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VAPOUR PRESSURE CURVES  
OF THE DIPHENYL BENZENE MIXTURES

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DIPHENYL BENZENE MIXTURES

by

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## ABSTRACT

The paper deals with the measurement of the bubble point curve of diphenyl-benzene mixture. The pressure range covered by the measurements was 5-25 atm. The results show that the relationship between the saturation temperature and pressure may satisfactorily be determined by the Calingaert-Davis equation:  $\ln p = a - \frac{b}{t + 230}$

The constants "a" and "b" in the equation, which are functions of the concentration, were calculated from a great deal of experimental points by fitting using the least square method.

## KIVONAT

A dolgozat difenil-benzol elegy forráspont-görbéjének mérését ismerteti. A mérés 5-25 ata nyomástartományban számos összetétel mellett történt. A mérési eredmények szerint a telítési nyomás és hőmérséklet közötti összefüggés jól leírható a Calingaert-Davis egyenlettel:  $\ln p = a - \frac{b}{t + 230}$

Az egyenlet "a" és "b" állandóit - amelyek a koncentráció függvényei - nagyszámu mérésből a legkisebb négyzetek módszerével történő illesztéssel határoztuk meg.

## РЕЗЮМЕ

В данной работе представлены результаты экспериментального определения точек кривой кипения дифенил-бензоловой смеси. Измерения производились в интервале давлений 5-25 атм. для большого числа относительной концентрации веществ в смеси. Согласно результатам зависимость между давлением насыщения и температурой хорошо описывается уравнением:  $\ln p = a - \frac{b}{t + 230}$

Постоянные  $a$  и  $b$  в уравнении, являющиеся функциями относительной концентрации, определены на основе большого числа измерений применением метода наименьших квадратов.

## INTRODUCTION

The liquid vapour equilibrium diagrams of the diphenyl benzene mixture were plotted with the help of the loop device described in paper [2]. By comparing the obtained results with the data published in paper [1] it was found that

- 1/ the obtained dew points showed a good agreement in both measurements
- 2/ between the bubble points there appeared - especially at higher pressures - deviations.

Therefore we have plotted again in the course of control measurements the vapour pressure versus concentration in the pressure range of  $p = 5 - 25$  atm. In order to eliminate any possible systematic errors we have used deliberately a device of different system for the control measurement. The measuring device and the obtained results are described and analyzed in the following.

## THE APPARATUS

The used simple apparatus consisted of the stainless steel vessel shown schematically in Fig. 1. By filling an appropriate amount of the material under investigation into the vessel, then heating it up to the desired temperature and measuring the pressure of the saturated vapour over the liquid the individual points of the vapour pressure curve are given by the conjugate pressure and temperature values. The quality of the measurement depends obviously on the uniformity of the

temperature distribution attained in the vessel.

In order to ensure uniform wall and fluid temperature the vessel was provided with an inner copper shell. The volume of the vessel was  $V = 5$  Lit. In the temperature and concentration ranges of the measurement the minimum specific weight of the material was  $0,6$  kg/L and so an initial filling of  $G_0 = 3$  kg resulted which was reduced for securing the actual saturated vapour state at all times to  $G = 2,8$  kg.

## TEMPERATURE MEASUREMENT

As it is known, the temperature of the boiling liquid and the vapour over it is not perfectly identical. When bubbles escape from the surface, the temperature of the liquid is higher than that of the saturated vapour over it. The lower the temperature difference, the smaller the intensity of the bubble formation. In order to avoid the bubble formation disturbing the surface we heated the liquid up to the maximum temperature then under a very low cooling rate we measured the temperature and the pressure. The saturated vapour is in thermal equilibrium with the surface liquid, therefore it is to the purpose to measure the temperature of the vapour and of the liquid surface.

For measuring the vapour temperature we placed the thermometer at a distance of 2 cm from the top of the apparatus where vapour state prevailed in the whole range of the measurement. But the liquid surface changed as a function of the temperature in consequence of the change of the liquid density and so the fixed thermometer measured the liquid temperature in various depths under the surface. A third thermometer was also placed in the lower regions of the liquid at about 10 cm from the bottom.

The above three thermometers were platinum resistance thermometers of 100 Ohm. We measured the wall temperature of

the vessel as well at several points /Fig.1./, with the help of NiCr-Ni thermoelements.

