THE PURIFICATION OF ORGANIC SOLVENTS BY THE COMBINED APPLICATION OF NORMAL FREEZING AND ZONE MELTING

By

E. Brandt-Petrik and J. Nagy

Department for Inorganic Chemistry, Technical University, Budapest

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In numerous fields of modern chemical research, especially in determining the dielectric constant and the ultraviolet spectrum of compounds, reliable purity of the employed solvents i.e. exemptness of foreign matter, is an absolute necessity. Commercial solvents of pro analyse purity fail this requirement.

The production of solvents of 99.99 mole% or higher purity is rather difficult and practically impossible by distillation.

One of the latest and most effective methods of the purification is zone refining, applied widely for refining metals (semiconductors), permitting impurities as low as $10^{-7}\%$ [1].

Several publications are known on extending the method of zone melting to the purification of organic materials [2, 3] that may exceed in efficiency the preparative gas chromatography. Zone melting is widely used both in research and industry for separation, refining, and concentration of organic compounds. Namely, there are materials melting at a favourable temperature without loss of quality, while other methods are unlikely to produce such extremely high degrees of purity. Various refining concepts have already been realized by the zone melting technique such as the extraction of anthracene from naphthalene [4], the separation of benzene [5, 6, 7] and water — acetic azeotropic mixtures, p- and o-toluene as well as the separation of normal and heavy water, not to speak but of the most significant ones. These achievements induced to develop a method for producing high-purity organic solvents solidifying at medium temperatures, by the zone refining technique, on the principle that the material already prerefined to a high degree by normal freezing is brought by zone refining to a high purity state. Consideration was given to economic possibilities of application.

The expression *zone melting* is used in the literature as a collective term designating a series of techniques for the examination of the distribution of soluble impurities in crystalline materials. This method is essentially the repetitive process of fractional crystallization. When a liquid compound is chilled, the composition of the crystallizing solid phase is generally different from the composition of the liquid. This difference corresponds in nature to the equilibrium between solid and liquid phases of the binary solution-solvent system. This is at the basis of zone melting applied as a refining method.

The various types of solid-liquid states can be described by phase diagrams. From the aspect of zone melting the two extreme positions in the phase diagram are of importance, namely those ranges where the system is very poor in one of the components.

The crucial parameter for any material to be handled by zone melting is the distribution coefficient, the ratio of impurity concentrations in solid to liquid phase $\left(k = \frac{c}{x}\right)$. The k value is lower than unity ($k < 1$) if the impurity lowers the melting point of the main component, and $k > 1$ in the opposite case. The k value depends on parameters of both the material and the equipment. Material parameters can be obtained from the phase diagram, while equipment parameters are given by solidification conditions, such as zone length, progress rate of the solid-liquid interface, number of zone passages rate of stirring in the liquid, etc. Our work involved two types of zone melting methods:

a) *Normal freezing*, pertaining to the conceptual sphere of zone melting at the fundamental difference, however, that the material to be refined is fed in *liquid* state into a suitably designed cylinder where it starts solidifying by one end. The rate of impurity segregation may be increased by stirring the liquid, increasing hereby the actual diffusion.

b) In the case of *zone refining* the melted zone migrates from one end to the other of the material solidified in form of a cylinder. Here impurities can only diffuse within the melted liquid phase which may be one tenth of the total zone length. Stirring of the liquid phase to promote diffusion is not possible. Accordingly, zone refining is a process requiring for its final result — high-grade purity — repeated zone passes.

Description and discussion of experimental methods

For developing experimental methods and techniques for refining organic solvents, the use of benzene seemed to be the most suitable. Several research workers [5, 6, 7] have already worked with this industrially important solvent, published results served as useful guidance. To make experimental results surveyable, the benzene of pro analyse purity distilled in a column corresponding to a number of plates of approximately 20 was found by gas chromatography and refractometry to be pure. Impurity of 1 mole% methane alcohol was added, having hereby an exactly known quantity and quality of impurity the distribution of which was simple to follow.

The benzene with methane alcohol impurity was exposed to various zone melting operations. The effect of normal freezing was examined first, afterwards that of zone refining, finally the effect of their combination.

1. *Normal freezing*

The apparatus shown in Fig. 1 has been applied for refining organic solvents by normal freezing.

