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SHORT ARTICLE

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Solubilities of Amino and Nitro Substituted Stilbene Sulfonic Acids: Investigations and Applications

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S *Supporting Information*

ABSTRACT: The recovery of 4,4′-dinitrostilbene-2,2′-disulfonic acid (DNS) and 4,4′-diaminostilbene-2,2′-disulfonic acid (DSD) and the purification of 4-amino-4′-nitrostilbene-2,2′-disulfonic acid (ANSD) are important processes during their individual production. To increase the yields of DNS, DSD, and the purity of ANSD, detailed studies on the solubilities of these three stilbene sulfonic acids (SSA) are necessary. Herein, the static analytical method was used to investigate the effects of pH, temperature, and ionic strength on the solubilities of these three SSA. On the basis of the results, new processes were proposed to recover more DNS and DSD during their production. In addition, a new purification method was developed to obtain ANSD with a purity of > 99 %.

1. INTRODUCTION

Stilbene sulfonic acids (SSA) are important intermediates widely used in the production of optical brighteners and synthetic dyes.[1] Among these SSA, 4,4′-dinitrostilbene-2,2′-disulfonic acid (DNS) is the most important one. It can be widely used in producing direct dyes, fluorescent brighteners, and mothproofing agents, and nearly 100 kilotons of DNS are needed every year.[2,3] 4-Amino-4′-nitrostilbene-2,2′-disulfonic acid (ANSD) is also an important SSA, which is produced from partial reduction of DNS. Both DNS and ANSD can be further reduced into 4,4′-diaminostilbene-2,2′-disulfonic acid (DSD), another widely used industry intermediate. The relationship among DNS, ANSD, and DSD is shown in Figure 1.

Normally, the oxidation yield from NTS to DNS is ~85 %. However, DNS is highly soluble in water and is difficult to be separated from the oxidation products. The general method for its recovery from the oxidation products is to evaporate the water to precipitate the DNS, but this process will lead to undesired loss of DNS.[2] As to the ANSD, it is usually produced from DNS by partial reduction with stoichiometric amounts of reducing agents (NaHS). However, because this stoichiometric reduction process is difficult to control, some DNS and DSD are usually mixed in the products, resulting in a low purity of the ANSD (~83 %). DSD is usually reduced from DNS by iron powder, with a subsequent acidification process to obtain DSD products from the reaction mixtures.[4] However, the specific effect of pH on this acidification process is still unclear. All of these problems above are related to the solubilities of the three SSA (DNS, ANSD, and DSD), but these data are still not present.

In this study, the solubilities of these three SSA (DNS, ANSD, and DSD) under different conditions were systematically investigated.[5,6] On the basis of the results, effective solutions were proposed for the separation and purification of these three SSA.

2. MATERIALS AND METHODS

2.1. Materials. DNS, DSD, and ANSD were provided by Huayu Chemical Co. (China) with purities of > 99 % (determined by high-performance liquid chromatography (HPLC)). Other chemical reagents and solvents (Merck) were either analytical or chromatography grade and used without further purification.

2.2. Methods. *2.2.1. Apparatuses and Procedures.* The measurements were carried out in a jacketed equilibrium glass bottle (150 mL). The bottle with magnetic stirring was sealed with a rubber stopper to prevent the solvent evaporation. The temperature was strictly controlled within ± 0.1 °C of the desired temperature with refrigerated and heating circulators (Julabo, Germany). The deviation of the temperature measurements was estimated to be ± 0.1 °C for all of the experiments. The pH value was measured within ± 0.01 by microBench pH600 (Singapore). The quantitative determination of the compounds in the solution was done with an ultraviolet−visible spectrophotometer (UV-2802H, Unico, China) and an HPLC system. The HPLC is Finnigan Surveyor HPLC integrated with quaternary gradient pumps, photodiode array detector, auto injector, degasser, and system controller (all from Thermo Fisher Scientific, San Jose, CA). A reversed-phase Hypersil ODS-2 C18 column (250 × 4.6 mm inner diameter (i.d.), 5 μm particle size) (Thermo Scientific, US), with a guard column made of the same packing material, was used for separation. HPLC conditions were as follows: 15:85 acetonitrile/ water−0.01 M ammonium acetate, 335 nm (flow: 0.8 $\text{mL}\cdot\text{min}^{-1}$). The mobile phase was filtered through a 0.45 μm PTFE filter and degassed using ultrasound before passing through the column. All of the measurements were repeated three times, and the average of the three measurements was considered to be the final solubility.

