Physical Chemistry

The use of saturated vapor pressure at standard temperature in correlations of physicochemical properties

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The saturated vapor pressure (p_{st}) at the standard temperature can be a useful descriptor for correlations of physicochemical properties. Regression analysis of the standard heats of vaporization H_{st} of organic compounds, boiling temperatures T_b at the standard pressure, and the heats of vaporization at boiling temperature H_{vb} using the $\log p_{st}$ and $(\log p_{st})^2$ values as descriptors in combination with solvatochromic descriptors provided the regressions describing these properties for many organic compounds.

Key words: saturated vapor pressure, descriptor, regression analysis, heat of vaporization, boiling temperature, solvatochromic descriptors.

The physicochemical properties depend on the molecular structure and intermolecular interactions in a complicated manner. Therefore, a search for empirical structure—property correlations (SPC) based on statistical methods is an active area of investigation. Empirical regression models are often used for prediction of unknown values of the properties.[1,2] The most common SPC find use in prognostic computations for the properties of new compounds.[3—5] The quality of the SPC depends on descriptors used in the model, and the latter are often determined on the basis of the physicochemical parameters with some errors. The use of descriptors with a low accuracy increases errors in calculations of statistical models.

The saturated vapor pressure p is one of the most exactly measured physical properties of compounds. Usually a series of the p values is determined for the intervals of temperatures T and described by the $p = f(T)$ function. The parameters of the $p = f(T)$ functions for many compounds have been determined[1,6—10] in the temperature interval including the standard temperature (T_{st} = 298.15 K). Therefore, the saturation vapor pressure p_{st} (at T_{st}) can be calculated from these relations for several thousands of compounds.

This work was aimed at the construction of SPC in the framework of the regression model including the $\log p_{st}$ and $(\log p_{st})^2$ values as descriptors in combination with the solvatochromic descriptors.[11,12]

Calculation procedure

The $\log p_{st}$ values (Table 1) were calculated from the $p = f(T)$ relations for T_{st}. The parameters of the Antoine and Clausius—Clapeyron equations[1,6,7] were used for the temperature intervals including T_{st} in the calculation of $\log p_{st}$. The $\log p_{st}$ values determined earlier were used for some compounds.[13,14] The calculated $\log p_{st}$ values agree well with the latter.

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The solvatochromic descriptors (R_2, π_2^H, $\Sigma\alpha_2^H$, $\Sigma\beta_2^H$), estimating the ability of different compounds to intermolecular interactions with a medium, were taken from previously published works.[11,12] It is believed[15] that the excess molar refraction $R_2 = MR_X - MR_{alkane}$ (the difference between the molar refractions of the compound and alkane with the same V_X value) can characterize the interaction of n- and π-electrons of the compounds with the medium.[11] The π_2^H descriptor obtained at first from the solvatochromic shifts in the UV spectra of the indicator compounds was later refined[11] using the GLC data. It characterizes dipole-dipole interactions of the compounds with the medium. The $\Sigma\alpha_2^H$ and $\Sigma\beta_2^H$ descriptors, which were deter-

Table 1. The $\log p_{st}$ values for compounds with different structures (at 298.15 K)

