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PHYSICOCHEMICAL STUDIES OF SYSTEMS AND PROCESSES

Influence of the Molecular Structure on the Phase Transition Temperatures of Mononuclear Aromatic Compounds

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Abstract—Boiling and melting points in relation to the molecular structure were examined for 60 mononuclear aromatic compounds. Phase transition temperatures were analyzed as influenced by the structural isomerism and symmetry of the molecules.

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Aromatic compounds (benzene, toluene, xylenes) play an important role in science and technology. They find extensive and diverse application as solvents, in particular, in preparation of medicines, explosives (e.g., trotyl), plastics, photodevelopers, dyes, and many other compounds [1, 2]. Of much significance in choosing solvents for specific applications are their phase transition temperatures, boiling and melting points.

The boiling T_b and melting T_m points in relation to the molecular structure were analyzed for the first time for fairly simple compounds, hydrides of various elements, by Pauling in the 1940s and discussed in a number of monographs [3, 4]. Kitaigorodskii [5, 6], Bokii [7], and Kotel'nikova and Filatov [8] carried out crystal-chemical analysis of the structure and properties of various crystalline substances.

This research line underwent vigorous development in the years that followed, as suggested by tens of relevant theoretical, semiempirical, calculational, and experimental studies, which can be conditionally subdivided into two large groups.

The first group integrates studies that attempted establishing relationships for a set of molecular characteristics of a substance ("descriptors") and predicting their boiling (or melting) point in the most general form. Examples can be found in studies by Meissner [9], Todos et al. [10–12], Lydersen [13], Joback et al. [14], Somayajuluy [15], and other. Of much significance for those studies was the so-called "group contributions" method [16, 17].

Virtually all the generalizing studies employed the parachor concept [18]. For example, Meissner established a semiempirical relationship [9]

$$T_b = (637\, R_D^{1.27} + B)/P, \quad (1a)$$

where R_D is the molecular refraction for the D line of Na; B, constant for a specific class of compounds; and $P = M\sigma^{1/4}(\rho_1 - \rho_2)$. In the latter expression, P is parachor; M, molecular weight of the substance; σ, surface tension, dyne cm^{-1}; and ρ_1 and ρ_2, densities of the liquid and vapor, respectively, g cm^{-3}, at temperatures distant from the critical point. In this case $\rho_1 >> \rho_2$ and

$$P \approx V_1\sigma^{1/4}, \quad (1b)$$

where V_1/ρ_1 is the molar volume of the liquid.

Parachor is temperature-independent and exhibits the additivity property: The molar parachor (parachor per mole of substance) is the sum of the parachors of the atoms or molecular groups constituting the molecule.

Using relationship (1b), Steraski and Machwart [19] plotted a nomogram for determining T_b under

Characteristics of a series of mononuclear aromatic compounds[a]

No.	Compound	Formula	M [43]	T_m [43], °C	d_4^{20} [43, 44], mg mm^{-3}	T_b [43], °C	δ [43], D
1	Benzene	C_6H_6	78.11	5.53	0.879	80.1	0
2	Toluene	$C_6H_5CH_3$	92.15	–95	0.8669	110.6	0.39
3	Aminobenzo(aniline)	$C_6H_5NH_2$	93.12	–6.0	1.02173	184.4	1.51
4	Phenol	C_6H_5OH	94.108	40.9	1.057[b]	181.75	1.73
5	Fluorobenzene	C_6H_5F	96.10	–42.2	1.0240	84.7	1.47
6	Styrene	$C_6H_5CH{=}CH_2$	104.14	–30.6	0.90600	145.2	0.12
7	Ethylbenzene	$C_6H_5CH_2CH_3$	106.16	–94.975	0.86702	135.19	0.35
8	*o*-Xylene	$C_6H_4(CH_3)_2$	106.17	–25.18	0.8802	144.41	0.62
9	*m*-Xylene	$C_6H_4(CH_3)_2$	106.17	–47.87	0.8642	139.10	0.37
10	*p*-Xylene	$C_6H_4(CH_3)_2$	106.17	13.26	0.8611	138.35	0
11	*o*-Toluidine	$CH_3C_6H_4NH_2$	107.150	–16.25	0.99843	200.30	1.60
12	*m*-Toluidine	$CH_3C_6H_4NH_2$	107.150	–30.40	0.99302	203.40	1.45
13	*p*-Toluidine	$CH_3C_6H_4NH_2$	107.150	43.75	0.96589	200.55	1.52
14	Anisole	$C_6H_5OCH_3$	108.1	–37.5	0.99402	153.75	1.20
15	*o*-Cresol	$CH_3C_6H_4OH$	108.134	30.94	1.0273[b]	190.95	1.41
16	*m*-Cresol	$CH_3C_6H_4OH$	108.134	11.95	1.0380[b]	202.70	1.543
17	*p*-Cresol	$CH_3C_6H_4OH$	108.134	34.78	1.0179[b]	201.88	1.543
18	Benzyl alcohol	$C_6H_5CH_2OH$	108.134	–15.3	1.04127[b]	205.45	1.66
19	*o*-Fluorotoluene	$CH_3C_6H_5F$	110.13	–62.0	–	114.40	1.35
20	*m*-Fluorotoluene	$CH_3C_6H_5F$	110.13	–87.7	0.9974	116.5	1.85
21	*p*-Fluorotoluene	$CH_3C_6H_5F$	110.13	–56.8	0.9975	116.6	2.01
22	Chlorobenzene	C_6H_5Cl	112.557	–45.58	1.10630	131.7	1.56
23	Acetophenone (acetylbenzene)	$C_6H_5C(O)CH_3$	120.14	19.6	1.02810	202.1	2.77
24	Isopropylbenzene	$C_6H_5CH(CH_3)_2$	120.186	–96.028	0.86179	152.39	–
25	Nitrobenzene	$C_6H_5NO_2$	123.108	5.76	1.20824[b]	210.80	3.99
26	*o*-Chlorotoluene[b]	$ClC_6H_4CH_3$	126.586	–35.1	1.0825	159.1	–
27	*m*-Chlorotoluene[b]	$ClC_6H_4CH_3$	126.586	–47.8	1.0722	162	–
28	*p*-Chlorotoluene[b]	$ClC_6H_4CH_3$	126.586	7.5	1.069	162	–
29	*o*-Chloroaniline[b]	$ClC_6H_4NH_2$	127.57	–1.94	1.21251	208.84	1.81
30	2-Chlorophenol[b]	ClC_6H_4OH	128.558	8.7	1.235	175–176	–
31	3-Chlorophenol[b]	ClC_6H_4OH	128.558	32.8	–	214	–
32	4-Chlorophenol[b]	ClC_6H_4OH	128.558	42–43	–	217	–
33	*p*-Cymene	$CH_3C_6H_4CH(CH_3)_2$	134.2	–67.9	0.8573	177.1	0
34	Butylbenzene[b]	$C_6H_5CH_2CH_2CH_2CH_3$	134.218	–87.97	0.86013	183.27	–

