# Measurement and Prediction of Solubility of Four Arylamine Molecules in Benzene, Hexane, and Methanol

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In this paper, the solubility of selected arylamine molecules in methanol, hexane, and benzene has been investigated. Solubility of mmmTTA in hexane and benzene is the highest while mTTA has the lowest solubility in benzene and hexane. The UNIFAC and the UNIQUAC binary adjustable parameters have been determined. On the basis of these parameters, the solubility of these molecules has been predicted and compared with the experimental data. The effect of meta or para substitutions in arylamine molecules on their solubility in organic solvents was experimentally determined and theoretically established. The adjustable parameters of the UNIFAC equation obtained in this study will help estimate the solubility of macromolecules with the same constitutional groups or estimate the solubility of mixture of arylamine molecules. Thermal properties such as specific heat, melting point, boiling point, and heat of vaporization of the selected arylamine molecules have been determined.

## Introduction

Arylamine compounds are extensively used for many industrial applications. The pharmaceutical,[1] polymer,[2] and xerographic industries[3] are among the well-known communities that have interests in these compounds. High drift mobilities[4−6] make these molecules a good choice for the OLED (organic light-emitting diodes) or organic photoreceptors as a hole transport material.

In the OLED, the arylamine molecules form a thin solid film whereas in an organic photoreceptor they present a solid-state solution in a polymeric binder. In either case, the continuously increasing need on the improvement of these devices (durability, thermodynamic stability, and higher efficiency) necessitates stricter control over the properties and characteristics of the arylamine molecules.

Progress on the area of synthesis has been achieved, and still much work is being carried out in this area.[7−15] In the area of application, many researchers use arylamine molecules in optoelectronic diodes (both OLEDs[16−18] and organic photoreceptors[19−21]). However, to our knowledge, there is no published data on the solubility, purification, and crystallization of these molecules. In the area of synthesis, the solubility data for arylamine molecules in different solvents is important since many hydrocarbon solvents are usually utilized as the reaction medium.[3,22−24] On the basis of our study,[25] the success of the synthesis method necessitates that the catalyst, reactant, and product be soluble in one phase under homogeneous condition to reduce mass transfer limitations.

In the xerographic industry, a minor impurity in arylamine materials would result in poor quality and resolution. Besides, unwanted crystallization of these molecules as a result of aging has a serious consequence on the lifespan and functionality of the OLEDs.[26−29]

In this study, we present the solubility of selected arylamine molecules [tritolylamine or TTA (*N*,*N*,*N*-tris-(4-methylphenyl)amine, CAS Registry No. 1159-53-1); mTTA (*N*,*N*-bis-(4-methylphenyl)-*N*-(3-methylphenyl)amine, Beilstein Registry No. 9202276), mmTTA (*N*,*N*-bis-(3-methylphenyl)-*N*-(4-methylphenyl)amine, CAS Registry No. 97413-60-0); mmmTTA (*N*,*N*,*N*-tris-(3-methylphenyl)amine; CAS Registry No. 20676-79-3)] in hexane, methanol, and benzene. Figure 1 shows the structure of these molecules.

We want to show the effect of the substitution of a methyl group on the solubility of these molecules in polar-protic and nonpolar-aprotic solvents. Since these solvents cover a wide range of polarity index, the results can be extended to other solvents with a similar polarity index. For solubility estimation, the UNIQAC binary adjustable parameters of these molecules are obtained in the selected solvents. In addition, binary parameters of the constitutional group for the UNIFAC method are obtained. The estimated solubility by the ideal mixture and by UNIFAC and UNIQUAC are compared with the experimental data.

## Theory

In a binary system, the relationship between fugacities of the solute in solid and subcooled liquid forms is given:[30]

$$\ln\frac{f_2^{\mathrm{L}}}{f_2^{\mathrm{S}}} = \frac{\Delta_{\mathrm{fus}}H}{RT_{\mathrm{tp}}}\left(\frac{T_{\mathrm{tp}}}{T}-1\right) - \frac{\Delta C_p}{R}\left(\frac{T_{\mathrm{tp}}}{T}-1\right) + \frac{\Delta C_p}{R}\ln\left(\frac{T_{\mathrm{tp}}}{T}\right) \quad (1)$$

where $f_2^{\mathrm{S}}$ is the fugacity of pure solid, $f_2^{\mathrm{L}}$ is the fugacity of pure subcooled solute, $\Delta_{\mathrm{fus}}H$ is the enthalpy of fusion, and $\Delta C_{\mathrm{p}}$ is the difference in heat capacities of the solute between liquid state and solid state at temperature $T$. $T_{\mathrm{tp}}$ is the triple point of solute, which can be assumed as the melting point. This assumption creates only minor error.[15,30] This equation is true for all cases regardless of ideality or nonideality of the solution. To solve this equation one needs thermal properties of the pure solid. However, certain assumptions have to be made. First, $\Delta C_p$ is constant over the temperature range $T$ to $T_{\mathrm{tp}}$. Second, the effect of pressure on the properties of solid and subcooled liquid is negligible. This is true unless the pressure is high. Finally,

