivity for the investigated binary mixtures at (288.15, 293.15, 298.15, 303.15, and 308.15) K are reported in Table 2.

From the experimental values of relative permittivity, the excess values, ε_r^E, were calculated

$$\varepsilon_r^E = \varepsilon_r - (x_1 \cdot \varepsilon_{r1} + x_2 \cdot \varepsilon_{r2}) \tag{1}$$

and next they were fitted to the Redlich−Kister equation[33,34]

$$\varepsilon_r^E = x_1 \cdot x_2 \sum_{i=0}^{n} a_i (x_2 - x_1)^i \tag{2}$$

to obtain the parameters a_i. x_1, x_2 are the mole fraction and n is the degree of the polynomic expansion. The linear least-squares fitting procedure was used to fit the polynomials to the data. The adjustable parameters, a_i, their standard errors, and the standard deviations, $\sigma(\varepsilon_r^E)$, are listed in Table 3. The standard errors of all fits indicate that the above equation fits the experimental data very well.

The values of ε_r^E were used to determine the smoothed values of relative permittivity, $\varepsilon_{r\,(s)}$

$$\varepsilon_{r(s)} = x_1 \cdot \varepsilon_{r1} + x_2 \cdot \varepsilon_{r2} + \varepsilon_r^E \tag{3}$$

Figure 1 shows the relative permittivitties as a function of composition for all systems studied here at 298.15 K. The corresponding excess values, ε_r^E, were shown in Figure 2.

The relationships $\varepsilon_r = f(x_2)$ are monotonic, but there are many exceptions to the linearity. Their increasing or decreasing character depends on the value of ε_r for pure alcohol. For pure alcohols, it is possible to place the relative permittivity values in the order

$$\varepsilon_{r\,\mathrm{MeOH}} > \varepsilon_{r\,\mathrm{EtOH}} > \varepsilon_{r\,\text{1-PrOH}} > \varepsilon_{r\,i\text{-PrOH}} > \varepsilon_{r\,i\text{-BuOH}} > \varepsilon_{r\,\text{1-BuOH}} > \varepsilon_{r\,s\text{-BuOH}} > \varepsilon_{r\,t\text{-BuOH}}$$

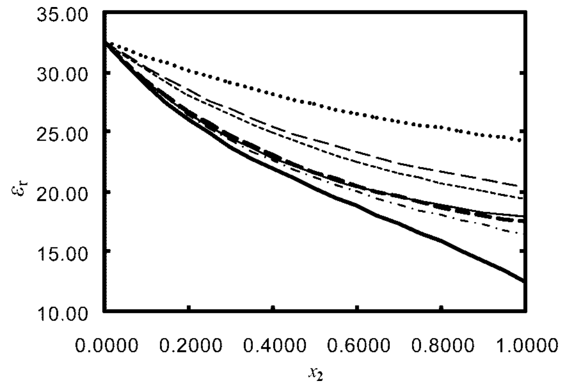

Figure 1. Relative permittivity, ε_r, as a function of the mole fraction for binary mixtures of alcohols at 298.15 K: ••••, EtOH; — — —, *n*-PrOH; ••••, *i*-PrOH; - - -, *n*-BuOH; —, *i*-BuOH; — • —, *s*-BuOH; bold —, *t*-BuOH.

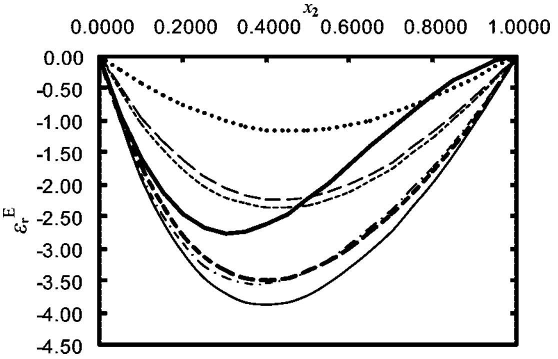

Figure 2. Excess relative permittivity, ε_r^E, as a function of the mole fraction for binary mixtures of alcohols at 298.15 K: ••••, EtOH; — — —, *n*-PrOH; ••••, *i*-PrOH; - - -, *n*-BuOH; —, *i*-BuOH; — • —, *s*-BuOH; bold —, *t*-BuOH

Table 4. Coefficients of the Redlich−Kister Equation and Their Standard Errors for Relative Temperature Coefficient Excess Values ((∂lnε_r)/(∂*T*))E at 298.15 K

