

TEMPERATURE DEPENDENCE OF SATURATED VAPOUR
PRESSURES OF METHYL ISOBUTYL KETONE,
DIISOBUTYL KETONE, 1,1-DIFLUOROTETRACHLOROETHANE,
AND 1,2-DIFLUOROTETRACHLOROETHANE

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Dedicated to late Academician Eduard Hála.

Temperature dependence of saturated vapour pressures of methyl isobutyl ketone, diisobutyl ketone, 1,1-difluorotetrachloroethane, and 1,2-difluorotetrachloroethane was measured. A static method was used, and the measurements were carried out in the temperature range of 261 to 353 K and in the pressure range of 0.5–49 kPa.

This work resumes our preceding studies from the region of thermodynamics of vapour–liquid phase equilibria referring to the groups of aliphatic ketones¹ and mixed halogenated ethanes^{2,3}. These groups are supplemented with four further substances by presenting their temperature dependence of saturated vapour pressures over the liquid and/or solid phases.

EXPERIMENTAL

Preparation and purity of substances. The substances studied were synthesized at laboratories of this Institute. They were purified by distillation in a rotary hundred-plate column with stainless steel packing. The substance purity was determined chromatographically. For all the substances it was higher than 99.95%.

Measurement: The temperature dependence of saturated vapour pressures was determined by a static method of direct saturated vapour pressure measurement. The apparatus was designed by Adamcová and Beneš and is described in detail in the literature⁴. It is characterized by these technical data: The design of thermostat and control units makes it possible to measure temperature with an accuracy of 0.05 K. The saturated vapour pressure of the substance measured is determined from the difference of mercury levels in the inside and outside manometers. The difference is established by means of cathetometer with an accuracy of ± 0.01 mm.

Each substance is degassed before the measurement. Degassing is carried out five times by repeated evacuation to a pressure of 10^{-3} Pa, the substance being cooled deep.

RESULTS

The measured data on the temperature dependence of saturated vapour pressures of methyl isobutyl ketone (thereinafter MIBK), diisobutyl ketone (DIBK), 1,1-difluorotetrachloroethane (1,1-DFTCE), and 1,2-difluorotetrachloroethane (1,2-DFTCE) are given in Table I. Since the experimental equipment makes it possible to determine, on using a cryostat, even the saturated vapour pressures of substances

TABLE I

Summary of the measured data on the temperature dependence of saturated vapour pressures p of substances studied

Temperature K	p kPa	Temperature K	p kPa
MIBK		DIBK	
288.09	1.704	288.07	0.528
293.25	2.415	293.13	0.753
298.10	3.186	298.15	1.010
303.04	4.006	303.26	1.215
308.19	5.247	308.17	1.531
313.09	6.701	313.14	1.813
318.10	8.441	318.19	2.277
323.12	10.623	323.18	2.657
333.27	16.253	328.15	3.231
342.90	23.717	333.10	3.878
353.06	34.378	338.15	4.614
		343.17	5.522
		353.15	7.712
1,1-DFTCE		1,2-DFTCE	
261.65	1.256	258.05	0.885
262.15	1.333	258.25	0.854
266.75	1.815	263.05	1.250
278.78	3.419	268.15	1.687
287.67	5.460	274.18	2.160
293.04	6.980	278.18	2.742
298.26	8.830	283.15	3.571
303.19	11.000	287.86	4.690
313.29	16.967	292.31	5.979
323.14	24.271	298.18	8.143
333.19	34.842		
343.15	48.870		

TABLE II
 Constans of Antoine vapour pressure equation

Substance	Phase ^a	A	B	C	Std. deviation σ_p kPa	Temperature interval K
MIBK	l	5.88818	1 242.35	205.546	0.040	288–353
DIBK	l	6.39916	2 159.44	311.715	0.042	288–353
1,1-DFTCE	s	8.75645	3 128.56	102.348	0.119	262–313
	l	6.84045	1 850.07	289.138	— ^b	313–343
1,2-DFTCE	s	8.34629	2 473.47	34.441	0.031	258–298

^a l liquid phase, s solid phase; ^b three constants evaluated from three experimental points.

at low temperatures, the saturated vapour pressures of 1,1-DFTCE both for the liquid and for the solid phase were measured. The data for the liquid and solid phases are divided in Table I by the dash line. In case of 1,2-DFTCE, the data by Dohnal and Novotná⁵ were supplemented with those on saturated vapour pressures over the solid phase.

The Antoine equation was used for calculating the experimental data:

$$\log p/\text{kPa} = A - B/(T/\text{K} + C),$$

where p denotes the pressure, T the temperature, and A , B , C are parameters of the equation. To calculate the parameters, a modification of the weighted least-squares method⁶ was used. The calculation starts with choosing the numerical value of parameter C_0 and calculating parameters A_0 and B_0 of the linearized form of the Antoine equation. The accurate values of the parameters were determined by an iterative procedure in terms of a residual function where the individual corrections to parameters A , B , C are determined by the weighted least-squares method.

The results of the measured data correlation are presented in Table II. The first and second columns give the substance name and phase which the numerical values of the Antoine equation parameters pertain to. Further, the standard deviation in pressure σ_p (kPa) and the temperature interval of validity of the values are given. The results of correlations correspond to the technical possibilities of the experimental equipment used.

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