The liquid to be refined is fed into the glass tube of 22 mm, dia 300 mm, length thus, of a capacity of about 70 ml of the material. The bottom of the tube is closed by a ground stopper exchangeable in the melting stade by a through-way pipe and a graduated receiver. The top end of the tube is closed

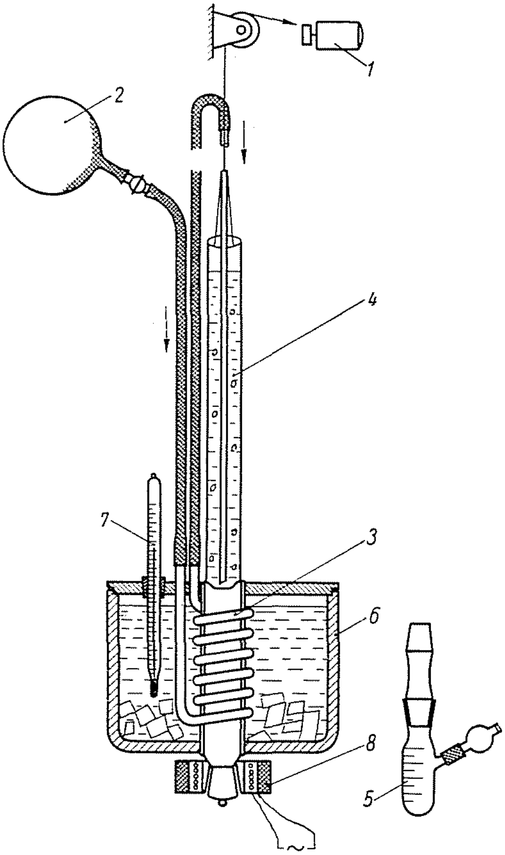

Fig. 1. Apparatus used for normal freezing. 1 Motor with speed reducer, 2 Rubber ball filled with N_2 gas, 3 Copper spiral, 4 Glas tube, 5 Graduated receiver, 6 Heat insulated vessel for the cooling medium, 7 Thermometer, 8 Heating ring

by a plastic stopper having a centre bore. Similarly here, it can be connected by way of a plastic string to the forwarding disc. Discs were prepared with ten different diameters, exchangeable on the shaft of the motor fitted with a speed reducer, thus advance speed could be adjusted in the range 1 to 10 cm/hour.

The rate of impurity segregation decisively depends on the conditions of the forwarding process within the liquid. Beside of selecting an optimum passage speed, also a complete stirring of the liquid phase (a perfectly homogenous liquid concentration) was to be ensured. In the apparatus shown in the figure, stirring was effected by passing micro gas bubbles through the liquid. Gas was supplied by the rubber ball shown in the figure. The gas flow, hence the intensity of stirring, could be adjusted by an inserted tap. A precooling of the gas is necessary so as to-ensure heat equilibrium (otherwise the gas at room temperature would melt the already solidified phase), therefore stirring gas into the liquid after having passed the copper spiral in the cooling space.

The cooling space is a double-wall heat insulated vessel, the ring shaped wall of which, surrounding the glass tube, is made of copper for good heat transfer. In our work of refining organic solvents a mixture of alcohol and dry ice was employed as cooling medium suitable for producing temperature as low as —70 °C.

The glass tube emerging of the cooling space passes a heating ring heated by alternating current of max. 1.5 A. intensity.

The molten liquid dripping was collected by the graduated receiver, in fractions of 1 to 5 ml. The liquid of appropriate volume was stored in tightly closed, numbered test tubes.

Purity was determined by the cyroscopic method [8], infrared spectroscopy, and refractometry. The percentage of impurities expressed in mole% is denoted by X_0 in the initial liquid and by C in the refined material.

Fig. 2 shows the change of purity grade of benzene with methane alcohol impurity upon normal freezing for varying stirring and solidification rate.

It is evident from the figure that at higher solidification rates (8 cm/hour), segregation was at a minimum without stirring. Purity was considerably improved if the liquid is stirred by gas bubbles directed to the solid-liquid interface, rate being kept unchanged. Even better results could be obtained by having the solidification rate 4 cm/hour maintaining optimum stirring.