Table (Contd.)

No.	Compound	Formula	M [43]	T_m [43], °C	d_4^{20} [43, 44], mg mm^{-3}	T_b [43], °C	δ [43], D
35	sec-Butylbenzene[b]	$C_6H_5CH(CH_3)CH_2CH_3$	134.218	–75.47	0.86207	173.30	–
36	*tert*-Butylbenzene	$C_6H_5C(CH_3)_3$	134.218	–57.85	0.86650	169.12	0.53
37	Benzoic acid methyl ester	$C_6H_5COOCH_3$	136.144	–12.10	1.09334	199.5	1.80
38	*o*-Nitrotoluene[b]	$NO_2C_6H_4CH_3$	137.138	–9.55	1.1629	227.1	–
39	*m*-Nitrotoluene[b]	$NO_2C_6H_4CH_3$	137.138	16.1	1.1571	232.6	–
40	*p*-Nitrotoluene[b]	$NO_2C_6H_4CH_3$	137.138	54.5	1.2860	238.3	–
41	*o*-Nitrophenol[b]	$NO_2C_6H_4OH$	139.11	45.3–46	1.294	216	–
42	*m*-Nitrophenol[b]	$NO_2C_6H_4OH$	139.11	97	–	194	–
43	*p*-Nitrophenol[b]	$NO_2C_6H_4OH$	139.11	114–115.6	1.479	279	–
44	*o*-Dichlorobenzene	$C_6H_4Cl_2$	147.006	–17.03	1.30589	180.48	2.26
45	*m*-Dichlorobenzene	$C_6H_4Cl_2$	147.006	–24.76	1.28844	173.00	1.48
46	*p*-Dichlorobenzene	$C_6H_4Cl_2$	147.006	52.99	1.24750	174.12	0
47	Acetic acid benzyl ester	$CH_3COOCH_2C_6H_5$	150.17	–51.5	1.055	213.5	1.80
48	Benzoic acid ethyl ester	$C_6H_5COOCH_2CH_3$	150.17	–34.7	1.05112[b]	212.40	1.99
49	*o*-Nitroanisole	$NO_2C_6H_4OCH_3$	153.13	9.4	1.2527	265	4.814
50	Bromobenzene	C_6H_5Br	157.0	–30.8	1.4951[b]	155.9	1.73
51	Benzoic acid propyl ester	$C_6H_5COOC_3H_7$	164.196	–51.6	1.0232	231.2	–
52	1,2,3-Trichloro-benzene[b]	$C_6H_3Cl_3$	181.4487	53.5	1.466[b]	218.5	–
53	1,2,4-Trichloro-benzene[b]	$C_6H_3Cl_3$	181.4487	17	1.4542	213	–
54	1,3,5-Trichloro-benzene[b]	$C_6H_3Cl_3$	181.4487	63.5	–	208.5	–
55	1-Fluoro-2,4-dinitrobenzene[b]	$FC_6H_3(NO_2)_2$	186.1	27	–	137	–
56	2,4,5-Trichloro-phenol[b]	$Cl_3C_6H_2OH$	212.4388	68–70	–	244–248	–
57	2,4,5-Trichloronitro-benzene[b]	$Cl_3C_6H_2NO_2$	226.4473	57–58	1.790	288	–
58	2,4,6-Trinitrotoluene (trotyl) [b]	$(NO_2)_3C_6H_2CH_3$	227.132	80.85	–	–	–
59	2,4,6-Trinitrophenol[b]	$(NO_2)_3C_6H_2OH$	229.104	122–122.5	–	195	–
60	2,4,6-Trinitroxylene[b]	$(NO_2)_3C_6H(CH_3)_2$	241.159	182	–	–	–

[a] Tm is the melting or freezing point, d_4^{20}, density, and δ, dipole moment. [b] Data from [44, 46].

any conditions and used other plotted nomograms for estimating the surface tension, molar refraction, and density at different temperatures.