	$a_i \cdot 10^3$			
mixture	$a_o \cdot 10^3$	$a_1 \cdot 10^3$	$a_2 \cdot 10^3$	$\sigma((\partial \ln \varepsilon_r)/(\partial T))^E \cdot 10^3/K^{-1}$
MeOH + EtOH	−1.17 ± 0.04	1.31 ± 0.05	−4.55 ± 0.11	0.018
MeOH + 1-PrOH	0.87 ± 0.03	−0.91 ± 0.04	0.02 ± 0.08	0.010
MeOH + *i*-PrOH	3.69 ± 0.04	3.15 ± 0.05	3.85 ± 0.10	0.016
MeOH + 1-BuOH	2.08 ± 0.03	1.60 ± 0.03	1.53 ± 0.07	0.010
MeOH + *i*-BuOH	2.54 ± 0.11	0.52 ± 0.14	0.98 ± 0.28	0.043
MeOH + *s*-BuOH	6.15 ± 0.07	1.91 ± 0.09	2.55 ± 0.18	0.022
MeOH + *t*-BuOH	13.20 ± 0.26	8.17 ± 0.32	1.37 ± 0.66	0.070

As can be seen, values become smaller with the increase in size of molecules as well as with the type of a given alcohol (the smallest for tertiary alcohol, the largest for primary one). This can be connected with an ability of alcohol to create intermolecular hydrogen bonds of the linear type or with the possibility of participation of such associated molecules in relation to the others. This follows from the fact that these possibilities are greater in the case of smaller molecules and from the fact that they are bigger for primary alcohols, which can be connected with steric hindrances. The character of changes of the relative permittivity is very clear as the function of the composition of mixtures in the case of excess value of ε_r.

As can be seen in Figure 2, the values of ε_r^E are always negative, and they can be ordered depending on the carbon chain length of the other ingredient

$$\varepsilon^E_{r\,\mathrm{EtOH}} > \varepsilon^E_{r\,\text{1-PrOH}} > \varepsilon^E_{r\,\text{1-BuOH}} \text{ and } \varepsilon^E_{r\,i\text{-PrOH}} > \varepsilon^E_{r\,s\text{-BuOH}}$$

and according to the type of the alcohol

$$\varepsilon^E_{r\,t\text{-BuOH}} > \varepsilon^E_{r\,s\text{-BuOH}} \approx \varepsilon^E_{r\,\text{1-BuOH}} \text{ and } \varepsilon^E_{r\,i\text{-PrOH}} > \varepsilon^E_{r\,\text{1-PrOH}}$$

To sum up, it is possible to state that ε_r^E values increase (they become less negative or more positive) with a decrease of the

Table 5. Values of Relative Temperature Coefficient, $(\partial \ln\varepsilon_r)/(\partial T)$, for Each Mixture at 298.15 K

	$(\partial \ln\varepsilon_r)/(\partial T)\cdot 10^3/\mathrm{K}^{-1}$						
x_2	MeOH + EtOH	MeOH + 1-PrOH	MeOH + *i*-PrOH	MeOH + 1-BuOH	MeOH + *i*-BuOH	MeOH + *s*-BuOH	MeOH + *t*-BuOH
0.0000	−5.98	−5.98	−5.98	−5.98	−5.98	−5.98	−5.98
0.0500	−6.28	−5.94	−5.94	−5.98	−5.96	−5.90	−6.17
0.1000	−6.47	−5.91	−5.94	−6.00	−5.96	−5.88	−6.34
0.1500	−6.57	−5.90	−5.98	−6.04	−5.99	−5.90	−6.50
0.2000	−6.61	−5.90	−6.04	−6.08	−6.03	−5.95	−6.66
0.2500	−6.61	−5.91	−6.12	−6.13	−6.08	−6.04	−6.81
0.3000	−6.57	−5.94	−6.20	−6.18	−6.15	−6.14	−6.97
0.3500	−6.53	−5.97	−6.28	−6.23	−6.23	−6.27	−7.15
0.4000	−6.48	−6.02	−6.35	−6.28	−6.31	−6.41	−7.35
0.4500	−6.44	−6.07	−6.42	−6.33	−6.40	−6.57	−7.59
0.5000	−6.41	−6.12	−6.48	−6.38	−6.50	−6.74	−7.88
0.5500	−6.40	−6.18	−6.55	−6.43	−6.60	−6.93	−8.23
0.6000	−6.41	−6.25	−6.62	−6.49	−6.72	−7.15	−8.65
0.6500	−6.43	−6.31	−6.70	−6.56	−6.85	−7.39	−9.15
0.7000	−6.46	−6.38	−6.81	−6.64	−6.98	−7.66	−9.75
0.7500	−6.50	−6.44	−6.95	−6.75	−7.14	−7.98	−10.47
0.8000	−6.53	−6.50	−7.15	−6.87	−7.31	−8.34	−11.32
0.8500	−6.53	−6.56	−7.41	−7.04	−7.51	−8.77	−12.31
0.9000	−6.50	−6.61	−7.77	−7.24	−7.73	−9.28	−13.47
0.9500	−6.42	−6.66	−8.23	−7.50	−7.99	−9.87	−14.82
1.0000	−6.26	−6.70	−8.83	−7.82	−8.29	−10.58	−16.37

