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# The Mathematical and Graphical Interpretation of Solubility Profile-Viscosity Behavior of Poly(MA-*alt*-NVP)

# Poly(MA-alt-NVP) Kopolimerinin Çözünürlük Profili-Vizkozite Davranışına Grafiksel ve Matematiksel Olarak Açıklık Getirilmesi

Research Article

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## ABSTRACT

Alternating copolymer of maleic anhydride (MA) with N-vinyl-2-pyrrolidone (NVP) is synthesized by free radical polymerization reaction. Solubility of the copolymer in certain solvents is investigated by different algorithmic approaches such as Van Krevelen Hoftyzer (VKH), Hoy and Askadskii. Spectral characterization of that copolymer is achieved by FTIR, $^{1}$H, $^{13}$C NMR spectroscopic methods whereas the polymer hydrodynamic behavior of the copolymer is investigated by viscometric method for comparison purpose with that obtained from the solubility profile through algorithmic calculations.

**Key Words**
Poly(MA-alt-NVP), Solubility parameter, Viscometry, FTIR.

## ÖZET

Maleik anhidritin (MA) N-vinil-2-pirolidon (NVP) ile ardışık kopolimeri serbest radikal kopolimerleşme reaksiyonu ile sentezlendi. Kopolimerin çeşitli çözücülerdeki çözünürlüğü, Van Krevelen Hoftyzer (VKH), Hoy ve Askadskii gibi değişik algoritmik yaklaşımlarla irdelendi. Kopolimerin spektral karakterizasyonu, FTIR, $^{1}$H, $^{13}$C NMR gibi spektroskopik yöntemlerle gerçekleştirilirken, polimer hidrodinamik davranışı ise algoritmik hesaplamalar yoluyla elde edilen çözünürlük profili verilerinin vizkometrik metod kullanılarak elde edilen verilerle karşılaştırılmasıyla araştırıldı.

**Anahtar Kelimeler**
Poli(MA-ard-NVP), Çözünürlük parametresi, Vizkometri, FTIR.

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## INTRODUCTION

A versatile polymer soluble in both water and organic solvents, poly(N-vinyl-2-pyrrolidone) (PVP) has been the focus of numerous applications including additives, cosmetics, coatings and biomedicines [1]. Homo- and copolymers of N-vinyl-2-pyrrolidone have been attracting much attention and have been widely investigated for their applications in the medicine and biotechnology [2]. It is frequently used as a comonomer [3-5] mainly because of its amphiphilic character. It contains a highly polar amide group, which confirms its hydrophobic and polar attracting properties, while the methylene and methine groups in the main and side chain confirm the hydrophobic properties.

Alternating copolymers of maleic anhydride can be regarded as preactivated polymers due to the presence of anhydride moieties susceptible to the reaction with the primary amine of a biomolecule [6]. Acrylamide and its derivatives can undergo alternating copolymerization with maleic anhydride under the given conditions reported in literature [7-9]. These copolymers are potentially useful as flocculants, for purification of industrial waste water, as coatings for microcapsule production and for paper dry-strength agents [10]. In a continuing effort to improve the quality of polymer- protein conjugates, it was envisioned using N-vinylpyrrolidone (NVP)-based maleic copolymers because poly(NVP) is known to be quite biocompatible and to improve adhesion [11].

Solubility parameter is one of the key parameters for selecting solvents in industry, characterizing surfaces, predicting solubility and degree of rubber swelling, polymer compatibility, chemical resistance, and permeation rates and for numerous other applications. There is also much interest in utilizing solubility parameter for rationally designing new processes such as the supercritical fluid, the coating, and the drug delivery processes [12-17].

The basic principle lying behind the use of $\delta$ is the oldests rule of solubility-like dissolves like. This rule can, indeed, be a good guide in the study of solubilty as long as we can also define with sufficient precision the degree of likeness in the given system. The enthalpy of mixing, given by,

$$\Delta H_m / V = f_1 f_2 (\delta_1 - \delta_2)^2 \qquad (1)$$

where $\delta_1$ and $\delta_2$ are the solubility parameters, $f_1$ and $f_2$ are the volume fractions of both substances and V is the total volume of the mixture, predicts that $\Delta H_m = 0$ if $\delta_1 = \delta_2$, so that two substances with equal solubility parameters should be mutually soluble due to the negative entropy factor. As the difference between $\delta_1$ and $\delta_2$ increases, the tendency towards dissolution decreases [18]. However, these predictions with the Hildebrand solubility parameters are made with the absence of any specific interactions, especially hydrogen bonds. They also do not account for the effects of morphology (crystallinity) and cross-linking. In addition, there may be (non-ideal) changes with changes in temperature and, in many cases, with changes in concentration.

Division of $\delta$ into its partial components or Hansen solubility parameters leads to the precision in the definition of likeness. Thus liquids with similar $\delta_d$, $\delta_p$, and $\delta_h$ are very likely to be miscible or soluble. The method of Hoftyzer and van Krevelen [19] estimates the individual solubility parameter components from group contributions. Another approach has been proposed by Hoy [20] for the estimation of the solubility parameter and its components. Askadskii [21] has used the total solubility parameter to predict the solubility of polymers in various solvents.

