

Prediction of physical properties for molecular design of solvents



José Scilipoti^a, Martín Cismondi^a, Esteban A. Brignole^{b,*}

^a IDTQ – Grupo Vinculado PLAPIQUI – CONICET, Facultad de Ciencias Exactas Físicas y Naturales, Universidad Nacional de Córdoba, Ciudad Universitaria, X5016GCA Córdoba, Argentina

^b PLAPIQUI – Universidad Nacional del Sur – CONICET, Bahía Blanca, Argentina

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ABSTRACT

An improved group contribution method is developed for the prediction of boiling points in the context of molecular design. Predictions are based exclusively on the molecular structure of the compound, and for this purpose, UNIFAC-type groups are used. This new model is based on a previous work, which was extended taking into account association effects and modifying the previous method's functionality to achieve a better qualitative and quantitative reproduction of the experimental data. An existing viscosity prediction model is revised and formulated as a group contribution method based also on UNIFAC functional groups.

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1. Introduction

The basis for any design process in the chemical industry is a reliable set of chemical and physical pure component and mixture properties. Experimental values of these properties are frequently not at hand and the measurements are often expensive or even difficult or impossible, which makes estimation methods of great interest. An extensive review on estimation methods of physical properties is available in the classic book "The properties of gases and liquids" last edition by Pöling et al. [1].

The design of separation processes based on mass separation agents begins with the selection of an appropriate solvent. To address this problem, in the last decades several methodologies have been developed focusing on generating molecular structures for components with specific pure component properties (boiling point, critical temperature and pressure, viscosity, etc.) and mixture properties. These methodologies, generally computer aided, generate a large number of structures and have to rely on the precision of the estimation methods employed.

Particularly, since the early eighties, a computer aided method for molecular design MOLDES has been developed for the optimum selection of solvents [2–5]. The MOLDES approach is based on the computer aided synthesis of molecular structures to identify those that satisfy a given set of physical properties. The

chemical structures are formed from the submolecular fragments of the UNIFAC group contribution thermodynamic model for predicting activity coefficients [6]. In this way, the MOLDES approach was first applied for the selection of solvents for extractive distillation and liquid–liquid extraction. This approach is known today as *computer aided molecular design* (CAMD). From the early work of Stephanopoulos and Townsend [7] on refrigerant design, a large number of CAMD applications have been proposed to design polymers, drugs, cleaning agents, etc. [8].

For the prediction of physical properties of pure components, MOLDES used a method developed by Pretel et al. [9] that is based on Riedel's equation and Lydersen method to predict normal boiling points and critical properties. The Lydersen group contribution method was modified by introducing UNIFAC functional groups instead of the molecular fragments of the original method. In the present work parameters of these models were re-estimated to improve the calculation of normal boiling point, together with the prediction of critical pressure, temperature and volume. The main limitations of the Pretel et al. [9] method were found in the estimation of the normal boiling point for compounds with associative groups. The goal in the present work is to improve the reproduction of experimental data by taking into account the effect of associative groups in the normal boiling point (T_b) estimation.

Another important liquid solvent property is viscosity. In this work a group contribution approach for viscosity prediction that makes use of normal boiling point predictions is developed. For this purpose the Sastri and Rao [10] method based in the

* Corresponding author. Tel.: +54 291 4861700x231; fax: +54 291 4861600.
E-mail address: ebrignole@plapiqui.edu.ar (E.A. Brignole).

relation between liquid viscosity and vapour pressure is revised and formulated in terms of UNIFAC groups.

2. Available predictive methods

The need of physical property prediction of pure components is always present in chemical process design and operation. In this regard a variety of methods have been developed to predict the normal boiling points, critical properties and densities of pure components on the basis of molecular structure. Poling et al. [1] make a thorough review on these methods, which are based on the concept of group contribution. Groups are selected taking into consideration atoms, atomic groups and types of characteristic links. A contribution is assigned to each group which allows the calculation of normal boiling points (or another property of interest) by adding algebraically the contributions of each part of the molecule (Jobak and Reid [11]). Some of these methods employ a large number of group contributions in order to improve the accuracy of predictions. Constantinou and Gani [12], for example, use a two level approach based on first-order and second-order contributions. Ericksen et al. [13] employed over 300 group contributions. Other method recently published is that of Marrero-Morejon and Pardillo-Fontdevila [17], employed 167 first-order, 106 second-order and 51 third-order (in total 324) contributions. These large number of contributions, even though improve the accuracy of predictions, makes more difficult the coding of molecular structures and the prediction of pure component properties within the framework of a CAMD approach based on the UNIFAC model. We use only 60 UNIFAC groups (Table 1) plus 10 groups in Table 2, which can be regarded as second-order.

3. Development of a method for physical properties prediction

The design of solvents for liquid extraction and extractive distillation requires a reliable method for predicting the normal boiling point (T_b) of the synthesized chemical structures. The difference in boiling points between the solvent and the component to be separated determines the operating conditions in the solvent recovery process and the possibility of formation of azeotropes.