Compound	$-\log(p_{st}/kbar)$	Refs.
Ethane (**1**)	1.387	7
Propane (**2**)	2.024	7
Butane (**3**)	2.614	6
2-Methylpropane (**4**)	2.458	7
Pentane (**5**)	3.165	7
2-Methylbutane (**6**)	3.040	7
2,2-Dimethylpropane (**7**)	2.766	7
Hexane (**8**)	3.695	6
2-Methylpentane (**9**)	3.549	6
3-Methylpentane (**10**)	3.596	6
2,2-Dimethylbutane (**11**)	3.371	6
2,3-Dimethylbutane (**12**)	3.504	7
Heptane (**13**)	4.215	7
2-Methylhexane (**14**)	4.056	7
3-Methylhexane (**15**)	4.085	6
2,2-Dimethylpentane (**16**)	3.853	6
2,3-Dimethylpentane (**17**)	4.037	7
2,4-Dimethylpentane (**18**)	3.882	7
3,3-Dimethylpentane (**19**)	3.956	6
Octane (**20**)	4.729	7
2-Methylheptane (**21**)	4.561	6
3-Methylheptane (**22**)	4.586	7
2,2,4-Trimethylpentane (**23**)	4.181	6
2,3,4-Trimethylpentane (**24**)	4.443	6
Nonane (**25**)	5.236	7
2,2,5-Trimethylhexane (**26**)	4.656	6
n-Decane (**27**)	5.738	7
n-Undecane (**28**)	6.242	7
n-Dodecane (**29**)	6.754	7
n-Tridecane (**30**)	7.276	7
n-Tetradecane (**31**)	7.806	7
n-Pentadecane (**32**)	8.351	7
n-Octadecane (**33**)	10.011	7
n-Nonadecane (**34**)	10.579	7
Eucosane (**35**)	11.172	7
Cyclopropane (**36**)	2.140	7
Cyclobutane (**37**)	2.805	6
Cyclopentane (**38**)	3.371	7
Methylcyclopentane (**39**)	3.737	7
Ethylcyclopentane (**40**)	4.274	6
Propylcyclopentane (**41**)	4.783	7
Cyclohexane (**42**)	3.886	7
Methylcyclohexane (**43**)	4.209	6
Z-1,2-Dimethylcyclohexane (**44**)	4.715	6
E-1,4-Dimethylcyclohexane (**45**)	4.519	6
Z-Decalin (**46**)	6.007	7
E-Decalin (**47**)	5.841	7
Ethene (**48**)	1.168	7
Propene (**49**)	1.940	7
But-1-ene (**50**)	2.527	7
Pent-1-ene (**51**)	3.070	7
Z-Pent-2-ene (**52**)	3.180	7
3-Methylbut-1-ene (**53**)	2.919	6
2-Methylbut-2-ene (**54**)	3.206	6
Hex-1-ene (**55**)	3.605	6
Hept-1-ene (**56**)	4.124	6
Oct-1-ene (**57**)	4.635	7
Non-1-ene (**58**)	5.147	7
Buta-1,3-diene (**59**)	2.552	7
2-Methylbuta-1,3-diene (**60**)	3.134	6
Penta-1,4-diene (**61**)	3.009	6
Hexa-1,5-diene (**62**)	3.557	6
Cyclopentene (**63**)	3.295	7
Cyclohexene (**64**)	3.926	7
1-Methylcyclohexene (**65**)	4.389	7
Cycloheptene (**66**)	4.477	7
Ethyne (**67**)	1.308	7
Propyne (**68**)	2.253	6
But-1-yne (**69**)	2.726	6
Pent-1-yne (**70**)	3.240	7
Hex-1-yne (**71**)	3.741	7
Hept-1-yne (**72**)	4.155	7
Oct-1-yne (**73**)	4.741	7
Fluoroethane (**74**)	2.065	7
Chloromethane (**75**)	2.240	7
Dichloromethane (**76**)	3.235	7
Trichlorofluoromethane (**77**)	2.974	6
Trichloromethane (**78**)	3.568	7
Tetrachloromethane (**79**)	3.812	7
Chloroethane (**80**)	2.796	7
1,1-Dichloroethane (**81**)	3.517	6
1,2-Dichloroethane (**82**)	3.976	7
1,1,1-Trichloroethane (**83**)	3.784	7
1,1,2-Trichloroethane (**84**)	4.523	7
1,1,2,2-Tetrachloroethane (**85**)	5.076	7
Pentachloroethane (**86**)	5.214	7
1-Chloropropane (**87**)	3.343	7
2-Chloropropane (**88**)	3.151	7
1,2-Dichloropropane (**89**)	4.179	7
1,3-Dichloropropane (**90**)	4.614	13
1-Chlorobutane (**91**)	3.865	7
2-Chlorobutane (**92**)	3.694	6

(*to be continued*)

Table 1 (*continued*)

