DILUTE-SOLUTION VISCOSIMETRY AND SOLUTION PROPERTIES OF COLLOIDAL POLYMERS

ESTUDIO POR VISCOSIMETRIA EN SOLUCION DILUIDA Y PROPIEDADES EN SOLUCION DE POLIMEROS COLOIDALES

J.I. Amalvy[1]

SUMMARY

The intrinsic viscosities of a terpolymer of methyl methacrylate, ethyl acrylate and methacrylic acid, prepared by semicontinuous emulsion polymerization (latex) were measured in acetone and THF at different temperatures. Data were analyzed with the aid of the equations of Huggins, Kraemer, Martin, Schulz-Blaschke and an equation recently suggested by Rao. Relationships between different parameters were also considered. The effects of low-molecular weight and water-soluble compounds on the intrinsic viscosities were observed for uncleaned samples of latex as compared to samples purified, by single precipitation or by dissolution and precipitation from THF. Solvent powers and effects of degree of purification and temperature on viscosity are discussed. Polymer-solvents interactions are discussed in terms of the acceptor / donor properties of the solvents.

It is concluded that purification of functionalized latices can lead to modifications of the original systems, through the elimination of different polymer chains.

Keywords: *DSV; solution properties; colloidal polymers; latices.*

INTRODUCTION

In latex synthesis by emulsion polymerization, the molecular weight (M) of the colloid polymer reaches relatively high values. Several methods for determination of molecular weight are avaliable, such as GPC, osmometry or dilute solution viscosimetry (DSV). DSV is based on the measurements of the increase in viscosity of a dilute polymer solution and allows determination of the intrinsic viscosity ability of a polymer to increase the viscosity of a particular solvent at a given temperature. This quantity provides a wealth of information relating to the size of the polymer molecule in solution, including the effects of polymer structure, molecular shape and degree of polymerization and polymer-solvent interactions upon chain dimensions. There are several equations that relate the intrinsic viscosity and other parameters reflecting solution properties, and relations between these parameters of these equations have also been suggested.

[1] Miembro de la Carrera del Investigador de la CIC

DSV also provides information on polymer - solvent interaction, which is of importance for systems used in products like paints and coatings. Understanding the interactions between polymers and solvents is therefore of practical importance.

If absolute molecular weight determination is not possible, the intrinsic viscosity determination can be used as a relative method to characterize polymers.

Berger [1] in his determination of molecular weight by viscosimetry, found that the presence of additives does not susbstantially affect the intrinsic viscosity of polymer solutions. However, Anzur et al. [2] studied the solution properties of acrylic emulsion copolymers and concluded that determination of Mw by viscosity measurement (as well as GPC) of uncleaned emulsion polymer samples is questionable due to the influence of residual emulsifier.

Most studies of DSV have been performed with homopolymers and the presence of a second or third type of repeat unit causes the dilute solution behaviour of copolymers and terpolymers to be more complex than in the homopolymer case. The most obvious factors which affect the intrinsic viscosities of co- or terpolymers are composition, composition distribution and the sequence length distributions.

In most practical applications of latices, a few percent of an acidic monomer (methacrylic acid for example) are commonly added during the synthesis to improve the freeze-thaw and mechanical stability of the final product. In functionalized latices the way and timing of functional monomer addition could have an important effect in the latex structure. Even in non-functionalized latices the surface of particles acquire carboxylic groups due to the hydrolysis of the ester linkage during the polymerization and storage [3]. This part of the latex particle could be of a hydrophilic nature and even water-soluble. The solution properties of cleaned samples should be different when compared with uncleaned samples, due to the elimination of the water-soluble fraction during the purification process.

The present study deals with the solution properties of a terpolymeric system composed of methyl methacrylate, ethyl acrylate and methacrylic acid in two common solvents used in DSV, acetone and tetrahydrofurane (THF), with and without purification and at different temperatures. In this work we also test the available relations between different parameters relating to polymer solution properties.

EXPERIMENTAL

The latex was prepared by a semicontinuous emulsion polymerization method with a variable monomer feed rate. Details of synthesis can be found in a previous paper [4].

The solvents for viscosity of polymer solutions used in this work were acetone and tetrahydrofuran (THF) of analytical grade.

Samples of uncleaned latex were prepared by air drying, and dissolving in the solvent. Cleaned samples were prepared by coagulation from the latex, by adding isopropanol drop-by-drop to the emulsion and shaking. The polymer was then filtered, washed exhaustively with water and dried to constant weight. Further purifications were carried out by solubilizing the polymer in THF, precipitating with water and drying it.

