

CCA-1839

YU ISSN 0011-1643

UDC 532.13

*Original Scientific Paper*

## Viscometric Studies of Poly(ethylene glycol), Poly(vinyl alcohol) and Poly(vinyl chloride) and Their Mixtures in Water and Chlorobenzene

*Harun Ur Rashid**20, Carpenter Court, Markham, Ontario, Canada L3P 6W2*

Received October 7, 1987

Absolute viscosities of semi-dilute solutions of poly(ethylene glycol) and poly(vinyl alcohol) and their mixtures in water and of poly(ethylene glycol) and poly(vinyl chloride) and their mixtures in chlorobenzene have been measured at 30°C. The viscosities of poly(vinyl alcohol) and poly(vinyl chloride) increase sharply with concentration. The plots of viscosity of polymer mixtures against composition deviate from linearity. The effect of total polymer content on the viscosity of mixtures has also been studied. The results are discussed in terms of the association of similar type macromolecules and compatibility between dissimilar types of macromolecules. Theoretical predictions of compatibility/incompatibility have also been made for these systems. It appears that poly(vinyl alcohol) and poly(vinyl chloride) macromolecules associate at higher concentrations and poly(ethylene glycol) is incompatible with poly(vinyl alcohol), but compatible with poly(vinyl chloride) in water and chlorobenzene, respectively.

### INTRODUCTION

Macromolecules remain isolated in polymer solution of infinite dilution without interacting with one another. As the concentration of the solution increases, the macromolecules come into contact with each other forming associates.<sup>1</sup> The higher the molecular mass of the polymer, the smaller is the concentration at which they come into contact. The attractive interaction between polymer chains is enhanced in a poor solvent and if the polymer chains have capability of forming hydrogen bonds with each other. The association of macromolecules may result in an increase of viscosity of the system.

Viscometric results of polymer mixtures in a common solvent have been interpreted in terms of compatibility between polymers. The nonlinear plot of viscosity against composition has been considered as the indication of incompatibility between polymers.<sup>2-6</sup> Other works<sup>7</sup>, however, have concluded that the deviation of the values of viscosity from additivity should not be regarded as a measure of incompatibility.

---

The full address of the author to whom correspondence should be sent: Department of Chemistry, Bayero University, P. M. B. 3011, Kano, Nigeria.

In the present work we have used the viscometry method to study semi-dilute aqueous solution of a low molar mass polymer, poly(ethylene glycol), and its high molar mass isomer, poly(vinyl alcohol). We have also presented the viscometric data of a mixture of poly(ethylene glycol) and poly(vinyl alcohol) in water and a mixture of poly(ethylene glycol) and poly(vinyl chloride) in chlorobenzene. Attempts have been made to explain the results in terms of the association of similar type macromolecules and compatibility between dissimilar types of macromolecules. Attempts have also been made to estimate roughly the extent of compatibility between the macromolecules through theoretical approach.

#### EXPERIMENTAL

##### *Materials*

Commercial samples of poly(vinyl alcohol) (PVA), poly(vinyl chloride) (PVC) and poly(ethylene glycol) (PEG) were used in this work. The molecular weights of the samples as indicated by the supplier, BDH Ltd., England are PVA, 125000 (Degree of hydrolysis: 87–89%) and PVC, 100000. The molecular weight of PEG 1000, also supplied by BDH, was determined by end group analysis<sup>8</sup> as 995. Chlorobenzene and water were fractionally distilled. Only middle fractions were used.

##### *Preparation of Solutions*

Accurately weighed amounts of polymers were simultaneously dissolved in the solvent. For PEG/PVA/water system, the range of polymer composition and the total polymer concentrations studied were 0–100% and 2–8% (w/v), respectively. For PEG/PVC/chlorobenzene system, solutions of 2% total polymer concentration were prepared from a whole range of composition. But clear, homogeneous solutions of 8% total polymer content were obtained only from 10, 20 and 40% of PVC. Gelation was observed in solutions of higher proportions of PVC. At least 24 hours were allowed (for the polymers to dissolve completely) before the solutions were filtered using sintered glass filters.

