

$D_2PO_4^-$ ion). Their solutions were made up in such a way that the last term in this equation is zero. Their experimental measurements gave values of the third term on the right-hand side of this equation; they are independent of the concentration scale used. They made five determinations of this term; their average value was 0.052 with a mean deviation from the average of ± 0.013 . The measurements were made at 18°C.; at this temperature, $pK(D_2PO_4^- \text{ in } D_2O) = 7.804$ (4) and $pK(H_2PO_4^- \text{ in } H_2O) = 7.221$ (1, 3), so that ΔpK (buffer acid) = 0.587. Hence, for dinitrophenol at 18°C., the work of Martin and Butler gives $\Delta pK = 0.639$, which compares with our value of 0.613 at 25°C.; little is known about the influence of temperature on ΔpK but ΔpK for the second stage of dissociation of phosphoric acid is 0.007 greater at 18° than at 25°C. We conclude that our results are in substantial agreement with those of Martin and Butler and that the ΔpK value for 3,5-dinitrophenol is anomalously higher than the values for other nitrophenols.

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NOMENCLATURE

- a_{D^+} = deuterium ion activity
 C_i = concentration of i species
 D_1, D_2, D = absorbances of solutions of 3,5-dinitrophenol in acid, alkaline, and buffer solutions, respectively
 I = total ionic strength
 m = molality, mole/kg.
 K = dissociation constant on molality scale, mole/kg.
 γ_i = activity coefficient (molal scale) of i species

LITERATURE CITED

- (1) Bates, R.G., Acree, S.F., *J. Res. Natl. Bur. Std.* **30**, 129 (1943).
- (2) Bell, R.P., "The Proton in Chemistry," Fig. 18, p. 189, Cornell University Press, Ithaca, N. Y., 1959.
- (3) Datta, S.P., Grzybowski, A.K., *J. Phys. Chem.* **62**, 555 (1958).
- (4) Gary, R., Bates, R.G., Robinson, R.A., *Ibid.*, **68**, 3806 (1964).
- (5) Martin, D.C., Butler, J.A.V., *J. Chem. Soc.* **1939**, 1366.
- (6) Robinson, R.A., Davis, M.M., Paabo, M., Bower, V.E., *J. Res. Natl. Bur. Std.* **64A**, 347 (1960).
- (7) Robinson, R.A., Kiang, A.K., *Trans. Faraday Soc.* **51**, 1398 (1955).

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Vapor Pressures of Fluorine- and Silicon-Containing Derivatives of Some Hydroxylic Compounds

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The vapor pressures of the acetates, trifluoroacetates, pentafluoropropionates, and trimethylsilyl ethers of 1-butanol, cyclohexanol, *m*-cresol, and *p*-cresol, and *n*-butyl *tert*-butyl ether were measured in the 80° to 130° C. range. Antoine constants have been calculated. Where comparison is possible, the results of this work are in reasonable agreement with data reported in the literature.

IN A GAS chromatographic study of some esters and ethers of certain alcoholic and phenolic compounds, it became necessary to know vapor pressure *vs.* temperature relationships in the 80° to 130° C. range. Since the literature contained little more than a few boiling ranges, the data had to be experimentally determined. It was felt that this information would be of interest because some of the compounds are common, while others are of a hybrid chemical composition and have been rather incompletely characterized.

EXPERIMENTAL

The compounds investigated were the acetates, trifluoroacetates, pentafluoropropionates, and trimethylsilyl ethers of 1-butanol, cyclohexanol, *m*-cresol, and *p*-cresol, and also *n*-butyl *tert*-butyl ether. The parent compounds and acetates were obtained commercially and used without further purification, as were the butyl fluoroesters (Peninsular ChemResearch Corp.). Gas chromatographic analyses revealed no impurities. Other fluoroesters were made

according to Shulgin (17) using trifluoroacetic anhydride (Aldrich Chemical Co.) and pentafluoropropionic anhydride (Pierce Chemical Co.). The trimethylsilyl ethers were made using Freedman and Croitoru's (6) modification of Langer *et al.*'s hexamethyldisilazane (Aldrich) procedure (10). The *n*-butyl *tert*-butyl ether was prepared by a Williamson synthesis from sodium *tert*-butoxide (sodium hydride plus *tert*-butyl alcohol) and *n*-butyl bromide. All compounds were purified by distilling at least twice, with the center cut retained each time. Chromatographic analyses showed a minimum purity of 99.3% with the exception of the *n*-butyl *tert*-butyl ether, which had a 4% impurity of slightly higher boiling point.