3.1. Prediction of the normal boiling points and related properties

The original approach was based in the Riedel's equation (1) for estimating critical volumes:

$$V_c = \frac{RT_c}{P_c} [3.72 + 0.26(\alpha c - 7.0)]^{-1} \quad (1)$$

where

$$\alpha c = 0.9076 \left[1.0 + \frac{(T_b/T_c) \ln P_c}{1.0 - (T_b/T_c)} \right]$$

with $R=82.06$ [cm³ atm/(K mol g)]; T_c the critical temperature [K]; P_c the critical pressure [atm]; and V_c the critical volume [cm³/g mol]. Spencer and Daubert [14] have demonstrated that Eq. (1) is very reliable when is used with experimental critical values. This equation provides a way of predicting the boiling point as a function of critical properties. By introducing the definition of αc in Eq. (1) and the value of the constant R , we obtain:

$$T_b = V_c P_c \left(\frac{T_b}{T_c} \right) \left[0.02876 \ln \left(\frac{(T_b/T_c)}{1 - (T_b/T_c)} \right) + 0.02603 \right] \quad (2)$$

Eq. (2) allows the calculation of T_b as a function of the critical properties V_c , P_c and the T_b/T_c ratio. Therefore T_b can be estimated from group contribution methods that predict critical properties and

Table 1
Group contributions for the estimation of boiling points and critical properties.

Group number	Group	ΔT_i	ΔP_i	ΔV_i
1	(CH ₃)	0.81657	0.227	27.00
2	(CH ₂)	0.21255	0.227	21.00
3	(CH)	-0.47637	0.210	14.00
4	(C)	-1.12485	0.210	7.00
5	(CH ₂ =CH)	0.72378	0.328	42.00
6	(CH=CH)	0.41659	0.396	35.00
7	(CH ₂ =C)	0.36748	0.396	35.00
8	(CH=C)	-0.16239	0.396	28.00
9	(C=C)	-1.36322	0.396	14.00
10	(ACH)	0.32794	0.154	14.00
11	(AC)	-0.14141	0.154	7.00
12	(ACCH ₃)	0.53988	0.381	37.00
13	(ACCH ₂)	-0.06893	0.381	28.00
14	(ACCH)	-0.74388	0.364	21.00
15	(OH)	0.34054	0.060	12.00
16	(ACOH)	-0.15581	0.134	3.00
17	(CH ₃ CO)	0.80272	0.517	48.00
18	(CH ₂ CO)	-0.14346	0.517	46.00
19	(CHO)	0.69690	0.330	33.00
20	(CH ₃ COO)	0.03480	0.697	58.00
21	(CH ₂ COO)	0.06700	0.697	52.00
22	(HCOO)	0.04700	0.470	38.00
23	(CH ₃ O)	0.66342	0.387	38.50
24	(CH ₂ O)	0.06030	0.387	31.50
25	(CH-O)	-0.38482	0.370	24.50
26	(FCH ₂ O)	0.02700	0.304	31.50
27	(CH ₂ NH ₂)	0.75214	0.322	42.00
28	(CHNH ₂)	0.00928	0.305	35.00
29	(CH ₃ NH)	1.02921	0.362	42.00
30	(CH ₂ NH)	0.07506	0.362	35.00
31	(CHNH)	-0.60478	0.345	28.00
32	(CH ₃ N)	0.11552	0.397	35.00
33	(CH ₂ N)	-0.33848	0.397	28.00
34	(ACNH ₂)	0.91529	0.249	28.00
35	(C ₅ H ₄ N)	1.23375	0.900	92.60
36	(C ₅ H ₃ N)	0.46621	0.900	85.60
37	(CH ₂ CN)	0.14900	0.587	49.00
38	(COOH)	0.94178	0.400	38.00
39	(CH ₂ Cl)	0.04200	0.547	45.50
40	(CHCl)	0.03150	0.530	38.50
41	(CCl)	0.01700	0.530	31.50
42	(CHCl ₂)	0.04900	0.850	63.00
43	(CCl ₂)	0.03400	0.850	56.00
44	(CCl ₃)	0.05100	1.170	80.50
45	(ACCl)	0.02800	0.474	33.50
46	(CH ₂ NO ₂)	0.07500	0.647	53.20
47	(CHNO ₂)	0.06700	0.630	46.20
48	(ACNO ₂)	0.06600	0.574	41.20
49	(CH ₂ SH)	0.03500	0.497	49.00
50	(I)	0.01200	0.830	38.50
51	(Br)	0.07015	0.500	31.50
52	(CH=C)	1.28148	0.306	21.00
53	(C=C)	0.87037	0.306	14.00
54	Cl-(C=C)	0.01700	0.320	35.50
55	(ACF)	0.02900	0.378	19.50
56	(DMF-2)	0.06200	0.954	29.30
57	(CF ₃)	0.05400	0.882	38.50
58	(CF ₂)	0.03600	0.658	28.00
59	(CF)	0.01800	0.434	17.50
60	(COO)	0.04700	0.470	21.00

the T_b/T_c ratio. Lydersen's method [15] for calculation of critical pressures is formulated and revised in terms of UNIFAC groups, the critical pressure is obtained as follows:

$$P_c = \frac{MW}{\left(\sum_i v_i \Delta P_i + 0.34 \right)^2} \quad (3)$$

where MW is the compound molecular weight; P_c is given in [atm]; v_i is the number of groups of type i and ΔP_i are the contribution of group i to P_c . The group contributions estimated in terms of UNIFAC functional groups are given in Table 1.