Three heaters were arranged on the apparatus; one of them in the tube introduced in the lower part of the apparatus, another one on the lower part and the third one on the upper part of the outer shell. The supply of the three heaters were correspondingly regulated during the measurement for obtaining the slow cooling rate and the uniform temperature distribution in the vessel. By this regulation of the three heaters we attained the result that under a cooling rate of about  $0,3^{\circ}\text{C}/\text{min}$  in the vessel the maximum values of the temperature difference did not exceed  $2^{\circ}\text{C}$ , thus limiting the gradient of concentration in the liquid volume to a maximum of 0,5 weight percent. Not considering the period of heating up, the highest situated thermometer measuring the temperature of the saturated vapour measured in most cases a temperature, which was higher by some tenth centigrade then that measured by the thermometer immersed in the liquid below it and we took always this saturated vapour temperature into consideration.

## PRESSURE MEASUREMENT

The pressure was measured by a Bourdon tube type manometer of 0,5 accuracy class which was calibrated before and during the measurement several times. The pressure tap was joined to the liquid volume. To avoid freezing, a pressure transmitter diaphragm - which was heated together with the tube section leading to the apparatus - was placed between the apparatus and the manometers.

Three manometers were installed with the measuring limits of 4 ata, 10 ata and 25 ata respectively, which could be turned off individually. With the three manometers we wished to enhance the accuracy of the measurements in the lower pressure ranges. As seen in Fig. 1., the manometers are arranged at the height of the middle liquid level in order to avoid

considerable changes of the hydrostatic pressure. In this way a fluctuation of  $\Delta p = 70 \text{ kg/m}^2$  around the accurate value - which is within the accuracy limit of our manometers - is obtained in the case of a level change of  $\Delta h_{\text{max}} = \pm 0,1 \text{ m}$  with a supposed specific weight of  $\gamma = 700 \text{ kg/m}^3$ .

## CONCENTRATION MEASUREMENT

The accurate measurement of the concentration caused always the greatest trouble during the investigation of the mixture. In the cases of the measurements described in papers [1] and [2] Abbe type refractometers were used for measuring the concentration. The error of the measurement was greatly increased by the following factors:

- a/ at higher temperatures a loss of benzene occurs during the sampling in consequence of the relatively high volatility of the benzene;
- b/ at the temperature of the refractive coefficient measurement /room temperature/ the sample had to be diluted in most cases because of the freezing of the high diphenyl concentration samples;
- c/ the equilibrium conditions are disturbed in a not negligible measure in the overwhelming majority of the cases by the sampling itself.

In order to eliminate the above factors the benzene concentration of the studied sample was determined by high accuracy weighing. The pure homogeneous mixture with the desired concentration, as ready for measurement in the apparatus was prepared as follows:

The necessary amount of diphenyl was filled into the apparatus, the moisture content of the diphenyl was expelled by heating on  $170^\circ\text{C}$  for 1 hour, then after freezing the diphenyl the weighed amount of benzene was filled into the

evacuated vessel, followed by shaking for homogenisation at a temperature of 70 °C.

In the measurements diphenyl produced by Monsanto and pro anal quality benzene were used.

Scales of  $2 \cdot 10^{-3}$  kg accuracy was used for weighing.

The amount and concentration of the material in the vapour volume changes during the measurement and so does the concentration of the liquid as well. If this change of liquid concentration is not negligible, a correction must be applied. The weights of the liquid and the vapour can be calculated by the relations:

$$G_f = \frac{Gv'' - V}{v'' - v'}$$

and

$$G_g = \frac{V - Gv'}{v'' - v'}$$

In the knowledge of these weights the change of the liquid concentration can be evaluated by the relation:

$$\Delta \chi = \chi_o - \frac{\chi_o G_{fo} - \left( \frac{y}{G_g} G_g - \frac{y_o}{G_{go}} G_{go} \right)}{G_f}$$

where:  $G$  = weight of the total filling, g

$V$  = volume of the vessel,  $\text{cm}^3$

$G_g$  = weight of the vapour, g

$G_f$  = weight of the liquid, g

$v''$  = specific volume of the vapour,  $\text{cm}^3/\text{g}$

$v'$  = specific volume of the liquid,  $\text{cm}^3/\text{g}$

$\chi$  = concentration of benzene in the liquid, g/g

$y$  = concentration of benzene in the vapour, g/g

Subscript "o" denotes the initial  $t = 70^{\circ}\text{C}$  state, whereas the quantities without the subscript "o" belong to the actual temperature and pressure.

