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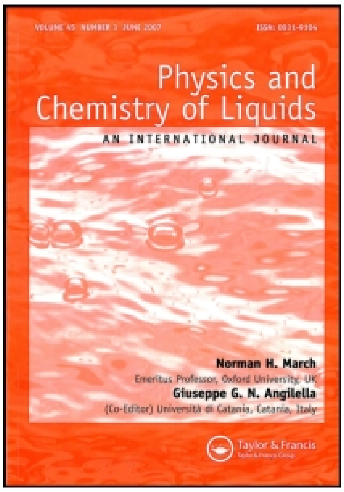

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H-NMR Spectral and Dielectric Behaviours of the 2-Metoxyethanol-Tetrahydrofuran Solvent System

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^{1}H-NMR SPECTRAL AND DIELECTRIC BEHAVIOURS OF THE 2-METOXYETHANOL – TETRAHYDROFURAN SOLVENT SYSTEM

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Relative permittivities (ε_{12}) have been measured for 2-metoxyethanol (ME)-tetrahydrofuran (THF) binary liquid mixtures over the whole compositions range at various temperatures ranging from 291.15 K to 308.15 K. The experimental data were used to test some empirical equations of the type: $y_{12} = y_{12}(t)$ and $y_{12} = y_{12}(X_1)$ [where: $y_{12} - \varepsilon_{12}$]. From all these data, the temperature coefficients of relative permittivities (α_{12}) and the excess extrathermodynamic parameters ε^E were calculated. The ^{1}H-NMR spectra of liquid binary mixtures of ME and THF, were recorded at 298 K over almost the whole range of the mixed solvent compositions. From these data the values of the values of the spectral structural parameters were found, $\Delta\delta$(ME – THF). These structural parameters as a function concentration suggest the formation of stable 3ME·THF types intermolecular complexes.

Keywords: Binary liquid mixtures; Physicochemical properties; Intermolecular interactions

INTRODUCTION

This paper is part of our research concerning the real behaviour of binary solvent mixtures upon intermolecular interactions that take place in solutions of two organic cosolvents [1–4]. In the course

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of these investigations, we plan to extend our studies to the 2-metoxyethanol (ME) – tetrahydrofuran (THF) binary system in wide temperature range and over the whole composition range. The relative permittivity and ^{1}H-NMR spectra are the first properties investigated.

EXPERIMENTAL

Presently ^{1}H-NMR spectral studies and the measurements of relative permittivities of mixtures of chemical pure 2-metoxyethanol (Fluka) and THF (Fluka) were carried. They were dried and purified according to known procedures [5, 6]. The ^{1}H-NMR spectra were recorded using a Tesla BS 467 (60 MHz) spectrometer, at 298 ± 1 K. The proton chemical shifts of ME and THF were measured with an accuracy of ca. ± 0.2 Hz with respect to an external standard HMDS (hexamethyldisiloxane). The relative permittivity measurements were carried out at 3 MHz, with an accuracy of ± 0.1%, using a bridge of the type OH – 301 (made in Radelcis, Hungary). The thermostatic stainless steel measuring cells were of C3 ($10 < \varepsilon < 25$) and C4 ($25 < \varepsilon < 100$) type. The sample cells are of the covered coaxial capacitor type with vacuum capacitances of 2.5 pF (C3) and 0.5 pF (C4). The cells were calibrated with standard pure liquids, such as acetone, butan-1-ol and dichloromethane (C3); methanol, ethanol and dioxane – water mixtures (C4). With the exception of the deionized water, all these solvent were of spectrograde quality or higher. The relative permittivities for the standards were taken from literature [6]. Each temperature was maintained constant with an accuracy of ± 0.01 K. All the solutions were prepared by weight.

RESULT AND DISCUSSION

The experimental data of relative permittivity (ε_{12}) obtained from the measurements of the pure solvents and for the analysed binary mixtures at all investigated temperatures are summarized in Table I.