difference in the length of chains of alcohol in the mixture, as well as with an increase of the difference of types of alcohols added (primary, secondary, or tertiary). Adding molecules of a longer chain alcohol to methanol probably reduces more effectively the amount of methanol associates. This effect is smaller for secondary, and especially for tertiary alcohols, probably on account of growing steric hindrances in interactions between methanol and the other alcohol. When examining the influence of the addition of methanol to the examined alcohol, it should be stated that the decrease of the amount of hydrogen bonds is less rapid.

Additional information about intermolecular interactions is provided from the analysis of the changes in the relative temperature coefficient

$$\frac{\partial \ln\varepsilon_r}{\partial T} = \frac{\partial \varepsilon_r}{\varepsilon_r\,\partial T} \qquad (4)$$

From the experimental values of relative permittivity, the values of relative temperature coefficient, $(\partial \ln\varepsilon_r)/(\partial T)$, were calculated, and next the excess values, $((\partial \ln\varepsilon_r)/(\partial T))^E$, were calculated. The Redlich−Kister procedure was adjusted to the calculated values, in a similar way as previously (see eq 2)

$$\left(\frac{\partial \ln\varepsilon_r}{\partial T}\right)^E = x_1\cdot x_2 \sum_{i=0}^{n} a_i (x_2 - x_1)^i \qquad (5)$$

Coefficients of received polynomials were given in Table 4.

Smoothed excess values of the relative temperature coefficient were used to determine the smoothed values of relative temperature coefficient, collected next in Table 5.

$$\frac{\partial \ln\varepsilon_r}{\partial T} = x_1\cdot\left(\frac{\partial \ln\varepsilon_r}{\partial T}\right)_1 + x_2\cdot\left(\frac{\partial \ln\varepsilon_r}{\partial T}\right)_2 + \left(\frac{\partial \ln\varepsilon_r}{\partial T}\right)^E \qquad (6)$$

Figure 3 shows the plot of the relative temperature coefficient, $(\partial \ln\varepsilon_r)/(\partial T)$, versus mole fraction of alcohol at the temperature 298.15 K.

If addition of the second component of a mixture to the first does not cause drastic changes in the amount of hydrogen bonds as a result of bigger amounts of 1−2 associates (between methanol (1) and the other alcohol (2)) being formed in mixtures with large contents of the first component, the values of this coefficient should not change significantly. These changes should increase with the decrease of the competition between the interactions of type 1−2 compared with interactions of type 1−1. On the other hand, if the competitiveness of interactions 1−1 and 1−2 is similar, in mixtures with high concentration of the second component, one should not find significant changes in the coefficient value, and the relationship between relative temperature coefficient, $(\partial \ln\varepsilon_r)/(\partial T)$, and the composition of mixture should be closer to additive.

In the case of mixtures of methanol with other alcohols (Figure 3), one may expect that the biggest deviations from additivity will depend on the carbon chain length of the other ingredient

$$\left(\frac{\partial \ln\varepsilon_r}{\partial T}\right)_{\text{1-BuOH}} > \left(\frac{\partial \ln\varepsilon_r}{\partial T}\right)_{\text{1-PrOH}} > \left(\frac{\partial \ln\varepsilon_r}{\partial T}\right)_{\text{EtOH}} \text{ and } \left(\frac{\partial \ln\varepsilon_r}{\partial T}\right)_{s\text{-BuOH}} > \left(\frac{\partial \ln\varepsilon_r}{\partial T}\right)_{i\text{-PrOH}}$$