The values of  $\Delta\chi$  were calculated by the above relations and the results are given in Figs. 2 and 3. The calculations were based on the data found in refs. [6], [7] and [8]. According to the obtained results the liquid concentrations need corrections which was carried out by the following average values:

| $\chi$       | 0-0,1 | 0,1-0,2 | 0,2-0,3 | 0,3-0,4 | 0,4-0,5 | 0,5-0,6 | 0,6-0,7 | 0,7-1,0 |
|--------------|-------|---------|---------|---------|---------|---------|---------|---------|
| $\Delta\chi$ | 0,002 | 0,004   | 0,005   | 0,006   | 0,005   | 0,004   | 0,002   | 0       |

## MEASUREMENT RESULTS

The results of our measurements are shown in Fig.4. in the diagram  $\ln p - \frac{1}{T}$

The relation between the pressure and temperature of the saturated vapour is most generally expressed by the Antoine equation:

$$\lg p = A - \frac{B}{t+C}$$

where  $p$  = pressure of the saturated vapour

$t$  = temperature of the saturated vapour,  $^{\circ}\text{C}$

$A$  and  $B$  = constants determined by the experimental data

$C$  =  $271 - 7,6n$  for hydrocarbons with  $n$  C-atoms.

We found, that for not too extensive pressure ranges the Calingaert - Davis equation gives for low pressures a less favourable agreement than the Antoine equation, yet for the higher pressures, which are of a greater interest for us, it is better [3], [4]. Therefore we fitted straight lines to the points of measurement by the least squares method on the basis of the Calingaert-Davis equation:

$$\ln p = a - \frac{b}{t + 230}$$

The constants obtained by the fitting are shown as functions of the benzene concentration in Fig.5. and the straight lines calculated for round concentration values in Fig.6. The maximum relative error of the fitting is 6,85 % whereas the average relative error is less than 1,0 %.

The apparatus was calibrated by checking the vapour pressure of the pure components, in the course of which the data published in ref. [7] for diphenyl by the firm MONSANTO were reproduced by our measurements to a maximum relative error of 1,95 % in the pressure range of 8-20 atm whereas for benzene there was a deviation of  $\left| \frac{\Delta p}{p} \right|_{\max} = 0,65 \%$  between the boiling point published in ref. [9] for benzene and the one obtained by us in the pressure range of 10-20 atm.

The data measured at constant temperature show an unambiguous negative, but not too great deviation from the Raoult law. For the sake of illustration in one case, for  $T = 250^{\circ}\text{C}$  we plotted the course of the pressure as a function of the benzene concentration in Fig.7.

## SUMMARY

We measured the saturated vapour pressure of the diphenyl benzene mixture with an error of  $\left| \frac{\Delta p}{p} \right|_{\max} < 7 \%$  with the help of the described apparatus. The vapour pressure curves constructed on the basis of the obtained results for constant pressure agreed excellently with the data of ref. [2] i.e. with the results obtained by the large scale loop arrangement.

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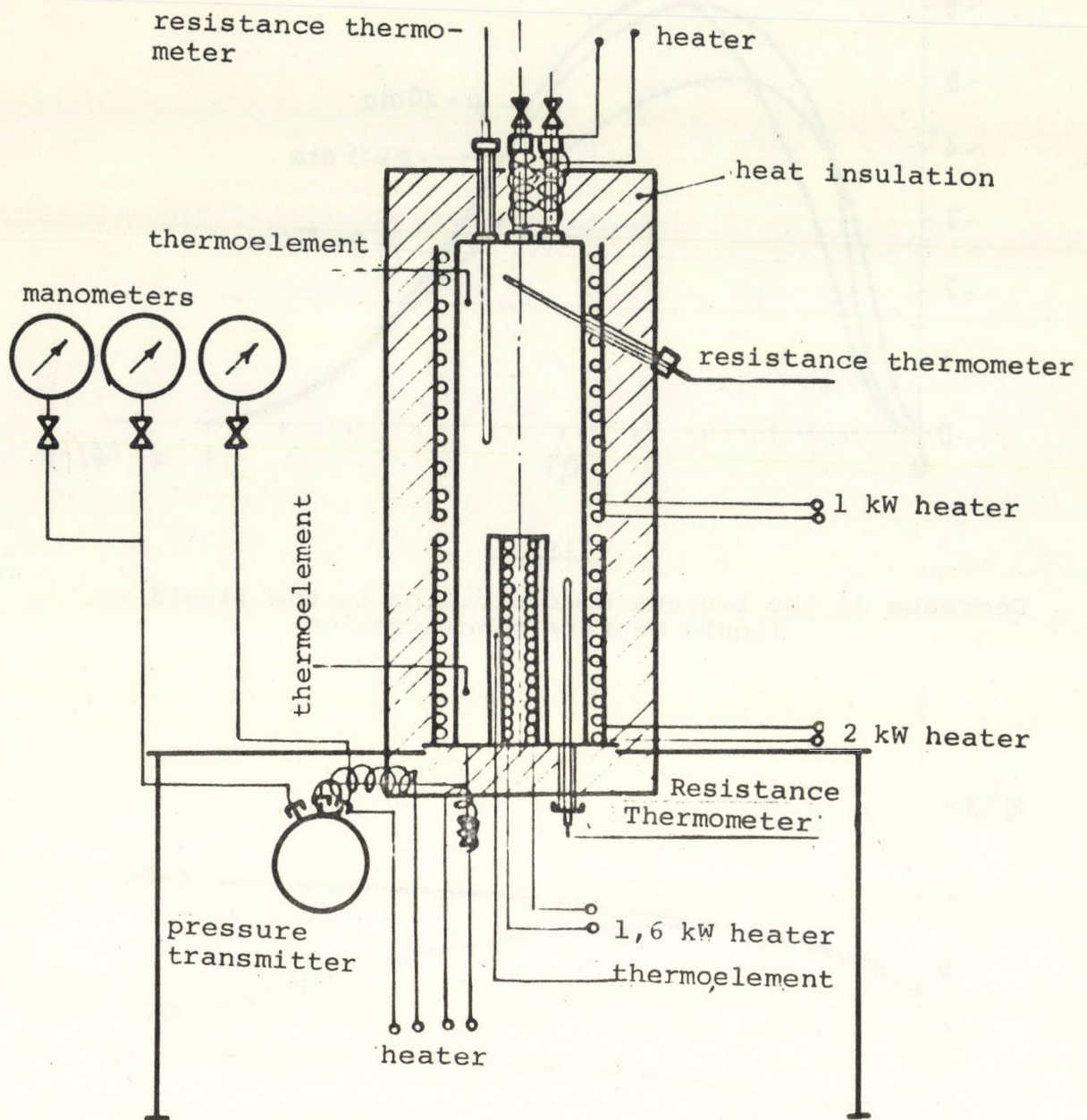


