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Kinematic Viscosities for Ether + Alkane Mixtures: Experimental Results and UNIFAC-VISCO Parameters

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Abstract Kinematic viscosities for the binary mixtures of diisopropylether, dibutylether or methyl ter-butyl ether with 3-methylpentane, hexane or heptane have been measured at 283.15 K, 298.15 K, and 313.15 K. The experimental values have been correlated by the McAllister equation. Using these results, new UNIFAC-VISCO parameters, $O_{ether}-CH_2$ and $O_{ether}-CH_3$, have been calculated.

Keywords Alkane · Ether · Kinematic viscosities · UNIFAC-VISCO

1 Introduction

In recent years, our research group has studied the viscosities of binary liquid mixtures containing a cyclic ether [1–4]. Following this research work, in this article we report the kinematic viscosities of mixtures containing linear ethers such as diisopropylether, dibutylether, and methyl tert-butyl ether and several alkanes such as 3-methylpentane, hexane, and heptane at temperatures of 283.15 K, 298.15 K, and 313.15 K.

The study of these types of mixtures is important since they are normally used in the petroleum industry; first of all, these ethers are added to the fuel in order to enhance the octane number, improving the combustion efficiency of it. Furthermore, they act as anti-knocking agents, substituting for the formally used lead compounds and reducing toxic air emissions. Due to the importance of these liquids, there are numerous articles that report thermophysical properties at various temperatures of mixtures containing linear ethers like diisopropylether and methyl tert-butyl ether and alkanes with the aim to reproduce the effect of the additives and the hydrocarbons, respectively, in gasoline

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[5–11]. We have found some previous references of viscosities of the studied binary mixtures at several temperatures [12–14].

Moreover, the viscosity is very useful for designing chemical industrial processes involving heat and mass transfer phenomena. Due to its importance, several models based on the group contribution method have been developed to predict the viscosity of liquid mixtures. The Wu model [15] combines the Eyring equation and the UNIFAC group contribution method [16]; the GC-UNIMOD [17] uses both a group contribution viscosity equation and an activity coefficient equation; the Asfour method [18,19] calculates the McAllister equation parameters using the group contribution concept; and the UNIFAC-VISCO method [20,21], which is also based on the Eyring equation, uses kinematic viscosity data to obtain group interaction parameters. From these methods, the UNIFAC-VISCO is one of the most frequently used [22–26]. Recently, in order to improve and extend the model proposed by Chevalier, some authors have recalculated and presented some interaction parameters among different groups [27–31]. Here, we use our experimental data to obtain new interaction parameters involving the ether group.

2 Experimental

The liquids used were diisopropylether (purity better than 99%), dibutylether (purity better than 99%), methyl tert-butyl ether (purity better than 99.7%), and 3-methylpentane, hexane, and heptane (purities better than 99%) obtained from Aldrich. No additional purification has been carried out.

Kinematic viscosities, ν, were determined using an Ubbelohde viscometer with a Schoot-Geräte automatic measuring unit Model AVS-440. The temperature was kept constant within ±0.01 K by means of a Schoot-Geräte thermostat. The viscometer was calibrated with doubly-distilled deionized water. The uncertainty of the time flow measurements was ±0.01 s, and the corresponding uncertainty in the kinematic viscosity was $\pm 1 \times 10^{-4}\ \mathrm{mm}^2 \cdot \mathrm{s}^{-1}$. Kinetic energy corrections were applied to the experimental data.

The kinematic viscosity values of the pure components measured at three temperatures are reported together with literature values at 298.15 K [9,12,32,33] in Table 1.