Table 2
Associative group contributions.

Group number	Group	ΔA_i	Group number	Group	ΔA_i
15	(OH)	3.26990	29	(CH ₃ NH)	0.42421
16	(ACOH)	6.72246	30	(CH ₂ NH)	1.35171
17	(CH ₃ CO)	3.12579	31	(CHNH)	0.54872
18	(CH ₂ CO)	5.24096	32	(CH ₃ N)	1.10779
19	(CHO)	2.56732	33	(CH ₂ N)	0.69218
23	(CH ₃ O)	1.52582	34	(ACNH ₂)	-2.37065
24	(CH ₂ O)	1.33862	35	(C ₅ H ₄ N)	-0.40481
25	(CH—O)	-1.18554	36	(C ₅ H ₃ N)	0.06607
27	(CH ₂ NH ₂)	0.92518	38	(COOH)	2.80158
28	(CHNH ₂)	0.86706	51	(Br)	-13.63086

V_c is related to the liquid molar volume at the normal boiling point (V_b) by means of the equation proposed by Tyn and Calus, as cited by Reid et al. [16]:

$$V_b = 0.285V_c^{1.048} \quad (4)$$

where V_b is given in [cm³/mol]. V_b can be obtained by the additive volume methods of Schroeder and Le Bas (as cited by Reid et al.) [16] where the bond type and atomic contributions of this method are converted to UNIFAC groups, therefore, V_c may be estimated through:

$$V_c = 3.3127 \left(\sum_i v_i \Delta V_i \right)^{0.9542} \quad (5)$$

where V_c is given in [cm³/(g mol)]. The ΔV_i contribution for the computation of V_b is given in Table 1 for each group. In the case of aromatic compounds, V_b should be increased in 12 units, while for cyclic compounds it should be decreased in 7 units.

In the previous method, the T_b/T_c ratio is calculated on the basis of the equation proposed by Lydersen [15]:

$$\left(\frac{T_b}{T_c} \right) = 0.567 + \sum_i v_i \Delta T_i - \left(\sum_i v_i \Delta T_i \right)^2 \quad (6)$$

where ΔT_i is the group contribution of group i to the T_b/T_c ratio. Eq. (6) has two disadvantages: first, does not take into account association effects and, second, its functionality does not reproduce qualitative trends in the experimental data. In homologous series such as n -alkanols or unsaturated fatty acids, the relative effect of association is greater for the components of lower molecular weight. These associative effects result in an increase of the experimental T_b . This effect diminishes with the increase of the number of CH₂ groups in the molecule, when van der Waals forces begin to dominate. Fig. 1 shows this effect by comparing the experimental values of T_b for n -alkanes and n -alkanols. Figs. 2 and 3 show the predictions of T_b values for both families of compounds respectively, by the different methods previously mentioned. In particular it is observed that, although it provides good predictions for low and medium molecular weight compounds (especially for alkanes), the original method of Pretel et al. predicts a maximum value in the curve T_b versus molecular weight, which is qualitatively and physically wrong. Moreover, it presents the largest underestimation of the T_b value for 1-propanol (Fig. 3).

In this work, the calculation for the T_b/T_c ratio was revised and modified. The new proposed equation has the following form:

$$\frac{T_b}{T_c} = 1 - \frac{MW^a}{d + \sum_i v_i \Delta T_i} + \frac{\sum_i v_i \Delta A_i}{0.122 + MW^c b} \quad (7)$$

where MW is the molecular weight of compound; ΔT_i is the group contribution of group i ; ΔA_i is the association contribution of group i ; and a , b and c are adjustable parameters ($a=0.0268$, $b=0.1219$, $c=1.3769$); $d=1.0$ for non-cyclic compounds, and $d=3.0$ for cyclic structures. Table 2 shows typical associative groups and