The difference of polymer (P) and solvent (S) solubility parameters are taken as a measure of mixing. In case this difference is small, the idea of mixing probability is widely accepted.

$$\Delta\delta = [(\delta_{d,P} - \delta_{d,S})^2 + (\delta_{p,P} - \delta_{p,S})^2 + (\delta_{h,P} - \delta_{h,S})^2]^{1/2} \qquad (2)$$

The condition of solubility parameter difference being less than 5 is assumed to be the limit of solubility where $\Delta\delta$ is in $(J/cm^3)^{1/2}$ [18].

Synthesis of poly(maleic anhydride- alt-N-vinyl-pyrrolidone) [poly(MA-alt-NVP)] was carried out by radical initiated solution polymerization under the given conditions. The copolymer structure was characterized by using FTIR, $^1$H NMR and $^{13}$C NMR spectrophotometric methods. The $^1$H NMR and

$^{13}C$ NMR chemical shifts of poly(MA-alt-NVP) were assigned and discussed. FTIR spectra of MA/NVP copolymer indicated successful polymerization. Solubility parameters of poly(MA-alt-NVP) were calculated and interactions between different polymer/solvent pairs were empirically investigated on the basis of Hoy, van Krevelen-Hoftyzer (VKH) and Askadskii's approaches. The values obtained from the methods of Hoy and Askadskii are in good agreement with each other. The viscometric method was used to compare the correlation of the results with those obtained from algorithmic calculations.

## EXPERIMENTAL

### Materials

MA monomer (Fluka) was purified by recrystallization from anhydrous benzene and sublimation in vacuum: m.p. 52.8 °C. NVP monomer (Fluka) was purified before use by distillation at reduced pressure. $\alpha,\acute{\alpha}$-azobisisobutyronitrile (AIBN) (Fluka) was twice recrystallized from methanol: m.p. 102.5 °C. Methanol (MeOH), dimethylformamide (DMF), dimethylsulfoxide (DMSO) and water were used as solvent in viscometric studies.

### Copolymerization

The copolymerization of MA with NVP using monomer feed ratio MA:NVP = 50:50 was carried out in benzene at 65 °C with AIBN radical initiator at constant total concentration of monomers under nitrogen atmosphere. Reaction conditions for system: $[M]_{total}$ = 2.78 mol/L, [AIBN] = $6.5\times10^{-3}$ mol/L.

### Measurements

Fourier transform infrared (FTIR) spectra of KBr pellets of the samples prepared in both solvents were taken by Mattson 1000 FTIR spectrophotometer in the 4000-400 $cm^{-1}$ range, where 40 scans were taken at 16 $cm^{-1}$ resolution. The microstructure of the copolymers was investigated by NMR using a Bruker 400 MHz Ultrashield spectrometer. Spectra were recorded in a deuterated DMSO.

Intrinsic viscosities of the copolymer were determined in MeOH, DMF, DMSO, water at 20±0.1 °C by Ubbelohde viscometer. The calculated solubility parameters of the copolymer were obtained from their chemical structures of repeating units by using the explained methods of van Krevelen-Hoftyzer pair, Hoy and Askadskii.

## RESULTS AND DISCUSSION

### Alternating copolymerization

MA was copolymerized with NVP monomer in benzene by free radical polymerization in the presence of AIBN as initiator and in the absence of oxygen at 65 °C. Studies show that the obtained copolymers of MA/VP monomer pair consist of equimolar amounts of the two comonomer units, which are alternatingly arranged along the macromolecular length. Such a copolymer is formed independent of the initial ratio of the comonomers [22]. The dominating tendency toward alternation is due to the charge-transfer complex (CTC) of VP and MA [23, 24], which takes part in the reaction process as an independent monomer. The complex is attached to the growing polymer chain anticipated with respect to the free VP and MA, due to the affinity of CTC, which is greatest toward the growing radical [25].

### Functional group analysis

In this study, FTIR, $^{1}H$ NMR and $^{13}C$ NMR spectroscopic methods were used to confirm the structures of the synthesized copolymer.

The FTIR spectrum of the synthesized alternating copolymer of MA with NVP is characterized by the typical absorption bands for NVP and MA units. As shown Figure 1, the characteristic peaks for the MA/NVP copolymer synthesized in this work are given as; 3429 $cm^{-1}$ ascribes C–N streching, 2976 and 2905 $cm^{-1}$ belongs to characteristic vibration of polymer backbone, 1783 $cm^{-1}$ is assigned to the streching vibration of C=O group in anhydride ring, 1680 $cm^{-1}$ broad streching band for C=O in NVP unit, 1727 $cm^{-1}$ for intramolecular hydrogen bonded C=O of NVP unit to the neighboring hydrogen atom, 1095 $cm^{-1}$ for C–O–C streching band, 935 $cm^{-1}$ belongs to C–C streching of the main chain. The streching band at 1853 $cm^{-1}$ belongs to C=O of unreacted anhydride moities.

