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Solubilities of 3-Methoxy-*N*-phenylaniline and 3-(Methylthio)-*N*-phenylaniline in Five Organic Solvents (285 K to 333.75 K)

Yin-xia Jia, Chao Qian,* Xin-zhi Chen, and Chao-hong He

State Key Laboratory of Chemical Engineering (Zhejiang University), Department of Chemical and Biological Engineering, Zhejiang University, Hangzhou, 310027, China

ABSTRACT: The solubilities of 3-methoxy-*N*-phenylaniline and 3-(methylthio)-*N*-phenylaniline in pure organic solvents of methanol, acetone, ethyl acetate, chloroform, and 1,2-dichloroethane were measured at temperatures ranging from 285 K to 333.75 K using the laser monitoring dynamic method. The experimental data were correlated with the Apelblat equation; the solubilities correlated by the model are in good agreement with experimental values. The mean relative deviations σ are less than 1.5 % and the root-mean-square deviations (rmsd) less than 0.10 %.

INTRODUCTION

3-Methoxy-*N*-phenylaniline and 3-(methylthio)-*N*-phenylaniline are two important intermediates for producing negative photosensitizers, phenothiazine and its derivatives, and fluorane heat sensitive dyes. The molecular structures for 3-methoxy-*N*-phenylaniline (CAS Registry No. 101-16-6) and 3-(methylthio)-*N*-phenylaniline (CAS Registry No. 13313-45-6) are illustrated in Figures 1 and 2.

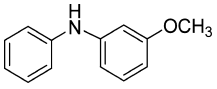

Figure 1. Molecular structure of 3-methoxy-*N*-phenylaniline.

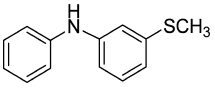

Figure 2. Molecular structure of 3-(methylthio)-*N*-phenylaniline.

The knowledge of the thermophysical properties is important not only for the design of separation, extraction, and absorption processes but also to take decisions regarding the influences of solvents on reaction rates and drug design and formulation development in the pharmaceutical industry.[1,2] Widely used in medicine, dyes, and printing industries, the thermophysical properties of 3-methoxy-*N*-phenylaniline and 3-(methylthio)-*N*-phenylaniline, such as the solubility, density, activity, and coefficient, are essential data for product development and process design in industrial production, especially since their solubilities are of crucial importance in the determination of proper solvents and the development and operation of crystallization processes.[3,4] Therefore, it is necessary to determine the solubility data of 3-methoxy-*N*-phenylaniline and 3-(methylthio)-*N*-phenylaniline in different solvents. To our knowledge, this is the first time the solubilities of 3-methoxy-*N*-phenylaniline and 3-(methylthio)-*N*-phenylaniline are reported.

The measurements of the solid−liquid equilibrium (SLE) and the foundation of thermodynamic models are important work. Many scholars have made fruitful efforts in this area, such as the solid−liquid equilibrium of binary systems[5] and liquid−solid equilibrium in a quinary system.[6] There are many equations proposed to study the solubilities of solids, like the Wilson equation,[7] universal quasichemical (UNIQUAC) equation,[8] nonrandom two-liquid (NRTL) equation,[9] universal functional (UNIFAC) equation,[10] Apelblat equation, DISQUAC equation,[11] and the Hansen equation.[12−14]

Recently, more and more solubilities determined by the laser monitoring observation technique have been published.[15−17] Compared to other methods, the laser monitoring dynamic method has the advantages of higher sensibility, higher accuracy, ease of use, wilder applicable scope, and quicker dynamic response.

In the present paper, the solubilities of 3-methoxy-*N*-phenylaniline and 3-(methylthio)-*N*-phenylaniline in methanol, acetone, ethyl acetate, chloroform, and 1,2-dichloroethane were measured at temperatures ranging from 285 K to 333.75 K at atmospheric pressure using the laser monitoring dynamic method.

EXPERIMENTAL SECTION

Materials. All of the solvents, methanol, acetone, ethyl acetate, chloroform, and 1,2-dichloroethane, were obtained from Shanghai Aibi Chemistry Preparation Co., Ltd.; they were all analytical-grade research reagents, and their purities were higher than 0.998 ascertained by high-performance liquid chromatgraphy (HPLC) or gas chromatography (GC). These pure organic solvents were dried over 0.4 nm molecular sieves and degassed in an ultrasonic bath before use.

