Nucleophilicity Evaluation for Primary and Secondary Amines

MADIAN RAFAILA, MIHAI MEDELEANU*, CORNELIU MIRCEA DAVIDESCU
"Politehnica" University of Timişoara, Faculty of Industrial Chemistry and Environmental Engineering, 6 Vasile Pârvan Blvd, 300223, Timisoara, Romania

Two nucleophilicity indices were evaluated for a series of N-nucleophiles. The first index is the one defined by Jaramillo et al. in 2006 while the second is a new index proposed for the first time in this paper. Both indices are based on information concerning the frontier molecular orbital of the nucleophile and its electrophilic partner. The models based on these indices were validated against existent kinetic data for the nucleophilic substitution of benzhydrylium cations with primary and secondary amines in water at 20°C. The predictive character of the models was also tested.

Keywords: amines, nucleophilicity, electrophilicity, HOMO, LUMO

The use of the electrophilicity and nucleophilicity concepts to define the electron-deficient (electrophile) and the electron-rich (nucleophile) species has gained a continuous interest in classifying atoms, molecules, charged species and their reactivity centers within empirical scales of electrophilicity and nucleophilicity [1-6]. Also, the availability of experimental scales of electrophilicity and nucleophilicity, usually based on kinetic parameters, provides useful information for the rationalization of chemical reactivity. Both of these concepts have been defined in a kinetic sense [7, 8]. While the electrophilicity concept represent the stabilization in energy when the electrophile species acquires an additional electronic charge from the environment, a quantitative definition of the nucleophilicity concept is more difficult to postulate. The reason lies in the fact that when a nucleophile loses an electronic charge, its frontier orbital energy will increase. Therefore, one cannot use a variational calculation such as the one introduced by Parr et al. [9] to define the electrophilicity:

$$\omega = \frac{\mu^2}{2\eta} \qquad (1)$$

Equation (1) represents the electrophilicity index, where μ and η are the electronic chemical potential and the chemical hardness of the electrophile, defined by the following relations:

$$\mu = \frac{\varepsilon_{LUMO} + \varepsilon_{HOMO}}{2} \qquad (2)$$

$$\eta = \frac{\varepsilon_{LUMO} - \varepsilon_{HOMO}}{2} \qquad (3)$$

The first attempt to quantify nucleophilicity was reported in 1953 by Swain and Scott [10], who proposed equation (4):

$$\lg k = \lg k_0 + s_E' \cdot n \qquad (4)$$

where:
k = experimental rate constant of the reaction;
k_o = experimental rate constant of the etalon reaction;
s_E = sensitivity of the electrophile;
n = nucleophilicity constant.

A second attempt to quantify nucleophilicity was reported by Ritchie in 1972 [10] and is described by equation (5):

$$\lg k = \lg k_0 + N_+ \qquad (5)$$

where N_+ is the electrophile-independent nucleophilicity parameter.

The third attempt to quantify nucleophilicity was reported by Mayr and Patz in 1994 [10] in the form of equation (6):

$$\lg k = s_N \cdot (E + N) \qquad (6)$$

where:
s_N = solvent-dependent nucleophile-specific slope;
E = nucleophile-independent electrophilicity parameter;
N = electrophile-independent nucleophilicity parameter.

In 2002, while trying to unify the above relations, Mayr et al. [11] rewrote equation (6) in the form of equation (7):

$$\lg k = s_E \cdot s_N \cdot (E + N) \qquad (7)$$

with s_E = solvent-dependent electrophile-specific slope.

If s_E from equation (7) is replaced with $s_E = 1$ (the value for carbocations), the Mayr and Patz equation (6) is obtained. Furthermore if s_N from equation (6) is replaced with $s_N = 0.6$ ($s_N \approx 0.6$ for most *n*-nucleophiles), equation (8) is obtained [10]:

$$\lg k = 0.6E + 0.6N \qquad (8)$$

Ritchie equation (5) can be easily obtained from equation (8)[10].

If s_N from equation (7) is replaced with $s_N = 0.6$ ($s_N \approx 0.6$ for most *n*-nucleophiles), equation (9) is obtained [10]:

$$\lg k = 0.6 s_E \cdot E + 0.6 s_E \cdot N \qquad (9)$$

Swain and Scott equation (4) can be easily obtained from equation (9) [10].

