International Journal of Thermophysics, Vol. 26, No. 5, September 2005 (© 2005)
DOI: 10.1007/s10765-005-8092-7

New Group-Contribution Method for Predicting Temperature-Dependent Properties of Pure Organic Compounds

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Received September 24, 2004

A new method for predicting temperature-dependent properties of organic compounds is presented. It is a combination of a group-contribution method with the novel non-random hydrogen-bonding (NRHB) equation-of-state theory. First-order and second-order groups are used to predict the three characteristic scaling constants of the NRHB model. With these scaling constants, one is able to estimate/predict temperature-dependent properties of pure organic compounds such as vapor pressure, liquid density, heat of vaporization and more, in a wide range of temperatures. The influence parameter, κ, which is needed for the estimation of surface tension at any given temperature, is also predicted by the same group-contribution method.

KEY WORDS: equation of state; group-contribution method; NRHB theory; temperature-dependent properties.

1. INTRODUCTION

A number of methods that can predict thermodynamic properties of organic compounds in a range of temperatures is available in the open literature. Li et al. [1, 2] have invented a group-contribution method based on a theory of corresponding states (CSGC). This method has been applied to the prediction of surface tension [1] and heat of vaporization [2]. Yinghua et al. [3] have used a similar model for estimating the liquid viscosity of organic compounds at any temperature. Coutsikos et al. [4] have created a method for estimating the vapor pressure of solid organic compounds.

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A different category of estimation techniques for temperature-dependent properties includes those based on neural networks. Kuhne et al. [5] have estimated the vapor pressure of hydrocarbons and halogenated hydrocarbons at different temperatures with a method of this kind. Yaffe and Cohen [6] have also developed a neural-network method for the prediction of vapor pressures of hydrocarbons. The method of Chalk et al. [7] combines quantum mechanics with neural networks in order to estimate the vapor pressures of organic solvents at different temperatures.

The present paper introduces a different method for estimating temperature-dependent thermophysical properties at any given temperature. It is a combination of the Constantinou–Gani [8] group-contribution method with the novel NRHB equation-of-state theory [9]. The estimation of properties is exclusively based on the molecular structure of each organic compound. The present paper, the first part in a series of papers, covers the application of the NRHB model to the prediction of temperature-dependent properties of pure compounds that do not form hydrogen bonds.

2. THE PROPOSED METHOD

2.1. NRHB Model

The NRHB (non-random hydrogen-bonding) model [9] is a novel equation-of-state model which, in addition to the capabilities of the similar lattice-fluid type models [10], is able to estimate the non-random distribution of free volume in a system. This model can predict phase equilibria and interfacial properties of fluids. The NRHB model can be applied to pure fluids and to mixtures, to simple molecules as well as to polymers, to liquids, vapors and supercritical fluids. The model is also able to predict the same properties at different pressures.

The only parameters needed for the estimation of properties of each compound are the characteristic scaling constants. In the present model, it has been decided to use the ε^*, v^* and v^*_{sp} scaling constants, which are related to the equivalent set of T^*, P^*, and ρ^* scaling constants with the following equations:

$$\varepsilon^* = RT^* \tag{1}$$

$$v^* = \frac{\varepsilon^*}{P^*} \tag{2}$$

$$v^*_{\mathrm{sp}} = \frac{1}{\rho^*} \tag{3}$$

where ε^* is the average interaction energy per molecular segment, v^* is the average segmental volume, v^*_{sp} is the hard-core specific volume, T^* is the scaling temperature, P^* is the scaling pressure, ρ^* is the scaling density, and R is the universal gas constant [9, 10].

For the estimation of surface tension at any temperature, the influence parameter, κ, is also needed. The shift factor, β, is equal to 2 for all compounds that do not form hydrogen bonds [9]. Finally, it should be stressed that all mathematical expressions for the predicted properties and also the constants' definitions are adequately reported in a previous work and are not repeated in the present study [9].

2.2. Calculation of the Characteristic Scaling Constants

The aim of the present study was to predict the first-order and second-order group contributions to each of the three scaling constants ε^*, v^*, and v^*_{sp}. Through them, it is possible to estimate the temperature-dependent properties of organic compounds at any temperature.

There were only few scaling constants of pure compounds in the literature [9], basically concerning normal alkanes. The scaling constants of compounds that belong to other homologous series were needed in order to develop the group-contribution method for their prediction. The ε^*, v^* and v^*_{sp} constants were calculated through regression using as input, data of the DIPPR database.

The steps of our methodology were the following:

(a) Calculation of vapor pressure, liquid density, and heat of vaporization values in a selected temperature range for 334 compounds using the equations of the DIPPR database [11]. The temperature range was from $(17T_{\mathrm{m}} + T_{\mathrm{c}} - 10\ \mathrm{K})/18$ to $T_{\mathrm{c}} - 10$, where T_{m} is the normal melting point, and T_{c} is the critical temperature of each compound. This expression comes out from the division of the temperature range from T_{m} to $T_{\mathrm{c}} - 10$ into 18 equidistant points.

(b) Calculation of the surface-to-volume ratio, s, a geometric feature of each molecule. As previously [9], this was done by using the 78 UNIFAC group contributions to the surface area parameter, Q_{i}, and the volume parameter, R_{i}, for each group i [12]. The appropriate equation is $s = \Sigma Q_i / \Sigma R_i$.

(c) Fitting of ε^*, v^*, v^*_{sp} characteristic scaling constants and "s" to the DIPPR data by means of a FORTRAN algorithm which uses a Marquardt-type optimization subroutine.

