Silikáty 27, s. 355—363 (1983)

VAPORIZATION OF SIMPLE SUBSTANCES USED IN GLASS MELTING

I. High-temperature Transpiration Apparatus

JAN HLAVÁČ, MIROSLAV KARÁSEK, LUDMILA RYBAŘÍKOVÁ

Institute of Chemical Technology, Suchbátarova 5, 166 28 Prague 6

Received 13. 1. 1983

In the first of a series of papers, a description is presented of a transpiration apparatus suitable for measuring the density of vapours of solids and melts up to 1400 °C in reactive atmospheres. The function of the apparatus was verified by means of sodium chloride; a satisfactory agreement between the vapour pressures determined and data in the literature was found.

INTRODUCTION

Considerable attention has been paid in recent years in the literature to vaporization of volatile substances from melted glasses. It appears, however, that under operating conditions the vaporization occurs particularly in the initial stage of melting, when the individual components of the raw-material mix are capable of evaporating extensively before forming reaction products or melt with the other components. Under these conditions, the vaporization is distinctly different from that taking place during the usual experimental arrangement when measuring vapour pressures, which is generally carried out in vacuo or in an inert gas atmosphere. This is why the literature presents very little information on the vaporization of simple compounds, such as B_2O_3, Na_2CO_3, Na_2SO_4 etc. in the presence of reactive gases and water vapour. There is therefore a lack of essential data applicable for an explanation of the behaviour of these substances under real conditions and for practical engineering calculations. The present study had the aim to fill this gap at least partially. The transpiration method was chosen for the measurements, since it allows to study vaporization in the presence of reactive gases and vapours.

TRANSPIRATION METHOD

The transpiration method is one of the oldest and most effective ways of studying heterogeneous equilibria in the systems condensed phase-gas at high temperatures. It has been used mainly for measuring vapour pressures and dissociation pressures. It is virtually the only way of measuring these quantities in the presence of higher concentrations of other gases. The principles of the transpiration (also called transportation or saturation) method are described in comprehensive studies, such as those by Merten and Bell [1], Richardson and Alcock [2], and the like.

The principle of the method is based on passing a suitable gas (inert or reactive) above a solid sample or melt so as to saturate it with the respective vapours. The gaseous mixture is then analyzed or the amount of condensed vapours is determined on cooling down. The vapour pressure is calculated from these data and from the amount of gas passed over the specimen.

The saturating part of the apparatus is shown schematically in Fig. 1. The carrier gas flows through a tube around the specimen placed in the isothermal zone of a furnace. The narrowing of the tube in front of the specimen and behind it should suppress lossess of vapours by diffusion.

The time of dwell of the gas in the saturation space should be adequately long to create an equilibrial concentration of the vapours throughout the gas volume.

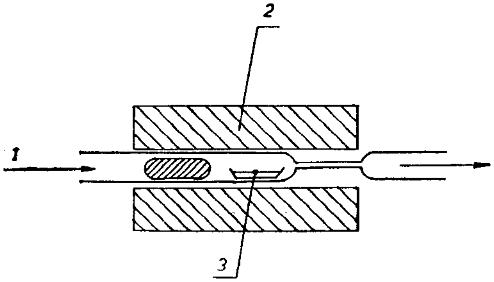

Fig. 1. Schematic diagram of the saturation part of the transpiration apparatus; 1 — carrier gas inlet 2 — furnace, 3 — boat with sample.

The saturation proceeds by diffusion and also involves convection. According to Merten and Bell [1], the following condition should be met for a laminar gas flow and for a 90 % saturation: $v < 5.46DL$, where D is the diffusion coefficient of the vapour and L is the length of the zone containing the specimen. This condition holds when a constant concentration of vapours is maintained at the specimen boundary. When the diffusion coefficient of the high-temperature vapours is of the order 1 cm^2 s^{-1}, the upper limit of the applicable rate of flow of the carrier gas in the apparatus described below amounts to $v = 38$ cm^3 s^{-1} (the volume is related to the measuring temperature).

Before entering the saturation space, the carrier gas should have a rate of flow sufficient for preventing the vapours from passing in the opposite direction by diffusion. This is ensured by narrowing the cross section, for which the following condition has to be met: $v > 4.6DA/l$, where A is the cross section area and l is the length of the narrowed supply tube. For example, for $A = 1$ cm^2 and $l = 3$ cm, the minimum rate of flow of the carrier gas $v = 1.5$ cm^3 s^{-1}, if the losses due to diffusion are not to exceed 1 %.

