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Vapor Pressures of 1,4-Dimethylbenzene, 1,4-Di(methyl-d_3)benzene, and 1,4-Dimethylbenzene-d_{10} at 20–50 °C

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The vapor pressures of p-$(CH_3)_2C_6H_4$ (d_0), p-$(CD_3)_2C_6H_4$ (d_6), and p-$(CD_3)_2C_6D_4$ (d_{10}) were measured by a static method from 20 to 50 °C. The ratio of the vapor pressure of d_6 to that of d_0 decreases from 1.07_2 at 20 °C to 1.05_7 at 50 °C, and that of d_{10} to that of d_0 decreases from 1.08_4 at 20 °C to 1.06_5 at 50 °C. For the vaporization process, $\Delta H°_{298}$ (kJ/mol) and $\Delta S°_{298}$ (J/(K mol)) were found to be 43.0 and 107.0 for d_0, 42.6 and 106.3 for d_6, and 42.5 and 106.1 for d_{10}, respectively. The substitution of a deuterium atom for a hydrogen on the methyl groups appears to affect the properties more than such a substitution on the aromatic ring.

Introduction

The vapor pressure of 1,4-dimethylbenzene (d_0) has been reported by several investigators, most extensively by the National Bureau of Standards (*1*) from 27 to 149 °C. Pitzer and Scott (*2*) also report values over a more limited temperature range, but there appear to be no published data on its two most common isotopomers, 1,4-di(methyl-d_3)benzene (d_6) and 1,4-dimethylbenzene-d_{10} (d_{10}). For these, the Aldrich Chemical Co. catalog, 1988–9, gives the normal boiling points as 135.4 and 135 °C, respectively, both lower than that of d_0, 138.350 °C (*1*). It became necessary to measure the ratios of the vapor pressures of d_6 and d_{10} to that of d_0 in the neighborhood of room temperature in order to interpret earlier data on the fractionation of isotopic molecules based on inclusion phenomena (*3*). An accuracy of about 1% in the vapor pressure ratios was all that was needed, and this required only an accuracy of about 0.7% in the individual vapor pressures. All three isomers, d_0, d_6, and d_{10}, were determined, the d_0 partly to confirm the reliability of the technique used.

Experimental Section

The three isomers were Aldrich Chemical Co. products. Gold Label d_0 (99+%) was distilled from $LiAlH_4$ under dry nitrogen, collected over a 0.5-deg range at atmospheric pressure, and stored under dry nitrogen. The d_6 and d_{10} were 99+ atom % deuterium and were given no further treatment except for drying with molten sodium, as was also the d_0, described below.

The apparatus, shown schematically in Figure 1, was patterned after that used by Davis and Schiessler (*4*), but the design and procedure were modified somewhat. Seven mercury float valves, a, were controlled by mercury in reservoirs attached by tubes b and b′ to the manifold, c, through stopcocks, s. With the mercury in place, only one (capillary) tube, b′, led out of the system itself. The manifold permitted evacuation or introduction of dry nitrogen and led to the usual large mercury manometer, a McLeod gauge capable of measuring pressures down to 5 μmHg, a dry ice trap, and a mechanical pump. Nitrogen was admitted when needed by passage through Drierite and a dry ice trap. The whole apparatus occupied a segment of a cylinder, as in ref 4, and could be immersed in a water thermostat, controlled to ±0.02 °C while still attached to the pump. All the stopcocks were below the water level. The differential mercury manometer, m, had an internal diameter of 15 mm. The differences in the levels in the two arms were measured to 0.01 mm with a Gaertner cathetometer outside of the thermostat, which was also used for measuring the meniscus heights in the two manometer arms. Temperatures were read with a −1 to 51 °C thermometer graduated in tenths and certified by the National Bureau of Standards. The readings were corrected for any differences in meniscus heights in the two arms, as well as to 0 °C.

The procedure was as follows. Although a few direct measurements of the difference between the vapor pressures of d_{10} and d_0 were made, it was found that more reliable results could be obtained by measuring the pure substances separately, with one arm of the manometer always evacuated. Furthermore, metallic sodium, not CaH_2, was used to remove any traces of water. The sodium was placed in the refluxing tube, r, which remained attached to, but could be isolated from, the apparatus by closing the appropriate valve. Further dehydration could then be accomplished, if desired, by returning the sample to r.