The values of the characteristic scaling constants for 334 organic compounds were obtained by following the above mentioned methodology. The compounds were specially selected so as to cover a large number of homologous series of organic compounds. All scaling constants defined by fitting the values from the DIPPR database from now on will be referred as "DIPPR-based scaling constants".

In Fig. 1, the ε^* scaling constants for the normal alkanes are presented. One can see three clearly distinguished regions. There is a steep rise of the average segmental interaction energies (ε^*) up to pentane. Right after pentane, the slope of the curve decreases due to some sort of "orientational order" behavior of the higher alkanes. Finally, after pentadecane, there is a slight decrease in the slope of the curve due to the capacity of "chain folding" which is observed when the number of carbon atoms is expanded further [9].

2.3. Estimation of Group Contributions to the ε^*, v^*, v^*_{sp} Characteristic Scaling Constants

For obtaining first-order and second-order group contributions to the $\varepsilon^*, v^*, v^*_{sp}$ scaling constants, the same methodology as that for temperature-independent properties was followed [8, 13]. Scaling constants for 334 compounds were used in the group-contribution regression. Normal

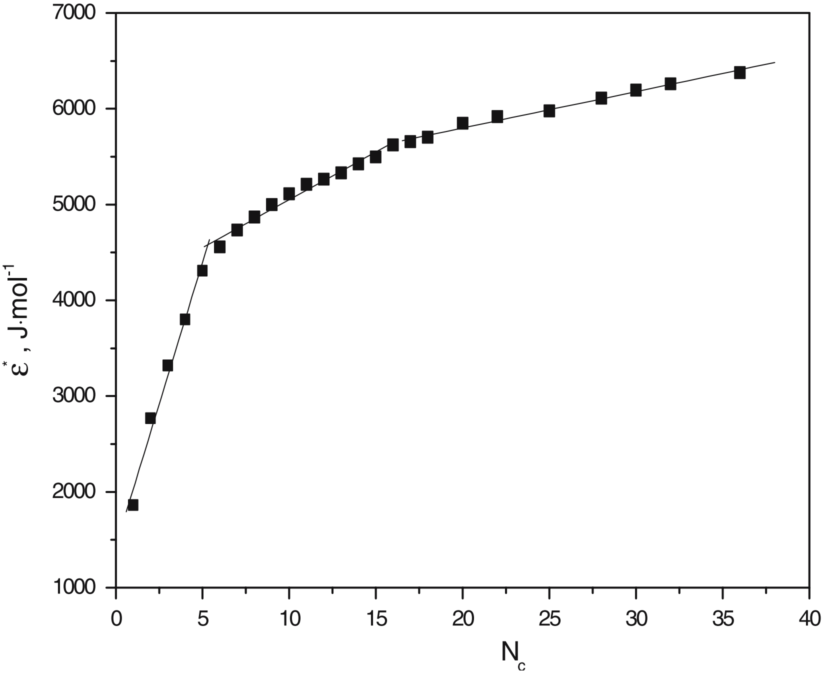

Fig. 1. Characteristic scaling constant, ε^*, as a function of the number of carbon atoms.

alkanes and normal alkenes with fewer than five or more than 15 carbon atoms were not included in these 334 compounds for reasons related to the behavior of ε^* scaling constants, when the number of carbon atoms increases (Fig. 1).

The best model found after least-square analysis for all scaling constants was the linear one. The equations that give the characteristic scaling constants through the first-order and second-order group contributions are the following:

$$\varepsilon^* = \sum_i n_i F_i + \sum_j m_j S_j + 4438 \ \mathrm{J \cdot mol^{-1}} \tag{4}$$

$$v^* = \sum_i n_i F_i + \sum_j m_j S_j + 8.8303 \ \mathrm{cm^3 \cdot mol^{-1}} \tag{5}$$

$$v^*_{\mathrm{sp}} = \sum_i n_i F_i + \sum_j m_j S_j + 1.19155 \ \mathrm{cm^3 \cdot g^{-1}} \tag{6}$$

The first-order and second-order group contributions to the characteristic scaling constants are shown in Tables I and II. Table III demonstrates the overall improvement of the estimation of scaling constants and the influence parameter, κ, which was achieved after the introduction of second-order-groups in the regression. The improvement of 10–20% is typical for the Constantinou–Gani group-contribution method. The reliability of the method was tested following the methodology reported elsewhere [8]. Figures 2, 3, and 4 illustrate the correlation of estimated values with the corresponding DIPPR-based values for the ε^*, v^*, and v^*_{sp} scaling constants, respectively.

3. SURFACE-TENSION ESTIMATION

In the case of surface-tension estimations, a knowledge of influence parameters, κ, is necessary. There is a lack of κ values in the literature. These parameters for 334 selected compounds were obtained after fitting experimental values of surface tension calculated by the DIPPR database equations [11]. The fitting has been done at a temperature equal to $0.6T_c$ for each compound, where T_c is the critical temperature. The calculated influence parameters were considered to be valid at any other temperature.