A few years ago Jaramillo et al. [12] proposed an empirical nucleophilicity index based on the first order energy changes due to changes in the electron number. Assuming that N is the nucleophile and E is the electrophile, the empirical nucleophilicity index model proposed by Jaramillo et al. is described by equation (10):

$$\omega^- = \frac{1}{2}\left(\frac{\mu_N - \mu_E}{\eta_N + \eta_E}\right)^2 \eta_N \qquad (10)$$

* email: mihai.medeleanu@chim.upt.ro, Tel.: 0256 404219

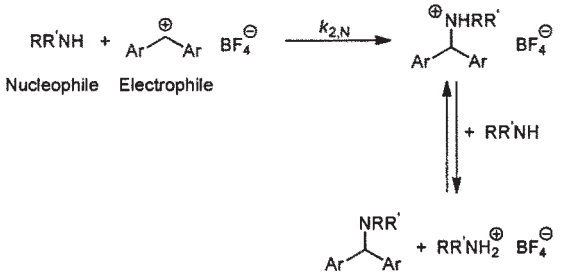

Fig. 1. Reaction mechanism [13]

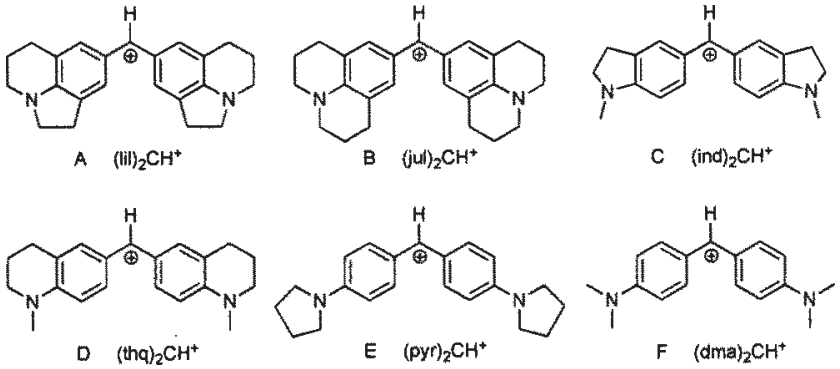

Fig. 2. Benzhydrylium cations used as electrophiles

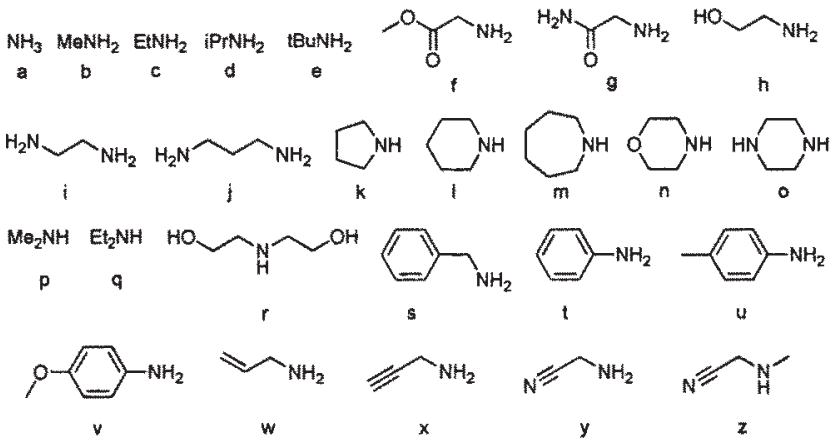

Fig. 3. Primary and secondary amines used as nucleophiles

where μ_N and μ_E are the corresponding electronic chemical potentials, while η_N and η_E are the chemical hardnesses.

The objectives of this paper were to test the empirical nucleophilicity index proposed by Jaramillo et al., on one hand, and elaboration of an improved nucleophilicity index based on LUMO and HOMO energies of the species involved in the reactions, similar in form with Mayr and Patz Equation (6), on the other hand. The study was made on the reactions of 26 (a-z) primary and secondary amines with 6 (A-F) benzhydrylium cations in water at 20°C [13]. The reaction evolve according to the mechanism [13] presented in figure 1.

Experimental part

Methods and materials

In figure 2 and figure 3 the selection of the electrophiles and the nucleophiles initially used by Brotzel [13] are depicted.

Full geometry optimization for the whole series of benzhydrylium cations and amines was performed at the B3LYP/6-31+G(d,p) level of theory implemented in the Gaussian 09 package [14].

