

2-METHOXYETHANOL–TETRAHYDROFURAN– BINARY LIQUID SYSTEM

Viscosities, densities, excess molar volumes and excess Gibbs activation energies of viscous flow at various temperatures

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Abstract

Densities (d_{12}) and viscosities (η_{12}) have been measured for 2-methoxyethanol (ME) with tetrahydrofuran (THF) binary liquid mixtures over the whole composition range at various temperatures ranging from 291.15 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: $y_{12} = d_{12}$ or η_{12}]. From all these data, the excess molar volumes (V_{12}^E), the excess viscosities (η_{12}^E) and excess Gibbs activation energies (ΔG^*) of viscous flow were calculated. These structural parameters as a function of concentration suggest the formation of 3ME·THF and 2ME·THF types of intermolecular complexes.

Keywords: binary liquid mixtures, intermolecular interactions, physicochemical properties

Introduction

The knowledge of transport and thermodynamic properties of binary liquid mixtures formed by two components associated through hydrogen bonds is important from theoretical and process designing points of view.

This paper reports values of densities and viscosities of the 2-methoxyethanol (ME)–tetrahydrofuran (THF) binary mixtures at different temperatures.

2-Methoxyethanol (ME) is an ether alcohol showing physicochemical characteristics which are intermediate between protic and dipolar aprotic solvents [1–5]. The molecules of ME contain both hydroxylic and ether groups and they in their pure state are self-associated and form cyclic dimers in which the hydroxy proton of one ME molecule is bound to the ether oxygen atom of the other [6–8]. They can also form intermolecular hydrogen-bonded five membered ring monomers [8–10].

Tetrahydrofuran with a proton acceptor in its molecule (oxygen atom) is a weaker base than HMPT, amides, DMSO or acetone. This results from the fact that the electronegative oxygen atom in its molecule is enriched with a negative charge

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only to small extent due to a positive induction effect of alkyl groups [11–13]. The repulsion effects between hydrogen atoms and also free electron pair of the oxygen atom and electrons of adjacent C–H bonds bring about, however, an increase in the basicity of THF as compared with linear ethers (eq. diethyl ether). A very weak acidity of THF ($pK_a = -2.08$) excludes the possibility of self-association via formation of hydrogen bonds of the C–H \cdots O type [14].

Taking into account the published data concerning the structure of liquid ME and THF it seemed appropriate to extend these structural studies to ME–THF binary liquid mixtures.

Results and discussion

The experimental data of density (d_{12}) and viscosity (η_{12}) obtained from the measurements of the pure solvents and for the analysed binary mixtures at all investigated temperatures are summarized in Table 1.

Table 1 Experimental density (d_{12}) and viscosity (η_{12}) for ME–THF liquid mixtures

x_{ME}	$d_{12}/g\ cm^{-3}$					$\eta_{12}\cdot 10^2/P$		
	T/K	291.15	293.15	298.15	303.15	308.15	293.15	298.15
0.0000	0.88965	0.88746	0.88198	0.87649	0.87101	0.490	0.467	0.455
0.0499	0.89311	0.89100	0.88562	0.88021	0.87479	0.553	0.522	0.494
0.0958	0.89640	0.89433	0.88899	0.88364	0.87827	0.613	0.574	0.540
0.1503	0.90037	0.89833	0.89306	0.88778	0.88245	0.684	0.638	0.596
0.1915	0.90345	0.90143	0.89619	0.89093	0.88564	0.738	0.686	0.639
0.2498	0.90781	0.90583	0.90064	0.89544	0.89019	0.814	0.754	0.699
0.2886	0.91072	0.90875	0.90359	0.89844	0.89322	0.865	0.798	0.739
0.3496	0.91537	0.91342	0.90831	0.90320	0.89802	0.945	0.867	0.800
0.3872	0.91820	0.91628	0.91119	0.90611	0.90096	0.993	0.910	0.838
0.4491	0.92292	0.92102	0.91597	0.91095	0.90584	1.072	0.980	0.900
0.5009	0.92685	0.92498	0.91999	0.91501	0.90994	1.138	1.037	0.951
0.5486	0.93044	0.92859	0.92364	0.91870	0.91369	1.198	1.092	0.999
0.5867	0.93334	0.93151	0.92659	0.92169	0.91670	1.247	1.135	1.038
0.6423	0.93754	0.93574	0.93088	0.92605	0.92112	1.316	1.198	1.094
0.6886	0.94108	0.93927	0.93448	0.92970	0.92481	1.375	1.251	1.140
0.7475	0.94563	0.94387	0.93913	0.93440	0.92958	1.447	1.316	1.199
0.7997	0.94973	0.94801	0.94332	0.93864	0.93386	1.511	1.373	1.249
0.8511	0.95384	0.95213	0.94749	0.94286	0.93812	1.570	1.426	1.296
0.8996	0.95783	0.95613	0.95150	0.94692	0.94222	1.622	1.471	1.337
0.9503	0.96217	0.96045	0.95586	0.95132	0.94667	1.669	1.512	1.374
1.0000	0.96652	0.96488	0.96029	0.95576	0.95110	1.708	1.544	1.404