After obtaining the DIPPR-based influence parameter values, a group-contribution model has been developed for their prediction. Values for 334 organic compounds have been used in the group-contribution regression. The best model found for the influence parameter, κ, was again the linear one. The equation that gives the influence parameters, κ, by using the

Table I. First-Order Group Contributions to the ε^*, v^*, and v^*_{sp} Characteristic Scaling Constants

	Contributions		
First-order groups	ε^*	v^*	v^*_{sp}
$-CH_3$	−145.8	0.9281	0.03676
$-CH_2$	121.0	0.6323	0.00040
$-CH<$	366.6	0.9888	−0.02829
$>C<$	747.0	2.1785	−0.07202
$CH_2{=}CH-$	−95.4	0.9276	0.01785
$-CH{=}CH-$	349.7	1.3467	0.00447
$CH_2{=}C<$	280.9	1.8782	−0.02177
$-CH{=}C<$	586.2	1.5089	−0.05008
$>C{=}C<$	863.4	1.0716	−0.11808
CHEC–	86.5	0.6585	0.00249
CEC	589.2	1.8203	0.02413
ACH	125.4	0.3585	−0.01242
AC	220.6	−0.5645	−0.04080
$ACCH_3$	294.8	0.8643	−0.01672
$ACCH_2-$	476.6	0.9839	−0.03085
$ACCH<$	723.7	1.4434	−0.05639
CH_3CO	341.0	−0.3859	−0.11186
CH_2CO	655.1	−0.2091	−0.12761
CH_3COO	258.3	−0.0107	−0.19945
CH_2COO	559.1	−0.7785	−0.24905
HCOO	86.5	−0.9879	−0.22006
COO	521.5	−0.2883	−0.19770
CH_3O	118.0	0.0656	−0.09432
CH_2O	73.8	−0.5496	−0.11272
CHO	283.8	−0.0726	−0.14665
CH_2O (cyclic)	43.4	−0.8307	−0.17244
CH_3N	370.6	0.8713	−0.02569
CH_2N	634.1	1.3881	−0.08050
$CON(CH_3)_2$	1538.9	0.1841	−0.19338
CH_2SH	607.4	1.0368	−0.11702
CH_3S	536.3	1.0622	−0.13828
CH_2S	840.4	1.2446	−0.15283
Br	628.7	1.5593	−0.27167
CH_2CL	539.6	1.1667	−0.17669
CHCl	442.5	0.6639	−0.23553
CCl	747.3	3.0978	−0.24618
ACCl	440.4	0.3689	−0.15803
ACF	14.0	0.1660	−0.10648
$Cl{-}(C{=}C)$	87.0	0.2038	−0.25451
CF_3	−273.1	2.7573	−0.20341
CH_2NO_2	910.8	−1.2464	−0.29118

Table I. (*Continued*)

First-order groups	Contributions ε^*	v^*	v^*_{sp}
$CHNO_2$	1093.7	−1.2143	−0.32430
$ACNO_2$	729.3	−1.3249	−0.20984
CH_2CN	800.7	−0.7731	−0.06197
C_4H_3S	1184.8	0.6004	−0.27114

Table II. Second-Order Group Contributions to the ε^*, v^*, and v^*_{sp} Characteristic Scaling Constants

Second-order groups	Contributions ε^*	v^*	v^*_{sp}
$(CH_3)_2$–CH–	−34.5	−0.2003	−0.00353
$(CH_3)_3$–C–	−71.6	−0.0168	0.00868
–CH(CH_3)–CH(CH_3)–	107.1	−0.0043	−0.01230
–CH(CH_3)–C$(CH_3)_2$–	95.5	−0.0665	−0.01652
–C$(CH_3)_2$–C$(CH_3)_2$–	273.5	−0.1382	−0.04418
Ring of 5 carbons	−177.9	−0.4868	0.01401
Ring of 6 carbons	−24.8	0.2604	0.01309
–C=C–C=C–	−2.6	0.0130	0.01195
CH_3–C=	−33.0	−0.0070	0.00385
–CH_2–C=	13.8	0.0186	0.00482
>CH or C–C=	−37.9	0.2375	0.02229
String in cyclic	193.9	0.9800	−0.00801
CH_3(CO)CH_2–	16.9	0.0491	0.00565
C(cyclic)=O	292.9	−0.1394	−0.01525
(CO)O(CO)	−273.5	0.1570	0.01910
C–O–C=C	−8.1	0.0383	−0.00978
AC–O–C	388.7	0.6132	−0.00360
–S–(in cyclic)	362.4	−1.0670	−0.08022
ACBr	−1.9	−0.0025	−0.00047
CH_3(CO)CH<	22.1	0.0952	0.00089
Ring of 3 carbons	−920.7	−2.2781	0.14623
Ring of 4 carbons	−414.3	−1.0279	0.04392
Ring of 7 carbons	168.4	0.5391	−0.01962
ACCOO	123.8	0.7050	0.01579
AC$(ACHm)_2$AC$(ACHn)_2$	9.6	0.0125	0.00236
Ocyclic–Ccyclic=O	1354.1	−1.2561	−0.06007

Table III. Statistical Values of First-Order and Second-Order Approximation for the Estimation of the ε^*, v^*, and v_{sp}^* Scaling Constants and the κ Influence Parameters

		Standard deviation		AAE		AAPE (%)	
Scaling constant	Data Points	1st-order	2nd-order	1st-order	2nd-order	1st-order	2nd-order
ϵ^*	336	193	153	133	109	2.49	2.04
v^*	336	0.641	0.585	0.468	0.422	3.61	3.22
v_{sp}^*	336	0.033	0.030	0.023	0.021	2.18	2.00
κ	334	0.0129	0.0117	0.0088	0.0082	5.68	5.11