Katrizky et al. [20] successfully (correlation coefficient R^2=0.9544; standard deviation of approximation S = 16.2 K) applied CODESSA program in establishing quantitative relationships between the chemical structure and properties of compounds from various classes (298 organic and 9 elementary inorganic compounds). Fairly recently Yin H. et al. [21] employed a set of three known regression analysis methods for predicting the boiling points of 530 saturated hydrocarbons.

The second group of studies includes those focused on 1–2 classes of related compounds, in which no attempts were made to construct a general molecular theory of boiling (or melting) and only more special conclusions were made.

For example, Palatinus et al. [22] and Nohair et al. [23] restricted themselves to predicting T_b for acyclic alkanes; Plavšić et al. [24] examined condensed benzenoids, Murray et al. [25], fluorinated methanes, Hansen and Jurs [26], olefins, Sakka et al. [27], tetrahalomethanes, and Öberg [28] and Devotta and Pendyala [29], halogenated aliphatic compounds.

Taken together, those studies allowed the following conclusions: (1) all other conditions being the same, the larger the molecule, the higher T_b; (2) T_b varies with the shape of the molecules: Compounds with close to spherical molecules have lower boiling points than those with rod-shaped molecules; (3) T_b sharply increases in the presence of intermolecular hydrogen bonds (H-bonds); (4) typically, the larger the dipole moment of the molecule δ, the higher T_b; and (5) T_b decreases in the presence of a halogen atom in the molecule.

In the recent 10–15 years there has been increased interest in aromatic compounds that find extensive application as solvents in preparation and examination of fullerenes [30–32] and fullerene-containing systems. Those studies revealed a noticeable influence on the structure and properties of aromatic solvents, exerted by fullerenes, even when in very low concentrations [33–36]. The influence depends on the molecular structure of the solvent, in particular, on the symmetry of its molecules [37]. This stimulated analysis of how the molecular structure of aromatic compounds affects a broader spectrum of their properties.

Here, we restricted ourselves to analysis of mononuclear aromatic compounds and the influence exerted by their molecular structure above all on the phase transition temperatures, boiling and melting points.

Boiling points. Boiling is a very interesting and complex process examined in numerous works from the physical viewpoint [38–42]. For the chemicostructural analysis, we compiled reference data [43–47] for 60 compounds of the class of interest (see table). First, we constructed the plots of boiling point T_b (under normal conditions) vs. molecular weight M for selected compounds of the same type. Indeed, for a series of solvents including benzene (see table, no. 1), toluene (no. 2), and *p*-xylene (no. 10) the boiling points fall virtually perfectly on the straight line corresponding to the T_b(M) dependence (Fig. 1, curve *1*). It should be noted that the boiling points of *m*-xylene (no. 9) and *o*-xylene (no. 8) are very close to that of *p*-xylene, so that the general pattern remains unchanged. At the same time, by contrast to *p*-xylene having, like benzene, a zero dipole moment, *m*-xylene and *o*-xylene have the dipole moments of 0.62 and 0.37 D, respectively, and slightly higher boiling points. At least, the boiling point of *o*-xylene is much higher than that of *p*-xylene, 144.41 against 138.35°C.

At the same time, for a series of halogenated benzenes, including fluorobenzene (no. 5), chlorobenzene (no. 22), and bromobenzene (no. 50), even three points clearly do not fall on a straight line (Fig. 1, curve *2*), which suggests a complex nature of the phenomenon. Probably, a drastic change in the electronegativity of halogens [3] is manifested in this case. Fluorine is the most electronegative element (on the Pauling's scale its electronegativity is 4.0 [3]), and it is followed, in

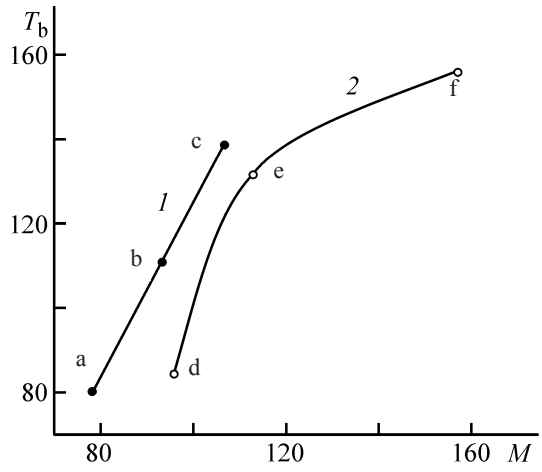

Fig. 1. Boiling point T_b,°C, vs. molecular weight M: (*1*): (a) benzene, (b) toluene, and (c) *p*-xylene and (*2*): (d) fluorobenzene, (e) chlorobenzene, and (f) bromobenzene.