##### *Measurement of Absolute Viscosity of Solutions*

The absolute viscosity,  $\eta$ , of solutions was evaluated from the following well known equation

$$\eta = \alpha \rho t - \frac{\beta \rho}{t} \quad (1)$$

where  $\rho$  and  $t$  are the density and flow time of the solution, respectively. An Ubbelohde suspended level type viscometer was used to measure the flow time of solutions at 30°C. The viscometer constants,  $\alpha$  and  $\beta$  were determined by measuring the flow time of water at different temperatures. The absolute viscosity values of water at various temperatures were taken from literature.<sup>9</sup>

##### *Measurement of Densities of Polymers and Their Solutions*

The densities of polymers were determined using the Archimedes principle and those of solvents and solutions by pycnometer.

#### RESULTS AND DISCUSSION

##### *PEG/PVA/Water System*

The absolute viscosities of aqueous solutions of PEG and PVA at different concentrations are given in Table I. As expected, the viscosity increases with an increase in concentration for both systems. For PEG/water system the increase is not very significant owing to the low molar mass of PEG and

TABLE I

*Absolute viscosities of aqueous solutions of poly(ethylene glycol) and poly(vinyl alcohol) at different concentrations measured at 30 °C*

% Concentration (w/v)	$\eta$ (PEG) $\times 10^3$ (N s m <sup>-2</sup> )	$\eta$ (PVA) $\times 10^3$ (N s m <sup>-2</sup> )
2	1.04	4.09
4	1.16	23.34
6	1.19	146.00
8	1.28	226.20

its incapacity of associating intermolecularly. On the other hand, in the PVA/water system an increase of concentration by 400 percent has increased the viscosity by about 5500 percent. The higher molar mass of PVA and its capability of associating through hydrogen bonds has resulted in this massive increase of viscosity.

The absolute viscosity of the mixture of PEG and PVA in water has been plotted against weight percentage of PVA for various total polymer concentrations in Figures 1 and 2. Non-linear plots are obtained for data points above 20% PVA.

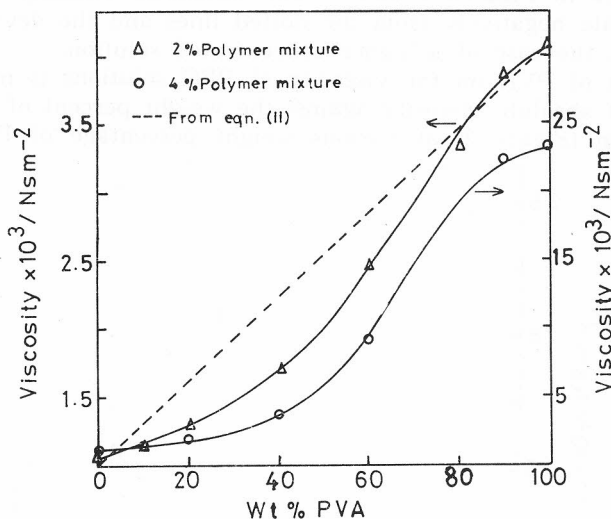


Figure 1. Absolute viscosity of 2% and 4% PEG — PVA mixture in water versus weight percent of PVA.

Absolute viscosity values have been calculated using additivity rule from the following equation for 2 and 6% solutions:

$$\eta = X_1\eta_1 + X_2\eta_2 \quad (2)$$

where  $X_1$  and  $X_2$  are the weight fraction of the component polymers in the mixture and  $\eta_1$  and  $\eta_2$  are the measured viscosities of the individual polymer solutions. These values have also been plotted against composition, as shown

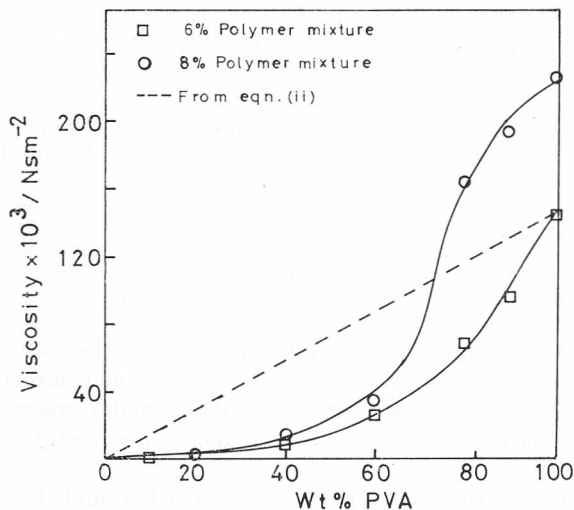


Figure 2. Absolute viscosity of 6% and 8% PEG — PVA mixture in water *versus* weight percent of PVA.

by dotted lines in Figures 1 and 2. The measured viscosity values of the mixtures deviate negatively from the dotted lines and the deviation is more pronounced in the case of a higher concentrated solution.