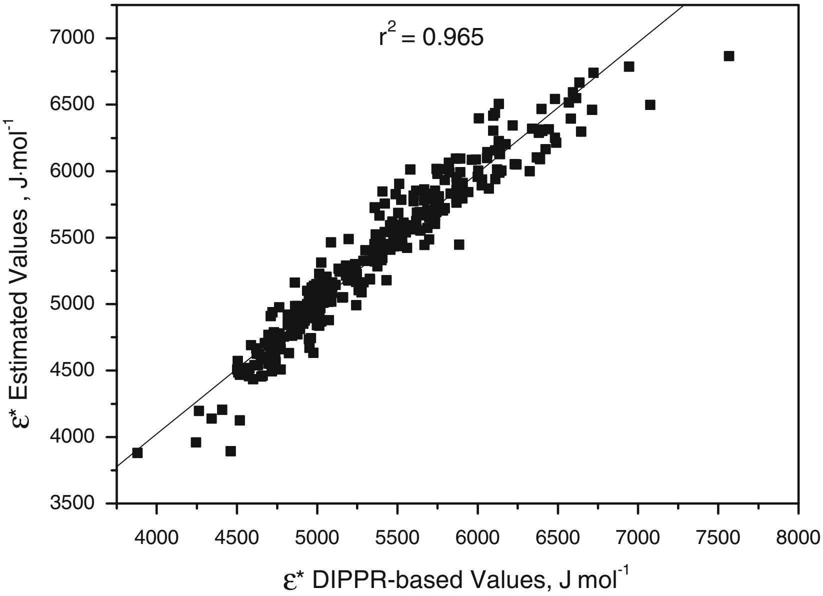

Fig. 2. Scatter plot of estimated vs. DIPPR-based ε^* scaling constants.

first-order and second-order group contributions is the following:

$$\kappa = \sum_i n_i F_i + \sum_j m_j S_j + 0.15595 \tag{7}$$

The first-order and second-order group contributions to the influence parameters are shown in Tables IV and V.

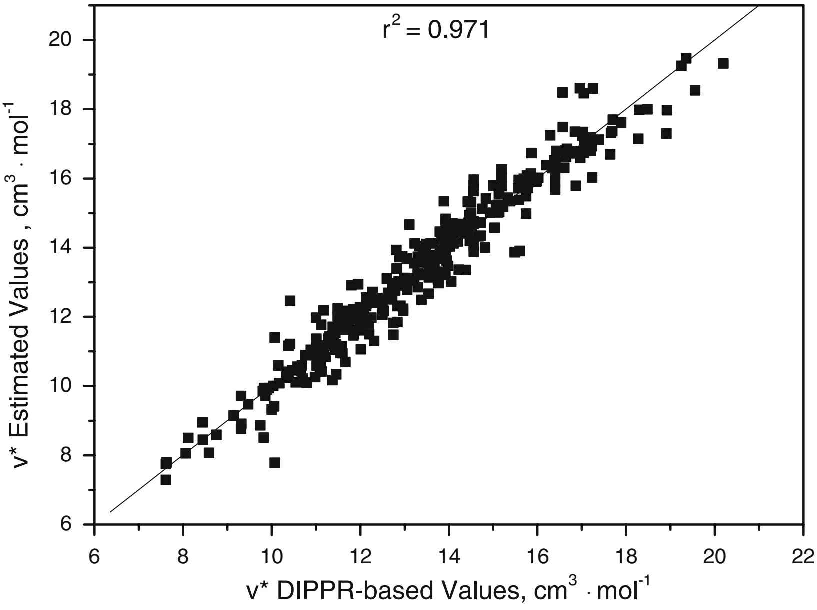

Fig. 3. Scatter plot of estimated vs. DIPPR-based v^* scaling constants.

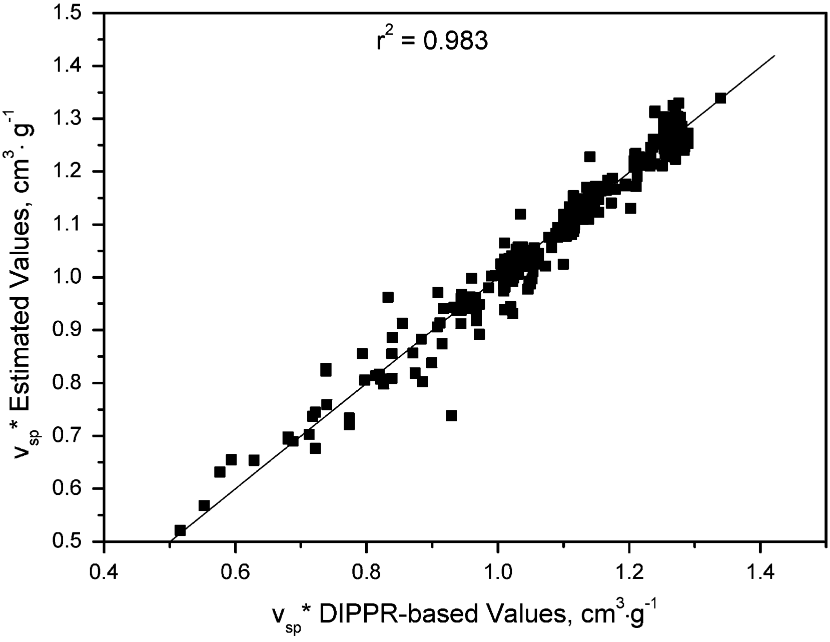

Fig. 4. Scatter plot of estimated vs. DIPPR-based v^*_{sp} scaling constants.

