Vapor Pressures of Phthalate Esters

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DEW-POINT METHOD

UCK and Wise (5) have described a dew-point method for the measurement of moderately low vapor pressures at room temperature. Their measurements extended from values of about 1 micron to about 20 mm. of mercury. This paper presents data on six specially purified phthalate esters obtained with a similar apparatus modified to include higher temperature measurements. At temperatures above room temperature, however, it was found that vapor pressures above approximately 200 microns could not be determined with this instrument. Hence, it was necessary to employ a tensimeter still for determination of higher vapor pressures.

The dew-point method was selected principally because of its apparently large range. At temperatures above room temperature, however, it was found that the sudden cooling of the hot nitrogen stream when it came in contact with air resulted in separation of the sample as a fog obscuring the mirror. For this reason, measurements by this method were restricted to vapor pressures below about 200 microns.

Essentially, the dew-point method consists of directing a gaseous stream of sample and nitrogen of known variable composi-



- Manometer Nitrogen preheater Thermally insulated connecting line copper
- 13 Vaporizer
- 14. Syringe extension

21

Constant temperature bath

- 28 Synchronous motor

November 1952

tion against a thermostated mirror until a spot just forms on the mirror. At this point, the dew and the vapor are in equilibrium and the vapor pressure of the material is equal to its partial pressure in the gas stream. This can be readily calculated from the known composition.

APPARATUS. A schematic diagram of the apparatus is shown in Figure 1.

The liquid sample was fed at a known, constant rate of speed from a hypodermic syringe, 16, through a capillary extension



Figure 2. Tensimeter Assembly

Pirani gage
Stopcock
Dibutyl phthalate manometer
Air inlet valve
Ball joint
Ballast flask
Thermometer
Rubber stopper
Tensimeter

14, and a hypodermic needle, 10, to a 30-ohm constantan-wound heater, 13. The hypodermic needle was embedded in a piece of glass-fiber tape with one strand laid across the needle opening to eliminate drop formation. The needle and a copper-constantan thermocouple, 12, were then securely wired to the heater. The syringe plunger was driven by a ram, 25, operated by a screw mechanism. The motive power for the latter was provided by a synchronous motor, 28, and reducing gears, 27. The apparatus was so arranged that the motor, reducing gears, and syringe could be readily changed, making it possible to vary the feed rate to obtain any vapor pressure within the range of the instrument. During the determination of any one point, the liquid feed rate could not be varied.

For the measurements on dicyclohexyl phthalate, which melts at 63.6° C., a heated syringe was necessary. A steam-jacketed syringe was used; thus it was possible to maintain the molten ester at a constant and readily reproducible temperature.

The steam-heated syringe was calibrated with dicyclohexyl phthalate directly. The other syringes were calibrated with dibutyl phthalate and corrected to the various esters by means of the known densities.

The nitrogen feed rate was measured by Fischer and Porter Flowrators, 4. Two Flowrators were available, covering the range 0 to 58 liters per minute. Before entering the Flowrator, the nitrogen passed through a coil immersed in a constant temperature bath, 3, at 25° C. After leaving the Flowrator, the nitrogen was preheated by passing it through a coil in a sandbath, 6.

The nitrogen-sample mixture passed through a mixing baffle, 17, before impinging on the thermostated mirror, 22. This baffle, as well as the vaporizer, was enclosed by an asbestos-insulated glass tee, 9, which was maintained at a sufficiently high temperature by a Nichrome element to prevent condensation of the sample. A copper-constant thermocouple, 20, placed in the gas stream at the exit from the tee, was provided to make sure that the exit gas stream temperature was always slightly higher than the mirror temperature. The mirror was a chrome-plated copper disk, 0 008 inch thick and 3 inches in diameter, recessed 1.5 inches into an oil bath, 21, kept at a constant temperature by means of a mercury thermoregulator. The temperature of the mirror was measured with a thermocouple formed by soldering a copper and a constantan wire to the mirror about 1 mm. apart. In this way, the copperconstantan junction was located exactly at the face of the mirror. To eliminate heat leak along the leads, they were passed through a 1/4-inch copper tube, 24, immersed in the oil bath before going to the potentiometer. A thermocouple prepared from adjacent sections of the same wire spools showed no deviation from the standard copper-constantan tables when calibrated at 100° C. All thermocouple potentials were determined with a Rubicon Precision portable potentiometer.

