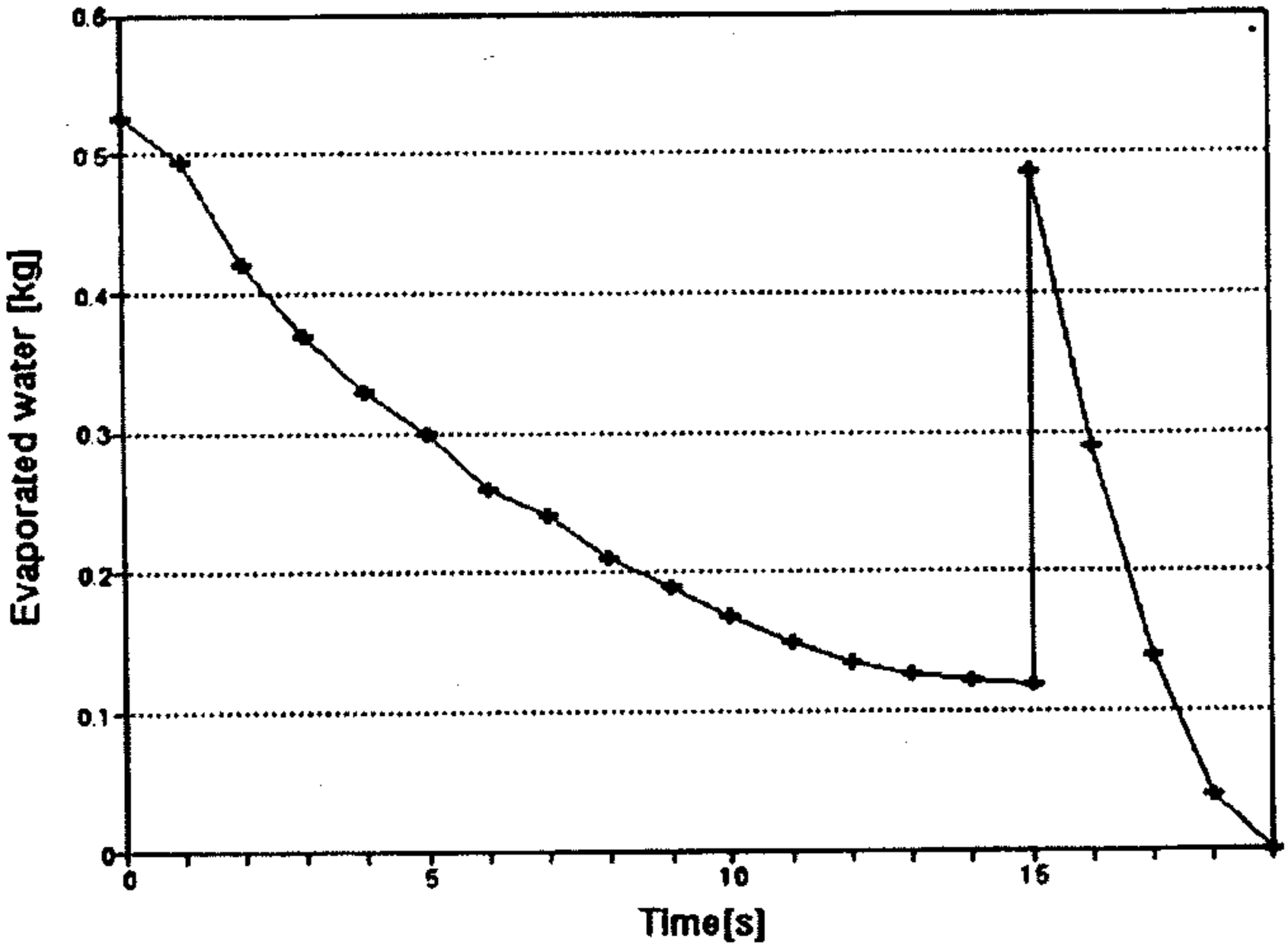


Fig.21 The dependence of the intensity of evaporation on time

## Problem No.13 – Spirits

Assuming a bottle is defined as transparent and a vessel as opaque, the concentration of ethylalcohol in the water may be determined by one of the following methods.