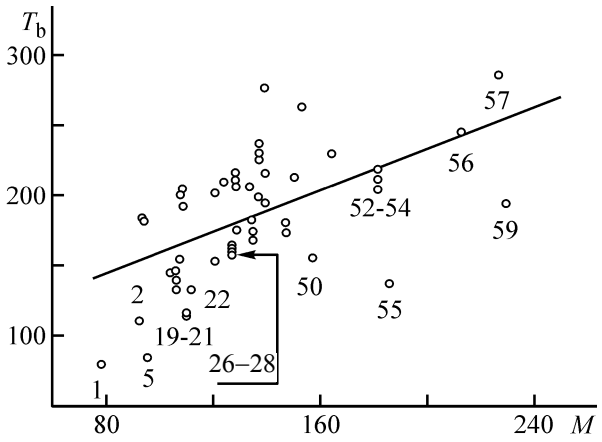

Fig. 2. Boiling point T_b,°C, vs. molecular weight M for 60 mononuclear aromatic compounds: (*1*) benzene and (*2*) toluene; other numbered points correspond to most of the halogenated compounds listed in Table 1; unnumbered points are correlated to formulas in Figs. 3–5.

the order of decreasing electronegativity, by oxygen (3.5), nitrogen (3.0), and chlorine (3.0). Only these four elements are able of forming H-bonds, whose strength should decrease in the same order [3]. However, the lack of hydrogen bonding in the presence of halogens in aromatic compounds leads to lower boiling point, which is fully consistent with the general trend. Apparently, in the first approximation this can be attributed to shifting

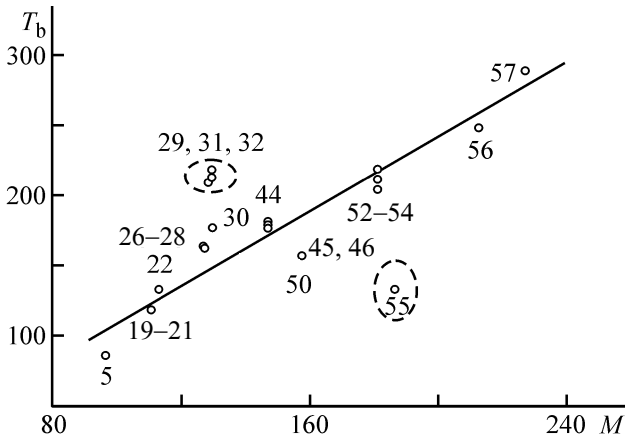

Fig. 3. Boiling point T_b,°C, vs. molecular weight M for all the halogenated aromatic compounds listed in Table 1. The points corresponding to *o*-chloroaniline (no. 29), 3-chlorophenol (no. 31), and 4-chlorophenol (no. 32), exhibiting appreciable shifts of the boiling point to high temperatures, and the point corresponding to 1-fluoro-2,4-dinitribenzene (no. 55), exhibiting an abnormal shift to low temperatures, are circled with dotted lines; they were discarded in mathematical processing (for explanations, see text); correlation coefficient $R^2 = 0.968$; standard approximation error $S = 13$ K.

of the electron density to the halogen atom, which concerns, above all, π-electrons. Despite nonzero dipole moment, ππ-interaction of the benzene rings tends to weaken, and this effect is the stronger, the higher the electronegativity of the halogen atom. Thus, boiling point of chlorobenzene, and especially fluorobenzene, is lower than that of bromobenzene.

In the following step of analysis we attempted to establish a general $T_b(M)$ dependence for all the compounds listed in the table. In the resulting dependence, shown in Fig. 2, it is hardly possible to identify any clear trend, though least-squares processing (by ORIGIN program) for the a priori set straight-line $T_b(M)$ dependence gave a different from zero correlation coefficient $R^2 = 0.450$. Figure 2 shows that many of the lowest boiling points correspond to compounds containing halogen atoms in their molecular structure (due apparently to the above-mentioned high electronegativity [3]).

Taking this into account, we further plotted the T_b(M) dependence for halogenated compounds only. We found that this dependence should be adequately described by a straight line, except for three points that were strongly shifted to high temperatures (nos. 29, 31, 32), and one point, to low temperatures (no. 55). Discarding these four points afforded a good correlation of the T_b(M) dependence with a straight line (Fig. 3).

The three points characterized by "increased" boiling points correspond to *o*-chloroaniline (no. 29) and 3- and 4-chlorophenol (nos. 31, 32, respectively). Along with chlorine atoms, these compounds contain hydroxy (chlorophenols) and amine (chloroaniline) groups prone to strong intermolecular hydrogen bonding [3]. Thus, specifically intermolecular H-bonds cause the boiling points of chlorophenols and chloroaniline to increase. As to 2-chlorophenol containing chlorine and hydroxy group in the *ortho* position with respect to each other, this obviously results in intramolecular hydrogen bonding and decreased boiling point.

A low boiling point of 1-fluoro-2,4-dinitrobenzene (no. 55) is probably associated with the symmetric positions of the nitro groups with respect to the benzene ring and high electronegativity of fluorine, which can weaken internuclear interactions, as mentioned above.

In the case of dichlorobenzenes (nos. 44–46), there is no hydrogen bonding, and *ortho* position of the chlorine atoms is responsible for enhanced attraction of electrons and a large dipole moment, –2.26 D, against zero in the *para* isomer. This leads to strong dipole–dipole

interaction in the *ortho* isomer and an appreciable increase of its boiling (not melting!) point.

