



## Prediction of physical properties for molecular design of solvents



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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

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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  $R=82.06$  [cm<sup>3</sup> atm/(K mol g)];  $T_c$  the critical temperature [K];  $P_c$  the critical pressure [atm]; and  $V_c$  the critical volume [cm<sup>3</sup>/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  $\alpha c$  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	$\Delta T_i$	$\Delta P_i$	$\Delta V_i$
1	(CH <sub>3</sub> )	0.81657	0.227	27.00
2	(CH <sub>2</sub> )	0.21255	0.227	21.00
3	(CH)	-0.47637	0.210	14.00
4	(C)	-1.12485	0.210	7.00
5	(CH <sub>2</sub> =CH)	0.72378	0.328	42.00
6	(CH=CH)	0.41659	0.396	35.00
7	(CH <sub>2</sub> =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 <sub>3</sub> )	0.53988	0.381	37.00
13	(ACCH <sub>2</sub> )	-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 <sub>3</sub> CO)	0.80272	0.517	48.00
18	(CH <sub>2</sub> CO)	-0.14346	0.517	46.00
19	(CHO)	0.69690	0.330	33.00
20	(CH <sub>3</sub> COO)	0.03480	0.697	58.00
21	(CH <sub>2</sub> COO)	0.06700	0.697	52.00
22	(HCOO)	0.04700	0.470	38.00
23	(CH <sub>3</sub> O)	0.66342	0.387	38.50
24	(CH <sub>2</sub> O)	0.06030	0.387	31.50
25	(CH-O)	-0.38482	0.370	24.50
26	(FCH <sub>2</sub> O)	0.02700	0.304	31.50
27	(CH <sub>2</sub> NH <sub>2</sub> )	0.75214	0.322	42.00
28	(CHNH <sub>2</sub> )	0.00928	0.305	35.00
29	(CH <sub>3</sub> NH)	1.02921	0.362	42.00
30	(CH <sub>2</sub> NH)	0.07506	0.362	35.00
31	(CHNH)	-0.60478	0.345	28.00
32	(CH <sub>3</sub> N)	0.11552	0.397	35.00
33	(CH <sub>2</sub> N)	-0.33848	0.397	28.00
34	(ACNH <sub>2</sub> )	0.91529	0.249	28.00
35	(C <sub>5</sub> H <sub>4</sub> N)	1.23375	0.900	92.60
36	(C <sub>5</sub> H <sub>3</sub> N)	0.46621	0.900	85.60
37	(CH <sub>2</sub> CN)	0.14900	0.587	49.00
38	(COOH)	0.94178	0.400	38.00
39	(CH <sub>2</sub> 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 <sub>2</sub> )	0.04900	0.850	63.00
43	(CCl <sub>2</sub> )	0.03400	0.850	56.00
44	(CCl <sub>3</sub> )	0.05100	1.170	80.50
45	(ACCl)	0.02800	0.474	33.50
46	(CH <sub>2</sub> NO <sub>2</sub> )	0.07500	0.647	53.20
47	(CHNO <sub>2</sub> )	0.06700	0.630	46.20
48	(ACNO <sub>2</sub> )	0.06600	0.574	41.20
49	(CH <sub>2</sub> 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 <sub>3</sub> )	0.05400	0.882	38.50
58	(CF <sub>2</sub> )	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  $\Delta P_i$  are the contribution of group  $i$  to  $P_c$ . The group contributions estimated in terms of UNIFAC functional groups are given in Table 1.

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