The effect of PVA on the viscosity of PEG solutions is more revealing in the plots of absolute viscosity against the weight percent of total polymer in the solution (Figure 3) at various weight percentage of PVA. Addition

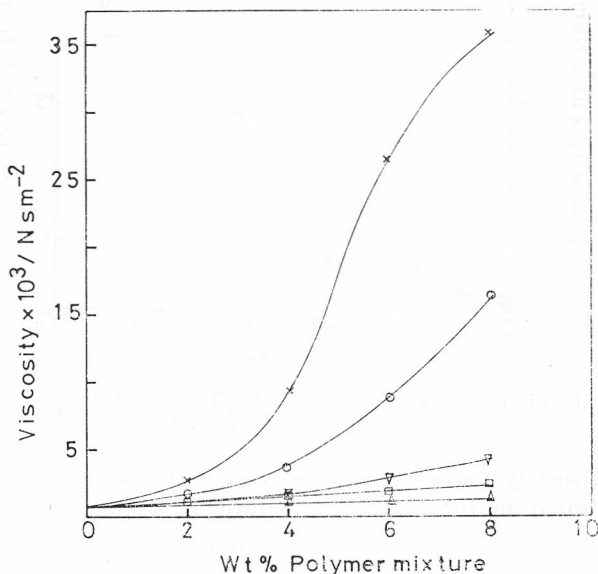


Figure 3. Absolute viscosity of PEG — PVA mixture *versus* weight percent of polymer mixture at different PVA concentrations;  $\Delta$  0%,  $\square$  10%,  $\nabla$  20%,  $\circ$  40% and  $\times$  60% PVA.

of 10, 20% of PVA does not alter much the viscosity of the solution. We may observe a rapid increase of viscosity in solutions containing more than 20% PVA and a total polymer content higher than 4%.

In solution of a lower concentration of PVA, isolated PVA molecules may interact with isolated PEG molecules forming polycomplexes through hydrogen bonds (Illustration 1).

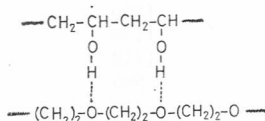


Illustration 1. Polycomplex formation through hydrogen bonds between PVA and PEG macromolecules.

When the concentration of a solution increases, macromolecules begin to come into contact with one another, forming associates. The higher the molecular mass of a dissolved polymer, the lower is the concentration at which they come into contact. In solutions of higher concentration of PVA and also due to larger PVA molecular size, contacts among PVA molecules are more likely than those between PVA and PEG molecules. Association of PVA is formed also through hydrogen bonds between hydroxyl groups (Illustration 2). Association is enhanced in poor solvents like water where the polymer contacts are more likely to predominate. Single polymer molecules no longer diffuse separately, but drag along neighbours. This leads to a larger dissipation of energy and a higher viscosity.

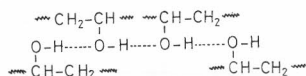


Illustration 2. Intermolecular association of PVA.

The non-linear behaviour of viscosity with composition has been considered as the indication of incompatibility between polymers.<sup>2-6</sup> In PEG/PVA/water system, the incompatibility between PEG and PVA at higher concentrations may arise due to this tendency of PVA molecules to associate. Deviation from the linear behaviour of viscosity with composition, however, may not be considered as an unambiguous measure of incompatibility between polymers.<sup>7</sup>

Methods are available which may be used to predict the extent of compatibility between polymers. One of the methods is to calculate the heat of mixing,  $\Delta H_m$  for the whole range of composition of the polymer mixture and compare the values with  $42 \times 10^{-3} \text{ J mol}^{-1}$ , which has been regarded as the upper limit for a polymer pair to be compatible.<sup>10</sup> Schneier<sup>10</sup> deduced the following equation for the heat of mixing for two component polymer blends.