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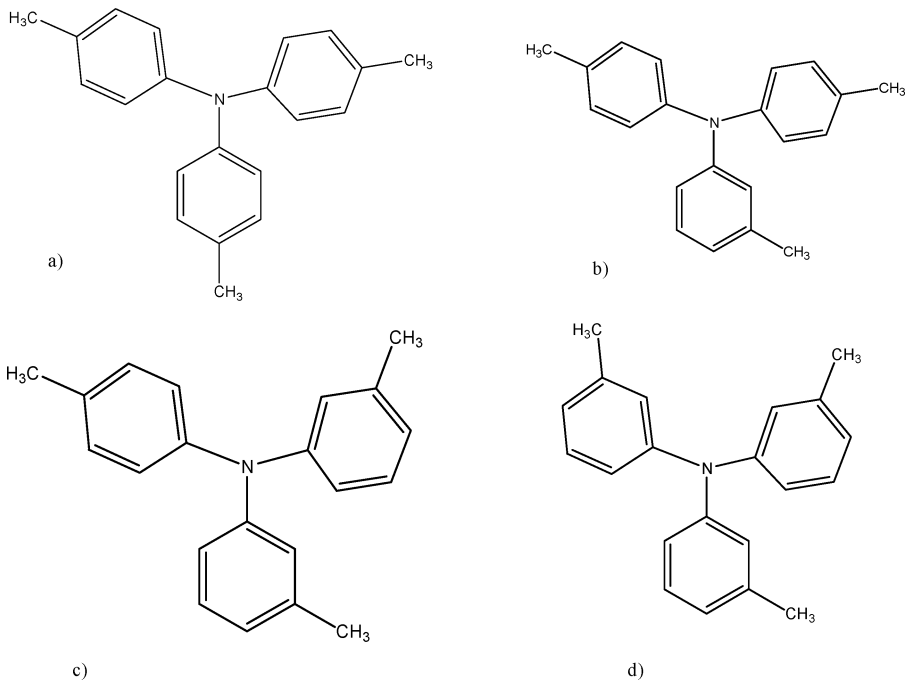


**Figure 1.** (a) TTA, (b) mTTA, (c) mmTTA, and (d) mmmTTA molecule.

there is no solid−solid-phase transition and no solid solution formed. It should be noted that the first term on the right-hand side of eq 1 is the dominant term. The second and third terms are of comparable magnitude and tend to cancel each other.[30]

Fugacities are related through the activity coefficient by

$$x_2\gamma_2 = \frac{f_2^S}{f_2^L} \tag{2}$$

where $x_2$ is the molar solubility of solute in solvent and $\gamma_2$ is the activity coefficient of solute in the solvent. Therefore, calculation of this ratio by eq 1 renders the mole fraction of the solute in the solvent presuming that the activity coefficient is known.

For the ideal case $\gamma_2$ is assumed to be one. For the nonideal solutions, $\gamma_2$ has to be calculated. There are many different methods such as the Scatchard−Hildebrand, NRTL, Van Laar, Wilson,[31,32] UNIQUAC,[33,34] and UNIFAC[30,35] methods that can be use for the calculation of the activity coefficient of a solute in a solvent. The theory behind the UNIQUAC model[33−36] and its application to arylamines has been discussed.[15] However, the application of the UNIFAC method for arylamine molecules will be addressed in this paper. The UNIFAC method of estimation for activity coefficient is suitable for creating a group contribution correlation. Table 1 presents the group description and dimensionless $r$ and $q$ associated to each individual group.[30,37−39]

## Experimental Section

***Materials.*** Hexane was purchased from Avocado Research Chemicals Ltd. (Lancaster, PA). All other materials were from Sigma-Aldrich Chemical Co. Inc. (Milwaukee, WI) and used as received. The selected arylamine molecules in this study were synthesized in our laboratory by the method that is described in the General Synthetic Method section. They were purified using the method described in the Typical Synthetic Method for Tritolylamine section. All solvents were HPLC grade.

**Table 1. Group Description, Volume, and Specific Area Parameters[30,36−39]**

| main group | subgroup | $R_k$ | $Q_k$ |
|---|---|---|---|
| $CH_2$ | $CH_2$ | 0.674 | 0.540 |
| | $CH_3$ | 0.901 | 0.848 |
| ACH | ACH | 0.531 | 0.400 |
| $ACCH_2$ (para position) | $ACCH_2$ | 1.039 | 0.660 |
| | $ACCH_3$ | 1.266 | 0.968 |
| $ACCH_2$ (meta position) | $ACCH_3$ | 1.266 | 0.968 |
| OH | OH | 1 | 1.200 |
| $CH_3OH$ | $CH_3OH$ | 1.431 | 1.432 |
| $AC_2NH$ (arylamines with two substitutions) | $AC_2NH$ | 1.463 | 1.204 |
| $AC_3N$ (arylamine with three substitutions) | $AC_3N$ | 1.866 | 1.592 |

***General Synthetic Method.*** All reactions for the synthesis of TTA, mTTA, mmTTA, and mmmTTA were carried out in glassware under an inert atmosphere created by argon. For synthesis, we used the copper-ligated synthesis method, first proposed by Goodbrand and Hu[3] and modified by our team.[25] The progress of each reaction was monitored by HPLC (Varian, Inc., R-18, acetonitrile:methanol 1.0 mL/min:0.2 mL/min) until the reaction came to completion. Samples were smaller than 1 mL, and their withdrawal did not disturb the process.