In the MA/NVP copolymer, the characteristic peaks belong to NVP unit of the copolymer. Erdemi and Bozkurt [26] reported that in the $^{1}H$ NMR spectrum of poly(vinylpryrrolidone-covinylphosphonic acid) copolymer, the peak at 2.05 ppm is assigned to the –$CH_2$– group protons of VP, the signals at 2.34 and 2.47 ppm are attributed to methylene protons in –$CH_2$-CO– group and the resonance signals of –CH–N– protons are altered to higher chemical shift which are observed at 3.65 and 3.82 ppm due to electronegative effect of nitrogen. Brar and Kumar [27] also reported characteristic peaks for NVP unit (2H, $^2CH_2$ at 2.15-2.30 ppm; 2H, $^3CH_2$ at 1.85-2.05 ppm; 2H $^4CH_2$ at 3.2-3.35 ppm; the β-methylene and methine signals at 1.65-1.80 ppm and 4.10-4.25 ppm, respectively).

The $^1$H NMR spectrum of the MA/NVP copolymer synthesized in this study is represented in Figure 2. As can be seen from Figure 2 the characteristic peaks in the $^1$H NMR spectra of the copolymer of MA with NVP can be identified as: (2) 2H, $CH_2$ of VP unit at 2.1-2.4 ppm; (3) 2H $CH_2$ of VP unit at 1.7-2.0 ppm; (4) 2H, $CH_2$ of VP unit at 3.0-3.4 ppm. The methylene ($CH_2$) resonances of polymer backbone and side chain methylene signals are very broadly overlapped. The β-methylene ($CH_2$) signal and methine (CH) signals of both VP and MA resonate around 0.8-2.4 and 3.8-4.1 ppm, respectively.

The structure of the copolymer was also confirmed by using $^{13}$C NMR analysis. $^{13}$C NMR spectrum of poly(MA-alt-NVP) copolymer is given in Figure 3. The characteristic peaks for this copolymer belong to NVP unit. The carbonyl (C1) carbon signals for NVP resonate around 173.28-177.71 ppm and is assigned for MA (C5, C6) at 167.19 ppm as a single peak. The side chain ring methylene carbon peaks of NVP are recorded around 40.39 ($^4CH_2$), 30.37 ($^2CH_2$), and 18.24 ($^3CH_2$) ppm, respectively. The β-methylene carbon resonates around 40.9-50.5 ppm. The methine carbon (CH) resonances of both NVP and MA unit are assigned around 41.84-44.10 ppm. The methine carbon (CH) resonances and side chain methylene carbon resonance of NVP overlap. The characteristic resonances found in literature for NVP in agreement with the above values are as follows; peaks around 175.44-174.09 ppm for C=O; 40.40, 30.32, and 16.98 ppm for $^4CH_2$, $^2CH_2$ and $^3CH_2$ respectively; at around 34.70-31.41 ppm, methylene resonances of polymer backbone [28, 29].

## Algorithmic Calculations for the

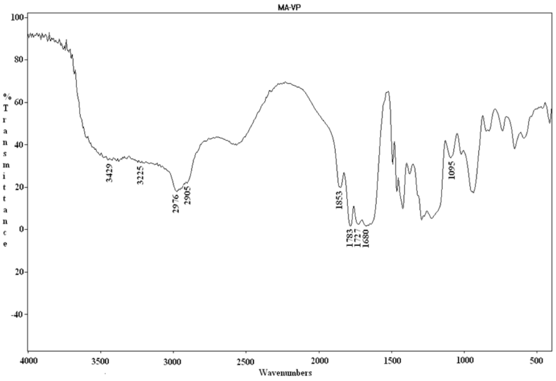

**Figure 1.** FTIR spectrum of poly(MA-alt-NVP)

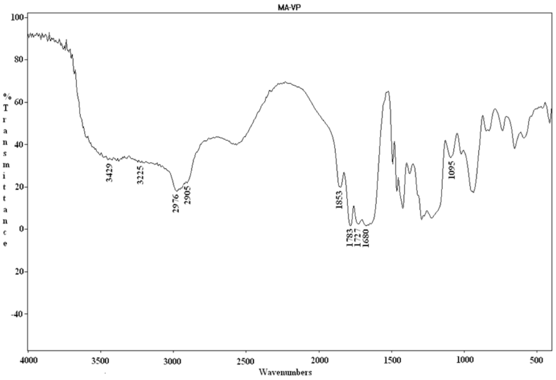

**Figure 2.** $^1$H NMR spectrum of poly(MA-alt-NVP)

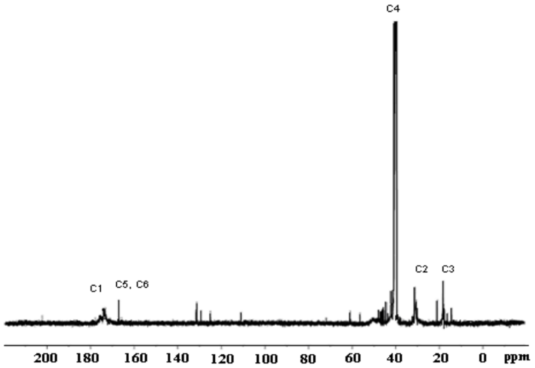

**Figure 3.** $^{13}$C-NMR spectrum of poly(MA-alt-NVP)

## Determination of the Solubility Profile of poly(MA-alt-NVP)

The solubility parameter of poly(MA-alt-NVP) has been calculated with regard to the methods of Van Krevelen-Hoftyzer [19], Hoy [20] and Askadskii [21].

