Critical Temperatures and Pressures of 12 Phthalates Using the Pulse-Heating Method

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The critical temperatures and pressures of phthalates with the straight side alkyl chains $C_6H_4{-}1,2\text{-}[COO(CH_2)_nH]_2$ (*n* is from 1 to 11) as well as bis(2-ethylhexyl) phthalate have been measured. No literature data are available for the critical properties of phthalates. Since phthalates decompose at temperatures well below their critical temperatures, the method of pulse heating of a wire probe immersed into the liquid under study has been used. The method minimizes the effect of thermal decomposition because residence times are only from (0.035 to 1) ms. The experimental critical properties of phthalates have been compared with the values calculated using the group-contribution methods by Constantinou and Gani and Marrero and Gani.

Introduction

Phthalates (esters of 1,2-benzenedicarboxylic acid) are primarily used as plasticizers for poly(vinyl chloride). They are also used in other plastics, solid rocket propellants, lacquers, coating agents, printing inks, perfume oil solvents, etc. The critical properties of phthalates have probably never been measured. In this paper, we report experimental critical temperatures and pressures of 11 di-*n*-alkyl phthalates with the straight side alkyl chains $C_6H_4{-}1,2\text{-}[COO(CH_2)_nH]_2$ (*n* is from 1 to 11) as well as bis(2-ethylhexyl) phthalate. The critical temperatures of phthalates investigated by us are from (772 to 886) K. The thermal decomposition of phthalates begins at temperatures about (525 to 575) K.[1] Consequently, phthalates are thermally unstable at their critical points, and the pulse-heating method with an ultralow residence time was used for the measurements.

Experimental Section

Method. The pulse-heating method and apparatus have been described in detail in previous publications.[2−4] The method is based on measuring the pressure dependence of the temperature of the attainable superheat (spontaneous boiling-up) of a liquid with the help of a thin wire probe heated by pulses of electric current. When the pressure in the liquid approaches the critical pressure, the temperature of the attainable superheat approaches the critical temperature. The liquid under investigation fills a chamber, the pressure in which may be changed with a press and is measured with a dial gauge. In the liquid, a thin wire probe is placed. The probe is heated by pulses of electric current in such a manner that by the end of a pulse the liquid boils-up at the surface of the probe. At the moment of boiling-up a perturbation of the probe temperature arises. The pressure in the chamber increases until the negative temperature perturbation decreases to the level of apparatus sensitivity. The probe temperature is determined from its resistance. The values of the critical pressure p_c^m and the critical temperature T_c^m determined in such a way are always lesser than the true ones. It is an inherent feature of the pulse-heating method. The true critical constants p_c and T_c of a stable compound are calculated by the following equation:

$$p_c = p_c^m/\pi_0 \quad T_c = T_c^m/\tau_0 \tag{1}$$

Here $1/\pi_0$ and $1/\tau_0$ are correction factors.[2,5] To calculate the correction factors, the thermophysical properties of the substance under study near the critical point are required. They are estimated by the principle of corresponding states using the formulas given in our previous paper.[5] These formulas contain a similarity parameter of the compound under investigation. Usually we use the acentric factor or the analogous parameter suggested by Filippov:[6]

$$A = 100\frac{p_{vp}(T/T_c = 0.625)}{p_c}$$

where p_{vp} is the vapor pressure. The Filippov parameters and the critical properties of phthalates were calculated by an iteration method. For the first iteration, p_c^m and T_c^m were used as the critical constants. The vapor pressure of phthalates with $n = 2$ and 4 was calculated by the Antoine equation using the parameters taken from the NIST Chemistry WebBook.[7] The vapor pressure of phthalates with $n = 1$, 3, and 8 and for bis(2-ethylhexyl) phthalate was estimated by the following equation:

$$\ln p_{vp} = B - \frac{C}{T} \tag{2}$$

which is sometimes called the Clapeyron equation.[8] The

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Table 1. Sources and Purities of Phthalates Used in Critical Point Measurements

