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Miscibility Studies of Polyethersulfone (PES), N – Methyl – 2 – Pyrrolidone (NMP) and Alkanolamines on the Basis of Hansen Solubility Parameters

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Abstract— **in advance materials, it is very necessary to find the best solvent which can dissolve the polymer and other additives to form the homogenous solution. The simplest way to explore this science is based on Hansen solubility parameters. In this work the Hansen solubility parameters of Polyethersulfone (PES), N – Methyl – 2 – Pyrrolidone (NMP), Diethanolamine (DEA), and Methyldiethanolamine (MDEA) were calculated. The miscibility of polymer in solvent and amines has been estimated by using of Hoftzyer / Van Krevelen method for the determination of Hansen solubility parameter.**

Keywords— **Solubility, Alkanolamines, Miscibility Studies, Polyethersulfone**

I. Introduction

The successful processing of advance materials can be achieved by formulating the stable solution. Besides various physical and chemical properties involved (viscosity, surface tension, density, etc.), the fine selection of a set of solvents that are able to solubilize the solute of interest, represents an enormous step towards the achievement of a thermodynamically stable solution [1]. In order to get the stabilize solution; it is needed to know about the solubility parameters of chemicals which will be used in the preparation of the solution.

Solubility parameters have found their greatest use in the coating industry to aid in the selection of solvents. They are used in other industries; however, the solubility parameters are used to predict compatibility of polymers, chemical resistance, permeation rates. Liquids with similar solubility parameters will be miscible, and polymers will dissolve in solvents whose solubility parameters are not too different from their own. The basic principle has been "like dissolves like"[2].

Solubility parameter can be used to find the widely used solubility parameter approach to predicting polymer solubility. The basis of these so-called Hansen solubility parameters (HSP) is that the total energy of vaporization of a liquid consists of several individual parts [3, 4]. These arise from (atomic) dispersion forces (*d*), (molecular) permanent dipole–permanent dipole forces (*p*), and (molecular) hydrogen bonding (*h*) (electron exchange).

The basic equation [2] which governs the assignment of Hansen parameters is that the total cohesion energy *E* must be the sum of the individual energies which make it up.

$$E = E_d + E_p + E_h \quad (1)$$

Dividing these energies by molar volume gives the square of the total (or Hildebrand) solubility parameter as the sum of the squares of the Hansen *d*, *p*, and *h* components [2].

$$\frac{E}{V} = \frac{E_d}{V} + \frac{E_p}{V} + \frac{E_h}{V} \quad (2)$$

$$\delta^2 = \delta_d^2 + \delta_p^2 + \delta_h^2 \quad (3)$$

The concept, fundamental approaches, applications and importance of solubility parameter has been discussed by various researchers [5-12].

This study is the preliminary investigation for miscibility study of MDEA and DEA with polymer and solvent in order to develop the new membrane material for gas separation.

II. Material and Methodology

Polyethersulfone PES (ULTRASON E 6020P) was purchased from BASF Germany, its molecular weight is 50,000g/mol. N – Methyl – 2 – Pyrrolidone (NMP) was obtained from Merck Germany. NMP was used as solvent for the preparation of polymeric solution. Diethanolamine, (DEA) and methyl di ethanol amine (MDEA) was purchased from Merck Germany.

Table 1 Physical Properties of Chemicals

	PES	NMP	DEA	MDEA
Molecular weight	236	99.13	105.14	119.16
Density (g/cm^3)	1.37	1.03	1.09	1.04
Molar Volume (cm^3/mol)	172.26	94.24	96.54	114.57

Characteristics of the Polymer Solutions

A. Overall Solubility Parameter of Dope Solution

The overall solubility parameter can be calculated by following equation:

$$\delta = \sqrt{\delta_d^2 + \delta_p^2 + \delta_h^2} \quad (4)$$

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Where δ_d, δ_p and δ_h are the dispersive, polar and hydrogen bonding solubility parameters, respectively, calculated by Van-Kravelen and Hoftyzer's method [13].