Compound	$-\log(p_{st}/\text{kbar})$	Refs.
2-Chloro-2-methylpropane (**93**)	3.577	6
1-Chloropentane (**94**)	4.383	13
Z-1,2-Dichloroethene (**95**)	3.554	7
E-1,2-Dichloroethene(**96**)	3.357	7
Trichloroethene (**97**)	4.004	7
Tetrachloroethene (**98**)	4.609	7
1-Chloropropyl-2-ene (**99**)	3.317	6
Bromomethane (**100**)	2.662	7
Dibromomethane (**101**)	4.230	13
Tribromomethane (**102**)	5.079	13
Bromoethane (**103**)	3.207	7
1,2-Dibromoethane (**104**)	4.814	7
1-Bromopropane (**105**)	3.735	7
2-Bromopropane (**106**)	3.541	7
1-Bromobutane (**107**)	4.259	13
1-Bromo-2-methylpropane (**108**)	4.036	13
1-Bromopentane (**109**)	4.804	14
Iodomethane (**110**)	3.262	7
Iodoethane (**111**)	3.741	13
1-Iodopropane (**112**)	4.238	7
1-Iodobutane (**113**)	4.733	13
Dimethyl ether (**114**)	2.207	6
Methyl ethyl ether (**115**)	2.849	7
Diethyl ether (**116**)	3.147	6
Dipropyl ether (**117**)	4.062	7
Di-*iso*-propyl ether (**118**)	3.709	6
Dibutyl ether (**119**)	5.063	6
Furan (**120**)	3.097	6
Tetrahydrofuran (**121**)	3.665	6
1,4-Dioxane (**122**)	4.272	7
Formaldehyde (**123**)	2.291	6
Acetaldehyde (**124**)	2.908	7
Propanal (**125**)	3.372	6
Butanal (**126**)	3.847	7
iso-Butanal (**127**)	3.638	6
Pentanal (**128**)	4.339	6
Hexanal (**129**)	4.864	14
Heptanal (**130**)	5.424	14
Propanone (**131**)	3.513	6
Butan-2-one (**132**)	3.897	7
Pentan-2-one (**133**)	4.284	7
Pentan-3-one (**134**)	4.314	6
3-Methylbutan-2-one (**135**)	4.144	7
Hexan-2-one (**136**)	4.791	7
4-Methylpentan-2-one (**137**)	4.556	7
Heptan-2-one (**138**)	5.283	7
Octan-2-one (**139**)	5.836	9
Decan-2-one (**140**)	6.446	9
Cyclopentanone (**141**)	4.866	6
Cyclohexanone (**142**)	5.204	14
Methyl formate (**143**)	3.095	7
Ethyl formate (**144**)	3.487	7
Propyl formate (**145**)	3.941	7
iso-Propyl formate (**146**)	3.721	7
Butyl formate (**147**)	4.408	7
iso-Butyl formate (**148**)	4.242	7
iso-Pentyl formate (**149**)	4.690	13
Vinyl formate (**150**)	3.392	13
Methyl acetate (**151**)	3.539	6
Ethyl acetate (**152**)	3.889	6
Propyl acetate (**153**)	4.358	6
iso-Propyl acetate (**154**)	4.086	8
Butyl acetate (**155**)	4.822	6
iso-Butyl acetate (**156**)	4.641	6
Pentyl acetate (**157**)	5.268	7
iso-Pentyl acetate (**158**)	5.134	14
Methyl propionate (**159**)	3.943	6
Ethyl propionate (**160**)	4.303	6
Propyl propionate (**161**)	4.693	7
Methyl butyrate (**162**)	4.366	13
Ethyl butyrate (**163**)	4.634	6
Propyl butyrate (**164**)	5.224	14
iso-Butyl *iso*-butyrate (**165**)	5.204	14
Vinyl acetate (**166**)	3.812	7
Acetonitrile (**167**)	3.888	7
Propionitrile (**168**)	4.201	6
Butyronitrile (**169**)	4.582	6
Valeronitrile (**170**)	4.994	14
Ammonia (**171**)	2.007	6
Methylamine (**172**)	2.447	6
Ethylamine (**173**)	2.849	6
Propylamine (**174**)	3.379	6
Butylamine (**175**)	3.912	6
Pentylamine (**176**)	4.336	13
Hexylamine (**177**)	4.816	13
Octylamine (**178**)	5.746	6
Dimethylamine (**179**)	2.706	6
Diethylamine (**180**)	3.504	7
Dipropylamine (**181**)	4.493	6
Dibutylamine (**182**)	5.516	6
Trimethylamine (**183**)	2.618	7
Triethylamine (**184**)	3.980	7
Pyrrole (**185**)	4.958	6
Pyrrolidine (**186**)	4.075	6
Piperidine (**187**)	4.408	6
Morpholine (**188**)	4.871	7
Nitromethane (**189**)	4.321	7
Nitroethane (**190**)	4.564	14
1-Nitropropane (**191**)	4.866	13
2-Nitropropane (**192**)	4.634	13
N,N-Dimethylformamide (**193**)	5.266	13
Formic acid (**194**)	4.243	6
Acetic acid (**195**)	4.674	7
Propionic acid (**196**)	5.243	7
Butyric acid (**197**)	5.854	6
Water (**198**)	4.485	7
Methanol (**199**)	3.680	7
Ethanol (**200**)	4.103	6
Propan-1-ol (**201**)	4.564	6