Table IV. First-Order Group Contributions to the Influence Parameters, κ

First-order groups	κ Contributions
$-CH_3$	0.00788
$-CH_2$	0.00043
$-CH<$	−0.00534
$>C<$	−0.00577
$CH_2=CH-$	0.00738
$-CH=CH-$	−0.00864
$CH_2=C<$	0.00544
$-CH=C<$	−0.00476
$>C=C<$	0.03738
CHEC–	0.00672
CEC	−0.00684
ACH	−0.00087
AC	−0.00336
$ACCH_3$	0.00137
$ACCH_2-$	−0.00479
$ACCH<$	−0.00660
CH_3CO	−0.00805
CH_2CO	−0.01205
CH_3COO	0.00995
CH_2COO	−0.01006
HCOO	0.00909
COO	0.00030
CH_3O	0.00771
CH_2O	0.01489
CHO	−0.00419
CH_2O (Cyclic)	0.02314
CH_3N	0.00442
CH_2N	0.00239
$CON(CH_3)_2$	−0.06573
CH_2SH	−0.00416
CH_3S	−0.00030
CH_2S	−0.00796
Br	0.01114
CH_2Cl	0.00951
CHCl	0.02216
CCl	0.01121
ACCl	0.00603
ACF	0.00162
CL–(C=C)	0.01302
CF_3	0.02175
CH_2NO_2	−0.03576
$CHNO_2$	−0.03931
$ACNO_2$	−0.00270
CH_2CN	−0.02411
C_4H_3S	−0.02028

Table V. Second-Order Group Contributions to the Influence Parameters, κ

Second-order groups	κ contributions
$(CH_3)_2$–CH–	−0.00096
$(CH_3)_3$–C–	−0.00163
–CH(CH_3)–CH(CH_3)–	0.00151
–CH(CH_3)C–(CH_3)$_2$–	0.00421
–C(CH_3)$_2$–C(CH_3)$_2$–	0.00118
Ring of 5 carbons	0.00524
Ring of 6 carbons	0.00824
–C=C–C=C–	−0.00282
CH_3–C=	−0.00626
–CH_2C–=	−0.00128
>C{H or C}–C=	0.00589
String in cyclic	−0.00786
CH_3(CO)CH_2–	0.00305
C(cyclic)=O	−0.00938
(CO)O(CO)	0.00176
C–O–C=C	0.00471
AC–O–C	−0.01439
–S–(in cyclic)	−0.01378
ACBr	0.00122
CH_3(CO)CH<	0.00012
Ring of 3 carbons	0.01466
Ring of 4 carbons	0.02074
Ring of 7 carbons	0.01359
ACCOO	0.00264
AC(ACHm)$_2$AC(ACHn)$_2$	−0.00609
Ocyclic–Ccyclic=O	−0.07105

4. RESULTS AND DISCUSSION

A detailed example of the application of the method to the estimation of various temperature-dependent properties for ethyl benzoate is given in the Appendix (Fig 5). The average percentage errors in the estimation of temperature-dependent properties for different classes of compounds using DIPPR-based scaling constants are presented in Table VI. Table VII depicts the errors in the calculation of the same properties using the scaling constants predicted by the group-contribution method.

The NRHB model provides a useful method for the estimation of basic temperature-dependent thermophysical properties of pure fluids and mixtures. Its main advantage is that, with a set of scaling constants, more than one temperature-dependent property, such as vapor pressure, liquid and vapor density, heat of vaporization, solubility parameters, etc. can be

Table VI. Average Error for Each Class of Compounds Using DIPPR-Based Scaling Constants and DIPPR-based Influence Parameters

	Number of compounds	Liquid density (%)	Heat of vaporization (%)	Vapor pressure (%)	Surface tension (%)
Alkanes	55	1.67	7.61	0.69	1.33
Alkenes	54	1.43	8.88	1.17	1.73
Alkynes	5	1.47	9.47	2.04	1.60
Cyclic Hydrocarbons	23	1.33	9.86	1.46	3.03
Aromatics	42	1.63	9.96	1.48	3.82
Naphthalenes	26	1.61	10.22	1.32	4.39
Ethers	14	1.74	6.24	1.18	1.72
Ketones	15	1.41	7.26	1.23	2.46
Esters	29	1.70	6.17	1.37	1.93
Formates	5	1.50	6.92	1.34	3.23
Anhydrides	3	1.70	5.22	1.62	3.40
Halohydrocarbons	26	1.54	8.78	0.93	2.71
Sulfocompounds	16	1.42	9.41	1.53	2.38
Nitrogen Compounds	21	1.33	8.55	1.62	3.99
Total	334	1.55	8.45	1.19	2.58

Table VII. Average Error for Each Class of Compounds Using Group-Contribution Estimated Scaling Constants and Influence Parameters

	Number of compounds	Liquid density (%)	Heat of vaporization (%)	Vapor pressure (%)	Surface tension (%)
Alkanes	55	3.13	7.28	7.31	4.57
Alkenes	54	2.74	9.26	7.38	5.02
Alkynes	5	2.40	8.72	5.43	4.87
Cyclic Hydrocarbons	23	2.24	10.03	6.30	5.01
Aromatics	42	3.51	9.78	11.03	7.82
Naphthalenes	26	6.70	12.06	14.81	12.76
Ethers	14	3.75	10.15	17.77	9.07
Ketones	15	1.72	7.61	5.31	4.09
Esters	29	3.87	10.05	19.09	6.95
Formates	5	2.65	7.26	10.57	8.23
Anhydrides	3	7.30	9.11	19.33	9.10
Halohydrocarbons	26	4.59	10.00	13.65	6.50
Sulfocompounds	16	2.71	9.51	6.77	4.69
Nitrogen Compounds	21	6.26	9.43	16.45	9.82
Total	334	3.29	9.68	10.82	6.66

estimated simultaneously for pure fluids. The same properties can also be predicted for mixtures if the scaling constants of the pure fluids, that are components of the mixture are known.

