J. Chem. Thermodynamics 74 (2014) 16–21

Contents lists available at ScienceDirect

J. Chem. Thermodynamics

journal homepage: www.elsevier.com/locate/jct

Vapor pressure data for ethyl-2-methylbutyrate, hexanal and (*E*)-2-hexenal at a pressure range of (25 to 190) kPa

David A. Meneses [a], Arturo Bejarano [a], Juan C. de la Fuente [a,b,*]

[a] *Departamento de Ingeniería Química y Ambiental, Universidad Técnica Federico Santa María, Avda. España 1680, Valparaíso, Chile*
[b] *Centro Regional de Estudios en Alimentos Saludables, Blanco 1623, Valparaíso, Chile*

ARTICLE INFO

Article history:
Received 7 October 2013
Received in revised form 28 February 2014
Accepted 5 March 2014
Available online 22 March 2014

Keywords:
Dynamic recirculation method
Ethyl-2-methylbutyrate
Hexanal
(*E*)-2-hexenal
Vapor pressure
Apple aroma

ABSTRACT

The saturated vapor pressures of pure ethyl-2-methylbutyrate, hexanal and (*E*)-2-hexenal, which are volatile compounds characteristic of apple aroma, were measured with a dynamic recirculation apparatus at a pressure range of (24.5 to 190.0) kPa. Measurements were made over the temperature range of (362.1 to 429.9) K for ethyl-2-methylbutyrate, (358.1 to 425.8) K for hexanal, and (373.5 to 446.2) K for (*E*)-2-hexenal. The maximum likelihood method was used to estimate the parameters of the Antoine equation, whereas the parameters of an extended Antoine equation and the Wagner equation were determined by non linear least square method. The three models showed root mean square deviations (*rmsd*) of 0.29%, 0.28%, and 0.27% for ethyl-2-methylbutyrate, 0.58%, 0.48%, and 0.38% for hexanal, and 0.89%, 0.62% and 0.36% for (*E*)-2-hexenal, respectively. Additionally, the experimental data and correlation were compared with those available in the literature.

1. Introduction

Fruit aroma is a complex mixture of a large number of volatile compounds that contribute to the overall sensory quality of fruit specific to species and cultivar [1]. Over 300 volatile compounds have been measured in the aroma profile of apples. These compounds include alcohols, aldehydes, carboxylic esters, ketones, and ethers [2]. Flath *et al.* [3] studied odor thresholds of the volatile compounds of "Delicious" apples and pointed out ethyl-2-methylbutyrate, hexanal, and (*E*)-2-hexenal as essential constituents of apple aroma.

The use of (counter-current) supercritical CO_2 fractionation (CC-SCF) is an alternative technology for the recovery and concentration of fruit aromas [4]. The applications of CC-SCF of aqueous solutions are mainly related to alcoholic beverages. The topics of most intense scientific research are the dealcoholization [5–9] and recovery and separation of the aroma [10–14] of wine and other spirits. However, the information on recovery and concentration of aromas from non-alcoholic beverages (*e.g.*, natural fruit aromas) using CC-SCF is very limited in the literature, and the existence of commercial scale CC-SCF processes is currently low [15].

To successfully apply CC-SCF to the fruit aroma recovery, (vapor + liquid) equilibrium data are required for the mixture of CO_2 + volatile compounds. Data of vapor pressure of pure volatile compounds is a relevant property on which the (vapor + liquid) calculations have a strong dependence and therefore it is of great importance in the design of separation processes. Moreover, other (physical + chemical) properties can be derived based on the vapor pressure data [16]. Additionally, limited information regarding vapor pressure data were reported in the literature, mainly for ethyl-2-methylbutyrate and (*E*)-2-hexenal.