			before measuring critical constants			after measuring critical constants		
			acidity	purity/%		acidity	purity/%	
phthalate	CASRN[a]	supplier	wt % as phthalic acid	chrom	pms	wt % as phthalic acid	chrom	pms
dimethyl	131-11-3	Eastman	0.0028[b]	99.97[b]	99.9		99.9[c]	99.9
diethyl	84-66-2	Eastman	0.0016[b]	99.95[b]	99.9		99.9[c]	99.8
dipropyl	131-16-8	IOS[d]	0.13	99.9[c]	99.9	0.18	99.9[c]	99.9
dibutyl	84-74-2	Eastman		99+[b]			99.8[c]	99.9
dipentyl	131-18-0	IOS[d]	0.074	99.9[c]	99.8	0.059	99.7[c]	99.9
dihexyl	84-75-3	IOS[d]	0.030	99.9[c]	99.9	0.12	99.9[c]	99.9
diheptyl	3648-21-3	IOS[d]	0.089	99.9[c]	99.9	0.030	99.9[c]	99.9
dioctyl	117-84-0	IOS[d]	0.059	99.7[e]	99.9	0.089	99.5[e]	99.8
bis(2-ethylhexyl)	117-81-7	IOS[d]	0.37	99.1[e]	99.9	0.33	98.9[e]	99.9
dinonyl	84-76-4	IOS[d]	0.059	99.9[e]	99.9	0.074	99.8[e]	99.9
didecyl	84-77-5	IOS[d]	0.059	99.7[e]	99.9	0.059	99.9[e]	99.9
diundecyl	3648-20-2	IOS[d]	0.089	99.8[e]	99.9	0.089	99.9[e]	99.9

[a] Chemical Abstracts Service Registry Number. [b] Supplier data. [c] Gas chromatography data. [d] Institute of Organic Synthesis, Ural Branch of the Russian Academy of Sciences. [e] Liquid chromatography data.

Table 2. Critical Temperatures of Phthalates: Experimental Values and Comparison with Predictive Methods

	1	T_c/K		
substance	τ_0[a]	exptl	ref 9	ref 17
dimethyl phthalate	1.003	772 ± 9	755.9	742.3
diethyl phthalate	1.004	776 ± 9	774.4	765.9
dipropyl phthalate	1.004	784 ± 9	791.2	787.4
dibutyl phthalate	1.005	797 ± 9	806.6	807.0
dipentyl phthalate	1.005	811 ± 9	820.7	825.1
dihexyl phthalate	1.005	817 ± 9	833.9	841.8
diheptyl phthalate	1.005	830 ± 9	846.1	857.5
dioctyl phthalate	1.005	840 ± 9	857.6	872.1
bis(2-ethylhexyl) phthalate	1.005	835 ± 9	853.5	868.7
dinonyl phthalate	1.005	858 ± 9	868.4	885.9
didecyl phthalate	1.006	870 ± 10	878.6	898.9
diundecyl phthalate	1.006	886 ± 10	888.2	911.2
AAE[b]/K			10.6	21.3

[a] $1/\tau_0$ is the correction factor in eq 1. [b] AAE $= (1/N)(\sum|T_c^{\exp} - T_c^{\text{calc}}|)$, where N is the number of experimental data points, $T_c^{\exp}$ is the experimental value of the critical temperature, and T_c^{calc} is the calculated value of the critical temperature.

Table 3. Critical Pressures of Phthalates: Experimental Values and Comparison with Predictive Methods

	1	p_c/MPa		
substance	π_0[a]	exptl	ref 9	ref 17
dimethyl phthalate	1.048	2.77 ± 0.1	2.741	2.788
diethyl phthalate	1.054	2.26 ± 0.08	2.259	2.323
dipropyl phthalate	1.057	1.90 ± 0.07	1.899	1.992
dibutyl phthalate	1.061	1.66 ± 0.06	1.624	1.748
dipentyl phthalate	1.064	1.43 ± 0.05	1.409	1.562
dihexyl phthalate	1.067	1.34 ± 0.05	1.237	1.419
diheptyl phthalate	1.070	1.24 ± 0.04	1.098	1.305
dioctyl phthalate	1.074	1.08 ± 0.04	0.983	1.213
bis(2-ethylhexyl) phthalate	1.074	1.07 ± 0.04	0.982	1.220
dinonyl phthalate	1.077	1.02 ± 0.04	0.888	1.138
didecyl phthalate	1.080	0.94 ± 0.03	0.808	1.076
diundecyl phthalate	1.083	0.89 ± 0.03	0.740	1.024
AAE[b]/MPa			0.076	0.097