OPERATION. Since the liquid feed rate could not be varied during the determination of any one point, the concentration of the ester in the nitrogen stream was controlled by changing the nitrogen flow. The equilibrium nitrogen flow rate at any temperature was determined by starting at too high a flow and gradually decreasing it until a dew could be observed just forming on the mirror. It was necessary to approach the equilibrium point slowly because the rate of nitrogen flow affected the vaporizer temperature. A sudden decrease in the flow rate resulted in an



Figure 3. Vapor Pressure of Dibutyl Phthalate

increase in the vaporizer temperature. This in turn caused an expansion of the liquid in the needle producing a premature end point.

It was necessary to degas the sample before use, especially at low liquid feed rates; otherwise bubbles were formed in the needle ejecting the sample spasmodically. It was sufficient to degas the sample by warming gently while pumping under vacuum and then filling the syringe immediately.

Puck and Wise used a photoelectric cell to indicate dew formation on the mirror. This was not attempted here, since operating



Figure 4. Vapor Pressure of Dioctyl Phthalate

at temperatures above room temperature resulted in fog formation. This fog limited measurements to pressures below about 200 microns for the present study. At higher pressures, the fog became so dense that it was impossible to see the mirror.

Puck and Wise stated that since the rate of evaporation is materially hastened by the swiftly flowing gas stream, complete vaporization is secured at temperatures below the normal boiling point of the liquid. However, it was found in this investigation that if temperatures much below the boiling point were used, incomplete vaporization was obtained as evidenced by the continuance of fog formation for some time after stopping the liquid feed. Nevertheless, it is possible, as mentioned by Puck and Wise, to obtain measurements on materials which decompose at their boiling points. Thus, data were obtained on dicapryl phthalate in the dewpoint apparatus, whereas it decomposed rapidly in the tensimeter.

TENSIMETER METHOD

APPARATUS. A schematic diagram of the apparatus is shown in Figure 2.

The ordinary type of ebulliometer is not suitable for the determination of low vapor pressures because of the large pressure drop encountered between the boiling liquid and the thermometer. For moderately low vapor pressures, Hickman, Hecker, and Embree (3) have described a special wide-necked tensimeter. Their design was used here except that a hot plate was substituted for the built-in heater.

Temperatures in the dioctyl phthalate measurements were determined with a copper-constant n thermocouple in conjunction with a Rubicon Precision portable potentiometer. Several turns of the thermocouple leads were taken around the ends of the support to eliminate heat conduction along the leads. With the other esters, temperatures were determined with a mercury thermometer.

Pressures were measured with a dibutyl phthalate manometer. The low pressure leg of this manometer was continuously pumped out and the pressure on it determined with a Pirani gage. This pressure was added to that read on the manometer to give the total pressure.

OPERATION. Measurements were started at the highest pressure in each case. When vapors were observed in the con-

denser, readings were taken and the pressure was reduced. If the system was at equilibrium, an immediate decrease in the temperature occurred. Further readings were then taken at successively lower pressures.

MATERIALS

The dibutyl phthalate, dicyclohexyl phthalate, and dioctyl phthalate (bis-2-ethylhexyl phthalate) were obtained by distilling Barrett commercial dibutyl phthalate, Elastex DCHP plasticizer and Elastex 28-P plasticizer at average pressures of 7.4, 25.2, and 15.0 microns of mercury, respectively. The fraction distilling between 50 and 75 volume % of the charge was used for the measurements. The dicyclohexyl phthalate melted at 63.6°C. and had a saponification number of 338 (theoretical is 340). The other two materials had saponification numbers equal to the theoretical values.



Figure 5. Vapor Pressure of Dicyclohexyl Phthalate

The dicapryl phthalate was prepared in the laboratory from carefully fractionated capryl alcohol. It was distilled at an average pressure of 9.2 microns of mercury, and the 50 to 70 volume % fraction was used. It had a saponification number equal to the theoretical.