Next, we considered the compounds from the analyzed group of mononuclear compounds that have relatively high boiling points. We found that they contain hydroxy and amino groups able of hydrogen bonding, as well as strongly polar nitrile and carboxy groups. The $T_b(M)$ dependence plotted for these compounds exhibited a satisfactory correlation with a straight line (Fig. 4; $R^2 = 0.90$), except for the points corresponding to nitrophenols (nos. 41–43). Specifically, for *p*-nitrophenol we obtained a strongly "increased" boiling point of 279°C (due to intermolecular hydrogen bonding). At the same time, its *ortho* analog forms intramolecular hydrogen bonds [4], which causes the intermolecular interactions to weaken, and this is responsible for lowering of the boiling point (216°C). In a similar way, the *para* and *ortho* positions of substituents in nitrophenols affect their melting points. The behavior of *m*-nitrophenol whose boiling point is the lowest among those of the stereo isomers (194°C) is somewhat puzzling. We can only presume in this connection formation of highly strained intramolecular cycles comprising hydrogen bonds.

Hence, like in the case of 3- and 4-chlorophenol and *o*-chloroaniline, we classed *o*- and *m*-nitrophenol with the third group compounds. It integrates the rest of compounds boiling at "medium" temperatures, for which the $T_b(M)$ plot was also represented by a straight line exhibiting a good correlation with the experiment (correlation coefficient $R^2 = 0.80$). If we discard "abnormally" high boiling points of *p*-nitrophenol, *o*-chloroaniline, and 3- and 4-chlorophenol, the $T_b(M)$ dependence can be adequately described by a straight lime (Fig. 5) with the correlation coefficient R^2=0.916.

The three $T_b(M)$ dependences we obtained (Figs. 3–5) will apparently provide satisfactory predictions of T_b for compounds that escaped our consideration or new compounds that still remain to be examined. The same is true of explosives (trotyl) whose heating poses hazard (probably, for this reason there are no data on their boiling points in handbooks, or they were not reported by researchers; extrapolation in Fig. 5 gave a close to 330°C boiling point of trotyl).

It should be emphasized that the boiling points are approximately identical for most of *ortho*, *meta*, and *para* isomers, e.g., for xylenes (nos. 8–10), toluidines (nos. 11–13), fluorotoluenes (nos. 19–21), and chlorotoluenes (nos. 26–28). The boiling points of sec- and *tert*-butylbenzenes (nos. 35, 36) are close. At the same time, for some isomers the boiling points differ appreciably, e.g., for nitrophenols (nos. 41–43), which is explained by the above-discussed reasons.

Melting point. Pauling [3] analyzed how the melting point T_m depends on the molecular weight of the isoelectronic series of hydrides of elements jointly with the analogous dependences for the boiling point. The

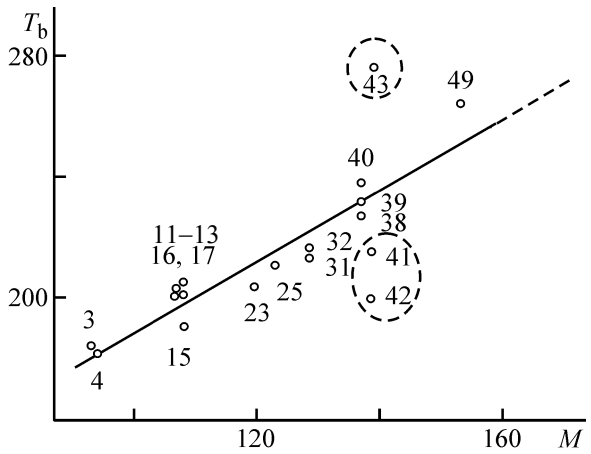

Fig. 4. Boiling point T_b,°C, vs. molecular weight M for the aromatic compounds listed in Table 1, characterized by increased boiling points. Mathematical processing discarded point nos. 41–43 corresponding to nitrophenols (for explanations, see text); $R^2 = 0.90$; $S = 6.9$ K.

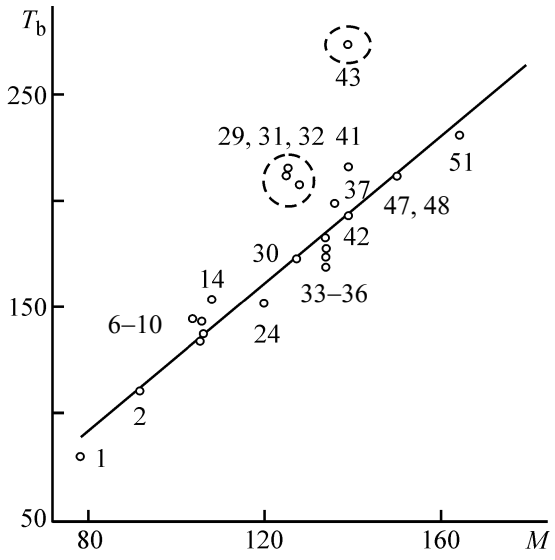

Fig. 5. Boiling point T_b,°C, vs. molecular weight M for the aromatic compounds listed in Table 1, characterized by "intermediate" boiling points. The points for *o*-chloroaniline (no. 29), 3-chlorophenol (no. 31), and 4-chlorophenol (no. 32), discarded in mathematical processing, are circled with dotted line (for explanations, see text); $R^2 = 0.916$; $S = 5$ K.

characteristic features of the resulting curves were also interpreted within a single framework.