2.2.2. Solubility Measurements.

2.2.2.1. Effect of pH Values. The solubilities were measured by the static analytical method. For each experiment, excess amounts of DNS, ANSD, or DSD were added to 100 ± 5 mL of distilled water. The temperature was kept constant at 25 °C. Then, the solution was adjusted to the desired pH values by

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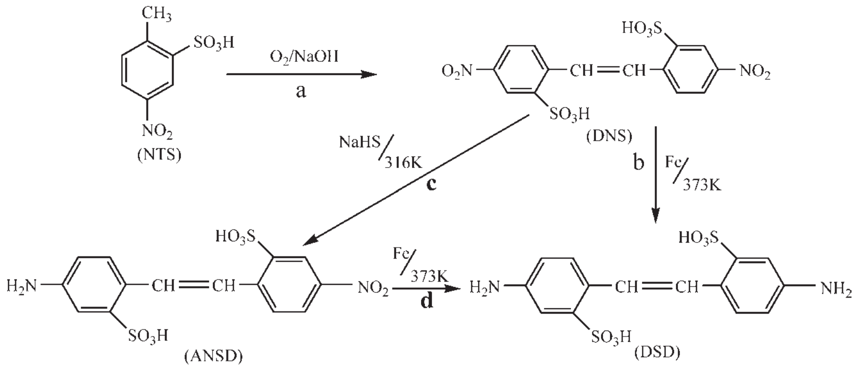

Figure 1. Production of DNS from oxidation of NTS (a); reduction of DNS to DSD by iron powder (b); reduction of DNS to ANSD by NaHS (c), and reduction of ANSD to DSD by iron powder (d).

addition of either sulfuric acid or sodium hydroxide aqueous solution with constant stirring. The solution was then allowed to stand to obtain the saturated solution in the upper layer without any undissolved substance. This dissolve process was also monitored by the UV−vis until the absorption of upper layer sample kept stable. Then, the pH of the saturated solution was measured again to get the real value used in the pH-solubility curve. After that, the samples were taken out and analyzed by UV−vis. Different dissolution and standing times were tested to determine suitable equilibrium time, and it was found that (5 and 10) h were enough for stirring and stillness, respectively.

2.2.2.2. Effect of Temperature at Different pH Values. An excess amount of DNS, ANSD, or DSD was added to 100 ± 5 mL of solvent. Then, the solution was adjusted to desired pH values with constant stirring. After that, the solution was heated to the desired temperatures ((20 to 50) °C). The stirring and stillness time were the same as in Section 2.2.2.2. Then, the pH was measured according to Section 2.2.2.1 and the samples taken out for analysis with UV−vis.

2.2.2.3. Effect of Ionic Strength. An excess amount of DNS, ANSD, or DSD and desired amounts of inorganic salt (KCl, NaCl, or NH_4Cl) were added into the jacketed bottle. Then, distilled water was added until the volume reached 100 mL. The temperature was kept constant at 25 °C. The stirring and stillness time were the same as Section 2.2.2.2. Finally, the samples were taken out and analyzed by UV−vis.

2.2.2.4. Purification of ANSD. The acidification recrystal process was as follows: First, 5 g of crude ANSD was dissolved with 20 mL of 1.5 M NaOH aqueous solution to get a homogeneous solution. KCl (0.3 g) was then added. The solution was stirred for 30 min and then filtered to remove the deposition. After that, the mother liquor was adjusted to pH 1.8 to precipitate ANSD (acidification recrystal product).

The alkalization recrystal process was as follows: The obtained ANSD was dissolved with 40 mL of 0.5 M NaOH aqueous solution at 50 °C. The solution was cooled down to 20 °C and then filtered to remove the DSD. The obtained filter cake was the final ANSD (alkalization recrystal product) with a higher purity. The analysis of the products in every process was performed by the HPLC system.

3. RESULTS AND DISCUSSION

3.1. Selection of Measure Method. All of these three SSA have cis−trans isomers, and the trans-isomers will be converted into their corresponding cis ones if they are exposed to light. In addition, the cis-isomers can be degraded to aldehydes as well as to the corresponding carboxylic acids with oxygen (Figure 2), and this will result in the deviation of the measurement.[7] Therefore, the static analytical method was selected to measure the solubilities of these three SSA to prevent the use of laser monitoring system in the dynamic method.[8,9] The detailed external calibration methods during the measurement are listed in the Supporting Information.