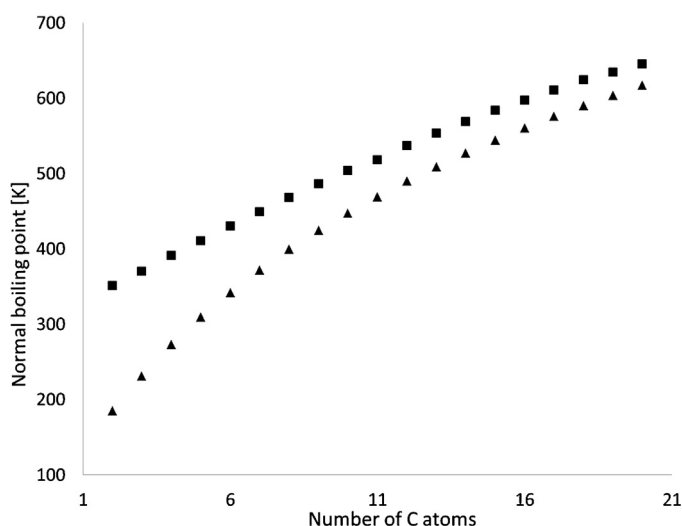


Fig. 1. Normal boiling points of n -alkanes (▲) and n -alkanols (■) as a function of number of C atoms.

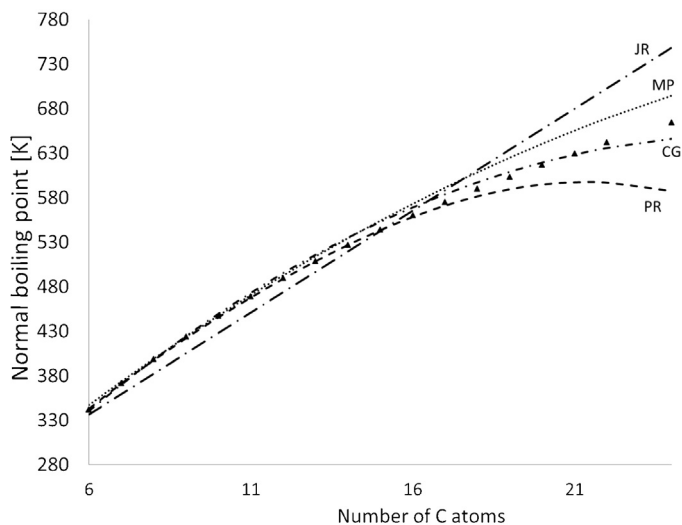


Fig. 2. Normal boiling points of n -alkanes (▲) [19] as a function of number of C atoms, together with the results of some predictive methods ([11] (JR), [17] (MP), [12] (CG), [17] (PR)).

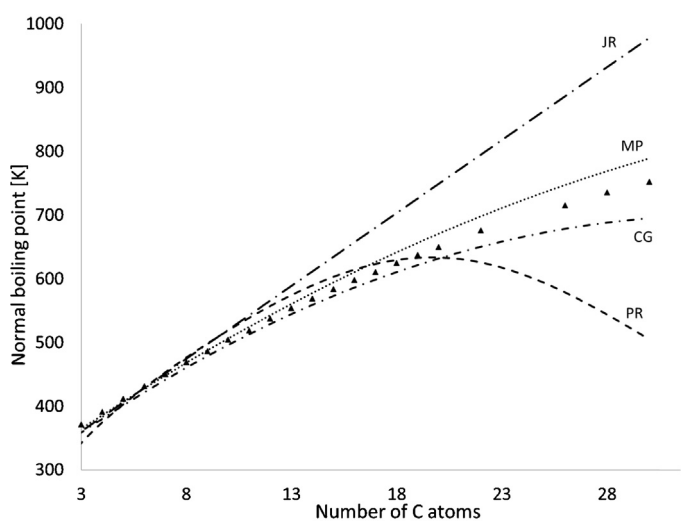


Fig. 3. Normal boiling points of n -alkanols (▲) [19] as a function of number of C atoms, together with the results of some predictive methods ([11] (JR), [17] (MP), [12] (CG), [17] (PR)).

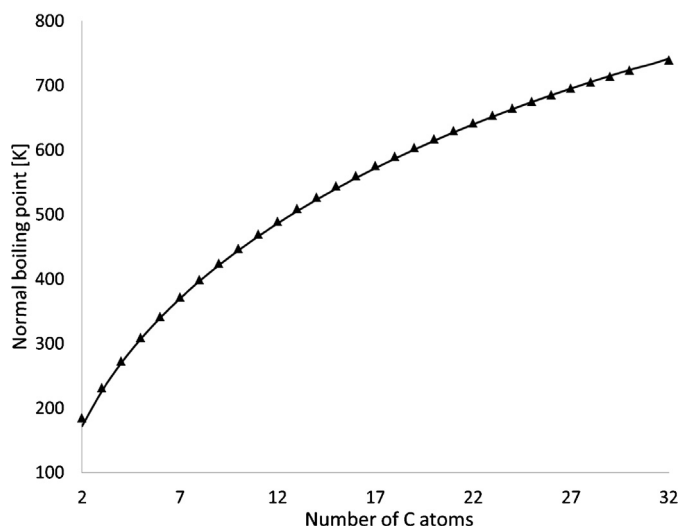


Fig. 4. Normal boiling points of *n*-alkanes [19] as a function of number of C atoms, together with the predictions of the proposed method.

its contributions. The third term in Eq. (7) takes into account the associative effect when one or more associative groups are present in the structure. When the molecular weight of the compound increases, for a given homologous series, the relative effect of association decreases. The proposed modification clearly incorporates this effect for the predictions of T_b for associating compounds.