Vapor pressures were determined using the ebulliometer and experimental method of Hoover *et al.* (8). A few boiling stones were needed to prevent bumping. The apparatus had to be wrapped in asbestos to prevent excessive heat loss which led to condensation in the bottom portion only. The thermometer was calibrated in a liquid bath against a National Bureau of Standards corrected thermometer. Temperatures were read to 0.1°C. with a magnifier, the

thermometer having 1°C. graduations. The pressure was controlled by a Cartesian manostat (Roger Gilmont Instruments, Inc.) with a small bleed into the system through a needle valve to give dynamic conditions. A 4-liter filter flask helped to damp pressure fluctuations. Pressure measurements were made with a 0- to 800-mm. Hg barometer (Gilmont). Experimental tests with water, benzene, and butyl acetate gave pressures within $\pm 1.2\%$ of accepted or published values at a given temperature. A small amount of sample was distilled into the side arm of the ebulliometer during each run, thus removing a portion of any low boiling impurities.

RESULTS

Our results are presented in Table I. Based on the raw experimental data, constants for the Antoine equation

$$\text{Log}_{10} P = A - B/(C + t)$$

were calculated by a computer program which solved three simultaneous equations. P is the vapor pressure in millimeters of Hg, t is the temperature in °C., and A , B , and C are constants characteristic of the compound. Where there are four data points, the constants are the average of all possible combinations of values available at that point in the calculation procedure. Since, strictly by chance, some of the data yielded operations in the calculation where the difference of two almost equal numbers occurred, small experimental errors caused the Antoine constants to be unreasonable in size; in some instances negative constants

were generated. Small trial and error adjustments in the input data were made until the conditions that the Antoine constants were of reasonable magnitude and the experimental points were regenerated almost exactly by these constants were met simultaneously. Since these adjustments were occasionally necessary, and in some instances the Antoine equations were tested against only three experimental points, there may be serious disagreements from actual behavior outside the experimental range. However, $\log P$ vs. $1/T$ plots show little scatter and the Antoine equations can be used with some confidence within about 10°C. of the range studied.

Values calculated from the Antoine equations and assorted data from the literature are compared in the table. Some of the temperatures reported were listed only as boiling points without atmospheric pressure, so that values at 760 mm. may not be a good comparison. The most extensive comparison is with butyl acetate, and here two sets of reportedly accurate data from the literature are in moderate agreement.

DISCUSSION

To illustrate some of the effects of chemical structure on vapor pressure and relative volatility, the table includes a compilation of vapor pressures at 100°C. calculated from the Antoine equation. Again, the experimental range and discussion must be noted, and application of the tabulated Antoine constants should be restricted to the range of experimentation until further verification. Several interest-