***Typical Synthetic Method for Tritolylamine (TTA).*** A 500 mL round-bottom three-necked flask was used as the reactor. The reactor was equipped with a paddle-like mechanical stirrer, an argon gas purge, a Dean−Stark trap under reflux condenser, and a heating mantle. At the outset of the reaction, 100 g of 4-iodotoluene, 17.43 g of *p*-toluidine, 110 g of KOH pellets, 1.16 g of CuBr, and 1.265 g of 2,2′-dipyridyl (ligand) were weighed and added to the 100 g of hydrocarbon solvent as the reaction medium. Using a reflux condenser, as well as the choice of hydrocarbons, enabled us to control the temperature and maintain isothermal condition during the course of the reaction. After reaction completion, the mixture was cooled and partitioned between dichloromethane and water for purification.

***Typical Purification Method for Tritolylamine (TTA).*** The organic portion obtained from the synthesis

was diluted in toluene and then treated with a mixture of acidic alumina and acid-leached bentonite at 80 °C for about 2 h. The solution was filtered while hot, and then the resulting mixture was further treated by a Rotavapor system to remove all the liquid (dichloromethane and toluene). The resulting viscous liquid was dissolved in methanol and crystallized, except for mTTA and mmmTTA, where a yellowish oil as a stable second-phase liquid was formed. To overcome the oiling-out problem for mTTA and mmmTTA, large quantities of methanol were used, reducing the concentration of mTTA and mmmTTA. After cooling the mixture, crystals formed and were separated by filtration. The HPLC results confirmed the high purity of the compound, close to 100%.

***Solubility Measurement.*** Several methods can be utilized for the measurement of solubility: refractive index,[40,41] an online density meter,[42−45] turbidity,[46] spectrophotometer,[47,48] NMR,[47] HPLC,[48] GC,[48] gravimetric,[34] and FTIR. We used the gravimetric method.

***Solubility Measurement Using Gravimetric Method.*** A number of 5 mL screw-capped vials were prepared. Each vial was weighed and marked. Different amounts of crystals were added to the vials and then weighed. An approximately identical volume of the solvent (under investigation) was added to each vial and weighed. Vials were immersed in a constant-temperature bath while shaking. The temperature was gradually increased by 0.1 °C every (30 to 45) min to find the saturation temperature by visual observation. At the saturation point, no crystals were observed in the solution. A focused light (Leica CLS 150) was applied for visual monitoring and reducing the errors associated in this step. It was found that (30 to 45) min of shaking provided sufficient time for dissolution of the samples at each temperature increment.

Errors originate from different sources related to the measurement of solubility and thermal parameters. In solubility measurement, errors associated with weighing were minimized by using a precise balance (Metller Toledo, AX205) with a resolution of ± 0.01 mg. The precision of the thermometer was ± 0.1 °C. Error associated with evaporation of solvents was minimized by employing tightly closed screw-cap vials. The largest experimental error was attributed to the exact determination of the saturation temperature by visual inspection. This error was minimized using a small temperature increment (0.1 °C) and allowing enough time, (30 to 45 min) for the dissolution of solids to take place.

In DSC analysis, although the crucible of sample was not thermally isolated, using a reference crucible minimized the error. The calibration of the DSC instrument (Mettler Toledo, Switzerland) was performed using pure indium. The acceptable deviation in enthalpy of fusion was 27.85 J/g to 29.05 J/g, and deviation in temperature of melting was 156.3 °C to 159.9 °C. Precise weighing of samples ensured minimizing the errors associated with the differential calorimetry (DSC).

## Optimization of the Adjustable Parameters of Activity Coefficient Model

Using the experimental thermal properties of pure solids as well as the experimental solubility data, the activity coefficients of selected arylamine molecules in different solvents were calculated. The activity coefficients were then used to find the adjustable parameters of the UNIQUAC and the UNIFAC models by minimization procedure. These parameters can be used for further equilibrium calculation (e.g., vapor−liquid equilibrium) for highly nonideal solutions.