$$\Delta H_m = [\bar{X}_1 M_1 \rho_1 (\delta_1 - \delta_2)^2 (\bar{X}_2 / (1 - \bar{X}_2) M_2 \rho_2 + (1 - \bar{X}_1) M_1 \rho_1)^{1/2}] \quad (3)$$

where  $\bar{X}$ ,  $M$ ,  $\rho$  and  $\delta$  are the weight fraction, repeat unit molecular weight, density and the solubility parameter, respectively.  $\Delta H_m$  has been calculated using equation (3) for PEG/PVA mixture and plotted against the composition

TABLE II  
Density and solubility parameters of polymers and solvents

	*Density (kg m <sup>-3</sup> )	Solubility Parameter × 10 <sup>-3</sup> (J m <sup>-3</sup> ) <sup>1/2</sup>
PVA	1270	25.8 <sup>a</sup>
PVC	1350	19.4 <sup>b</sup>
PEG	1150	18.8 <sup>c</sup>
Chlorobenzene	1172	19.6 <sup>b</sup>
Water	995	48.1 <sup>b</sup>

\* Measured at 30 °C.

<sup>a</sup> J. Brundrup and E. H. Immergut, Eds., *Polymer Handbook*, 2nd Ed., New York, Wiley — Interscience, 1975, pp. IV—354.

<sup>b</sup> C. M. Hansen, *J. Paint Tech.* 39 (1967) 505.

<sup>c</sup> H. U. Rashid and S. C. Zakka, unpublished work.

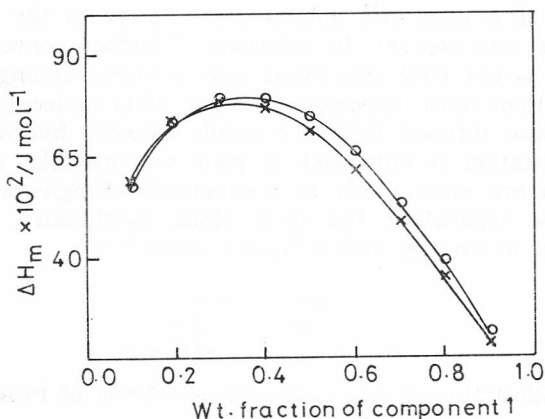


Figure 4. Heat of mixing,  $\Delta H_m$  (equation 3) of PEG and PVA versus weight fraction of component 1;  $\circ$  PVA component 1 and  $\times$  PEG component 1.

(Figure 4). Density and solubility parameters of polymers which have been used to evaluate  $\Delta H_m$  are shown in Table II. According to Schneier's criterion, incompatibility may be predicted in the present system as all  $\Delta H_m$  values are above the limit of  $42 \times 10^{-3} \text{ J mol}^{-1}$ . The maximum points of the curves are independent of the choice of polymer as component 1.

Another method of estimating the extent of compatibility is to compare the values of  $\chi_{12}$  and  $(\chi_{12})_{cr}$ , the interaction parameter and the critical interaction parameters between polymers. The interaction parameter between polymers is related to their solubility parameters by equation (4).<sup>11,12</sup>

$$\chi_{12} = \frac{V_r}{RT} (\delta_1 - \delta_2)^2 \quad (4)$$

where  $V_r$  is the molar volume of repeat unit. The critical interaction parameter is given by equation (5).<sup>13</sup>

$$(\chi_{12})_{(cr)} = 1/2 \left( \frac{1}{x_1^{1/2}} + \frac{1}{x_2^{1/2}} \right)^2 \quad (5)$$

$x_1$  and  $x_2$  are the degrees of polymerization of polymers 1 and 2, respectively.

In general, if  $\chi_{12} > (\chi_{12})_{(cr)}$ , then the two polymers should be incompatible. The greater the difference between  $\chi_{12}$  and  $(\chi_{12})_{(cr)}$ , the more incompatible should the polymers be. If  $\chi_{12} \leq (\chi_{12})_{(cr)}$ , then the two polymers may be expected to be compatible. The calculated values of  $\chi_{12}$  and  $(\chi_{12})_{(cr)}$  are given in Table III. Molar volumes of repeat units of both polymers have been used to calculate  $\chi_{12}$ . For the PEG/PVA system, extensive incompatibility may be envisaged.