Table I. Vapor Pressure Relationships

Compound	Temperature, °C.				Antoine Constants			Vapor Pressure at 100° C.	This Work ^a	Literature
	Vapor Pressure, Mm. Hg				A	B	C			
<i>n</i> -Butyl acetate	67.9	96.3	124.0		6.9688	1326.7	199.2	342.5	80/164.8	80/161.2, 100/334.1, 125.53/760 (9)
	100.4	301.4	730.0							
Cyclohexyl acetate	95.5	109.7	129.5	172.2	7.6975	1959.7	233.5	66.3	75/22.2	75/20 (13)
	55.1	97.3	198.2	739.1						
<i>m</i> -Tolyl acetate	112.0	127.6	140.0		9.0365	2967.5	277.0	14.6	205/760	
	26.0	49.9	83.2							
<i>p</i> -Tolyl acetate	112.6	127.1	140.6		9.0325	2962.5	276.1	14.3	205/760	
	26.0	48.9	83.5							
<i>n</i> -Butyl trimethylsilyl ether	71.2	95.2	110.6	124.1	7.8899	1977.6	270.1	351.9	124.7/760	124/760 (15), 123.7-5.0/740 (10)
	124.4	300.0	495.3	746.8						
Cyclohexyl trimethylsilyl ether	90.7	104.9	125.1	168.1	7.7488	2014.9	244.7	80.0	169.2/760	170/760 (19)
	55.1	96.8	198.5	740.4						
<i>m</i> -Tolyl trimethylsilyl ether	97.8	111.9	125.8		8.3389	2548.1	269.7	28.0	47.8/113	50/113 (20)
	25.4	45.9	78.8							
<i>p</i> -Tolyl trimethylsilyl ether	101.2	115.6	129.1		8.2412	2481.9	264.2	26.7	59/3.6	59/1 (20)
	28.0	51.3	84.9							
<i>n</i> -Butyl trifluoroacetate	70.9	85.5	94.3	103.5	7.6792	1676.2	245.0	661.5	104.3/760	B.p. 102.7-.8 (4), 104/745 (3), 104.8/760 (12)
	235.3	399.7	548.2	740.7						
Cyclohexyl trifluoroacetate	72.0	93.5	117.8	146.9	7.7345	1905.8	244.8	161.1	147.9/760	B.p. 148.5 (18)
	52.3	126.3	300.5	740.0						
<i>m</i> -Tolyl trifluoroacetate	90.6	106.5	125.0	166.0	7.8830	2017.3	236.3	76.6	167.0/760	B.p. 166.5-7.5 (17)
	51.3	100.2	199.7	736.8						
<i>p</i> -Tolyl trifluoroacetate	92.4	108.6	127.2	168.3	7.6838	1890.0	224.0	70.9	169.5/760	B.p. 169-70 (17)
	51.3	100.4	199.7	736.7						
<i>n</i> -Butyl pentafluoropropionate	81.7	96.8	106.0	116.0	7.5655	1669.7	239.8	446.7	116.7/760	
	234.2	400.5	547.1	740.6						
Cyclohexyl pentafluoropropionate	82.0	103.3	126.5	155.0	8.2517	2226.4	258.8	111.3	155.7/760	
	52.3	126.3	299.9	740.1						
<i>m</i> -Tolyl pentafluoropropionate	98.4	113.0	131.4	172.6	7.9857	2107.1	239.1	59.1	173.7/760	
	54.6	100.2	199.9	732.9						
<i>p</i> -Tolyl pentafluoropropionate	98.8	113.5	133.0	174.4	7.6389	1886.7	220.9	57.5	175.6/760	
	54.6	100.2	200.6	732.6						
<i>n</i> -Butyl <i>tert</i> -butyl ether	83.3	101.4	112.0	123.5	7.2222	1518.2	225.1	356.3	124.6/760	124/760 (14), b.p. 124 (15)
	199.1	372.3	524.5	734.2						

^a Calculated from Antoine equation

ing relationships are apparent upon inspection of the table.

Vapor pressures of *m*-tolyl derivatives are higher than those of *p*-tolyl derivatives for all compounds examined here. This is also true for the *m*-cresol-*p*-cresol parent compounds, where the vapor pressure ratio is 1.025 at 100°C. However, this behavior continues to the boiling point for the derivatives, whereas with the cresols the meta-isomer has the higher boiling point at atmospheric pressure. The greatest vapor pressure difference occurs with the trifluoroacetates where a ratio of 1.080, *m*-/*p*-, exists at 100°C. The ratio at 100°C. for the pentafluoropropionates is 1.028, indicating that any isomeric effect diminishes when the presence of a larger ester group makes the aromatic portion a smaller fraction of the total molecule. Fluorination of the acetate causes both a marked increase in vapor pressure and an increase in the *m*-/*p*- ratio, the acetate ratio being 1.021.

The butyl esters show a similar vapor pressure increase upon fluorination. The vapor pressure of the *n*-butyl *tert*-butyl ether is slightly higher than that of the trimethylsilyl analog, which might be expected in view of the higher atomic weight of silicon.