Fig. 1

Equipment

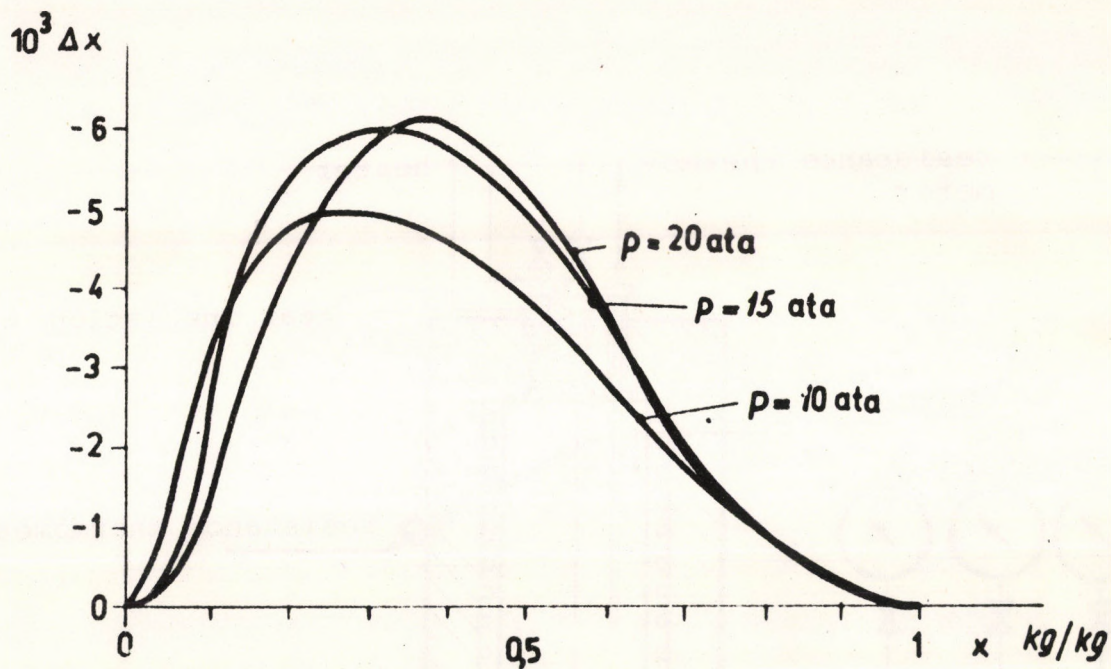


Fig. 2

Decrease of the benzene concentration in the liquid vs.  
liquid benzene concentration