The construction materials have to be chosen with regard to the measuring temperatures (quartz glass, mullite or corundum ceramics, nickel, platinum, etc.). Argon and nitrogen are mostly used as the inert carrier gas, and hydrogen serves as a nonreactive carrier gas for measuring the pressures of metallic vapours. The reactive carrier gas should either prevent dissociation, or form the required compounds; for instance, H_2 behaves as a reactive gas with respect to Ge and Si, forming their volatile hydrides, and the measurement then yields apparent vapour pressures [3] which are effective pressures with respect to vapour transport. Another example is provided by the vaporization of Mo or W in an oxygen stream. The effect of changes in partial pressure of the reactive gas sometimes allows to determine the type of molecules comprising the vapour [1].

The measurements are usually carried out under pressures close to atmospherical pressure, but it is also possible to measure under higher pressures or at pressures reduced down to about 0.01 MPa. The partial pressure of the vapour in question is calculated on the assumption of ideal behaviour using the equation:

$$p = \frac{n_V}{n_V + n_C} P,$$

where n_V and n_C are the numbers of vapour and carrier gas moles respectively, and P is total pressure. To calculate n_V from analytical data or from a known amount of the condensed vapour, one has to know the composition of molecules present in the vapour; this is usually determined by mass spectroscopy. For some purposes, particularly for engineering calculations of mass transport, one only needs to know the total vapour density without knowing the molecular composition. The authors of older studies dealing with the transpiration method had assumed that even at a low rate of flow the carrier gas is unsaturated, and could only be saturated under static conditions. For this reason they extrapolated the diagrams of apparent vapour pressure in terms of carrier gas flow rate to a zero rate of flow. This method mostly yielded excessively high values. Suitable conditions for correct measurements have therefore to be determined experimentally in the way indicated in Fig. 2. This shows the curves of vapour density and vaporization rate, both in dependence on the flow rate of the carrier gas. Region I is characterized by diffusion effects, i.e. a loss of some of the vapours by diffusion, which is relatively fast compared to the carrier gas flow. Regular saturation takes place in the region II; the vapour density remains constant, the amount of vapour increases linearly with the carrier gas rate of flow. The actual vapour pressure is evaluated within this region. In region III, the rate of flow of the carrier gas is so fast that it cannot be saturated with the vapours; the region may be suitable for providing information on the vaporization kinetics. Complete saturation of the carrier gas, which is indicated by a distinct horizontal section of the vapour density curve, can be ensured only with a suitable design of the saturating part of the apparatus.

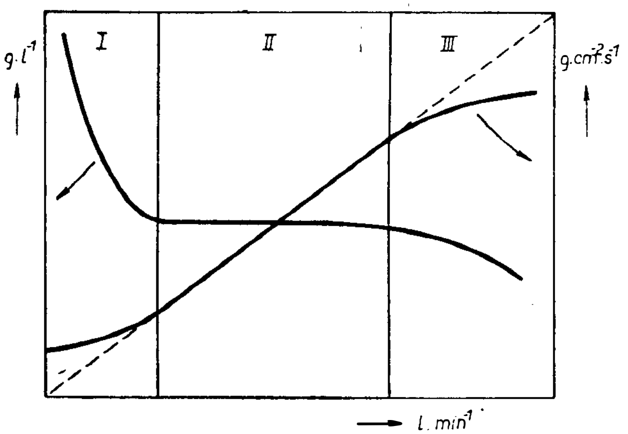

Fig. 2. Vapour density [g litre^{-1}] and vaporization rate [g cm^{-2} s^{-1}] vs. carrier gas rate of flow [litres min^{-1}].

APPARATUS

The design of the apparatus was based above all on the experience published in [4 through 8]. A similar method has more recently been described, e.g. in [9]. A schematic diagram of our apparatus is shown in Fig. 3.