Jaramillo empirical nucleophilicity index (10) was tested against kinetic data reported by Brotzel [13] and compared with the new nucleophilicity index proposed in this study (11).

$$\omega^* = E^* + N^* \quad (11)$$

where:

E* = electrophilicity parameter

N* = nucleophilicity parameter

$E^* = -\varepsilon_{LUMO\ E}$

$N^* = -\varepsilon_{HOMOE} - \varepsilon_{LUMO\ E}$ (E and N describing the electrophile and nucleophile respectively)

Results and discussions

The energies of the frontier molecular orbitals HOMO and LUMO were obtained after full geometry optimization of the involved species (N, E) and were used to calculate Jaramillo empirical nucleophilicity index ω^- and the nucleophilicity index ω^* proposed in this study.

While a plot of the logarithm of the experimental rate constant lgk versus the nucleophilicity index ω^- yields a linear correlation with r = 0.809 (fig. 4) and versus the nucleophilicity parameter N* yields a better linear correlation (r = 0.828, fig. 5), when plotting versus the nucleophilicity index ω^* it gives an even better linear correlation (r = 0.843, fig. 6,) for the one hundred and thirty two reactions considered in the study and presented in table 1.

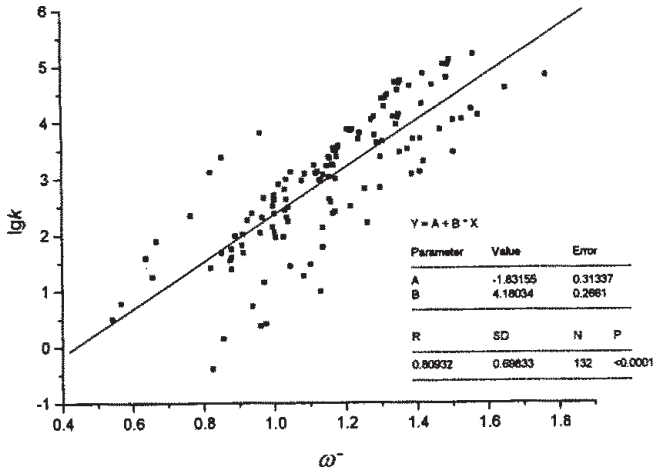

Fig. 4. Comparison between logarithm of the experimental rate constant lgk [13] and the calculated Jaramillo nucleophilicity index ω^-

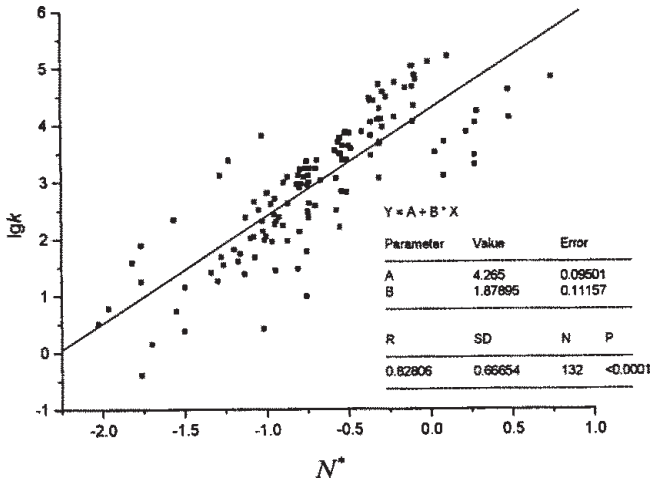

Fig. 5. Comparison between logarithm of the experimental rate constant lgk [13] and the calculated nucleophilicity parameter proposed in this study N*

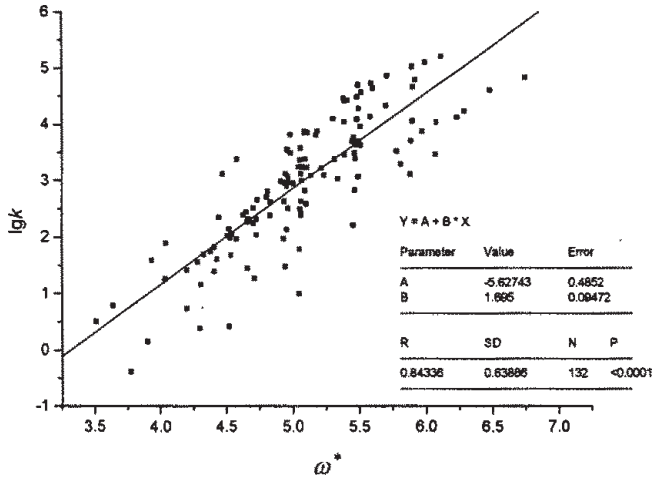

Fig. 6. Comparison between logarithm of the experimental rate constant lgk [13] and the calculated nucleophilicity index proposed in this study ω^-