Table 1 Kinematic viscosities, ν, of the pure compounds

	$\nu(\mathrm{mm}^2 \cdot \mathrm{s}^{-1})$			
	$T = 283.15\ \mathrm{K}$	$T = 298.15\ \mathrm{K}$		$T = 313.15\ \mathrm{K}$
Compound	Exptl.	Exptl.	Lit.	Exptl.
Diisopropylether	0.4959	0.4392	0.4412 [9]	0.3861
Dibutylether	1.0295	0.8563		0.7187
Methyl tert-butyl ether	0.5191	0.4529	0.456 [12]	0.3961
3-Methylpentane	0.4928	0.4366	0.4411 [12]	0.3881
Hexane	0.5125	0.4493	0.4490 [32]	0.4039
Heptane	0.6697	0.5754	0.574 [33]	0.4986

Table 2 Experimental kinematic viscosities, ν, of the binary mixtures

x_1	$\nu(\mathrm{mm}^2 \cdot \mathrm{s}^{-1})$		
	$T = 283.15\,\mathrm{K}$	$T = 298.15\,\mathrm{K}$	$T = 313.15\,\mathrm{K}$
Diisopropylether (1) + 3-methylpentane (2)			
0.0498	0.4914	0.4364	0.3872
0.1011	0.4903	0.4355	0.3861
0.2010	0.4886	0.4348	0.3847
0.3018	0.4877	0.4342	0.3837
0.4014	0.4871	0.4339	0.3830
0.5010	0.4876	0.4338	0.3827
0.5993	0.4883	0.4344	0.3831
0.6973	0.4897	0.4352	0.3833
0.8014	0.4912	0.4366	0.3842
0.8997	0.4934	0.4377	0.3849
0.9501	0.4947	0.4385	0.3854
Diisopropylether (1) + hexane (2)			
0.0523	0.5094	0.4477	0.4011
0.0915	0.5076	0.4467	0.3994
0.1890	0.5031	0.4446	0.3961
0.3016	0.4990	0.4426	0.3929
0.3980	0.4963	0.4409	0.3907
0.4998	0.4944	0.4397	0.3889
0.6007	0.4931	0.4383	0.3874
0.6975	0.4932	0.4381	0.3866
0.7976	0.4934	0.4381	0.3859
0.8959	0.4945	0.4386	0.3856
0.9432	0.4953	0.4385	0.3860
Diisopropylether (1) + heptane (2)			
0.0508	0.6578	0.5658	0.4910
0.1002	0.6473	0.5567	0.4831
0.1986	0.6265	0.5387	0.4719
0.2973	0.6068	0.5218	0.4610
0.3992	0.5880	0.5055	0.4498
0.4991	0.5693	0.4900	0.4385
0.5979	0.5533	0.4779	0.4273
0.7009	0.5372	0.4679	0.4166
0.8008	0.5215	0.4588	0.4058
0.8954	0.5091	0.4496	0.3960
0.9500	0.5016	0.4443	0.3909
Dibutylether (1) + 3-methylpentane (2)			
0.0498	0.5151	0.4505	0.4026
0.1011	0.5383	0.4655	0.4176
0.1884	0.5796	0.4975	0.4427
0.2989	0.6320	0.5415	0.4712
0.4033	0.6843	0.5846	0.5031
0.4999	0.7344	0.6244	0.5374
0.5992	0.7877	0.6669	0.5730
0.7016	0.8460	0.7116	0.6088
0.7990	0.9030	0.7548	0.6442
0.9001	0.9657	0.8021	0.6804
0.9496	0.9979	0.8257	0.6992