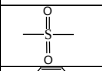
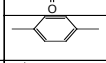
$$\delta_d = \sum \frac{F_{d_i}}{V} \quad (5)$$

$$\delta_P = \frac{\sqrt{\sum {F_{P_i}}^2}}{V} \quad (6)$$

$$\delta_h = \sqrt{\frac{\sum E_{h_i}}{V}} \quad (7)$$

F_{di}, F_{pi}, E_{hi} are the respective dispersion, dipole force and hydrogen bonding force components of the solubility parameter and V denotes the molar volume. The numerical values assigned to each structural component of the organic compounds can be obtained readily from the following table. [14, 15]

Table 2 Numerical value of each structural component of Compound

Compounds	Functional Groups	Components			Frequency
		F_{di} ($KJ^{1/2}$. $cm^{3/2}$. mol^{-1})	F_{pi} ($KJ^{1/2}$. $cm^{3/2}$. mol^{-1})	E_{hi} (KJ. mol^{-1})	
PES		591	0	13490	1
		1270	110	0	2
NMP		290	770	2000	1
	—CH_2—	270	0	0	3
	—CH_3	420	0	0	1
	Tertiary amine	20	800	5000	1
DEA	$-OH$	210	500	20,000	2
	$-CH_2$	270	0	0	4
	$-NH_2$	137	0	2,006	1
MDEA	$-OH$	210	500	20,000	2
	$-CH_2$	270	0	0	4
	$-CH_3$	420	0	0	1
	$-N<$	20	800	5,000	1

B. Solubility Parameter of Dope Solutions

The solubility parameter δ of the binary mixture (solvent / amine) is calculated using the following equation [16, 17].

$$\delta_{i,s} = \frac{X_1 V_1 \delta_{i,1} + X_2 V_2 \delta_{i,2}}{X_1 V_1 + X_2 V_2} \quad (8)$$

$i = d, p, h$

The equation has been modified for the solvent / amine mixture.

$$\delta_{i,mix} = \frac{X_s V_s \delta_{i,s} + X_A V_A \delta_{i,A}}{X_s V_s + X_A V_A} \quad (9)$$

$i = d, p, h$

Where X is the molar fraction V corresponds to the molar volume, and the subscripts s and A mean the solvent (NMP) and amines respectively. Subscript d represents the dispersion interaction, p corresponds to the polar bonding, and h denotes the hydrogen bonding components. Thus, the solubility parameter between PES and solvent, solvent and amine mixture can be expressed by the Hansen equation as [16]:

$$\Delta\delta_{s-P} = \left[\left(\delta_{d,s} - \delta_{d,P}\right)^2 + \left(\delta_{p,s} - \delta_{p,P}\right)^2 + \left(\delta_{h,s} - \delta_{h,P}\right)^2\right]^{0.5} \quad (10)$$

The equation has been modified in term of mixture (solvent / amines) and polymer:

$$\Delta\delta_{mix-PES} = \left[\left(\delta_{d,mix} - \delta_{d,PES}\right)^2 + \left(\delta_{p,mix} - \delta_{p,PES}\right)^2 + \left(\delta_{h,mix} - \delta_{h,PES}\right)^2\right]^{0.5} \quad (11)$$

III. Results and Discussion

A. Overall Solubility Parameter

The overall solubility parameter has been calculated for the compounds by using Eq. 4 and tabulated in the Table 3. The results shows that the overall solubility parameter of PES and NMP is close enough to each other. Thus it shows that the polymer PES has strong affinity with solvent NMP. The polymer and solvent compatibility also proved from the small difference in overall solubility parameter. The literature reported that if the compounds having the large difference in solubility parameter are immiscible with each other [18].

In this study the amines used as the additives and it is very necessary to know the overall solubility parameter of these amines. In the Table 3 shows that both amines have slightly higher value of overall solubility parameter than polymer and solvent.

The difference between the total solubility parameters of the polymer and solvent increases, tendency towards dissolution decreases. The necessity of small differences between these parameters became a rule of thumb in solvent and additives selection. It was also concluded that substances with a $\Delta\delta <$ 7.0 $MPa^{1/2}$ are likely to be miscible, whereas those with $\Delta\delta >$ 10$MPa^{1/2}$ are likely to be immiscible [2].

So on the basis of overall solubility study results, it found that all chemicals of this study have strong affinity and compatibility with each other.

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Table 3 Overall Solubility Parameter of Compounds

Compound	δ_d $(MPa)^{1/2}$	δ_p $(MPa)^{1/2}$	δ_h $(MPa)^{1/2}$	$\delta_{Overall}$ $(MPa)^{1/2}$
PES [2]	19.6	10.8	9.2	24.19
NMP [2]	18.0	12.3	7.2	21.48
DEA [2]	17.2	10.8	21.2	29.35
MDEA	16.9	11.1	19.8	28.35

B. Solubility Parameter of Solvent /Amines Mixture

The solubility parameters of mixture (solvent / amine) were calculated numerically with the help of Eq. 9. The results have been tabulated in the Table 4. The overall solubility parameter of mixture is almost same. It is because of the energy of mixing released by interactions within the components is balanced by the energy released by interaction between the components [19]. It shows the solvent has strong affinity with both amines, and they can mix well with each other. The concentration amines also have no effect on the overall solubility parameter. The overall solubility parameter of mixture with DEA and MDEA is almost equal. So we can get the stabilize solution with the help of this mixture.