(*to be continued*)

Table 1 (*continued*)

Compound	$-\log(p_{st}/\text{kbar})$	Refs.
Propan-2-ol (**202**)	4.220	6
Butanol (**203**)	5.086	6
2-Methylpropan-1-ol (**204**)	4.858	6
Butan-2-ol (**205**)	4.614	6
2-Methylpropan-2-ol (**206**)	4.252	6
Pentanol (**207**)	5.503	6
2-Methylbutan-1-ol (**208**)	5.381	6
3-Methylbutan-1-ol (**209**)	5.390	6
2-Methylbutan-2-ol (**210**)	4.740	6
Hexanol (**211**)	5.960	6
Hexan-3-ol (**212**)	5.214	14
2-Methylpentan-2-ol (**213**)	4.964	14
4-Methylpentan-2-ol (**214**)	5.138	13
2-Methylpentan-3-ol (**215**)	5.165	13
Heptanol (**216**)	6.294	14
Octanol (**217**)	6.874	14
Nonanol (**218**)	7.314	14
Decanol (**219**)	7.724	14
Cyclopentanol (**220**)	5.484	14
Cyclohexanol (**221**)	5.655	13
Allyl alcohol (**222**)	4.503	6
Methylmercaptane (**223**)	2.694	6
Ethylmercaptane (**224**)	3.145	7
Propylmercaptane (**225**)	3.680	7
Butylmercaptane (**226**)	4.224	14
Dimethyl sulfide (**227**)	3.190	6
Methyl ethyl sulfide (**228**)	3.676	7
Diethyl sulfide (**229**)	4.109	6
Dipropyl sulfide (**230**)	5.064	14
Thiophene (**231**)	3.974	7
2-Methylthiophene (**232**)	4.261	7
Diethyl disulfide (**233**)	5.248	6
Carbon disulfide (**234**)	3.317	6
Benzene (**235**)	3.896	7
Toluene (**236**)	4.421	7
Ethylbenzene (**237**)	4.916	7
o-Xylene (**238**)	5.049	7
m-Xylene (**239**)	4.951	7
p-Xylene (**240**)	4.928	7
Propylbenzene (**241**)	5.340	7
iso-Propylbenzene (**242**)	5.208	7
1,2,3-Trimethylbenzene (**243**)	5.686	7
1,2,4-Trimethylbenzene (**244**)	5.553	7
1,3,5-Trimethylbenzene (**245**)	5.479	7
2-Ethyltoluene (**246**)	5.473	7
4-Ethylbenzene (**247**)	5.396	7
Butylbenzene (**248**)	5.840	7
iso-Butylbenzene (**249**)	5.589	7
sec-Butylbenzene (**250**)	5.602	7
tert-Butylbenzene (**251**)	5.531	7
Pentylbenzene (**252**)	6.359	7
Pentamethylbenzene (**253**)	6.859	7
Hexylbenzene (**254**)	6.854	7
Styrene (**255**)	5.104	7
α-Methylstyrene (**256**)	5.477	7
Biphenyl (**257**)	7.842	1
Naphthalene (**258**)	6.546	7
1-Methylnaphthalene (**259**)	7.048	7
Diphenylmethane (**260**)	7.642	7
Indane (**261**)	5.618	1
Acenaphthene (**262**)	8.416	1
Fluorobenzene (**263**)	4.004	7
Chlorobenzene (**264**)	4.805	7
1,2-Dichlorobenzene (**265**)	5.726	7
1,3-Dichlorobenzene (**266**)	5.600	7
1,4-Dichlorobenzene (**267**)	5.644	7
1,2,4-Trichlorobenzene (**268**)	6.412	7
2-Chlorotoluene (**269**)	5.317	7
Bromobenzene (**270**)	5.253	7
Iodobenzene (**271**)	5.876	7
Anisol (**272**)	5.341	6
Phenetol (**273**)	5.726	6
Benzaldehyde (**274**)	5.790	6
Acetophenone (**275**)	6.305	7
Methyl benzoate (**276**)	6.277	7
Ethyl benzoate (**277**)	6.640	6
Benzonitrile (**278**)	5.954	14
Aniline (**279**)	6.048	7
o-Toluidine (**280**)	6.374	7
m-Toluidine (**281**)	6.436	7
p-Toluidine (**282**)	6.349	7
2-Chloroaniline (**283**)	6.472	7
3-Chloroaniline (**284**)	6.952	7
N-Methylaniline (**285**)	6.295	6
Nitrobenzene (**286**)	6.421	7
2-Nitrotoluene (**287**)	6.553	13
Phenol (**288**)	6.346	7
o-Cresol (**289**)	6.420	7
p-Cresol (**290**)	6.579	7
3-Ethylphenol (**291**)	7.070	7
4-Ethylphenol (**292**)	7.014	7
Benzyl alcohol (**293**)	6.757	6
Thiophenol (**294**)	5.411	7
Pyridine (**295**)	4.558	6
4-Methylpyridine (**296**)	5.12	6
Tetramethyltin (**297**)	3.813	7