3.2. Results

Table 3 compares the predictions of the new method with those from the original method of Pretel et al. In all cases, the method based on Eq. (7) gives more accurate T_b predictions. Both methods have difficulty in predicting aromatic compounds with a hydrogen substituted by COOH functional group, and in cyclic compounds with double bonds within the ring. This shows the need for the creation of new groups such as ACCOOH for aromatics and CH=CH, CH=C, C=C for cyclic compounds. Figs. 4–8 show T_b predictions for some homologous series of compounds predicted with both methods and their comparisons with experimental data. Tables 4a–4c provide examples of T_b estimation for 2,2,4,4,6,8,8-heptamethylnonane, benzidine and levulinic acid.

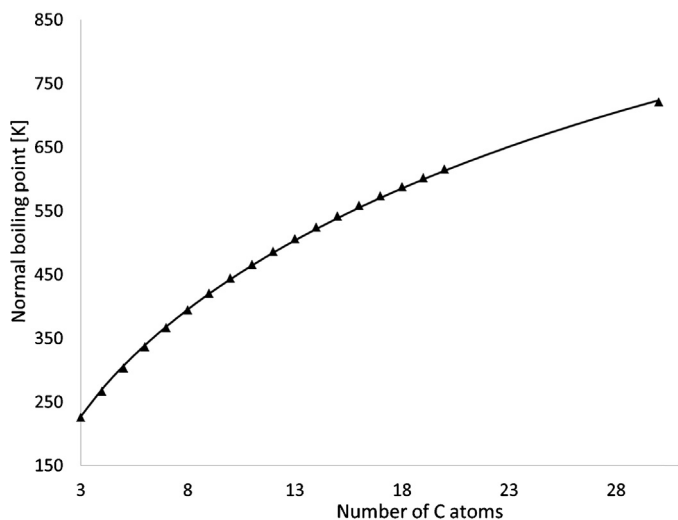


Fig. 5. Normal boiling points of *n*-alkenes [19] as a function of number of C atoms, together with the predictions of the proposed method.

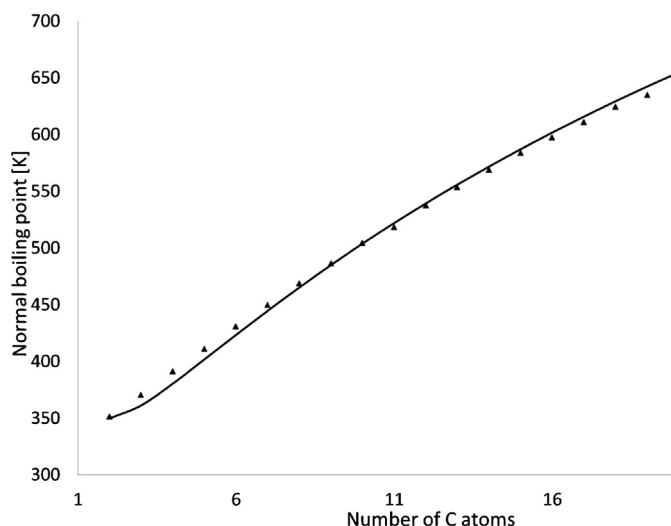


Fig. 6. Normal boiling points of *n*-alkanols [19] as a function of number of C atoms, together with the predictions of the proposed method.

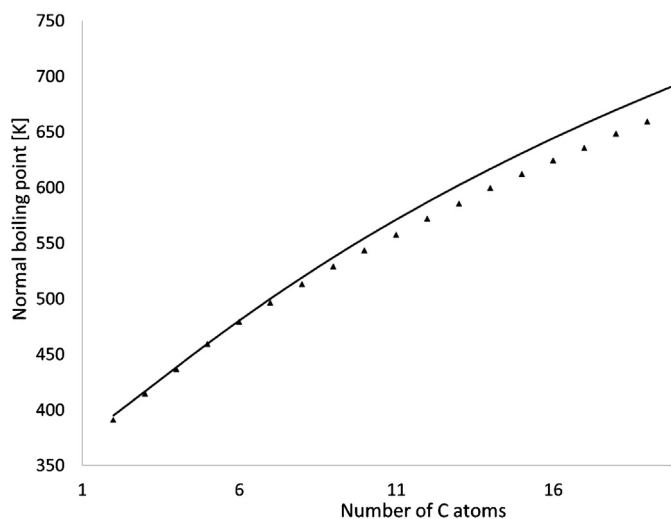


Fig. 7. Normal boiling points of fatty acids [19] as a function of number of C atoms, together with the predictions of the proposed method.