**Table 2. Melting Point, Boiling Point, Enthalpy of Vaporization, and Enthalpy of Fusion of TTA, mTTA, mmTTA, and mmmTTA**

| molecule | TTA | mTTA | mmTTA | mmmTTA |
|---|---|---|---|---|
| $T_{fus}$/°C | 115.59 | 56.70 | 89.5 | 39.81 |
| $\Delta_{fus}H$/J·g$^{-1}$ | 69.43 | 75.53 | 91.83 | 45.48 |
| $T_b$/°C | 300.89 | 315.94 | 274.15 | 294.84 |
| $\Delta_{vap}H$/J·g$^{-1}$ | 252.5 | 264.2 | 241.1 | 130.8 |
| $\delta$/(J·cm$^{-3}$)$^{0.5}$ [a] | 15.36 | 15.78 | 15.01 | 10.91 |

[a] These results are calculated based on $[(\Delta_{vap}H - RT)/\nu]^{0.5}$ where $\Delta_{vap}H$ is the molar heat of vaporization, $T$ is the melting point, and $\nu$ is the molar liquid volume in cm$^3$·mol$^{-1}$.

The optimization procedure was based on the minimization of the errors between the calculated and experimental values of the activity coefficients. Therefore, we have

$$\min_{a_{mn},a_{nm}} J = \sum_{k=1}^{n} (\gamma_{2,k}^{exp} - \gamma_{2,k}^{calc})^2 \quad (3)$$

where $\gamma_{2,k}^{exp}$ is the experimental activity coefficient of solute based on the solubility data and $\gamma_{2,k}^{calc}$ is the calculated activity coefficient. Minimization was carried out by using the function "fmincon" in Matlab (Mathwork, Massachusetts).

## Results and Discussion

The solubility of TTA in 12 solvents was reported previously by our group.[15] The solvents were chosen to cover a wide range of polarity index. From those solvents, methanol, hexane, and benzene were selected for further solubility studies. Some of the data are repeated here for comparison with the solubility of structurally similar arylamine molecules.

Solubility depends on the molecular attractive forces between the solute and the solvent molecules. The energy of vaporization is related to the molecular forces between solute molecules. According to the results of the differential scanning calorimeter (DSC) (Table 2), the order of enthalpy of vaporization ($\Delta_{vap}H$) of these arylamine molecules is

$$\Delta_{vap}H\ (\text{mTTA}) > \Delta_{vap}H\ (\text{TTA}) > \Delta_{vap}H\ (\text{mmTTA}) > \Delta_{vap}H\ (\text{mmmTTA})$$

This shows that mTTA has the strongest intermolecular forces, while mmmTTA has the weakest. Since there is no hydrogen bonding sites in the solute molecules, the van der Waals or dipole−dipole interactions must affect the solubility. Therefore, the tendency of these molecules dissolving in polar protic solvents is minimal. This suggests that the expected solubility in nonpolar solvents such as hexane or benzene must be high and follow

$$w^*_{\text{mmmTTA}} > w^*_{\text{mmTTA}} > w^*_{\text{TTA}} > w^*_{\text{mTTA}}$$

, which was confirmed by our experimental data. $w^*$, saturation concentration, represents mass in grams of solutes per 100 grams of the solvent. In some references $C^*$ is used instead. In crystallization, usually, the unit of solubility is expressed in terms of grams of solute per 100 grams of solvents is used. However, in thermodynamic equations, mole fraction or mole per volume is the common unit. These units are interchangeable. The following equations can be used to calculate the solubility ($w$) in terms of

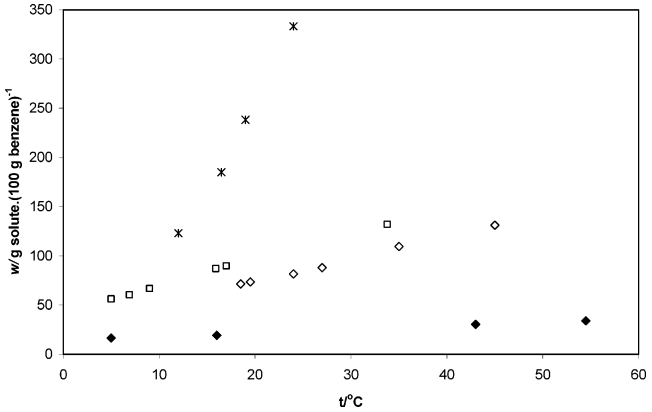


**Figure 2.** Experimental solubility of selected arylamines in benzene: ◇, $w$ TTA/(g of TTA/100 g of benzene); ◆, $w$ mTTA/(g of mTTA/100 g of benzene); □, $w$ mmTTA/(g of mmTTA/100 g of benzene); *, $w$ mmmTTA/(g of mmmTTA/100 g of benzene).