The viscosities of polymer solutions were determined in most cases at 15, 20, 25, 30 and 35 °C, by means of a commercial, calibrated Ubbelöhde-type viscometer. Triplicate measurements usually agreed within 0.3 seconds. Initial polymer concentrations were between 0.20-0.45 g of polymer per 100 ml of solution, prepared at 20 °C. The concentration at the other temperatures were calculated taking into account the density of the solvents at each temperature. Calibration of the viscometer was performed using flow times measured and reported viscosity of chloroform, acetone, THF and toluene at different temperatures.

For the calculations, the following relation was used:

$$\frac{\eta}{\eta_o} = \frac{\left(A \cdot t - \dfrac{B}{t^2}\right)}{\left(A \cdot t_o - \dfrac{B}{t_o^2}\right)} \tag{1}$$

where η and η_o are the viscosities and t and t_o the flow times of the solution and pure solvent respectively, and A and B are the constants of the viscometer.

In some cases the intrinsic viscosity were close to or even higher than 4 dL/g and a correction for non-Newtonian behaviour should have been applied [5], but for the purpose of this work this was not performed.

RESULTS AND DISCUSSION

Data from the polymer solutions were analyzed using least-squares analysis with the following mathematical equations:

- relationships for very dilute solutions:

Huggins

$$\left(\frac{\eta_{sp}}{C}\right) = [\eta] + K_H \cdot [\eta]^2 \cdot C \tag{2}$$

Kraemer

$$\left(\frac{\ln \eta_r}{C}\right) = [\eta] + K_K \cdot [\eta]^2 \cdot C \tag{3}$$

- relationships over a large concentration range:

Martin

$$\ln\left(\frac{\eta_{sp}}{C}\right) = \ln[\eta] + K_M \cdot [\eta] \cdot C \tag{4}$$

Schulz-Blaschke (SB)

$$\left(\frac{\eta_{sp}}{C}\right) = [\eta] + K_\eta \cdot [\eta] \cdot \eta_{sp} \tag{5}$$

- relationship for moderate to concentrated solution

Rao [6]

$$\left(\frac{1}{2(\eta_r^{1/2} - 1)}\right) = \left[\frac{1}{[\eta] \cdot C}\right] - \left[\frac{a-1}{2.5}\right] \tag{6}$$

where C is the concentration (grams of polymer per 100 ml), $\eta_r = \eta/\eta_o$ is the reduced viscosity, $\eta_{sp} = (\eta - \eta_o)/\eta_o$ is the specific viscosity, $[\eta]$ the intrinsic viscosity, K_i are coefficients and $a = 1/\phi_m$, where ϕ_m is the maximum volume fraction to which particles of polymers can pack in the solution.

For the determination of constants using Huggins' equation, an improved method suggested by Nagy et al. [7] was used. This method gives intrinsic viscosities and Huggins constants with lower standard deviations.

Whether a certain high molecular weight polymer solution falls into dilute, semi-dilute or concentrated regimes depends not only on its actual concentration, but also on temperatures, polymer type and solvent properties and only the appropiate equations for those conditions will describe the polymer-solvent behaviour correctly: the same polymer in different solvents and at different temperatures can be described by different equations. For these reasons it is useful to consider several equations and choose the most appropiate one.

The best fit results were obtained by using the equations of Huggins with the method of Nagy et al. [7] and Rao, with C and Schulz-Blaschke with η_{sp} as independent variable. The intrinsic viscosities determined by Rao's equation were comparable with those obtained by the Martin equation, both being able to describe the viscosity of polymer solutions over a large concentration range. In particular, the equation suggested by Rao[6] takes into account the solvent-polymer interaction effects. The $[\eta]$ values determined by the equation of Schulz-Blaschke were the highest.

Typical plots of the above mentioned equations are shown in **Fig. 1**. The method suggested by Nagy et al. [7] is also included, where the parameter α is $C_m + C_M$, being C_m and C_M the minimum and maximun concentrations.

