TURBIDIMETRIC STUDY OF THE DEMIXING PHENOMENON IN LIQUID – LIQUID SYSTEM POLYURETHANE – DIMETHYLFORMAMIDE - WATER

**Simona Ungureanu, Luminita Balau, C. Ciobanu,
M .I. Popa, M. O. Apostu[1], V. Melnig[1]**

*"Gh. Asachi" University Technique, Iasi, Faculty of Industrial
Chemistry, B-dul D. Mangeron, Nr. 71A, 6600 – Iasi, Romania
e-mail: mipopa@ch.tuiasi.ro*
[1] "Al.I.Cuza" University, Iasi, Faculty of Physics

ABSTRACT: The present research relates to liquid – liquid demixing phenomena encountered in polyurethane (PU)/N,N'-dimethylformamide (DMF)/water system. The cloud – points were determined by turbidimetric titration for various initial concentrations of PU in DMF.

It was experimentally observed that a small amount of water is needed to induce liquid – liquid demixing. The cloud – points were determined by turbidimetric titration for PU/DMF different concentrations between 1÷20 %.

The obtained phase diagram is a useful tool for the preparation of membranes with controlled morphology. Morphology and structure of the membranes was studied by Scanning Electronic Microscopy (SEM) technique and by Angular Total Reflection Fourier Transform InfraRred (ATR-FTIR) method.

The paper reveals that the morphology of the asymmetric membranes can be anticipated with the help of phase diagram and controlled by casting parameters such as: polymer concentration, coagulation bath composition and temperature.

KEYWORDS: *polyurethane, membranes, turbidimetric titration, SEM, FTIR*

INTRODUCTION

Polyurethanes have many applications such as: fibers, adhesives, synthetic leathers, and biomedical products. The preparation of synthetic leathers or biomedical products often involves formation of polyurethane membrane via in immersion precipitation process. In this process, the homogeneous polymer solution is contacted with nonsolvent, and subsequent exchange of solvent and nonsolvent across the interface result in phase separation into a polymer-rich phase and a polymer- lean phase.

The former results in rigid, structural part of the membrane, while the latter gives porous substructure. Phase separation is continued until the polymer-rich phase is solidified by gelation and/or crystallization of the polymer.

To investigate the final morphology obtained by immersion precipitation, we need to know both the thermodynamics and kinetics of phase separation.

Knowledge of the thermodynamics such as the phase diagrams enables one to change the compositions of the casting solution or the coagulation bath to obtain optimal membrane structure.

In this paper there have been established the best conditions of precipitations (volume of the precipitations solutions-temperature) for the polyurethans solutions of different concentrations. Parameters of interactions have been measured using the turbidimetric method.

METHOD

Turbidimetric method

In the case of the solutions and macromolecular substances (polymer and biopolymer) the method of turbidimetric titration allows the determination of molecular masses distribution as well as the obtaining of the value of some structural – termodynamic parameters of the biopolymer solvent-nonsolvent system. The method is used to obtain the phase diagrams in binary, ternary and quaternary system (for example the study of the phase equilibres in the water-gelatin-pectin-dextran system). The measurement of turbidity allows the study of the transport in the cellular membranes: the own volume of the cells/organoids depends on the osmotic equilibre between their interior and exterior. The moment in which the less molecular substances (sugars, aminoacids) are added to the watery suspension appears in an osmotic unbalance, which has as a result a swift increase of the water flux of the cell. As a consequence to that a decrease of the own volume of the cells/organoids takes place. This change of the volume can be followed by measuring the turbidity suspension. The method was used in the study of the actinium-myosin complex, a complex involved in the muscular contraction metabolism. Adding the ATP in an actinium-myosin suspension causes a decrease of the turbidity as a consequence of this dissociation complex.

The method is simple and accessible from the point of view of the necessary equipment. This necessary testing quantity for a proper determination is reduced, in milligrams figures.