3-Methoxy-*N*-phenylaniline and 3-(methylthio)-*N*-phenylaniline were obtained from Zhejiang Shou & Fu Chemical Co., Ltd. and were recrystallized several times from ethanol to yield purified samples. Their mass fraction purities determined by HPLC were greater than 0.996.

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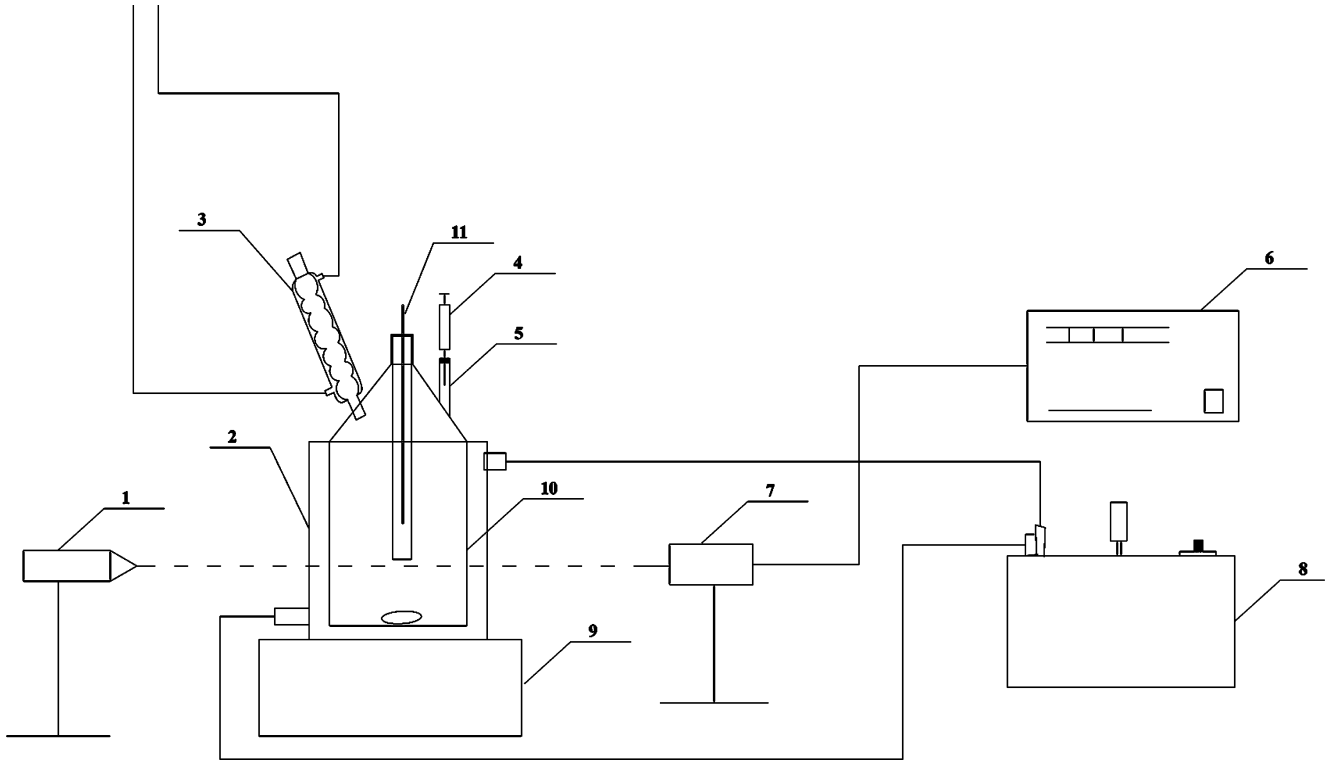

Figure 3. Schematic experiment: 1, laser generator; 2, jacked dissolution vessel; 3, condenser; 4, titration funnel; 5, feed inlet; 6, signal display; 7, laser acceptor; 8, thermostat; 9, magnetic stirring apparatus; 10, magnet stirrer; 11, precise mercurial thermometer.

Apparatus and Procedure. The solubility of solute in solvent complies with two principles, that is, similar polarity and similar solubility parameters (δ).

