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# Detection of the Liquid – Liquid Demixing by Differential Scanning Calorimetry

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## Summary

From theoretical considerations it is concluded that the demixing temperatures of moderately concentrated polymer solutions should manifest themselves in a change of the slope of the corresponding DSC trace; the effects are expected to suffice for detection by means of the commercially available dual furnace instrument DSC-2C from Perkin-Elmer.

Measurements with 17 mg samples (10 wt.% poly(decyl methacrylate) in iso-octane, lower critical solution temperature) and with 40 mg samples (10 wt.% polystyrene in tert. butyl acetate, upper and lower critical solution temperature) corroborate the above considerations. Since the effects are rather small, special care must be taken to exclude artifacts.

## 1. Introduction

The demixing of a homogeneous system produced for instance by temperature, pressure or shear stress can be followed by means of various methods such as turbidimetry, light scattering, viscometry or NMR /1/. Because of the small amounts of the sample required and of the frequent availability of precise calorimeters it would be advantageous to develop also a calorimetric procedure for the determination of the liquid-liquid demixing.
The main problems are the following: upon demixing, the differences in the composition of the coexisting phases are much smaller than on mixing the pure components, consequently the heat of demixing is also much smaller than the total heat of mixing. Moreover, if DSC methods are applied, the heat of demixing is not converted isothermally like in the mixing experiment, but only in tiny portions according to the change in composition of the coexisting phases produced by the changes in temperature.

Some early trials with DSC measurement of the liquid - liquid demixing of polymer solutions were undertaken by EMMERIC and SMOLDERS /2/, but their later results /3/ revealed the described effect to be the heat of crystallization. Recently it was reported /4/ that the phase separation can be followed calorimetrically by means of a self-built DTA apparatus, if sufficiently large amounts of the polymer solution (in the order of 5 ml) are employed. In the present study it is investigated whether a commercial DSC-2C apparatus with its small sample volumes (about 0,02 ml) suffices to detect the entrance into the two phase region in the case of polymer solutions.

## 2. Experimental part

Samples of poly(decyl methacrylate) (PDMA) were supplied by Röhm GmbH, Darmstadt (Germany); their weight average molecular weight $M_w$ is /5/ 250 000 and 470 000, respectively, the corresponding non-uniformities $U = M_w / M_n - 1$ ($M_n$ = number average molecular weight) amount to /5/ 0,13 and 0,20 . Polystyrene (PS) was bought from Pressure Chemical Company; according to the producer $M_w$ = 600 000 and U = 0,10 .
Iso-octane (IO) and tert.butyl acetate (TBA), both p.a.-grade from E.Merck, Darmstadt, were employed without further purification.

For the calorimetric measurements, the commercially available dual furnace instrument DSC-2C from Perkin-Elmer Corp., Norwalk, (USA), was used. Both types of capsules employed were first heated outside the instrument up to the maximum temperature of interest to test their tightness. Since the rehomogenization of a solution once demixed, may be rather slow, only the effects associated with the transition homogeneous-heterogeneous were determined.The apparatus sensitivity was always chosen to 0,4 mJ/s.

For IO/PDMA, the first system under investigation, high pressure, copper ring sealed capsules containing ca.17 mg of solution had to be applied; these cells are designed for measurements up to 400 °C and 150 bar /6/. Great attention must be paid to the weighing-in of the sample, since the volume of IO increases by a factor of about 2,5 /7/ going from 20 °C (weighing) to 270 °C (demixing range). Too small amounts of the solutions would deteriorate the quality of the thermogram and lead to a strong change in composition upon heating, too large amounts on the other hand can burst the capsules.

Base-line runs with pure IO gave surprising thermograms: About 30°C below the liquid-gas critical point, exothermal step jumps were observed on heating as well as on cooling. A similar behaviour was also observed with some solutions and with other pure liquids (cyclopentane, n-hexane, benzene),cf. Fig. 2 and 4, but never with empty capsules. An electronic deficiency can be ruled out, since another DSC-2C apparatus (at the Perkin-Elmer sales and service center in Offenbach) also yielded the effects.
The height of the step depends on the size of the sample, decreases as the rate of temperature change is lowered and vanishes if the absolute change in temperature falls below ca. 0,1 K/min. These findings suggest that the above phenomenon is caused by convection induced microstreams. With regard to these difficulties with the base-line, properly mass-adjusted (pieces of copper sheet) empty pans were taken instead of the normally used solvent filled capsules.

The second system under investigation, TBA/PS, exhibits an upper critical solution temperature (UCST) at 4 °C and a lower critical solution temperature (LCST) at 123 °C with the present molecular weight as can be estimated from published data /8/. Because of the lower vapour pressures as compared with the previous system, the DSC measurements could be performed in so called large volume capsules which are sealed by viton O-rings and contain ca. 40 mg of the solution. No convection induced step is observed with the present system, probably because of the greater distance to the gas-liquid critical point of the solvent.