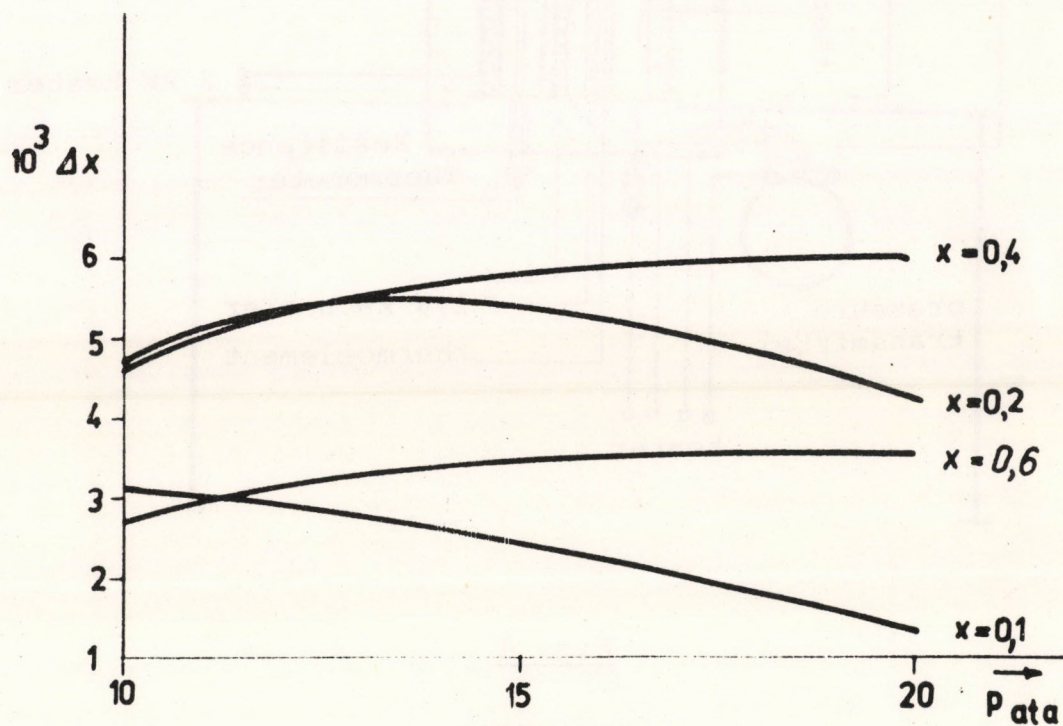


Fig. 3

Decrease of the benzene concentration in the liquid vs.  
pressure

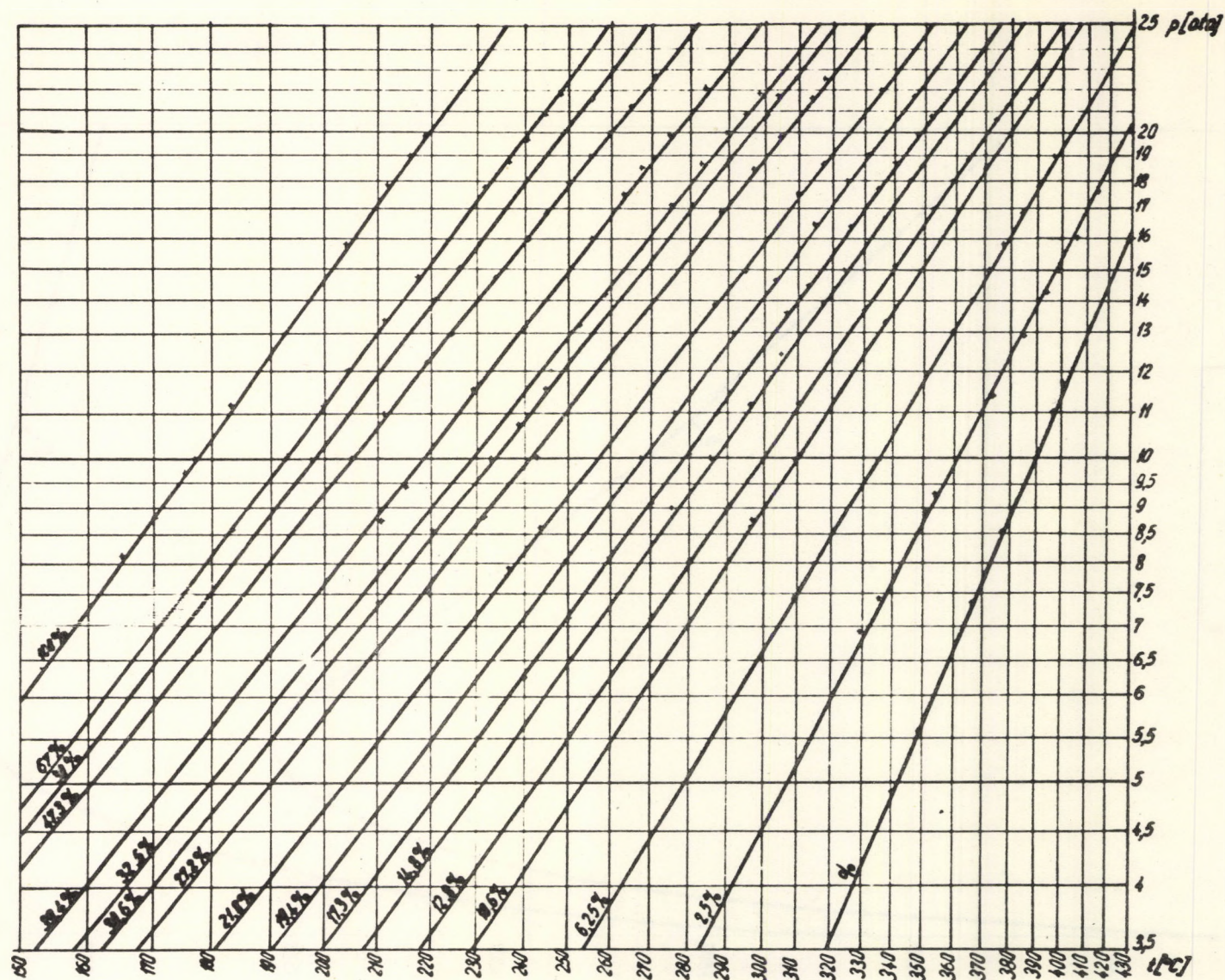


Fig. 4

Diphenyl-benzene tension measurements in  $\lg p = \frac{1}{t+230}$  diagram function of the benzene concentration