The main advantage of group contribution methods is that it is easy to estimate individual contributions such as dispersive ($\delta_d$), polar ($\delta_p$) and hydrogen bonding ($\delta_h$) of polymers/low molecular weight compounds, through which the overall solubility parameter ($\delta_t$) can be estimated. In many instances, the physical properties of polymers are found to correlate strongly with interconnections between the atoms of a molecule. Over the years the partial solubility parameters were determined for an enormous number of substances and lead to critical compilations as a most valuable source of information for the nature of the substances and their interactions [13-15]. The solubility parameter values were calculated by applying the dispersion and polar components of the molar attraction constant ($F_{di}$ and $F_{pi}$) and contribution of the H-bonding forces to the cohesive energy ($E_{hi}$) of the specific groups present in the structures of the studied copolymers for the method of VKH [18] and molar volume values derived by Fedors [30].

By using the methods of Van Krevelen-Hoftyzer (VKH), Hoy and Askadskii, the solubility parameter ($\delta_t$) and its components ($\delta_p$, $\delta_d$, $\delta_h$) were calculated for poly(MA-alt-NVP) by using the tabulated group contributions and the calculated parameters displayed in Table 1 and 2.

According to VKH approach, total solubility parameter determined with regard to the solubility parameter components of poly(MA-alt-NVP) is found as 41.7. The total solubility parameter respecting solubility parameter components calculated from Hoy's method is found as 25.3. Total solubility parameter value, achieved by Askadskii's method, yields a value of 26.6. As can be seen from the tables, calculated $\delta_t$ value of poly(MA-alt-NVP) indicates that values evaluated according to Askadskii and Hoy methods are much more in agreement with each other.

The solubility behavior of a polymer depends mainly on the structure of the polymer and on the interactions of solvent and polymer. It has been assumed for a long time that the like must dissolve in the like.

The poly(MA-alt-NVP)/solvent systems were employed for determining parameters on the basis of solubility parameter with regard to the theoretical methods of Hoy, VKH and Askadskii. There is a generally accepted rule that for a good solubility, the solubility parameters of both solvent and polymer must be close to each other. Various approaches have been developed for evaluating the solubility parameter values contributing from polymer and solvent pair individually. One of these methods is the calculation of $\Delta\delta$ values. For a good solubility $\Delta\delta$ should be small ($\leq 5$).

The solubility parameter components of the selected ten solvents are reported in literature with respect to Hoy and Hansen [31,32]. $\Delta\delta$ values were calculated by using both the Hoy and Van Krevelen-Hoftyzer systems where Hansen's and Hoy's solubility parameter components are employed for solvents displayed in 3 and 4 for poly(MA-alt-NVP) in the related solvents. According to the above calculations a sequence has been obtained interpreting the solvent power for poly(MA-alt-NVP) determined on the basis of $\Delta\delta$ values given in Table 5.

As can be seen from the tabulated values, water

**Table 1.** Calculated solubility parameter and its components for poly(MA-alt-NVP) according to VKH and Hoy methods

| Polymer | $\delta_p$ | | $\delta_d$ | | $\delta_h$ | | $\delta_t$ | |
|---|---|---|---|---|---|---|---|---|
| | VKH | Hoy | VKH | Hoy | VKH | Hoy | VKH | Hoy |
| MA-NVP | 27.6 | 15.8 | 29.2 | 15.5 | 11.1 | 12.3 | 41.7 | 25.3 |

**Table 2.** Calculated physical characteristics of poly(MA-alt-NVP) according to Askadskii's method

| Polymer | $\Delta E_i^*$(J/mol) | $\Delta V_i^*$ (Å$^3$) | $\delta_t$ (J/cm$^3$)$^{1/2}$ |
|---|---|---|---|
| poly(MA-alt-NVP) | 79412.5 | 186.9 | 26.6 |

**Table 3.** $\Delta\delta$ values for different MA-alt-NVP/related solvent systems by using Hansen's solubility parameter components of solvents.

| System | $\Delta\delta$ ( J/ cm$^3$) $^{1/2}$ | |
|---|---|---|
| | VKH | Hoy |
| DMSO/poly(MA- alt-NVP) | 8.5 | 3.3 |
| DMF/poly(MA- alt-NVP) | 10.9 | 1.7 |
| THF/poly(MA- alt-NVP) | 17.2 | 9.3 |
| 1-Butanol/poly(MA- alt-NVP) | 18.7 | 9.9 |
| Ethyl acetate/poly(MA- alt-NVP) | 18.2 | 9.9 |
| EtOH/poly(MA- alt-NVP) | 18.2 | 10.1 |
| MeOH/poly(MA- alt-NVP) | 18.7 | 11.5 |
| 1-Pentanol/poly(MA- alt-NVP) | 19.1 | 10.3 |
| Chloroform/poly(MA- alt-NVP) | 19.3 | 12.6 |
| Ethyleneglycol /poly(MA- alt-NVP) | 20.9 | 15.4 |
| Water/poly(MA- alt-NVP) | 34.7 | 31.3 |