and the type of the alcohol

$$\left(\frac{\partial \ln\varepsilon_r}{\partial T}\right)_{t\text{-BuOH}} > \left(\frac{\partial \ln\varepsilon_r}{\partial T}\right)_{s\text{-BuOH}} > \left(\frac{\partial \ln\varepsilon_r}{\partial T}\right)_{\text{1-BuOH}} \text{ and } \left(\frac{\partial \ln\varepsilon_r}{\partial T}\right)_{i\text{-PrOH}} > \left(\frac{\partial \ln\varepsilon_r}{\partial T}\right)_{\text{1-PrOH}}$$

It is difficult to present in the above dependences the values of $(\partial \ln\varepsilon_r)/(\partial T)$ (and ε_r^E also) for *i*-BuOH because it is a primary alcohol but with the branched carbon chain.

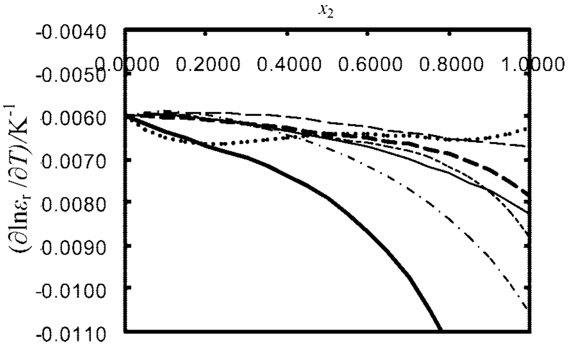

Figure 3. Relative temperature coefficient, $(\partial \ln\varepsilon_r)/(\partial T)$, as a function of the mole fraction for mixtures of alcohols at 298.15 K: ••••, EtOH; − − −, *n*-PrOH; ••••, *i*-PrOH; - - -, *n*-BuOH; −, *i*-BuOH; − • −, *s*-BuOH; bold −, *t*-BuOH.

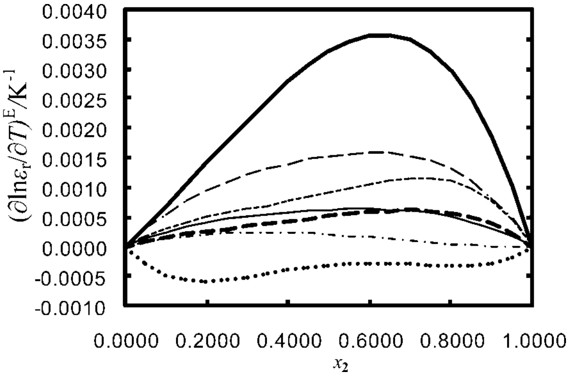

Figure 4. Excess values of relative temperature coefficient, $((\partial \ln\varepsilon_r)/(\partial T))^E$, as a function of the mole fraction for mixtures of alcohols at 298.15 K; ••••, EtOH; — — —, *n*-PrOH; ····, *i*-PrOH; - - -, *n*-BuOH; —, *i*-BuOH; — · —, *s*-BuOH; bold —, *t*-BuOH.

Table 6. Experimental and Literature Values of Relative Permittivity, ε_r, for Pure Alcohols at 298.15 K

	ε_r	
alcohol	this work	lit.
MeOH	32.60	32.70[2] 32.66[3,22] 32.78[17] 32.63[18,35]
EtOH	24.35	24.34[3] 24.55[4,22] 24.35[35]
1-PrOH	20.45	20.33[2] 20.28[17] 20.45[22] 20.44[35]
i-PrOH	19.43	19.41[4] 19.38[17] 19.92[22] 19.40[35]
1-BuOH	17.58	17.51[2,22] 17.43[35]
i-BuOH	17.96	17.93[4,22]
s-BuOH	16.60	16.56[4,22] 17.0[35]
t-BuOH	12.49[a]	12.47[4,22]

[a] Extrapolated value.

Analyzing the relation of the excess value of temperature coefficient, $((\partial \ln\varepsilon_r)/(\partial T))^E$, as the function of composition (Figure 4), these orders are the same, which confirms the above proposals completely.

Comparison with Literature Data. The relative permittvity values at 298.15 K reported in the literature for pure alcohols are in good agreement with data obtained in this work (Table 6).