After the introduction of the sodium (cut in a dry nitrogen atmosphere in a glovebag) into r with a stream of dry nitrogen sweeping through the apparatus, about 5 cm^3 of d_0, d_6, or d_{10} was added, similarly, the sample frozen in dry ice, and r sealed. The apparatus was evacuated, nitrogen admitted, and the sample refluxed for several minutes, during which time the sodium melted to form a shiny sphere. The sample was again frozen, the system evacuated, dry nitrogen introduced, and the refluxing repeated. The sample was again frozen, the system evacuated, and part of it distilled into bulb e, which contained a small Teflon-covered stirring bar. The remainder of the original sample, along with the sodium, was isolated in r. The mercury in the apparatus was then degassed by pumping at 5 μmHg or less while irradiating with a heat lamp. Finally, the sample in e was degassed by pumping at 25 °C (with magnetic stirring) for 2 or 3 min. While pumping was continued, the sample was frozen and pumped down to 5 μmHg for 10 or 15 min. The arms of the manometer were then divorced by closing the appropriate valve, the whole apparatus was immersed in the thermostat, and the left-hand side of the manometer kept continually at 5 μmHg or less by pumping. After

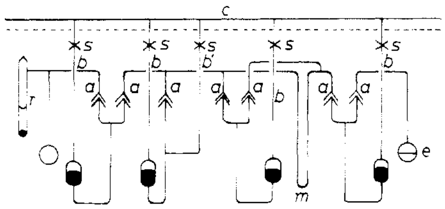

Figure 1. Vapor pressure apparatus (schematic).

Table I. Measured Vapor Pressures (Torr) of p-$(CH_3)_2C_6H_4$ (d_0), p-$(CD_3)_2C_6H_4$ (d_6), and p-$(CD_3)_2C_6D_4$ (d_{10}) at 20–50 °C

t, °C	d_0	d_6	d_{10}
20.00	6.49	6.92	7.03
25.00	8.74	9.34	9.40
30.00	11.56	12.42	12.49
35.13			16.56
35.15		16.42	
35.24	15.46		
40.00	19.84	21.12	21.30
44.27	24.80		
45.00			27.40
45.02		27.18	
50.00		34.51	34.75
50.07	32.81		

Table II. Parameters for $\ln p_{Torr} = A - B/(t\ (°C) + 215.367)$

	A	B
d_0	16.191 36	3371.18
d_6	16.140 26	3342.85
d_{10}	16.116 11	3334.52

$^1/_2$ h, the levels in the manometer showed no further change, and the difference was measured several times with the cathetometer to the nearest 0.01 mm. The mean deviation of the several results was usually 0.02 mm or less. The meniscus heights were also determined and corrections made accordingly. The latter were never more than 0.02 mm. The pressures (Torr) were then converted to 0 °C.

Results and Discussion

The resulting raw data are given in Table I. It is clear that at any one temperature the vapor pressures are in the order $d_0 < d_6 < d_{10}$. They were fitted to the Antoine equation, $\ln p_{torr} = A - B/(t + C)$, as was done in ref 1, where a value of 215.367 for C had been determined for d_0, with t in °C. Because of the relatively short temperature range covered by the present data, the value assigned to C is not important to the fit of the resulting equation: C can be changed by several degrees without seriously altering the fit, although, of course, changing C requires a change in A and B. For this reason C was kept at 215.367 and A and B were determined by least-squares method. The resulting values of A and B are presented in Table II with p in Torr. These parameters reproduce the data of Table I with an average deviation of 0.03 Torr for d_0 and d_{10} and of 0.02 Torr for d_6.