2. *Zone refining*

As a second method for refining benzene, zoning was employed. The equipment assembled to permit control of decisive parameters. Fig. 3 is a schematic drawing of the apparatus. In the case of zone refining liquid mate-

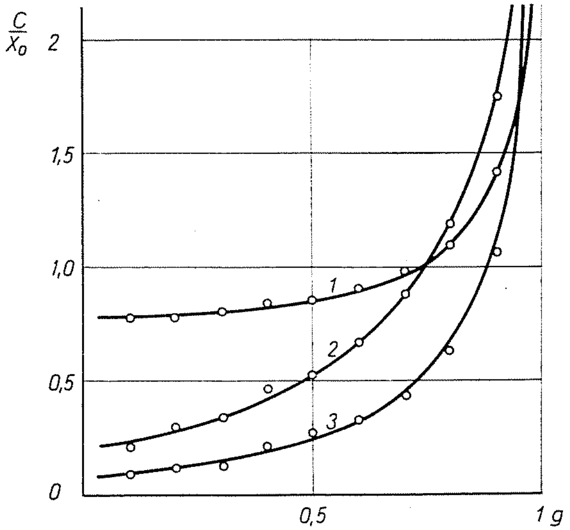

Fig. 2. Normal freezing with the same material couple at varying solidification rates
1 without stirring, 8 cm/hour 2 with stirring, 8 cm/hour 3 with stirring, 4 cm/hour

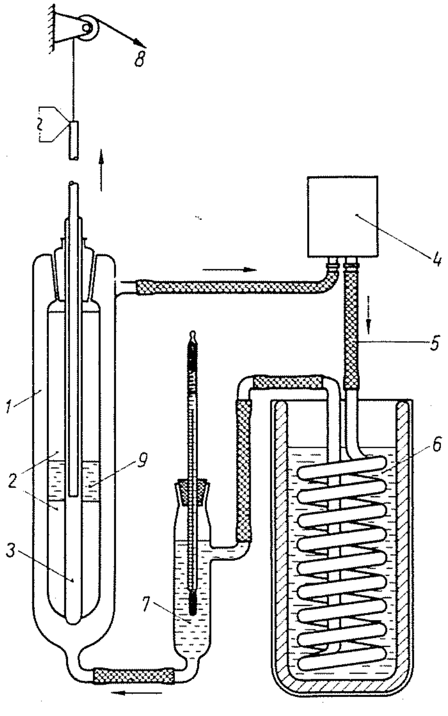

Fig. 3. Apparatus for zone refining
1 Glass cilinder with inlet and outlet opening, serving for cooling liquid flow; 2 Frozen liquid; 3 Internal tube in which heater spiral is moving; 4 Pump for circulating the cooling liquid; 5 Heat insulated rubber joint; 6 Dewar vacuum flask for the cooling mixture (alcohol + dry ice); 7 Recipient for measuring cooling liquid temperature; 8 Motor for moving; 9 Liquid (zone)

rials, the sample should be cooled along its whole length. The recipient for zone refining was made of three concentrical glass tubes of different diameters. In the external shell the alcohol precooled to the suitable temperature (always a function of the solidification point of the solvent) is circulating. The advantage of the glass recipient and of the circulation method are visibility of the process control over the intensity of heating and cooling, thus, over the width of the liquid zone. The liquid to be refined is fed into the central opening of annular cross section (radial dimension 6 mm, length 170 mm), then the opening is closed by a ground stopper. The heater is vertically raising inside the internal tube of a speed of 4 cm/hour, actuated by the motor and speed reducer. Heater current was adjusted in the range 0.9 to 1.2 A for ensuring constant width and shape of the zone. In this way a zone width equal to 1/10 of the whole length of the material could be realized.

A mixture of alcohol and dry ice was used as cooling medium in a Dewar vacuum flask. Temperature of the cooling medium and circulation speed of the alcohol were controlled so as to keep the temperature of the cooling liquid in the shell surrounding the material by 5 to 7 °C lower than the solidification point of the material zoned.

To provide unambiguous evaluation of results also these experiments were made with suitably prepared benzene, admixed with approximately 1 mole% methane alcohol impurity. In our case the melting point of the methane alcohol impurity (—97 °C) reduced the melting point of the benzene solvent (5.53 °C), which would move in the same direction as the zone, hence concentrate at the top of the material. After zoning the heater moved downwards and the gradually molten fractions of 2 to 5 ml were pipetted.

Impurity distribution was examined by refractometry and cryoscopy after 1, 3 and 5, zone passes. Solidification rate was 4 cm/hour in all three cases. Comparison of Fig. 2 and 4 shows that after $n = 5$ zone passes the benzene did not yet attain the grade of purity possible by normal freezing at the same crystallization rate, but at a constant stirring of the liquid phase.