In this paper, the Hansen[12−14] method was used to estimate the solubilities. Considering the applications of 3-methoxy-*N*-phenylaniline and 3-(methylthio)-*N*-phenylaniline, we choose five solvents that have similar solubility parameters with the two solutes to attain high solubilities, and their solubility parameters δ are: 3-methoxy-*N*-phenylaniline, 21.8 $MPa^{1/2}$; 3-(methylthio)-*N*-phenylaniline, 21.3 $MPa^{1/2}$; methanol, 29.7 $MPa^{1/2}$; ethyl acetate, 18.6 $MPa^{1/2}$; acetone, 20.3 $MPa^{1/2}$; toluene, 18.2 $MPa^{1/2}$; 1,2-dichloroethane, 19.8 $MPa^{1/2}$; chloroform, 19.0 $MPa^{1/2}$.

The solubilities of 3-methoxy-*N*-phenylaniline and 3-(methylthio)-*N*-phenylaniline were measured by a dynamic method at atmospheric pressure. The laser monitoring observation technique was used to determine the dissolution temperature of a solid−liquid mixture of known composition. Referring to our real experiment conditions, we set up a set of experimental facility to measure their solubilities. The experimental setup is shown in Figure 3.

The experiments were carried out in a magnetically stirred (type THS-51, China), jacketed glass vessel (100 mL). The temperature was maintained constant by circulating water (the temperature of the water circulator bath was controlled by a built-in thermoelectric thermometer at a precision of 0.1 K) from a thermostatic water circulator bath 8 (type 85-1, China). A condenser (3) was connected with the vessel (2) to prevent the solvent from evaporating and a mercury-in-glass thermometer (11) was inserted into the inner chamber of the vessels to measure the real temperature of the solution with the uncertainty of 0.1 K. The continuous stir in the vessel (2) was completed by the magnetic stirring system (9, 10). Solvents were fed through the titration funnel (4).

The masses of the solvents and solutes were weighed using a digital analytical balance (type AR2140, China) at a precision of 0.0001 g. The uncertainties in the solubility values are due to uncertainties in the temperature measurements, weighing procedures, and the stability of the temperature of the water.

The solubility of 3-methoxy-*N*-phenylaniline and 3-(methylthio)-*N*-phenylaniline were measured using an method similar to that described in the literature.[16,17] The interval of addition depended on the speed of dissolving at that temperature, and it should last more than 30 min. In this work, the uncertainty for solubility measurement is estimated on the basis of the principle of the error propagation to be 2.0 % at the 95 % confidence level.

■ RESULTS AND DISCUSSION

The solubilities of 3-methoxy-*N*-phenylaniline and 3-(methylthio)-*N*-phenylaniline in methanol, acetone, ethyl acetate, chloroform, and 1,2-dichloroethane between 285 K and 333.75 K were measured by experiments; all of the data are presented in Tables 1 and 2. The temperature dependence of 3-methoxy-*N*-phenylaniline and 3-(methylthio)-*N*-phenylaniline solubility in pure solvents is described by the modified Apelblat equation,[3,18−23] which is a semiempirical equation derived from the Clausius−Clapeyron equation.

$$\ln x = A + B/(T/\mathrm{K}) + C \ln(T/\mathrm{K}) \quad (1)$$

where *A*, *B*, and *C* are dimensionless parameters, which are also shown in Table 3 together with ε, σ; *T* is the absolute temperature; and *x* is the experimental mole fraction solubility of the 3-methoxy-*N*-phenylaniline and 3-(methylthio)-*N*-phenylaniline.

Table 1. Experimental Mole Fraction Solubilities of 3-Methoxy-*N*-phenylaniline in Liquid Solvents at Temperature *T* and Pressure *p* = 0.1 MPa and Their Relative Deviations