**Table 4.** $\Delta\delta$ values for different MA- alt-NVP/related solvent systems by using Hoy's solubility parameter components of solvents.

| System | $\Delta\delta$ ( J/ cm$^3$) $^{1/2}$ | |
|---|---|---|
| | VKH | Hoy |
| DMSO/poly(MA- alt-NVP) | 8.5 | 3.7 |
| DMF/poly(MA- alt-NVP) | 10.9 | 2.9 |
| THF/poly(MA- alt-NVP) | 15.9 | 7.6 |
| 1-Butanol/poly(MA- alt-NVP) | 16.1 | 6.5 |
| 1-Pentanol/poly(MA- alt-NVP) | 16.6 | 7.1 |
| Chloroform/poly(MA- alt-NVP) | 16.7 | 8.4 |
| Ethyl acetate/poly(MA- alt-NVP) | 17.1 | 8.2 |
| EtOH/poly(MA- alt-NVP) | 19.3 | 9.4 |
| MeOH/poly(MA- alt-NVP) | 21.7 | 17.1 |
| Ethyleneglycol /poly(MA- alt-NVP) | 26.3 | 15.1 |
| Water/poly(MA- alt-NVP) | 33.9 | 29.2 |

results with one of the highest $\Delta\delta$ values (much greater than the predicted value of 5 considered for good solubility) for this copolymer although it is water soluble. This is rather confusing when both approaches are considered which can however be interpreted by the acidic and basic contributions affecting the solubility parameter.

## Solubility Diagrams

Solubility behavior cannot accurately be predicted by the consideration of the Hildebrand solubility parameter ($\delta$), only. As mentioned before, solubility can be affected by any specific interactions, especially H-bonds, temperature, polymer morphology (crystallinity) and cross-linking. Also, of great importance, is the size and shape of the polymer and solvent molecules. Therefore, several plotting and modeling techniques have been improved facilitating the prediction of polymer solubility [33]. These solubility parameter diagrams give a quick insight to the decomposition of polymers by solvents, namely, the swelling of three-dimensional network structures by solvents, solvent crazing and cracking and the decrease in mechanical properties like tensile strength.

The use of measurable physical quantities besides the solubility parameter for expressing the solvent properties of a liquid was used by Beerbower, Kaye and Pattison [34], who expressed the amount of hydrogen bonding energy by the hydrogen bonding number, $\Delta\nu$. Beerbower, Kaye and Pattison [34] plotted the data for various solvents in a diagram with the solubility parameter $\delta$ along the horizontal axis and the hydrogen bonding number, $\Delta\nu$, along the vertical axis. All the solvents in which a given polymer are soluble fall within a certain region. Crowley, Teague, and Lowe [35,36] used an extension of this method by including the dipole moment of the solvent in the characterization. However, as this involves a comparison of a number of solvents in a three-dimensional system, the method is impratical.

For practical applications, a two-dimensional method is to be preferred. Thermodynamic considerations led Bagley, Nelson, and Scigliano [37] to the conclusion that the effects of $\delta_d$ and $\delta_p$ show close similarity, while the effect of $\delta_h$ is of a quite different nature. Accordingly, they introduced the parameter as $\delta_v = \sqrt{(\delta_d^2 + \delta_p^2)}$. This leads to a diagram in which $\delta_v$ and $\delta_h$ are plotted on both axes.

Other two-dimensional methods for the representation of solubility data are the $\delta_p$-$\delta_h$ diagram proposed by Henry [38] and the $\delta$-$\delta_h$ or the $\delta$-$\delta_a$ diagram proposed by Hoernschemeyer [39]. At present the $\delta_v$-$\delta_h$ diagram seems to be the most efficient way of representing polymer-solvent interactions. Table 6 shows the axes of these Diagrams [37, 38, 39].

All these diagrams have a common feature such that the solubility parameter component of polymer is placed at the center of the circle. The solubility parameter components of solvents remaining within the circle and closer to the solubility parameter of component of the polymer are all considered as good solvents whereas the one remaining outside the circle may be assumed as either slightly swelling the polymer or not affecting the solubility at all [40].

With respect to the solubility parameter components, variously chosen as the axes of these plots, the diagrams are presented in Figure 4. When these diagrams are examined, a sequence is obtained with respect to the solvent and with regard to the distance of the solubility parameter components of the solvent from the center of the circle. Regarding the distance of the solubility parameter components of the solvent from the center of the circle, various sequences for the solvents of poly(MA-alt-NVP) are displayed in Table 7 according to Bagley [37], Henry [38] and Hoernschemeyer [39] diagrams.