Intrinsic viscosity coefficients and their temperature dependence

In a good solvent where the energy of interaction between a polymer segment and a solvent molecule adjacent to it exceeds the mean of the energies of interaction between the polymer-polymer and solvent-solvent pairs, the polymer will tend to expand further so as to reduce the number of contacts between pairs of polymer elements. Therefore, the polymer molecule will be in a very extended form in a very good solvent. The value of the intrinsic viscosity will be high in a good solvent, as the molecule is very extended. In a poor solvent, on the other hand, where the energy of interaction is unfavourable, a small configuration in which polymer-polymer contacts occur more frequently will be favoured, and the polymer will tend to occupy a tightly coiled form, resulting in a lowering of the intrinsic viscosity.
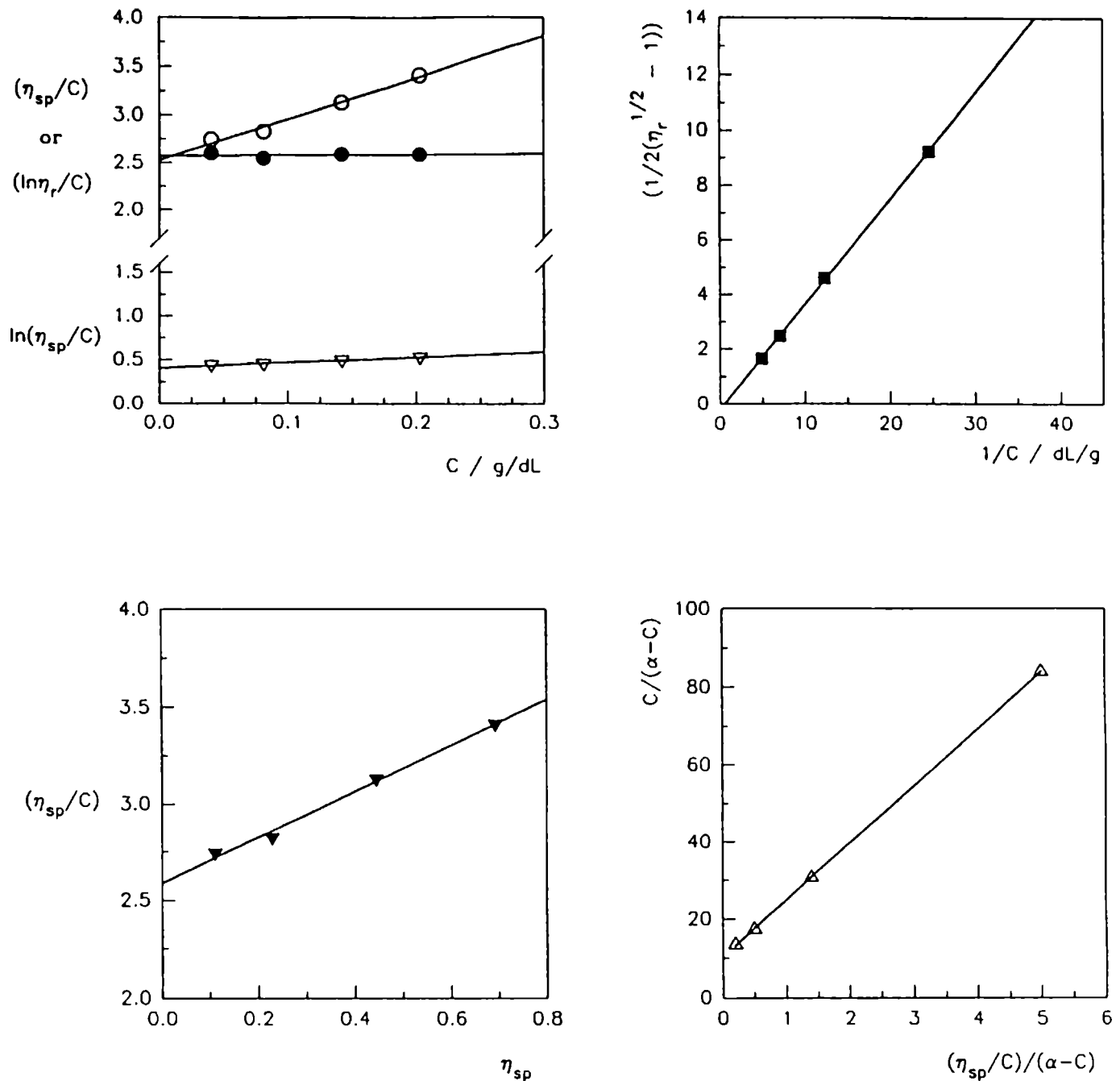
Fig. 1.- Huggins (O), Kraemers (●), Martin (∇), Schulz-Blaschke (◆) and Rao's (▼) plots for isopropanol precipitate samples in acetone at 20 °C. The plot method by Nagy et al. [7] is also shown (Δ).

In good solvents the plots given by equations 2 and 3 are linear and K_H is about 0.34 to 0.40 and in poor solvents the value of K_H increases [8]. For most random chain polymer systems $K_H \leq 0.5$, but if there is association of macromolecules in the solution, an effective Huggins coefficient $K_{eff.} > 0.5$ is obtained [9].