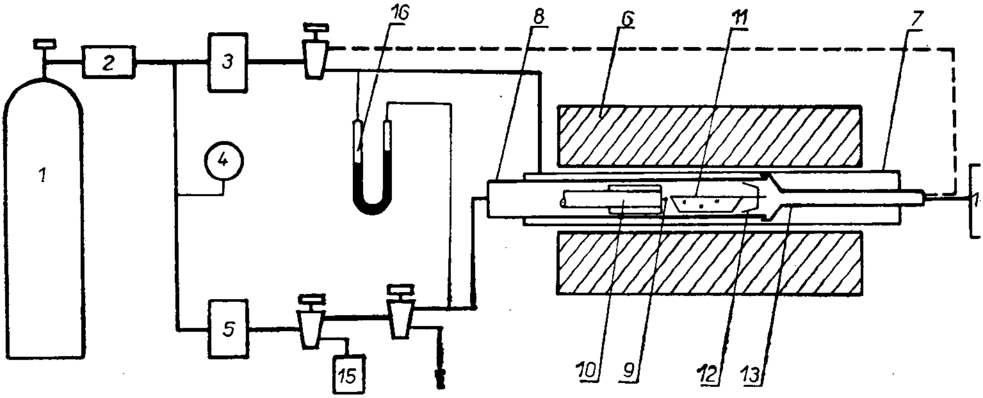

Fig. 3. Schematic diagram of the transpiration apparatus.

In an electric resistance furnace (6) there is a corundum or quartz tube (7), the so called „outer“ one, closed at both ends by metal flanges with union nuts and sealed with silicon rubber rings. Through the front flange (to the left) passes the platinum "internal" tube (8), 20 mm in diameter, terminating in the isothermic furnace zone. The tube is loosely closed with a platinum crucible (12) to slow down the gas flow (for better saturation) and to throttle the cross section (to suppress vapour losses due to diffusion). It is also possible to use corundum or quartz inner tubes and to protect their inner surface from the vapours by covering them with a platinum sheet.

In the saturation part of the inner tube, there is a platinum boat (11) 70×12×7 mm in size, containing the substance to be tested. Close to the boat there is the junction of thermocouple (9) which is protected with a corundum tube (10) provided with an element decreasing the furnace cross section, thus preventing the vapours from escaping from the heat zone by diffusion. The end of the inner tube (8) is inserted into the expanded end of platinum tube (13) serving as a condensate collector. This tube is fitted and sealed in the rear flange (to the right in the Figure) provided with cooling ribs. A Teflon holder for aerosol filter [14] is fitted to the collector outside the furnace. In another arrangement, the filter is replaced by a washing flask containing a suitable absorbing liquid.

The respective carrier gas is passed from a pressure cylinder (1) through dessicating column (2) containing silica gel and $CaCl_2$, or $CaCl_2$ and $Mg(ClO_4)_2$. The gas stream is then branched into two flow rate controllers (3 and 5) capable of maintaining, within 0.1—1 litre/min, a constant rate of flow independently of output pressure. From the controller (3) the gas passes through the front flange to the outer tube, rinsing it and then entering into the carrier gas flow through the gap between the inner tube and the collector. The manometer (16) installed in the rinse gas line serves for setting the overpressure in the outer tube, which prevents the carrier gas from escaping through untightness at the point where the collector is fitted. A mercury manometer or pressure gauge (4) serves for checking the tightness of the entire apparatus. From the other controller (5) the carrier gas*) passes into two two-way cocks which either direct the gas to the soap film flow meter (15) or pass it away from the furnace. The rinse gas can be passed through the collecting tube in the opposite direction (indicated by dashed line in Fig. 3); this connection is used during the period of tempering the furnace including the specimen, and should prevent the vapours from entering the collecting tube. Only when the temperature has equalized, the gas flow is reversed in the way described above, and this is also the moment of starting the time counter.

The carrier gas was saturated with water vapour in a ball condenser filled with ceramic beads. The condenser was placed between the flow rate controller (5) and the furnace. The carrier gas and the water being metered passed co-currently through the condenser, and the saturation temperature was maintained by means of an ultrathermostat. To prevent the water vapours from condensing, the connecting hoses leading to the furnace were heated. In another arrangement the carrier gas was saturated with water in washing bottles kept at the required constant temperature in a thermostat.

The electric furnace was provided with platinum wire winding divided into three sections with separate thermocouples. The increased input into the side windings should eliminate the losses through the front furnace walls, thus achieving a constant temperature zone about 12 cm in length. The temperature was controlled by Zepakomp regulators, which controlled the autotransformer output voltage. The temperature variations were within the limits of ±3 °C, and the interval tended to increase during long-term measurements only (more than 4 hours).