## Askadskii's method for predicting polymer solubility

Askadskii [21] has used the total solubility parameter to predict the solubility of polymers in various solvents. Taking into account the nature of molecules in liquids and polymers leads to the following equation for calculating the solubility parameter:

$$\delta_t^2 = \frac{\Delta E^*}{N_A \sum_i \Delta V_i} = \frac{\sum_i \Delta E_i^*}{N_A \sum_i \Delta V_i^*} \qquad (3)$$

where $\Delta E^* = k\Delta E_0$ is the cohesive energy of the liquid or repeat unit of the polymer, reduced by the number of times of the van-der-Waals volume of the molecule (or unit); k is the coefficient of molecular packing of the liquid or polymer. $N_A$ is taken as $6.023\text{x}10^{23}$ mol$^{-1}$, $\Delta E_i^*$ is expressed in Joule/mole, $\Delta V_i$ in ( Å$^3$), and $\delta_t$ in (J/cm$^3$)$^{1/2}$. The value of $\Delta E^*$ is additive and is represented as $\Delta E^* = \sum_i \Delta E_i^*$, where $\Delta E_i^*$ is the contribution of each atom and type of intermolecular interaction to $\Delta E^*$. Values of $\sum_i \Delta E_i^*$ for different atoms and types of intermolecular interaction.

For copolymers, the equation for the calculation of the solubility parameter is presented in the form:

$$\delta^2 = \frac{\alpha_1\left(\sum_i \Delta E_i^*\right)_1 + \alpha_2\left(\sum_i \Delta E_i^*\right)_2 + \ldots + \alpha_n\left(\sum_i \Delta E_i^*\right)_n}{N_A\left[\alpha_1\left(\sum_i \Delta V_i\right)_1 + \alpha_2\left(\sum_i \Delta V_i\right)_2 + \ldots + \alpha_n\left(\sum_i \Delta V_i\right)_n\right]} \qquad (4)$$

where $\alpha_1$, $\alpha_2$,...$\alpha_n$ are the molar parts of the components 1, 2,...,n; $(\Sigma\Delta V_i)$ ,$(\Sigma\Delta V_i)$ ,..., $(\Sigma\Delta V_i)$ are the van-der Waals volumes of the components 1, 2,...,n; $(\Sigma\Delta E_i^*)$ , $(\Sigma\Delta E_i^*)$ ,..., $(\Sigma\Delta E_i^*)$ are cohesive energies of

**Table 5.** Sequences of solvents for poly(MA- alt-NVP) according to $\Delta\delta$ values.

| Sequence of solvents | Calculation method | |
|---|---|---|
| [a]DMSO > DMF > THF > 1-Butanol > 1-Pentanol > Chloroform > Ethyl acetate >EtOH > MeOH > Ethyleneglycol > Water | $\delta_{polymer;\ VKH}$ | $\delta_{solvent;\ Hoy}$ |
| [b]DMSO > DMF > THF > Ethyl acetate = EtOH > 1-Butanol = MeOH > 1-Pentanol > Chloroform > Ethyleneglycol > Water | $\delta_{polymer;\ VKH}$ | $\delta_{solvent;\ Hansen}$ |
| [c]DMF > DMSO > 1-Butanol > 1-Pentanol > THF > Ethyl acetate > Chlorform > EtOH > Ethyleneglycol > MeOH > Water | $\delta_{polymer;\ Hoy}$ | $\delta_{solvent;\ Hoy}$ |
| [d]DMF > DMSO> THF > 1-Butanol = Ethyl acetate > EtOH > 1-Pentanol > MeOH > Chlorform > Ethyleneglycol > Water | $\delta_{polymer;\ Hoy}$ | $\delta_{solvent;\ Hansen}$ |

[a] Represents the sequence of solvent power obtained by using the VKH method for solubility parameter of the polymer whereas for thesolvents according to Hoy's values.

[b] Represents the sequence of solvent power obtained by using the VKH method for solubility parameter of the polymer whereas for the solvents according to Hansen's values.

[c] Represents the sequence of solvent power obtained by using the Hoy's method for solubility parameter of the polymer whereas for the solvents according to Hoy's values.

[d] Represents the sequence of solvents power obtained by using the Hoy's method for solubility parameter of the polymer whereas for the solvents according to Hansen's values.

**Table 6.** The coordinates of two-dimensional diagrams

| Specified by | Coordinates and combinations |
|---|---|
| Bagley [37] | $\delta_v$-$\delta_h$, $[\delta_v = (\delta_d^2 + \delta_p^2)^{1/2}]$ |
| Henry [38] | $\delta_p$-$\delta_h$ |
| Hoernschemeyer [39] | $\delta_t$-$\delta_h$, $[\delta = (\delta_d^2 + \delta_p^2 + \delta_h^2)^{1/2}]$ and $\delta_t$-$\delta_a$, $[\delta_a = (\delta_p^2 + \delta_h^2)^{1/2}]$ |

**Table 7.** The sequences of solvents for poly(MA-*alt*-NVP) according to different solubility diagrams.

| Used Diagram | Poly(MA-alt-NVP) |
|---|---|
| Bagley | DMSO > DMF > THF ≈ chloroform ≈ 1-butanol > 1-pentanol > ethyl acetate > EtOH > MeOH > ethyleneglycol > water |
| Henry | chloroform > DMSO > DMF > THF > ethyl acetate > 1-butanol ≈ EtOH ≈ MeOH > 1-pentanol > ethyleneglycol > water |
| Hoernschemeyer-1 | ethyleneglycol > MeOH > DMSO > EtOH > water > DMF > 1-butanol > 1-pentanol > THF ≈ chloroform > ethyl acetate |
| Hoernschemeyer-2 | ethyleneglycol > water ≈ MeOH > DMF > DMSO ↓ EtOH > 1-butanol > 1-pentanol > chloroform ≈ THF |

components 1, 2,...,n; $N_A$ is the Avagadro number.