Volumetric properties of the 2-methoxyethanol–tetrahydrofuran binary liquid mixtures

The first step of this study involves investigation of the dependence of density (d_{12}) on temperature, and the following relationship was used [15, 16]:

$$d_{12}(t) = \sum_0^i \alpha_i t^i \quad (1)$$

where t – temperature in °C.

The α_i coefficients, for $i=3$, summarized in Table 2 together with standard deviations [$\sigma(d_{12})$] for each mixture investigated. Equation (1) reproduces the experimental d_{12} values with an average uncertainty, evaluated by means of the relation:

$$\overline{\Delta d}_{12} = \frac{1}{N} \sum_N \left| d_{12}^{\text{calc.}} - d_{12}^{\text{exp.}} \right| \quad (2)$$

where N – number of experimental points.

Table 2 Coefficients α_i and standard deviations $\sigma(d_{12})$ of Eq. (1) for ME–THF mixtures

x_{ME}	$\alpha_4 \cdot 10^7$	$\alpha_3 \cdot 10^6$	$\alpha_2 \cdot 10^4$	$\alpha_0 \cdot 10$	$\sigma(d_{12})$
0.0000	1.8231	-1.4889	-10.5730	9.0906	$2.0 \cdot 10^{-6}$
0.0499	7.3192	-6.5217	-8.9164	9.1085	$3.0 \cdot 10^{-6}$
0.0958	9.1221	-8.0130	-8.4091	9.1361	$6.6 \cdot 10^{-6}$
0.1503	6.5153	-6.1874	-8.6856	9.1764	$7.6 \cdot 10^{-6}$
0.1915	6.3707	-6.3894	-8.5063	9.2047	$8.0 \cdot 10^{-6}$
0.2498	10.9890	-9.9583	-7.4870	9.2388	$9.9 \cdot 10^{-6}$
0.2886	7.6623	-7.2498	-8.1277	9.2727	$11.8 \cdot 10^{-6}$
0.3496	8.1904	-7.7710	-7.8780	9.3160	$10.4 \cdot 10^{-6}$
0.3872	11.1770	-10.2130	-7.1716	9.3378	$13.0 \cdot 10^{-6}$
0.4491	8.8093	-8.3121	-7.5698	9.3874	$14.7 \cdot 10^{-6}$
0.5009	10.8240	-10.1630	-6.9278	9.4200	$14.8 \cdot 10^{-6}$
0.5486	13.4140	-12.0980	-6.3723	9.4507	$15.3 \cdot 10^{-6}$
0.5867	12.2130	-11.2570	-6.4923	9.4798	$16.3 \cdot 10^{-6}$
0.6423	11.6680	-10.8460	-6.4631	9.5203	$17.9 \cdot 10^{-6}$
0.6886	5.6778	-6.0725	-7.5969	9.5641	$13.7 \cdot 10^{-6}$
0.7475	12.4220	-11.5090	-6.0568	9.5956	$16.4 \cdot 10^{-6}$
0.7997	14.6420	-13.5050	-5.3785	9.6296	$18.6 \cdot 10^{-6}$
0.8511	12.0690	-11.4590	-5.8130	9.6733	$16.8 \cdot 10^{-6}$
0.8996	9.9395	-9.4842	-6.3328	9.7175	$20.4 \cdot 10^{-6}$
0.9503	5.1631	-5.3343	-7.4247	9.7698	$16.0 \cdot 10^{-6}$
1.0000	1.0864	-2.0696	-8.2725	9.8213	$16.5 \cdot 10^{-6}$

The value of $\overline{\Delta d_{12}}$ is equal to $\pm 0.00004 \text{ g cm}^{-3}$ over the set of the experimental d_{12} values (Table 1).