The first step of this study involves investigation of the dependence of relative permittivity (ε_{12}) on temperature, and the following

TABLE I Experimental relative permittivity (ε_{12}) and chemical shifts δ(ME–THF) for ME – THF liquid mixtures

	d_{12} $[g\,cm^{-3}]$						$\delta(ME-THF)$ $[Hz]$
X_{ME}	$291.15K$	$293.15K$	$298.15K$	$303.15K$	$308.15K$	X_{ME}	$298K$
0.0000	7.69	7.56	7.36	7.25	7.17	0.0114	129.5
0.0499	8.12	8.00	7.81	7.69	7.60	0.0499	131.0
0.0958	8.50	8.39	8.19	8.07	7.98	0.0958	132.5
0.1503	8.95	8.84	8.61	8.49	8.38	0.1503	134.0
0.1915	9.25	9.18	8.97	8.83	8.71	0.1915	135.0
0.2498	9.75	9.66	9.45	9.30	9.16	0.2498	137.0
0.2886	10.05	9.97	9.76	9.61	9.45	0.2886	138.0
0.3496	10.54	10.46	10.24	10.07	9.89	0.3496	140.5
0.3872	10.83	10.77	10.54	10.38	10.20	0.3872	142.0
0.4491	11.31	11.27	11.07	10.90	10.72	0.4491	145.0
0.5009	11.73	11.70	11.51	11.34	11.14	0.5009	147.0
0.5486	12.11	12.09	11.92	11.74	11.54	0.5486	149.0
0.5867	12.45	12.43	12.25	12.07	11.86	0.5867	151.0
0.6423	12.95	12.91	12.73	12.56	12.33	0.6423	153.0
0.6886	13.39	13.34	13.13	12.97	12.74	0.6886	155.0
0.7475	13.98	13.93	13.71	13.53	13.28	0.7475	156.0
0.7997	14.58	14.51	14.24	14.05	13.79	0.7997	158.0
0.8511	15.13	15.12	14.78	14.62	14.33	0.8511	159.0
0.8996	15.79	15.73	15.39	15.19	14.87	0.8996	160.0
0.9503	16.61	16.54	16.16	15.86	15.49	0.9503	160.5
1.0000	17.54	17.41	16.96	16.59	16.16	0.9962	160.5

relationship was used [7, 8]:

$$\ln \varepsilon_{12} = \alpha_0^* + \alpha_i^* T \tag{1}$$

where: α_i ($i = 0$, 1) are empirical constants and T is the absolute temperature.

The α_i coefficients of this fitting procedure are listed in Table II, along with the standard deviations σ ($\ln\varepsilon_{12}$) for each solvent system.

Equation 1 reproduces the experimental ε_{12} values with an average uncertainty, evaluated by means of the relation (2):

$$\overline{\Delta\varepsilon_{12}} = \frac{1}{N}\sum_{N} |\varepsilon_{12}^{\text{calc.}} - \varepsilon_{12}^{\text{exp.}}| \tag{2}$$

where: N is the number of experimental points; $\overline{\Delta\varepsilon_{12}} = \pm 0.02$ units of over relative permittivity values (see Tab. I).

The second step, of this study, involves investigation of the variation of relative permittivity with binary composition was analyzed by using

TABLE II Coefficients α_i^* and standard deviations $\sigma(\ln\varepsilon_{12})$ of Eq. (1) for ME – THF mixtures

X_{ME}	$\alpha_1^*\ 10^3$	α_0^*	$\sigma\ (ln\varepsilon_{12})$
0.0000	−4.0349	3.2074	$3.7 \cdot 10^{-3}$
0.0499	−3,8279	3.2030	$3.0 \cdot 10^{-3}$
0.0958	−3.6854	3.2080	$2.7 \cdot 10^{-3}$
0.1503	−3.8492	3.3077	$2.6 \cdot 10^{-3}$
0.1915	−3.7563	3.3205	$1.6 \cdot 10^{-3}$
0.2498	−3.6753	3.3452	$1.3 \cdot 10^{-3}$
0.2886	−3.6196	3.3602	$0.8 \cdot 10^{-3}$
0.3496	−3.7501	3.4464	$0.6 \cdot 10^{-3}$
0.3872	−3.5627	3.4197	$0.7 \cdot 10^{-3}$
0.4491	−3.2106	3.3618	$0.5 \cdot 10^{-3}$
0.5009	−3.0853	3.3625	$0.9 \cdot 10^{-3}$
0.5486	−2.8957	3.3398	$1.2 \cdot 10^{-3}$
0.5867	−2.9088	3.3713	$1.2 \cdot 10^{-3}$
0.6423	−2.8832	3.4025	$1.1 \cdot 10^{-3}$
0.6886	−2.9209	3.4461	$0.8 \cdot 10^{-3}$
0.7475	−3.0134	3.5164	$0.9 \cdot 10^{-3}$
0.7997	−3.2767	3.6343	$0.7 \cdot 10^{-3}$
0.8511	−3.2626	3.6689	$1.8 \cdot 10^{-3}$
0.8996	−3.5444	3.7926	$1.3 \cdot 10^{-3}$
0.9503	−4.8363	4.2736	$0.7 \cdot 10^{-3}$
1.0000	−4.6089	2.9453	$1.7 \cdot 10^{-3}$