3. *The combined application of normal freezing and zone refining*

After evaluating zone experiments by both methods it was at hand to subject the liquid refined previously by normal freezing to a further zone refinement. The apparatus shown in Fig. 1 was only modified to increase the heat insulated recipient 6 (containing the cooling mixture) to the height of the useful space of the glass tube since in zone refinement the whole length of the liquid has to be cooled. The tube emerging of the heating ring is gradually immersed into a thermos flask filled previously with a mixture of alcohol and dry ice. Conditions of the experiment are more favourable for illustrated

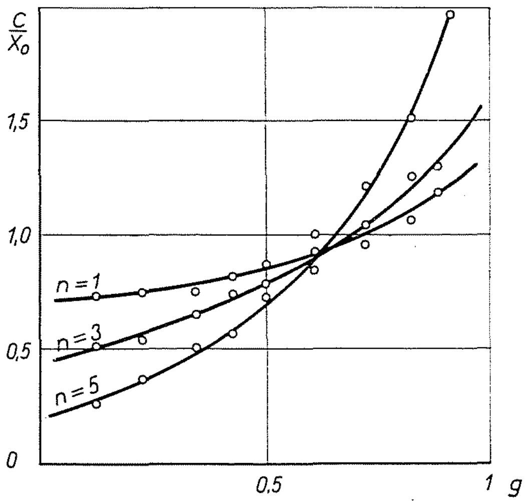

Fig. 4. Zone refining with the same material couple, varying zone passing

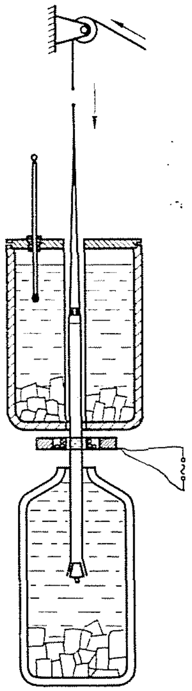

Fig. 5. Apparatus used for combined technique

method. Alternation of cooling and heating reduced the risk of overwarming or overcooling consequently, zone width can be kept strictly constant.

Fig. 6 shows results obtained with the three methods. Solidification rate was 4 cm/hour in all the four cases. The most remarkable result of the series of experiments was that single normal freezing process resulted in a better impurity distribution than five successive zone refining passages. The efficiency of normal freezing prior to zoning could further be increased by continuous zone refining operations. This observation is likely to indicate that impurity content can rapidly and effectively be reduced by a normal freezing as the first step, at a solidification rate proper for the couple of materials (solvent + impurity), with stirring best suited to the circumstances. Then after having removed approximately 1/5 from the end enriched in impurities, the remaining material is subject to some passages of zone refining. Omitting normal freezing as the first step, then favourable impurity distribution possible by the combined method can only be approached by a very high number of zone refining.

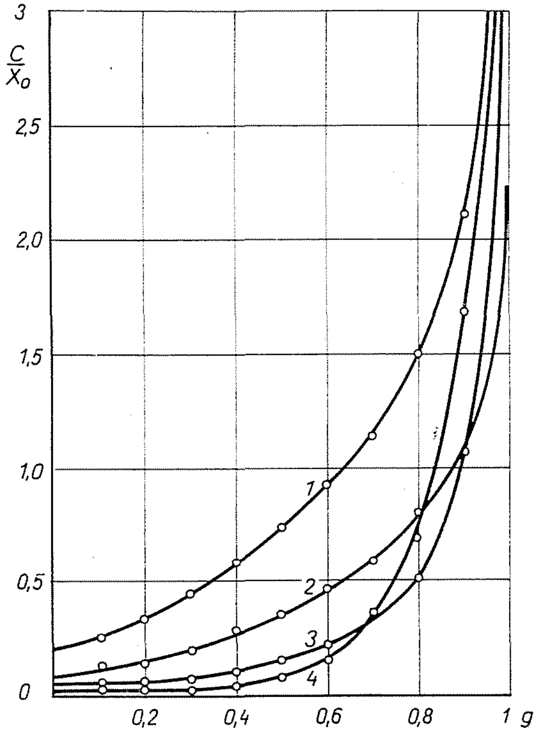

Fig. 6. Experimental results

1. Zone refining; 2. Normal freezing; 3. Normal freezing followed by a single zone refining; 4. Normal freezing followed by three zone refinings