MEASUREMENT PROCEDURE

The weighed boat with the substance to be examined is placed in the inner tube and plugged with a platinum crucible. By shifting the furnace the inner tube is inserted into the outer one to a depth ensuring placement of the specimen in the isothermic zone. The collector is inserted from the other side and the furnace is sealed by means of the flanges and rings. The apparatus tightness is checked. Following temperature equalization in the furnace, the required rates of flow of the carrier and rinsing gas are set and the exposure time counting is started. The temperature is read, the pressure in the apparatus checked and the carrier gas flow monitored during the exposure. After ending the thermal exposure, the carrier gas flow is turned off, the furnace dismantled, the loss in specimen weight determined and the amount of condensate from the collector, from the filter and possibly also from the washing bottles is measured. Vapour density or vapour pressure can then be calculated from the amount of vaporized substance and from the volume of gas passed through and expressed under normal conditions. The closer details or deviations from the procedure described are mentioned in the following paragraphs on measurements with the individual substances.

Notice: *) The gas is of identical composition; the designation carrier and rinsing is used solely for distinguishing the flow paths.

APPARATUS VERIFICATION

Function of the apparatus and the correctness of measurement were checked by means of sodium chloride of A. R. purity, for which there is enough data in the literature and which vaporizes perceptibly even at relative low temperatures. The only complication involved in its use is the fact that apart from NaCl molecules, the vapours likeweise contain the dimer Na_2Cl_2, so that the relationship between the vapour density and vapour pressure is not simple; it depends on the ratio of the two types of molecules.

The measurement was carried out according to the procedure described above. The NaCl sample was first fused into the boat, and the time of exposure in the transpiration apparatus was 60—120 minutes. The carrier gas was dry nitrogen at a flow rate corresponding to optimum saturation (cf. Fig. 4). The condensed NaCl from the collector and filter was transferred by hot distilled water into a quartz dish and its evaporation residue weight determined. A confrontation with the loss in sample weight indicated a satisfactory agreement; this comparison was somewhat complicated by the melt climbing up the boat walls to the pad. The vapour pressure taken as NaCl monomer was calculated from the amount of sample vaporized and from the volume of the nitrogen passed through the apparatus. The actual pressure is somewhat lower in dependence on the dimer content; for 100 % dimer the pressure would correspond to one half. According to the JANAF data [10], for instance, NaCl vapours contain 23 % of the dimer at 1360 K.

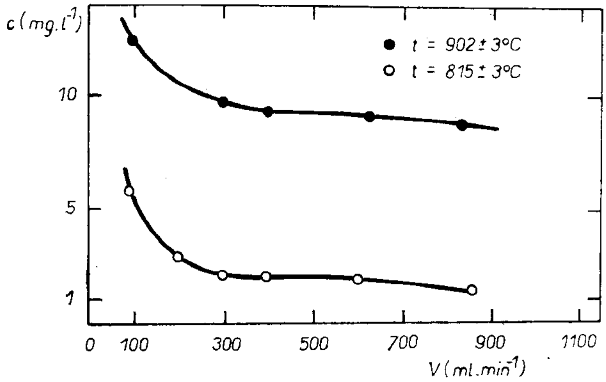

Fig. 4. Dependence of carrier gas saturation with NaCl *vapours on its rate of flow.*

Fig. 5 shows a comparison of the values established by the present authors with data from the literature. The older results by Fiock and Rodebush [11] obtained by direct pressure measurements, are in a very satisfactory agreement with the results by Barton and Bloom [12], obtained by measuring the boiling point of the melt at various pressures; the boiling point was indicated by a temperature hold at continuously increasing temperatures. The results are virtually identical with the measurements carried out earlier by Ruff and Mugdan [13] and also with those by Wartenberg and Albrecht [14]. The data by Stull [15] are the results of a critical evaluation of earlier data from 10 various sources. All of these studies mentioned so far have obviously specified the summary pressure of NaCl and Na_2Cl_2 vapours, even without stating it explicitly.

The more recent measurements by Ewing and Stern [16], carried out by Knudsen's method, take into account the molecular composition of the vapours; the authors confront their results with the extrapolated JANAF data [10]. The agreement is very good, within the limits of 1—8 % (the JANAF data are represented by the full line in Fig. 5). In spite of the diversity of the methods employed, the agreement of all the data can be assessed as being satisfactory and NaCl can therefore be used as a standard for calibrating or checking the equipment for vapour pressure or density measurements.