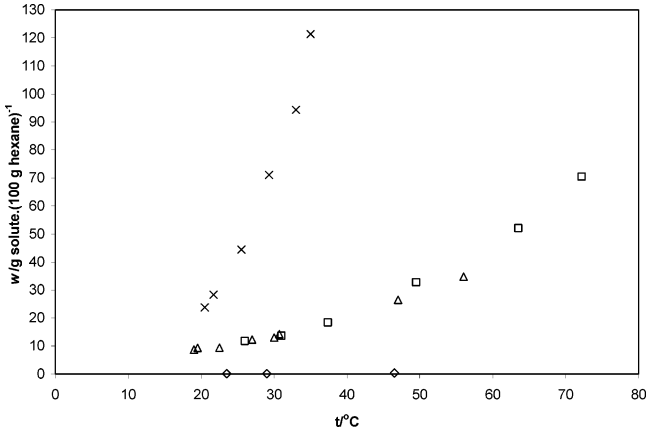


**Figure 3.** Experimental solubility of selected arylamines in hexane: □, $w$ TTA/(g of TTA/100 g of hexane); ◇, $w$ mTTA/(g of mTTA/100 g of hexane); △, $w$ mmTTA/(g of mmTTA/100 g of hexane); ×, $w$ mmmTTA/(g of mmmTTA/100 g of hexane).

**Table 3. $C_p$ Equation of Arylamines in Solid and Liquid Phase[a]**

| component | phase | $A$*10$^{+6}$ | $B$*10$^{+3}$ | $C$ | $R^2$ | temp validity range / K |
|---|---|---|---|---|---|---|
| TTA[b] | solid | 19.08 | −12.96 | 3.58 | 0.92 | 298 to 373 |
| | liquid | 97.81 | −26.05 | 3.35 | 0.80 | 393 to 413 |
| mTTA | solid | 2087.8 | −1288.00 | 199.87 | 0.92 | 298 to 325 |
| | liquid | −4.96 | 1.83 | 1.49 | 0.99 | 339 to 393 |
| mmTTA | solid | −1559.4 | 1039.20 | −172.72 | 0.99 | 330 to 340 |
| | liquid | −203.13 | 146.80 | −26.02 | 0.85 | 365 to 372 |
| mmmTTA | solid | 844.16 | −459.79 | 66.79 | 0.94 | 240 to 306 |
| | liquid | 59.33 | −40.94 | 11.41 | 0.99 | 336 to 381 |

[a] Equation is in the form: $C_p/\mathrm{J\cdot g^{-1}\cdot K^{-1}} = A(T^2/\mathrm{K^2}) + B(T/\mathrm{K}) + C$. [b] These results are from ref 15.

g of solute/100 g of solvent using the saturation mole fraction of the solute, $x_2$:

$$x = \frac{x_2}{1 - x_2} \text{ and } w = \frac{x \times \mathrm{M_{solute}}}{\mathrm{M_{solvent}}} \times 100$$

where M is the molar mass (g/mol).

Figures 2 and 3 present the experimental solubilities of the studied arylamines in benzene and hexane, respectively. The raw solubility data of all the arylamine molecules studies are listed in Table 4.

There is a huge difference between the enthalpy of vaporization of mmmTTA and TTA although both have symmetrical structures, suggesting that the intermolecular forces in mmmTTA are much weaker than in TTA. Substitution in the para position increases the electron cloud over the nitrogen atom and therefore increases the dipole moment of the molecule. On the other hand, substitution in the meta position does not affect the electron cloud over nitrogen. Therefore, it can be speculated that TTA has a stronger dipole moment as compared to mmmTTA and, consequently, a stronger bond energy than the van der Waals forces operating in mmmTTA. In addition, placing all methyl groups in the meta position reduces the volume of the molecule, and they may act like a shield for the nitrogen atom. Therefore, intermolecular forces between molecules of solutes decrease and lead to an increase in the solubility. In mTTA, there is both asymmetry and the effect of two para substitutions that make the molecular dipole−dipole strong, leading to the least solubility in nonpolar solvents. For mmTTA asymmetry exists, and it affects the polarity of the molecules. On the other hand, it has only one para substitution. From the results for mmTTA and mTTA, it may be concluded that the effect of asymmetry is less than the effect of the dipole moment caused by the substitution of an electron donor compound in the para position. Figures 2 and 3 demonstrate the effect of the polarity of the solvent. Increasing the polarity of the solvent from polarity index 0.4 (solubility parameter 14.9 $(\mathrm{J/cm^3})^{0.5}$) for hexane to polarity index 2.7 (solubility parameter 18.2 $(\mathrm{J/cm^3})^{0.5}$) for benzene, a large difference between the solubility of mmTTA and TTA molecules is noticed. Table 4 presents the solubility correlations for different arylamines and their validity range.