4. *Determination of the effective distribution coefficient*

The effective distribution coefficient (k) — crucial parameter of zone melting — was determined experimentally. Impurity concentration in the initial liquid (X_0) and in portions g of the specimen length (C) was determined. In the diagrams the relative concentration $\frac{C}{X_0}$ is plotted in function of g. The effective distribution coefficient is delivered by the equation

$$\frac{C}{X_0} = k(1 - g)^{k-1}$$

analytical expression for the impurity distribution at normal freezing. The k value obtained in this way is, however, valid only approximately. Namely it is physical impossibility to have a constant k value of benzene with methane alcohol impurity ranged between 0.06 and 0.1, a very low value. This can be readily explained by the fact of normal freezing. Solidification conditions in zone refining are nearly identical with those in normal freezing without stirring. In both cases k values of 0.25 to 0.4 were obtained. The k value below 0.5 indicates that the material can be considerably purified by n zone passages.

It follows from the experimental results that the purity of the system prerefined by normal freezing and then subjected to zone refining is superior to that of products after as many zone treatments. The main advantage of this method is to considerably shorten the time consuming zone refining operation. A given material with impurities can be purified at a shorter time if normal freezing is employed first followed by zone refinement n times. than by zone refining alone. The period of zone refining is considerably higher than n if the same purity is required, as that resulting from the combined application of the two methods.

Experimental

Commercial benzene of pro analyse purity was distilled in a 2 m high column filled with Rasching rings, adjusted to a reflux ratio of 1 : 5, corresponding to a number of plates of approximately 20. The main distillate was collected, simultaneously checking purity. To the pure benzene obtained in this way 1 mole% of methane alcohol was added as impurity. A solution of 70 ml was prepared for normal freezing, and 50 ml for zone refining, and after thorough stirring 5 ml was filled into the ground test tube marked X_0, while the rest of the liquid was filled into the freezing space of the zone apparatus.

Refinig performed by the three methods is described in details under the heading "Description and discussion of experimental methods". After completion of zoning, the benzene was melted gradually and the dripping liquid was caught in fractions of 1 to 5 ml, and stored in numbered, well closed test tubes.

Examination of purity

a) *Cryoscopic method*

The change of solution temperature was measured in function of the freezing time of the material. The test needed 3 ml of the solution which was stirred until complete crystallization. Gradually cooling ambience was provided by gradually exhausting the space above the acetone in recipient surrounding the sample. Temperature changes were measured by a Chromel-Alumel Thermocoax, values were automatically recorded by a DC Microvolt-Ammeter. From the slope of the time vs. crystallization temperature curves and in the knowledge of the cryoscopic constant (0.0196 mole fraction/°C), the quantity of impurities and the rate of the purification of the materials could be evaluated.

b) *Infrared spectroscopy*

On the infrared spectrophotometer UR 20 the quantity of impurities was measured in NaCl cuvette of 0.16 to 1.02 layer thickness, based on the intensity of the OH^- absorption line (valence oscillation of the OH^- ion). For the precise evaluation of the quantity of methane alcohol a calibration curve was plotted on the basis of measurements.

c) *Refractometry*

With an immersion-type refractometer the refractive index was measured by a T 5 prism thermostated at 25 °C, at an accuracy of 5 decimals. Accurate concentration values in mole percentages were obtained by a calibration curve.

Impurity concentrations were determined with all the three refining methods and values showed a good agreement (up to 10^{-2}).

Summary

The series of experiments has proved that in the case of zone melting handling of liquid materials, normal freezing shows an outstanding effect what can serve in every case as the basis for further zone refining.

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References

1. W. G. Pfann: Zone melting. New York, London, Sydney (1966)
2. E. F. G. Herington: Zone melting of organic compounds. Oxford (1963)
3. Schildknecht: Zonenschmelzen. Verlag Chemie Weinheim Berg Str (1964)
4. H. C. Wolf and H. P. Deutsch: Naturwissenschaften, **41**, 425 (1954)
5. W. R. Wilcox, R. Friedenberg and N. Black: Chem. Rev. **64**, 187 (1964)
6. A. G. Anikin, G. M. Dugacheva, U. M. Presnyakova and S. P. Bykova: Russ. J. Phys. Chem. **36**, 1115 (1962)
7. H. Rock: Naturwissenschaften **43**, 81 (1956)
8. A. G. Anikin, G. M. Dugacheva: Dkl. Akad. Nauk. SSSR. **119**, 939 (1958)

Dr. József Nagy
Edith Brandt-Petrik
} Budapest XI, Gellért tér 4, Hungary