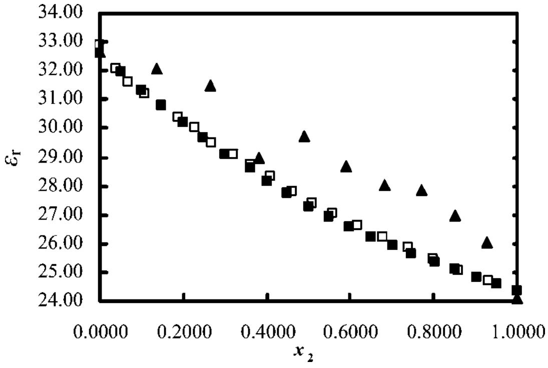

Figure 5. Comparison of experimental relative permittivitties, ε_r, for the MeOH + EtOH mixture at 298.15 K with those reported in the literature. The data points correspond to: ■, this work; □, ref 16; ▲, ref 12.

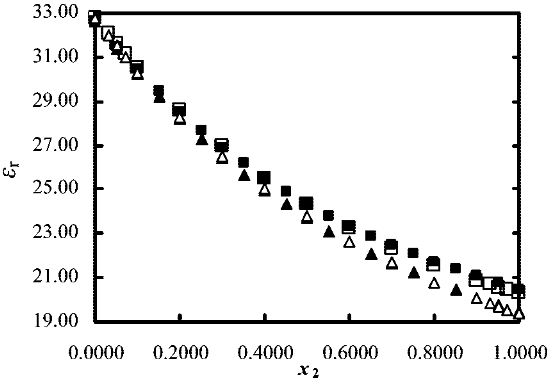

Figure 6. Comparison of experimental relative permittivitties, ε_r, for MeOH + 1-PrOH and MeOH + *i*-PrOH mixtures at 298.15 K with those reported in the literature. The data points correspond to: ■, this work; □, ref 17 (for MeOH + 1-PrOH); ▲, this work; Δ, ref 17 (for MeOH + *i* -PrOH).

Table 7. Values of the Relative Temperature Coefficient, $(\partial \ln\varepsilon_r)/(\partial T)$, for Pure Alcohols at 298.15 K

	$(\partial \ln\varepsilon_r)/(\partial T)/K^{-1}$	
alcohol	this work	lit.
MeOH	−0.00598	−0.00608,[36] −0.00577[17]
EtOH	−0.00626	−0.00622[36]
1-PrOH	−0.00670	−0.00650,[36] −0.00674[17]
i-PrOH	−0.00883	−0.00714,[36] −0.00859[17]
1-BuOH	−0.00782	−0.00771[36]
i-BuOH	−0.00829	−0.00860[36]
s-BuOH	−0.01058	−0.00990[37,38]
t-BuOH	−0.01637	−0.01460[37,38]

Figure 5 illustrates the comparison between experimental and literature ε_r values for the methanol + ethanol mixture at 298.15 K. The data reported by Sengwa et al.[16] (from the "capacitive measurement method") are in good agreement (a little worse in the middle range of composition) with data obtained in this work, while values of ε_r from ref 12 differ considerably because they are estimated values (in that paper, the TDR method was used).

In Figure 6, we compare our new data of ε_r for methanol + 1-propanol and methanol + 2-propanol with those reported previously.[17] In that paper, the relative permittivity was measured using the heterodyne-beat type dielectrometer with digital frequency readout. As can be seen in Figure 6, the relative permittivity values obtained in this paper agree satisfactorily with literature data.

Table 7 presents values of the relative temperature coefficient of examined pure alcohols at the temperature 298.15 K, taken from the literature and from our experiment. Good agreement of the data was obtained.

Conclusions

The relative permittivities of binary alcohol mixtures (methanol with ethanol, 1-propanol, 2-propanol, 1-butanol, 2-methyl-1-propanol, 2-butanol, and 2-methyl-2-propanol) at (288.15, 293.15, 298.15, 303.15, and 308.15) K have been measured over the whole composition range. The relations of ε_r, ε_r^E, $(\partial \ln\varepsilon_r)/(\partial T)$, $((\partial \ln\varepsilon_r)/(\partial T))^E$ values as the function of composition for all mixtures studied here at 298.15 K have been analyzed. It has been proved that the above values connected with the intermolecular interactions, as expected, depend on the carbon chain length of the other ingredient and on the type of alcohol added (primary, secondary, or tertiary). It follows from the observed dependences for the values of excess relative permittivity and relative temperature coefficients of ε_r.

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