Although we could measure the solubility of TTA and mmTTA in methanol (see Figure 4), the attempts to find

**Table 4. Experimental Solubility Data for Hexane (1), Methanol (2), and Benzene (3)[a]**

| system | $t$/°C | $w$ | system | $t$/°C | $w$ | system | $t$/°C | $w$ |
|---|---|---|---|---|---|---|---|---|
| mTTA + 1 | 23.5 | 0.04 | mTTA + 2 | na | na | mTTA+3 | 5.0 | 16.44 |
| | 29.0 | 0.08 | | | | | 16.0 | 19.23 |
| | 46.5 | 0.33 | | | | | 43.0 | 30.36 |
| | | | | | | | 54.5 | 34.05 |
| mmTTA + 1 | 19.0 | 8.70 | mmTTA + 2 | 15.5 | 0.43 | mmTTA + 3 | 5.0 | 56.17 |
| | 19.5 | 9.31 | | 19.0 | 0.49 | | 6.9 | 60.55 |
| | 22.5 | 9.37 | | 26.0 | 0.63 | | 9.0 | 66.75 |
| | 27.0 | 12.25 | | 30.7 | 0.84 | | 15.9 | 86.97 |
| | 30.0 | 12.96 | | 40.5 | 1.18 | | 17.0 | 89.66 |
| mmmTTA + 1 | 20.5 | 23.81 | mmmTTA + 2 | na | na | mmmTTA + 3 | 12.0 | 123.18 |
| | 21.7 | 28.28 | | | | | 16.5 | 185.09 |
| | 25.5 | 44.39 | | | | | 19.0 | 238.25 |
| | 29.3 | 71.08 | | | | | 24.0 | 333.12 |
| | 33.0 | 94.28 | | | | | | |

[a] $w$ is g of solute/100 g of solvent. na is not available.

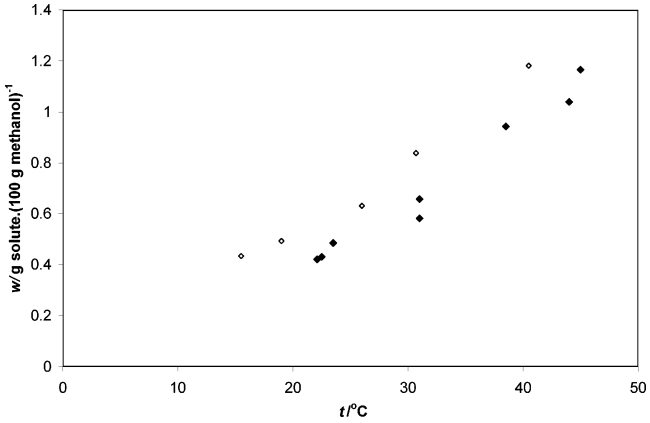


**Figure 4.** Experimental solubility of selected arylamines in methanol: ◆, $w$ TTA/(g of TTA/100 g of methanol); ◇, $w$ mmTTA/(g of mmTTA/100 g of methanol).

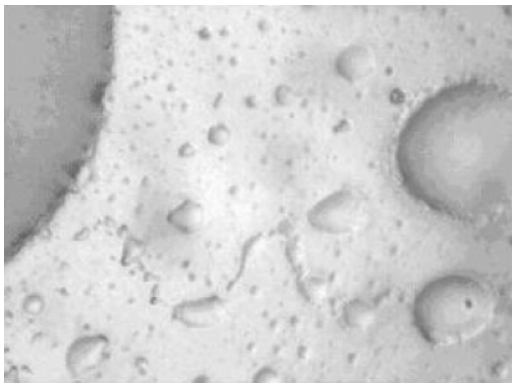

**Figure 5.** Oiling-out problem: oily mTTA in methanol.

the solubility of mTTA and mmmTTA in methanol was not successful since they formed an oily phase that was stable in the solvent (liquid phase). Figure 5 shows this phenomenon.

***Ideal Solubility.*** As it was stated earlier, in order to use eq 1, thermal properties of the solute are needed. The differential scanning calorimeter was used to measure these properties. Specific heats calculated from DSC studies are reported in Table 3. The DSC results also confirmed that there is no solid−solid enantiotropic transition over the temperature range studied for TTA, mTTA, mmTTA, and mmmTTA.[15,49]

Using the thermal properties in eqs 1 and 2 and assuming the activity coefficient is equal to 1 renders the ideal solubility. Figure 6 compares the experimental and theoretical solubilities of mmTTA in methanol, hexane, and benzene, expressed in mole fraction. Methanol and hexane show lower solubility than the predicted ideal behavior. However, the prediction for benzene is different. For solution of mmTTA in benzene $\gamma_2$ is less than one, and corresponding solubility is more than the ideal solubility. In solutions where only dispersion forces are important, $\gamma_2$ is generally larger than unity; therefore, solubility is lower than that corresponding to the ideal behavior. Methanol and hexane show the same behavior, but benzene has the activity coefficient less than unity. Benzene has partially a similar structure with mmTTA; therefore, the solution of mmTTA in benzene shows less deviation from the ideal behavior.