T/K	*x*	ε/%	*T*/K	*x*	ε/%
Methanol					
287.25	0.0134	0.7463	311.85	0.0478	2.3012
291.95	0.0174	1.7241	316.25	0.0579	0.1727
296.65	0.0214	1.8691	321.25	0.0724	1.3812
301.15	0.0268	2.2388	327.15	0.0972	0.3086
305.35	0.0339	0.2950			
Ethyl Acetate					
287.15	0.1950	3.0256	311.25	0.3661	0.4370
291.05	0.2246	0.6679	316.25	0.4075	0.1963
295.55	0.2538	1.2214	321.35	0.4423	2.3287
300.18	0.2831	0.6005	326.25	0.5003	0.1199
306.35	0.3288	0.8516	330.15	0.5432	0.7364
Acetone					
287.25	0.2375	0.8000	308.15	0.3608	0.8038
292.85	0.2643	0.1135	313.05	0.4074	0.3682
298.95	0.3000	0.9000	317.55	0.4562	0.3946
303.05	0.3272	0.9169	321.75	0.5134	0.4090
1,2-Dichloroethane					
287.65	0.1489	1.6118	313.15	0.3554	1.6882
292.30	0.1821	0.3844	318.85	0.4014	0.0997
297.35	0.2162	0.6013	324.25	0.4433	2.0528
302.55	0.2581	0.0000	329.55	0.5018	0.0598
308.65	0.3122	0.8648	333.75	0.5446	0.6978
Chloroform					
290.25	0.1807	0.3320	311.50	0.35041	0.3681
295.25	0.2176	0.1379	315.50	0.3861	0.2331
300.55	0.2580	0.2713	319.80	0.4240	0.2594
306.15	0.3083	0.9731	323.13	0.4556	0.2853

The relative deviations of 3-methoxy-*N*-phenylaniline and 3-(methylthio)-*N*-phenylaniline are also given in Tables 1 and 2, respectively. The relative deviation ε is defined as

$$\varepsilon = \frac{|x_{ci} - x_i|}{x_i} \cdot 100\ \% \tag{2}$$

where x_i represents the experimental solubility and x_{ci} represents the solubility calculated from Apelblat equation, and both are presented in Table 1.

The parameters *A*, *B*, and *C* were obtained by fitting the experimental solubility data and are presented in Table 3 together with the average relative deviations and the root-mean-square deviations. The average relative error σ is defined as

$$\sigma = \frac{1}{n}\sum_{i=1}^{n}\left|\frac{x_{ci} - x_i}{x_i} \cdot 100\ \%\right| \tag{3}$$

The root-mean-square deviation (rmsd) is defined as

$$\mathrm{rmsd} = \left[\frac{\sum_{i=1}^{n}(x_i - x_{ci})^2}{n}\right]^{1/2} \tag{4}$$

In the last two equations, *n* is the number of experimental points; x_i and x_{ci} represent the experimental and the calculated solubility values, respectively.

The calculated solubilities of 3-methoxy-*N*-phenylaniline and 3-(methylthio)-*N*-phenylaniline at different temperatures in five solvents (methanol, acetone, ethyl acetate, chloroform, and 1,2-dichloroethane) agree with the experimental data, which are also shown in Figures 4 and 5 as lines fitted from eq 1 and Table 3.

Table 2. Experimental Mole Fraction Solubilities of 3-(Methylthio)-*N*-phenylaniline in Liquid Solvents at Temperature *T* and Pressure *p* = 0.1 MPa and Their Relative Deviations

T/K	*x*	ε/%	*T*/K	*x*	ε/%
Methanol					
287.65	0.0115	2.6087	311.95	0.0608	0.4934
291.55	0.0160	2.5000	316.35	0.0761	0.2628
297.15	0.0235	1.7021	321.25	0.0951	0.0000
302.40	0.0342	0.2924	327.15	0.1209	0.0827
307.25	0.0460	0.8696			
Ethyl Acetate					
287.85	0.2309	2.5552	311.25	0.4522	0.0221
292.95	0.2810	2.0285	316.45	0.5163	0.2712
297.25	0.3110	0.0965	321.35	0.5732	1.0642
302.15	0.3573	0.2799	325.85	0.6435	0.0311
306.65	0.4033	0.3992	330.15	0.7112	0.3234
Acetone					
287.45	0.2543	1.5729	305.45	0.4384	0.0684
292.55	0.3058	0.6213	310.65	0.4996	0.0600
296.15	0.3431	1.2824	315.15	0.5513	0.7074
300.35	0.3808	0.2889	321.75	0.6434	0.3264
1,2-Dichloroethane					
287.65	0.1891	1.2692	315.15	0.4658	0.0215
292.30	0.2314	0.0864	319.75	0.5148	0.1166
296.85	0.2784	1.7241	324.25	0.5622	0.0711
300.95	0.3114	0.9313	329.55	0.615	0.0325
305.35	0.3602	0.0555	333.75	0.6544	0.0764
310.45	0.4154	0.1444			
Chloroform					
288.85	0.2260	0.5752	307.55	0.3912	0.1534
293.35	0.2630	0.1520	313.25	0.4487	0.3566
297.05	0.2960	0.7432	318.75	0.5114	0.3910
302.00	0.3378	0.1480	323.13	0.5575	0.1076