It should be noted, however, that, in the case of melting/crystallization, the phase transition temperature is determined not only by the molecular weight and intermolecular interactions, but also by other essential factors, specifically, possible dense packing of the molecules and, hence, the molecular symmetry [5–7].

Let us consider a small series of compounds including benzene, toluene, and xylenes (Fig. 6). The benzene molecule (Fig. 6a) has the highest symmetry in this series, specifically, seven symmetry elements; the melting point of benzene is +5.5°C. The situation drastically changes in the case of toluene whose molecule has only one symmetry element (Fig. 6b), and toluene melts at a temperature decreased to –95°C.

Clearly, the symmetry of the *p*-xylene molecule is higher than that of the toluene molecules (Fig. 6c): The former has two symmetry planes and one two-fold symmetry axis. The melting point of *p*-xylene is +13.26°C. The *o*- and *m*-xylene molecules (Figs. 6d, 6e) possess a low symmetry (one two-fold symmetry axis in each of them) and, correspondingly, melt at negative temperatures (see table).

A good illustration of how the symmetry of the molecules affects the melting point of a substance can be found in dichlorobenzenes (reproducing the symmetry of xylenes) (nos. 44–46): *p*-Dichlorobenzene melts at a fairly high positive temperature, while its *ortho* and *meta* analogs, at negative temperatures.

Fluorotoluenes (nos. 19–21) and toluidines (nos. 11–13) exemplify benzene derivatives containing different molecular/atomic groups in the *ortho, meta*, and *para* positions. However, in this case the melting point of the *para* isomer, whose molecules are formally lacking high symmetry, still appreciably exceeds those of the *ortho* and *meta* isomers.

It should be mentioned that the melting point of *p*-xylene slightly exceeds that of benzene. This is another evidence in favor of the fact that the melting point is determined by a set of factors, including the molecular weight, intermolecular interactions, and symmetry, rather than by the symmetry of the molecules solely.

Like with boiling, the case of nitrophenols (nos. 41–43) is highly indicative. The nitro and hydroxy groups in the *ortho* position form intramolecular hydrogen bonds [4]; hence, intermolecular interaction is substantially weakened, and the melting point is fairly low, 45–46°C. At the same time, in the case of *m*- and *p*-nitrophenol, the chains of intermolecular bonds permeate the entire system, and the melting point reaches 97 and ~115°C, respectively. The density of the *p*-nitrophenol also significantly increases relative to *o*-nitrophenol, 1.479 against 1.294 g cm^{-3}. As the temperature increases and approaches the boiling point, the intramolecular H-bonds apparently get largely destroyed, and the boiling point of *o*-nitrophenol is even appreciably higher than that of *m*-nitrophenol. However, the boiling point of *p*-nitrophenol is record high, considering its molecular weight (Fig. 4, no. 43). This is evidently due to both dense packing of the molecules and a "favorable" arrangement of the groups involved in intermolecular hydrogen bonding.

Role of molecular symmetry in formation of associates in C_{60} and C_{70} solutions. Earlier [37] we

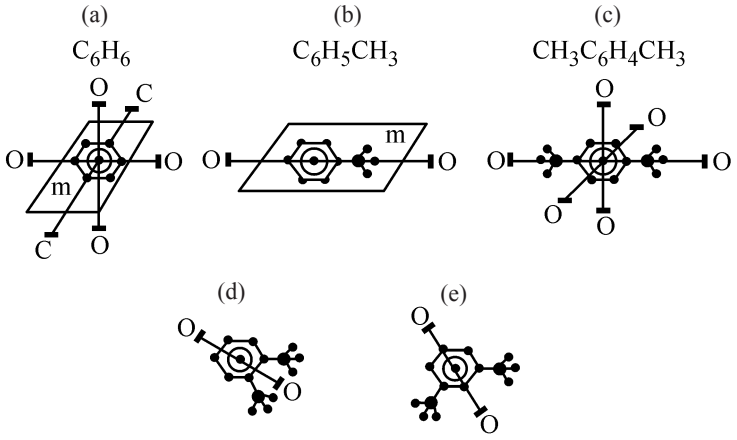

Fig. 6. Formulas, schematic molecular structures, and symmetry elements for (a) benzene, (b) toluene, (c) p-xylene, (d) o-xylene, and (e) *m*-xylene.

determined the concentration dependences of the volumetric boiling points T_b of solutions of fullerene C_{60} in four aromatic solvents, benzene, toluene, *p*-xylene, and *o*-dichlorobenzene. Also, solutions of C_{60} in bromobenzene were recently studied. In all the cases the plots of the concentration dependence of T_b can be divided into two sections: section 1, in which T_b sharply increases at the smallest concentrations of fullerene, and section 2 in which T_b increases more slowly or remains unchanged (Fig. 7). Section 1 was associated with structurization of solvents under the action of fullerene [33–36]. The difference in the runs of the two curves in section 2 was presumably attributed to that in the symmetry of the solvent molecules: More symmetric molecules (benzene, *p*-xylene) are characterized by ascending dependences (Fig. 7a), and for less symmetric molecules (toluene, *o*-dichlorobenzene, bromobenzene) T_b remains unchanged (Fig. 7b). Based on processing of the ascending dependences within section 2 in terms of the Raoult law, the size of the associates, or the cooperativity parameter of interaction between the fullerene and solvent molecules near the boiling point, was estimated at ~800 and ~80 molecules for benzene and *p*-xylene, respectively [37]. In the case of toluene, *o*-dichlorobenzene, and bromobenzene whose molecules have low symmetry, associates are evidently not formed under the boiling conditions.