mined[11] using the constants of formation of 1 : 1 complexes with the hydrogen bond in CCl_4, serve for the estimation of intermolecular interactions of the compounds with formation of hydrogen bonds by proton-donating ($\Sigma\alpha_2^H$) and proton-withdrawing ($\Sigma\beta_2^H$) groups.

The V_X and $\log L^{16}$ descriptors are used in combination with the solvatochromic descriptors. The V_X descriptor represents the molar volume ($1 \cdot 10^{-2}$ cm^3 mol^{-1}) calculated from the additive increments.[11] In the $\log L^{16}$ descriptor the L^{16} value is the partition coefficient of the compounds in the gas—hexadecane system.[12] The V_X and L^{16} descriptors serve to take into account the influence of the energy of cavity formation on the intermolecular interaction of the compounds with the medium. Both descriptors were also taken from the previously published works.[11,12]

The multiple regressions were calculated by the least-squares method using the STATGRAPHICS *Plus* program. The statistical qualities of the obtained regressions reflect the number of compounds in the subset n, the standard deviation for the subset s, the multiple correlation coefficient (calculated taking into account the number of degrees of freedom) r, and the statistical Fischer criterion F.

Results and Discussion

Unlike the critical pressure p_c, the p_{st} value is not almost used for SPC construction because tabulated p_{st} values are lacking from the reference literature.[6] The $\log(p_{st}/\text{kbar})$ values for 297 compounds (see Table 1) change in the interval >10 logarithmic units. This indicates that the $\log p_{st}$ parameter depends strongly on the structure of compounds. The following multiple regression reflects the influence of the volume of molecules and intermolecular interactions on the $\log p_{st}$ value:

$$\log p_{st} = (-0.375\pm0.069) - (0.861\pm0.057)R_2 - (1.786\pm0.061)\pi_2^H - (6.03\pm0.20)(\Sigma\alpha_2^H \cdot \Sigma\beta_2^H) - (2.97\pm0.11)V_X - (0.251\pm0.043)V_X^2, \quad (1)$$

