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Determination of the Molecular Weight of Linear Polymers From Viscosity Measurements Carried out in the Solvent Mixtures

by

E. PULAT And M. TALU

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Faculté des Sciences de l'Université d'Ankara
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Determination of the Molecular Weight of Linear Polymers From Viscosity Measurement Carried out in the Solvent Mixtures

E. PULAT And M. TALU.

Department of Physical Chemistry, University of Ankara, Turkey.

(*Received................*)

In this work polyvinyl acetate prepared by B. D. H Laboratory ·Chemicals Division has been used. The intirinsic viscosities have been determined in acetone-benzene mixtures of various percentages. By using these intrinsic viscosity values the viscosity average molecular weights of the same polyvinyl acetate sample have been calculated from this relationship:

$$[\eta] = K' M^{\alpha'} \qquad (1)$$

In this equation the values of K and α' are calculated from the following equations:

$$K' = K_1 - K_1 (1-f_1)^3 + K_2 (1-f_1)^3 \quad (2)$$

$$\alpha' = \alpha_1 f_1 + \alpha_2 (1-f_1) \qquad (3)$$

Where f_1 stands for the volume fraction of one solvent in the solution. K_1, α_1 and K_2, α_2 are constants for a given polymer-solvent system and temperature.

The values of K_1, α_1 and K_2, α_2 are given in the literatures [1, 2] for polyvinyl acetate-benzene and polyvinyl acetate-acetone systems.

The values of the molecular weight abtained by this method are satisfactorily good within experimental errors. The benzene-acetone mixture is better than pure benzene and acetone as solvent for the polyvinyl acetate. Especially the solution containing 20-40 % benzene is the most effective solvent for this polymer. Here polar and nonpolar parts of the polymer are respectively affected by acetone and benzene.

INTRODUCTION

It is known that the relationship

$$[\eta] = K M^{\alpha}$$

is used to calculate the molecular weight of the linear polymers from viscosity measurements.

In this relationship K and α are constants for a given polymer-solvent system and temparature at which intrinsic viscosity is determined.

In this work we have tried to apply the intrinsic viscosity-molecular weight relationship, which is so far used for only one solvent-polymer system, to the solvent mixtures-polymer systems to calculate the molecular weight of the linear polymers. For the purpose of investigation we have used acetone- benzene mixtures in different concentrations.

As it will be seen from our experimental results that the intrinsic viscosity-molecular weight relationship could also be used to calculate the molecular weight of the linear polymer samples from viscosity mearurements carried out in the solvent mixtures.

EXPERIMENTAL

Diluted polymer solutions and pure solvents were filtered to be sure that they are dust free. All the viscosity measurements were carried out in a thermostat whose temperature was kept constant at 30 ∓ 0.5° C. Ubbelohde viscometer was used; this viscometer is particularly convenient since the effective pressure head maintaining the flow is independent of the amount of liquid in the large bulb and hence of dilution.

The experimental results are tabulated in the following table.

TABLE I

The variation of the Intirinsic Viscosity with percentage of benzene in the acetone-benzene mixture.

Benzene % (By volume)	$[\eta]$ (dl/g)
100	0.270
90	0.294
80	0.312
40	0.360
20	0.362
0	0.295

Two points from this table deserve comment. Firstly, the solvation power of acetone is better than those of benzene for polyvinyl acetate.

Secondly, the highest value of $[\eta]$ corresponds to that mixture ranging between 20 % and 40 %. Therefore the best solvent of the polyvinyl acetate is the acetone-benzene mixture containing 40-20 % of benzene.

The viscosity average molecular weights of the same polyvinyl acetate sample calculated from the equation (1) are shown in Table II.

TABLE II

Benzene % (by volume)	α'	K'(dl/g)	$\bar{M}_v$
100	0.65 [1]	2.2×10^{-4} [1]	56500
90	0.66	2.19×10^{-4}	54900
80	0.67	2.15×10^{-4}	52500
40	0.70	1.73×10^{-4}	55000
20	0.72	1.37×10^{-4}	56500
0	0.74 [2]	0.9×10^{-4} [2]	56300

As it will be seen from Table II, the values of the viscsity average molecular weight calculated from solvent mixtures for the same polyvinyl acetate sample are in agreement with that obtained in pure solvents.

ÖZET

Bu çalışmada "B.D.H. Laboratory Chemicals Division" tarafından hazırlanan polivinil asetat kullanılmıştır. Farklı yüzdelerde aseton-benzen karışımında polimerin intirinsik viskoziteleri tayin edilmiş ve bu intirinsik viskoziteler kullanılarak aynı polivinil asetat nümunesi için

$$[\eta] = K' M^{\alpha'} \qquad (1)$$

bağıntısından viskozite ortalama molekül ağırlıkları hesaplanmıştır. Yukardaki bağıntıda yer alan K' ve α' sabitlerine ait değerler

$$K' = K_1 - K_1 (1-f_1)^3 + K_2 (1-f_1)^3 \qquad (2)$$

$$\alpha' = \alpha_1 f_1 + \alpha_2 (1-f_1) \qquad (3)$$

bağıntıları kullanılarak bulunmuştur. Bu bağıntılarda f_1 çözeltide çözücülerden birinin hacim kesrini göstermektedir. K_1, α_1 ve K_2, α_2 ise polivinil asetat-benzen ve polivinil asetat-Aseton sistemleri için literatürde [1,2] verilen sabitlerdir.

Her karışım için denel olarak tayin edilen intrinsik viskozite değerleri ile (2) ve (3) bağıntılarından bulunan K′ ve α' sabitleri kullanılarak (1) bağıntısından viskozite ortalama molekül ağırlığı değerleri hesaplanmıştır. Aynı polivinil asetat numunesine ait bulunan viskozite ortalama molekül ağırlığı değerlerinin birbirlerine oldukça yakın çıktıkları görülmüştür.

Bundan başka bu polimer için benzen ve aseton karışımının saf benzen ve asetondan daha iyi çözücü olduğu özellikle % 20–40 benzen bulunduran karışımın çözücü olarak en etkili olduğu da anlaşılmaktadır. Bu iki karışık çözücüden aseton polimerin polar kısmına, benzen ise apolar kısmına etki ederek makro molekülü çözerler.

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