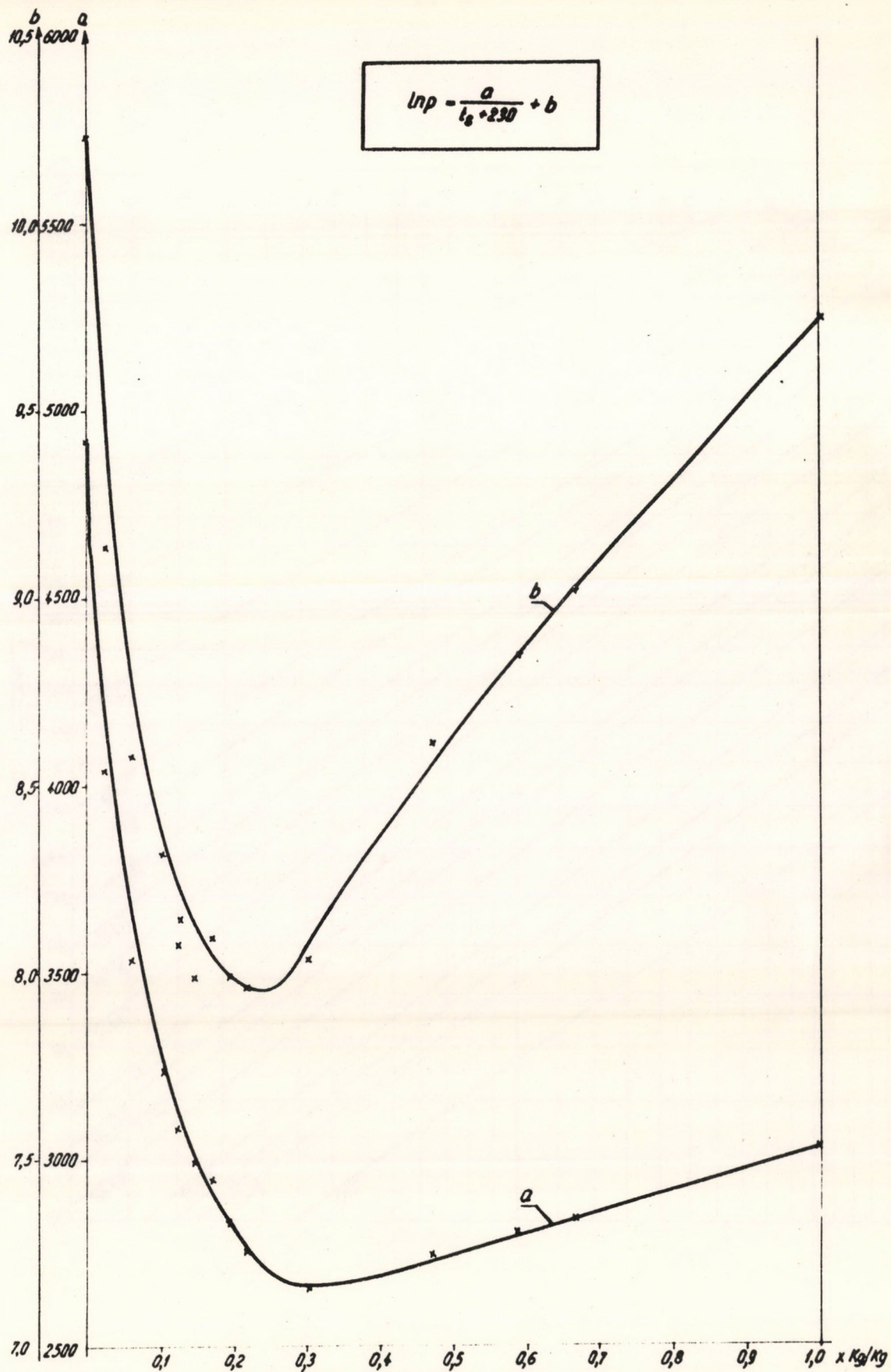


Fig. 5

The constants of the Calingaert - Davis equation vs. benzene concentration of the liquid