***Method I***

We can use the tabular values for the melting and solidification point temperatures of the water-ethylalcohol mixture in dependence on concentration (we have verified them – see Fig.22). The bottle will be cooled slowly in a cryostate, i.e. we will remove a known quantity of heat regularly and we will measure the temperature. The temperature will decrease gradually in a linear dependence on the removed heat. At the moment when the solidification temperature is reached, this linearity will be disturbed and the rest of the heat will be needed for the solidification of the mixture. The temperature will practically not change any more. The temperature corresponding to this state is dependent on the mixture concentration.

Using a reverse procedure, we can get another value which will allow us to obtain a more accurate determination of the mixture in the case that the bottle is not completely full. We will freeze the entire content of the bottle (vessel). Then we will regularly supply heat up to the point at what the temperature will stop changing (see above). It is necessary to determine this value because the mixture is marked by a difference between the melting and solidification point temperatures and because the tables give only values obtained by approximation of these two temperatures. The problem of this method is the existence of an eutectic point of this mixture, i.e. two concentration values are possible within a certain range for the same solidification point temperatures (see also Fig.22) – the melting temperature of the mixture which is given as a function of concentration, is not a simple function within a certain interval.

The state when the mixture begins to solidify may be determined by a comparison of the real temperature and the temperatures plotted on the graph. At the point when the temperature stops decreasing, although we continue in removing the heat, is the moment when we have attained the desired state, for the first solid paticles appear in the mixture. The other temperature value which we have been trying to determine may be obtained by a similar procedure, i.e. we freeze the mixture, then we heat it up slowly and determine again the stationary point of the temperature.

We used an East German cryostate MK70 for the practical testing of this method. It is a device equipped with an ammonia compressor system. Water-free denatured ethanol was used as a cooling medium. The concentration determined during our experiments was established with a 2% accuracy.

***Method II***

This method is based on the determination of the specific thermal capacity of the water-ethylalcohol mixture. We have to know the specific thermal capacity of the vessel material. If we do not know it, it may be determined using a very little piece obtained from the material of the bottle or the vessel.

To solve this problem we also need to know the volume of the mixture and the volume of the vessel material. These values may be obtained by using some ultrasound or X-ray methods. These values may be determined with the highest accuracy in the case that the vessel has the shape of a rotary body. In that case it will be enough to take just one ultrasound or X-ray image which will make it possible to determine the internal cross-section of the vessel and also water-ethylalcohol mixture (assumning the vessel is homogeneous). We will also determine the weight of the water-ethylalcohol mixture or – if we want to get a more precise calculation – we can also determine the weight of the air above the surface of the mixture. However, in this case it is better to cool the vessel with the mixture first to the lowest possible temperature making sure that the mixture does not start solidifying prematurely, so that the water-ethylalcohol mixture does not evaporate too much because this would result in changes in the specific thermal capacity and air density.

Now using the calorimeter, we may determine the heat necessary for cooling or heating the vessel with the mixture by a certain temperature, such as 10 K. From this established heat value, we will substract the heat needed for the cooling (heating) of the vessel (or even the air in the vessel), we will determine the specific thermal capacity of the mixture and finally we will get a value of its concentration from the graph.

We will have the same problem with this method, i.e. the dependence of the specific thermal capacity as a function of concentration is not a simple function (see Fig.23). However, by combinig this method with method I., we will obtain an unambiguous result in any case.

***Method III***

The third method is based on the determination of the mixture density. Again, with the aid of a chip from the vessel material, we will determine the vessel density. then, with the aid of the above mentioned methods, i.e. ultrasound or X-ray, we will determine the volume of the water-ethylacohol mixture and the volume of the air contained in the vessel. Using a densimeter, it is easy to determine the

density of the entire system, i.e. the vessel, mixture, air, and we can use this value to derive the density of the mixture.

With the aid of the established relation (see Fig.24) between the mixture density and its composition, we will determine the concentration corresponding to this density.

***Method IV***

This method is based on the different permissivity (or permeability) of the water/ethylalcohol mixtures of different concentrations. In practice, the measuerement would be carried out with the aid of two parallel plates between which the vessel would be placed. The plates will be charged to a certain voltage and we will measure the capacity of the capacitor. Since we know the distance and the area of the plates, we can determine the permissivity of the space between them, from which we can determine the permissivity of the mixture. Then we will proceed according to the graph establishing the dependence of permissivity on concentration of the mixture.