As to solutions of fullerene C_{70} in solvents with high (benzene) and low (toluene) symmetry, we observed dependences similar to those presented in Fig. 7b. Specifically, under conditions of boiling of C_{70} solutions, associates are not formed, whatever the symmetry of the solvent molecules.

In the case of C_{60} solutions, aggregation of the C_{60} molecules is probably precluded specifically by the solvate shell, and this effect is more pronounced in the case of symmetric solvent molecules. Hence, combined fullerene–polymer solutions in such solvents should give films with more uniformly spread fullerene.

CONCLUSIONS

(1) The boiling and melting points of mononuclear aromatic compounds were for the first time analyzed in relation to their molecular structure, based on the published data. Three linear dependences on the molecular weight were revealed for boiling point.

(2) The highest-temperature dependence was established for solvents characterized by strong intermolecular interaction due to the presence in their structure of specific groups, hydroxy, amino, amide, nitrile, ester, and other, able of forming hydrogen or strongly polar (dipole-dipole) bonds.

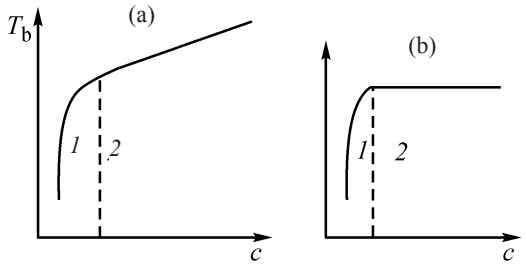

Fig. 7. Schematic dependences of the boiling point, T_b,°C, of solutions on the fullerene C_{60} concentration c in aromatic solvents with (a) high and (b) low molecular symmetry.

(3) The lowest-temperature dependence is characteristic for solvents whose molecular structure contains halogen atoms that do not form hydrogen bonds.

(4) The intermediate-temperature dependence was obtained for the rest of solvents, as well as for those among them that contain both the above-mentioned specific groups and halogen atoms.

(5) Special consideration was given to the role played by structural isomerism (and its associated symmetry of molecules) in disubstituted compounds. The symmetry of the molecules strongly affects the melting point of the aromatic compounds: Disubstituted compounds with substituents in the *para* position typically have substantially increased melting points, and compounds with substituents in the *ortho* position can have both increased and decreased boiling points .

(6) The symmetry of the solvent molecules affects the run of the concentration dependences of the boiling point of C_{60} fullerene solutions.