TABLE III Coefficients β_j and standard deviations $\sigma(\ln\varepsilon_{12})$ of Eq. (3) for ME – THF binary mixtures

T	$\beta_3 \cdot 10$	$\beta_2 \cdot 10$	β_1	β_0	$\sigma(ln\varepsilon_{12})$
291.15 K	5.2256	−8.2818	1.1270	2.0392	$8.8 \cdot 10^{-4}$
293.15 K	5.1563	−8.5013	1.1664	2.0224	$6.9 \cdot 10^{-4}$
298.15 K	4.4556	−7.8413	1.1690	1.9964	$13.5 \cdot 10^{-4}$
303.15 K	3.7477	−6.8774	1.1370	1.9830	$8.3 \cdot 10^{-4}$
308.15 K	3.2408	−6.1302	1.0972	1.9734	$9.3 \cdot 10^{-4}$

the following equation:

$$\ln\varepsilon_{12} = \sum_{0}^{j} \beta_j X_i^j \tag{3}$$

which could be fitted to the experimental data at each temperature using a least-squares method [8]. The values of β_j coefficients, for $j = 3$, and the standard deviations $\sigma(\ln\varepsilon_{12})$ are summarized in Table III. Eq. (3) reproduces the experimental data of ε_{12} (see Tab. I) with $\overline{\Delta\varepsilon_{12}} = \pm 0.02$ units.

In our studies on intermolecular interactions in liquid mixtures of ME with THF we have carried out the analysis of changes excess values of ε_{12} as a function of the composition of the mixed solvent. The study of this extrathermodynamic structural parameter of liquid binary mixtures represents a unique tool for investigating the formation of intermolecular complexes, and provides a valuable aid for determining their stoichiometric composition.

Therefore, a very slight shift of ε_{12} from the linear behavior of a non-interacting "ideal" system should correspond to very weak complexes.

The values of ε_{12}^E have been evaluated by means of the equation:

$$\varepsilon_{12}^E = \varepsilon_{12} - (\varepsilon_1 X_1 + \varepsilon_2 X_2) \tag{4}$$

The values of ε_{12}^E have been fitted in a Redlich – Kister equation of the type [7]:

$$\varepsilon_{12}^E = X_1 X_2 \sum_{j=0}^{k} a_j (2X_2 - 1)^j \tag{5}$$

where: X_i-molar fraction

The parameters a_j of Eq. (5) were evaluated by the method of least squares with points weighted and they are listed in Table IV along with standard deviations $\sigma(\varepsilon_{12}^E)$. This function reproduces the values ε_{12}^E with an average deviation $\overline{\Delta\varepsilon_{12}^E} = \pm 0.02$ units.

The results of ε_{12}^E calculations for the investigated systems are presented graphically as a function of mole fraction of ME (X_{ME}) in Figure 1.

As we can see, the excess of this extrathermodynamic parameter (ε_{12}^E) is always negative ($-1.14 \leq \varepsilon_{12}^E \leq 0$) over the whole composition range. At the lower temperatures, ε_{12}^E reaches a minimum at $X_{ME} = 0.7$.

As suggested by other authors, the study of this extrathermodynamic parameter of binary liquid mixtures represents a unique tool for investigating the formation of intermolecular complexes, and provides a valuable aid for determining their stoichiometry and their relative thermostability [9–11]. The position of the relative minima in plots of ε_{12}^E, could be taken as the true composition of these intermolecular complexes, while the relative height on the ordinate scale could be considered as their thermostability index.