$$n = 296,\ s = 0.22,\ r = 0.988,\ F = 2320.$$

The negative coefficients at the descriptors in Eq. (1) indicate that an increase in all types of intermolecular interactions and an increase in the volume of molecules decrease p_{st}. The presence of the quadratic term V_X^2 and descriptor product $(\Sigma\alpha_2^H \cdot \Sigma\beta_2^H)$ in regression (1) points to a nonadditive change in $\log p_{st}$ in a wide variety of the structure of organic compounds (see Table 1). The $\log p_{st}$ and $(\log p_{st})^2$ values can serve as descriptors for the correlation of the physicochemical properties and thermodynamic parameters of organic compounds, as shown below for several examples.

Standard heats of vaporization H_{st}. The Clausius—Clapeyron equation $\ln p = -H_v/RT + C$ reflects the linear dependence of the heat of vaporization H_v on $\ln p$ when accepting that H_v is independent of T (H_v = const).[6] The latter condition is fulfilled for all compounds at small changes in T. Taking into account this fact, it is reasonable to use the $\log p_{st}$ value (see Table 1) as a descriptor for the H_{st} parameter in the regression model.

The H_{st} value (at 298.15 K)[1] in the interval of 4.1—19.5 kcal mol^{-1} for liquid organic compounds is described by the regression

$$H_{st} = (0.45\pm0.21) - (0.401\pm0.083)R_2 + (9.94\pm0.34)(\Sigma\alpha_2^H \cdot \Sigma\beta_2^H) - (1.785\pm0.094)\log p_{st} + (0.0461\pm0.0097)(\log p_{st})^2, \quad (2)$$

$$n = 202,\ s = 0.28,\ r = 0.995,\ F = 4942,$$

which includes the $\log p_{st}$ and $(\log p_{st})^2$ values along with the solvatochromic descriptors. The subset included all classes of compounds presented in Table 1. The use of the solvatochromic descriptors in the regression model is necessary to take into account different effects of intermolecular interactions on the $\log p_{st}$ and H_{st} parameters. The statistical regression parameters based on the $\log p_{st}$ and $(\log p_{st})^2$ descriptors are much worse (n = 201, s = 0.69, r = 0.970) when ignoring the R_2 and $\Sigma\alpha_2^H \cdot \Sigma\beta_2^H$ terms.

The V_X and $\log L^{16}$ descriptors are commonly used[11,12,15] in SPC in combination with the solvatochromic descriptors. The replacement of the $\log p_{st}$ and $(\log p_{st})^2$ descriptors in regression (2) by the V_X and V_X^2 descriptors worsens considerably the statistical qualities (n = 201, s = 1.1, r = 0.925), as also does their replacement by $\log L^{16}$ and $(\log L^{16})^2$, which gives analogous results (n = 200, s = 0.85, r = 0.954). The worst statistical qualities in the latter two cases are induced in part by a less accuracy in determination of the V_X and $\log L^{16}$ values than that for $\log p_{st}$.

Regression (2) suggests a nonadditive change in the H_{st} value in variation of the structure of organic compounds. Due to this, the earlier proposed[1,16,17] methods for prediction of H_{st} on the basis of additive increments can result in errors in prognosis, in particular, for compounds with a high proton-donating or proton-withdrawing ability, *i.e.*, high $\Sigma\alpha_2^H \cdot \Sigma\beta_2^H$ values.

Boiling temperatures of liquids. Normal boiling temperatures of liquids T_b have received the most study among the physical properties. The T_b values for 293 organic compounds of different structures in the interval from 169 to 616 K (see Refs. 6, 7, and 18) are described by the multiple regression

$$T_b = (85.4\pm1.7) + (6.81\pm0.84)R_2 - (92.3\pm4.0)(\Sigma\alpha_2^H \cdot \Sigma\beta_2^H) - (79.89\pm0.69)\log p_{st} - (2.954\pm0.062)(\log p_{st})^2, \quad (3)$$

$$n = 293,\ s = 4.0,\ r = 0.998,\ F = 23256,$$

containing the $\log p_{st}$ and $(\log p_{st})^2$ values as descriptors and the solvatochromic descriptors.