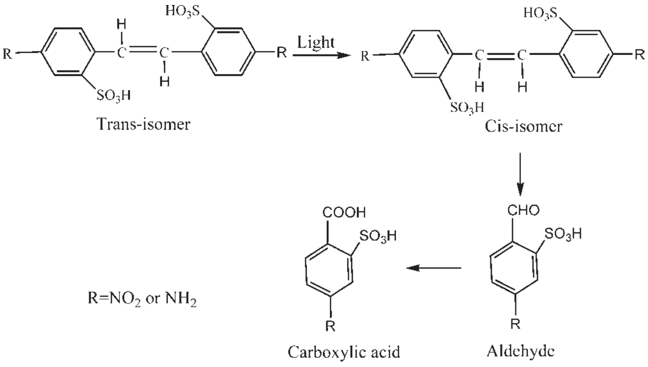

Figure 2. Degradation pathway of these SSA under the light.

Table 1. Solubilities of DNS, ANSD, and DSD at Different pH Values

DNS		ANSD		DSD	
pH	solubility/g·L^{-1}	pH	solubility/g·L^{-1}	pH	solubility/mg·L^{-1}
0.81	97.399	0.75	5.196	0.56	22.012
1.05	86.338	1.32	3.842	0.90	12.039
1.45	79.015	1.80	3.106	1.30	7.162
1.98	76.919	2.15	3.300	1.58	4.613
2.47	74.217	2.54	3.896	2.08	3.295
3.02	73.434	2.84	4.548	2.45	3.295
3.58	72.753	3.05	5.306	3.05	4.745
4.03	72.373	4.20	9.852	3.33	6.986
4.64	72.752	4.80	12.563	3.56	12.039
5.98	75.076	5.28	15.379	3.90	17.970
6.42	77.702	5.82	18.302	4.21	58.770
7.42	81.035	6.18	20.198	4.31	106.292

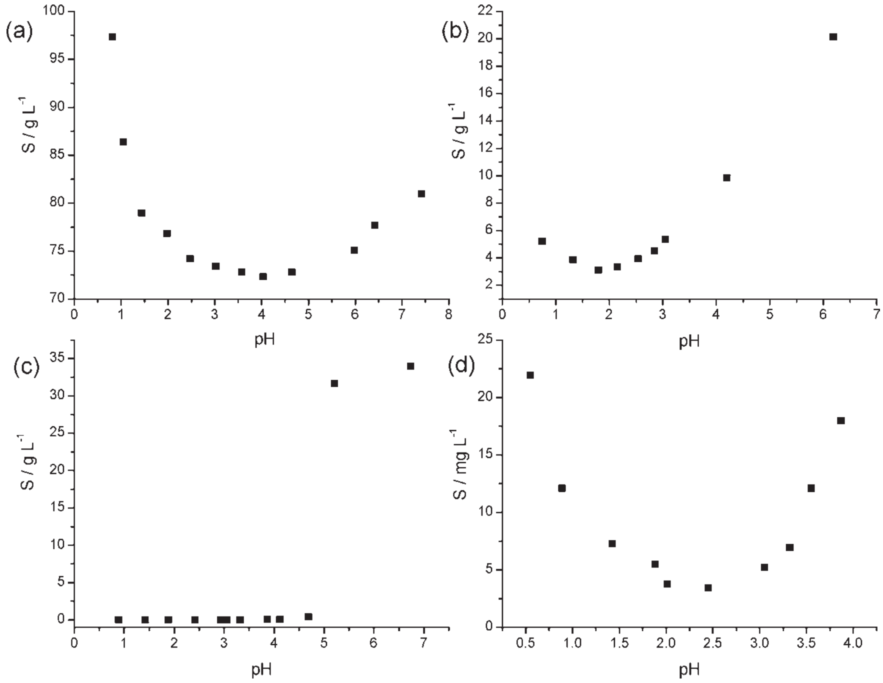

Figure 3. Solubility of DNS (a), ANSD (b), and DSD (c, d) with increasing pH values; d is intercepted from c (pH < 4.0) to show the curve of c clearly.