The turbidimetric method is also used for the characterization of present interactions in the solutions of polymers. In this way one may obtain the θ conditions (the composition and the temperature) as well as the solubility parameters values.

The principle of the method

The turbidimetric titration method is based on the light intensity transmitted or distributed to the diffusion centers of the solution.
The describe phenomena which take place in a measurement experiment of the turbidity one should take into account a polymer/ solvent/nonsolvent system. The increase of the turbidity system can be followed by decreasing the transmitted light intensity or by increasing the light intensity diffused to the θ angle. Starting with the Lambert- Beer law, turbidity τ is defined for a certain wavelength in the following relation:

$$\tau = \frac{1}{L}\ln\frac{I_0(\lambda)}{I(\lambda)} = \frac{2,303}{L}\lg\frac{I_0(\lambda)}{I(\lambda)} = \frac{2,303}{L}D \tag{1}$$

where L is the optic way, $I_0(\lambda)$ and $I(\lambda)$ are the incident light intensity respectively the one transmitted and D is the optic density.
Lord Rayleigh established that in the case of spherical particles (monodisperses), with more dimensionless than the wavelength of the utilized radiation, the turbidity is given by the relation:

$$\tau = \frac{32\pi^3 n_0^2 \left[(n - n_0)/c\right]^2 cM}{3\lambda^4 N_A} \tag{2}$$

Where n and n_0 are the indexes of refraction of the solution as well as of the solvent, c is the diffused particles concentration, N_A is the Avogadro's number and M is molecular mass. Thus, if the diffused particles are spherical a mass, molecular determination is possible by using the simple measure of the turbidity.
For macromolecules with moderate dimensions the turbidity, is related to the massic concentrations c by the relation:

$$\frac{Hc}{\tau} = \frac{1}{\overline{M}_w}\left(1 + 2Bc + ...\right) \tag{3}$$

where H parameter is proportional with the variation of the refraction index, with the concentration and $\overline{M}_w$ represent the gravimetric average molecular mass.
The typical size order for turbidity is comprised between 10^{-5} cm^{-1} for pure transparent liquids, 10^{-3} cm^{-1} for polymers with 1% concentration and 10 cm^{-1} for milk.
When analyzing the diffusion data of the light one has to take into account the dimension of the particles in suspension.
When the wave length of the incident radiation is comparable to the particles dimensions, the light diffusion takes place to the level of a single particle, on many centers of diffusion. As a consequence to that the diffusion intensity deviates from the Rayleigh intensity due to the interference phenomenon. A measure of this distortion is the relation:

$$P = \frac{I}{I_R} \qquad (4)$$

Where I is a noticed intensity and I_R is the intensity for the Rayleigh diffusion following the same conditions.

When the molecule is much lesser than the wavelength of the incident radiation (the particle dimension $< \lambda/20$) then:

$$P - 1 \propto R_g^2 \qquad (5)$$

where R_g represents the molecule gyration ray.

The value of the turbidity system is a measure of the polymer fractions mass, which precipitated of the solution.

Considering we note V_0 the initial volume of the solution in work and with V_{ns} the volume of the nonsolvent in different moments of the titration, then the volume fraction of nonsolvent (γ) will be:

$$\gamma = V_{NS} / (V_0 + V_{ns}) \qquad (6)$$

Due to the adding of the nonsolvent the concentration variates continually in such a way, that the concentration must be corrected by the relation:

$$C = C_0 (1 - \gamma) \qquad (7)$$

where C_0 is the initial concentration and C is the momentary concentration. As a consequence to that, one will have to operate a correction even for the D optic density by diving to ($1-\gamma$):

$$D_c = D / (1 - \gamma) \qquad (8)$$

where D_c represents the optic density corrected for the dilution. The maxim value of the optic density (noted with D_m) corresponds to the moments in which all the polymer precipitated; its value corrected for the dilution will be:

$$D_{mc} = D_m / (1 - \gamma) \qquad (9)$$

The relation D_c/D_{mc} represents the fractions of precipitated polymer.

