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Thermodynamic Properties of 1,5-Pentanediamine Adipate Dihydrate in Three Binary Solvent Systems from 278.15 K to 313.15 K

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Abstract: In this work, solubility data of 1,5-pentanediamine adipate dihydrate in binary solvent systems of water + methanol, water + ethanol and water + N,N-dimethylformamide were experimentally measured via a static gravimetric method in the temperature range from 278.15 K to 313.15 K under atmospheric pressure. The results indicated that the solubility of 1,5-pentanediamine adipate dihydrate increased with the rising of temperature in all the selected binary solvent systems. For water + N,N-dimethylformamide, solubility increased as the mole fraction of water increased. However, the rising tendency changed when the temperature was higher than 303.15 K for water + methanol, and it would show a cosolvency phenomenon for water + ethanol. Furthermore, the solubility data were fitted with modified an Apelblat equation, NRTL model, combined nearly ideal binary solvent/Redlich Kister (CNIBS/R-K) model and Jouban–Acree model. The calculation results agreed well with the experimental data. Finally, the mixing thermodynamic properties of 1,5-pentanediamine adipate dihydrate in all tested solvents were calculated based on the experimental data and NRTL model.

Keywords: 1,5-pentanediamine adipate dihydrate; solubility; mixing thermodynamics

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1. Introduction

1,5-pentanediamine adipate dihydrate ($C_{11}H_{24}O_4N_2 \cdot 2H_2O$, CAS registry No. 2156592-12-8, Figure 1), is major monomer for the synthesis of bio-based polyamide 56 fiber [1]. Due to its excellent mechanical properties, heat resistance, abrasion resistance and self-lubricity, polyamide 56 is not only a renewable substitute for traditional materials, but also a unique and novel polymer applied in the textile and industrial plastics [2].

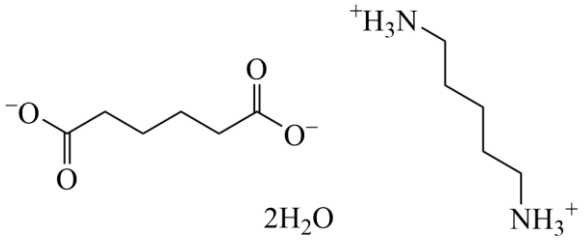

Figure 1. Molecular structure of 1,5-pentanediamine adipate dihydrate.

The performance of the polymer material is directly related to the purity of the polymerized monomer since it is greatly sensitive to impurities [3]. Therefore, the purification stage of 1,5-pentanediamine adipate dihydrate plays a critical role during the manufacturing process [4,5]. Crystallization, as a vital separation and purification process, is widely used in the pharmaceutical and food industries. As such, it is essential to know the physicochemical and thermodynamic properties of 1,5-pentanediamine adipate dihydrate to design and optimize the crystallization process [6]. Considering the high solubility of 1,5-pentanediamine adipate dihydrate in water, anti-solvent crystallization is a reasonable and efficient crystallization method for purifying it [7,8]. Besides, the temperature range from 278.15 K to 313.15 K is commonly used in industrial manufacturing and the product contains two molecules of water. However, no reports about the solubility of 1,5-pentanediamine adipate dihydrate in this temperature range have been published.

In this work, the solubility data of 1,5-pentanediamine adipate dihydrate in water + methanol, water + ethanol and water + N,N-dimethylformamide were determined in the range of 278.15 K to 313.15 K under 0.1 MPa. Besides, the modified Apelblat equation model, NRTL model, combined nearly ideal binary solvent/Redlich Kister (CNIBS/R-K) model, and Jouyban–Acree model were applied to the fitting of the experimental solubility data, respectively. Finally, the mixing thermodynamic properties, including the mixing enthalpy, the mixing entropy and the Gibbs free energy of 1,5-pentanediamine adipate dihydrate in different binary solvents were calculated and discussed.

2. Experimental Section

2.1. Materials

1,5-pentanediamine adipate dihydrate (≥0.99 mass fraction) was offered by Hebei Meibang Engineering Technology Co., Ltd. (Hebei, China). Deionized water was prepared by an ultrapure water system (YPYD Co., Nanjing, China) in the laboratory. Methanol and ethanol were purchased from Guangda Pharmaceutical Co., Ltd. (Tianjin, China), and N,N-dimethylformamide was purchased from Benchmark Chemical Reagent Co., Ltd. (Tianjin, China). More details about the materials are listed in Table 1. All chemicals were used without further purification.

Table 1. Sources and mass fraction purity of chemicals.

Chemical Name	CAS Reg. No.	Mass Fraction Purity	Source	Analysis Method
1,5-pentanediamine adipate dihydrate	2156592-12-8	≥0.99	Hebei Meibang Engineering Technology Co., Ltd., of China	HPLC [a]
1,5-pentanediamine adipate	13534-23-1	≥0.99	Hebei Meibang Engineering Technology Co., Ltd., of China	HPLC [a]
methanol	67-56-1	≥0.995	Tianjin Guangda Pharmaceutical Co., Ltd., China	GC [b]
ethanol	64-17-5	≥0.997	Tianjin Guangda Pharmaceutical Co., Ltd., China	GC [b]
DMF	68-12-2	≥0.995	Tianjin Benchmark Chemical Reagent Co., Ltd., China	GC [c]

[a] High performance liquid chromatography, determined by Hebei Meibang Engineering Technology Co., Ltd., of China. [b] Gas chromatography, determined by Tianjin Guangda Pharmaceutical Co., Ltd., China. [c] Gas chromatography, determined by Tianjin Benchmark Chemical Reagent Co., Ltd., China.

2.2. Apparatus and Methods

The gravimetric method was used to determine the solubility of 1,5-pentanediamine adipate dihydrate in different binary solvent mixtures [9]. Known mass of solvent and excess 1,5-pentanediamine adipate dihydrate were added to a 100 mL crystallizer. A constant temperature water bath (Nanjing Xianou Instrument Manufacturing Co., Ltd., China) was used to control the solution at specified temperature. The solution was agitated for 12 h to ensure that the solution reaches solid-liquid equilibrium. Then, the stirring was stopped and the solution was kept static for 3 h until the suspended particles settled down.

After that, the samples were drawn with a 5 mL syringe and filtered through a 0.45 μm nylon membrane into 50 mL pre-weighed beakers and the total weight was measured immediately. Besides, KF analyzer (C20s, Mettler Toledo, Switzerland) was used to determine the amount of water in the saturated solution after equilibration. Finally, the beakers were put into a vacuum oven and dried at temperature of 323.15 K. The quality of the beaker with the samples was recorded periodically until the total weight did not change any more, to ensure that there were no solvents in the solid after the drying treatment. The solubility data of 1,5-pentanediamine adipate dihydrate were calculated from the mass of the remaining solid. The crystal form of the dried solid was determined using powder X-ray diffraction (PXRD). All the samples were weighed by an analytic balance (AL204, Mettler Toledo, Switzerland) with an accuracy of ±0.0001 g. The procedure was repeated three times to determine the error of the experiments.

The solubility of 1,5-pentanediamine adipate dihydrate described in the mole percentage x_p was calculated by Equation (1):

$$x_p = \frac{\frac{m_p}{M_p}}{\frac{m_p}{M_p} + \frac{m_w}{M_w} + \frac{m_i}{M_i}} \tag{1}$$

where x, m and M represent the mole fraction solubility, mass and molar mass, respectively. The subscript p, w, and i represent 1,5-pentanediamine adipate dihydrate, water and the other organic solvents, respectively. The mass of 1,5-pentanediamine adipate dihydrate (m_p) was calculated by using experimental results. Besides, the masses of water and organic solvents were determined by the pre-designed mixed solvents of different compositions.