***Conclusion:***

We have not been able to establish an absolutely universal method, however, in any case we will always find a method which will make it possible to determine the concentration of alcohol. We can always use the first point, the accuracy will be better than 5%, while we will obtain the concentration values by calculating the mean values of the established values.

By using a combination of several methods, we will obtain a significantly higher level of accuracy as confirmed by experimental results (see above), we can obtain satisfactory results when measuring concentration.

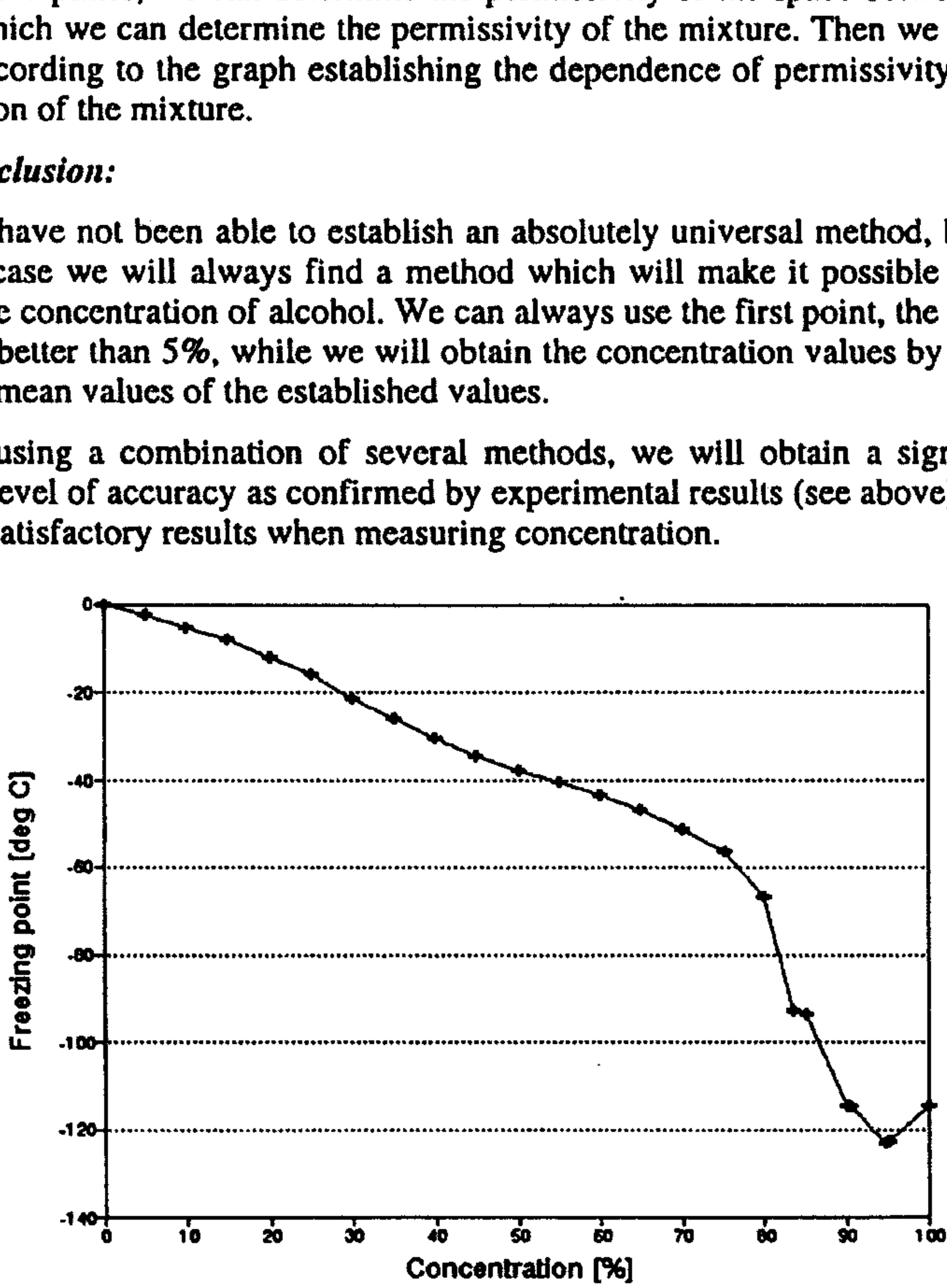


Fig.22 Freezing point in dependence on the concentration of the mixture

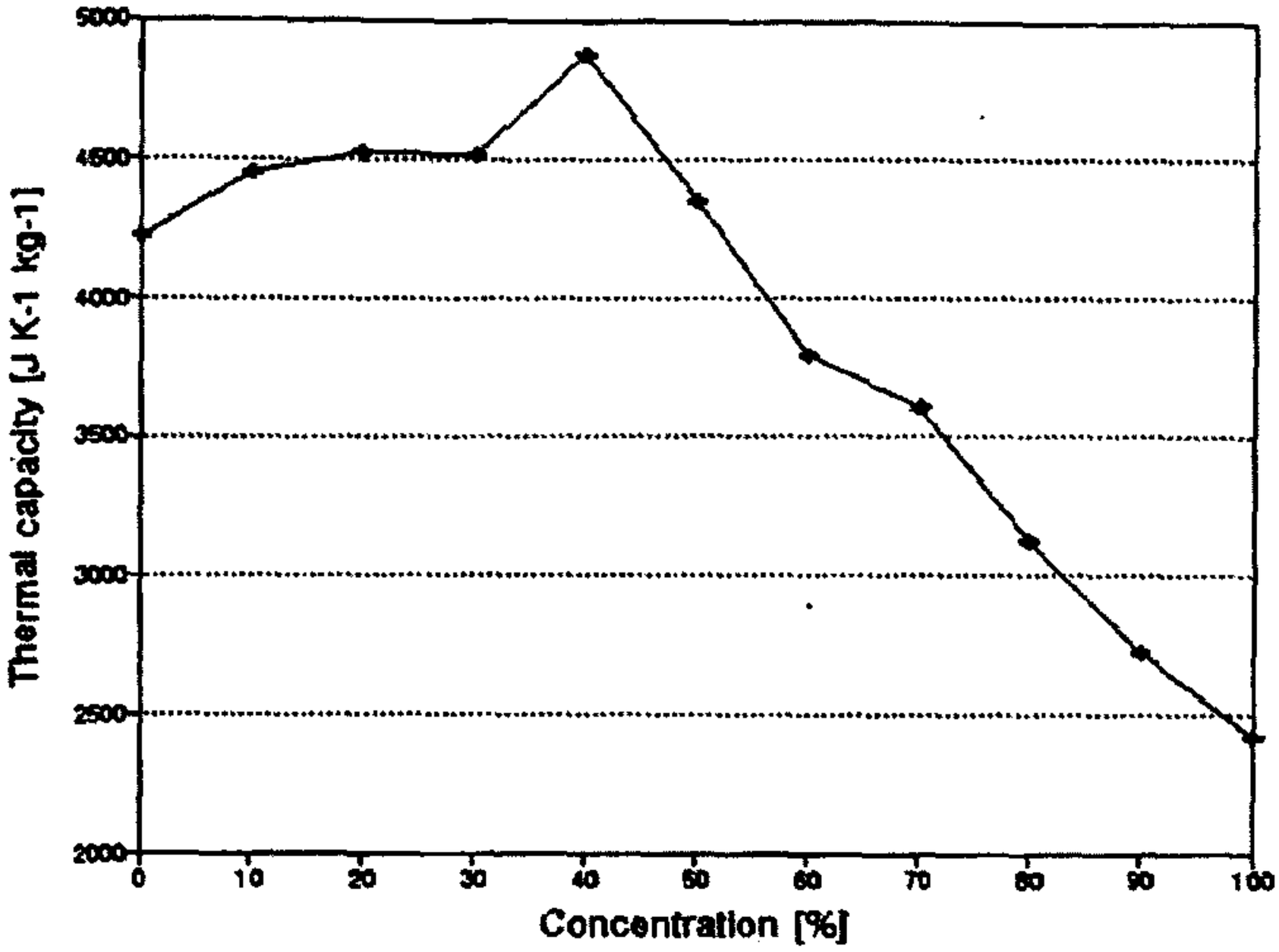


Fig.23 Dependence of the specific thermal capacity on the concentration of the mixture