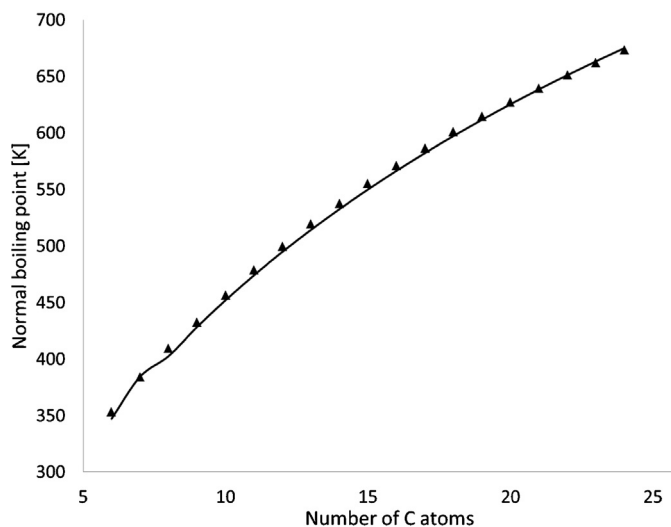


Fig. 8. Normal boiling points of alkylbenzenes [19] as a function of number of C atoms, together with the predictions of the proposed method. Note that the kink observed is due to the (AC) group that begins to appear from ethylbenzene.

Table 3
Comparison between original and new method.

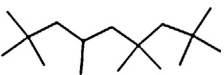
Compounds	No. of compounds	A.A.E. (Pretel et al.)	A.R.E. (Pretel et al.)	A.A.E. (This work)	A.R.E. (This work)
Alkanes	94	26.97	4.41%	3.67	0.92%
Alkenes	75	16.13	4.21%	3.34	0.90%
Alkynes	16	50.16	15.34%	10.37	3.30%
Cycloalkanes	14	28.32	8.73%	10.92	3.22%
Alcohols	45	17.04	3.90%	5.80	1.35%
Aldehydes	29	22.72	5.31%	8.21	2.09%
Ethers	31	8.66	2.56%	2.94	0.82%
Ketones	27	20.67	4.91%	10.24	2.38%
Acids	49	17.69	3.33%	12.78	2.21%
Amines	30	15.39	3.87%	5.63	1.17%
Aromats ^a	63	14.96	3.02%	4.40	0.91%
Aromats ^b	77	24.65	4.51%	21.69	3.84%
Terpenes	6	93.28	20.61%	41.58	9.19%
All compounds	556	27.43	6.52%	10.89	2.49%

A.A.E., Average absolute error; A.R.E., Average relative error.

^a Aromatic compounds with hydrogen substituted by aliphatic chains without functional groups.

^b Aromatic compounds with hydrogen substituted by functional groups and aliphatic chains with functional groups.

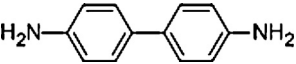
Table 4a
Estimation of the normal boiling point temperature of 2,2,4,4,6,8,8-heptamethylnonane.



Group	Frequency	Contribution			
		ΔT_i	ΔP_i	ΔV_i	ΔA_i
1	9	0.81657	0.23	27.00	0.00
2	3	0.21255	0.23	21.00	0.00
3	1	-0.47637	0.21	14.00	0.00
4	3	-1.12485	0.21	7.00	0.00

Predicted $T_b = 523.810$ K; experimental $T_b = 519.5$ K.

Table 4b
Estimation of the normal boiling point temperature of benzidine.

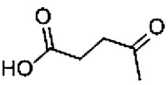


Group	Frequency	Contribution			
		ΔT_i	ΔP_i	ΔV_i	ΔA_i
10	8	0.32794	0.15	14.00	0.00
11	2	-0.14141	0.15	7.00	0.00
34	2	0.91529	0.25	28.00	-2.37

Predicted $T_b = 685.19$ K; experimental $T_b = 674.85$ K.

Even though more complex methods with a multilevel approach can obtain even more accurate results [12,13,17,20], our method has proven to be sufficiently reliable to be used in the context of molecular design of solvents based on UNIFAC groups.

Table 4c
Estimation of the normal boiling point temperature of levulinic acid.



Group	Frequency	Contribution			
		ΔT_i	ΔP_i	ΔV_i	ΔA_i
2	2	0.21255	0.23	21.00	0.00
17	1	0.80272	0.52	48.00	3.13
38	1	0.94178	0.40	38.00	2.80

Predicted $T_b = 499.89$ K; experimental $T_b = 518.15$ K.

4. Liquid viscosity prediction

Liquid viscosity is a key solvent property in many separation processes like liquid–liquid chromatography, liquid extraction and gas absorption. In general the separation efficiency is reduced if the solvent viscosity is high. Usually low viscosity solvents (no more than 0.5 cp) are preferred.