The samples were dried to completely convert into anhydrous 1,5-pentanediamine adipate and the mass of dissolved 1,5-pentanediamine adipate dihydrate was calculated by Equation (2):

$$m_p = \frac{M_p}{M_a} m_a \tag{2}$$

where m_a and M_a represent the mass and molar mass of anhydrous 1,5-pentanediamine adipate, respectively. The mole fraction solubility of anhydrous 1,5-pentanediamine adipate was calculated as follows:

$$x_a = \frac{\frac{m_p}{M_p}}{\frac{m_w}{M_w} + \frac{m_i}{M_i} + 3\frac{m_p}{M_p}} \tag{3}$$

The initial mole fraction of water x_w in the mixed solution was calculated as follows:

$$x_w = \frac{\frac{m_w}{M_w}}{\frac{m_w}{M_w} + \frac{m_i}{M_i}} \tag{4}$$

where m_w and m_i were determined by an analytic balance during the process of preparing mixing solvent. The final mole fraction of water x_w^0 in three binary solvent mixtures was calculated as follows:

$$x_w^0 = \frac{\frac{m_w}{M_w} + 2\frac{m_p}{M_p}}{\frac{m_w}{M_w} + \frac{m_i}{M_i} + 2\frac{m_p}{M_p}} \tag{5}$$

2.3. Characterization of 1,5-Pentanediamine Adipate Dihydrate

The crystal form of 1,5-pentanediamine adipate dihydrate, before and after solubility measurement, was determined using powder X-ray diffraction (PXRD), which was carried out on Rigaku D/max-2500 (Rigaku, Japan). The diffraction angle (2θ) ranged from 2° to 40° with a scanning rate of 8°/min and step size of 0.02°.

In order to characterize the melting temperature and melting enthalpy of 1,5-pentanedi amine adipate dihydrate, the thermal behaviors of 1,5-pentanediamine adipate dihydrate were measured using TGA/DSC (Mettler Toledo, Zurich, Switzerland) under the protection

of nitrogen. Besides, the thermal behaviors of dehydrated raw materials were also detected to eliminate the influence of dehydration peaks. The measurements were conducted within the temperature ranging from 298.15 K to 473.15 K at a heating rate of 3 K/min. The DSC instrument was calibrated by indium and zinc, of which the melting temperature was measured three times. The standard uncertainties of melting points and solid-to-solid transition temperature were estimated to be 1 K while the relative standard uncertainties of melting enthalpy and solid-to-solid transition enthalpy were estimated to be 5%.

3. Thermodynamic Models

3.1. The Modified Apelblat Equation

Combined with the Clausius–Clapeyron relationship, Apelblat et al. proposed a semi-empirical model in 1999 as Equation (6) [10,11].

$$\ln x = A + \frac{B}{T} + C \ln T \tag{6}$$

where x is the mole fraction solubility of solute at absolute temperature T. A, B and C are model constants.

3.2. NRTL Equation

The solubility of solute can be expressed by a general thermodynamic model, which is written as follows [12].

$$\ln x = -\ln \gamma_i + \frac{\Delta_f H}{R}\left(\frac{1}{T_m} - \frac{1}{T}\right) - \frac{1}{RT}\int_{T_m}^{T} \Delta C_p dT + \frac{1}{R}\int_{T_m}^{T} \frac{\Delta C_p}{T} dT \tag{7}$$

where γ_i stands for the activity coefficient, $\Delta_f H$ is the enthalpy of fusion, R is the gas constant; T and T_m refer to the solution temperature and the melting point of solute, respectively, ΔC_p refers to the difference of the molar heat capacity between melting state and solid state of the solute. When a solid undergoes a phase transition, the solubility equation should include a term for the contribution of the transition as following [13].

$$\ln x = -\ln \gamma_i + \frac{\Delta_f H}{R}\left(\frac{1}{T_m} - \frac{1}{T}\right) + \frac{\Delta_{tr} H}{R}\left(\frac{1}{T_{tr}} - \frac{1}{T}\right) - \frac{1}{RT}\int_{T_m}^{T} \Delta C_p dT + \frac{1}{R}\int_{T_m}^{T} \frac{\Delta C_p}{T} dT \tag{8}$$

where $\Delta_{tr} H$ and T_{tr} stand for the enthalpy of the transition and the transition temperature of the solute, respectively.

Considering the last two parts of the Equation (8) are less important than the first three parts due to the negligible value of ΔC_p, the solubility of the solute can be expressed by a simplified thermodynamic model, which is written as follows [14].

$$\ln x = \frac{\Delta_f H}{R}\left(\frac{1}{T_m} - \frac{1}{T}\right) + \frac{\Delta_{tr} H}{R}\left(\frac{1}{T_{\mathrm{tr}}} - \frac{1}{T}\right) - \ln \gamma_i \tag{9}$$

The nonrandom two-liquid (NRTL) model, which is based on the theory of solid–liquid phase equilibrium can be used to calculate the activity coefficients. It can be shown as Equations (10)–(13) [15,16].

$$\begin{aligned} \ln \gamma_i = {} & \frac{\left(G_{ji}x_j + G_{ki}x_k\right)\left(\tau_{ji}G_{ji}x_j + \tau_{ki}G_{ki}x_k\right)}{\left(x_i + G_{ji}x_j + G_{ki}x_k\right)^2} + \frac{\tau_{ij}G_{ij}x_j^2 + G_{ij}G_{kj}x_j x_k\left(\tau_{ij} - \tau_{kj}\right)}{\left(x_j + G_{ij}x_i + G_{kj}x_k\right)^2} \\ & + \frac{\tau_{ik}G_{ik}x_k^2 + G_{ik}G_{jk}x_j x_k\left(\tau_{ik} - \tau_{jk}\right)}{\left(x_k + G_{ik}x_i + G_{jk}x_j\right)^2} \end{aligned} \tag{10}$$

where i, j, k are the three components of the solution system. Model parameters τ_{ij} and G_{ij} can be calculated as follows:

$$G_{ij} = \exp\left(-\alpha_{ij}\tau_{ij}\right) \tag{11}$$

$$\tau_{ij} = \frac{\Delta g_{ij}}{RT} \tag{12}$$

$$\alpha_{ij} = \alpha_{ji} \tag{13}$$

where α_{ij} represents the non-randomness between i and j components and Δg_{ij} stands for the cross-interaction energy.

3.3. The CNIBS/R-K Model

The combined nearly ideal binary solvent/Redlich–Kister (CNIBS/R–K) model, which describes the relationship between solubility and solvent composition, is suitable for binary solvent systems [17]. It describes the relationship between solubility and solvent composition as Equation (14).

$$\ln x = x_a \ln X_a + x_b \ln X_b + x_a x_b \sum_{i=0}^{N} S_i (x_a - x_b)^i \tag{14}$$

where x_a, x_b stand for the initial mole fraction of water and organic solvents in binary solvent mixtures, respectively. X_a, X_b are the mole fraction solubility of 1,5-pentanediamine adipate dihydrate in pure water and organic solvents, respectively. S_i is the model constant and N refers to the number of the solvents.

For binary solvent systems, substituting $N = 2$ and $x_a = 1 - x_b$ into Equation (14) can result in a new simplified equation as following.

$$\ln x = B_0 + B_1 x_a + B_2 x_a^2 + B_3 x_a^3 + B_4 x_a^4 \tag{15}$$

where B_0 to B_4 are empirical model parameters.

3.4. The Jouyban–Acree Model

The Jouyban–Acree model is widely used to describe the solubility by considering both the composition of the solution and the temperature [18]. The model is expressed as Equation (16):

$$\ln x = x_a \ln X_a + x_b \ln X_b + x_a x_b \sum_{i=0}^{N} \frac{J_i (x_a - x_b)^i}{T} \tag{16}$$

Subsequently, Jouyban et al. proposed to combine the Jouyban–Acree model with the van't Hoff model to obtain a seven-parameters mixed model [19] as Equation (17).

$$\ln x = A_0 + A_1 x_a + \frac{A_2 + A_3 x_a + A_4 x_a^2 + A_5 x_a^3 + A_6 x_a^4}{T} \tag{17}$$

where A_0 to A_6 are empirical model parameters.

To evaluate the fitting accuracy, the average relative deviation (*ARD*) and root mean-square deviations (*RMSD*) were calculated [20,21].

$$ARD = \frac{1}{N} \sum_{i=1}^{N} \left| \frac{x_i^{\text{cal}} - x_i^{\text{exp}}}{x_i^{\text{exp}}} \right| \tag{18}$$

$$RMSD = \sqrt{\frac{\sum_{i=1}^{N} \left(x_i^{\text{cal}} - x_i^{\text{exp}} \right)^2}{N}} \tag{19}$$

where N stands for the total number of experiments. x_i^{exp} and x_i^{cal} refer to the experimental mole fraction solubility and calculated mole fraction solubility of 1,5-pentanediamine adipate dihydrate, respectively.