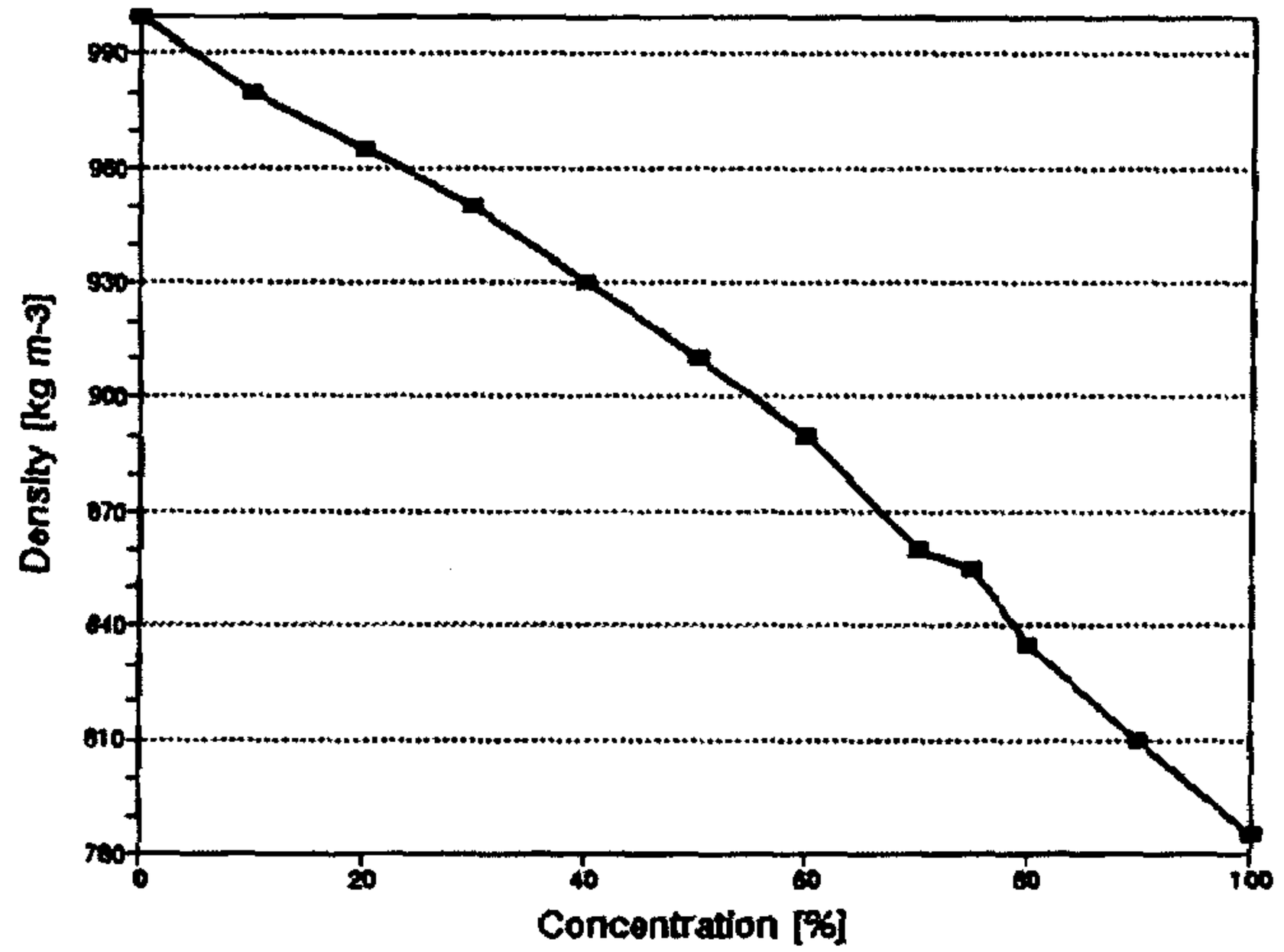


Fig.24 Dependence of the density of the mixture on its concentration