Table 2 continued

x_1	$\nu(\mathrm{mm}^2 \cdot \mathrm{s}^{-1})$ $T = 283.15\,\mathrm{K}$	$T = 298.15\,\mathrm{K}$	$T = 313.15\,\mathrm{K}$
Dibutylether (1) + hexane (2)			
0.0506	0.5334	0.4626	0.4167
0.1050	0.5573	0.4812	0.4309
0.1974	0.5962	0.5131	0.4530
0.2961	0.6404	0.5510	0.4771
0.3967	0.6883	0.5884	0.5079
0.4991	0.7393	0.6293	0.5414
0.5974	0.7897	0.6690	0.5757
0.7004	0.8479	0.7126	0.6104
0.8272	0.920	0.7686	0.6552
0.9125	0.9723	0.8077	0.6851
0.9514	0.9985	0.8287	0.7017
Dibutylether (1) + heptane (2)			
0.0479	0.6828	0.5867	0.5078
0.0951	0.6970	0.5979	0.5170
0.1907	0.7247	0.6200	0.5355
0.2992	0.7599	0.6468	0.5579
0.3990	0.7945	0.6723	0.5790
0.4989	0.8296	0.6985	0.6001
0.5993	0.8666	0.7269	0.6225
0.6973	0.9023	0.7551	0.6445
0.7993	0.9451	0.7861	0.6687
0.8986	0.9862	0.8170	0.6933
0.9501	1.0088	0.8332	0.7051
Methyl tert-butyl ether (1) + 3-methylpentane (2)			
0.0480	0.4915	0.4361	0.3870
0.0967	0.4906	0.4357	0.3859
0.1961	0.4893	0.4348	0.3843
0.2982	0.4895	0.4347	0.3836
0.3995	0.4906	0.4351	0.3834
0.4983	0.4923	0.4361	0.3836
0.5992	0.4954	0.4379	0.3850
0.6984	0.4995	0.4406	0.3863
0.7978	0.5048	0.4435	0.3888
0.8996	0.5113	0.4478	0.3918
0.9491	0.5145	0.4502	0.3937
Methyl tert-butyl ether (1) + hexane (2)			
0.0479	0.5097	0.4478	0.4017
0.0974	0.5074	0.4465	0.3994
0.1983	0.5034	0.4442	0.3960
0.2988	0.5004	0.4427	0.3932
0.3979	0.4990	0.4418	0.3910
0.4975	0.4990	0.4413	0.3897
0.5974	0.4996	0.4419	0.3895
0.6968	0.5025	0.4431	0.3895
0.7911	0.5059	0.445	0.3913
0.8976	0.5125	0.4484	0.3926
0.9486	0.5147	0.4505	0.3940

Table 2 continued

x_1	$\nu(\mathrm{mm}^2 \cdot \mathrm{s}^{-1})$ $T = 283.15\,\mathrm{K}$	$T = 298.15\,\mathrm{K}$	$T = 313.15\,\mathrm{K}$
Methyl tert-butyl ether (1) + heptane (2)			
0.0431	0.6606	0.5683	0.4926
0.0987	0.6512	0.5599	0.4862
0.1892	0.6353	0.5461	0.4767
0.2958	0.6168	0.5300	0.4658
0.3844	0.6030	0.5169	0.4569
0.4986	0.5845	0.5012	0.4454
0.6007	0.5700	0.4881	0.4347
0.6999	0.5567	0.4777	0.4246
0.7998	0.5421	0.4680	0.4144
0.8997	0.5298	0.4604	0.4047
0.9499	0.5241	0.4566	0.4004

The mixtures were prepared using a Sartorious semi-microbalance CP225-D. The maximum estimated error in the mole fraction is $\pm 1 \times 10^{-4}$.

3 Results and Discussion

The kinematic viscosities, ν, for the binary mixtures are given in Table 2 and graphically represented in Figs. 1–3. The kinematic viscosity data were correlated by using the McAllister [34] equation:

$$\begin{aligned}\ln \nu = {} & x_1^3 \ln \nu_1 + 3x_1^2 x_2 \ln \nu_{12} + 3x_1 x_2^2 \ln \nu_{21} + x_2^3 \ln \nu_2 \\ & - \ln\left[x_1 + x_2 M_2/M_1\right] + 3x_1^2 x_2 \ln\left[(2 + M_2/M_1)/3\right] \\ & + 3x_1 x_2^2 \ln\left[(1 + 2M_2/M_1)/3\right] + x_2^3 \ln(M_2/M_1) \qquad (1)\end{aligned}$$

where ν refers to the kinematic viscosity of the mixture, ν_1 and ν_2 are the kinematic viscosities of components 1 and 2, M_1 and M_2 are their corresponding molar masses, and ν_{12} and ν_{21} are adjustable parameters characteristic of the system.