[a] $1/\pi_0$ is the correction factor in eq 1. [b] AAE $= (1/N)(\sum|p_c^{\exp} - p_c^{\text{calc}}|)$, where N is the number of experimental data points, $p_c^{\exp}$ is the experimental value of the critical temperature, and p_c^{calc} is the calculated value of the critical temperature.

parameters B and C were determined from the values of p_c^m and T_c^m and normal boiling points also taken from the Internet.[7] For phthalates with n from 5 to 7 and from 9 to 11, we calculated the normal boiling temperatures using the group-contribution method by Constantinou and Gani[9] and then the vapor pressure by eq 2. One can find in the NIST Chemistry WebBook the boiling points of these phthalates but without referring to the origin of these data, so we prefer the way of using the method by Constantinou and Gani as being more understandable. In addition, even if there is a reliable boiling point but measured at a low pressure, our experience shows that using eq 2 frequently gives an unreal, high acentric factor. After that, the values of π_0 and τ_0 and with the use of eq 1, p_c and T_c were calculated. For the second iteration, the Filippov parameter and the critical constants were calculated using the values obtained after the first iteration. Two iterations were enough because the values of π_0 and τ_0 have little sensitivity to the variations of Filippov's parameter. For example, for di-*n*-octyl phthalate, a change of 10 % in A causes a change about 0.2 % in π_0 and 0.01 % in τ_0. This warrants using the calculated normal boiling points for phthalates with $n = 5$, 6, 7, 9, 10, and 11.

The values of the corrections factors $1/\pi_0$ and $1/\tau_0$ are given in Tables 2 and 3. The magnitude of the correction factors depends on the thermophysical properties of a substance under study. The main tendency is as follows: the greater is the acentric factor ω or the lower is the Filippov parameter A of a substance, the greater are the corrections factors. For instance, for such compounds as *n*-pentane ($\omega = 0.252$, $A = 1.70$) or *n*-hexane ($\omega = 0.300$, $A = 1.44$) $1/\pi_0 = 1.006$, $1/\tau_0 = 1.0006$, and $1/\pi_0 = 1.010$ and $1/\tau_0 = 1.001$, respectively.[2] According to our estimations, the acentric factors and the Filippov parameters of phthalates vary from $\omega = 0.557$, $A = 0.620$ for dimethyl phthalate to $\omega = 0.656$, $A = 0.481$ for diundecyl phthalate, so the corrections factors of the phthalates are larger than those of *n*-pentane or *n*-hexane.

The ideal gas heat capacity of the compound under study and the factor G_T are also needed to calculate the correction factors. The ideal gas heat capacity was estimated by the method of Rihani and Doraiswamy as presented by Reid et al.[8] The factor $G_T \equiv \partial \ln J/\partial T$, where J is the rate of bubble nucleation in a superheated liquid, was measured as described in our previous paper[2] and estimated at 1.5 K^{-1}.

A thermally unstable compound decomposes in the course of heating so that the critical pressure and the critical temperature of such a compound determined as described above may depend on the time from the beginning of the heating pulse to the moment of boiling-up t^*. The true critical constants of an unstable substance are determined in this case by extrapolating the dependencies $p_c(t^*)$ and $T_c(t^*)$ to $t^* = 0$. The procedure of extrapolation was given in detail previously.[10] To use the

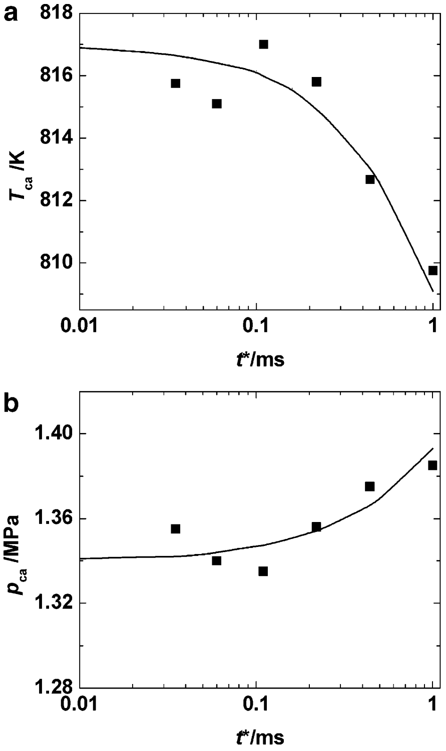

Figure 1. Apparent critical temperature (a) and critical pressure (b) of di-*n*-hexyl phthalate in the pulse-heating experiments; t^* is the time from the beginning of a heating pulse to the moment of boiling-up. The solid lines correspond to the extrapolation procedure.[10]