3.5. Solution Mixing Thermodynamics

For the ideal solution, its mixing properties, including Gibbs energy, enthalpy, and entropy, can be expressed as follows [22].

$$\Delta_m G^{id} = RT \sum_{i=1}^{n} x_i \ln x_i \tag{20}$$

$$\Delta_m H^{id} = 0 \tag{21}$$

$$\Delta_m S^{id} = -R \sum_{i=1}^{n} x_i \ln x_i \tag{22}$$

where x_i represent the mole fraction of each component. The mixing thermodynamic properties of the real solution system can be calculated by using Equation (23).

$$\Delta_m M = M^E + \Delta_m M^{id} \tag{23}$$

where M refers to the Gibbs free energy (G), enthalpy (H) or entropy (S); $\Delta_m M^{id}$ and M^E represent the mixing properties of the ideal solution and excess properties, respectively. Excess mixing properties (M^E) can be calculated using the Equations (24)–(26).

$$G^E = RT \sum_{i=1}^{n} x_i \ln \gamma_i \tag{24}$$

$$H^E = -RT^2 \sum_{i=1}^{n} x_i \left(\frac{\partial \ln \gamma_i}{\partial T} \right)_{P,x} \tag{25}$$

$$S^E = \frac{H^E - G^E}{T} \tag{26}$$

where γ_i refer to the activity coefficient, which will be calculated by the NRTL model in this work.

4. Results and Discussion

4.1. Identification and Characterization of Materials

The powder X-ray diffraction (PXRD) patterns of 1,5-pentanediamine adipate dihydrate are shown in Figure 2. It can be found that the 1,5-pentanediamine adipate dihydrate crystals obtained in this work remained unchanged in each experiment, indicating no phase transformation occurred during solid–liquid equilibrium. Furthermore, the results of random KF titration experiments for the cases with a large organic solvent content at the highest studied temperatures are shown in Table 2. It can be found that the amount of water $x_w^{0,KF}$ agrees with the calculated data in Tables 3–5, indicating no additional release of water from the hydrated solid phase upon equilibration.

Table 2. The amount of water x_w^0 upon equilibration.

Sample	$x_w^{0,KF}$
water + methanol (x_w = 0.360, T = 313.15 K)	0.562
water + ethanol (x_w = 0.447, T = 313.15 K)	0.553
water + DMF (x_w = 0.648, T = 313.15 K)	0.656

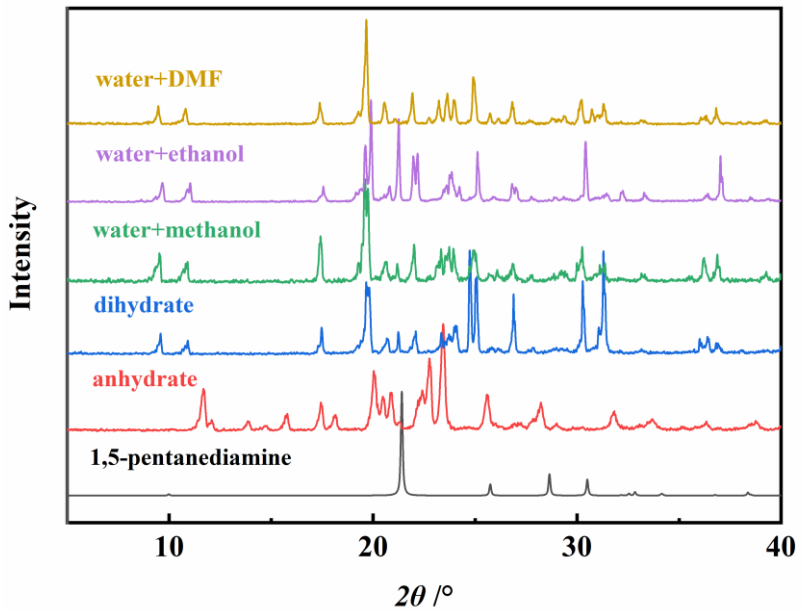

Figure 2. Powder X-ray diffraction pattern of raw material and residual solid in mixed systems: water + DMF (x_w = 0.648), water + ethanol (x_w = 0.447) and water + methanol (x_w = 0.360) at T = 298.15 K.

Table 3. Mole fraction solubility of 1,5-pentanediamine adipate dihydrate in water + methanol from 278.15 K to 313.15 K (p = 0.1 MPa) [a,b].

T/K	x_w^0	10^2x_a	$10^2x_p^{exp}$	$10^2x_p^{Apel}$	$10^2x_p^{NRTL}$	$10^2x_p^{RK}$	$10^2x_p^{JA}$
			x_w = 0.360				
278.15	0.432	5.412	6.029	5.738	5.934	6.036	5.795
283.15	0.440	5.896	6.641	6.837	7.027	6.641	6.944
288.15	0.455	6.976	8.055	8.132	8.117	8.062	8.270
293.15	0.474	8.233	9.793	9.654	9.439	9.793	9.789
298.15	0.488	9.158	11.14	11.43	11.27	11.14	11.52
303.15	0.520	11.17	14.29	13.53	13.05	13.74	13.49
308.15	0.535	11.74	15.85	15.97	15.93	15.87	15.71
313.15	0.569	13.86	19.01	18.82	18.98	18.89	18.21
			x_w = 0.491				
278.15	0.554	5.827	6.552	6.308	6.608	6.503	6.270
283.15	0.562	6.544	7.480	7.340	7.383	7.483	7.365
288.15	0.570	7.265	8.446	8.529	8.399	8.407	8.603
293.15	0.583	8.303	9.893	9.897	9.602	9.891	9.996
298.15	0.591	8.995	10.89	11.46	11.26	10.90	11.55
303.15	0.610	10.53	13.26	13.27	13.09	13.26	13.29
308.15	0.629	11.97	15.70	15.33	15.47	15.58	15.22
313.15	0.644	13.10	17.65	17.70	18.66	17.65	17.36
			x_w = 0.600				
278.15	0.651	6.044	6.830	6.730	7.161	6.956	6.703
283.15	0.658	6.797	7.816	7.692	7.777	7.794	7.744
288.15	0.664	7.455	8.704	8.786	8.652	8.772	8.901
293.15	0.673	8.434	10.08	10.02	9.708	10.09	10.18
298.15	0.679	9.043	10.97	11.44	11.18	10.94	11.59
303.15	0.693	10.48	13.19	13.04	12.86	13.19	13.14
308.15	0.704	11.61	15.04	14.85	15.12	15.22	14.84
313.15	0.715	12.66	16.85	16.90	18.05	16.83	16.70

Table 3. *Cont.*

T/K	x_w^0	10^2x_a	$10^2x_p^{exp}$	$10^2x_p^{Apel}$	$10^2x_p^{NRTL}$	$10^2x_p^{RK}$	$10^2x_p^{JA}$
			$x_w = 0.692$				
278.15	0.735	6.571	7.517	7.241	7.496	7.371	7.086
283.15	0.738	6.900	7.952	8.123	8.136	8.004	8.071
288.15	0.744	7.761	9.127	9.117	8.823	9.108	9.151
293.15	0.750	8.590	10.30	10.23	9.784	10.26	10.33
298.15	0.754	9.099	11.05	11.50	11.11	11.08	11.61
303.15	0.763	10.39	13.04	12.92	12.67	13.06	13.01
308.15	0.771	11.43	14.72	14.52	14.76	14.71	14.52
313.15	0.779	12.33	16.28	16.33	17.45	16.30	16.15
			$x_w = 0.771$				
278.15	0.804	6.687	7.670	7.513	7.887	7.730	7.418
283.15	0.806	7.136	8.270	8.360	8.382	8.225	8.348
288.15	0.811	7.971	9.422	9.304	8.977	9.380	9.356
293.15	0.814	8.604	10.32	10.35	9.874	10.36	10.44
298.15	0.818	9.221	11.23	11.52	11.05	11.22	11.61
303.15	0.824	10.28	12.86	12.82	12.51	12.84	12.87
308.15	0.829	11.19	14.32	14.27	14.44	14.19	14.22
313.15	0.834	12.14	16.15	15.88	16.00	15.93	15.66
			$x_w = 0.900$				
278.15	0.915	7.119	8.247	8.028	8.415	8.250	7.947
283.15	0.916	7.406	8.638	8.760	8.797	8.654	8.771
288.15	0.918	8.117	9.628	9.567	9.259	9.664	9.647
293.15	0.919	8.710	10.48	10.45	9.991	10.46	10.57
298.15	0.920	9.293	11.34	11.43	10.98	11.34	11.55
303.15	0.922	9.977	12.38	12.51	12.26	12.39	12.59
308.15	0.924	10.59	13.36	13.69	13.91	13.45	13.68
313.15	0.927	11.48	15.36	14.99	16.09	15.37	14.83
			$x_w = 1.000$				
278.15	1.000	7.313	8.512	8.263	8.843	8.509	8.334
283.15	1.000	7.506	8.869	8.945	9.107	8.865	9.060
288.15	1.000	8.106	9.613	9.691	9.490	9.603	9.821
293.15	1.000	8.774	10.57	10.50	10.07	10.57	10.61
298.15	1.000	9.152	11.18	11.39	10.94	11.18	11.44
303.15	1.000	9.869	12.27	12.37	12.06	12.27	12.31
308.15	1.000	10.62	13.40	13.43	13.53	13.37	13.21
313.15	1.000	11.50	14.78	14.59	15.46	14.78	14.14