3.2. Effect of pH Values.

The solubilities of these three SSA are affected strongly by pH values, so they are usually recovered by precipitation in acidic conditions during their production. To get their accurate solubility data responding to the change of pH, the effects of pH values on their solubilites were investigated in Section 2.2.2.1, and the results are shown in Table 1 and Figure 3.

Figure 3a shows the solubility of the DNS decreases with pH increasing from 0.5 to 4.0 and then increases with pH increasing from 4.0 to 7.5. Similar trends were also observed for ANSD and DSD, with different lowest solubilities at pH 1.8 and 2.45, respectively (Figure 3b and c). In addition, the solubility of DNS is the best, but its variety is the smallest with the change of pH. The solubility of DSD is the worst, as only 3.295 $\text{mg} \cdot \text{L}^{-1}$ at pH 2.45. However, the variety of DSD solubility is the largest, and it is 10^4 times more than that at pH 2.5.

All of these three SSA are strong acids, and the most acidic $\text{p}K_\text{a}$ of them are −1.61, −1.31, and −1.58 for DNS, ANSD, and DSD, individually (counted by ACD/Laboratories Software V11.02). Therefore, there will be too much deviation to investigate the effects of pH on their solubilities. Herein, the effects of pH on their solubilities were described by the parabolic equation:

$$S - S_0 = a(\text{pH} - \text{pH}_0)^2 \tag{1}$$

where S is the factual solubility of some SSA, S_0 is the smallest solubility, the corresponding pH of the solution is pH_0, and a is a empirical constant (pH range from 1.0 to 4.0). The values of a, pH_0, and corresponding S_0 obtained from the experimental solubility data in the systems are listed in Table 2. The root-mean-square deviations (rmsd's) for the parabolic equation are also listed in Table 2. The rmsd is defined as:

$$\text{rmsd} = \left[\sum_{i=1}^{N} (x_i^{\text{cal}} - x_i^{\text{exp}})^2/N\right]^{1/2} \tag{2}$$

where x_A^{cal} is the solubility calculated from eq 1, x_A^{exp} is the experimental value of solubility, and N is the number of experimental points.

Table 2. Parameters of eq 1 and rmsd Values

compound	pH_0	$S_0/\text{g} \cdot \text{L}^{-1}$	a	rmsd
DNS	4.46	70.754	1.449	2.175
ANSD	1.84	3.331	1.183	0.158
DSD	2.25	$2.227 \cdot 10^{-3}$	5.450	0.820

It can be found from Table 2 that the calculated solubilities of the three SSA are in good agreement with the experimental data, which indicates that the parabolic equation can be used to describe the effects of the pH value on the solubilities of them.

3.3. Effect of Temperature at Different pH Values.

Temperature is another important factor that affects the solubilities of these SSA, so the effects of temperature at different pH values were investigated in Section 2.2.2.2. The results are shown in Table 3 and Figure 4. It can be found in Figure 4 that the solubilities of these three SSA increase with increasing temperature. The largest solubility variety is DNS at pH 7.42, while the smallest is DSD at pH 2.01. Therefore, during the recovery of DNS, a lower temperature is necessary, and the pH does not have the obvious effect. Conversely, during the recovery of DSD, a lower pH value ~2.0 is necessary, and the temperature does not have obvious effect on its solubility. For ANSD, a lower pH as well as lower temperature is beneficial to get a higher recovery yield.

The obtained solubilities were used to calculate the mole fraction solubility (x_A) based on the following equation:

$$x_\text{A} = \frac{m_\text{A}/M_\text{A}}{m_\text{A}/M_\text{A} + m_\text{S}/M_\text{S}} \tag{3}$$

where m_A and m_S represent the mass of the solute and solvent, respectively, and M_A and M_S are the molecular weight of the solute and solvent, respectively. The relationship between the mole fraction and the temperature can be described by the modified Apelblat equation:

Table 3. Solubilities of DNS, ANSD, and DSD at Different pH Values and Temperatures

	DNS/g·L^{-1}			ANSD/g·L^{-1}			DSD/mg·L^{-1}		
pH =	7.42	3.53	2.05	4.30	3.01	2.04	4.31	3.50	2.01
20 °C	68.618	65.018	65.346	5.237	4.261	2.985	99.074	10.074	2.910
25 °C	83.028	75.030	76.913	6.842	5.025	3.272	106.186	12.089	3.588
30 °C	97.986	84.947	87.706	7.946	5.645	3.893	134.055	14.586	4.035
35 °C	120.213	104.289	107.804	9.458	6.364	4.357	185.775	17.220	4.793
40 °C	149.596	125.635	129.676	11.976	7.612	4.862	266.545	20.031	5.455
45 °C	183.924	149.897	157.608	13.915	9.553	6.725	429.319	23.715	5.988
50 °C	219.082	193.247	199.712	17.370	13.236	9.874	707.267	29.430	6.879