The scaling constants are temperature-independent and can be easily estimated by the Constantinou–Gani group-contribution method. The relevant group contributions and the equations of estimation are reported in the present paper, and the method can be applied to multifunctional compounds.

The NRHB theory is an approximate model for estimating thermodynamic properties using scaling constants only. Thus, the prediction ability of the whole method featured in the present study depends, first of all, on the accuracy of NRHB model and, in addition, on the ability of the group-contribution method to predict the scaling constants. The majority of the analogous methods in the literature predict thermophysical properties directly, while our method predicts scaling constants as input to the NRHB model which in turn evaluates the desired thermophysical properties. From the above, it is clear that no direct comparison can be made between the methods.

The novelty of our method lies in the prediction of all basic thermodynamic properties of fluids at any external conditions when no experimental data are available, since it is based on an equation-of-state theory. This fact is very important in the design of new compounds with desired properties. The calculations using DIPPR-based scaling constants are, in general, of quite satisfactory accuracy. When these properties are predicted using the scaling constants that have been estimated with group contributions, the results are relatively accurate except for vapor pressure. Figures 2, 3, and 4 show that the correlation between experimental and estimated scaling constants is, in general, sufficiently good and this is an important parameter for the success of the predictions.

In the example of the Appendix, the values of properties estimated by experimental ε^*, v^*, v^*_{sp} scaling constants (circular symbols) in some cases overlap with those predicted by estimated (by group contributions) scaling constants (solid line). This is due to the significant accuracy of estimated values of scaling constants that the group contributions gave and the result is that the predicted values of all properties are very close to the values of DIPPR equations (triangular symbols).

5. CONCLUSION

The combination of the Constantinou–Gani method with the NRHB theory has expanded the potential of this group-contribution method significantly. For the first time, this method can predict temperature-dependent properties. The three characteristic scaling constants of the NRHB model, which are able to estimate the temperature-dependent properties of pure organic compounds in a wide range of temperatures, are easily predicted using first-order and second-order group contributions. An extension of the method to the prediction of properties of compounds that contain hydrogen bonds will be a future goal of our work.

APPENDIX

Example of application of the group-contribution method to ethyl benzoate:

(A) ε^* characteristic scaling constant (Table VIII).
First-order approximation value:

$$\varepsilon^* = \sum_i n_i F_i + 4438 = 5782 \ \mathrm{J \cdot mol^{-1}}$$

First-order approximation error: $(5782 - 5910)/5910 = -2.17\%$.

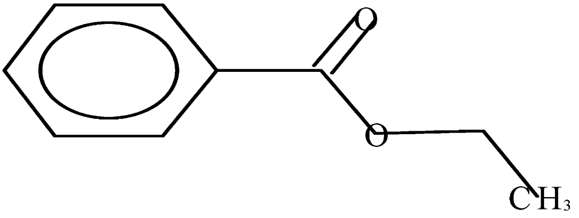

Fig. 5. Chemical structure of ethyl benzoate.

Table VIII. ε^* Characteristic Scaling Constant Estimation

First-order groups	Occurences, n_i	Contributions, F_i	n_iF_i
$-CH_3$	1	−145.8	−145.8
$-CH_2$	1	121	121
ACH	5	125.4	627
AC	1	220.6	220.6
–COO	1	521.5	521.5
$\Sigma n_i F_i$			1344.3
Universal constant, C			4438
Second-order groups	Occurences, m_j	Contributions, S_j	m_jS_j
ACCOO	1	123.8	123.8
$\Sigma m_j S_j$			123.8

Table IX. v^* Characteristic Scaling Constant Estimation

First-order groups	Occurences, n_i	Contributions, F_i	n_iF_i
$-CH_3$	1	0.9281	0.9281
$-CH_2$	1	0.6323	0.6323
ACH	5	0.3585	1.7925
AC	1	−0.5645	−0.5645
–COO	1	−0.2883	−0.2883
$\Sigma n_i F_i$			2.5001
Universal constant, C			8.8303
Second-order groups	Occurences, m_j	Contributions, S_j	m_jS_j
ACCOO	1	0.7050	0.7050
$\Sigma m_j S_j$			0.7050

Second-order approximation value:

$$\varepsilon^* = \sum_i n_i F_i + \sum_j m_j S_j + 4438 = 5906 \text{ J} \cdot \text{mol}^{-1}$$

Estimated characteristic scaling constant $\varepsilon^* = 5906 \text{ J} \cdot \text{mol}^{-1}$
DIPPR-based characteristic scaling constant $\varepsilon^* = 5910 \text{ J} \cdot \text{mol}^{-1}$

Error= (5906 − 5910)/5910 = 0.07%.

(B) v^* characteristic scaling constant (Table IX).
First-order approximation value:

$$v^* = \sum_i n_i F_i + 8.8303 = 11.330 \text{ cm}^3 \cdot \text{mol}^{-1}$$

First-order approximation error: (11.330 − 12.049)/12.049 = −5.97%.
Second-order approximation value:

$$v^* = \sum_i n_i F_i + \sum_j m_j S_j + 8.8303 = 12.035 \text{ cm}^3 \cdot \text{mol}^{-1}$$

Estimated v^* characteristic scaling constant = 12.035 $\text{cm}^3 \cdot \text{mol}^{-1}$
DIPPR-based v^* characteristic scaling constant = 12.049 $\text{cm}^3 \cdot \text{mol}^{-1}$

Error= (12.035 − 12.049)/12.049 = −0.11%.