A group contribution model for prediction of viscosities of pure organic liquids was developed from the relationship between viscosity and vapour pressure presented by Sastri and Rao [10]. They observed that the viscosity versus vapour pressure plot is a straight line in logarithmic coordinates and can therefore be expressed as:

$$\mu = AP_{sat}^{-N} \quad (8)$$

where μ (mPa s^{-1}) is the viscosity of the liquid at temperature T and P_{sat} is the liquid vapour pressure at that temperature and A and N are constants. If P_{sat} is given in (atm) then the constant A is equal to the viscosity at the normal boiling point μ_B , therefore:

$$\mu = \mu_B P_{sat}^{-N} \quad (9)$$

It was found that the μ_B and N values do not change significantly for similar liquids, as those of homologous series. Vapor pressure

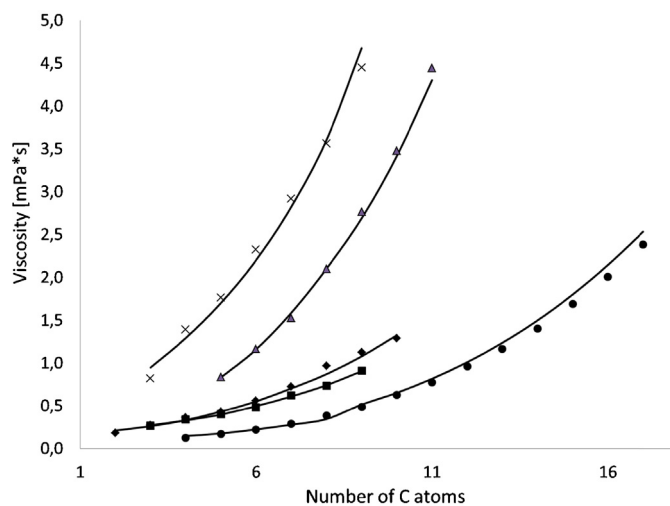


Fig. 9. Prediction of viscosities of various homologous series at 313 K compared with experimental values [19] (n -alkanols (\times), fatty acids (\blacktriangle), ketones (\blacksquare), aldehydes (\blacklozenge) and n -alkenes (\bullet)).

Table 5

The UNIFAC group contributions for the estimation of pure organic liquid viscosities.

Group number	Group	$\Delta\mu_i$	ΔN_i	Group number	Group	$\Delta\mu_i$	ΔN_i
1	(CH ₃) ^a	0.105	0.000	40	(C ₅ H ₅ N)	-0.150	0.050
2	(CH ₂)	0.00	0.00	41	(CH ₃ CN) ^e	0.345	0.000
3	(CH)	-0.110	0.050	42	(CH ₂ CN)	0.110	0.050
4	(C)	-0.180	0.100	43	(COOH) ^f	0.220	0.100
5	(CH ₂ =CH) ^b	0.085	0.000	44	(HCOOH)	1.630	0.000
6	(CH=CH)	-0.005	0.000	45	(CH ₂ Cl)	0.185	0.000
7	(CH ₂ =C)	0.085	0.000	46	(CHCl)	0.060	0.050
8	(CH=C)	-0.005	0.000	47	(CCl)	-0.010	0.100
9	(C=C)	-0.100	0.000	48	(CH ₂ Cl ₂)	0.180	0.000
10	(ACH)	0.050	0.000	49	(CHCl ₂)	0.230	0.050
11	(AC)	-0.120	0.000	50	(CCl ₂)	0.160	0.100
12	(ACCH ₃)	-0.015	0.050	51	(CHCl ₃)	0.540	0.000
13	(ACCH ₂)	-0.120	0.025	52	(CCl ₃)	0.330	0.100
14	(ACCH)	-0.230	0.000	53	(CCl ₄)	0.920	0.000
15	(OH) ^c	0.280	0.350	54	(ACCl)	0.030	0.025
16	(CH ₃ OH)	0.544	0.000	55	(CH ₃ NO ₂)	0.640	0.000
17	(H ₂ O)	0.900	0.000	56	(CH ₂ NO ₂)	0.180	0.050
18	(ACOH)	0.090	0.275	57	(CHNO ₂)	0.070	0.050
19	(CH ₃ CO)	0.135	0.025	58	(ACNO ₂)	0.040	0.050
20	(CH ₂ CO)	0.030	0.025	59	(CS ₂)	0.345	0.000
21	(CHO)	0.140	0.050	60	(CH ₃ SH)	0.180	0.000
22	(CH ₃ COO)	0.145	0.050	61	(CH ₂ SH)	0.150	0.025
23	(CH ₂ COO)	0.040	0.050	62	(FURF)	1.480	0.000
24	(HCOO)	0.205	0.050	63	(CH ₂ OH) ₂	17.500	0.000
25	(CH ₃ O)	0.125	0.050	64	(I)	0.000	0.000
26	(CH ₂ O)	0.020	0.050	65	(Br)	0.000	0.000
27	(CH—O)	-0.090	0.100	66	(CH=C) ^g	0.190	0.000
28	(FCH ₂ O)	0.080	0.050	67	(C=C)	0.190	0.000
29	(CH ₃ NH ₂) ^d	0.180	0.000	68	(ME ₂ SO)	2.098	0.000
30	(CH ₂ NH ₂)	0.170	0.100	69	(ACRY)	0.336	0.000
31	(CHNH ₂)	0.090	0.100	70	Cl—(C=C)	0.150	0.000
32	(CH ₃ NH)	0.125	0.075	71	(ACF)	-1.020	0.025
33	(CH ₂ NH)	0.020	0.075	72	(DMFA)	0.800	0.000
34	(CHNH)	0.090	0.075	73	(DMF-2)	0.185	0.300
35	(CH ₃ N)	-0.010	0.050	74	(CF ₂)	0.210	0.150
36	(CH ₂ N)	-0.115	0.050	75	(CF ₂)	0.000	0.150
37	(ACNH ₂)	0.030	0.100	76	(CF)	-0.080	0.200
38	(C ₅ H ₅ N)	0.920	0.000	77	(COO)	0.460	0.000
39	(C ₅ H ₄ N)	0.020	0.050				