The value of fraction of they nonsolvent volume γ, to which is separated the polymer of the solution depends on the fallowing factors:

- the molecular mass M_i of the present fractions in solution;
- the concentration C_i of each molecular specie situated in the solution at the precipitation moment;
- the polymer nature;
- the system temperature;
- the system solvent/nonsolvent utilized

In a given experiment the last three parameters are fixed.

The form of turbidimetric titration curves offers qualitative and quantitative informations over the dispersity of the studied polymer molecular mass, being similar from the qualitative point of view to the integral curve of molecular mass distribution. If the slope of this curve is bigger, then the polymer is becoming closer to a monodispers polymer and in the opposite case the molecular mass dispersity is bigger.

The use of the laser radiation leads to a supplementary improvement in the applications and interpretation of the light diffusion. All those allowed the determination of time dependence of the atoms position and the macromolecules orientation into the solution by measuring the frequency change of place on a mobile target a method called the dynamic diffusion of the light.

EXPERIMENTAL

The device used for the measurement of the turbidity is presented in the figure 1. There was utilized a thermostat quartz cell; the thermostat precision being of ± 0.3 K. The homogenization of the system was made using an agitator with constant turation at the initial volume of the solution was of 25 mL.
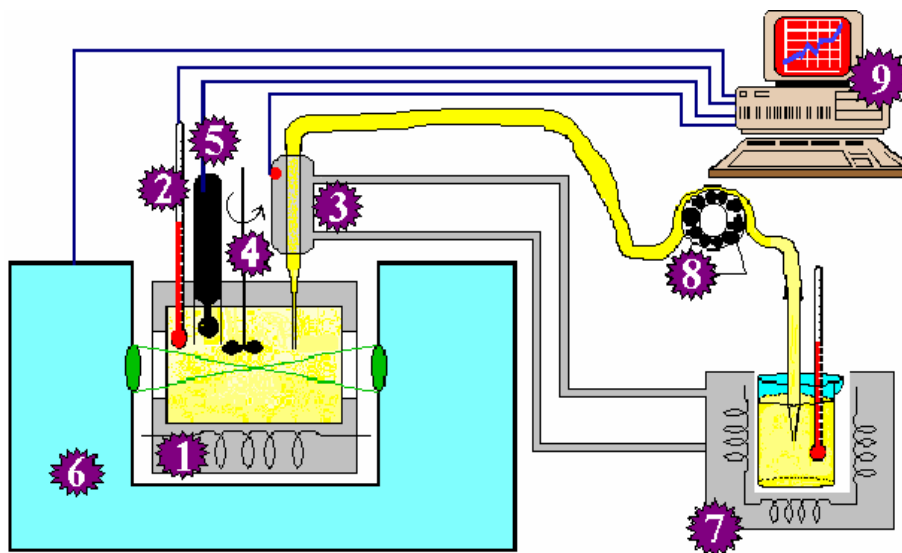

Figure 1. The scheme of the experimental device: 1-thermostat spectrophotometer cell;
2-thermocouple; 3-the thermostat cycle with thermocouple; 4-mechanical agitator;
5- pH measuring electrod ; 6-spectrophotometer; 7-thermostat; 8- peristaltic pump;
9-computer; 10-acquisition system

The nonsolvent adding was made using a peristaltic pump, with a constant flow of 0.2 mL/min. The nonsolvent was maintained at the same temperature as well as titrant system due to a thermostatic boucle. The system also permits the pH solution following. The transmitted fascicle intensity was caused by a spectrophotometer LKB ULTROSPEC 4052 TDS. The signal was obtained using a DAS 1600 plate piloted by the ViewDac utilitarian.