(C) v^*_{sp} characteristic scaling constant (Table X).
First-order approximation value:

$$v_{\text{sp}}* = \sum_i n_i F_i + 1.19155 = 0.9281 \text{cm}^3 \cdot g^{-1}$$

First-order approximation error: $(0.9281-0.9380)/0.9380=-1.06\%$.
Second-order approximation value:

$$v_{sp}{*}=\sum_{i} n_i\, F_i+\sum_{j} m_j\, S_j+1.19155=0.9439\ \mathrm{cm}^3\cdot \mathrm{g}^{-1}$$

Estimated characteristic scaling constant $v^*_{sp}=0.9439$
DIPPR-based characteristic scaling constant $v^*_{sp}=0.9380$

Error$=(0.9439-0.9380)/0.9380=0.63\%$.

In Figs. 6, 7, and 8, the charts of vapor pressure, liquid density, and the heat of vaporization at the whole range of temperatures are presented. Triangular symbols represent the experimental values calculated by the DIPPR equations. The properties estimated by the DIPPR-based values of scaling constants ε^*, v^*, and v^*_{sp} are depicted with circular symbols. The solid line represents the values of the properties estimated by the scaling constants predicted by the group-contribution method (Examples A, B, C).

(D) Influence parameter, κ (Table XI).

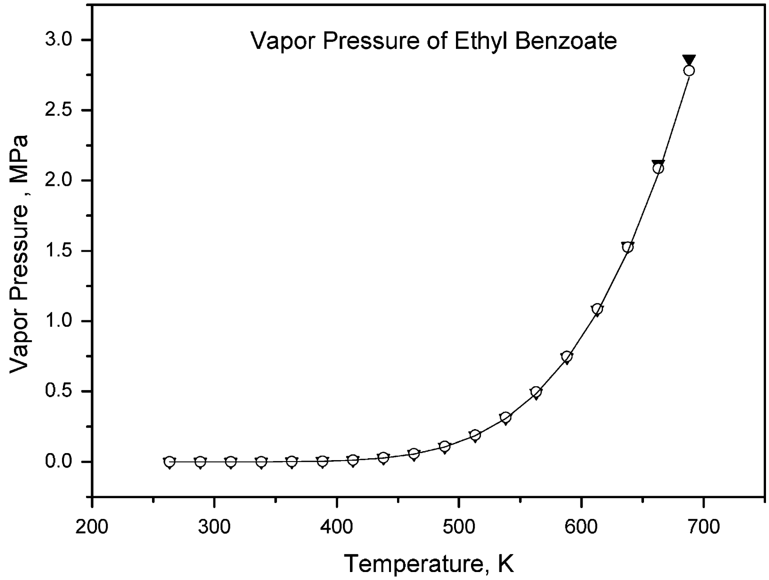

Fig. 6. Vapor pressure calculated by DIPPR equations (triangular symbols), by DIPPR-based scaling constants (circular symbols), and by estimated scaling constants (solid line).

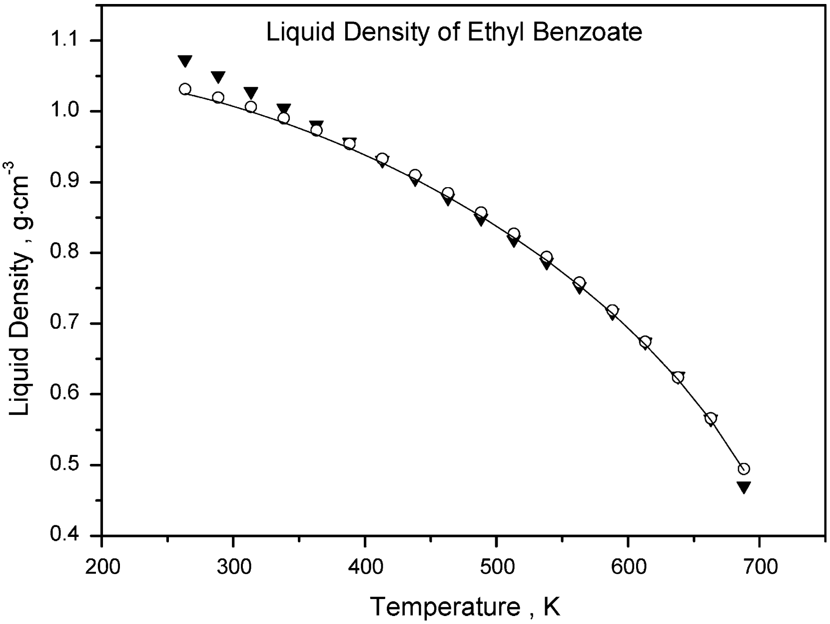

Fig. 7. Liquid density calculated by DIPPR equations (triangular symbols), by DIPPR-based scaling constants (circular symbols), and by estimated scaling constants (solid line).

Table X. v^*_{sp} Characteristic Scaling Constant Estimation

First-order groups	Occurences, n_i	Contributions, F_i	n_iF_i
$-CH_3$	1	0.03676	0.03676
$-CH_2$	1	0.00040	0.00040
ACH	5	−0.01242	−0.0621
AC	1	−0.04080	−0.04080
–COO	1	−0.19770	−0.19770
$\Sigma n_i F_i$			−0.26344
Universal constant, C			1.19155
Second-order groups	Occurences, m_j	Contributions, S_j	m_jS_j
ACCOO	1	0.01579	0.01579
$\Sigma m_j S_j$			0.01579

First-order approximation value:

$$\kappa = \sum_i n_i \, F_i + 0.15595 = 0.15956$$

First-order approximation error: $(0.15956 - 0.1652)/0.1652 = -3.41\%$.