***Solubility Prediction by the UNIQUAC and UNIFAC Method.*** The two adjustable parameters of the UNIQUAC, $a_{mn}$ and $a_{nm}$ ($m = 1$ and $n = 2$) for TTA, mTTA, mmTTA, and mmmTTA in hexane, methanol, and benzene

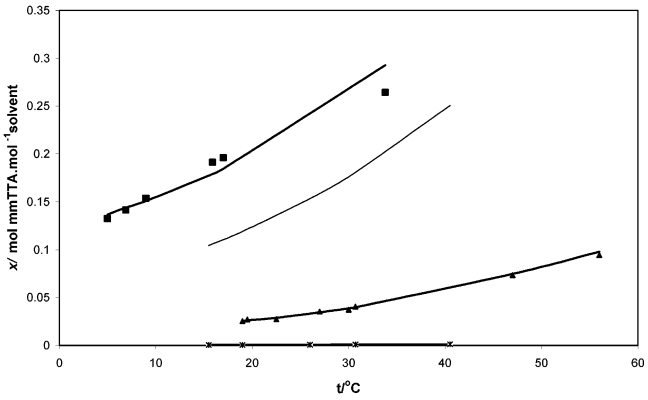


**Figure 6.** Comparison of ideal solubility of mmTTA with experimental results in methanol, hexane, and benzene: *, $x$ mmTTA/(mol of mmTTA/mol of solution of methanol); ■, $x$ mmTTA/(mol of mmTTA/mol of solution of benzene); ▲, $x$ mmTTA/(mol of mmTTA/mol of solution of hexane); —, UNIQUAC; −, the ideal law.

**Table 5. Pure Component Volume Constant ($r$) and Pure Component Area Parameter ($q$) Used in Calculation of the UNIQUAC Parameters**

| molecule | $r$ | $q$ | molecule | $r$ | $q$ |
|---|---|---|---|---|---|
| hexane | 4.499 | 3.852 | mTTA | 12.041 | 9.296 |
| benzene | 3.190 | 2.400 | mmTTA | 12.041 | 9.296 |
| methanol | 1.432 | 1.432 | mmmTTA | 12.041 | 9.296 |
| TTA | 12.041 | 9.296 | | | |

**Table 6. UNIQUAC Method Adjustable Parameters, Minimized Value $J = \sum_{k=1}^{n} (\gamma_{2,k}^{exp} - \gamma_{2,k}^{calc})^2$ and Average Error $= (\sum_{k=1}^{n} (C_{exp} - C_{calc})^2)/n$[a]**

| solution mixture[b] | $a_{12}$/K | $a_{21}$/K | $J$ minimized value | average error |
|---|---|---|---|---|
| TTA + 1[c] | 420.31 | −241.71 | 0.12 | 1.73 |
| TTA + 2[c] | 204.89 | −90.83 | 540.43 | 0.01 |
| TTA + 3[c] | 653.86 | 23.09 | 0.01 | 36.94 |
| mTTA+ 1 | 1387.72 | −193.41 | 0.25 | 0 |
| mTTA + 2 | −20.77 | 284.82 | 5.69E5 | 0 |
| mmTTA + 1 | −8.20 | 12.41 | 0.01 | 0 |
| mmTTA + 2 | 304.29 | −124.91 | 0.16 | 0 |
| mmTTA + 3 | 997.57 | 0.53 | 177.16 | 0 |
| mmmTTA + 1 | 127.15 | 125.60 | 0.49 | 0 |
| mmmTTA + 2 | 207.68 | −43.20 | 0.38 | 0.01 |

[a] $\gamma_{2,k}^{exp}$ is the experimental activity coefficient of solute based on the solubility data; $\gamma_{2,k}^{calc}$ is the calculated activity coefficient; $C_{exp}$/(g of solute/100 g of solvent) is the experimental concentration; and $C_{est}$/(g of solute/100 g of solvent) is the estimated concentration. [b] 1, benzene; 2, hexane; 3, methanol. [c] Data from ref 15.

using eq 3 were calculated. The calculation was based on the procedure described in our previous contribution[15] and using pure component van der Waals volume ($r$) and pure component area parameters ($q$) in Table 5. Results shown in Table 6 include minimized function values and average errors. The estimated solubility of mmTTA in methanol, hexane, and benzene by the UNIQUAC method is shown in Figure 6.

The UNIFAC $R$ and $Q$ parameters and $a_{12}$ and $a_{21}$ are listed in Tables 1 and 7, respectively. The group interaction parameters were calculated using the minimization algorithm (eq 3). It was necessary to calculate activity coefficients from the experimental solubility data and thermal properties in order to calculate the group interaction parameters. The functional groups that were considered in this work were those given in Table 1. While each group listed has its own values of $R$ and $Q$, the subgroups within the same main group (like $CH_2$ and $CH_3$ in group $CH_2$) are assumed to have the same group energy interaction parameters.[37]