The butyl cyclohexyl phthalate was a laboratory product prepared by treating the silver salt of monocyclohexyl phthalate with butyl iodide. The constancy of the refractive index of successive fractions obtained by distillation at an average pressure of 35.8 microns of mercury demonstrated that this was a pure mixed ester.

The name diiso-octyl phthalate indicates the ester obtained from a commercial primary alcohol manufactured from a petroleum fraction consisting principally of seven-carbon olefins. The resulting alcohol consists principally of a mixture of eightcarbon alcohols. Minor variations in composition of this alcohol are probable; these variations can affect the vapor pressure results.

November 1952

INDUSTRIAL AND ENGINEERING CHEMISTRY



Figure 6. Vapor Pressure of Butyl Cyclohexyl Phthalate

The diiso-octyl phthalate was Barrett Elastex 10-P plasticizer distilled at 11.0 microns of mercury average pressure.

RESULTS AND DISCUSSION

The results are shown graphically in Figures 3 to 8. For dibutyl phthalate and dioctyl phthalate, the data were fitted to an Antoine equation, $\log P = -\frac{A}{T+C} + B$. For the remaining esters the Clausius-Clapeyron equation, $\log P = -\frac{A}{T} + B$ fits the data equally as well. In all cases, the constants were determined by the method of least squares. The values of the constants are listed in Table I.

TABLE I. VAPOR	Pressure 1	Equation Com	ISTANTS
Material	Α	в	С
Dibutyl phthalate Dioctyl phthalate (Bis- 2-ethylheyyl phthalate)	$2872 \\ 3811$	$\begin{array}{c} 11.008\\ 12.639\end{array}$	176.5 201.2
Diso-octyl phthalate Dicyclohexyl phthalate Butyl cyclohexyl phthalate	4829 5069 4924	$13.262 \\ 13.940 \\ 14.194$	• • • •
Dicapryl phthalate	4864	13.283	

Numerous investigators have measured the vapor pressure of dibutyl phthalate by a variety of methods (1-4, 7-9). Small, Small, and Cowley (8) have combined these data into the equation

$$\log P = 10.065 - \frac{1666}{T} - \frac{547,700}{T^2}$$

To test the agreement between the literature data and the data reported here, the literature data were fitted to an Antoine equation over the range 70° to 170° C. with the same value for the constant, C, determined for the present data. Since the curves for the two Antoine equations intersect at about 140° C., it is sufficient to demonstrate that the slopes agree within the experimental error. The standard deviation of the slope for the present data is 258, compared with a difference of 63 between the slopes of the two Antoine equations. Hence, the agreement is demonstrated.



Figure 7. Vapor Pressure of Dicapryl Phthalate



Figure 8. Vapor Pressure of Diiso-octyl Phthalate

The vapor pressure of dioctyl phthalate has been determined by Hickman, Hecker, and Embree (3), Small, Small, and Cowley (3), and Ratchford and Rehberg (6). Agreement between the present data and those of Small, Small, and Cowley is indicated by the fact that their values fall well within the 90% confidence limits calculated from the standard deviation of the values reported here. The values of Hickman, Hecker, and Embree and of Ratchford and Rehberg are indicated in Figure 4 along with the present values. Excellent agreement is obtained between the values reported here and those of Ratchford and Rehberg at higher temperature, the values coinciding at 220° C.

Dicapryl phthalate decomposed very rapidly in the tensimeter. Hence, only the results obtained in the dew-point apparatus are reported.

Diiso-octyl phthalate is a mixture of phthalate esters made from alcohol mixtures containing small amounts of seven- and nine-carbon alcohols, in addition to eight-carbon alcohols. Hence, any method of determining vapor pressures is subject to error because of possible fractionation. Thus, in the dew-point method, the vapor pressure equilibrium is established between the condensate and a vapor composition equal to that of the original sample. Hence, results may be lower than values determined by a static method by an amount depending on the vapor pressures and mole fractions of the constituents of the sample. In the tensimeter method, low values would again be obtained, but the effect would be smaller since only a small fraction of the sample is volatilized. This discrepancy would be significant only for materials having a wide distillation range.