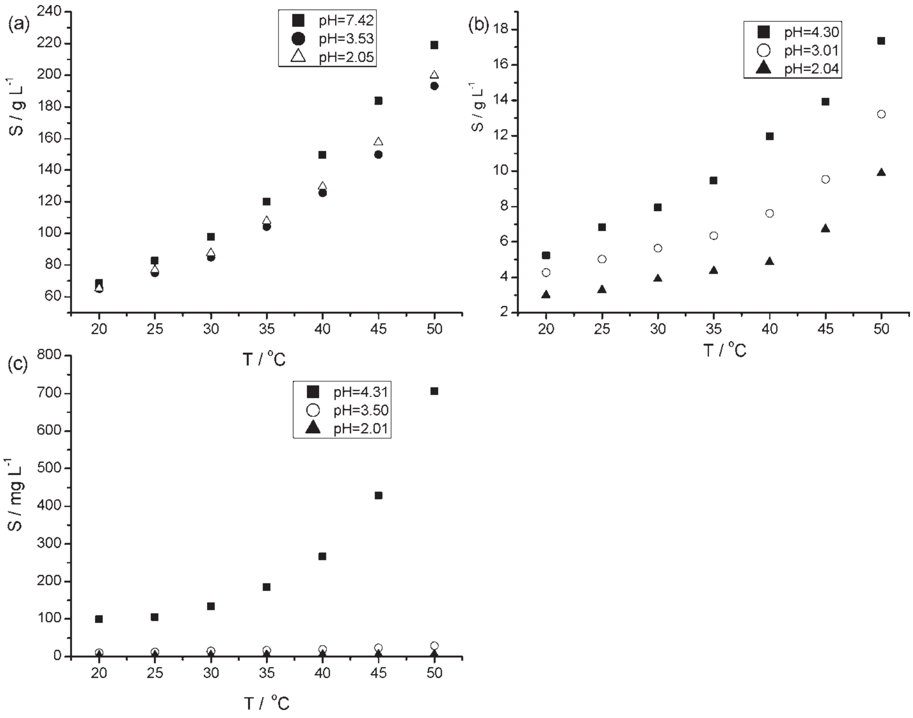

Figure 4. Solubilities of DNS (a), ANSD (b), and DSD (c) with increasing temperature at three different pH values.

$$\ln x_A = A + \frac{B}{T} + C \ln T \qquad (4)$$

where T is the absolute temperature and A, B, and C are empirical constants. The values of A, B, and C obtained from the experimental solubility data in the systems are listed in Table 4. The rmsd's for the modified Apelblat equation are also listed in Table 4.

It can be found from Table 4 that the calculated solubilities of the three SSA are in good agreement with the experimental data, which indicate that the modified Apelblat equation can be used to correlate the solubility data of these three compounds.

Table 4. Parameters of eq 4 and rmsd in Water at Different pH Values

compound	pH	A	B	C	10^4 rmsd
DNS	7.42	−262.261	8595.363	39.975	0.825
	3.53	−605.514	24538.106	90.817	0.711
	2.05	−518.104	20468.720	77.875	0.471
ANSD	4.30	−1194.700	51180.085	178.006	0.154
	3.01	−792.709	32986.367	118.232	0.151
	2.04	−74.832	−71.610	11.750	0.177
DSD	4.31	−2291.868	99103.823	342.591	0.205
	3.5	−169.226	4490.698	25.348	0.0181
	2.01	196.005	−11704.17	−29.438	0.00364

3.4. Effect of Ionic Strength. Although the effects of pH and temperature on the solubilities of these three SSA were investigated above, satisfactory solutions for the recovery of DNS were still not found. Therefore, the effects of ionic strength on the solubilities of them were investigated in Section 2.2.2.3, and the results were shown in Table 5 and Figure 5. As for DNS, we take its disodium salt (Na_2DNS) for the investigation. This is because the produced DNS was present in the form of disodium before the separation. As for DSD and ANSD, the ionization did not affect the pH of their solution too much for two reasons: (1) their solubilities are very small; (2) the presence of $-NH_2$

(alkaline group). Therefore, we investigated the solublities of ANSD and DSD in their intrinsic forms.