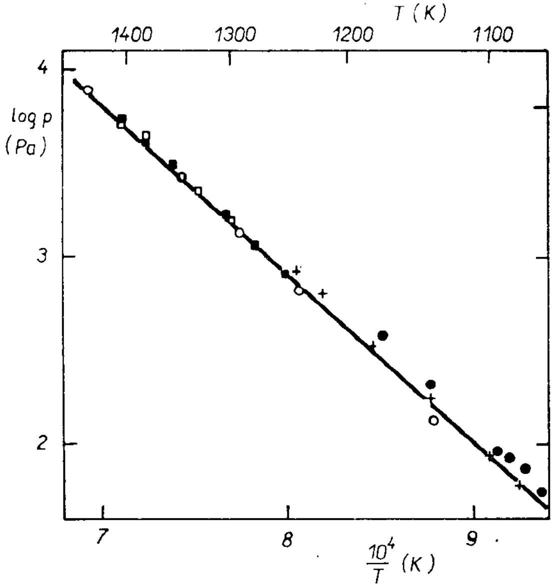

Fig. 5. Comparison of NaCl *vapour pressures with data from the literature; + Ewing and Stern [16], o Stull [15], ▪ Fiock and Rodebush [11].* □ *Barton and Bloom [12], • transpiration measurements [17].*

The references quoted do not include the transpiration method, probably because its lower precision is considered to be less suitable for accurate physico-chemical measurements. The results of measurements obtained by the transpiration method within the framework of the present study are plotted in Fig. 5. The respective values are somewhat higher (by max. 25 %) than those by Ewing and Stern or than the JANAF values. This difference is probably due, at least partially, to the calculation of the vapour pressure for the monomer regardless of the presence of dimer, the proportion of which cannot be determined by the method employed. The results can be regarded as satisfactory, particularly when taking into account that a significantly lower measuring accuracy is generally ascribed to the transpiration method compared to that of effusion methods; critical assessments specify an absolute accuracy of ±25 %. The cause obviously lies in the problems with carrier gas saturation.

In view of the aim of the present study, that is measurement of vapour density and pressures in reactive atmosphere, where it is possible to expect differences of up to one order of magnitude, the accuracy established and the agreement of the results for NaCl achieved may be considered as satisfactory.

References

[1] Merten N., Bell W. E. in: *The Characterization of High Temperature Vapours*. Edited by J. L. Margrave. J. Wiley and Sons, New York 1967, p. 91—114.

[2] Richardson F. D., Alcock C. B. in: *Physicochemical Measurements at High Temperatures*. Edited by J. O'M. Bockris. Academic Press, New York 1959, p. 135—170.

[3] *High Temperature Vapors*. J. W. Hastie, Academic Press, 1975, p. 66; see also (1), p. 93.

[4] Sense K. A., Snyder M. J., Clegg J. W.: J. Phys. Chem. *58*, 223 (1954).

[5] Popov M. M.: Zh. neorg. chimii *4*, 1707 (1959).

[6] Bell W. E., Merten U., Tagami M.: J. Phys. Chem. *65*, 510 (1961).

[7] Alcock C. B., Hooper G. W. in: *Physical Chemistry of Process Metallurgy*. Interscience, N. York 1961, Part I, p. 325.340.

[8] Cubicciotti D., Keneshea F. J.: High Temperature Science *4*, 32 (1972).

[9] Murai S., Wenzel J., Sanders D.: Phys. and Chem. of Glasses *21*, 150 (1980).

[10] *JANAF Thermochemical Tables* (Stull D. R., Prophet H.): Nat. Stand. Ref. Data Ser., Nat. Bur. Stand. No 37 (1971).

[11] Fiock E. F., Rodebush W. H.: J. Am. Chem. Soc. *48*, 2522 (1926).

[12] Barton J. L., Bloom H.: J. Phys. Chem. *60*, 1413 (1956).

[13] Ruff O., Mugdan S.: Z. anorg. allg. Chem. *117*, 147 (1921).

[14] Wartenberg H. von, Albrecht P.: Z. Elektrochem. *27*, 162 (1921).

[15] Stull D. R.: Ind. Eng. Chem. *39*, 517 (1947).