The aim of this research was to measure the isobaric (vapor + liquid) equilibrium in terms of temperature and vapor pressure for these three representative flavor compounds, namely, ethyl-2-methylbutyrate, hexanal and (*E*)-2-hexenal, for a pressure range of (24.5 to 190) kPa. The ester group was represented by ethyl-2-methylbutyrate, while hexanal and (*E*)-2-hexenal belonged to the aldehyde group. The experimental values were fit to the Antoine, extended Antoine, and Wagner vapor pressure equations.

2. Experimental

2.1. Materials

The reagents, ethyl-2-methylbutyrate (99%), hexanal (98%), and (*E*)-2-hexenal ($\geqslant$95%) were purchased from Sigma–Aldrich (St. Louis, MO). These materials were used without further purification.

2.2. Apparatus and procedures

The vapor pressure was measured using a commercial all-glass dynamic recirculation isobaric (vapor + liquid) equilibrium (VLE)

---

* Corresponding author. Tel.: +56 32 2654110; fax: +56 32 2654478.
E-mail address: juan.delafuente@usm.cl (J.C. de la Fuente).

http://dx.doi.org/10.1016/j.jct.2014.03.006
0021-9614/© 2014 Elsevier Ltd. All rights reserved.

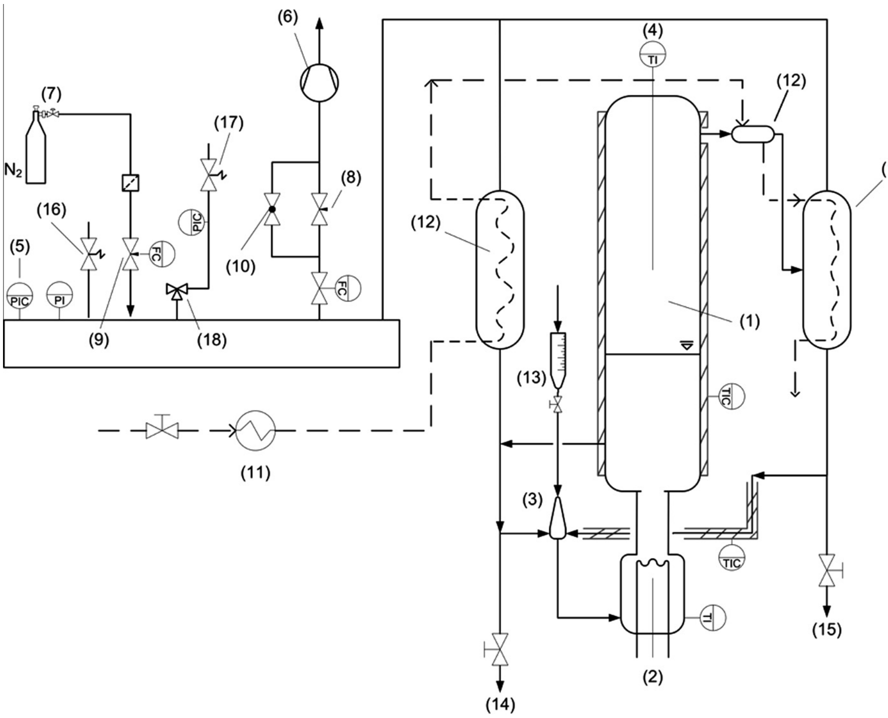

FIGURE 1. Experimental apparatus: (1), Cottrell pump; (2), immersion heater; (3), mixing chamber; (4), vapor Pt-100 temperature probe; (5) pressure controller; (6), vacuum pump; (7), N_2 supply; (8), vacuum throttle valve; (9), pressure throttle valve; (10), vacuum by-pass; (11), thermo regulated bath; (12), vapor condensers; (13), filling tunnel; (14) and (15), liquid and vapor samplers; (16), overpressure relief valve; (17), vacuum relief valve; (18), 3/2 way valve.