The intrinsic viscosity is given as follows [10]:

$$[\eta] = K \cdot M^{\frac{1}{2}} \cdot \alpha^3 \tag{7}$$

where K is a constant independent of the polymer molecular weight M, and of the solvent and α is the isotropic swelling factor given by:

$$\left(\overline{r^2}\right)^{\frac{1}{2}} = \alpha\left(\overline{r_0^2}\right)^{\frac{1}{2}} \qquad (8)$$

and $\left(\overline{r^2}\right)^{\frac{1}{2}}$ is the root-mean-square end to end distance of the polymer chain and $\left(\overline{r_0^2}\right)^{\frac{1}{2}}$ indicates unperturbed conditions.

The root-mean-square end to end distance is related to the molecular expansion and the greater the value, the better the solvent and the "swelling" of the molecule [10]. The intrinsic viscosity is a measure of the shape and size of the isolated macromolecule and a measure of the solvent power and K_H is a measure of the hydrodynamic interaction.

A change of temperature affects [η] and the coefficient values [10], due to modifications in the polymer-polymer and polymer-solvents interactions. Thus the interpretation of different temperature data provides a useful way to obtain information about the interactions particularly.

Although the temperature dependence on [η] is not very well-defined, it is possible to conclude from the effect of this variable on the coefficients (in particular K_H) how the solubilizing power changes.

A maximum in the [η] - T relation seems to be a general phenomenon for polymer solutions [11-12]. Kawai and Ueyama [11] found this behavior for PMMA in acetone and they concluded that there is a T_m for a given polymer-solvent combination and the polymer molecules take on the most expanded conformation. T_m is affected by the chain flexibility and its measurement will provide a characteristic parameter of the polymer. Radic and Gargallo [12] found that intrinsic viscosities of several fractions of poly(4-ter-butylcyclohexyl methacrylate) in cyclohexane present a maximum at $T_m \approx 25\,°C$ and fractions of poly(pentachlorophenyl methacrylate) in o-dichlorobenzene at $T_m \approx 30\,°C$. They concluded that this behaviour should be observed generally for polymer solutions.

Fig. 2a shows the dependence of the intrinsic viscosity with temperature for the evaporated latex (uncleaned sample) in acetone and THF.

For acetone, the intrinsic viscosity has a maximum value at about 20 °C, which is in agreement with the observations of Kawai and Ueyama [11]. The solution properties are described correctly by all equations, but in particular by those of Kraemer and Schulz-Blaschke.

In THF, it can be seen that no maximum is observed, in the range of temperature covered here, and the intrinsic viscosity decreases slightly with temperature. This behaviour is characteristic of solvents with low theta temperature [10].

Except at 20 °C, where the K_H values are about 0.4 and K_K about 0.13, the values of K_H are higher than 0.5, and the plots of equations 2 and 3, become slightly curved indicating the contribution of higher terms in these equations [13] or association. Equation 6 describes

the behaviour better indicating that in this case the system is in the moderatly to concentrated regime.

When the polymer samples obtained by coagulation of latex with isopropanol were tested, the dependence of the intrinsic viscosities with temperature were those shown in **Fig. 1b.**

In THF, the $[\eta]$ values are the highest and there is a minimum at 20 °C. The appearance of a minimum in the $[\eta]$ vs. T curve is rather peculiar and was also reported by Vasudevan and Santappa [14]. It may be noted that in this region the value of the Huggins constant decreased with decreasing temperature and at 20 °C had the maximum value. Equation 6 is the best to describe the solution properties. For acetone the behaviour is different and the $[\eta]$ values decrease slightly with temperature. In this case, equations 5 and 6 are able to describe the behaviour. Equations 2 and 3 show a slightly curve up at $\eta_{sp} \sim 0.7$, indicating again a contribution of higher terms.

In THF, the Huggins coefficients change between 0.23 and 0.38 and the Kraemer coefficients between 0.11 and 0.20, indicating that THF is a good solvent for this polymer. The K_H value for acetone rises with temperature and varies between 0.56 and 0.81, therefore the quality of solvent decreases with temperature and the polymer-polymer interaction is higher than the polymer-solvent interaction.

When the terpolymer was purified by solubilization in THF and precipitation with water, the behaviour of the intrinsic viscosities with temperature, are those in **Fig. 1c.** In THF the intrinsic viscosity decreases slightly with temperature and the K_H values range between 0.32 and 0.42 and K_K between 0.11 - 0.16. These values indicate that for this case THF is a good solvent. For acetone the intrinsic viscosity increases with temperature and the Huggins coefficients decrease. The higher temperature improves the solvent quality.