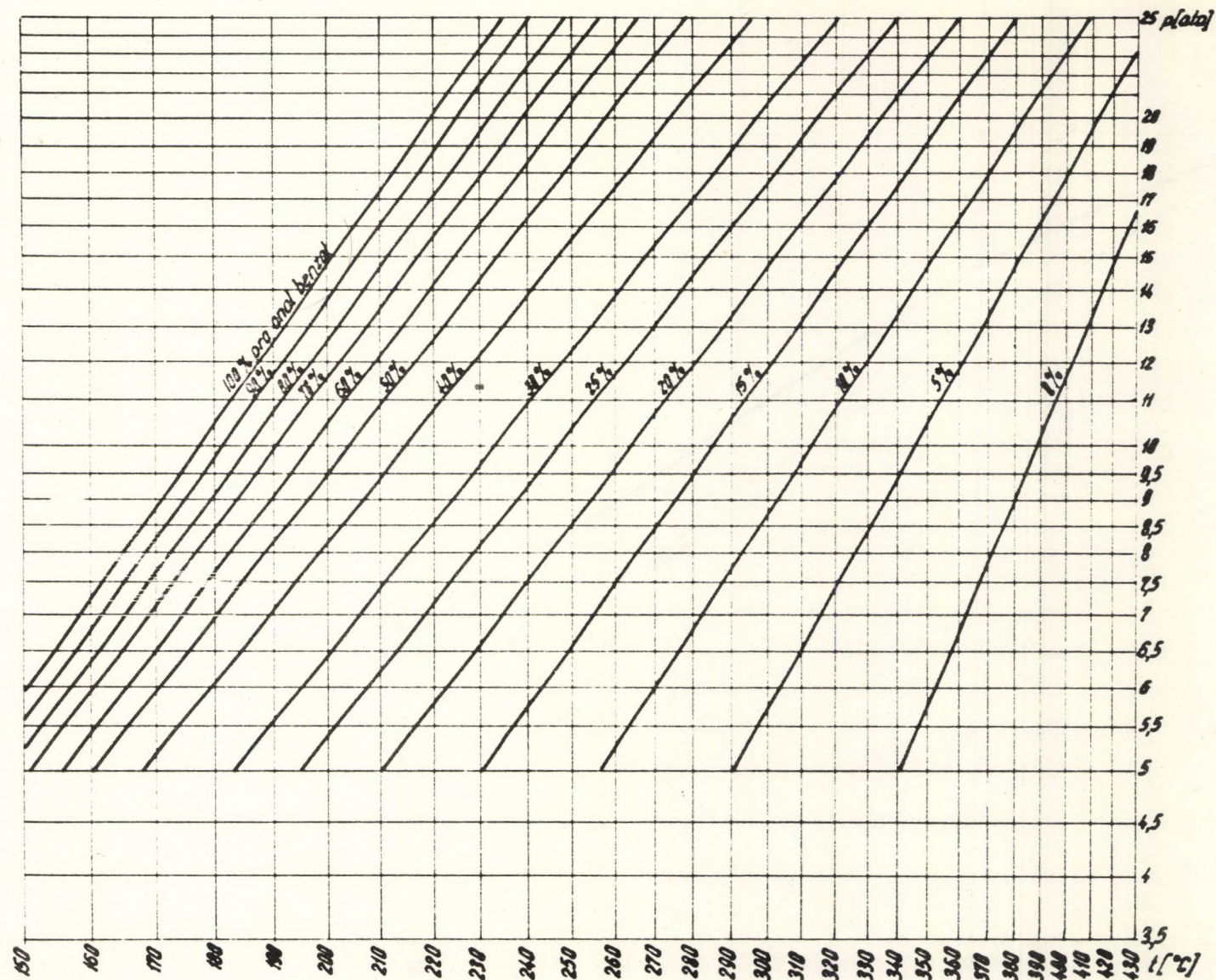


Fig. 6

Vapour pressure curves of the diphenyl-benzene mixture /parameter: the benzene concentration in weight percent/

