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Vapor−Liquid Critical Properties of Phenol and (C_8 to C_{10}) Phenylalkanols

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The critical pressures and temperatures of phenol and three phenylalkanols $C_6H_5(CH_2)_nOH$ with $n = 2$ to 4 have been measured. These substances are thermally unstable at their critical points. The pulse-heating method with ultralow residence times has been used. Residence times are from (0.03 to 1) ms. The experimental critical properties of phenol and phenylalkanols have been compared with the values calculated using the group-contribution methods by Constantinou and Gani and by Marrero and Gani.

Introduction

The paper presents the critical temperatures and pressures of phenol and phenylalkanols $C_6H_5(CH_2)_nOH$ with a straight alkyl chain and $n = 2$ to 4. The critical properties of phenol and 2-phenyl-1-ethanol have been previously measured.[1−6] Phenol, benzyl alcohol ($n = 1$), and 2-phenyl-1-ethanol ($n = 2$) are unstable at their critical points;[3,6,7] we can expect that all the phenylalkanols studied by us are unstable too. The pulse-heating method with ultralow residence times was used for measurements.

Experimental Section

Methods. The procedure of measuring the critical constants of phenol and phenylalkanols was standard for our experiments. The pulse-heating method has been described in previous publications.[8−10] The method consists in 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 immersed into the liquid and 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 time from the beginning of a pulse to the moment of boiling-up is from (0.03 to 1) ms. The values of the critical pressure p_c^m and the critical temperature T_c^m obtained in the course of the measurements are always lesser than the true ones. It is an inherent feature of the pulse-heating technique. The true critical constants of a stable compound are calculated by the following equations:

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

Here $1/\pi_0$ and $1/\tau_0$ are correction factors.[8,11] For the substances investigated, the correction factors vary from $1/\pi_0 = 1.032$, $1/\tau_0 = 1.003$ (phenol) to $1/\pi_0 = 1.058$, $1/\tau_0 = 1.004$ (phenylbutanol). 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 a previous paper.[11] The formulas contain a similarity parameter of the compound under investigation: the acentric factor or the analogous parameter suggested by Filippov:[12]

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

where p_{vp} is the vapor pressure.

We used an iteration method for calculating the Filippov parameters and the critical constants of phenyl alcohols. For the first iteration, p_c^m and T_c^m were used as the critical constants; the vapor pressure of phenol, phenylethanol, and phenylpropanol was calculated by the Antoine equation with parameters taken from the NIST Chemistry WebBook.[13] The vapor pressure of phenylbutanol was estimated by the following equation:

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

The parameters B and C were determined from the values of p_c^m and T_c^m and the reduced pressure boiling point also taken from the NIST Chemistry WebBook.[13] Then 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 are little affected by the variations of Filippov's parameter.

In the calculation of the correction factors, the ideal gas heat capacity of the substance under study and the factor G_T are also used. The ideal gas heat capacity was estimated by the method of Rihani and Doraiswamy as presented by Reid et al.[14] The factor $G_T \equiv \partial \ln J/\partial T$, where J is the rate of bubble nucleation in a superheated liquid, was measured in one experiment with

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Table 1. Sources and Purities of Compounds Used in Critical Point Measurement

			purity/%				
			before measuring critical constants			after measuring critical constants	
compound	CASRN[a]	supplier	supplier[b]	GC	PMS	GC	PMS
phenol	108-95-2	Fluka	99.99	99.9	99.9	99.1[c]	99.9
2-phenyl-1-ethanol	60-12-8	Fluka	99.9	99.9	99.9	99.8	99.9
3-phenyl-1-propanol	122-97-4	Aldrich	99.1	99.7	99.6	99.4[d]	99.5
4-phenyl-1-butanol	3360-41-6	Aldrich	99.6	99.9	99.9	99.9	99.9

[a] Chemical Abstracts Service Registry Number. [b] For a given lot. [c] Water ≤0.9%. [d] 1-Tetralone ≤0.6%.