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REFERENCES

1. Pauling, L., *General Chemistry*, Dover Publications, 3rd edn., 1988.

2. Efros, L.S., and Gorelik, M.V., *Khimiya i tekhnologiya promezhutochnykh produktov* (Chemistry and Technology of Intermediates), Leningrad: Khimiya, 1980.
3. Pauling, L., *The Nature of the Chemical Bond, and the Structure of Molecules and Crystals. An Introduction to Modern Structural Chemistry*, Ithaca: Cornell Univ., 1940, 2nd ed.
4. Spice, J. E., *Chemical Bonding and Structure*, Oxford: Pergamon Press Ltd., 1964.
5. Kitaigorodskii, A.I., *Organicheskaya kristallokhimiya* (Organic Crystal Chemistry). Moscow: Akad, Nauk SSSR, 1955.
6. Kitaigorodskii, A.I., *Molekulyarnye kristally* (Molecular Crystals), Moscow: Nauka, 1971.
7. Bokii, G.B., *Kristallokhimiya* (Crystal Chemistry), Moscow: Nauka, 1971.
8. Kotel'nikova, E.N. and Filatov, S.K., *Kristallokhimiya Parafinov* (Crystal Chemistry of Paraffins), St. Petersburg: Zhurnal "Neva", 2002.
9. Meissner, H.P., *Chem. Eng. Progr.*, 1949, vol. 45. pp. 149–155.
10. Gomez-Nieto, M. and Thodos, G., *Am. Inst. Chem. Eng. J.,* 1977, vol. 23, no. 6. pp. 904–913.
11. Gomez-Nieto, M. and Thodos, G., *Canad. J. Chem. Eng.,* 1977, vol. 55, p. 445.
12. Misic, D. and Thodos, G., *J. Chem. Eng. Data,* 1963, vol. 9, p. 540.
13. Lydersen, A.L., *Estimation of Critical Properties of Organic Compounds. Univ. Wisconsin Coll. Eng., Madison (Wisconsin),* April 1955, RPS, pp. 12–15.
14. Joback, K.G. and Reid, R.C., *Chem. Eng. Commun.,* 1987, vol. 57, pp. 233–243.
15. Somayajulu, G.R., *J. Chem. Eng. Data*, 1986, vol. 31, pp. 438–447.
16. Wen, X. and Quiang, Y., *Ind. Eng. Chem. Res.*, 2001, vol. 40, pp. 6245–6250.
17. Wen, X. and Qiang, Y., *J. Chem. Eng. Data,* 2002, vol. 47, no. 2, pp. 286–288.
18. Knotts, T.A., Wilding, W.V., Oscarson, J.L., et al., *J. Chem. Eng. Data*, 2001, vol. 46, no. 5, pp. 1007–1012.
19. Steraski, R. and Machwart, G.M., *Ind. Eng. Chem.*, 1960, vol. 52, no. 10, pp. 869–870.
20. Katrizky, A.R., Mu, L., Lobanov, V.S., and Karelson, M., *J. Phys. Chem.*, 1996. vol. 100, no. 24, pp. 10400–10407.
21. Yin, H., Liang, Y., and Hu, Q., *J. Data Sci.*, 2003, vol. 1, pp. 461–480.
22. Palatinus, J.A., Sams, C.M., Beeston, Ch. M., et al., *Ind. Eng. Chem. Res.*, 2006, vol. 45, no. 20, pp. 6860–6863.
23. Nohair, M., Zakarja, D., and Niassi, H., *J. Mol. Modelling,* 2001, vol. 7, no. 4, pp. 65–69.
24. Plavšić, D., Trinajstić, N., Amić, D., et al., *New J. Chem.,* 1998, pp. 1075–1078.
25. Murray, J.S., Lane, P., and Politzer, P., *J. Mol. Structure (Theochem.),* 1995, vol. 342, no. 20, pp. 15–21.
26. Hansen, P.J. and Jurs, P.C., *Anal. Chem.,* 1987, vol. 59, no. 19, pp. 2332–2337.
27. Sakka, T., Ogata, Y., and Iwasaki, M., *J. Fluorine Chem.,* 1996, vol. 76, no. 2, pp. 203–207.
28. Öberg, *T., Presentation at the Third Indo-US Workshop on Mathematical Chemistry, Duluth (Minnesota, US),* August 2–7, 2003. www.tomasoberg.com/english/pre-sentations.htm.
29. Devotta, S. and Pendyala, V.R., *Ind. Eng. Chem. Res.*, 1992, vol. 31, no. 8, pp. 2042–2046.
30. Bezmel'nitsyn, V.N., Eletskii, A.V., and Okun', M.V., *Usp. Fiz. Nauk*, 1998, vol. 168, no. 11, pp. 1195–1220.
31. Mekalova, N.V., *Fullereny v rastvorakh* (Fullerenes in Solutions), Ufa: Ufim. Gos. Neft. Tekh. Univ., 2001.
32. Krätschmer, W. and Huffman, D.R., *Phil. Trans. Royal Soc. London. A*, 1993, vol. 667, no. 343, pp. 33–38.
33. Ginzburg, B.M., Tuichiev, Sh., Tabarov, S.Kh., and Shepelevskii, A.A., *Kristallografiya*, 2005, vol. 50, no. 4, pp. 597–600.
34. Ginzburg, B.M. and Tuichiev, Sh., *Kristallografiya*, 2007, vol. 52, no. 1, pp. 109–112.
35. Ginzburg, B.M., Tuichiev, Sh., Tabarov, S.Kh., et al., *Zh. Prikl. Khim.*, 2005, vol. 78, no. 8, pp. 1047–1049.
36. Ginzburg, B.M. and Tuichiev, Sh., *J. Macromol. Sci. B. Phys.*, 2005, vol. 44, no. 4, pp. 517–530.
37. Ginzburg, B.M., Tuichiev, Sh., and Tabarov, S.Kh., *Zh. Prikl. Khim.,* 2009, vol. 82, no. 3, pp. 395–398.
38. Skripov, V.P., *Metastabil'naya zhidkost'* (Metastable Liquid), Moscow: Nauka, 1972.
39. Kutateladze, S.S., *Osnovy teorii teploobmena* (Fundamentals of Heat Exchange Theory), Moscow: Nauka, 1962.
40. Kutateladze, S.S. and Nakoryakov, V.E., *Teploobmen i volny v gazozhidkostnykh sistemakh* (Heat Exchange and Waves in Gas-Liquid Systems), Novosibirsk: Nauka, 1984.
41. Nesis, E.I., *Kipenie zhidkostei* (Boiling of Liquids), Moscow: Nauka, 1973.

42. Nesis, E.I., *Usp. Fiz. Nauk,* 1965, vol. 87, issue 4, pp. 615–653.

43. Weissberger, A., Proskauer, E.S., Riddick, J.A., and Toops, E.E., Jr., *Organic Solvents: Physical Properties and Methods of Purification*, 2nd edn., NewYork: Interscience, 1955.

44. *Khimicheskii entsiklopedicheskii slovar'* (Chemical Encyclopedic Dictionary), Knunyants, I.L., Ed., Moscow: Sov. Entsikl, 1983.

45. *Khimicheskaya entsiklopediya* (Chemical Encyclopedy), Knunyants, I.L., Ed., Moscow: Sov. Entsikl, 1988–1995.

46. *Vrednye khimicheskie veshchestva: galogen- i kislorod-soderzhashchie organicheskie soedineniya: spravochnik* (Harmful Chemical Substances: Halogen- and Oxygen-Containing Organic Compounds: Handbook), Filov, V.A. and Tiunov, L.A., Eds., St. Petersburg, Khimiya, 1994.

47. Gordon, A.J. and Ford, R.A., *The Chemist's Companion*, New York: Wiley, 1972.