## 3. Results and Discussion

First the shape of the thermogram that has to be expected theoretically will be discussed. To this end $H_M$ , the heat of mixing per gram of mixture, is calculated for the system IO/PDMA using the Flory-Huggins theory which yields the following expression

$$H_M = \chi_H \cdot R \cdot T \; \frac{x_1 \varphi_2}{x_1 M_1 + x_2 M_2} \qquad (1)$$

in which $x$, $\varphi$ and $M$ are the mole fraction, volume fraction and molar mass, respectively. The index 1 stands for the solvent, 2 for the polymer; RT has its usual meaning. The evaluation of LCSTs /9/ according to Shultz-Flory yields a value of -1,5 for $\chi_H$ , the enthalpy part of the interaction parameter. The function $H_M(\varphi_2)$ resulting therewith by means of eq.1 is shown in Fig. 1 together with the corresponding phase diagram. Although the assumption of $\chi_H \neq f(\varphi_2)$ can cause considerable errors (with trans-decalin / polystyrene for instance up to +300% /10/ ) the order of magnitude of the expected heat effects should remain correct.

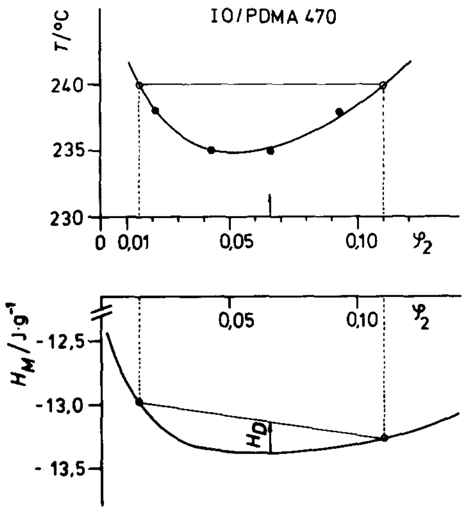

*Fig. 1:*

*Top: Phase diagram for solutions of poly(decyl methacrylate), $M_w$ = 470 000 g/mol , in iso-octane. $\varphi_2$ = volume fraction of the polymer. The two phase region lies above the curve;*

*Bottom: Enthalpy of mixing per gram solution as a function of $\varphi_2$ calculated according to the Flory-Huggins theory (cf. text)*

If a moderately concentrated solution, like that indicated in the upper part of Fig. 1 by an arrow, is warmed up, $H_D$ , the heat of demixing starts to be converted as soon as one enters the two-phase region at ca. 235 °C. Increasing the temperature further, this process proceeds according to the corresponding changes in the composition of the coexisting phases. The total heat effect resulting for instance from the demixing of a homogeneous solution of the indicated composition into the phases that coexist at 240 °C can be constructed from $H_M(\varphi_2)$ shown in the lower part of Fig. 1: The heat of demixing for a given amount of a polymer solution simply constitutes the sum of the (extensive) heats of mixing of the coexisting phases minus that of the corresponding homogeneous solution, since H is a variable of state and $H_M$ can be taken to be independent of temperature within the narrow interval of present interest. According to the construction in Fig. 1 $H_D$ the heat of demixing per gram of the solution is ca. +230 mJ/g for the given sample. Since this heat is however consumed within a temperature interval of ca. 5 K and not isothermally, like the heat of melting, the corresponding DSC trace can only be expected to show a change in the slope but no peak. With a heating rate of 10 K/min the heat flux of a 20 mg sample would consequently amount to 0,15 mJ/s assuming $\partial H_D/\partial T$ to be constant. According to the high sensitivity of the DSC-2C apparatus and to its low noise level (less than 0,017mJ/s), the entrance into the two phase region should be measurable from the change in the slope of the DSC trace at the demixing temperature. In the present example $H_D$ should for instance produce a deflection of about 1/3 of the full scale on the 10 mV - recorder, unless the formation of new phases were hindered kinetically. At least with the present system such difficulties are however absent as is demonstrated by the fact /9/ that the equilibrium turbidity is developed within less than a few seconds, when the conditions are changed. Concerning the measurement of small heat effects it should be noted, that comparable precision was required for the measuring of the heats of melting of 0,04 - 0,06 mg samples of polyethylene with the same DSC apparatus /11/.

The actually measured thermograms for the high temperature demixing of IO/PDMA reveal the expected bend at the demixing temperature independently determined by cloud-point experiments (s. Fig. s 2 and 3). The bend direction agrees with the thermodynamic considerations, i.e. $H_D$ results endothermal.