In the calculation of regression (3), the T_b values for carboxylic acids (see Table 1, compounds **194—197**) were not included into the subset because they give unusually large deviations from the values calculated using Eq. (3). In the absence of the R_2 and $\Sigma\alpha_2^H \cdot \Sigma\beta_2^H$ terms, the statistical qualities of regression based on the $\log p_{st}$ and $(\log p_{st})^2$ descriptors are much worse (n = 293, s = 7.1, r = 0.995). The replacement of the $\log p_{st}$ and $(\log p_{st})^2$ descriptors in regression (3) by V_X and V_X^2 or $\log L^{16}$ and $(\log L^{16})^2$ also worsen the statistical qualities (n = 292, s = 25, r = 0.936 and n = 289, s = 18, r = 0.967, respectively).

Regression (3) allows the prediction of the T_b values for organic compounds with a mean error of ±0.7%, *i.e.*, at the level of errors of other modern methods for estimation of these values.[19,20]

Heats of vaporization at the boiling temperature. Heats of vaporization at the boiling temperatures of liquids H_{vb} are of great practical significance. The H_{vb} values (kcal mol^{-1}) for various organic compounds in the interval from 3.2 to 13.7 kcal mol^{-1} (see Ref. 6) are described by the multiple regression

$$H_{vb} = (1.41\pm0.12) - (0.190\pm0.066)R_2 + \\ + (7.38\pm0.29)(\Sigma\alpha_2^H \cdot \Sigma\beta_2^H) - (1.750\pm0.048)\log p_{st} - \\ - (0.0599\pm0.0042)(\log p_{st})^2, \quad (4)$$

$n = 208$, $s = 0.25$, $r = 0.991$, $F = 2893$.

Like regressions (1)—(3), Eq. (4) reflects the nonadditive change in the H_{vb} values for the compounds included into the subset. The H_{vb} values for carboxylic acids (see Table 1, compounds **194—197**), which result in high systematical deviations from Eq. (4), were not either used in the calculation of regression (4).

When the R_2 and $\Sigma\alpha_2^H \cdot \Sigma\beta_2^H$ descriptors are excluded from regression (4), the statistical qualities of the two-parameter regression with the $\log p_{st}$ and $(\log p_{st})^2$ descriptors become much worse ($n = 208$, $s = 0.52$, $r = 0.963$). The replacement of the $\log p_{st}$ and $(\log p_{st})^2$ descriptors in regression (4) by V_X and V_X^2 or $\log L^{16}$ and $(\log L^{16})^2$ substantially worsen the statistical qualities ($n = 208$, $s = 0.69$, $r = 0.932$ и $n = 205$, $s = 0.55$, $r = 0.958$, respectively).

This study showed the applicability of the p_{st} parameter in the corresponding $\log p_{st}$ and $(\log p_{st})^2$ forms for using in the SPC. Unlike the earlier published works,[1,16,17,21] regressions (1)—(4) suggest that the $\log p_{st}$, H_{st}, T_b, and H_{vb} parameters are nonadditive in a wide variety of the structures of organic compounds. The new regression model including the $\log p_{st}$ and $(\log p_{st})^2$ values as descriptors in combination with the solvatochromic descriptors provides the best statistical qualities compared to the models in which V_X and V_X^2 or $\log L^{16}$ and $(\log L^{16})^2$ serve as descriptors instead of $\log p_{st}$ and $(\log p_{st})^2$. Using very wide subsets, regressions (1)—(4) describe the properties of organic compounds with different structures. The only exceptions for regressions (3) and (4) are compounds with an enhanced proton-donating ability (carboxylic acids), while the description of similar compounds by regressions (1) and (2) is the same as that for organic compounds of other classes.

Regressions (2)—(4) with good statistical qualities are appropriate for using in the systems for prognosis of physicochemical properties. Solvatochromic descriptors of organic compounds necessary for the application of these regressions are presented in several works.[11,12,22] The system of additive increments for the calculation of the solvatochromic descriptors on the basis of the structure of organic compounds has recently been developed.[23] Two models of the SPC for prediction of the p_{st} values for organic compounds on the basis of molecular structures have also been proposed.[24]

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