[a] x_p^{exp} is the experimental mole fraction solubility of 1,5-pentanediamine adipate dihydrate; x_p^{Apel}, x_p^{NRTL}, x_p^{RK} and x_p^{JA} refer to the calculated mole fraction solubility according to the modified Apelblat equation, NRTL model, CNIBS/R-K model and Jouyban–Acree model, respectively. x_w is the initial mole fraction of water in three binary solvent mixtures; x_w^0 is the final mole fraction of water in three binary solvent mixtures; x_a is the mole fraction solubility of anhydrous 1,5-pentanediamine adipate. [b] Standard uncertainty is $u(T)$ = 0.03 K, $u(p)$ = 0.3 kPa. The relative standard uncertainty is $u_r(x_w)$ = 0.03, $u_r(x_p)$ = 0.05, $u_r(x_w^0)$ = 0.03.

Table 4. Mole fraction solubility of 1,5-pentanediamine adipate dihydrate in water + ethanol from 278.15 K to 313.15 K (p = 0.1 MPa) [a,b].

T/K	x_w^0	10^2x_a	$10^2x_p^{exp}$	$10^2x_p^{Apel}$	$10^2x_p^{NRTL}$	$10^2x_p^{RK}$	$10^2x_p^{JA}$
			$x_w = 0.447$				
278.15	0.469	1.975	2.042	1.885	2.194	2.039	2.120
283.15	0.475	2.469	2.580	2.421	2.641	2.575	2.673
288.15	0.482	3.110	3.293	3.106	3.236	3.291	3.345
293.15	0.488	3.620	3.877	3.978	3.976	3.872	4.153
298.15	0.497	4.382	4.771	5.087	4.839	4.766	5.120
303.15	0.514	5.751	6.455	6.495	6.224	6.451	6.268
308.15	0.530	7.075	8.188	8.280	7.987	8.193	7.623
313.15	0.555	8.863	10.70	10.54	10.66	10.69	9.213

Table 4. *Cont.*

T/K	x_w^0	10^2x_a	$10^2x_p^{exp}$	$10^2x_p^{Apel}$	$10^2x_p^{NRTL}$	$10^2x_p^{RK}$	$10^2x_p^{JA}$
			x_w = 0.581				
278.15	0.613	3.790	4.074	4.175	4.364	4.114	4.041
283.15	0.621	4.678	5.126	4.951	4.912	5.198	4.874
288.15	0.626	5.189	5.751	5.852	5.636	5.783	5.840
293.15	0.634	6.055	6.844	6.892	6.573	6.899	6.954
298.15	0.644	7.110	8.235	8.090	7.761	8.297	8.233
303.15	0.654	8.069	9.561	9.466	9.328	9.605	9.693
308.15	0.662	8.940	10.81	11.04	11.29	10.77	11.35
313.15	0.677	10.33	12.94	12.84	13.94	12.99	13.22
			x_w = 0.683				
278.15	0.719	5.392	6.004	6.092	6.136	5.879	5.564
283.15	0.725	6.278	7.132	6.899	6.627	6.904	6.504
288.15	0.728	6.743	7.743	7.810	7.382	7.620	7.562
293.15	0.735	7.650	8.974	8.837	8.280	8.807	8.747
298.15	0.740	8.327	9.928	9.995	9.507	9.804	10.069
303.15	0.747	9.222	11.23	11.29	11.04	11.12	11.53
308.15	0.752	9.963	12.36	12.76	13.02	12.46	13.16
313.15	0.765	11.53	14.74	14.41	15.57	14.60	14.94
			x_w = 0.764				
278.15	0.794	6.131	6.943	6.824	7.398	7.011	6.600
283.15	0.797	6.674	7.652	7.620	7.861	7.840	7.539
288.15	0.801	7.344	8.553	8.516	8.487	8.724	8.572
293.15	0.805	8.074	9.567	9.522	9.337	9.705	9.703
298.15	0.808	8.699	10.46	10.65	10.48	10.42	10.93
303.15	0.813	9.558	11.74	11.92	11.93	11.80	12.28
308.15	0.819	10.54	13.27	13.34	13.81	13.24	13.74
313.15	0.826	11.91	15.15	14.94	16.23	15.28	15.31
			x_w = 0.829				
278.15	0.853	6.607	7.564	7.454	8.143	7.645	7.292
283.15	0.855	7.167	8.313	8.228	8.494	8.345	8.180
288.15	0.859	7.948	9.390	9.089	9.004	9.305	9.140
293.15	0.860	8.405	10.04	10.04	9.852	10.06	10.17
298.15	0.862	8.755	10.54	11.10	10.96	10.75	11.28
303.15	0.866	9.759	12.05	12.28	12.28	12.10	12.47
308.15	0.870	10.72	13.57	13.59	14.04	13.47	13.74
313.15	0.875	12.03	15.38	15.04	16.33	15.37	15.09
			x_w = 0.928				
278.15	0.939	7.163	8.307	8.151	8.558	8.205	8.152
283.15	0.940	7.588	8.889	8.855	8.833	8.781	8.904
288.15	0.941	8.140	9.662	9.628	9.274	9.660	9.696
293.15	0.942	8.632	10.36	10.47	9.956	10.29	10.52
298.15	0.943	9.255	11.28	11.40	10.86	11.12	11.39
303.15	0.944	9.959	12.35	12.42	12.06	12.29	12.30
308.15	0.945	10.56	13.31	13.53	13.62	13.39	13.25
313.15	0.947	12.13	15.05	14.76	15.65	15.01	14.24

[a] x_p^{exp} is the experimental mole fraction solubility of 1,5-pentanediamine adipate dihydrate; x_p^{Apel}, x_p^{NRTL}, x_p^{RK} and x_p^{JA} refer to the calculated mole fraction solubility according to the modified Apelblat equation, NRTL model, CNIBS/R-K model and Jouyban–Acree model, respectively. x_w is the initial mole fraction of water in three binary solvent mixtures; x_w^0 is the final mole fraction of water in three binary solvent mixtures; x_a is the mole fraction solubility of anhydrous 1,5-pentanediamine adipate. [b] Standard uncertainty is $u(T)$ = 0.03 K, $u(p)$ = 0.3 kPa. The relative standard uncertainty is $u_r(x_w)$ = 0.03, $u_r(x_p)$ = 0.05, $u_r(x_w^0)$ = 0.03.

Table 5. Mole fraction solubility of 1,5-pentanediamine adipate dihydrate in water + DMF from 278.15 K to 313.15 K (p = 0.1 MPa) [a,b].