TABLE IV Coefficients α_j and standard deviations $\sigma(\varepsilon_{12}^E)$ of Eq. (5) for ME – THF binary mixtures

T	α_6	α_5	α_4	α_3	α_2	α_1	α_0	$\sigma(V_m^E)$
291.15 K	3.8841	−4.1583	2.9755	0.2480	−1.7151	−1.2351	0.0021	$9.5 \cdot 10^{-4}$
293.15 K	5.1828	−7.4482	4.3576	1.1236	−2.2055	−1.0127	0.0024	$8.7 \cdot 10^{-4}$
298.15 K	0.2395	14.1990	−28.865	22.4920	−7.6499	−0.4062	0.0011	$9.9 \cdot 10^{-4}$
303.15 K	−7.1253	32.2160	−47.0310	32.2320	−10.2701	−0.0216	0.0004	$9.4 \cdot 10^{-4}$
308.15 K	−12.1990	47.4320	−65.7610	43.6030	−13.4892	0.4161	−0.0012	$8.6 \cdot 10^{-4}$

In the case our research in this paper, a very slight shift ε_{12} from the linear behaviour of non-interacting ideal system (see Fig. 1) should correspond to a very small stabilization energy for ME – THF binary

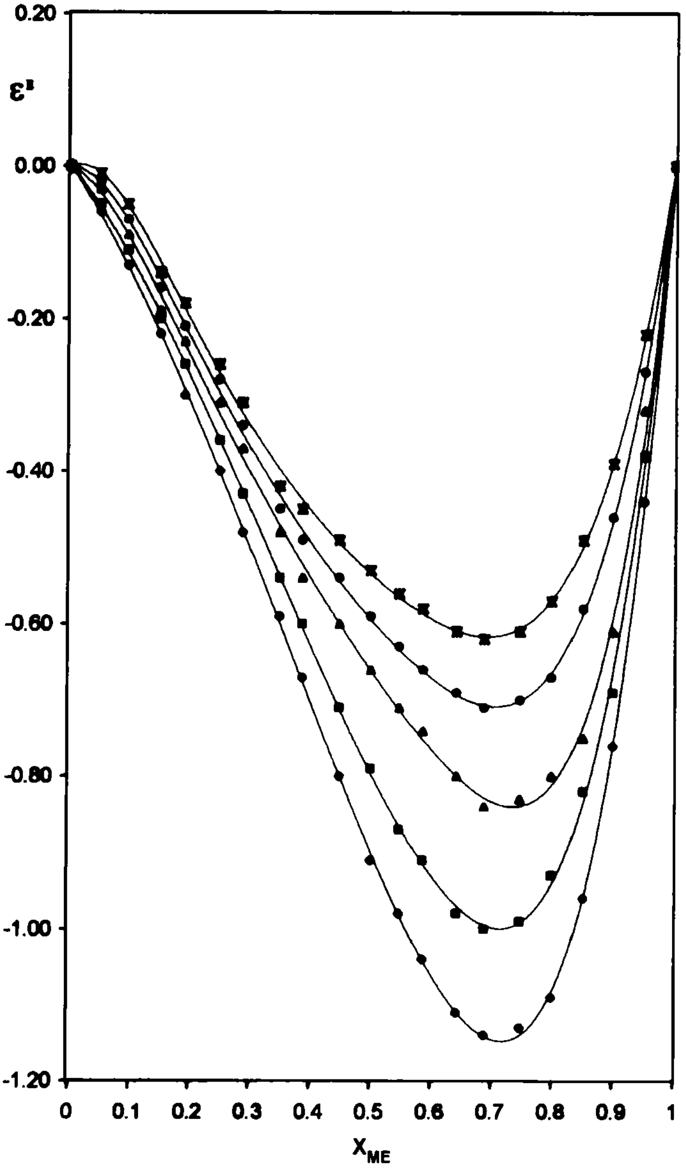

FIGURE 1 Excess of relative permittivities for the liquid ME–THF mixtures, at 291.15 K (■), 293.15 K(□), 298.15 K(▲), 303.15 K(•) and 308.15 K(×).

mixtures and the formation of very weak complexes with stoichiometry ME:THF = 3:1, at all the investigated temperatures.

Similar conclusions can be drawn from the analysis of the temperature coefficients of the relative permittivity.