The estimated parameters of the McAllister equation are shown in Table 3 together with the corresponding average absolute deviation, *AAD*, between experimental and correlated values:

$$AAD \quad (\%) = \frac{1}{N} \times \sum_{i=1}^{N} \left| \frac{\nu_{i,\mathrm{exp}} - \nu_{i,\mathrm{cal}}}{\nu_{i,\mathrm{exp}}} \right| \times 100 \qquad (2)$$

where N is the number of experimental data.

The *AAD* values are in all cases less than 0.5%, so we can conclude that the McAllister equation can be used to correlate the kinematic viscosity data with good accuracy.

As we have noted before, we have found literature viscosity data for the methyl tert-butyl ether + 3-methylpentane mixture at 298.15 K [12], and for the methyl

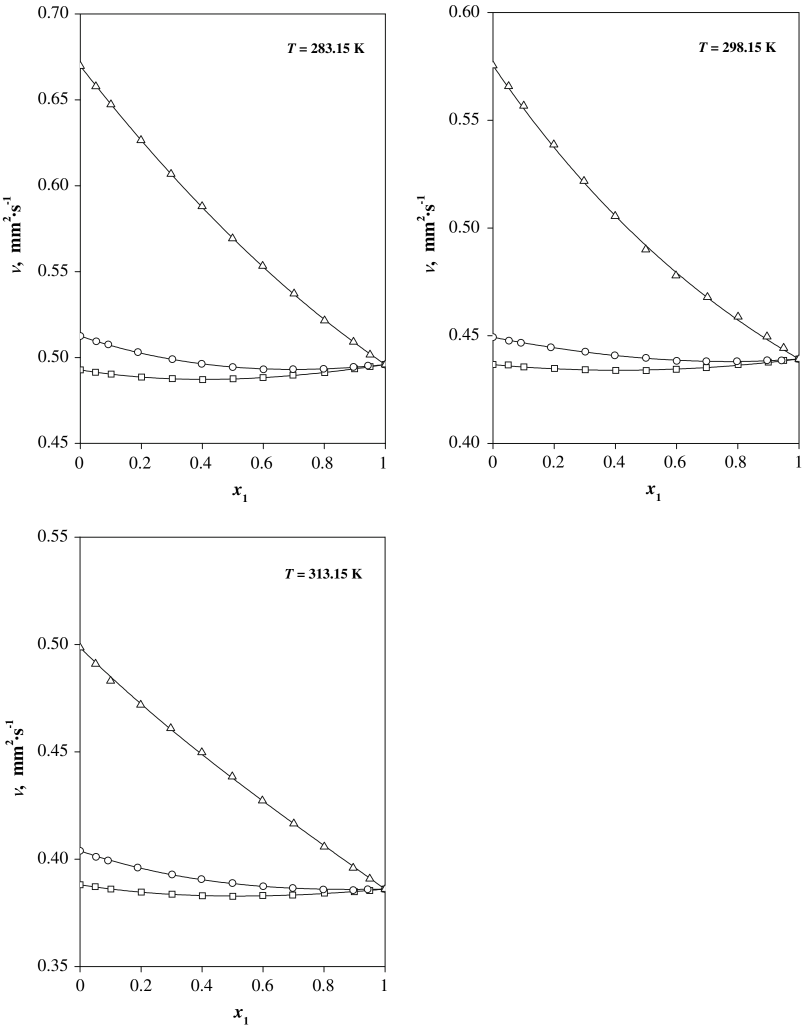

Fig. 1 Kinematic viscosities, ν, for diisopropylether (1) + alkane (2): (□) 3-methylpentane; (○) hexane; (△) heptane; (—) McAllister equation

tert-butyl ether + heptane mixture at 283.15 K, 298.15 K, and 313.15 K [13]; the difference between their and our data is less than 1%.