T/K	x_w^0	$10^2 x_a$	$10^2 x_p^{exp}$	$10^2 x_p^{Apel}$	$10^2 x_p^{NRTL}$	$10^2 x_p^{RK}$	$10^2 x_p^{JA}$
			x_w = 0.648				
278.15	0.648	0.1082	0.1084	0.1350	0.1095	0.1075	0.1237
283.15	0.649	0.2164	0.2173	0.1930	0.1630	0.2158	0.1806
288.15	0.649	0.2624	0.2637	0.2740	0.2402	0.2619	0.2602
293.15	0.650	0.3792	0.3820	0.3860	0.3571	0.3640	0.3701
298.15	0.651	0.4628	0.4671	0.5420	0.5190	0.4649	0.5204
303.15	0.652	0.6523	0.6609	0.7550	0.7410	0.6558	0.7234
308.15	0.655	1.059	1.081	1.046	1.116	1.073	0.9948
313.15	0.658	1.483	1.528	1.441	1.632	1.509	1.354
			x_w = 0.741				
278.15	0.745	0.8593	0.8940	1.030	1.003	0.8944	1.018
283.15	0.747	1.214	1.241	1.347	1.305	1.217	1.340
288.15	0.749	1.703	1.756	1.754	1.693	1.758	1.748
293.15	0.752	2.159	2.239	2.274	2.177	2.226	2.259
298.15	0.757	3.134	3.265	2.937	2.835	3.244	2.895
303.15	0.759	3.485	3.729	3.779	3.613	3.749	3.679
308.15	0.764	4.369	4.777	4.843	4.607	4.809	4.640
313.15	0.771	5.526	6.197	6.184	5.848	6.240	5.808
			x_w = 0.811				
278.15	0.823	3.087	3.291	2.997	3.079	3.108	2.677
283.15	0.823	3.292	3.465	3.535	3.625	3.553	3.298
288.15	0.826	3.835	4.090	4.167	4.242	4.107	4.034
293.15	0.828	4.498	4.918	4.911	4.955	4.950	4.900
298.15	0.830	4.949	5.711	5.785	5.839	5.665	5.914
303.15	0.835	6.023	6.762	6.810	6.724	6.726	7.093
308.15	0.839	7.030	8.026	8.013	7.787	7.980	8.457
313.15	0.843	8.013	9.374	9.422	9.078	9.295	10.02
			x_w = 0.866				
278.15	0.877	4.411	4.837	4.949	5.193	4.965	4.431
283.15	0.880	5.226	5.858	5.566	5.551	5.746	5.204
288.15	0.881	5.504	6.196	6.252	6.353	6.162	6.079
293.15	0.883	6.630	7.152	7.012	6.954	7.125	7.063
298.15	0.884	6.767	7.429	7.855	7.903	7.567	8.165
303.15	0.887	7.424	8.715	8.788	8.959	8.739	9.393
308.15	0.889	8.328	10.05	9.818	9.993	10.07	10.75
313.15	0.892	9.029	11.07	10.95	11.42	11.13	12.26
			x_w = 0.9453				
278.15	0.952	6.432	7.071	7.404	7.526	7.262	7.157
283.15	0.953	7.160	8.265	8.021	7.754	8.327	7.884
288.15	0.953	7.435	8.645	8.698	8.549	8.670	8.654
293.15	0.954	8.069	9.568	9.442	9.148	9.579	9.470
298.15	0.955	8.451	10.07	10.25	10.40	9.962	10.33
303.15	0.956	9.033	10.92	11.15	11.48	10.92	11.24
308.15	0.957	9.937	12.25	12.13	12.15	12.25	12.19
313.15	0.958	10.55	13.22	13.20	13.69	13.21	13.19

[a] x_p^{exp} is the experimental mole fraction solubility of 1,5-pentanediamine adipate dihydrate; x_p^{Apel}, x_p^{NRTL}, x_p^{RK} and x_p^{JA} refer to the calculated mole fraction solubility according to the modified Apelblat equation, NRTL model, CNIBS/R-K model and Jouyban–Acree model, respectively. x_w is the initial mole fraction of water in three binary solvent mixtures; x_w^0 is the final mole fraction of water in three binary solvent mixtures;x_a is the mole fraction solubility of anhydrous 1,5-pentanediamine adipate. [b] Standard uncertainty is $u(T)$ = 0.03 K, $u(p)$ = 0.3 kPa. The relative standard uncertainty is $u_r(x_w)$ = 0.03, $u_r(x_p)$ = 0.05, $u_r(x_w^0)$ = 0.03.

As shown in Figure 3, the dried solid was proved to completely convert into anhydrous 1,5-pentanediamine adipate by PXRD. The mass of dissolved 1,5-pentanediamine adipate dihydrate was calculated from the measured value of anhydrous 1,5-pentanediamine adipate.

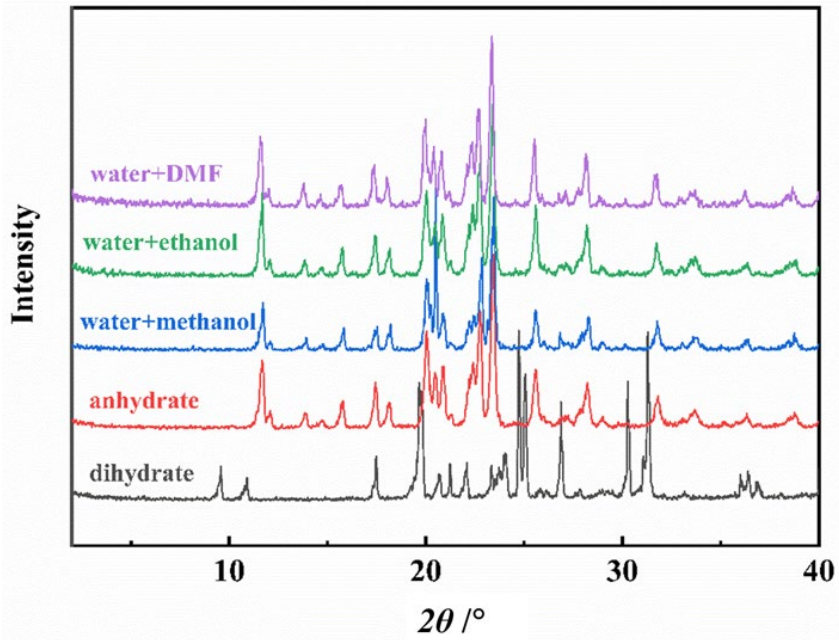

Figure 3. Powder X-ray diffraction pattern of dried solid in mixed systems: water + DMF (x_w = 0.648), water + ethanol (x_w = 0.447) and water + methanol (x_w = 0.360) at T = 298.15 K.

The TG/DSC results for the 1,5-pentanediamine adipate dihydrate crystal are shown in Figure 4. It was found that there was 12.49% weight loss between room temperature and 428.15 K, which is consistent with the theoretical water content of 1,5-pentanediamine adipate dihydrate (12.66 wt%). Meanwhile, there are two sharp endothermic peaks in the DSC curve, representing the dehydration process of two crystal waters in crystal. The loss of water from the lattice was divided into two stages, occurring at 341.71 K and 347.47 K, and the total dehydration enthalpy is 40.13 kJ·mol^{-1}, respectively. The broad endothermic peak at about 380 K indicated that the dehydration of polyamide 56 salt dihydrate was a slow process, accompanied by the endothermic phenomena related to the melting and dissolution in water. The endothermic peak at 456.10 K represents the decomposition process.

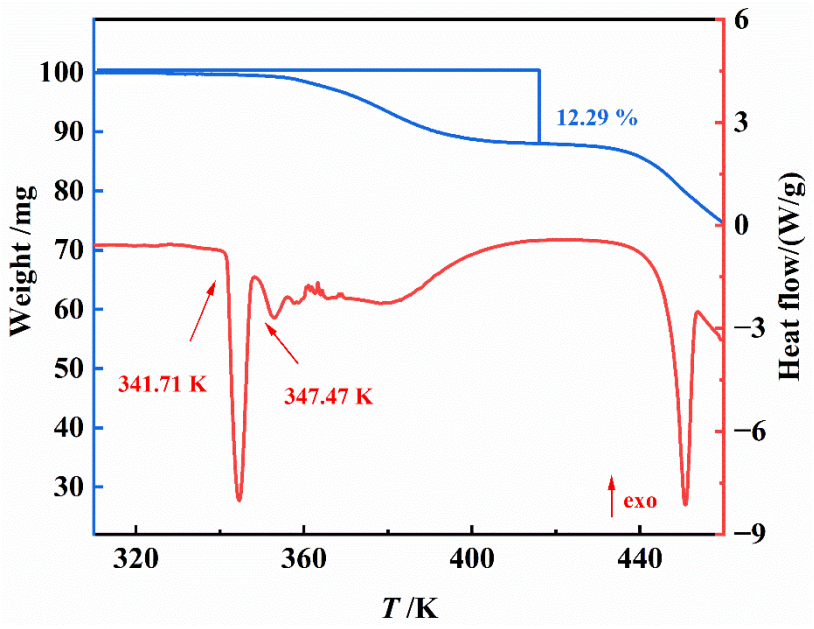

Figure 4. Thermal analysis (TG-DSC) of 1,5-pentanediamine adipate dihydrate.