TABLE III  
Interaction parameters calculated from equations (4) and (5)

System	$\chi_{12}$	$\chi_{12} (cr)$
PEG/PVA	0.818 0.753	0.026
PEG/PVC	$0.076 \times 10^{-2}$ $0.092 \times 10^{-2}$	$2.8 \times 10^{-2}$

Although both of these theoretical methods indicate incompatibility between PEG and PVA, one must realize the limitation of these methods. Equation (3) and (4) contain solubility parameters of polymers. The concept of solubility parameters is usually useful in the case of polymeric systems where specific interactions are negligible. Hydrogen bonds are present in PVA. Therefore, the prediction of incompatibility in PEG/PVA (and compatibility in PEG/PVC as predicted below) by these methods must be confirmed by definitive experimental methods such as dynamic mechanical analysis and differential scanning calorimetry. Rough estimations of compatibility/incompatibility by these methods have also been made for other polymer pairs with specific interactions.<sup>6,14,15</sup>

#### PEG/PVC/Chlorobenzene System

The absolute viscosity of the solution of PEG and PVC in chlorobenzene is plotted as a function of weight percent PVC in Figure 5. The shapes of the plots are distinctly different from those obtained for the PEG/PVA/water system for which we can see elongated S-type curves in Figures 1 and 2. The viscosity values have also been calculated using equation (2) for 2% solution. The dotted line in Figure 5 represents this values against composition. The measured viscosity values of the mixture for this system also deviate negatively from the additive values.

The plot in Figure 5 for 2% polymer is linear up to about 60% of PVC. For a higher concentrated solution (8%), the plot is linear only about 10% of PVC.

The heat of mixing,  $\Delta H_m$  of the PEG/PVC system has also been calculated using equation (3) and plotted against the composition in Figure 6. It may

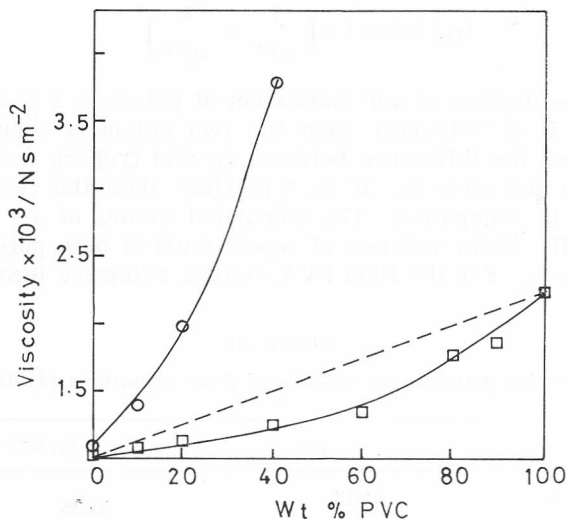


Figure 5. Absolute viscosity of PEG — PVC mixture in chlorobenzene *versus* weight percent of PVC;  $\square$  2% polymer mixture,  $\circ$  8% polymer mixture and — data calculated from equation (2).

be seen that all  $\Delta H_m$  values are below the upper limit  $42 \times 10^{-3} \text{ J mol}^{-1}$  indicating compatibility between PEG and PVC in all proportions. The maximum points of the curves are not, however, independent of the choice of polymer as component 1. The  $\chi_{12}$  values are lower than the  $(\chi_{12})_{(cr)}$  (Table III) for this system, also predicting compatibility. The nearly equal solubility parameters of PEG and PVC (Table II) may also suggest compatibility between them. It has been suggested<sup>16</sup> that PVC is a weak proton donor and, therefore, PVC is capable of forming polycomplexes with the oxygen atom of PEG through hydrogen bonds. At a higher concentration (*e. g.* 8% solution), this

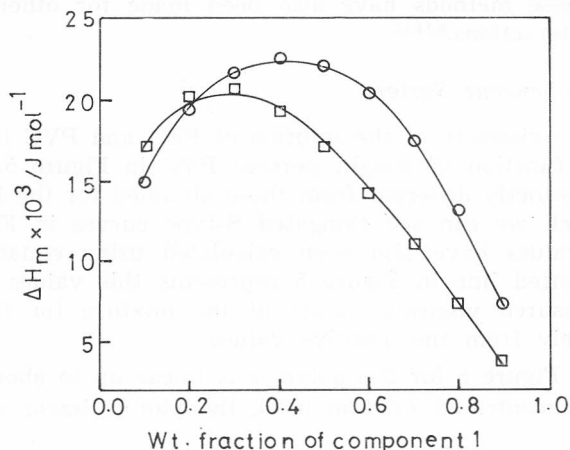


Figure 6. Heat of mixing,  $\Delta H_m$  (equation 3) of PEG and PVC *versus* weight fraction of component 1;  $\circ$  PVC component 1 and  $\square$  PEG component 1.



capacity of forming hydrogen bonds may also result in association of PVC macromolecules<sup>17</sup> causing a sharp increase in viscosity.