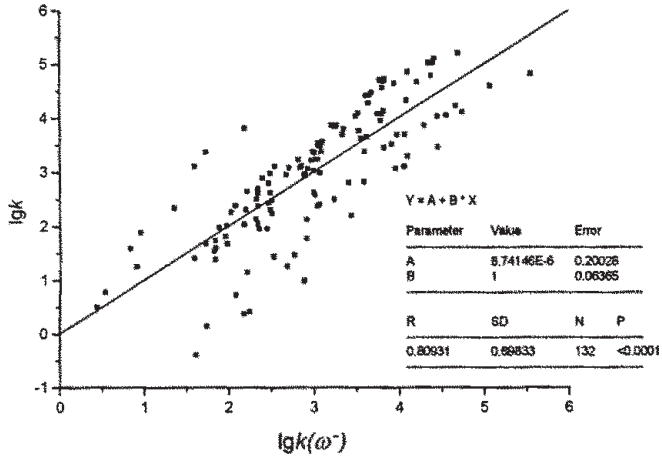

Fig. 7. Comparison between logarithm of the experimental rate constant lgk [13] and the calculated rate constant $lgk(\omega^-)$

The predictive character of the models was tested by plotting the logarithm of the experimental rate constant lgk versus the calculated rate constant $lgk(\omega^-)^-$, $lgk(N^*)$, $lgk(\omega^*)$ which gave similar results (figs.7- 9).

The calculated rate constant $lgk(\omega^-)$ is obtained by parametric equation from figure 4:

$$lgk(\omega^-)^- = -1.83155 + 4.18034 \cdot \omega^-$$

No.	Reaction	lgk	ε_{HOMO} (eV)	ε_{LUMO} (eV)	ε_{HOMO} E (eV)	ε_{LUMO} E (eV)	ω^* (eV)
1	A + a	-0.39041	-7.29679	0.43974	-7.95123	-5.53593	3.77507
2	B + a	0.14922	-7.29679	0.43974	-7.99477	-5.59933	3.90187
3	C + a	0.37840	-7.29679	0.43974	-8.21164	-5.79798	4.29916
4	D + a	0.73159	-7.29679	0.43974	-8.21219	-5.74791	4.19902
5	E + a	1.15534	-7.29679	0.43974	-8.32430	-5.80097	4.30515
6	F + a	1.26717	-7.29679	0.43974	-8.54308	-6.00261	4.70842
7	A + b	2.04532	-6.53405	0.06857	-7.95123	-5.53593	4.53781
8	B + b	2.30750	-6.53405	0.06857	-7.99477	-5.59933	4.66461
9	C + b	2.62737	-6.53405	0.06857	-8.21164	-5.79798	5.06190
10	D + b	2.96426	-6.53405	0.06857	-8.21219	-5.74791	4.96176
11	E + b	3.23553	-6.53405	0.06857	-8.32430	-5.80097	5.06789
12	F + b	3.62839	-6.53405	0.06857	-8.54308	-6.00261	5.47116
13	C + c	2.37291	-6.53731	0.11810	-8.21164	-5.79798	5.05864
14	E + c	2.98677	-6.53731	0.11810	-8.32430	-5.80097	5.06462
15	F + c	3.37840	-6.53731	0.11810	-8.54308	-6.00261	5.46790
16	B + d	1.44560	-6.54140	0.12082	-7.99477	-5.59933	4.65727
17	D + d	2.12710	-6.54140	0.12082	-8.21219	-5.74791	4.95442
18	E + d	2.40140	-6.54140	0.12082	-8.32430	-5.80097	5.06054
19	F + d	2.82607	-6.54140	0.12082	-8.54308	-6.00261	5.46382
20	A + e	0.41664	-6.55310	-0.01605	-7.95123	-5.53593	4.51876
21	C + e	0.99564	-6.55310	-0.01605	-8.21164	-5.79798	5.04285
22	D + e	1.47276	-6.55310	-0.01605	-8.21219	-5.74791	4.94272
23	E + e	1.77887	-6.55310	-0.01605	-8.32430	-5.80097	5.04884
24	F + e	2.20412	-6.55310	-0.01605	-8.54308	-6.00261	5.45212
25	B + f	1.60423	-6.76997	-0.27756	-7.99477	-5.59933	4.42869
26	D + f	2.30963	-6.76997	-0.27756	-8.21219	-5.74791	4.72584
27	E + f	2.61172	-6.76997	-0.27756	-8.32430	-5.80097	4.83196
28	F + f	3.08279	-6.76997	-0.27756	-8.54308	-6.00261	5.23524
29	A + g	1.38917	-6.66630	-0.28872	-7.95123	-5.53593	4.40556
30	B + g	1.67852	-6.66630	-0.28872	-7.99477	-5.59933	4.53236
31	C + g	1.96473	-6.66630	-0.28872	-8.21164	-5.79798	4.92965
32	D + g	2.37658	-6.66630	-0.28872	-8.21219	-5.74791	4.82951
33	E + g	2.62221	-6.66630	-0.28872	-8.32430	-5.80097	4.93564
34	F + g	3.02119	-6.66630	-0.28872	-8.54308	-6.00261	5.33892
35	A + h	1.54407	-6.79256	-0.10286	-7.95123	-5.53593	4.27930
36	B + h	1.81224	-6.79256	-0.10286	-7.99477	-5.59933	4.40610
37	D + h	2.50920	-6.79256	-0.10286	-8.21219	-5.74791	4.70325
38	E + h	2.80482	-6.79256	-0.10286	-8.32430	-5.80097	4.80938
39	F + h	3.21484	-6.79256	-0.10286	-8.54308	-6.00261	5.21265
40	A + i	1.95569	-6.49568	0.02095	-7.95123	-5.53593	4.57617
41	B + i	2.24055	-6.49568	0.02095	-7.99477	-5.59933	4.70298
42	C + i	2.57749	-6.49568	0.02095	-8.21164	-5.79798	5.10027
43	D + i	2.93802	-6.49568	0.02095	-8.21219	-5.74791	5.00013
44	E + i	3.22789	-6.49568	0.02095	-8.32430	-5.80097	5.10626
45	F + i	3.62221	-6.49568	0.02095	-8.54308	-6.00261	5.50953
46	A + j	2.13988	-6.55038	0.07238	-7.95123	-5.53593	4.52148
47	B + j	2.43616	-6.55038	0.07238	-7.99477	-5.59933	4.64829
48	D + j	3.11394	-6.55038	0.07238	-8.21219	-5.74791	4.94544
49	E + j	3.35793	-6.55038	0.07238	-8.32430	-5.80097	5.05156
50	F + j	3.76343	-6.55038	0.07238	-8.54308	-6.00261	5.45484
51	A + k	3.53275	-6.11091	0.10449	-7.95123	-5.53593	4.96095
52	B + k	3.86510	-6.11091	0.10449	-7.99477	-5.59933	5.08775
53	C + k	4.08636	-6.11091	0.10449	-8.21164	-5.79798	5.48504
54	D + k	4.41830	-6.11091	0.10449	-8.21219	-5.74791	5.38490
55	E + k	4.70586	-6.11091	0.10449	-8.32430	-5.80097	5.49103
56	F + k	5.02531	-6.11091	0.10449	-8.54308	-6.00261	5.89430
57	A + l	3.48430	-6.08805	0.09823	-7.95123	-5.53593	4.98380
58	B + l	3.84448	-6.08805	0.09823	-7.99477	-5.59933	5.11061
59	C + l	3.95472	-6.08805	0.09823	-8.21164	-5.79798	5.50790
60	D + l	4.42160	-6.08805	0.09823	-8.21219	-5.74791	5.40776
61	E + l	4.56585	-6.08805	0.09823	-8.32430	-5.80097	5.51389
62	F + l	4.78462	-6.08805	0.09823	-8.54308	-6.00261	5.91716
63	A + m	3.80414	-5.89567	0.04708	-7.95123	-5.53593	5.17619
64	B + m	4.08991	-5.89567	0.04708	-7.99477	-5.59933	5.30300
65	C + m	4.32838	-5.89567	0.04708	-8.21164	-5.79798	5.70029