**Table 7. Adjustable UNIFAC Energy Parameters for Pairs Obtained by Minimization (the unit of the numbers is in K)**

| | $AC_3N$ | ACH | p-$ACCH_2$ | meta $ACCH_2$ | $CH_2$ | OH |
|---|---|---|---|---|---|---|
| $AC_3N$ | 0 | −2303.0[a] | −2261.2[a] | −2219.5[a] | −2343.0[a] | 2500.0[a] |
| ACH | −2224.7[a] | 0 | 167 | −1338.3[a] | −11.12 | 636.1 |
| p-$ACCH_2$ | −437.5[a] | −146.8 | 0 | −167.3[a] | −69.7 | 803.2 |
| meta $ACCH_2$ | −224.3[a] | −1662.4[a] | −1993.5[a] | 0 | −2433.3[a] | 2468.6[a] |
| $CH_2$ | 541.3[a] | 61.13 | 76.5 | −371.1[a] | 0 | 986.5 |
| OH | 1903.2[a] | 89.6 | 25.82 | −257.6[a] | 156.4 | 0 |

[a] Calculated in the present study.

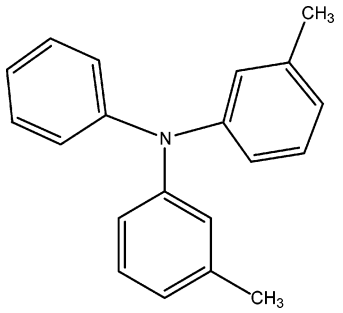


**Figure 7.** 3,3′-Dimethyltriphenylamine (phenyl-di-*m*-tolylamine) molecule.

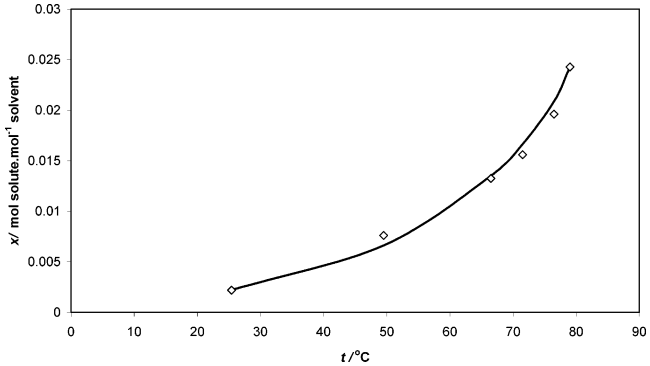


**Figure 8.** UNIFAC solubility prediction for phenyl-di-*m*-tolylaminehexane solution: ◇, experimental data; —, estimated data by UNIFAC; *x*/(mol of solute/mol of solution in hexane).

Based on previous studies by Fredenslund et al.,[35] interaction parameters for methyl substitution in the meta position and para position are the same. An exception to this rule is noted in the solubility of TTA and mTTA molecules that have the same group contributions. In both molecules there are 12 ACH (aromatic carbon), 3 $ACCH_3$ (aromatic methyl substitution), and 1 $AC_3N$ that is a core amine molecule with three aryl substitutions. However, there is a big difference in their solubility. Therefore, methyl groups substituted in the meta or para positions should be differentiated.

The resulting parameters can be used in calculation of the activity coefficient and consequently the solubilities of the arylamine molecules that have similar constitutional groups. To check the predictive capability of the UNIFAC model using the estimated constitutional group interaction parameters, we synthesized and purified 3,3′-dimethyltriphenylamine (Figure 7) in our lab. This molecule has similar constitutional groups to TTA and m-TTA. It consists of 13 ACH (aromatic carbon), 2 meta $ACCH_3$ (aromatic methyl substitution), and 1 $AC_3N$ that is a core amine molecule with three aryl substitutions. Hexane consists of 2 $CH_3$ and 4 $CH_2$ molecules. We measured the solubility of this arylamine molecule in hexane and also predicted its solubility by using the UNIFAC method with the data presented in Tables 1 and 7. As it is shown in Figure 8, there is a good agreement between the predicted and experimental solubility results. The $R^2$ value for this estimation is 0.9926, and the average error for the data based on the formula given in Table 6 is 0.

## Conclusions

The UNIFAC and UNIQUAC adjustable binary parameters for selected arylamines have been calculated and reported. The UNIQUAC adjustable binary parameters yield estimation of selected arylamines solubility in different solvents with good accuracy. Utilization of the UNIFAC adjustable parameters obtained in this study can be generalized for any arylamine molecules with defined group or subgroup constituent. Based on the experimental results presented in this paper, the effect of methyl group substituted in the para and meta position on the solubility of arylamine compounds can be differentiated and predicted by UNIFAC model. Ideal solution theory is not capable of precisely estimating the solubility of arylamines in polar solvents. However, it can be used for solubility estimation of arylamines in nonpolar-aprotic solvents.

Melting point, boiling point, enthalpies of vaporization, and fusion of these molecules were found and reported. As a result, it can be concluded that replacing each electron donor group like a methyl substitution from the para position to the meta position may render a higher solubility in nonpolar solvents and reduces the heat of vaporization with the exception of the first substitution. Also from our results, it can be concluded that the effect of substitution on the solubility is more than the effect of asymmetry of dipole−dipole formation.

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