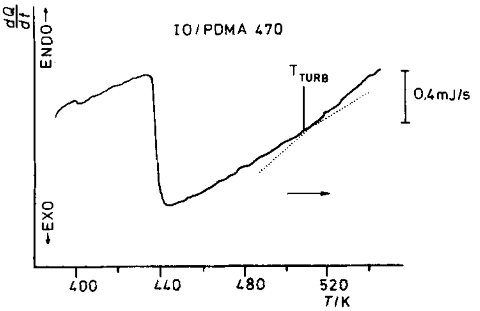

*Fig. 2:*

*Heating run (10 K/min) with 17 mg of a solution of poly(decyl methacrylate), $M_w$ = 470 000, in iso-octane; in copper sealed pans, sensitivity (range) 0,4 mJ/s. The huge exotherm step jump (here at 436 K) is likely to be caused by convection phenomena (cf. text)*

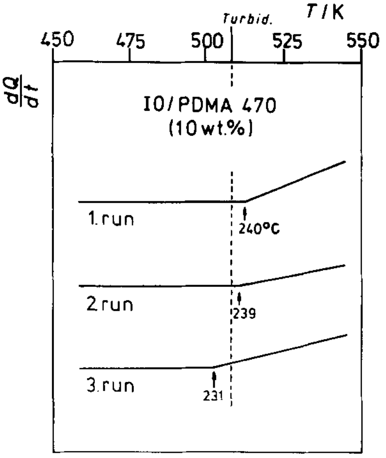

*Fig. 3:*

*Repetitions of the experiment shown in Fig. 2. The pronounced change between the 2nd and 3rd run is likely to be an autocatalytic thermal degradation.*

At the low temperature end of the scale, a strong convection-induced step appears (s. introduction).

Repeated scans of the same sample yielded thermograms as shown in Fig. 3. The discrepancies of the measured demixing temperature are probably due to two phenomena ; (i) the DSC experiments seem to yield somewhat higher values, unless extremely low heating rates are applied, (ii) the polymer sample is degraded, probably autocatalytically , when it was heated higher than 560 K, as described in the former work /12/. Typical DSC degradation endotherms were actually registered on 20 wt% solution of PDMA 250 000 in iso-octane (Fig. 4).

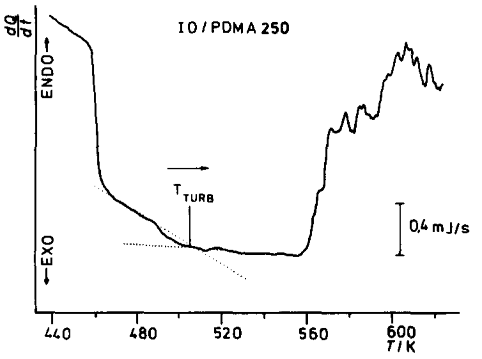

*Fig. 4:*

*Thermal degradation endotherms found above 560 K in a 20 wt-% solution of poly(decyl methacrylate) in iso-octane, $M_w$ = 250 000, 10 K/min, range 0,4 mJ/s, copper sealed pans.*

*The nature of a small exotherm at 490-510 K is likely random. The value of the demixing temperature (determined by cross over of dotted lines at 505 K) is justified by the turbidimetrically measured demixing temperature $T_{Turb}$ =507 K*

The second system for which the present approach has been tried, namely TBA / PS , also shows the characteristic demixing bends. Both low and high temperature demixing could be detected calorimetrically in agreement with the turbidimetric data of SAEKI et al. (Fig. 5).

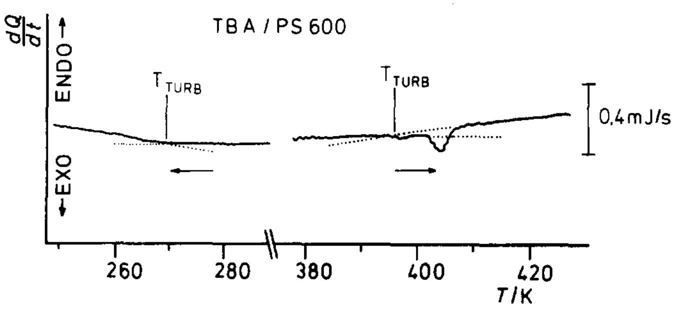

*Fig. 5:*

*Typical cooling and heating runs with a solution of polystyrene $M_w$=600 000 in tert-butyl acetate; $w_2$ = 10 wt-%, 40 mg solution, 5 K/min, sensitivity 0,4 mJ/s, viton sealed pans. $T_{Turb}$ indicates the critical solution temperatures estimated from published data /8/. (The small exotherm at 404 K is probably of random nature).*

At the first glance the endothermal heat of demixing observed upon cooling surprises, since it is well known that the corresponding enthalpy of dilution is also positive /13/. This does, however, not necessarily indicate that the measurements are in error, a possible explanation could simply lie in a point of inflection of $H_M(x_2)$ .

The present results demonstrate that the demixing of moderately concentrated polymer solutions can in principle be registered by commercially available DSC instrument with minute amounts of material. At the current state of the method it is however indispensable to check the results by an independent method. Cumulative registration of DSC trace for a given sample could already improve the situation considerably.

## Acknowledgement

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