LITERATURE CITED

- (1) Auwers, K.V., Schmelzer, A., *Sitzber. Ges. Beförder Ges. Naturw. Marburg* **62**, No. 4, 113.
- (2) Belov, V.N., Rudol'fi, T.A., *Sb. Statei Obshch. Khim., Akad. Nauk SSSR* **1**, 266 (1953).
- (3) Bourne, E.J., Stacey, M., Tatlow, J.C., Worrall, R., *J. Chem. Soc.* **1958**, 3268.
- (4) Campbell, K.N., Knobloch, J.O., Campbell, B.K., *J. Am. Chem. Soc.* **72**, 4380 (1950).
- (5) Fajkas, J., *Chem. Listy* **52**, 1320 (1958).
- (6) Freedman, R.W., Croitoru, P.P., *Anal. Chem.* **36**, 1389 (1964).
- (7) Henglein, F.A., Kramer, J., *Chem. Ber.* **92**, 2585 (1959).
- (8) Hoover, S.R., John, H., Mellon, E.F., *Anal. Chem.* **25**, 1940 (1953).
- (9) Kliment, V., Fried, V., Pick, J., *Collection Czech. Chem. Commun.* **29**, 2008 (1964).
- (10) Langer, S.H., Connell, S., Wender, I., *J. Org. Chem.* **23**, 50 (1958).
- (11) Langer, S.H., Pantages, P., Wender, I., *Chem. Ind. (London)* **1958**, 1664.
- (12) Macey, W.A.T., *J. Phys. Chem.* **64**, 254 (1960).
- (13) Mousseron, M., Jacquier, R., *Bull. Soc. Chim. France* **1950**, 698.
- (14) Norris, J.W., Rigby, G.W., *J. Am. Chem. Soc.* **54**, 2088 (1932).
- (15) Sauer, R.O., *Ibid.*, **66**, 1707 (1944).
- (16) Schiopu, M., Bot, O., Onu, V., *Bul. Inst. Politeh. Iasi* **7**, No. 3-4, 115 (1961).
- (17) Shulgin, A.T., *Anal. Chem.* **36**, 920 (1964).
- (18) Staab, H.A., Walther, G., *Angew. Chem.* **72**, 35 (1960).
- (19) Voronkov, M.G., Shabarova, Z.I., *Zh. Obshch. Khim.* **29**, 1528 (1959).
- (20) *Ibid.*, **30**, 1955 (1960).
- (21) Zavgorodniĭ, S.V., *Ibid.*, **14**, 270 (1944).

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CaCl₂-Rich Region of the CaCl₂-CaF₂-CaO System

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Thermal analysis studies of the CaCl₂-CaF₂-CaO system show that it contains a ternary eutectic at 625°C. at the composition CaCl₂-17 mole % CaF₂-4 mole % CaO, plus ternary peritectics at CaCl₂-23 mole % CaF₂-10 mole % CaO and CaCl₂-23 mole % CaF₂-13 mole % CaO at 660° and 670°C., respectively. The CaCl₂-CaF₂ binary phase diagram determined in this work differs only slightly from those in the literature. However, the CaCl₂-CaO diagram was found to have a peritectic point at 18.5 mole % CaO and 835°C. which has not previously been reported. The corresponding incongruently melting compound is CaO · 2CaCl₂.

DURING the development, in this laboratory, of nuclear reactor fuel reprocessing methods utilizing molten salts and metals as reaction media, it became necessary to know the liquidus surface of the CaCl₂ corner of the CaCl₂-CaF₂-CaO phase diagram. Information is available in the literature for each of the three binary systems (1-5), but none for the ternary system. Therefore, the portion of the CaCl₂-CaF₂-CaO phase diagram of interest was determined by thermal analysis techniques.

EXPERIMENTAL

Procedure. The salt mixture to be investigated was placed in a 1.5-inch diameter Type 304 stainless steel crucible, which was then put into a 2.5-inch tantalum crucible. The space between the two crucibles was filled with powdered zirconia for thermal insulation. These two crucibles were then lowered into a furnace well attached to the bottom

of an inert atmosphere (He) glovebox. The salt mixture was heated 50° to 100°C. above the melting point and stirred with a tantalum agitator for at least 1 hour to ensure solution of all components. The salts did not noticeably attack the stainless steel crucible.

A Type 304 stainless steel-sheathed Chromel-Alumel thermocouple was placed in the salt and another was located outside the crucible containing the salt, and insulated from it. The temperatures of the two thermocouples were measured using a two-pen Bristol recorder when heating and cooling curves (both at a rate of about 4° to 5°C. per minute) were run. The heating rate was determined by the voltage applied to the furnace, and the cooling rate was the inherent cooling rate of the furnace after the power was turned off. The temperatures of thermal halts corresponding to the liquidus, eutectic, and other points were determined by comparing the heating and cooling curves of the thermocouple in the salt with that