PU was synthesized utilizing a copolyester obtained by the condensation of adipic acid, ethylenglycol, diethylenglicol (in molars relations 1:0.5:0.6) with 4,4'-diphenil-methane-diisocyanate [8]. This copolyester has a gravimetric average molecular mass equal to 2000 and an acidity index of 0.2 mg KOH g^{-1}. PU was obtained in DMF and has a gravimetric average molecular mass of 45800.

PS and PU weighted tests were dissolved in DMF. To obtain a solution steady from the thermodynamic point of view the phials of solution were agitated in a thermostatic recipient. Thermodynamic equilibrium was obtained by the reproducibility measures of viscosity solutions. In the case of PU there have been made solution in the concentration field of 0.01÷6 % (mass percents).

The turbidimetric measurements were made at different temperatures in the range 25÷60 °C.

RESULTS AND DISCUSSIONS

In the figure 2 there are presented the curves of turbidimetric titration obtained in the case of PU-DMF-water system.

The titration curves of the figure 2 correspond to the 0.1 and 0.5 % concentrations the temperature field being of 30÷60 °C.
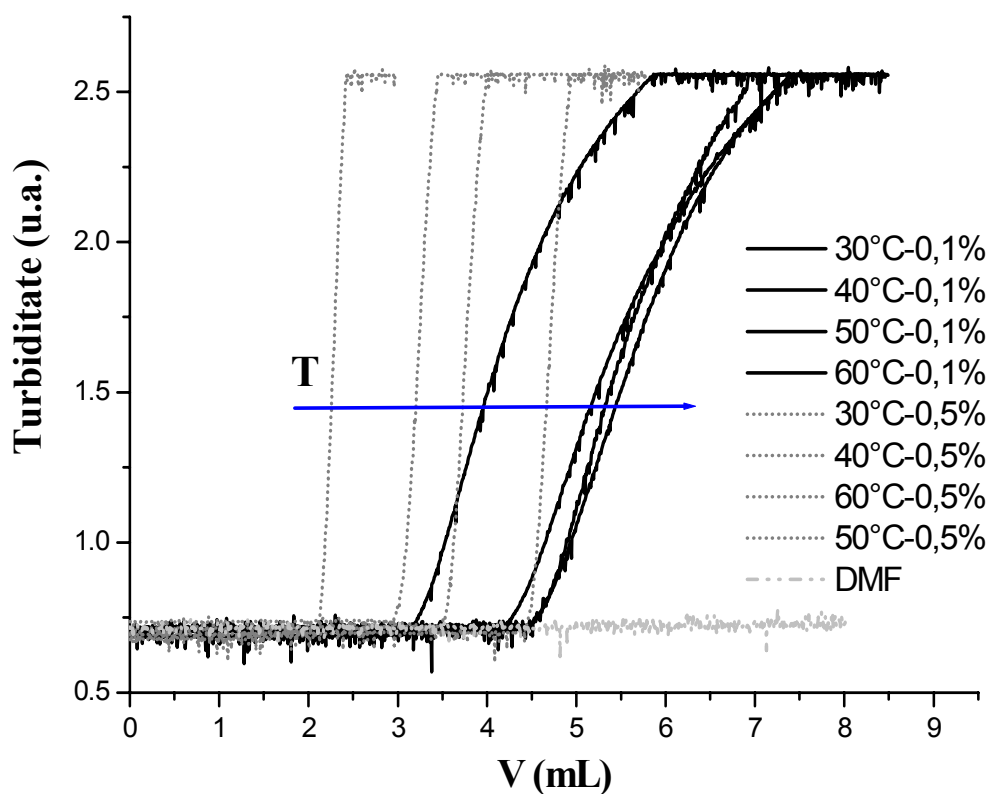

Figure 2. Curves of turbidimetric titration in PU-DMF-water system

One observation consists in the influence of the initial concentration over the solvent-nonsolvent relation in which the precipitation phenomenon appears. One may also notice the decrease of the nonsolvent volume necessary for the precipitation inductions together with the temperature increase.

The basic line in figure represents the registration obtained in titration case of a sample, which does not contain PU.