Table 2. Critical Temperatures and Pressures of Phenylalkanols: Experimental and Calculated Values

	T_c/K			p_c/MPa		
compound	exptl	ref 16	ref 17	exptl	ref 16	ref 17
phenol	695 ± 7[a] 692.4[b] 694.2 ± 0.1[c]	687.8	687.1	5.67 ± 0.17[a] 6.13 ± 0.05[d] 5.93[e]	6.010	5.965
phenylmethanol	715 ± 3[f]	662.3	658.9	4.3 ± 0.1[f]	4.284	4.460
2-phenyl-1-ethanol	720 ± 7[a] 723.5 ± 2[g]	677.9	688.3	3.85 ± 0.12[a] 3.99 ± 0.08[g]	3.773	3.997
3-phenyl-1-propanol	732 ± 7[a]	692.3	703.5	3.46 ± 0.10[a]	3.351	3.518
4-phenyl-1-butanol	746 ± 7[a]	705.6	717.8	3.07 ± 0.09[a]	2.998	3.133
AAPE[h]		5.02	4.21		2.77	3.29
MAPE[i]		7.37	7.85		6.00	5.20

[a] This work. [b] Data from ref 1. [c] Data from ref 3. [d] Data from ref 2. [e] Data from ref 4. [f] Data from ref 7. [g] Data from ref 6. [h] AAPE = $(1/N)(\sum|Y_c^{\mathrm{exp}} - Y_c^{\mathrm{calc}}|/Y_c^{\mathrm{exp}}) \times 100$, where N is the number of experimental data points, Y_c^{exp} is the experimental value of the critical property, and Y_c^{calc} is the calculated value of the critical property. [i] MAPE = $(|Y_c^{\mathrm{exp}} - Y_c^{\mathrm{calc}}|_{\mathrm{max}}/Y_c^{\mathrm{exp}}) \times 100$.

the critical constants and estimated at 1.5 K^{-1}. The procedure of measuring this factor was described in our previous paper.[8]

For a thermally unstable compound, the critical constants determined as described above may depend on the time from the beginning of a heating pulse to the moment of boiling-up t^* due to the decomposition of a substance under study in the course of heating. The critical properties of phenylalkanols were measured with the help of probes (1, 2, and 3) cm in length at heating times $t^* = (0.03, 0.06, 0.11, 0.22, 0.45, \text{and } 1.00)$ ms. Several samples (from 2 to 4) of each compound were used. All the substances studied by us are unstable at their critical points. However, the rate of decomposition is low enough. For example, in experiments by Ambrose the change of the critical temperature was about 0.01 $K{\cdot}min^{-1}$ for phenol.[3] For benzyl alcohol, the rate was so that it was possible to measure the critical temperature and the critical pressure using sealed tube and comparative ebulliometry methods which required long heating.[7] It is not surprising that no thermal decomposition was observed in the course of our measurements; so the experimental data were averaged over all the probe lengths, heating times, and samples.

Sources and Purities of the Compounds Used in the Critical Point Measurement. The sources and purities of phenylalkanols are given in Table 1. Before and after measuring the critical constants, the purities of the samples were determined using gas chromatography (Shimadzu GS-Ha) and proton magnetic spectroscopy (Bruker DRX 400). The purity of the samples is little changed in the course of the measurement of the critical properties. After measuring the critical constants, only the samples of phenol contained water while those of 3-phenyl-1-propanol contained 1-tetralone.

Uncertainties. The uncertainties of the critical constants measured by the pulse-heating method were discussed in detail in our recent paper.[15] We estimate the uncertainties for phenylalkanols at 0.03 p_c and 0.01T_c, where T_c is the absolute temperature. It corresponds to from (± 0.17 to ± 0.09) MPa for the critical pressure and ± 7 K for the critical temperature (see Table 2).

Results and Discussion

The critical temperatures and pressures of phenol and phenylalkanols included in this study are given in Table 2. To our knowledge, the critical properties of phenol and 2-phenyl-1-ethanol have ever been measured. The critical temperature of phenol measured by us is in good agreement with that determined by Radice[1] and Ambrose.[3] The critical pressure reported by Herz and Neukirch[2] seems to be overestimated due to the thermal decomposition of phenol. Judging by their paper they did not take this phenomenon into account. Delaunois[4] measured the vapor pressure of phenol at temperatures from (473 to 748) K and suggested an equation for the calculation of the vapor pressure. Then he calculated the critical pressure by substituting into the equation the critical temperature obtained by Ambrose.[3] The equation suggested by Delaunois somewhat overestimates the vapor pressure of phenol. For instance, it gives for the normal boiling temperature the value $T_b = 449.7$ K, while according to the NIST recommendations[13] obtained by averaging over the data of 26 studies $T_b = 455 \pm 0.6$ K. We believe our data on the critical pressure of phenol are more correct although the difference between the values of the critical pressure measured by Delaunois and us is not great.