Thus, it follows from the presented viscometric data that poly(vinyl alcohol) and poly(vinyl chloride) macromolecules tend to associate at higher concentrations in water and chlorobenzene, respectively. Poly(ethylene glycol) does not associate appreciably in water. The incompatibility of poly(ethylene glycol) with poly(vinyl alcohol) in water and its limited compatibility with poly(vinyl chloride) in chlorobenzene may also be predicted from these data and from theoretical calculations.

## REFERENCES

1. A. Tager, *Physical Chemistry of Polymers*, Translated from the Russian by D. Sobolev and N. Bobrov, Moscow, Mir Publishers, 1978, Ch. 17.
2. G. R. Williams and B. Wright, *J. Polym. Sci.* **A3** (1965) 3885.
3. D. Feldman and M. Rusu, *Eur. Polym. J.* **6** (1970) 627.
4. C. Hugelin and A. Dondos, *Makromolek. Chem.* **126** (1969) 206.
5. V. E. Gul, E. A. Penskaya, and V. N. Kuleznev, *Colloid J. USSR* **27** (1965) 283.
6. Y. P. Singh and R. P. Singh, *Eur. Polym. J.* **19** (1983) 535.
7. O. Quadrat, *Makromol. Chem., Rapid Commun.* **1** (1980) 651.
8. C. L. Ogg and W. L. Porter, *Ind. Eng. Chem. Anal. Ed.* **17** (1945) 394.
9. R. C. Weast (Ed.), *Handbook of Chemistry and Physics*, 58th Edn., Ohio, CRC Press Inc., 1977—1978, F-51.
10. B. O. Schneier, *J. Appl. Polym. Sci.* **17** (1973) 3175.
11. J. H. Hildebrand and R. L. Scott, *The Solubility of Non-electrolytes*, 3rd Edn., New York, Dover Publications, 1964.
12. J. H. Hildebrand and R. L. Scott, *Regular Solutions*, New Jersey, Prentice-Hall, Englewood Cliffs, 1962.
13. R. L. Scott, *J. Chem. Phys.* **17** (1949) 279.
14. D. J. Hourston and I. D. Hughes, *Polymer* **19** (1978) 1181.
15. S. P. Mishra and B. L. Deopura, *Polym. Commun.* **26** (1985) 5.
16. P. A. Small, *J. Appl. Chem.* **3** (1953) 71.
17. J. Spěvāček and B. Schneider, *Makromol. Chem.* **176** (1975) 3409.

## SAŽETAK

**Studij viskoznosti poli(etilen-glikola), poli(vinil-alkohola) i poli(vinil-klorida) i njihovih smjesa u vodi i klorbenzenu**

H. U. Rashid

Mjerena je apsolutna viskoznost polurazrijeđenih otopina poli(etilen-glikola) i poli(vinil-alkohola) i njihovih smjesa u vodi, te poli(etilen-glikola) i poli(vinil-klorida) i njihovih smjesa u klorbenzenu pri 30 °C. Viskoznost poli(vinil-alkohola) i poli(vinil-klorida) naglo raste s koncentracijom. Ovisnost viskoznosti polimernih smjesa o sastavu odstupa od linearnosti. Također je proučavan i utjecaj ukupnog sadržaja polimera na viskoznost smjesa. Rezultati su razmatrani u smislu asocijacije makromolekula iste vrste i kompatibilnosti između makromolekula nejednakih vrsta. Dane su i teorijske pretpostavke o kompatibilnosti i nekompatibilnosti. Proizlazi da se molekule poli(vinil-alkohola) i poli(vinil-klorida) asociiraju pri višim koncentracijama, te da je poli(etilen-glikol) nekompatibilan s poli(vinil-alkoholom), a kompatibilan s poli(vinil-kloridom) u vodi i klorbenzenu.