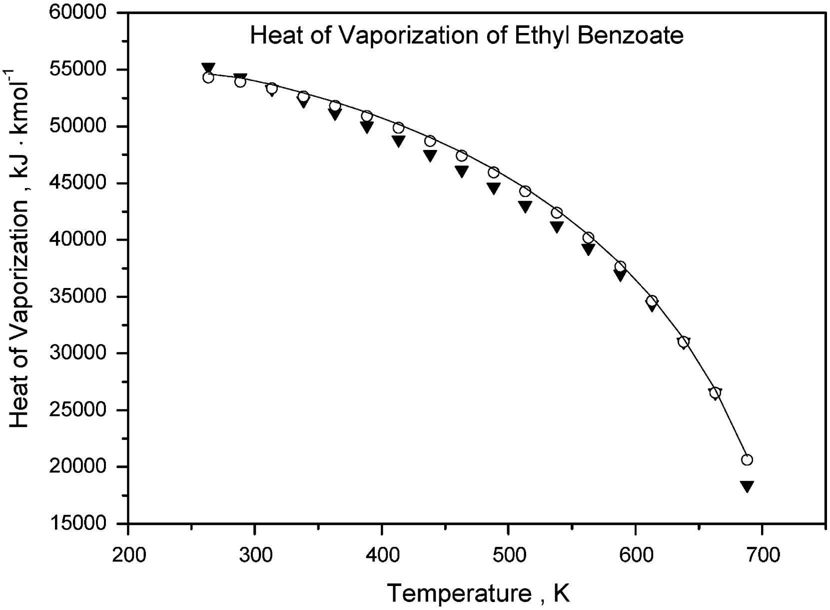

Fig. 8. Heat of vaporization calculated by DIPPR equations (triangular symbols), by DIPPR-based scaling constants (circular symbols), and by estimated scaling constants (solid line).

Table XI. "κ" Influence Parameter Estimation

First-order groups	Occurences, n_i	Contributions, F_i	n_iF_i
$-CH_3$	1	0.00788	0.00788
$-CH_2$	1	0.00043	0.00043
ACH	5	−0.00087	−0.00104
AC	1	−0.00336	−0.00336
–COO	1	−0.00030	−0.00030
Σn_iF_i			0.00361
Universal constant, C			0.15595
Second-order groups	Occurences, m_j	Contributions, S_j	m_jS_j
ACCOO	1	0.00264	0.00264
Σm_jS_j			0.00264

Second-order approximation value:

$$\kappa=\sum_i n_i\, F_i+\sum_j m_j\, S_j+0.15595=0.1603$$

Estimated influence parameter, $\kappa=0.1603$

DIPPR-based influence parameter, $\kappa = 0.1652$

$\text{Error} = (0.1622 - 0.1652)/0.1652 = -1.82\%$.

In Fig. 9, the chart of surface tension at any temperature is presented. Triangular symbols represent the surface tension values calculated by the DIPPR equations. The surface tension estimated by the DIPPR-based scaling constants ε^*, v^*, and v^*_{sp} and of the DIPPR-based influence parameter, κ, is depicted with circular symbols. The solid line represents the values of surface tension estimated by the scaling constants and the influence parameter predicted by the group-contribution method (Examples A, B, C, and D).

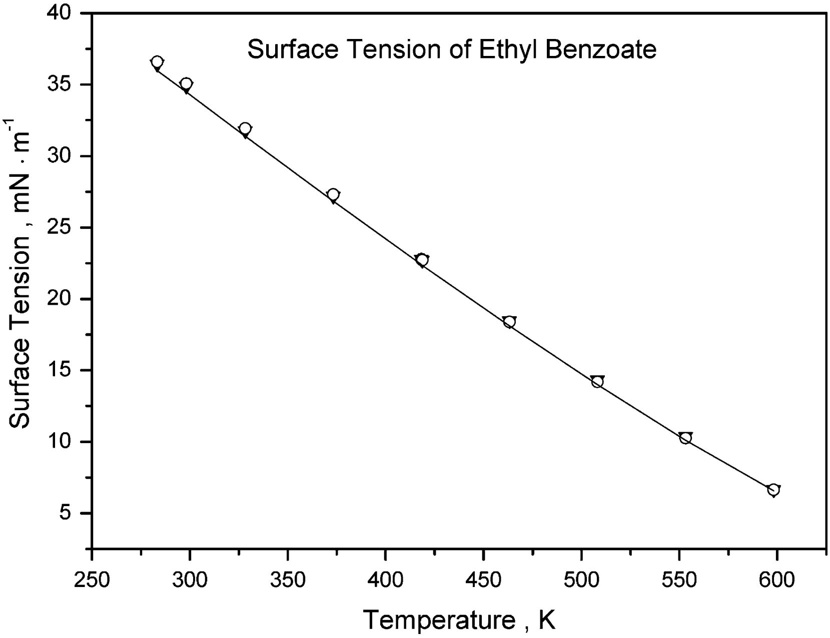

Fig. 9. Surface tension calculated by DIPPR equations (triangular symbols), by DIPPR-based scaling constants (circular symbols), and by estimated scaling constants (solid line).

ACKNOWLEDGMENTS

The authors would like to express their appreciation to Cyprus Science Foundation for the partial financial support of the project and to the State Scholarships Foundation of Greece (I.K.Y.).

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