[16] Ewing C. T., Stern K. H.: J. Phys. Chem. *78*, 1998 (1974).

[17] Čtvrtníček M. and Matheisl J.: unpublished work, Institute of Chemical Technology, Prague.

ИССЛЕДОВАНИЕ ИСПАРЕНИЯ НЕСЛОЖНЫХ ВЕЩЕСТВ, ИСПОЛЬЗУЕМЫХ ДЛЯ ВАРКИ СТЕКЛА I. ВЫСОКОТЕМПЕРАТУРНАЯ ТРАНСПИРАЦИОННАЯ АППАРАТУРА

Ян Главач, Мирослав Карасек, Лудмила Рибаржикова

Химико-технологический институт, 166 28 Прага

Была собрана транспирационная аппаратура для измерения давлений паров над твердыми веществами и расплавами до температуры 1400 °С. В электрической печи с отопительной зоной длиной 12 см, удерживаемой во время измерения при температуре ±3 °С, имеется Pt трубка, соединенная со сборником конденсата. Проба помещена на Pt лодочке. В качестве газа-носителя применяется азот, аргон и др. или их смеси с водяным паром или другими газами. Количество испаряемого вещества определяется на основании убыли веса пробы или количества конденсата и объема протекшего газа-носителя. Условия полного насыщения определяют на основании зависимости плотности паров от объема протока газа. Проверку функции аппаратуры и правильность измерения проводили с помощью NaCl, относительно которого имеется в литературе достаточное количество данных; было установлено достаточно надежное совпадение.

Рис. 1. Схема насыщающей части транспирационной аппаратуры; 1 — подводка газа-носителя, 2 — печь, 3 — лодочка с пробой.

Рис. 2. Зависимость плотности паров ($г\ л^{-1}$) и скорости испарения ($гсм^{-2}с^{-1}$) от протока газа-носителя ($л\ мин^{-1}$).

Рис. 3. Схема транспирационной аппаратуры

Рис. 4. Зависимость насыщения газа-носителя парами NaCl *от скорости протока.*

Рис. 5. Сопоставление измеренных давлений пара NaCl *с литературными данными: + Эвинг и Штерн [16], ○ Штулл [15], ■ Фиок и Родебуш [11], * Бартон и Блум [12], ● транспирационные измерения [17].*

Vaporization of Simple Substances Used in Glass Melting

STUDIUM VYPAŘOVÁNÍ JEDNODUCHÝCH LÁTEK POUŽÍVANÝCH K TAVENÍ SKLA

I. VYSOKOTEPLOTNÍ TRANSPIRAČNÍ APARATURA

Jan Hlaváč, Miroslav Karásek, Ludmila Rybaříková

Vysoká škola chemicko-technologická, 166 28 Praha

Byla konstruována transpirační aparatura pro měření tlaků par nad pevnými látkami a taveninami do 1400 °C. V elektrické peci s topným pásmem délky 12 cm, udržovaným po dobu měření na ± 3 °C, je zasunuta Pt trubice spojená s jímačem kondenzátu. Vzorek je umístěn na Pt lodičce. Jako nosný plyn se používá dusík, argon aj., popř. jejich směsi s vodní parou nebo jinými plyny. Množství vypařené látky se určuje z úbytku hmotnosti vzorku nebo z množství kondenzátu a z objemu prošlého nosného plynu. Podmínky úplného sycení se určují ze závislosti hustoty par na objemovém průtoku plynu. Ověření funkce aparatury a správnosti měření bylo provedeno pomocí NaCl, pro který je v literatuře dostatek údajů; byla zjištěna uspokojivá shoda.

Obr. 1. Schéma sytící části transpirační aparatury; 1 — vstup nosného plynu, 2 — pec, 3 — lodička se vzorkem.

Obr. 2. Závislost hustoty par (gl^{-1}) *a rychlosti vypařování* ($gcm^{-2}s^{-1}$) *na průtoku nosného plynu* ($l\ min^{-1}$).

Obr. 3. Schéma transpirační aparatury.

Obr. 4. Závislost sycení nosného plynu parami NaCl *na jeho průtoku.*

Obr. 5. Srovnání tlaků páry NaCl *s literárními údaji; + Ewing a Stern* [*16*], *o Stull* [*15*], ■ *Fiock a Rodebush* [*11*], □ *Barton a Bloom* [*12*], ● *transpirační* měření [17].