4 UNIFAC-VISCO

The UNIFAC-VISCO method, which is based on the Eyring theory, was initially proposed by Chevalier et al. [20,21]. The Eyring theory provided an equation for the viscosity of non-ideal mixtures:

$$\ln(\nu M) = \sum_i x_i \ln(\nu_i M_i) + \frac{\Delta G^{*\mathrm{E}}}{RT} \tag{3}$$

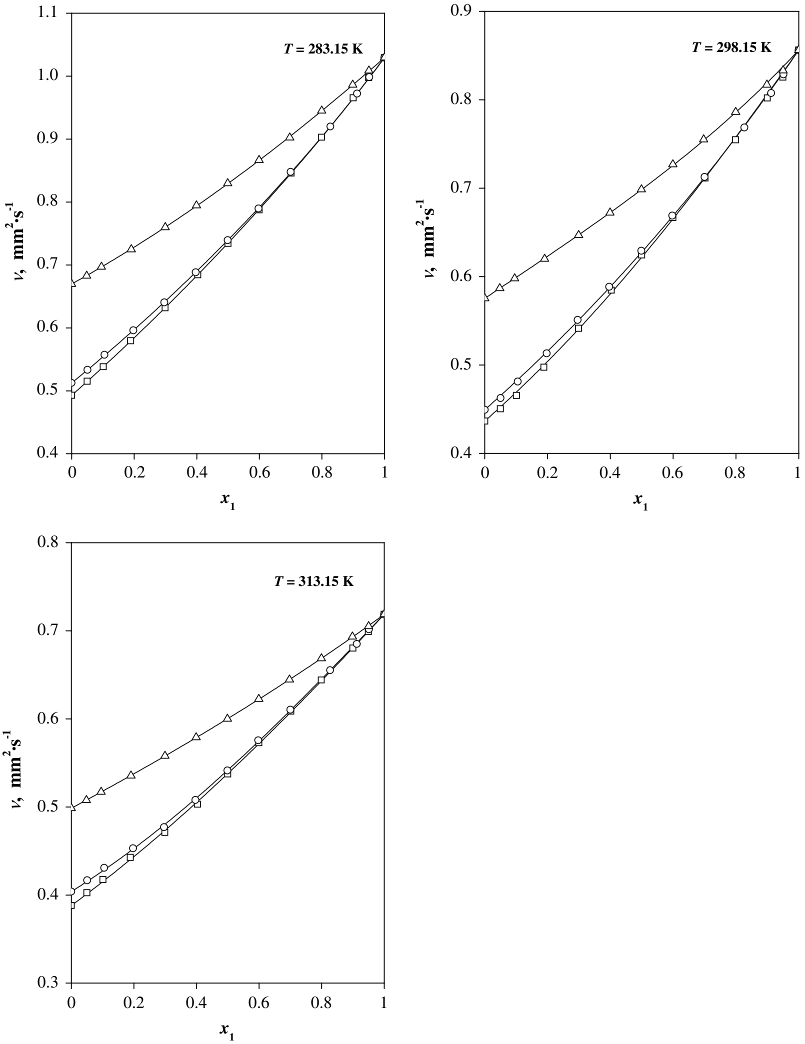

Fig. 2 Kinematic viscosities, ν, for dibutylether (1) + alkane (2): (□) 3-methylpentane; (○) hexane; (△) heptane; (—) McAllister equation

where x_i, M_i, and ν_i are, respectively, the mole fraction, the molar mass, and the kinematic viscosity of component i, M and ν are the molar mass and the kinematic viscosity of the mixture, $\Delta G^{*\mathrm{E}}$ is the excess Gibbs function of the activation for flow, R is the universal gas constant, and T is the absolute temperature.