^a For *n*-alkanes C > 8 $\Delta N_c = 0.05$.^b For *n*-alkenes C > 8 $\Delta N_c = 0.05$.^c For *n*-alkanols C < 11 $\Delta\mu_c = 0.615 - 0.092C + 0.004C^2 - 10^{-0.58C}$.^d $\Delta\mu_i = 0.220$ in NH₂-(CH₂)_n-NH₂.^e $\Delta\mu_i = 0.135$ in CN-(CH₂)_n-CN.^f $\Delta\mu_i = 0.250$ in saturates acid, $\Delta\mu_i = 0.195$ and $\Delta N_i = 0.175$ in aromatic acid.^g For *n*-alkynes C > 8 $\Delta N_c = 0.05$.

can be estimated from the following equation [18]:

$$\ln P_{sat} = (4.5398 + 1.0309 \ln T_b) \left[1 - \frac{(3 - 2T/T_b)^{0.19}}{T/T_b} - 0.38(3 - 2T/T_b)^{-0.81} \ln \left(\frac{T}{T_b} \right) \right] \quad (10)$$

The values of μ_B and N can be obtained from functional group contribution parameters that are correlated using experimental viscosity data:

$$\mu_B = \sum v_i \Delta\mu_{Bi} + \sum v_i \Delta\mu_{Bc} \quad (11)$$

$$N = 0.2 + \sum v_i \Delta N_i + \sum v_i \Delta N_c \quad (12)$$

Table 6

Viscosities prediction for some homologous series (viscosity predicted for each compound at 100 different points between the freezing and normal boiling points).

Compounds	No. of compounds	Cumulative percentage of predicted values with errors less than					
		10	20	30	40	50	60
<i>n</i> -Alkane	29	93.1	96.6	100			
Branched alkanes	37	87.5	100				
Unsaturated aliphatics	34	77.8	100				
Aromatics	78	78.9	85.3	94.1	100		
Alcohols	45	68.4	78.9	78.9	89.5	100	
Acids	31	77.8	88.9	100			
Amines	54	53.3	80.0	86.7	93.3	100	
Ketones	26	61.5	76.9	88.5	100		
Aldehydes	29	60.9	78.3	91.3	100		
Ethers	31	79.2	87.5	95.8	100		

where $\Delta\mu_{Bi}$ (mPa s^{-1}) and ΔN_i are the functional group “i” contributions to the molecular viscosity of the liquid at T_b and to the exponent N . In addition $\Delta\mu_{Bc}$ and ΔN_c are corrections due to special structures of functional groups. The functional group contributions considered in this model were transformed in UNIFAC group contributions and the new parameters are presented in Table 5. The objective function utilized for the parameters optimization was the classic summation of error squares.

In summary, liquid viscosity predictions at different temperatures up to the normal boiling point can be readily obtained from Eqs. (9)–(12) together with parameters from Table 5.

The errors in viscosity predictions for different homologous series are reported in Table 6, where for each family of compounds the % of compounds with relative error less than a given value are reported. For instance, for branched alkanes, the error is less than 20% for all the compounds investigated. The experimental data are taken from the DIPPR database [19]. Fig. 9 shows the prediction of viscosity for various homologous series as a function of number of C atoms at 313 K.

5. Conclusions

Improved methods for the prediction of normal boiling points and liquid viscosities by group contributions based on UNIFAC-types groups in the context of molecular design of solvents were developed. These predictions are based exclusively on the molecular structure of the compound. The methods developed in the present work are particularly useful in the context of CAMD methods based on the UNIFAC model. Even though the present method has certain limitations with regard to the detail description of molecular structures, the predictions obtained in this work have accuracy comparable with methods that use a significantly larger number of groups. Furthermore, the use of a lower number of molecular subgroups facilitates the coding of structures and the design of algorithms for the systematic screening of solvents for particular applications.

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