When an additional purification of the sample is performed, the intrinsic viscosity in THF at 20 °C rises to 4.45 dL/g, and the coefficients are $K_H = 0.37$ and $K_K = 0.14$.

The removal of low molecular weight compounds and water soluble fractions resulted in changes of the intrinsic viscosity values, and in the solution properties behaviour. In acetone, the change in the intrinsic viscosity is smaller compared with THF. In the first case, the purifications cause a decrease and in the second case, the values increase notably.

In the purification process, as the low molecular weight portion is eliminated, the average value of M should increase. According to eq. 7, the α value should decrease by a similar amount, so that $[\eta]$ did not change very much. In THF, the intrinsic viscosity value increases in the purified samples Therefore acetone is a poorer solvent than THF.

The $[\eta]$ values of the samples without purification in acetone and THF, are rather similar, but when the terpolymer was purified, the higher $[\eta]$ value corresponds to THF, which indicates that the polymer-solvent interaction is the highest in this case, and therefore it is a better solvent.

In the evaporated sample case, as acetone is an amphoteric molecule, both types of polymers are able to interact with the solvent and the [η] value is the highest.

In THF as a predominant electron-donor solvent, the water soluble component will not interact efficiently. The high value of $K_H \approx 0.9$ could indicate some association of the macromolecules.

When comparing the linearity of experimental data of equations 2 - 6, it was found that in the evaporated and isopropanol precipitated samples, some departure from linearity is observed, especially in the low concentration region, due to the fact that these equations are valid for non-ionic polymers and not for the water-soluble components.

In samples with one or two purification cycles the linearity of those equations is notably improved, due perhaps to the elimination of the ionic component.

The observations outlined above are in agreement with the nature of the terpolymer. The latex was prepared by a semicontinuous method with the MAA monomer added in the second part of the feed. The relatively concentrated addition of MAA results in the formation of water-soluble polymer blocks, heavily enriched with acid and of a hydrophilic nature. Purifications of terpolymer by dissolving in THF and precipitation from water, left a less enriched acidic polymer. When solutions of these fractions (with and without purification) are prepared in THF and acetone, different situations occur, due to the different acid-base characteristics of solvents; THF is a predominant basic (proton aceptor) solvent and acetone acts both as acidic (proton donor) and basic (proton aceptor) i.e. an amphoteric solvent.

When the polymer is further purified with THF, the [η] value increases again and this considerable increment should correspond to the elimination of the additional low molecular weight components, leaving only the highest molecular weight fraction.

The different behaviour of latex samples with and without purifications decribed above indicates the inhomogenity of the original latex sample, due to the presence of water-soluble components, and of SDS in the unpurified samples and to a lesser extent in singly precipitated samples. The presence of these polymers and surfactant should be treated as a mixture of components. In our case, the non-linear trend of equations 2 and 3 observed in some cases, does not seem to follow the ideal condition that each component contributes to the η of the mixture. A further contribution due to some interaction should be taken into account.

Relation between K_H and [η]

Stern [15] proposed an empirical relation for the Huggins' constant and the intrinsic viscosities in the form:

$$K_H = D + E \cdot [\eta]^{-2} \qquad (9)$$

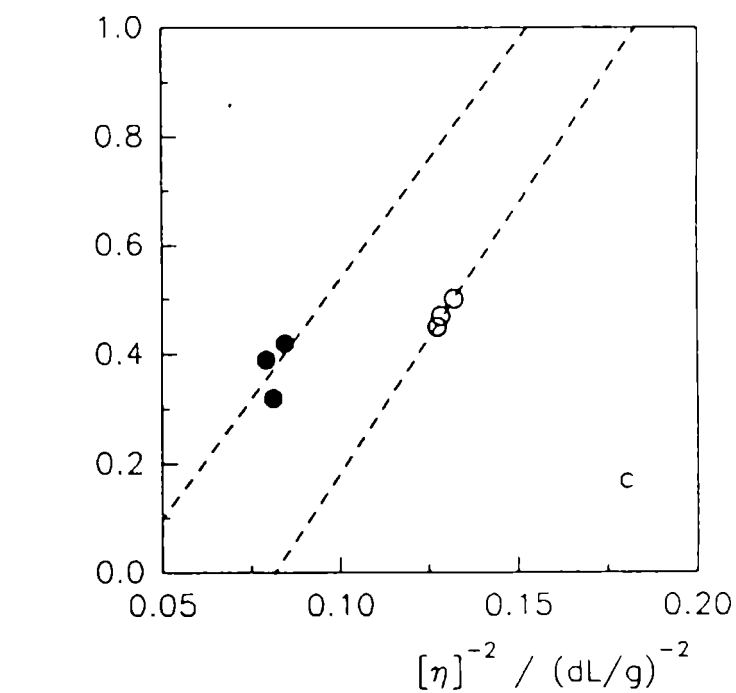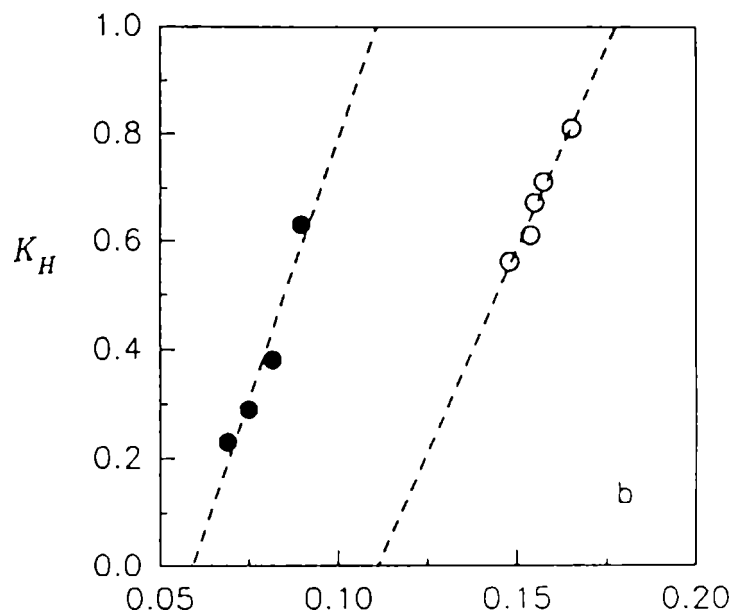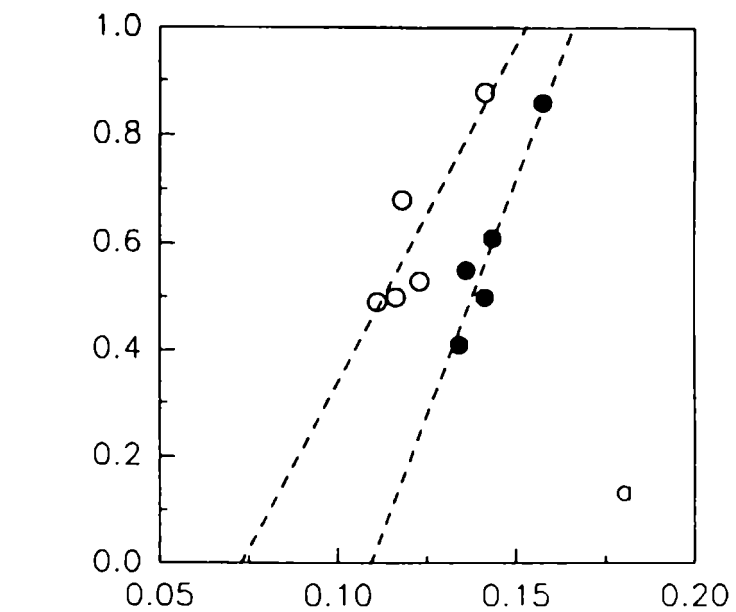