The UNIFAC-VISCO method attempts to represent the excess Gibbs function of the activation for flow by the UNIFAC group contribution method. It assumes that $\Delta G^{*\mathrm{E}}$ is the sum of two contributions: the combinatorial part, $\Delta G^{*\mathrm{EC}}$, arising from structural differences of the molecules in the mixture and the residual part, $\Delta G^{*\mathrm{ER}}$, due to energetic interactions among structural groups. To evaluate the residual part, it

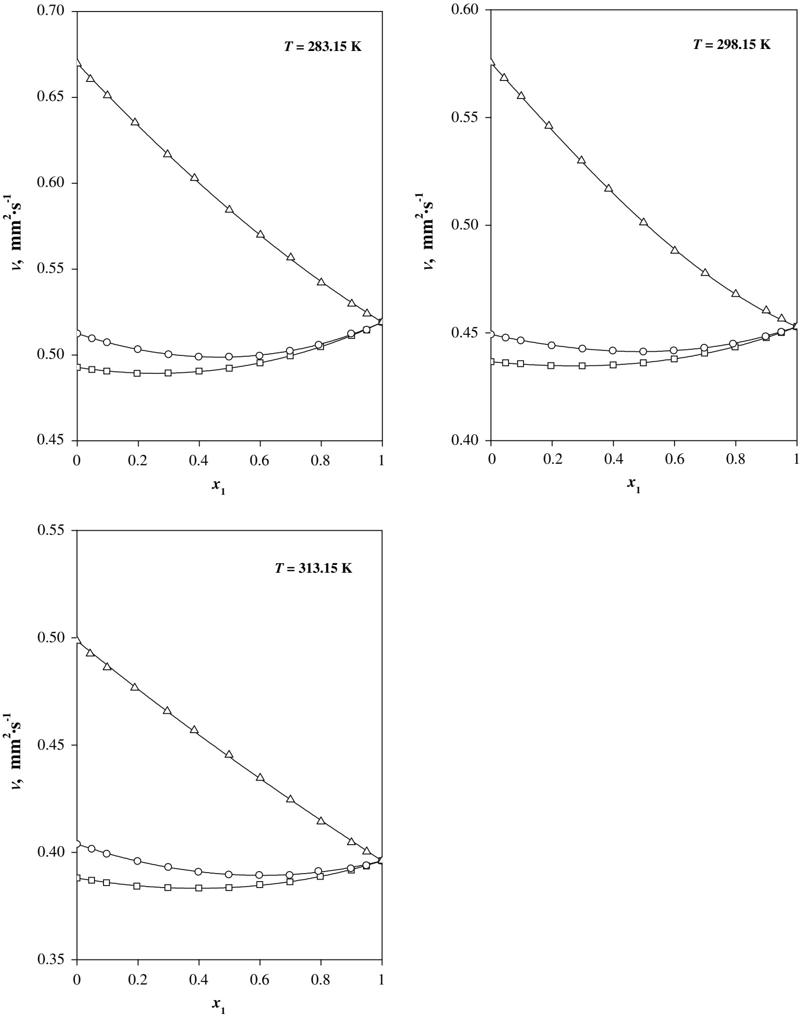

Fig. 3 Kinematic viscosities, ν, for methyl tert-butyl ether (1) + alkane (2): (□) 3-methylpentane; (○) hexane; (△) heptane; (—) McAllister equation

is necessary to know ψ^*_{nm}, which is defined as

$$\psi^*_{nm} = \exp\left(-\frac{\alpha_{nm}}{T}\right) \tag{4}$$

where α_{nm} is the group interaction parameter between the different functional groups n and m. It is significant that this parameter is obtained from experimental viscosities of several mixtures, and the larger the number of experimental data used for calculating them, the better is the prediction of kinematic viscosities.