Table III gives the smoothed values for d_0, d_6, and d_{10}, and compares those for d_0 with the results of the National Bureau of Standards (*1*) and of Pitzer and Scott (*2*). It may be noted, first, that in spite of the additional purification steps taken in the careful studies reported in refs 1 and 2 the vapor pressures differ appreciably from each other, especially at the lower temperatures. The fact that Pitzer and Scott used a cathetometer sensitive to only 0.05 mm would account for only a portion of this difference. Moreover, a dynamic method was used in ref 1 but a static one in ref 2 and in the present work. Second, at all but the highest temperature the agreement of the present results with those of ref 1 is better than that between refs 1 and 2. The present values for d_0 agree with those of

Table III. Smoothed Values of Vapor Pressure (Torr) at Rounded Temperatures

t, °C	d_0 present work	d_0 ref 1	d_0 ref 2	d_6	d_{10}
20	6.48	6.52[a]	6.63	6.94	7.02
25	8.73	8.76[a]	8.88	9.33	9.43
30	11.61	11.64	11.76	12.38	12.51
35	15.28	15.28	15.40	16.26	16.40
40	19.89	19.85	19.96	21.11	21.29
45	25.62	25.54	25.63	27.15	27.36
50	32.70	32.54	32.60	34.57	34.83

[a] Extrapolated, but with negligible uncertainty.

Table IV. Standard Enthalpies and Entropies of Vaporization at 25 °C

	d_0	d_6	d_{10}
$\Delta H°_{298}$, kJ/mol	42.98 ± 0.08	42.61 ± 0.09	42.50 ± 0.08
$\Delta S°_{298}$, J/(K mol)	107.0 ± 0.3	106.3 ± 0.3	106.1 ± 0.3

ref 1 within 0.3% on the average, well within the requirements for this project stated above, and gave confidence in the technique.

It follows from Table III that, at 20 °C, the vapor pressure ratio of d_6 to d_0 is 1.07_2 and that of d_{10} to d_0 is 1.08_4. These ratios decrease to 1.05_7 and 1.06_5, respectively, at 50 °C. The implications of these quantities in connection with the inclusion compounds of the p-xylenes, referred to above, will be considered in another paper. The relative values for all seven temperatures were fitted to the Bigeleisen expression (*5*), $\ln (p'/p) = A/T^2 - B/T$, where p' and p refer to the lighter and heavier isotopomers, respectively, with the following results:

$$\ln [p(d_0)/p(d_6)] = -6728.5\ (\pm 0.3)/T^2 + 2.77\ (\pm 0.96)/T$$

and

$$\ln [p(d_0)/p(d_{10})] = -9971.9\ (\pm 0.4)/T^2 + 10.47\ (\pm 1.28)/T$$

These were obtained by using the smoothed (Antoine) data for all three p-xylenes. The values of the resulting parameters were unexpected and, for the present, remain unexplained. For this reason, various other ways of fitting the data to the Bigeleisen expression were tried, such as using the raw data adjusted to common temperatures, but with essentially the same results.

Thermodynamic information for d_0, d_6, and d_{10} was obtained from the present data by first finding the heat capacity, C_p, of d_0(l) and d_0(g) as functions of T (K). The values of C_p(l) (*6*) and of C_p(g) (*7*) fit the expression ΔC_p (J K^{-1} mol^{-1}) = $-133.590 + 0.4462T - 6.108 \times 10^{-4}T^2$ for the vaporization of d_0 in the temperature range studied. This leads, by well-known methods, to $-R \ln f - 133.590 \ln T + 0.2231T - 1.018 \times 10^{-4}T^2 = \Delta H°_0/T + I$, where R is the gas constant, $\Delta H°_0$ and I are integration constants, and f is fugacity. Fugacities were estimated from the raw data by means of the modified van der Waals equation of state suggested by Brewer and Searcy (*8*), taking the normal boiling point to be 411.50 K (*1*) and the liquid molar volumes from Timmermans (*9*). (The fugacities differed from the vapor pressures negligibly at 20 °C and by only 0.25% at 50 °C.) A plot of the left-hand side of the foregoing thermodynamic equation against $1/T$ gave a straight line with slope $\Delta H°_0$ and intercept I. These, in turn, led to $\Delta H°_{298}$ and $\Delta S°_{298}$ for d_0(l) → d_0(g). The same treatment was given to the data for d_6 and d_{10}, using the same molar volumes as for d_0 and the normal boiling points stated earlier. (Use of molar volumes estimated by reducing those for d_0 by 0.06% per deuterium atom (*10*) made no difference in the results.) The standard enthalpies and entropies of vaporization found in this way are presented in Table IV, along with their standard deviations. The values for d_0 may be compared with those of the National Bureau of Standards (11), ΔH°_{298} = 42.38 kJ/mol and ΔS°_{298} = 105.06 J/K mol. The latter were obtained from measurements covering a much wider temperature range, and on more highly purified material; they are doubtless more accurate.