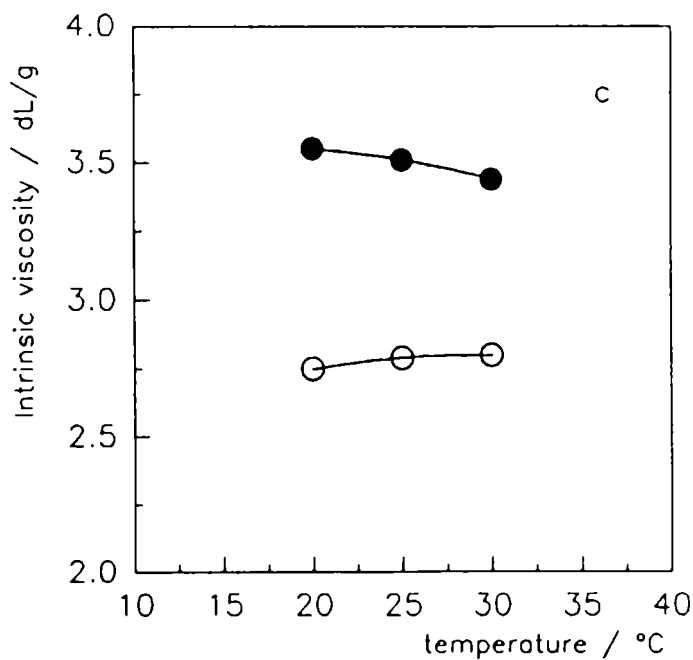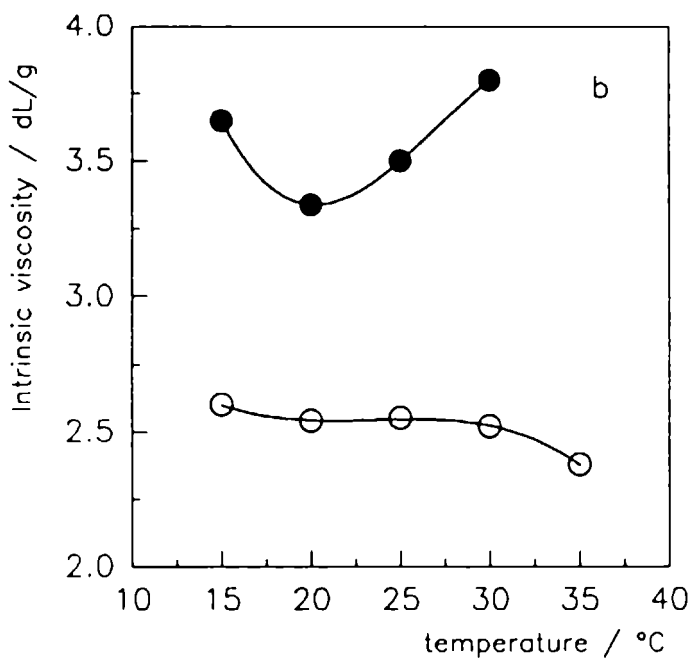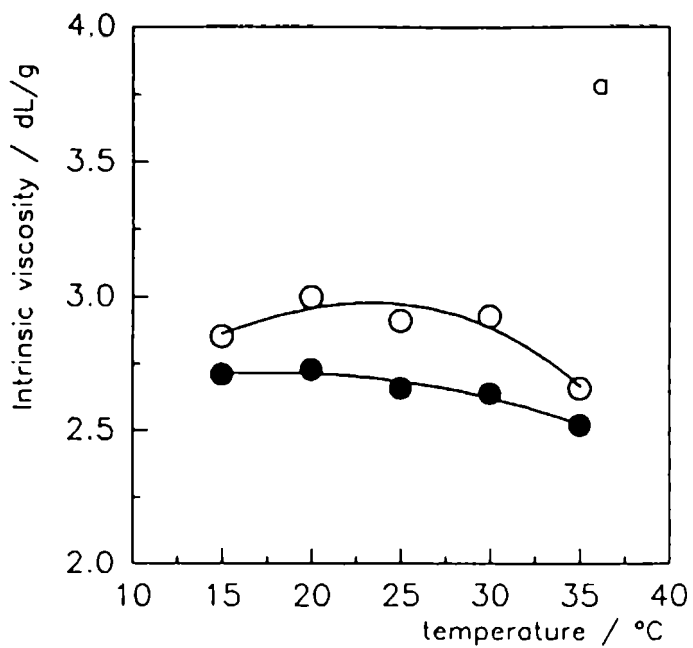where D and E are empirical constants independent of molecular weight.