apparatus shown in figure 1 (Labodest model 602D, *i*-Fischer Engineering GmbH, Waldbüttelbrunn, Germany) [17]. Its operation procedure relies on the principle of the recirculation of both liquid and vapor phases at controlled pressure. The advantage of the recirculation method is the rapid appearance of the equilibrium simultaneously with the exact measurement of the boiling temperature. The experimental procedure used was as follows: the pure compound was charged in the apparatus by the filling tunnel (13), the N_2 supply (7) to the system was opened, once the liquid is at the desired level the magnetic stirrer bar was activated (3), the pressure throttle valve (9) is opened, and the vacuum pump (10) was started to work. The desired value of pressure was set on the controller panel, the immersion heater (2) was activated and finally, fine adjustments of pressure were made by manual operation of valve (8). In order to verify that system reached the equilibrium, the temperature stability had to remain constant (within ±0.1 K) for a period of time of (15 to 30) min [17]. The experimental uncertainty was the uncertainty associated to the equipment, which was estimated <0.2% [18]. This estimation was calculated by comparison between the measurements for *n*-heptane made in our equipment and those reported in literature. The comparison, the apparatus and methodology are described in more detail in a previous work [18].

3. Results and discussion

Experimental temperature and vapor pressures are listed in table 1, along with the percent deviations $(10^2 \cdot (p - p_{\text{cal}})/p)$ between the observed and calculated (p_{cal}) pressures from the Wagner equation (4), for ethyl-2-methylbutyrate, hexanal, and (*E*)-2-hexenal.

The maximum likelihood method was used to estimate the parameters of the Antoine equation (1) in order to take into account its non-linear mathematical form and the fact that both temperature and pressure are subject to experimental variability [19].

$$\ln\{p_{\text{cal}}/\text{kPa}\} = A - \frac{B}{T/K + C}, \tag{1}$$

where *A*, *B* and *C* are adjustable parameters. The maximum likelihood objective function to be minimized has the form:

$$S = \sum_i \left[\left(\frac{T - T_{\text{cal}}}{\sigma_{T,i}} \right)^2 + \left(\frac{p - p_{\text{cal}}}{\sigma_{p,i}} \right)^2 \right], \tag{2}$$

where $\sigma_{T,i}$ and $\sigma_{p,i}$ are estimated standard deviations in the measured temperature and pressure for the *i*th observation. These values were assigned from the experimental set up as $\sigma_{T,i} = 0.1$ K and $\sigma_{p,i} = 0.1$ kPa.

The extended Antoine equation (3) [20] has the form:

$$\ln\{p_{\text{cal}}/\text{kPa}\} = A + \frac{B}{T/K} + C \cdot \{T/K\} + D \cdot \ln\{T/K\} + E \cdot \{T/K\}^6, \tag{3}$$

where *A*, *B*, *C*, *D* and *E* are adjustable parameters.

The Wagner equation (4) [21] with four different functional forms, with exponent $i \leqslant 6$, was evaluated to represent the measured vapor pressures. The results for the regression analysis have shown that there were not significant differences, in terms of root mean square deviation (*rmsd*), among the four functional forms selected for the ester and both aldehydes. However, the functional form depicted by equation (4), with parameters ($c_3 = c_6 = 0$), showed the best representation for the vapor pressures measured for ethyl-2-methylbutyrate and (*E*)-2-hexenal, while the same functional form, with parameters ($c_{2.5} = c_5 = 0$), showed the best representation for hexanal.

$$\ln(p_{\text{cal}}/p_c) = \{T_c/(T/K)\}\left(c_1 \cdot \tau + c_{1.5} \cdot \tau^{1.5} + c_{2.5} \cdot \tau^{2.5} + c_3 \cdot \tau^3 + c_5 \cdot \tau^5 + c_6 \cdot \tau^6\right), \tag{4}$$

where p_{cal} is the calculated vapor pressure, T_c and p_c are the critical temperature and pressure, c_i are the fitting model parameters, and, $\tau = 1 - T/T_c$ is a reversed reduced temperature variable. The critical