The second step, of this study, involves investigation of the dependence of density (d_{12}) on mole fraction (x_1) of ME, and the following relationship was used:

$$d_{12}(x_1) = \sum_0^j \beta_j x_1^j \quad (3)$$

The values of β_j coefficients, for $j=4$, are listed in Table 3 together with the standard deviations, at each investigated temperature.

Equation (3) reproduces the experimental data of d_{12} (Table 1) with $\overline{\Delta d_{12}} = \pm 0.00005 \text{ g cm}^{-3}$.

Table 3 Coefficients α_j and standard deviations $\sigma(d_{12})$ of Eq. (3) for ME–THF binary mixtures

T/K	$\beta_4 \cdot 10^2$	$\beta_3 \cdot 10^2$	$\beta_2 \cdot 10^2$	$\beta_1 \cdot 10^2$	$\beta_0 \cdot 10$	$\sigma(d_{12})$
291.15	2.4479	-4.3867	2.8399	6.7930	8.8966	$6.0 \cdot 10^{-6}$
293.15	2.1875	-3.8712	2.4913	6.9319	8.8747	$8.5 \cdot 10^{-6}$
298.15	1.8372	-3.1803	2.0529	7.1180	8.8200	$8.0 \cdot 10^{-6}$
303.15	1.6089	-2.7104	1.7363	7.2894	8.7651	$6.5 \cdot 10^{-6}$
308.15	1.3761	-2.2559	1.4608	7.4260	8.7103	$6.3 \cdot 10^{-6}$

From the measured densities (d_{12}) (Table 1) the excess molar volumes (V_m^E) of the mixtures, at each investigated temperature, were fitted in the equation:

$$V_m^E = X_1 M_1 (d_{12}^{-1} - d_1^{-1}) + X_2 M_2 (d_{12}^{-1} - d_2^{-1}) \quad (4)$$

where M_i , d_i and x_i are the molar mass, density and mole fraction of component i , with $i=1$ for 2-methoxyethanol and $i=2$ for THF while d_{12} is the density of the mixture.

The excess molar volumes (V_m^E) values have been fitted in a Redlich–Kister equation of the type [15]:

$$V_m^E = x_1 x_2 \sum_{j=0}^k a_j (2x_2 - 1)^j \quad (5)$$

where x_i – mole fraction.

The parameters a_j of Eq. (5) were evaluated by the method of least squares with points weighed and they are listed in Table 4 along with standard deviations $\sigma(V_m^E)$. The results of V_m^E calculations for the investigated systems are presented in graphic form in Fig. 1.

As we can see, V_m^E is always positive at all temperatures investigated and for the whole composition range and it has an absolute maximum at $x_{ME} \approx 0.75$ of ME. This composition range corresponds to the least dense and packed mixed solvent.

For these binaries, there are different effects that may contribute to V_m^E and these will be taken into account in order to rationalize the non-ideal behaviour of this solvent system.

Table 4 Coefficients α_j and standard deviations $\sigma(V_m^E)$ of Eq. (5) for various ME–THF binary mixtures

T/K	α_4	α_3	α_2	$\alpha_1 \cdot 10$	$\alpha_0 \cdot 10^4$	$\sigma(V_m^E)$
291.15	-2.0611	3.7334	-2.2692	5.9583	4.1115	$6.5 \cdot 10^{-3}$
293.15	-1.8338	3.2802	-1.9574	5.1073	0.6979	$4.6 \cdot 10^{-3}$
298.15	-1.5498	2.7039	-1.5650	4.0979	6.4827	$3.8 \cdot 10^{-3}$
303.15	-1.3861	2.3653	-1.3222	3.4244	1.9283	$1.9 \cdot 10^{-3}$
308.15	-1.1556	1.9114	-1.0343	2.7839	2.2154	$1.7 \cdot 10^{-3}$

In general, positive excess volumes can be ascribed to breaking of hydrogen bonds in 2-methoxyethanol by the addition of THF. It has been pointed out in literature that ME can exist in two conformations that may be represented as *gauche* or *anti* with respect to the substituting groups ($-\text{OH}$ and $-\text{OCH}_3$) in the alkyl chain. In the *gauche* form, a strong intermolecular hydrogen bond is present between the two groups, reducing in this way the possibility of interaction with the neighbouring molecules, which occur only via weak dipolar interactions [17]. In the ME–THF binary mixtures one of the effects that may contribute to V_m^E is homocooperative interactions of ME and THF molecules on mixing. This should correspond to a volumetric expansion and a positive contribution to V_m^E should be expected.