3-Methoxy-*N*-phenylaniline and 3-(methylthio)-*N*-phenylaniline have similar solubilities in these solvents due to similar structures. From Figures 4 and 5, it can be seen that the solubilities of the two solutes in all selected solvents increase with the increase of temperature, and it is also shown that the solubilities have huge differences in different types of solvents. Their solubilities in acetone, ethyl acetate, chloroform, and 1,2-dichloroethane are sensitive to temperature, while their solubilities in methanol have slight sensitivity to temperature. In the defined range of temperature, the solubilities of 3-methoxy-*N*-phenylaniline and 3-(methylthio)-*N*-phenylaniline in different solvents are in the following order: acetone > ethyl acetate > chloroform > 1,2-dichloroethane > methanol.

Corresponding to the empirical rule "like dissolves like" including "similar polarity" and "similar solubility parameter", the solubilities of 3-methoxy-*N*-phenylaniline and 3-(methylthio)-*N*-phenylaniline in hydrophilic solvents are higher than in hydrophobic solvents. Therefore, both 3-methoxy-*N*-phenylaniline and 3-(methylthio)-*N*-phenylaniline have low solubilities in polar hydrophilic methanol, while higher solubilities are present in hydrophobic acetone, ethyl acetate, chloroform, 1,2-dichloroethane, and toluene. Furthermore, the solubility of 3-methoxy-*N*-phenylaniline is higher than that of 3-(methylthio)-*N*-phenylaniline in the same solvent results from the discrepancies probably caused by crystalline form, melting point, and fusion enthalpy.

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Table 3. Parameters of the Modified Apelblat Equation and Deviations for 3-Methoxy-*N*-phenylaniline and 3-(Methylthio)-*N*-phenylaniline in Different Solvents

solute	solvent	A	B	C	r^2	σ/%	rmsd/%
3-methoxy-*N*-phenyl-benzenamine	methanol	−89.4819	−52.0402	15.0778	0.9994	0.9707	0.0006
	ethyl acetate	31.2580	−3331.9286	−3.7561	0.9981	1.0185	0.0043
	acetone	−269.9572	10432.6158	41.0237	0.9992	0.5882	0.0022
	1,2-dichloroethane	222.3408	−12530.4904	−31.9102	0.9989	0.8890	0.0039
	chloroform	250.4769	−13687.0610	−36.1554	0.9997	0.3575	0.0014
3-methylthio-*N*-phenyl-benzenamine	methanol	540.8698	−29609.2049	−78.1421	0.9999	0.9791	0.0003
	ethyl acetate	18.5608	−2987.2826	−1.6996	0.9994	0.7071	0.0034
	acetone	117.0435	−7423.1613	−16.3527	0.9993	0.6160	0.0027
	1,2-dichloroethane	300.6121	−16036.2253	−43.5407	0.9998	0.4117	0.0019
	chloroform	136.2206	−8315.6189	−19.2226	0.9998	0.3284	0.0013