As shown in Figure 5, K^+ is the most effective ionic to decrease the solubility of DNS, while NH_4^+ has the slightest effect. The solubility of DNS can decrease from (82.88 to 0.54) $g \cdot L^{-1}$ with the concentration of K^+ increasing from (0 to 0.2) $mol \cdot L^{-1}$. The effects of these ionics on decreasing the solubility of ANSD follow the same order with that of DNS: $K^+ > Na^+ > NH_4^+$. Surprisingly, the solubility of ANSD can increase with the concentration of NH_4^+ increasing, and the so-called salting in effect should have occurred.[10] As for DSD, a different order of $Na^+ > NH_4^+ > K^+$ was found. However, low concentrations ($< 0.1\ mol \cdot L^{-1}$) of K^+ and NH_4^+ can increase the solubility of DSD, which should be caused by salting-in effects, too.

The effects of the ionic strength (I) on the solubilities of these three SSA can be described by the Cohn equation:

$$\log S = \beta - K_s I \tag{5}$$

where S is the solubility, β is the empirical constant, and K_s is salting constant. The values of β and K_s obtained from the experimental solubility data in the systems and the rmsd's for this equation are all listed in Table 6.

It can also be found from Table 6 that the calculated solubilities of the three SSA are in agreement with the experimental data, which indicate that the Cohn equation can be used to correlate the solubility data of these three compounds with different ion species present.

3.5. Separation and Purification. Based on the results above, effective methods to recover and purify these three SSA can be proposed. For DNS, the addition of 0.2 $mol \cdot L^{-1}$ KCl can decrease the solubility from (82.88 to 0.54) $g \cdot L^{-1}$, and more than 98.3 % of the DNS dissolved in the water can be

Table 5. Solubilities of DNS, ANSD, and DSD with Different Ionic Strengths

	DNS/$g \cdot L^{-1}$			ANSD/$g \cdot L^{-1}$			DSD/$mg \cdot L^{-1}$		
	Na^+	K^+	NH_4^+	Na^+	K^+	NH_4^+	Na^+	K^+	NH_4^+
0[a]	82.88	82.88	82.88	5.326	5.326	5.326	106.7	106.7	106.7
0.1	78.656	56.849	28.023	5.793	4.867	4.948	110.421	98.267	120.402
0.2	58.51	39.091	1.898	5.895	3.682	4.131	96.869	85.408	104.36
0.3	52.579	21.618	0.02146	6.049	3.105	4.004	80.752	69.625	91.437
0.4	37.94	14.027	0.0065	6.499	2.764	3.94	73.853	55.434	83.295

[a] The concentrations of Na^+, K^+, and NH_4^+.

Table 6. Parameters of eq 5 and rmsd Values

compound	ion species	β	K_s	rmsd
DNS	NH^+_4	1.94745	0.85517	0.0265
	K^+	2.22362	11.56672	0.437
	Na^+	1.94245	1.96443	0.0240
ANSD	NH^+_4	0.73226	−0.19258	0.00728
	K^+	0.71747	0.35305	0.0196
	Na^+	0.73538	0.76401	0.0187
DSD	NH^+_4	−0.94496	0.43758	0.0189
	K^+	−0.92666	0.37096	0.0224
	Na^+	−0.95199	0.69491	0.0170

Table 7. Purity Data of ANSD

sample	DNS (%)[a]	DSD (%)[b]	ANSD (%)[c]
crude product	15.17	1.58	83.26
acidification recrystal product	0.23	1.82	97.95
alkalization recrystal product	0.15	0.01	99.84

[a] Mass percent of DNS. [b] Mass percent of DSD. [c] Mass percent of ANSD.