From the experimental values of relative permittivities (ε_{12}) (see Tab. I), the temperature coefficients of the relative permittivity, denoted α_{12}, *viz.*:

$$\alpha_{12} = \frac{1}{\varepsilon_{12}} \cdot \left[\frac{d\varepsilon_{12}}{d(1/T)}\right] \tag{6}$$

at 298.15 K, were calculated (see Fig. 2).

The composition range of liquid binary mixtures within which α_{12} or its excess (α_{12}^E) attain their highest values (maximum or minimum) should be interpreted (as shown in Räetzsch *et al.*'s thermodynamic considerations [12]) as a region characterized by maximal intermolecular interactions between two different components of the given liquid mixture. But, the negative shifts α_{12} or ε_{12}^E from the linear behaviour of a non-interacting ideal system should correspond to the formation of very weak complexes.

In the case of ME – THF mixtures, we observed the tendency to achieve the minimum by the function α_{12} at ca. $X_{ME} = 0.70$. This effect can be accounted for by maximal intermolecular interactions between THF and ME molecules, which lead to the formation of very weak 3ME – THF intermolecular complex.

Additional information about intermolecular interactions in liquid binary mixtures is provided by the analysis of the values of chemical shift differences δ(ME – THF) at 298 K, between the centre of ^{1}H-NMR signals of the -OH group of ME and the centre of the ^{1}H-NMR signal of -CH_2 group of THF molecules over a wide range of solvent compositions *i.e.*, from $0.0114 \leq X_{ME} \leq 0.9962$. Subsequently, to obtain more conclusive experimental evidence from the chemical shifts δ(ME – THF), shown in Table I and explained above, their deviations from the additive properties, *viz.* $\Delta\delta$(ME – THF) values, have been calculated.

The procedure to fit these values has been discussed in detail previously [1–4]. The values of these structural parameters or, more precisely, the locations of their maximum values correspond

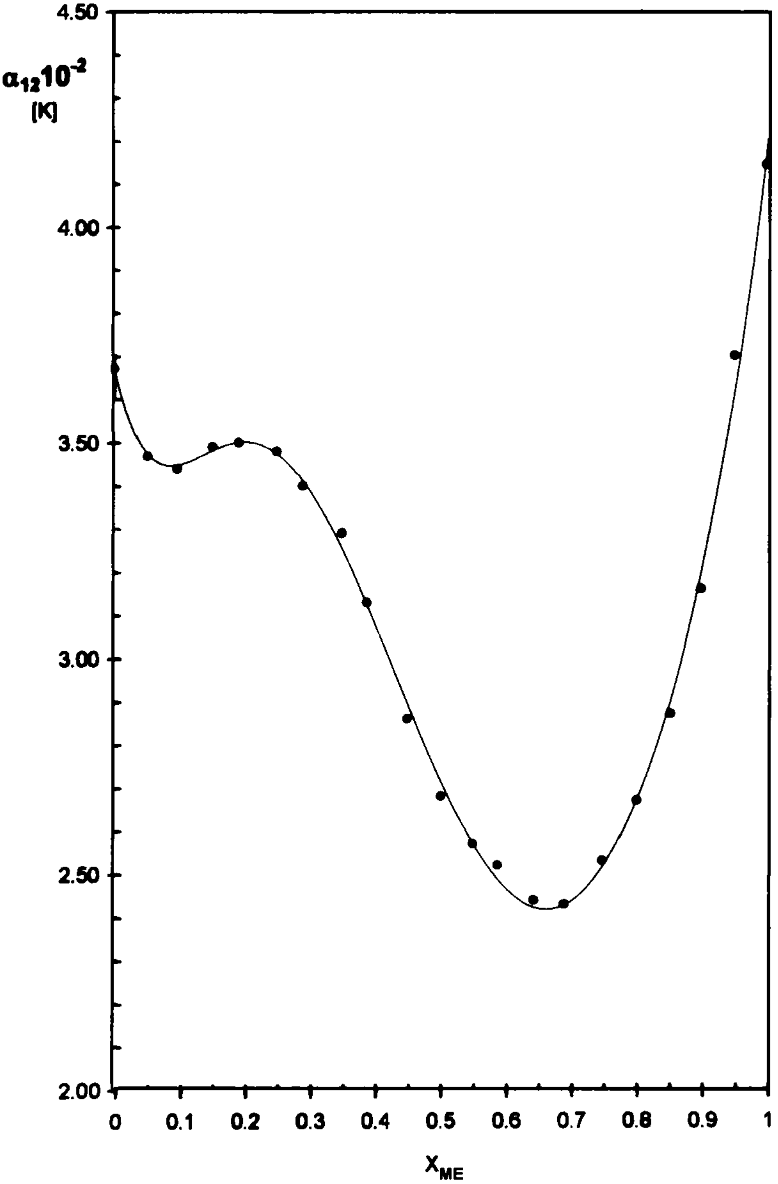

FIGURE 2 Changes in the temperature coefficient of the relative permittivity in the liquid ME–THF mixtures, at 298.15 K.