66	D + m	4.64345	-5.89567	0.04708	-8.21219	-5.74791	5.60015
67	E + m	4.86273	-5.89567	0.04708	-8.32430	-5.80097	5.70627
68	F + m	5.20412	-5.89567	0.04708	-8.54308	-6.00261	6.10955
69	A + n	3.05690	-6.10737	-0.02857	-7.95123	-5.53593	4.96448
70	B + n	3.37291	-6.10737	-0.02857	-7.99477	-5.59933	5.09129
71	C + n	3.65418	-6.10737	-0.02857	-8.21164	-5.79798	5.48858
72	D + n	4.03342	-6.10737	-0.02857	-8.21219	-5.74791	5.38844
73	E + n	4.27646	-6.10737	-0.02857	-8.32430	-5.80097	5.49457
74	F + n	4.66370	-6.10737	-0.02857	-8.54308	-6.00261	5.89784
75	A + o	3.57287	-6.01404	-0.00299	-7.95123	-5.53593	5.05782
76	B + o	3.87390	-6.01404	-0.00299	-7.99477	-5.59933	5.18463
77	C + o	4.13354	-6.01404	-0.00299	-8.21164	-5.79798	5.58192
78	D + o	4.48287	-6.01404	-0.00299	-8.21219	-5.74791	5.48178
79	E + o	4.72754	-6.01404	-0.00299	-8.32430	-5.80097	5.58790
80	F+ 1o	5.10380	-6.01404	-0.00299	-8.54308	-6.00261	5.99118
81	A + p	3.54654	-6.11445	0.16354	-7.95123	-5.53593	4.95741
82	B + p	3.84880	-6.11445	0.16354	-7.99477	-5.59933	5.08422
83	C + p	4.07918	-6.11445	0.16354	-8.21164	-5.79798	5.48150
84	D + p	4.45788	-6.11445	0.16354	-8.21219	-5.74791	5.38137
85	E + p	4.68931	-6.11445	0.16354	-8.32430	-5.80097	5.48749
86	F + p	5.02119	-6.11445	0.16354	-8.54308	-6.00261	5.89077
87	A + q	2.49969	-6.10656	0.30423	-7.95123	-5.53593	4.96530
88	B + q	2.81023	-6.10656	0.30423	-7.99477	-5.59933	5.09211
89	C + q	3.06446	-6.10656	0.30423	-8.21164	-5.79798	5.48940
90	D + q	3.45332	-6.10656	0.30423	-8.21219	-5.74791	5.38926
91	E + q	3.68842	-6.10656	0.30423	-8.32430	-5.80097	5.49538
92	F + q	4.04922	-6.10656	0.30423	-8.54308	-6.00261	5.89866
93	D + r	2.95472	-6.55936	-0.11075	-8.21219	-5.74791	4.93646
94	E + r	3.23045	-6.55936	-0.11075	-8.32430	-5.80097	5.04258
95	F + r	3.68842	-6.55936	-0.11075	-8.54308	-6.00261	5.44586
96	A + s	1.97589	-6.54248	-0.43403	-7.95123	-5.53593	4.52937
97	B + s	2.26007	-6.54248	-0.43403	-7.99477	-5.59933	4.65618
98	C + s	2.48572	-6.54248	-0.43403	-8.21164	-5.79798	5.05347
99	D + s	2.89321	-6.54248	-0.43403	-8.21219	-5.74791	4.95333
100	E + s	3.11059	-6.54248	-0.43403	-8.32430	-5.80097	5.05945
101	F + s	3.48287	-6.54248	-0.43403	-8.54308	-6.00261	5.46273
102	C + t	3.10380	-5.71580	-0.30232	-8.21164	-5.79798	5.88015
103	D + t	3.51322	-5.71580	-0.30232	-8.21219	-5.74791	5.78002
104	E + t	3.69723	-5.71580	-0.30232	-8.32430	-5.80097	5.88614
105	F + t	4.23045	-5.71580	-0.30232	-8.54308	-6.00261	6.28942
106	C + u	3.45939	-5.52559	-0.28137	-8.21164	-5.79798	6.07036
107	D + u	3.86570	-5.52559	-0.28137	-8.21219	-5.74791	5.97023
108	E + u	4.02938	-5.52559	-0.28137	-8.32430	-5.80097	6.07635
109	F + 1u	4.60097	-5.52559	-0.28137	-8.54308	-6.00261	6.47963
110	A + v	3.29226	-5.26300	-0.34341	-7.95123	-5.53593	5.80886
111	D + v	4.11727	-5.26300	-0.34341	-8.21219	-5.74791	6.23282
112	F + v	4.82478	-5.26300	-0.34341	-8.54308	-6.00261	6.74222
113	A + w	1.74273	-6.69242	-0.24735	-7.95123	-5.53593	4.37943
114	B + w	2.01284	-6.69242	-0.24735	-7.99477	-5.59933	4.50624
115	D + w	2.69723	-6.69242	-0.24735	-8.21219	-5.74791	4.80339
116	E + w	2.98000	-6.69242	-0.24735	-8.32430	-5.80097	4.90952
117	F + w	3.37107	-6.69242	-0.24735	-8.54308	-6.00261	5.31279
118	A + x	1.40993	-6.87011	-0.25307	-7.95123	-5.53593	4.20174
119	B + x	1.68215	-6.87011	-0.25307	-7.99477	-5.59933	4.32855
120	C + x	2.03743	-6.87011	-0.25307	-8.21164	-5.79798	4.72584
121	D + x	2.38382	-6.87011	-0.25307	-8.21219	-5.74791	4.62570
122	E + x	2.65031	-6.87011	-0.25307	-8.32430	-5.80097	4.73183
123	F + x	3.07918	-6.87011	-0.25307	-8.54308	-6.00261	5.13510
124	A + y	0.50515	-7.56238	-0.71349	-7.95123	-5.53593	3.50948
125	B + y	0.78390	-7.56238	-0.71349	-7.99477	-5.59933	3.63629
126	C + y	1.25285	-7.56238	-0.71349	-8.21164	-5.79798	4.03358
127	D + y	1.59218	-7.56238	-0.71349	-8.21219	-5.74791	3.93344
128	E + y	1.88874	-7.56238	-0.71349	-8.32430	-5.80097	4.03956
129	F + y	2.34044	-7.56238	-0.71349	-8.54308	-6.00261	4.44284
130	D + z	3.11059	-7.02495	-0.57961	-8.21219	-5.74791	4.47087
131	E + z	3.37475	-7.02495	-0.57961	-8.32430	-5.80097	4.57699
132	F + z	3.81090	-7.02495	-0.57961	-8.54308	-6.00261	4.98027