LITERATURE CITED

- (1) Burrows, G., J. Soc. Chem. Ind. (London), 65, 360 (1946).
- (2) Gardner, G. S., and Brewer, J. E., IND. ENG. CHEM., 29, 179 (1937).
- (3) Hickman, K. C. D., Hecker, J. C., and Embree, N. D., IND. ENG. CHEM, ANAL. ED., 9, 264 (1937).
- (4) Kapff, S. F., and Jacobs, R. B., Rev. Sci. Instruments, 18, 581 (1947).
- (5) Puck, T. T., and Wise, H., J. Phys. Chem., 50, 329 (1946).
- (6) Ratchford, W. P., and Rehberg, C. E., Anal. Chem., 21, 1417 (1949).
- (7) Schicktanz, S. T., J. Research Natl. Bur. Standards, 14, 685 (1935).
- (8) Small, P. A., Small, K. W., and Cowley, P., Trans. Faraday Soc., 44, 810 (1948).
 (1) Verball, F. H. and Marshell, A. L. L. Am. Chem. Soc. 61, 0727
- (9) Verhoek, F. H., and Marshall, A. L., J. Am. Chem. Soc., 61, 2737 (1939).

RECEIVED for review July 14, 1951. ACCEPTED June 5, 1952. Presented before the Fourth Meeting-in-Miniature, Philadelphia Section, AMERICAN CHEMICAL SOCIETY, Philadelphia, Pa., Jan. 18, 1951.

Dehydration of Aqueous Methyl Ethyl Ketone with 2-Methyl Furan

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ETHYL ethyl ketone is a common solvent in cloth-coating operations. It is vaporized into an air stream in the course of the operation and recovered from the mixture by absorption in water. The aqueous solution is stripped to obtain an azeotropic mixture from which anhydrous methyl ethyl ketone can be obtained at normal pressure only by the addition of some third component. The azeotrope cannot be resolved into its components by phase separation and fractionation, as is possible with the *n*butyl alcohol azeotrope for example, because of an abnormal solubility-temperature relation. This characteristic has been discussed recently by Newman *et al.* (13). They reviewed methods which have been suggested for breaking the azeotrope and proposed the use of butyl cellosolve in extractive distillation. A liquid-liquid extraction operation with a chlorinated hydrocarbon was suggested for recovery of methyl ethyl ketone from a dilute development. 2-Methyl furan was apparently available in Russia in 1940 where it was obtained from a fraction of a wood distillate. Some properties of the compound were published at that time, including the statement that it does not form azeotropes with methyl acetate, methyl ethyl ketone, or propionaldehyde (15). Other entrainers with known desirable physical properties are isopropyl formate and 1-chloro-2-methylpropane. These compounds are nonazeotropic with methyl ethyl ketone and, like 2-methyl furan, are azeotropic with water. The behavior of ternary mixtures of the possible entrainers was unknown. The use of 2-methyl furan as a nonselective entrainer for the dehydration of aqueous ethyl, isopropyl, and butyl alcohols is claimed in a recent patent (4).

Industrial dehydration processes use sodium or calcium chloride as the third component. Justification for the use of a different

aqueous solution. A method not included in the review employs a 40% caustic solution to dehydrate the azeotrope (3). Pressure distillation to effect a change in the composition of the azeotrope has been patented recently (θ). The possibility of using 2methyl furan as a selective entrainer for water in the methyl

methyl furan as a selective entrainer for water in the methyl ethyl ketone azeotrope was investigated several years ago. Physical data on the system were subsequently obtained when this compound became commercially available for

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method would be based on the elimination of corrosion problems and on improved economy of operation. This paper presents physical data on 2-methyl furan mixtures with water and methyl ethyl ketone. The data were obtained to evaluate a process in which aqueous methyl ethyl ketone is concentrated by extraction using 2-methyl furan which then serves as a selective entrainer to remove residual water by azeotropic distillation. The data include solubility and equilibrium in the system 2methyl furan-water-methyl ethyl ketone, and vapor-liquid