to the compositions with the strongest intermolecular interactions between the components, where hydrogen bonds are involved [1–4].

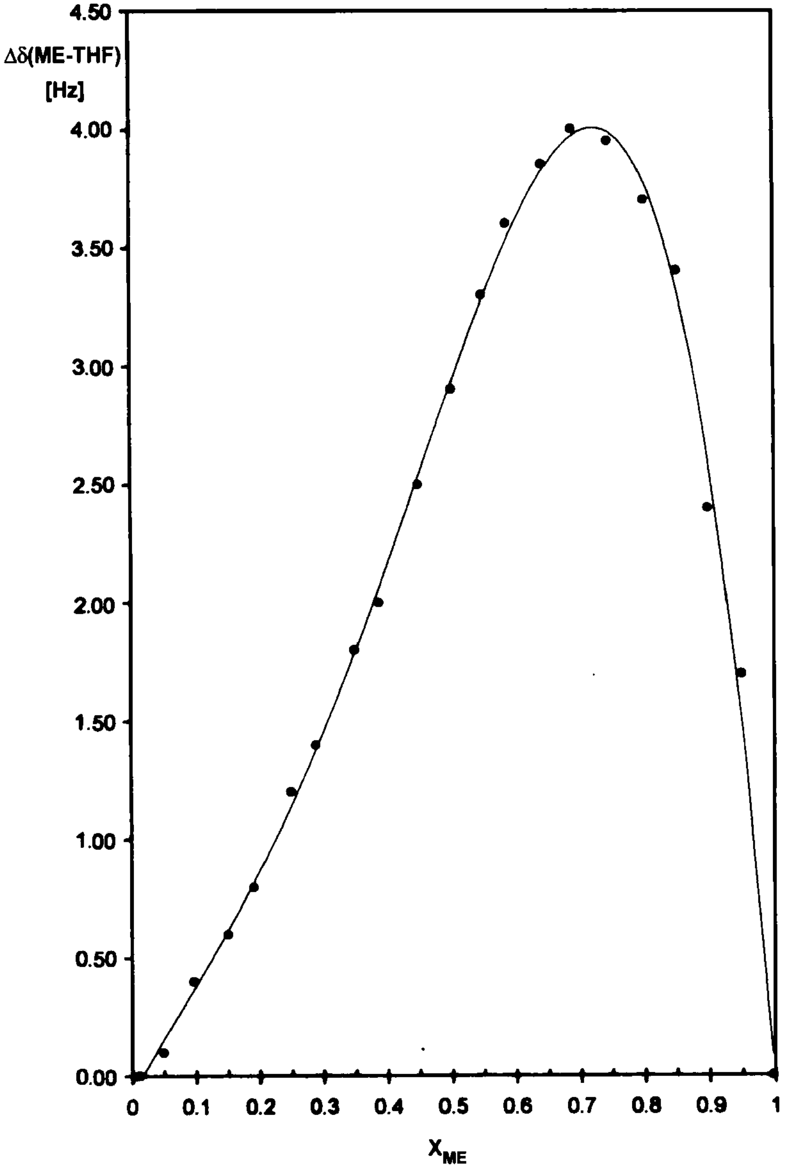

FIGURE 3 Changes in the spectral structural parameter, $\Delta\delta$(ME − THF), in the liquid ME − THF mixtures, at 298 K.

The $\Delta\delta$(ME − THF) values are visualised in Figure 3 as a function of the mixture compositions.

The analysis of the data indicates the presence of a maximum $\Delta\delta$(ME−THF) at ca. $X_{ME} \approx 0.7$. Thus, at this composition the intermolecular interactions between components involving hydrogen bonds, are observed, and the complex is 3ME·THF.

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