Furthermore, the DSC results for anhydrous 1,5-pentanediamine adipate (Figure 5) show a sharp endothermic peak at 397.32 K, which should be the melting process, and the melting enthalpy is 22.13 kJ·mol^{-1}. As shown in Figure 6, the melting process of anhydrous 1,5-pentanediamine adipate at 397.32 K was proved through polarized optical microscopy.

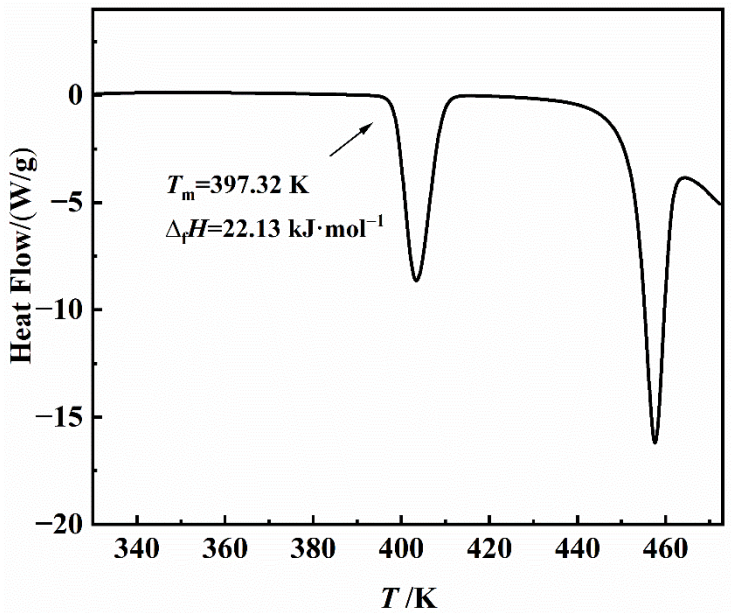

Figure 5. DSC of 1,5-pentanediamine adipate dihydrate after dehydration.

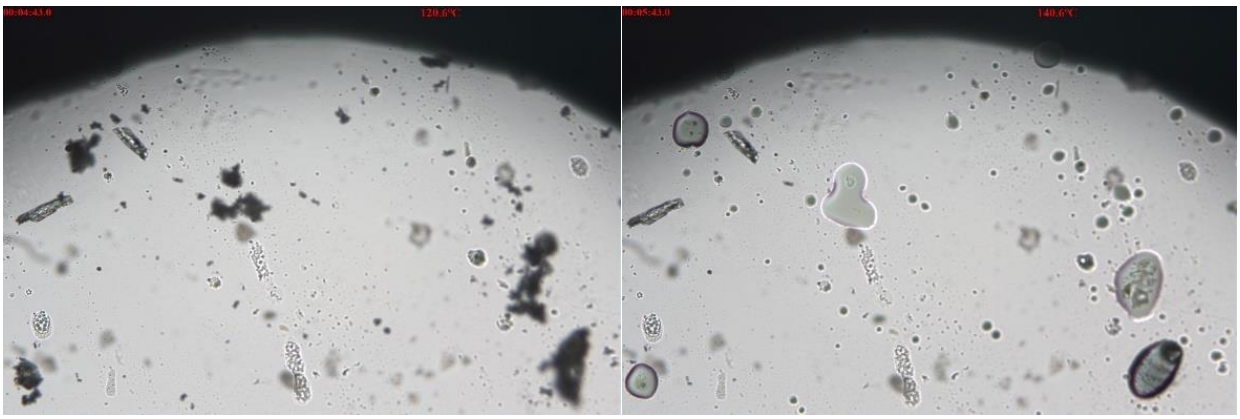

Figure 6. Polarized optical microscopy of anhydrous 1,5-pentanediamine adipate (**left**: 120.6 °C, **right**: 140.6 °C).

4.2. Solubility of 1,5-Pentanediamine Adipate Dihydrate in Binary Mixed Solvents

The experimental solubility data of 1,5-pentanediamine adipate dihydrate are listed in Tables 3–5 and are plotted in 3D mode in Figures 7–9. The results show that the solubility of 1,5-pentanediamine adipate dihydrate is positively correlated with temperature in all the tested three solvent systems. At a fixed temperature and solvent composition, the solubility order of 1,5-pentanediamine adipate dihydrate in the tested solvent systems follows the trend: (water + methanol) > (water + ethanol) > (water + DMF), which is consistent with the solvent polarity of methanol, ethanol and DMF. Taking into account the intense polarity of the molecule, the solvent effect on solubility could be explained by the "like dissolves like" rule, in which polar solute and polar solvent can result in strong interactions [23].

Solvent composition is the most important factor, which could affect the solubility of 1,5-pentanediamine adipate dihydrate in the solvent mixtures. Interestingly, the solubility values show different characteristics in the three binary mixture solvent systems. For

water + methanol, a progressive rise of initial content of water result in ever-increasing solubility at lower temperature, while the trend changes when the temperature is higher than 303.15 K. Besides, cosolvency phenomenon can be observed in water + ethanol mixture, which means that there is a peak in solubility curve versus solvent composition [24]. The peak position slightly shifts with temperature and it gives the highest solubility at x_w in between 0.8 and 0.9 for water + ethanol. While, the solubility of 1,5-pentanediamine adipate dihydrate increases with the rising mole fraction of water for the binary mixed solvents water + DMF. From the above results, ethanol and DMF can be chosen as antisolvent since 1,5-pentanediamine adipate dihydrate is almost insoluble in them.

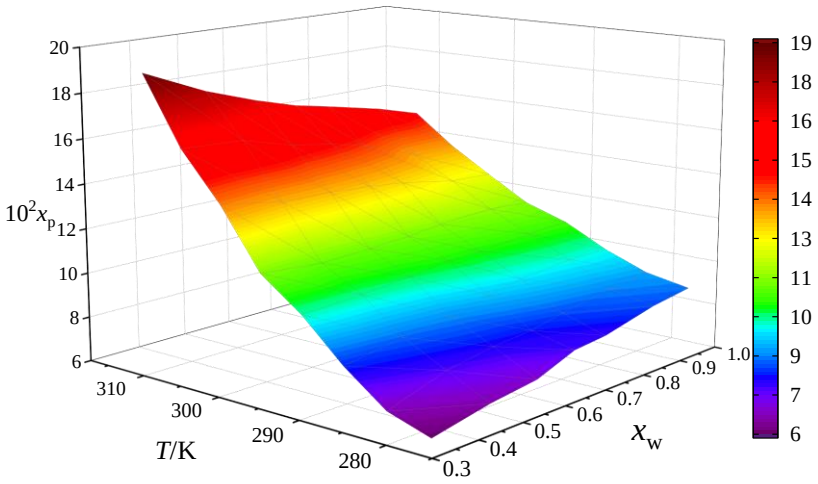

Figure 7. Mole fraction solubility of 1,5-pentanediamine adipate dihydrate in (water + methanol) mixed solvents with different mole fractions at various temperatures.

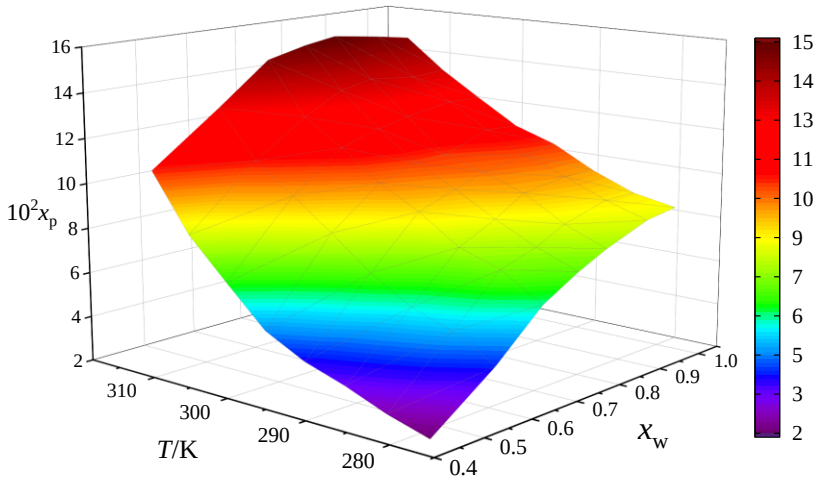

Figure 8. Mole fraction solubility of 1,5-pentanediamine adipate dihydrate in (water + ethanol) mixed solvents with different mole fractions at various temperatures.