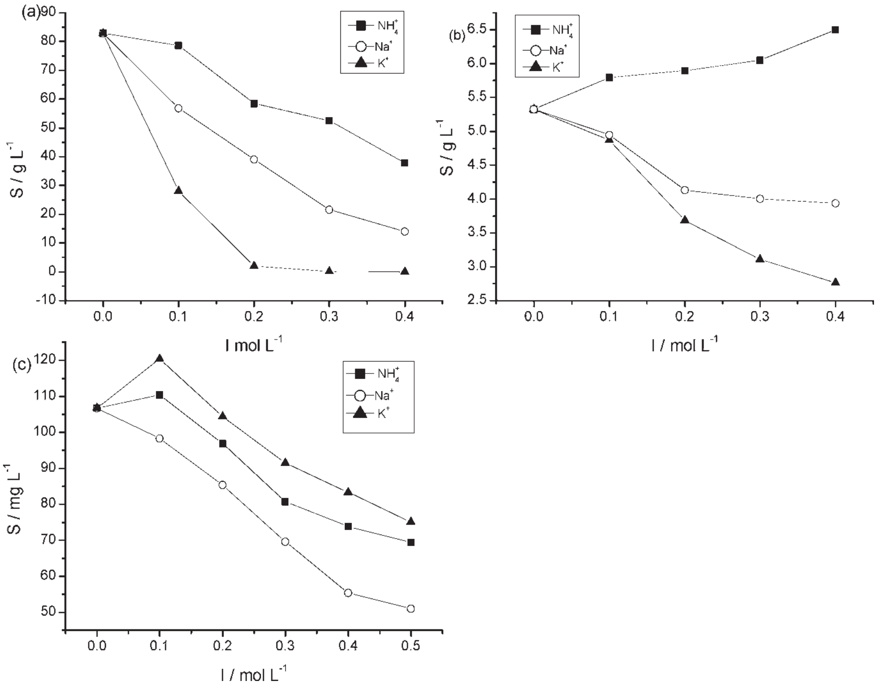

Figure 5. Effects of different ionics (K^+, Na^+, NH_4^+) on the solubilities of Na_2DNS (a), ANSD (b), and DSD (c); I: ionic strength.

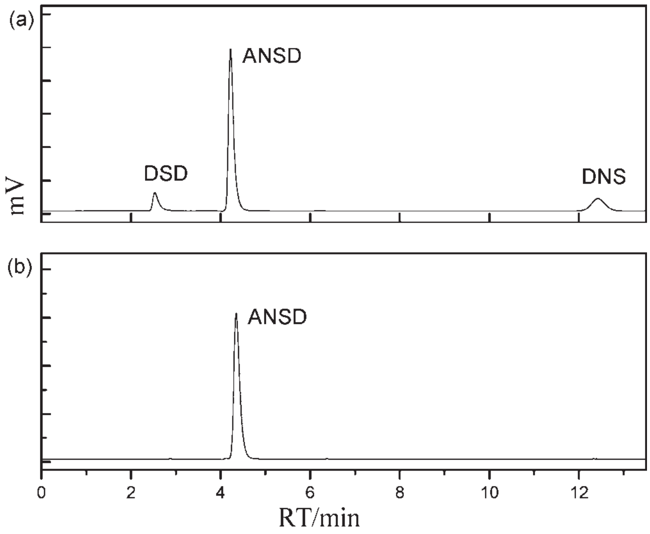

Figure 6. Chromatograph of (a) crude ANSD and (b) final ANSD after purification.

recovered. As for the recovery of DSD, a lower pH was thought to be beneficial for a long time, so pH ∼1 was selected before. However, it can be found from Figure 2d that the selection of pH 2.5 can get more DSD. This new pH value can also decrease the waste of acid during the acidification process.

As for ANSD, purification has always been a difficult problem, and the purity of its industry product is only 83 % mixed with DNS and DSD. Therefore, a new purification method including two recrystal processes (Section 2.2.2.4) was developed, and the results are listed in Table 7. The so-called acidification process was used to remove the DNS in the crude ANSD, and the alkalization process was used to remove the DSD. The chromatographs of the crude ANSD and purified ANSD were shown in Figure 6a and b. After the complete purification process, the purity of final ANSD can be > 99 %.

4. CONCLUSION

The static analytical method was used to investigate the effects of pH value, temperature, and ionic strength on the solubilites of DNS, ANSD, and DSD. Surprising solubility—pH and solubility—ionic strength curves were obtained for them, and these curves can be described by the parabolic equation and Cohn equation, individually. On the basis of these results, new processes were proposed to recover more DNS and DSD during their production. In addition, a new purification method was also developed to produce ANSD with a purity of > 99 %.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. External calibration of DNS, ANSD, and DSD in Table S1 (for UV—vis) and Table S2 (for HPLC). This material is available free of charge via the Internet at http://pubs.acs.org.

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