*Askadskii's solubility criterion* is given below:

$$\mu \langle 2\rho\phi\left(\phi - \sqrt{\phi^2 - 1 + a'}\right) \tag{5}$$

where,

$$\phi = \frac{4(V_s V_p)^{1/3}}{\left(V_s^{1/3} + V_p^{1/3}\right)^2} \tag{6}$$

$$\eta = \delta_p^2 / \delta_s^2 \tag{7}$$

$$a' = \gamma_{s-p} / \gamma_s \tag{8}$$

$\rho$ is a constant ($2\rho$ =1.374), $\delta_p$ and $\delta_s$ are the Askadskii's solubility parameters for the polymer and solvent, $\gamma_{s-p}$ and $\gamma_s$ present the ratio of interfacial tension/surface tension of solvent, respectively.

Table 8 presents the calculated values of physical characteristics of related solvents and the results of the application of Askadskii's solubility criterion verifying the solubility of poly(MA-alt-NVP) in these solvents.

After the evaluation of solubility parameters yielding the solvent power sequence, it is possible to say that DMSO has been found as the best solvent, whereas water remains as a poor solvent for poly(MA-alt-NVP) according to Hoy and Van Krevelen-Hoftyzer methods. On the other hand, according to Askadskii's method, water still seems to be a good solvent for poly(MA-alt-NVP) besides

**Table 8.** Calculated physical characteristics of related solvents and the results of the application of Askadskii's solubility criterion for poly(MA-*alt*-NVP).

| Solvent | $\delta_{solv.}$ | $V_{m,solv.}$ | $\gamma_{solv}$ | L.H.S.*. of Eqn. 2.23 | R.H.S.*. of Eqn. 2.23 | Solubility |
|---|---|---|---|---|---|---|
| Water | 48.14 | 18.0 | 65.39 | 0.733 | 0.914 | + |
| DMSO | 27.25 | 71.3 | 52.95 | 1.117 | 1.366 | + |
| Ethyene glycol | 25.24 | 56.0 | 27.35 | 4.188 | 0.629 | - |
| MeOH | 30.21 | 40.4 | 33.03 | 2.872 | 0.705 | - |
| Ethyl acetate | 18.44 | 97.8 | 26.50 | 4.461 | 0.699 | - |
| EtOH | 26.56 | 54.0 | 29.02 | 3.719 | 0.676 | - |
| 1-Butanol | 23.09 | 91.7 | 25.84 | 4.692 | 0.666 | - |
| 1-Pentanol | 22.11 | 108.2 | 25.15 | 4.953 | 0.660 | - |
| DMF | 25.94 | 77.0 | 29.92 | 3.499 | 0.777 | - |

* L.H.S. and R.H.S. refer to left and right hand sides, respectively.

**Table 9.** The linear and polyelectrolyte behavior characterizations in terms of intrinsic viscosity for poly(MA-*alt*-NVP)/ solvent system

| Solvent | Concentration (g/dL) | | $[\eta]_H$ dL/g |
|---|---|---|---|
| MeOH | >0.74 | linear | 0.076 |
| DMF | - | linear | 0.097 |
| DMSO | - | linear | 0.108 |
| Water | >6.3 | linear | 0.116 |

DMSO. In theory, water and DMSO, both being polar in nature are good solvents for the copolymer having highly polar groups. This behavior of water, exhibiting large $\Delta\delta$ value, seems to be confusing for poly(MA-alt-NVP) which is a water-soluble polymer [41]. The controversy of this behavior depends on the dense hydrogen bonding character of the copolymer and the solvent. Karger, Synder and Eon [42] reported that there exists two more solubility parameter components such as acidic ($\delta_a$) and basic ($\delta_b$) contributions affecting the solubility parameter besides dipole ($\delta_d$), polar ($\delta_p$) and hydrogen bonding ($\delta_h$) contributions. The conflict for the undesired results seems to rise from the fact that the effects of ($\delta_a$) and ($\delta_b$) values have not been taken into account in the existing values of $\Delta\delta$ in literature until now.

In our study, viscosity studies have been carried out with the purpose of comparing the agreement of these results with those obtained from algorithmic calculations. For the viscometric studies, solvents with varying solvent power have been employed, such as MeOH, DMF, DMSO and water. Since during the dissolution process of the copolymer, alcohols seem to be less effective, water takes place in the last row, whilst DMF and DMSO behave as good solvents. In the selection of these solvents, the algorithmic calculations have also been a valuable guide.

The viscosity behaviour of poly(MA-alt-NVP) in the selected solvents are displayed in Figure 5. Among these solvents MeOH and water systems exhibit a linear behaviour at high concentrations whereas a polyelectrolyte behavior has been observed at lower concentrations.