Table 4 Solubility Parameter of Mixture (Solvent / Amines)

Amin/Concentration		5 %	10 %	15 %
DEA	$\delta_{d(mixture)}$ $(MPa)^{1/2}$	17.9	17.9	17.9
	$\delta_{P(mixture)}$ $(MPa)^{1/2}$	12.2	12.2	12.2
	$\delta_{h(mixture)}$ $(MPa)^{1/2}$	7.6	7.4	7.6
	$\delta_{Overall(mixture)}$ $(MPa)^{1/2}$	23.1	23.1	23.1
MDEA	$\delta_{d(mixture)}$ $(MPa)^{1/2}$	17.9	17.9	17.9
	$\delta_{P(mixture)}$ $(MPa)^{1/2}$	12.2	12.2	12.2
	$\delta_{h(mixture)}$ $(MPa)^{1/2}$	7.6	7.4	7.5
	$\delta_{Overall(mixture)}$ $(MPa)^{1/2}$	23.0	23.0	23.0

C. Solubility Parameter Difference of mixture (Solvent / Amine) with polymer

The addition of solvent and amines can also affect the solubility parameter difference between solvent / amine mixture and polymer $\delta_{mix\text{-}PES}$. The results presented in Table 5 and 6 were calculated by using Eq. 11. The results show that the $\Delta\delta_{mix-PES}$ is same for DEA and MDEA.

Table 5 Effect of DEA Concentration on Solubility Parameter Difference of Mixture and Polymer

DEA Concentration	$\delta_{d(mixture)}$ $(MPa)^{1/2}$	$\delta_{P(mixture)}$ $(MPa)^{1/2}$	$\delta_{h(mixture)}$ $(MPa)^{1/2}$	$\Delta\delta_{mix-PES}$ $(MPa)^{1/2}$
5%	17.9	12.2	7.6	2.7
10%	17.9	12.2	7.4	2.8
15%	17.9	12.2	7.5	2.7

Table 6 Effect of MDEA Concentration on Solubility Parameter Difference of Mixture and Polymer

MDEA Concentration	$\delta_{d(mixture)}$ $(MPa)^{1/2}$	$\delta_{P(mixture)}$ $(MPa)^{1/2}$	$\delta_{h(mixture)}$ $(MPa)^{1/2}$	$\Delta\delta_{mix-PES}$ $(MPa)^{1/2}$
5%	17.9	12.2	7.6	2.7
10%	17.9	12.2	7.4	2.8
15%	17.9	12.2	7.5	2.8

IV. Conclusions

The solubility parameters were calculated numerically and found that the all chemicals of this study have good interaction with each other. The solubility parameter of the mixture (solvent /amine) and solubility parameter difference $\Delta\delta_{mix-PES}$ of mixture (solvent / amine) and polymer also similar. All the chemicals satisfy the rules of thumb for miscibility. The solubility approach is initial estimation; the selected chemicals should also satisfy some other standards.

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Symbol Used

E	-	Sum of individual energies
E_d	-	Dispersion force
E_p	-	Dipole force
E_h	-	Hydrogen bonding force
V	cm^3/mol	Molar volume
δ	$MPa^{1/2}$	Overall Solubility parameter
δ_d	$MPa^{1/2}$	Dispersive Solubility parameter
δ_p	$MPa^{1/2}$	Polar Solubility parameter
δ_h	$MPa^{1/2}$	Hydrogen Bonding Solubility parameter
F_{di}	$(KJ^{1/2}.\ cm^{3/2}.\ mol^{-1})$	Dispersion force of Specie i
F_{pi}	$(KJ^{1/2}.\ cm^{3/2}.\ mol^{-1})$	Dipole Force
E_{hi}	$(KJ.\ mol^{-1})$	Hydrogen bonding force
X_s	-	Mole fraction of solvent
X_A	-	Mole fraction of amine
S	-	Solvent
P	-	Polymer
mix	-	Mixture (solvent /amine)

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