The other effects that may have a positive contributions to V_m^E are the interactions between the hydrophobic and apolar groups (groups in alkyl chains) of one spe-

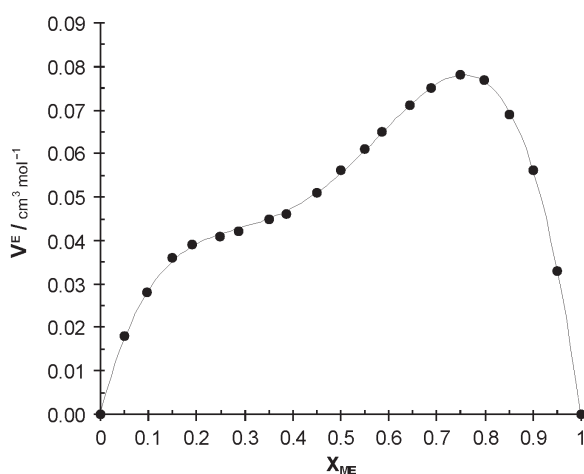


Fig. 1 Excess molar volumes (V^E) for 2-methoxyethanol–tetrahydrofuran, at 298.15 K

cies and the polar groups of the other, thus producing valuable microheterogeneity at molecular level.

After these considerations, we may assume that in the ME–THF liquid mixtures all the effects, discussed above, should be taken into account and may contribute to V_m^E values. In our opinion, the appropriate positive contributions may be expected for formation of the weak 3ME·THF adduct in this binary solvent system.

Viscosity properties of the 2-methoxyethanol–tetrahydrofuran binary liquid mixtures

The effect of temperature on the viscosity of the mixtures was examined by assuming validity of the general equation offered by Arrhenius [18]:

$$\eta = A \exp(B/RT) \quad (6)$$

where R being the gas constant and T the absolute temperature.

Calculated viscosity data, by use of the equation:

$$\eta_{12}^{1/8} = \frac{1}{M} \frac{d_0 + d_1 x_1 + \dots + d_5 x_5}{d_0 + d_1 x_1 + \dots + d_5 x_5} \quad (7)$$

where used in the plots of η_{12} vs. $1/T$. The mole fraction of ME, x_1 , for a given solution was kept there as constant parameter. Straight lines were obtained for each composition with a correlation coefficient better than 0.998.

The corresponding constants, A and B , were calculated by the least-squares method. Based on these data the following relations were found:

$$A = 0.2918x^6 - 1.0141x^5 + 1.3738x^4 - 0.9377x^3 + 0.3648x^2 - 0.1017x + 0.0275$$

standard deviations $\sigma(A) = 2.63 \cdot 10^{-5}$

$$B = -13.9450x^6 + 60.9890x^5 - 92.5400x^4 + 64.9131x^3 - 24.7783x^2 + 12.8443x + 7.0218$$

standard deviations $\sigma(B) = 1.28 \cdot 10^{-3}$

From the measured viscosities (η_{12}) (Table 1) the excess viscosity η_{12}^E of the mixtures, at the each investigated temperature, were fitted in the equation:

$$\eta_{12}^E = \eta_{12} - (\eta_1 x_1 + \eta_2 x_2) \quad (8)$$

where η_i and x_i are the viscosity and mole fraction of component i , with $i=1$ for 2-methoxyethanol and $i=2$ for THF, while η_{12} is the viscosity of the mixture.

The excess viscosity (η_{12}^E) values have been fitted in a Redlich–Kister equation of the type [15]:

$$\eta_{12}^E = x_1 x_2 \sum_{j=0}^k a_j (2x_2 - 1)^j \quad (9)$$

where x_i – mole fraction.