It is quite well-known that intrinsic viscosity values of dilute polymer solutions are rather high due to the extension of the copolymer chain whereas the polymer molecules remain coiled as the polymer concentration increases, decreasing intrinsic viscosity. However, the viscosities of dilute polymer solutions show minima in "poor solvents" which is quite expected since the polymer chains will naturally conform into a coiled structure rather than extending in the solvent. Thus, there is a "changeover" in the expected behavior.

In Table 9, the linear and polyelectrolyte behaviour characterizations are presented in terms of intrinsic viscosities within a given range of concentration. When carefully observed, the intrinsic viscosity values obtained in DMF and DMSO appear to be high. It is rather contradictory with regard to Hoy and Van Krevelen because water seems to be the best solvent owing to the highest intrinsic viscosity. The maleic anhydride (MA) copolymers are usually hydrolyzed in aqueous solutions when two carboxyl groups are formed on the MA unit which results in a behaviour characteristic to dibasic polyacids [43]. The behaviours of polyelectrolytes in aqueous solutions show some pecularities due to the modifications probably due to the competition between the electrostatic repulsion within the charged polymer chain sequences [44,45]. On the other hand, some attractive forces, such as hydrogen bonds between the carboxyl and carboxylate groups [45,46], van der Waals or hydrophobe interactions between the methyl groups are also present in the copolymer structure [47,48]. The polyelectrolyte character can be evidently proved by means of viscometric measurements [49].

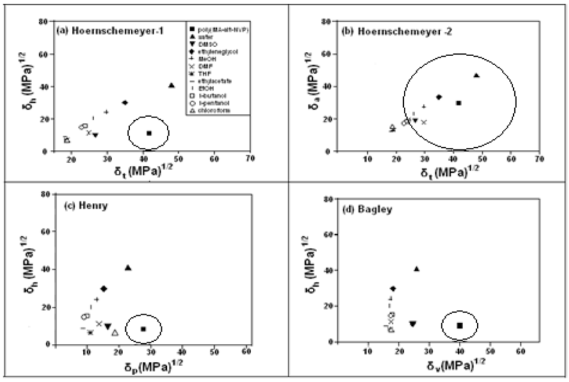

**Figure 4.** (a) solubility diagram according to Hoernschemeyer-1; (b) solubility diagram according to Hoernschemeyer-2; (c) solubility diagram according to Henry; (d) solubility diagram according to Bagley.

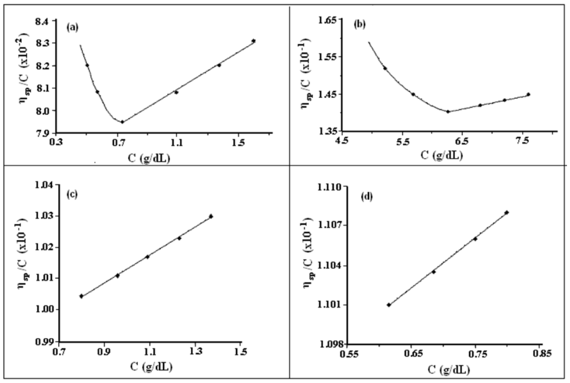

**Figure 5.** [a]The reduced viscosity $\eta_{sp}/C$ vs. concentration for poly(MA-alt-NVP) in MeOH at 20°C (Dilution effect and polyelectrolyte behaviour). [b]The reduced viscosity $\eta_{sp}/C$ vs. concentration for poly(MA-alt-NVP) in water at 20°C (Dilution effect and polyelectrolyte behaviour). [c]The reduced viscosity $\eta_{sp}/C$ vs. concentration for poly(MA-alt-NVP) in DMF at 20°C (Dilution effect and polyelectrolyte behaviour). [d]The reduced viscosity $\eta_{sp}/C$ vs. concentration for poly(MA-alt-NVP) in DMSO at 20°C (Dilution effect and polyelectrolyte behaviour).

Consequently, the acid and base constants which play an important role in viscosity behaviour of copolymers should be strongly considered as well. Unfortunately, no such equality exists in algorithmic methods to reveal the important contribution of the acidic $\delta_a$ and basic $\delta_b$ partial solubility parameters [42], thus, yielding contradictory results of $\Delta\delta$ as in the case of water.

## CONCLUSION

Solubility parameters of poly(MA-alt-NVP) were calculated and interactions between different polymer/solvent pairs were empirically investigated on the basis of Hoy, van Krevelen-Hoftyzer and Askadskii's approaches. $\delta_t$ values of the copolymers were determined by Hoy, van Krevelen-Hoftyzer and Askadskii's methods. The values obtained from the methods of Hoy and Askadskii are in good agreement with each other.

With regard to the total solubility parameter values, and concerning Askadskii's approach, DMSO and water appear to be the best solvents for MA/NVP copolymer. However, on the basis of solubility parameter differences ($\Delta\delta$), DMSO appears to be the best solvent. As a consequence of the evaluation of solubility parameter diagrams, for poly(MA-alt-NVP) copolymer, it is most probable to conclude that DMSO is usually the best solvent among all other solvents employed in this study.

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