Table 1

EXPERIMENTAL RATE CONSTANT OF THE REACTIONS [13], THE ENERGIES OF THE FRONTIER MOLECULAR ORBITALS FOR EACH ELECTROPHILE (A-F) AND NUCLEOPHILE (a-z) INVOLVED IN REACTIONS AND THE ω^* INDEX

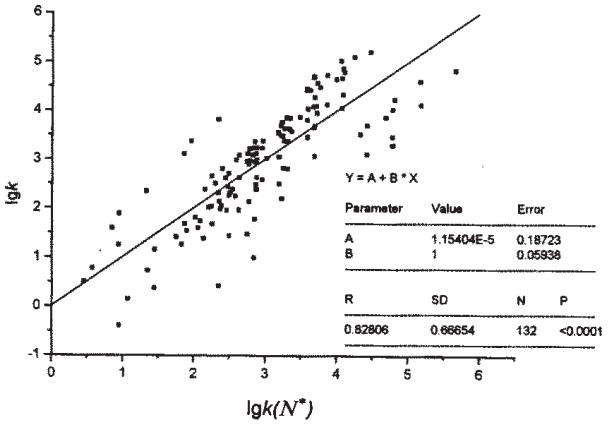

Fig. 8. Comparison between logarithm of the experimental rate constant lgk [13] and the calculated rate constant lgk(N*)

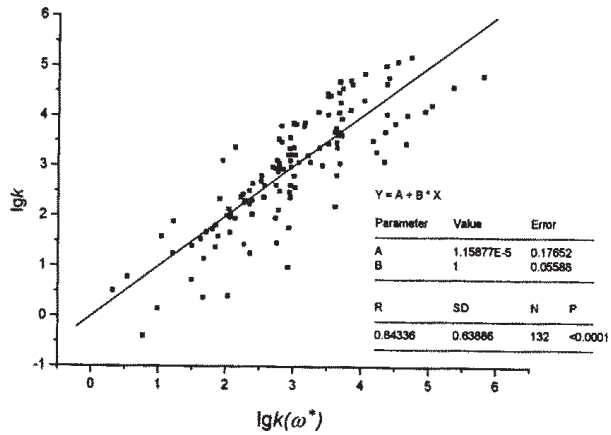

Fig. 9. Comparison between logarithm of the experimental rate constant lgk [13] and the calculated rate constant lgk(ω-)

The calculated rate constant lgk(N*) is obtained by parametric equation from figure 5:

$$lgk(N^*) = 4.26500 + 1.87895 \cdot N^*$$

The calculated rate constant lgk(ω^*) is obtained by parametric equation from figure 6:

$$lgk(\omega^*) = -5.62743 + 1.69500 \cdot \omega^*$$

Conclusions

The nucleophilicity index proposed in this study (ω^*) leads to better results than the empirical nucleophilicity index proposed by Jaramillo et al. The new index is formed by two terms, the electrophilicity parameter and the nucleophilicity parameter. The first is a nucleophile-independent electrophilicity parameter, expressed by LUMO energy of the electrophile. The second is an electrophile-dependent nucleophilicity parameter, expressed by the difference between HOMO energy of the nucleophile and LUMO energy of the electrophile. The next step of improvement of the proposed index could involve the solvent effect on both the electrophilicity and nucleophilicity parameters and the influence of the transition state (TS) and the intermediate species (I) for each reaction.