procedure, it is necessary to know the kinetic parameters of the reaction of decomposition: the order of reaction *m*, the activation energy *E*, and the preexponential factor *B*, as well as the derivatives $\alpha = (dT_c/dx_p)_c$ and $\beta = (dp_c/dx_p)_c$ that characterize the critical curve of the system (the substance under study + products of decomposition) near the critical point of the pure substance. Here x_p is the mole fraction of decomposition products; the derivatives are calculated at the critical point.

The critical constants of phthalates were measured by us with the help of probes (1, 2, and 3) cm in length at heating times $t^* = (0.035, 0.06, 0.11, 0.22, 0.44, \text{and } 1.00)$ ms. Several samples (from 2 to 3) of each compound were used. The volume of the sample was about 2 cm^3. The sample volume has no effect on the values of the experimental critical properties because during the pulse only a layer near the probe about 10^{-6} m in thickness is heated. As an example, the results of measuring the critical temperature and pressure of dihexyl phthalate are shown in Figure 1. Each point in Figure 1 is the result of averaging over all of the samples and all of the wire lengths. As a rule, the results reported are an average over about 10 measurements. Saido and co-workers[11,12] experimentally found the kinetic parameters of decomposition for dibutyl, dihexyl, bis(2-ethylhexyl), dioctyl, and didecyl phthalates. However, the parameters α and β are unknown. They and the critical constants of a pure substance $T_c(t^* = 0)$ and $p_c(t^* = 0)$ were calculated by processing the experimental data using the least-squares method and the formulas given in ref 10. The solid lines in Figure 1 are the result of the calculation. The critical properties of phthalates investigated by Saido and co-workers were estimated in such a way. For the rest of phthalates, the critical constants were determined by averaging the apparent critical constants over the heating times from (0.035 to 0.22) ms because our measurements showed that the apparent critical temperatures and pressures did not depend on the heating time in this interval.

Uncertainties. The uncertainties of the critical properties measured by the pulse-heating method were discussed in detail in our previous papers.[10,13,14] The uncertainties of the results of measuring the critical pressure and temperature of a stable compound may be written as follows:

$$u(p_c) = u_1 + u_2 + u_3$$

$$v(T_c) = v_1 + v_2 + v_3$$

Here u_1 is the uncertainty with which an experimenter determines the pressure at which the temperature perturbation decreases to the level of the apparatus sensitivity, u_2 is the uncertainty of measuring this pressure with a dial gauge, and u_3 is the uncertainty of calculating the correction factor $1/\pi_0$. The uncertainty v_1 has the same nature as u_1, v_2 is the uncertainty of measuring the probe temperature from its resistance, and v_3 is the uncertainty of estimating the correction factor $1/\tau_0$. The uncertainties u_1 and v_1 can be reduced by repeated experiments to the values $0.01p_c^m$ and $0.001T_c^m$. The uncertainties u_2 and v_2 depend on the equipment used and are evaluated by us to about $0.004p_c^m$ and $0.007T_c^m$. The uncertainties of calculating the correction factors are not easy to estimate because the formulas for their calculation[2] were obtained by solving a rather complex thermophysical problem.[15] Up to now we have preferred to evaluate the total uncertainties *u* and *v* by comparing the values obtained in the measurements with the literature data on the critical constants of some "standard" substances (pentane, hexane, heptane, water, naphthalene, and benzene). However, today, having measured the critical constants of about 130 substances of different chemical nature, we are able to draw some conclusions. We estimate the values u_3 and v_3 at $0.016p_c$ and $0.002T_c$ for "usual" substances and at $0.026p_c$ and $0.007T_c$ for compounds with hydrogen bonding or with high acentric factors $\omega \geq 1$.

For unstable compounds, additional uncertainties u_4 and v_4 appear if the procedure of extrapolation[10] is used. The magnitude of these uncertainties depends on the rate of decomposition of a substance under study. The higher the rate is, the larger the uncertainties are.