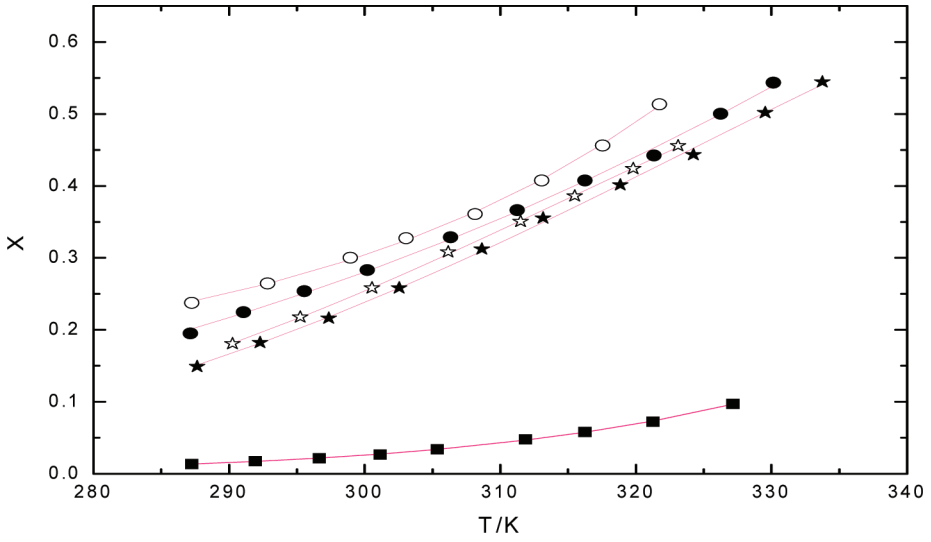

Figure 4. Experimental solubilities of 3-methoxy-*N*-phenylaniline in five solvents: ■, methanol; ★, 1,2-dichloroethane; ☆, chloroform; ●, ethyl acetate; ○, acetone and fitted lines.

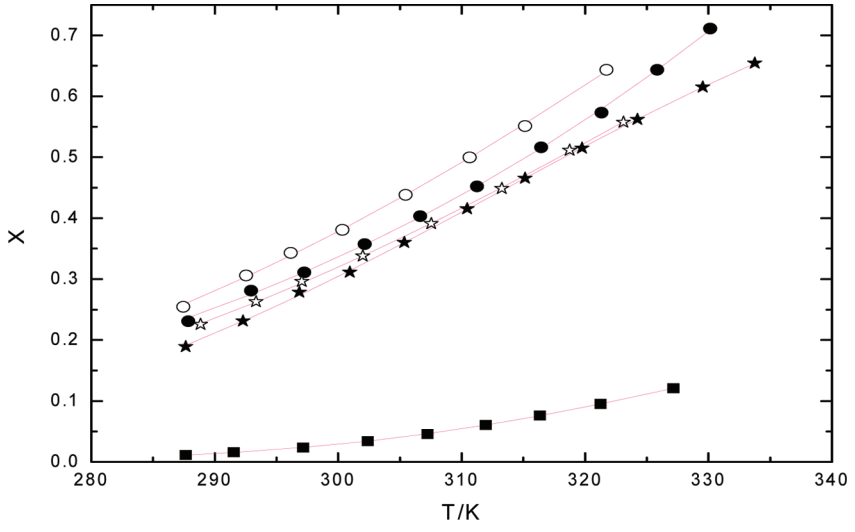

Figure 5. Experimental solubilities of 3-(methylthio)-*N*-phenylaniline in five solvents: ■, methanol; ★, 1,2-dichloroethane; ☆, chloroform; ●, ethyl acetate; ○, acetone and fitted lines.

From the results in Tables 1 and 2, we found that the solubilities of 3-methoxy-*N*-phenylaniline and 3-(methylthio)-*N*-phenylaniline were well-correlated with the Apelblat equation, and the relative errors ε were all almost less than 3 %.

CONCUSIONS

The solubilities of 3-methoxy-*N*-phenylaniline and 3-(methylthio)-*N*-phenylaniline in the studied organic solvents are functions of temperature and increase with the increase of temperature.

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Both 3-methoxy-*N*-phenylaniline and 3-(methylthio)-*N*-phenylaniline have low solubilities in polar hydrophilic methanol, while higher solubilities are present in hydrophobic acetone, ethyl acetate, chloroform, and 1,2-dichloroethane, which is because they can generate hydrogen bonds in polar hydrophilic solvents and only combine with hydrophobic solvents by van der Waals forces.

Furthermore, the solubility of 3-methoxy-*N*-phenylaniline in a solvent is higher than that of 3-(methylthio)-*N*-phenylaniline in the same solvent.

The solubilities in acetone, ethyl acetate, chloroform, and 1,2-dichloroethane vary more obviously with temperature than in methanol. The values calculated by the Apelblat model show good agreement with the experimental data with the related coefficients r^2 larger than 0.999. The experimental solubilities and correlation equation in this work can be used as essential data and a model in the purification process of 3-methoxy-*N*-phenylaniline and 3-(methylthio)-*N*-phenylaniline.

AUTHOR INFORMATION

Corresponding Author

*Tel.: +86-571-87951615; fax: +86-571-87951742; e-mail: supmoney@163.com.

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Notes

The authors declare no competing financial interest.

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