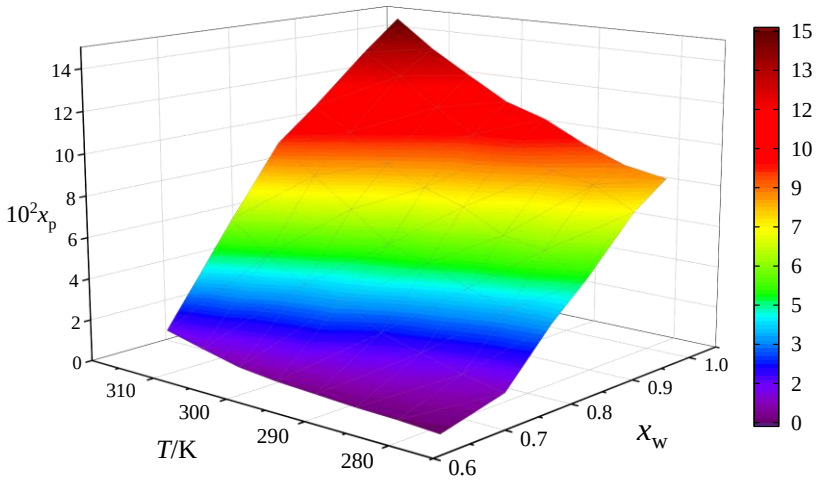

Figure 9. Mole fraction solubility of 1,5-pentanediamine adipate dihydrate in (water + DMF) mixed solvents with different mole fractions at various temperatures.

Furthermore, the experimental solubility data of this work were fitted by using the modified Apelblat Equation, NRTL model, the CNIBS/R–K model, and the Jouyban–Acree model. The values of model parameters and the calculated *ARD* and *RMSD* are shown in Tables 6–9. It can be observed the *ARD*% values of the four models used in this work and are generally lower than 5%, and the *RMSD* values are all lower than 0.006. It implies that the results fitted by these models show satisfactory consistency with the experimental values. Among them, the *ARD*% values of CNIBS/R-K model are lower than 1%, and the *RMSD* values are generally lower than 0.001. The CNIBS/R-K model shows best consistency among the four models, and as such, it was chosen to calculate the solubility of 1,5-pentanediamine adipate dihydrate in the above-mentioned solvents.

Table 6. Model parameters of modified Apelblat model for 1,5-pentanediamine adipate dihydrate in the investigated binary solvent mixtures [a,b,c].

x_w	*A*	*B*	*C*	*ARD*%	10^3*RMSD*
		water + methanol			
0.360	−82.8340	1038.99	13.5462	1.941	1.947
0.491	−77.8719	1151.40	12.6096	1.811	2.613
0.600	−82.4102	1586.55	13.1495	1.435	1.987
0.692	−95.1411	2376.78	14.9197	1.652	2.144
0.771	−80.2515	1856.47	12.6131	1.032	1.322
0.900	−81.0116	2152.54	12.5708	1.459	2.062
1.000	−75.7757	2039.99	11.7175	1.187	1.464
		water + ethanol			
0.447	−147.562	2728.03	23.7703	4.009	1.704
0.581	−44.1974	−544.343	7.63630	1.744	1.340
0.683	−81.2629	1656.53	12.8833	1.729	2.126
0.764	−94.6552	2414.27	14.7989	1.037	1.308
0.829	−85.2548	2175.21	13.2970	1.915	2.722
0.928	−78.0544	2088.14	12.0892	1.113	1.571
		water + DMF			
0.648	−103.155	−706.687	17.6053	10.73	0.553
0.741	−98.5924	393.332	16.4535	5.559	1.575
0.811	−111.074	2345.03	17.6142	2.312	1.586
0.866	−55.1677	636.236	8.86159	1.817	1.342
0.945	−81.6357	2273.41	12.5901	1.723	2.044

[a] *A*, *B* and *C* are the parameters of the modified Apelblat equation. [b] *ARD* is the average relative deviation. [c] *RMSD* is the root mean-square deviation.

Table 7. Model parameters of NRTL model for 1,5-pentanediamine adipate dihydrate in the investigated binary solvent mixtures [a,b,c].

Parameters	Water + Methanol	Water + Ethanol	Water + DMF
Δg_{ij}	−345,527	−347,351	360,083
Δg_{ik}	−12,636.6	−8875.18	−3418.04
Δg_{ji}	392,075	394,734	−319,133
Δg_{jk}	854.483	4455.60	−55,130.0
Δg_{ki}	13,260.8	14,444.6	8333.05
Δg_{kj}	4300.47	4725.49	14,778.7
ARD%	2.678	3.652	5.387
10^3*RMSD*	4.226	4.035	2.430

[a] Δg_{ij}, Δg_{ik}, Δg_{ji}, Δg_{jk}, Δg_{ki} and Δg_{kj} are the parameters of NRTL model. [b] *ARD* is the average relative deviation. [c] *RMSD* is the root mean-square deviation.

Table 8. Model parameters of CNIBS/R-K model for 1,5-pentanediamine adipate dihydrate in the investigated binary solvent mixtures [a,b,c].

T/K	B_0	B_1	B_2	B_3	B_4	*ARD*%	10^3*RMSD*
			water + methanol				
278.15	−2.98656	0.535550	−0.420300	1.13613	−0.728910	0.785	0.848
283.15	−4.53891	10.7029	−22.1239	20.5480	−7.011	0.252	0.303
288.15	−2.60732	0.359600	−0.853370	1.93184	−1.17388	0.349	0.397
293.15	−1.91604	−2.84662	6.86270	−6.66656	2.32015	0.166	0.255
298.15	−1.97239	−0.888080	0.450860	1.18540	−0.966630	0.101	0.167
303.15	−0.914890	−6.90305	15.9257	−15.9672	5.76152	0.060	0.116
308.15	−1.38438	−3.35065	−9.15557	−10.9973	4.56526	0.571	1.103
313.15	−1.57444	0.361170	−2.86611	3.78493	−1.61709	0.052	0.125
			water + ethanol				
278.15	−6.85983	3.86505	15.6193	−25.9248	10.8407	0.990	0.805
283.15	−12.0539	35.5145	−50.4952	32.8953	−8.27872	1.334	1.328
288.15	−7.14881	11.4357	−6.18013	−2.53752	2.08915	0.740	0.935
293.15	−7.32735	11.6185	−1.76807	−11.6445	6.87737	0.770	0.965
298.15	−13.5664	50.5021	−86.0459	66.1292	−19.2053	0.909	1.230
303.15	−8.03959	23.0644	−34.1683	22.9691	−5.92156	0.455	0.644
308.15	−1.81365	−9.83320	31.2860	−34.0285	12.3666	0.431	0.690
313.15	−0.181820	−16.3140	42.2165	−42.3819	14.7509	0.376	0.809
			water + DMF				
278.15	219.485	−1234.93	2423.09	−2035.12	625.028	4.045	2.264
283.15	92.4160	−562.581	1120.79	−934.259	281.209	0.510	0.327
288.15	−88.0758	293.604	−381.254	223.373	−49.9886	0.423	0.294
293.15	−83.1875	272.112	−340.998	188.063	−38.2364	0.095	0.077
298.15	−330.881	1465.47	−2470.41	1859.26	−525.636	2.276	1.976
303.15	−166.220	669.528	−1035.38	716.822	−186.839	0.295	0.296
308.15	−143.599	580.109	−902.644	630.033	−165.907	0.621	0.723
313.15	−180.185	758.701	−1219.05	873.296	−234.665	0.568	0.742

[a] B_0, B_1, B_2, B_3 and B_4 are the parameters of CNIBS/R-K model. [b] *ARD* is the average relative deviation. [c] *RMSD* is the root mean-square deviation.