We estimate the uncertainties for phthalates at $0.04p_c$ and $0.011T_c$, where T_c is the absolute temperature. It corresponds to from (± 0.03 to ± 0.1) MPa for the critical pressure and from (± 9 to ± 10) K for the critical temperature (see Tables 2 and 3).

Sources and Purities of the Compounds Studied. The sources and purities of the phthalates studied are given in Table 1. Dimethyl, diethyl, and dibutyl phthalates were obtained from Eastman Chemical Company; the rest of the phthalates were synthesized and purified by Y. Yatluk from the Institute of Organic Synthesis of the Russian Academy of Sciences (Ekaterinburg) using the standard procedure.[16] Before and after measuring the critical constants, the purities of the samples were determined using proton magnetic spectroscopy (Bruker DRX 400). Additionally, gas chromatography (Shimadzu GS-Ha) for dimethyl to diheptyl phthalates and liquid chromatography (Merck-Hitachi) for dioctyl to diundecyl phthalates were used. The acid values of the phthalates were determined by titration versus KOH; then they were recalculated into the mass fraction of phthalic acid.

Results and Discussion

The critical temperatures and pressures of the phthalates measured in this work are presented in Tables 2 and 3 and in

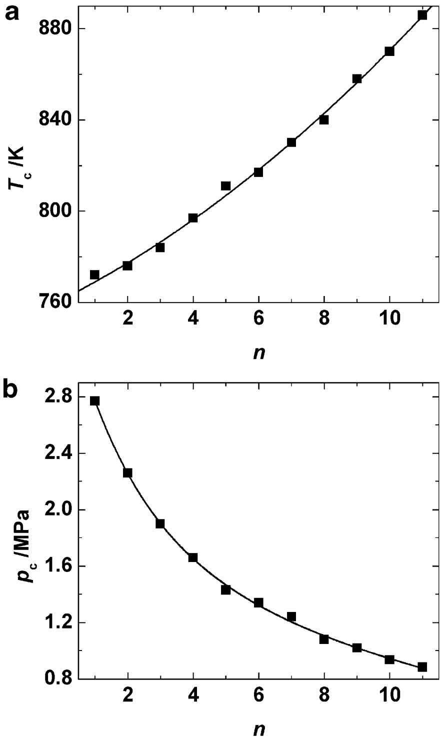

Figure 2. Critical temperature (a) and critical pressure (b) of di-*n*-alkyl phthalates $C_6H_4-1,2\text{-}[COO(CH_2)_nH]_2$ vs the number of CH_2 groups in the side chains.

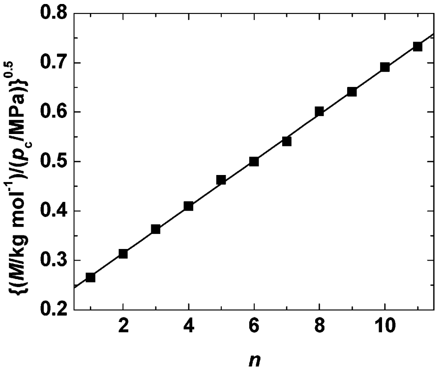

Figure 3. Correlation of the critical pressure of di-*n*-alkyl phthalates $C_6H_4-1,2\text{-}[COO(CH_2)_nH]_2$ as a function of the number of CH_2 groups in the side chains and molar mass.

Figure 2. The internal consistency of the critical pressure data was checked by plotting $(M/p_c)^{0.5}$ against n (Figure 3), where M is the molar mass and n is the number of CH_2 groups in the side chains of phthalates $C_6H_4-1,2\text{-}[COO(CH_2)_nH]_2$. A way to check the self-consistency of the critical temperature is to consider the ratio T_c/T_b as a function of n, where T_b is the normal boiling temperature (Figure 4). We, however, were able to find in the literature the normal boiling temperatures only for dimethyl to dibutyl and for dioctyl phthalates.[7]

Tables 2 and 3 also contain the values calculated by the group-contribution methods by Constantinou and Gani[9] and Marrero and Gani.[17] Both the Constantinou and Gani method and the Marrero and Gani method give the critical temperatures that are higher than the experimental ones for all the phthalates studied except for dimethyl and diethyl phthalates (see Figure 5). The method by Constantinou and Gani predicts the critical temperatures of the phthalates with an average absolute error of 10.6 K, which is close to the uncertainty of the experimental data; for the method by Marrero and Gani, this quantity is equal to 21.3 K. In our opinion, it is not a bad result as well because the critical temperatures of the phthalates investigated lie in the range (772 to 886) K. The method by Constantinou and Gani underestimates the critical pressures of phthalates whereas that of Marrero and Gani overestimates them (see Figure 6). Both methods give values that are close to the experimental critical pressures for comparatively low molar mass phthalates. However, the greater the molar mass is, the larger is the deviation of the estimated values from the experimental ones.