Table 3 Parameters of the McAllister equation and the corresponding average absolute deviations, AAD

System	T (K)	ν_{12}	ν_{21}	AAD (%)
Diisopropylether +				
3-Methylpentane	283.15	0.4879	0.4842	0.02
	298.15	0.4340	0.4331	0.04
	313.15	0.3826	0.3815	0.02
Hexane	283.15	0.4906	0.4936	0.03
	298.15	0.4364	0.4410	0.03
	313.15	0.3857	0.3888	0.05
Heptane	283.15	0.4675	0.5099	0.21
	298.15	0.4215	0.4540	0.13
	313.15	0.5379	0.5981	0.06
Dibutylether +				
3-Methylpentane	283.15	0.8357	0.6722	0.06
	298.15	0.7091	0.5621	0.42
	313.15	0.6057	0.4926	0.29
Hexane	283.15	0.8352	0.6759	0.07
	298.15	0.7036	0.5752	0.31
	313.15	0.6101	0.4921	0.23
Heptane	283.15	0.8974	0.7719	0.07
	298.15	0.7395	0.6628	0.12
	313.15	0.6394	0.5691	0.03
Methyl tert-butyl ether +				
3-Methylpentane	283.15	0.4287	0.4617	0.12
	298.15	0.4920	0.4840	0.03
	313.15	0.4347	0.4322	0.04
Hexane	283.15	0.4933	0.4933	0.04
	298.15	0.4369	0.4394	0.02
	313.15	0.3846	0.3883	0.05
Heptane	283.15	0.5574	0.6104	0.09
	298.15	0.4733	0.5254	0.06
	313.15	0.4287	0.4617	0.12

Table 4 Group volume, *R*, and surface area, *Q*

Group	R	Q
CH_3	0.9011	0.848
CH_2	0.6744	0.540
O_{ether}	0.2439	0.240

The van der Waals properties of the CH_2, CH_3, and O_{ether} groups [16] used in the calculation routines are compiled in Table 4, and the CH_2-CH_3 interaction parameters needed for the calculations were obtained from Tojo et al. [28].

The $O_{ether}-CH_2$ and $O_{ether}-CH_3$ parameters of the UNIFAC-VISCO method have been calculated by minimizing the following equation:

$$F = \frac{1}{N} \times \sum_{i=1}^{N} \left| \frac{\nu_{i,\text{exp}} - \nu_{i,\text{cal}}}{\nu_{i,\text{exp}}} \right| \tag{5}$$

where N is the number of experimental data points, $N = 297$.

Table 5 UNIFAC-VISCO interaction parameters, α_{nm}

α_{nm}	CH_3	CH_2	O_{ether}
CH_3	0	−872.51	767.54
CH_2	194.26	0	2257.45
O_{ether}	−361.04	−1167.02	0

Table 6 UNIFAC-VISCO predictions

	AAD (%)		
System	$T = 283.15\,K$	$T = 298.15\,K$	$T = 313.15\,K$
Diisopropylether +			
3-Methylpentane	1.0	0.7	1.0
Hexane	1.3	0.9	1.3
Heptane	1.1	0.3	1.2
Dibutylether +			
3-Methylpentane	2.8	1.8	2.2
Hexane	1.9	1.5	1.4
Heptane	0.5	0.8	0.2
Methyl tert-butyl ether +			
3-Methylpentane	0.2	0.2	0.2
Hexane	0.5	0.9	0.4
Heptane	4.6	3.7	4.4
Average overall		1.0	

This optimization was performed by using the simulated annealing method [35,36]. The UNIFAC-VISCO interaction parameters are collected in Table 5 together with the CH_2-CH_3 interaction parameters.

The kinematic viscosities obtained experimentally were compared with the predictions provided by UNIFAC-VISCO using the calculated parameters, and the corresponding average absolute deviations *AAD* are given in Table 6. The smallest deviations are shown for the system of dibutylether with heptane and the largest ones by the system of methyl tert-butyl ether with heptane; the overall *AAD* is 1.0%, which indicates good agreement between experimental and predicted values.

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