Table IV shows, furthermore, that replacement of hydrogen by deuterium decreases the enthalpy of vaporization and therefore increases the vapor pressure at a given temperature. This is consistent with the behavior of other nonpolar compounds (12). Calculation of the ratio $[\Delta H^\circ_{298}(d_0) - \Delta H^\circ_{298}(d_6)]/[\Delta H^\circ_{298}(d_0) - \Delta H^\circ_{298}(d_{10})]$ gives the value 0.77 ± 0.31, and if replacement of a hydrogen by a deuterium atom always decreases the enthalpy of vaporization by the same amount, this ratio would be 0.60. There is reason to believe, however, that substitution of a deuterium for a hydrogen atom on the methyl group affects the properties more than substitution on the aromatic ring (13). (The normal boiling points quoted earlier can also be interpreted in this way.) If this were so, the ratio of the enthalpy differences would be greater than 0.60, as found. It must be admitted, however, that the uncertainties in the ΔH°_{298} values are such as to make the value 0.77 and the resulting inferences tenuous. Several other methods of treating the data, such as using smoothed rather than raw data or using vapor pressures for d_6 and d_{10} calculated from the d_0 values through the Bigeleisen expressions given above, were tried with virtually the same results.

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Vapor–Liquid Equilibria of Coal-Derived Liquids. 1. Binary Systems with Tetraline at 200 mmHg

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Vapor–liquid equilibrium (VLE) data for the binary systems of tetraline with o-toluidine, m-toluidine, and m-cresol were measured at 200-mmHg pressure. These systems show positive deviations from Raoult's law and form azeotropic mixtures for molar fractions of 0.632 (o-toluidine), 0.551 (m-toluidine), and 0.482 (m-cresol). Data reduction based on the Margules, Van Laar, Wilson, NRTL, and UNIQUAC models provides a correlation for γ_i.

Introduction

Manufacturing synthetic fuels from coal is considered uneconomical under the present competition of petroleum. In coal liquefaction processes, hydrogen is added to a coal suspension in a solvent such as tetraline. Some of the major problems encountered in hydrogenation plants are related to separation processes, i.e. removal of solid particles from the slurry and separation of hydrogenation fractions for recycling of the solvent.

The need for vapor–liquid equilibrium (VLE) data regarding mixtures of coal-derived liquids, which would allow prediction of data for the design of separation equipment, has been indicated elsewhere (1).

Table I. Physical Properties of the Chemicals[a]

compound	property	exptl	lit.	ref
o-toluidine	d(25 °C)	0.9943	0.994 30	2
	n_D(25 °C)	1.5700	1.569 87	2
	bp (200 mmHg)	153.30		
m-toluidine	d(25 °C)	0.9846		
	d(20 °C)	0.9890	0.9889	3
	n_D(25 °C)	1.5658	1.565 70	2
	bp(200 mmHg)	156.15		
tetraline	d(25 °C)	0.9660	0.9662	2
	n_D(25 °C)	1.5393	1.539 19	2
	bp(200 mmHg)	157.00		
m-cresol	d(25 °C)	1.0303	1.030 19	2
	n_D(25 °C)	1.5397	1.5396	2
	bp(200 mmHg)	157.10		

[a] Units: d, g/cm^3; bp, °C.

In this work, VLE data for binary mixtures of a hydroaromatic compound, tetraline, a typical hydrogen donor molecule in liquefaction processes, with two aromatic nitrogen isomers, o-toluidine and m-toluidine, and a phenolic compound, m-cresol, are reported at 200 mmHg. VLE data for the tetraline/m-cresol system have been previously reported at isothermic

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