The critical temperature and the critical pressure of bis(2-ethylhexyl) phthalate are lower than those of its isomer with straight side chains, di-*n*-octyl phthalate, but the differences are small.

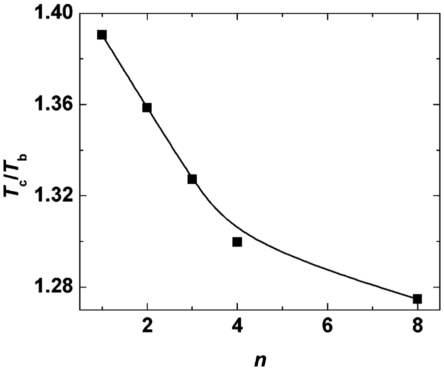

Figure 4. Correlation of the critical temperature of di-*n*-alkyl phthalates $C_6H_4-1,2\text{-}[COO(CH_2)_nH]_2$ as a function of the number of CH_2 groups in the side chains n and the normal boiling point T_b.

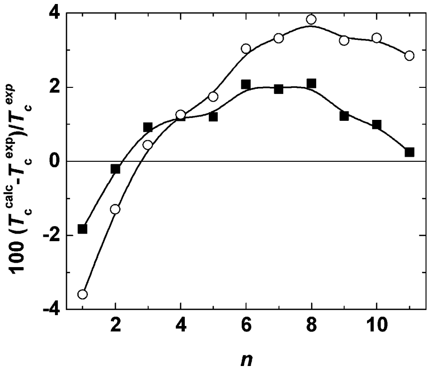

Figure 5. Percent deviations of the experimental critical temperatures from the values calculated by group-contribution methods as a function of the number of CH_2 groups in the side chains n for di-*n*-alkyl phthalates $C_6H_4-1,2\text{-}[COO(CH_2)_nH]_2$. GC methods: ■, Constantinou and Gani;[9] ○, Marrero and Gani.[17]

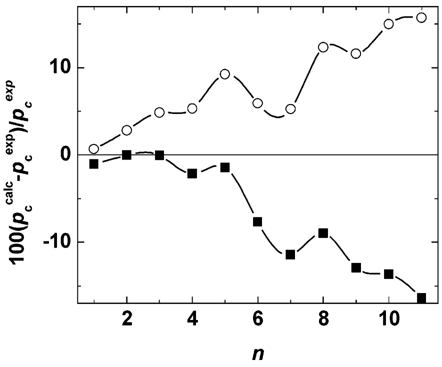

Figure 6. Percent deviations of the experimental critical pressures from the values calculated by group-contribution methods as a function of the number of CH_2 groups in the side chains n for di-*n*-alkyl phthalates $C_6H_4-1,2\text{-}[COO(CH_2)_nH]_2$. GC methods: ■, Constantinou and Gani;[9] ○, Marrero and Gani.[17]

Conclusion

The critical temperatures and pressures of phthalates with straight side alkyl chains from dimethyl to diundecyl phthalate as well as bis(2-ethylhexyl) phthalate have been measured by the pulse-heating technique. No literature data are available for the critical properties of phthalates. The critical constants of phthalates have been calculated using the group-contribution methods of Constantinou and Gani and Marrero and Gani. The method of Constantinou and Gani predicts the critical temperatures of the phthalates studied quite well, with an average absolute error that is approximately equal to the uncertainty of the measurements. The method of Marrero and Gani gives the average absolute error for the critical temperature about twice as large as the uncertainty of the measurements. Both methods predict the critical pressure well enough in the beginning of the homologous series of di-*n*-alkyl phthalates, but the deviation of the estimated values from the experimental ones rises with increasing molar mass.

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