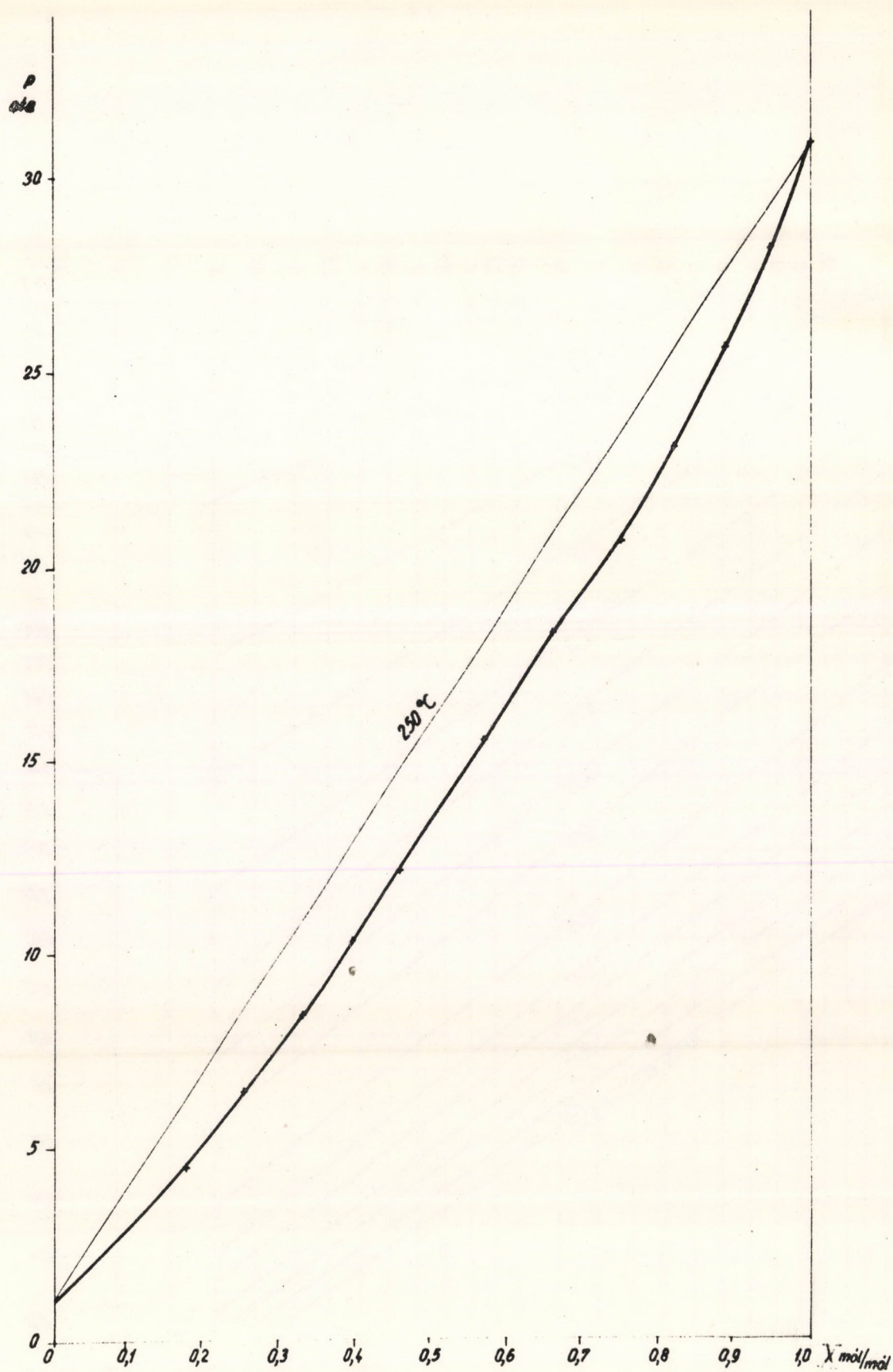


Fig. 7

Total pressure as a function of the liquid benzene concentration



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