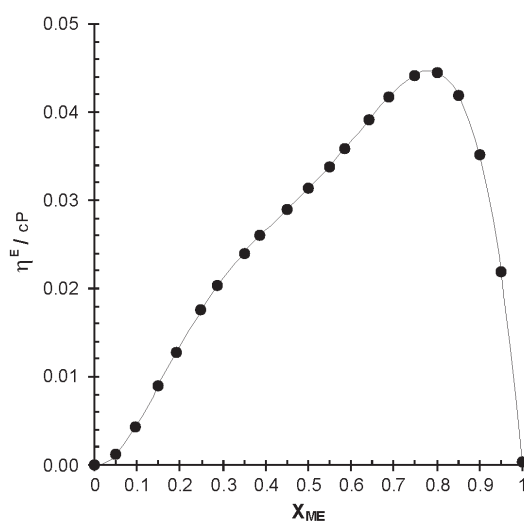


Fig. 2 Excess viscosities (η^E) for 2-methoxyethanol–tetrahydrofuran binary mixtures, at 298.15 K

The parameters a_i of Eq. (9) were evaluated by the method of least squares with points weighed and they are listed in Table 5 along with standard deviations $\sigma(\eta_{12}^E)$. The results of η_{12}^E calculations for the investigated systems are presented in graphic form in Fig. 2.

Table 5 Coefficients α_j and standard deviations $\sigma(\eta^E)$ of Eq. (9) for various ME–THF binary mixtures

T/K	$\alpha_6 \cdot 10$	α_5	α_4	α_3	$\alpha_2 \cdot 10$	$\alpha_1 \cdot 10^2$	$\alpha_0 \cdot 10^6$	$\sigma(\eta_{12}^E)$
293.15	-3.5998	-0.2065	1.4914	-1.4511	5.0085	2.5330	2.0156	$8.7 \cdot 10^{-4}$
298.15	3.8690	-2.5720	4.2310	-2.8410	8.0530	-0.9895	1.0640	$8.8 \cdot 10^{-4}$
303.15	3.3673	-2.1703	3.5619	-2.4171	7.0440	-1.5698	-3.6965	$4.9 \cdot 10^{-4}$

As we can see, η_{12}^E is always positive at all temperatures investigated and for the whole composition range and it has an absolute maximum at $x_{ME} \approx 0.75$ of ME.

This effect, in reference to the internal structure of ME and THF, should be interpreted in the analogous way as it has been done while discussing the change of V_m^E for the composition range corresponding to ca $x_{ME} \approx 0.75$ mole fraction of ME in the binary ME–THF mixtures. Thus, at this composition the intermolecular interactions between components involving intermolecular bonds, are observed, and the weak complex of the type $3ME \cdot THF$ is formed.

Viscosity data can be analyzed from thermodynamic view point in order to obtain further information about these mixed solvents. A more suitable treatment of experimental η_{12} values was suggested in literature by Eyring who, starting from Andrades approach to the viscosity theory, provided the following equation [19]:

$$\eta_{12} = \frac{hN}{V_m} \exp(\Delta H^*/RT - \Delta S^*/R) \quad (10)$$

where η_{12} is viscosity of the solution, h is the Planck constant, N the Avogadro number, R the universal gas constant, T the absolute temperature and V_m the molar volume.

When $\ln(\eta_{12}V_m/hN)$ is plotted vs. $1/T$, the slope is equal to $\Delta H^*/R$, and the intercept is equal to $-\Delta S^*/R$. Using both the graphical and least-squares methods, the activation parameters ΔH^* and ΔS^* were obtained, and then ΔG^* was obtained using the equation:

$$\Delta G^* = \Delta H^* - T\Delta S^* \quad (11)$$

From the obtained values of ΔG^* the excess free energy of viscous flow ΔG^{*E} , at 298.15 K, were fitted in the equation:

$$\Delta G^{*E} = \Delta G_{12}^* - (x_1\Delta G_1^* + x_2\Delta G_2^*) \quad (12)$$

These values, so obtained, are presented in Table 6 and Fig. 3.

In the case of ME–THF binaries, the analysis of the course of changes of ΔG^{*E} as a function of the composition of the studied mixtures points at two characteristic composition regions of mixed solvent within which the appearance of intermolecular interactions may be expected (Fig. 3). The first of them corresponds to ca. 0.40 mole fraction of ME and the second of them corresponds to ca. 0.9 mole fraction of ME. Within these regions the maximum and minimum of ΔG^{*E} are observed.