Fig. 2.- Dependence of intrinsic viscosity on temperature for solutions of uncleaned samples (a), isopropanol precipitated fraction (b) and samples with one purification cycle (c); in acetone (open circles) and THF (closed circles).

Fig.3.- Relation between K_H and [η]. See Figure 2 for explanation.

The data available from this work were used to test this equation. **Fig. 3** shows the relation for the systems studied. From this figure it was concluded that the relation is suitable in our case.

Relation between ϕ_m and K_H

Rao [6] found that the ϕ_m value of equation 6 is always less than unity and that a polymer-solvent system having lower K_H tends to give higher values of ϕ_m. For those polymer-solvent systems having $K_H = 0.25$ the value of ϕ_m should be near to or equal to unity. As this is possible only in dilute solutions and good solvents, Rao concluded that ϕ_m can be taken as a good measure of solvent quality.

Fig. 4 shows the relation of ϕ_m and K_H for the polymer-solutions systems studied in this work. A good negative correlation can be seen between the two variables, supporting the observations of Rao.
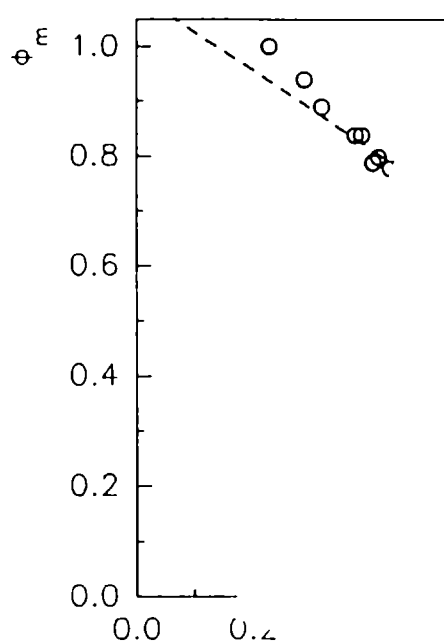

Fig. 4.- Relation between ϕ_m and K_H.

By comparing the values of the ϕ_m parameters it appears that for the uncleaned polymer latex, acetone and THF at 20 °C with $\phi_m \sim 0.8$ are good solvents. When latex was precipitated with isopropanol, THF seemed to be the best solvent. With ϕ_m values in THF ranging between 0.8 - 0.9 and those in acetone ca. 0.75, THF is the best solvent for samples purified by solubilizing the polymer in THF and precipitated with water.

CONCLUSIONS

Different fractions of an acrylic copolymer prepared by a semicontinuous emulsion polymerization method with a variable monomer feed and functionalized with an acidic acrylic monomer, were studied by solution viscosimetry. Results were interpreted using different equations for cases with different degrees of purification.

Different behaviours were observed in each case and no general rules can be given to choose the best conditions (solvent and temperatures) to perform a study of solution properties.

From the above results, it can be concluded that care must be taken when dilute solution viscometry or another technique depending on the polymer-solvent interactions is used to characterize functionalized latex samples. The most appropiate model for describing solution properties of this type of latices seems to be that for polymer mixtures with interactions.

It should be taken into account that purification of functionalized latices can lead to modifications of the original systems, through the elimination of different polymer chains, modified by the presence of functional monomers added during the synthesis.

A detailed study of solution properties including their variations with temperature, together with the knowledge of the synthesis characteristics of samples, should give the best method and working conditions.

Further study with similar compounds might help to clarify the various polymer properties differences, arising from the different synthesis procedures.

Acknowledgements

REFERENCES

[1] Berger H.W.- **J. Paint Technol,** **39,** 310 (1967).

[2] Anzur I., Osredkar U.,Ukmar I. and Vizovisek I.- **Makromol. Chem. Suppl,** **10/11,** 311 (1985).

[3] Fitch, R.M. Gajria, C and Tarcha, P.J.- **J. Colloid Interface Sci.,** **71,** 107 (1979).

[4] Amalvy, J.I.- **J. Appl. Polym. Sci.,** **59,** 339 (1996).

[5] Lovell P.A.- In "Comprehensive Polymer Science", Allen G. and Bevington J.C. (eds.), Pergamon Press, Oxford, 1989, Ch. 1 Vol. 9, page 179.

[6] Rao, M.V.S.- **Polymer, 34,** 592 (1993).

[7] Nagy, T.T., Kelen, T. and Tüdos, F.- **Polymer, 19,** 1360 (1978).

[8] Fox T.G. and Flory P.J.- **J. Am. Chem. Soc**, **73**, 1909 (1951).

[9] Wolff C., Silberberg A., Priel Z., Layec-Raphalen M.N.- **Polymer**, **20**, 281 (1979).

[10] Flory, P.J.- *Principles of Polymer Chemistry*, Cornell University, Press, Ithaca, NY (1953).

[11] Kawai, T. and Ueyama, T.- **J. Appl. Polym. Sci**, **8**, 227 (1960).

[12] Radic, D. and Gargallo, L.- **Polymer**, **22**, 410 (1981).

[13] Berry G.C.- **J. Chem. Phys**, **46**, 1338 (1967).

[14] Vasudevan P. and Santappa M.- **Makromol. Chem**, **137**, 261 (1970).

[15] Stern M.D.- Paper presented at the 142nd National Meeting of the American Chemical Society, Atlantic City, N.J. September 1962, see also Stobayashi H. **Makromol. Chem.**, **73**, 235 (1964).