The critical properties of 2-phenyl-1-ethanol have been measured by VonNiederhausern et al.[6] using a low residence time flow method. The critical temperatures of this alkanol obtained by us and VonNiederhausern and co-workers coincide within the limits of experimental uncertainties. The difference between the values of the critical pressure measured by us and VonNiesderhausern et al. is considerably greater. Frequently but not always, the pulse-heating method underestimates the critical temperature and pressure. However, in the case of

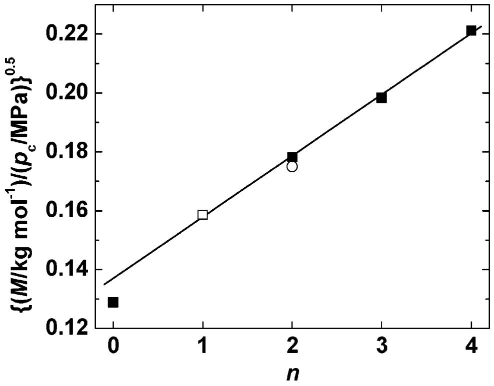

Figure 1. Correlation of the critical pressure of phenylalkanols $C_6H_5(CH_2)_n$-OH and phenol ($n = 0$) with the number of CH_2 groups n and molar mass M. ■, this work; □, ref 7; ○, ref 6.

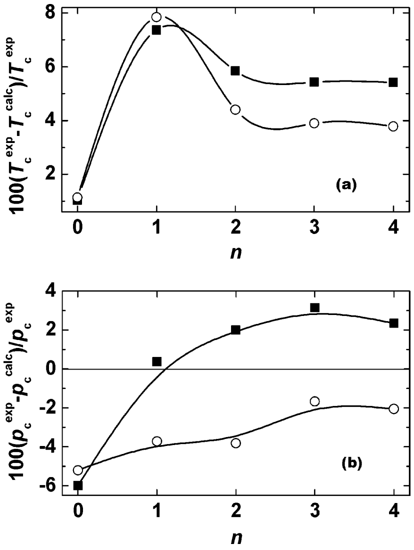

Figure 2. Percent deviations of the experimental critical temperatures (a) and pressures (b) from the values calculated using group contribution methods as a function of the number of CH_2 groups in a molecule of phenylalkanols $C_6H_5(CH_2)_nOH$ and phenol ($n = 0$). GC methods: ■, ref 16; ○, ref 17.

2-phenyl-1-ethanol, we think that our value of the critical pressure is closer to the true value than that by VonNiederhausern et al. The quantity $(M/p_c)^{1/2}$, where M is the molar mass, is well-known to be a linear function of the number of CH_2 groups in a molecule n within a given homologous series, at least for the lower members of the series. The straight line in Figure 1 was passed through the points that correspond to the data by us and Ambrose and Ghiassee.[7] It is not surprising that the point corresponding to phenol ($n = 0$) lies out of the line because phenol is not alkanol. Figure 1 shows as well that the critical pressure of 2-phenyl-1-ethanol ($n = 2$) obtained by VonNiederhausern et al.[6] is probably overestimated a bit.

Table 2 also contains the critical properties calculated using the well-known group-contribution methods by Constantinou and Gani[16] and by Marrero and Gani.[17] Percent deviations of the experimental critical constants from the values calculated by these methods are shown in Figure 2. The methods of both refs 16 and 17 underestimate the critical temperatures of phenol and phenylalkanols and predict that the critical temperature of phenylmethanol is lower than that of phenol. However, the experiments do not support this. For phenol, the difference between experimental and calculated values is of the order of 1 %, which is close to the uncertainty of the measurements; for phenylalkanols this difference lies in the range from (4 to 8)%. In contrast to the critical temperature, the critical pressure of phenol is predicted worse than for phenylalkanols.

Conclusion

The critical temperatures and pressures of phenol and phenylalkanols from 2-phenyl-1-ethanol to 4-phenyl-1-butanol have been measured by the pulse-heating technique. The critical properties of 3-phenyl-1-propanol and 4-phenyl-1-butanol have probably never been determined experimentally. The critical temperatures of phenol and 2-phenyl-1-ethanol obtained by us are in good agreement with the literature data. The critical pressure of these compounds determined by us is lower than the results of previous experiments. In our opinion, this fact is explained by the lesser decomposition of the substances under study in the course of our measurements.

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