As suggested by other authors [21–22], positive deviations of ΔG^{*E} should be detected in binary mixtures where strong specific interactions between unlike molecules, such as hydrogen bonding, take place. In this case, these specific interactions

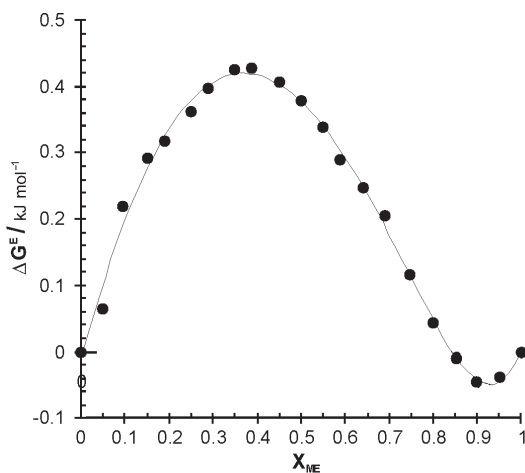


Fig. 3 Excess free energy of activation of viscous flow (ΔG^{*E}) for 2-methoxyethanol–tetrahydrofuran binary mixtures, at 298.15 K

should be predominant over all other interactions of any kind, classifiable as dispersion forces, which generally are responsible for negative deviations in the property.

Table 6 Activation parameters for the viscous flow for various ME–THF liquid mixtures

x_{ME}	$\Delta H_{12}^*/\text{KJ mol}^{-1}$	$\Delta S_{12}^*/\text{J mol}^{-1} \text{K}^{-1}$	$\Delta G_{12}^*/\text{KJ mol}^{-1}$
0.0000	6.28	−6.63	8.26
0.0499	6.74	−6.51	8.68
0.0958	7.29	−6.35	9.18
0.1503	7.89	−6.15	9.72
0.1915	8.22	−6.09	10.04
0.2498	8.61	−6.01	10.40
0.2886	8.94	−5.93	10.71
0.3496	9.44	−5.80	11.17
0.3872	9.76	−5.72	11.47
0.4491	10.18	−5.62	11.86
0.5009	10.61	−5.51	12.25
0.5486	10.87	−5.46	12.50
0.5867	11.09	−5.42	12.71
0.6423	11.50	−5.32	13.09
0.6886	11.79	−5.25	13.36
0.7475	12.15	−5.17	13.69
0.7997	12.47	−5.10	13.99
0.8511	12.80	−5.03	14.30
0.8996	13.14	−4.94	14.61
0.9503	13.52	−4.83	14.96
1.0000	13.97	−4.70	15.37

Thus, the conclusion can be drawn that for the composition corresponding to ca 0.40 mole fraction of ME the strongest interactions between ME and THF molecules are displayed and it suggests the formation of the stable 2ME·3THF intermolecular complex.

In our opinion the minimum of ΔG^{*E} values centred on $x_{ME} \approx 0.9$ would be preferably attributed to interstitial solvation phenomena rather than to a complex species involving such a high number of molecules.

The results obtained in the present paper indicate to formation of two different intermolecular complexes, namely 3ME·THF and 2ME·3THF. The intermolecular complex in which there are two ME molecules per three THF molecules, is characterized by the highest stability.

Experimental

Materials

2-Methoxyethanol and tetrahydrofuran, Merck, pro-analysis, containing less than 0.055 (mass/mass) of water, respectively (determined by Karl–Fischer method), were used.

2-Methoxyethanol and tetrahydrofuran were further purified by the methods described by Piekarski [23] and Riddick *et al.* [24]. The mixtures were prepared by mass, with weighings accuracy to $\pm 1 \cdot 10^{-4}$ g. Conversion to molar quantities was based on the relative atomic mass table of 1985 issued by IUPAC in 1986. The uncertainty in the mole fractions is less than $1 \cdot 10^{-4}$.

Measurements

Solvent densities were measured with a bicapillary type Lipkin pycnometer, with a capacity of ca 90 cm³. The maximum error in the density measurements was $5 \cdot 10^{-5}$ g cm⁻³. Viscosities of the pure components and the mixtures were determined at 293.15, 298.15 and 303.15 K with a calibrated Ubbelohde suspended level viscometer. The viscometers were calibrated by using high-purity dioxane, toluene and deionized water at the working temperatures. The viscosities were measured with an accuracy of ca $\pm 2 \cdot 10^{-5}$ Pa. Each temperature was maintained with an accuracy of ± 0.01 K.

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