Acknowledgments: This work was partially supported by the strategic grant POSDRU/88/1.5/S/50783, Project ID50783 (2009), co-financed by the European Social Fund – Investing in People, within the Sectoral Operational Programme Human Resources Development 2007 – 2013.

References

1.A. C. LEGON, D. J. MILLEN, J. Am. Chem. Soc., **109**, 1987, p. 356;
2.A. C. LEGON, D. J. MILLEN, H.M. NORTH, J. Chem. Phys., **86**, 1987, p. 2530;
3.H. MAYR, K. H. MÜLLER, A. R. OFIAL, M. BÜHL, J. Am. Chem. Soc., **121**, 1999, p. 2418;
4.P. CAMPODÓNICO, J. G. SANTOS, J. ANDRES, R. CONTRERAS, J. Phys. Org. Chem., **17**, 2004, p. 273;
5.P. PÉREZ, A. TORO-LABBÉ, A. AIZMAN, R. CONTRERAS, J. Org. Chem., **67**, 2002, p. 4747 ;
6.P. JARAMILLO, L. R. DOMINGO, P. PÉREZ, Chem. Phys. Lett., **420**, 2006, p. 95;
7.H. MAYR, A. R. OFIAL, Tetrahedron Lett., **38**, 1997, p. 3503;
8.H. MAYR, A. R. OFIAL, J. Am. Chem. Soc., **123**, 2001, p. 9500;
9.R. G. PARR, L. SZENTP LY, S. LIU, J. Am. Chem. Soc., **121**, 1999, p. 1922;
10.T. B. PHAN, M. BREUGST, H. MAYR, Angew. Chem. Int. Ed., **45**, 2006, p. 3869;
11.R. LUCIUS, R. LOOS, H. MAYR, Angew. Chem., **114**, 2002, p. 97; Angew. Chem. Int. Ed., **41**, 2002, p. 91;
12.P. JARAMILLO, P. PÉREZ, W. TIZNADO, R. CONTRERAS, P. FUENTEALBA, J. Phys. Chem. A, **110**, 2006, p. 8181;
13.F. BROTZEL, Nucleophilicities of Amines, Amino Acids and Pyridines, Dissertation zur Erlangung des Doktorgrades (PhD Thesis), München, 2008;
14.M. J. FRISCH, G. W. TRUCKS, H. B. SCHLEGEL, G. E. SCUSERIA, M. A. ROBB, J. R. CHEESEMAN, G. SCALMANI, V. BARONE, B. MENNUCCI, G. A. PETERSSON, H. NAKATSUJI, M. CARICATO, X. LI, H. P. HRATCHIAN, A. F. IZMAYLOV, J. BLOINO, G. ZHENG, J. L. SONNENBERG, M. HADA, M. EHARA, K. TOYOTA, R. FUKUDA, J. HASEGAWA, M. ISHIDA, T. NAKAJIMA, Y. HONDA, O. KITAO, H. NAKAI, T. VREVEN, J. A. MONTGOMERY, JR., J. E. PERALTA, F. OGLIARO, M. BEARPARK, J. J. HEYD, E. BROTHERS, K. N. KUDIN, V. N. STAROVEROV, T. KEITH, R. KOBAYASHI, J. NORMAND, K. RAGHAVACHARI, A. RENDELL, J. C. BURANT, S. S. IYENGAR, J. TOMASI, M. COSSI, N. REGA, J. M. MILLAM, M. KLENE, J. E. KNOX, J. B. CROSS, V. BAKKEN, C. ADAMO, J. JARAMILLO, R. GOMPERTS, R. E. STRATMANN, O. YAZYEV, A. J. AUSTIN, R. CAMMI, C. POMELLI, J. W. OCHTERSKI, R. L. MARTIN, K. MOROKUMA, V. G. ZAKRZEWSKI, G. A. VOTH, P. SALVADOR, J. J. DANNENBERG, S. DAPPRICH, A. D. DANIELS, O. FARKAS, J. B. FORESMAN, J. V. ORTIZ, J. CIOSLOWSKI, AND D. J. FOX, Gaussian 09, Revision B.01, Gaussian, Inc., Wallingford CT, 201

Manuscript received: 21.01.2013