In the figure 3 it is presented titrant volume-temperature diagram, having as a parameter the concentration of the polymer solution.

One can notice that at PU small concentrations, the best precipitation conditions are made at low temperatures (25-30 °C), while at high concentrations the best precipitation conditions are made at high temperatures (45-50°C). A possible explication of this behavior could be the different packaging way of PU at low concentrations comparing to the high ones.
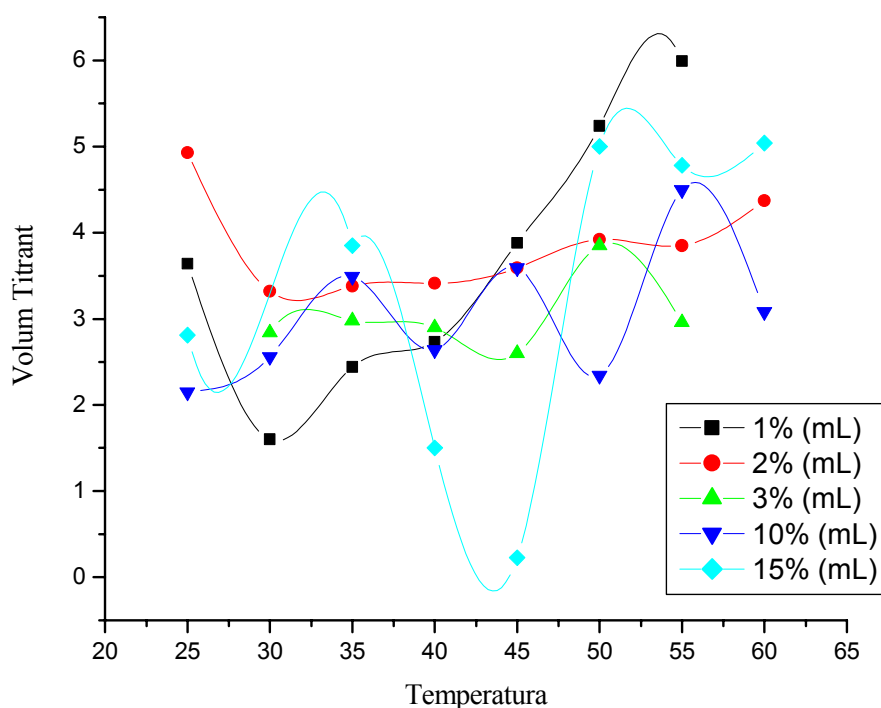

Figure 3. Diagram titrant volume against temperature

CONCLUSIONS

1.   Measurements made in the case of PU-DMF-water system, using the turbidimetric method demonstrate the accuracy of the obtained data.
2.   The results evidence the different behavior of polymer solutions at small concentrations and at high concentrations, this one depending on the macromolecules packaging way.
3.   In the case of PU-DMF-water system there were established the best precipitation conditions; the results being valuated in practice, a fact that lead to the improvement of experimental protocol.

REFERENCES

1. Debye P., *J. Phys. Colloid Chem.*, **1947, 51**, 18
2. Scholtan W., Ges Z., - *Exptl. Med.*, **1959, 130**, 556,
3. Nath S**.**, - *J. Chem. Techn. and Biotechn***., 1995, 62**(3), 295
4. Antonov Yu.A., Zubova O.M., - *International Journal of Biological Macromolecules,* **2001, 29**, 67–71.
5. Shu X. Z., Zhu K. J., Song W., - *International Journal of Pharmaceutics,* **2001, 212**, 19–28
6. Atkins P.W., - *Tratat de Chimie fizică*, 1996, Ed. Tehnică, Bucureşti
7. Onu A., - *Chimia fizică a stării macromoleculare*, **2002** Ed. Tehnopress, Iaşi
8. Ciobanu C., Afloarei P., Bîrlădeanu C. and Culic C. V., - *Brevet Ro.* 93590/25.06. **1997**