Table 9. Model parameters of Jouyban–Acree equation for 1,5-pentanediamine adipate dihydrate in the investigated binary solvent mixtures [a,b,c].

Parameters	Water + Methanol	Water + Ethanol	Water + DMF
A_0	10.2963	15.6173	40.6254
A_1	−8.04828	−14.1420	−39.9894
A_2	−3704.93	−6730.11	−35,615.2
A_3	2326.55	8302.08	87,378.6
A_4	167.587	−3422.17	−90,712.4
A_5	−127.038	285.814	46,058.6
A_6	20.3783	475.704	−7948.44
ARD%	2.022	3.270	6.128
10^3*RMSD*	2.459	3.707	4.389

[a] A_0, A_1, A_2, A_3, A_4, A_5 and A_6 are the parameters of Jouyban-Acree equation. [b] *ARD* is the average relative deviation. [c] *RMSD* is the root mean-square deviation.

4.3. The Mixing Thermodynamic Properties

The mixing properties, including mixing Gibbs free energy ($\Delta_m G$), mixing enthalpy ($\Delta_m H$), and mixing entropy ($\Delta_m S$), are essential for non-ideal binary solution mixtures and NRTL model can be adopted to calculate these data. The results are shown in Tables 10–12. It can be found that the values of $\Delta_m G$ are negative, indicating that the mixing processes in the investigated solution systems are spontaneous. Besides, the values of $\Delta_m H$ are mostly negative, which means the mixing processes are mainly exothermic. Generally, the thermodynamic properties of mixing are affected by the properties of solvents.

Table 10. Mixing thermodynamic properties of 1,5-pentanediamine adipate dihydrate in water + methanol mixtures [a,b].

x_w	$\Delta_m H$/kJ·mol^{-1}	$\Delta_m G$/kJ·mol^{-1}	$\Delta_m S$/J·mol^{-1}·K^{-1}
	T = 278.15 K		
0.360	−3.767	−1.873	−6.813
0.491	−4.283	−1.997	−8.223
0.600	−4.480	−2.017	−8.858
0.692	−4.879	−2.050	−10.17
0.771	−4.992	−1.983	−10.82
0.900	−5.399	−1.814	−12.89
1.000	−5.435	−1.450	−14.33
	T = 283.15 K		
0.360	−4.036	−1.953	−7.360
0.491	−4.676	−2.100	−9.102
0.600	−4.882	−2.119	−9.763
0.692	−4.961	−2.072	−10.20
0.771	−5.152	−2.019	−11.06
0.900	−5.435	−1.810	−12.80
1.000	−5.464	−1.434	−14.24
	T = 288.15 K		
0.360	−4.656	−2.114	−8.825
0.491	−5.038	−2.195	−9.872
0.600	−5.184	−2.197	−10.37
0.692	−5.388	−2.176	−11.15
0.771	−5.555	−2.113	−11.95
0.900	−5.758	−1.876	−13.48
1.000	−5.692	−1.464	−14.68

Table 10. *Cont.*

x_w	$\Delta_m H$/kJ·mol^{-1}	$\Delta_m G$/kJ·mol^{-1}	$\Delta_m S$/J·mol^{-1}·K^{-1}
	T = 293.15 K		
0.360	−5.315	−2.290	−10.32
0.491	−5.563	−2.330	−11.03
0.600	−5.658	−2.315	−11.41
0.692	−5.754	−2.265	−11.90
0.771	−5.789	−2.165	−12.36
0.900	−5.976	−1.911	−13.87
1.000	−5.999	−1.495	−15.37
	T = 298.15 K		
0.360	−5.714	−2.408	−11.09
0.491	−5.828	−2.404	−11.48
0.600	−5.862	−2.370	−11.71
0.692	−5.888	−2.297	−12.04
0.771	−5.988	−2.207	−12.68
0.900	−6.167	−1.936	−14.19
1.000	−6.105	−1.483	−15.50
	T = 303.15 K		
0.360	−6.579	−2.667	−12.91
0.491	−6.507	−2.589	−12.92
0.600	−6.490	−2.533	−13.05
0.692	−6.439	−2.434	−13.21
0.771	−6.413	−2.305	−13.55
0.900	−6.400	−1.970	−14.62
1.000	−6.415	−1.499	−16.22
	T = 308.15 K		
0.360	−6.809	−2.764	−13.13
0.491	−7.018	−2.748	−13.86
0.600	−6.859	−2.638	−13.70
0.692	−6.775	−2.520	−13.81
0.771	−6.705	−2.368	−14.08
0.900	−6.572	−1.986	−14.88
1.000	−6.710	−1.532	−16.81
	T = 313.15 K		
0.360	−7.245	−2.957	−13.69
0.491	−7.265	−2.847	−14.11
0.600	−7.115	−2.721	−14.03
0.692	−6.993	−2.578	−14.10
0.771	−7.378	−2.063	−16.98
0.900	−7.056	−2.077	−15.90
1.000	−7.068	−1.579	−17.53

[a] The values of $\Delta_m G$, $\Delta_m H$ and $\Delta_m S$ were calculated by Equation (23). [b] The standard uncertainty are $u(T)$ = 0.03 K, $u(p)$ = 0.3 kPa. The combined expanded uncertainties are $u_c(\Delta_m H) = 0.060\Delta_m H$, $u_c(\Delta_m S) = 0.065\Delta_m S$, $u_c(\Delta_m G) = 0.070\Delta_m G$ (0.95 level of confidence).

Table 11. Mixing thermodynamic properties of 1,5-pentanediamine adipate dihydrate in water + ethanol mixtures [a,b].

x_w	$\Delta_m H$/kJ·mol^{-1}	$\Delta_m G$/kJ·mol^{-1}	$\Delta_m S$/J·mol^{-1}·K^{-1}
	T = 278.15 K		
0.447	−0.3891	−0.1108	−1.000
0.581	−1.808	−0.4737	−4.801
0.683	−3.093	−0.8665	−8.010
0.764	−3.769	−1.114	−9.550
0.829	−4.291	−1.295	−10.77
0.928	−5.100	−1.499	−12.95
	T = 283.15 K		
0.447	−0.7009	−0.1980	−1.776
0.581	−2.368	−0.6156	−6.194
0.683	−3.602	−0.9993	−9.197
0.764	−4.012	−1.177	−10.01
0.829	−4.530	−1.352	−11.22
0.928	−5.242	−1.517	−13.16
	T = 288.15 K		
0.447	−1.096	−0.3010	−2.762
0.581	−2.626	−0.6872	−6.734
0.683	−3.782	−1.050	−9.488
0.764	−4.318	−1.255	−10.63
0.829	−4.900	−1.440	−12.01
0.928	−5.458	−1.552	−13.56
	T = 293.15 K		
0.447	−1.382	−0.3795	−3.423
0.581	−3.102	−0.8079	−7.830
0.683	−4.231	−1.165	−10.46
0.764	−4.634	−1.334	−11.26
0.829	−5.026	−1.466	−12.15
0.928	−5.611	−1.570	−13.79
	T = 298.15 K		
0.447	−1.807	−0.4852	−4.436
0.581	−3.654	−0.9458	−9.090
0.683	−4.496	−1.236	−10.93
0.764	−4.854	−1.389	−11.62
0.829	−5.069	−1.469	−12.08
0.928	−5.835	−1.603	−14.20
	T = 303.15 K		
0.447	−2.575	−0.6620	−6.314
0.581	−4.098	−1.061	−10.02
0.683	−4.858	−1.332	−11.63
0.764	−5.186	−1.471	−12.25
0.829	−5.493	−1.566	−12.96
0.928	−6.092	−1.639	−14.69
	T = 308.15 K		
0.447	−3.240	−0.8211	−7.854
0.581	−4.444	−1.155	−10.67
0.683	−5.092	−1.397	−11.99
0.764	−5.543	−1.561	−12.96
0.829	−5.848	−1.646	−13.64
0.928	−6.264	−1.654	−14.96
	T = 313.15 K		
0.447	−4.078	−1.029	−9.741
0.581	−5.004	−1.310	−11.80
0.683	−5.648	−1.353	−13.08
0.764	−5.932	−1.664	−13.63
0.829	−6.356	−1.764	−14.67
0.928	−6.692	−1.722	−15.88

[a] The values of $\Delta_m G$, $\Delta_m H$ and $\Delta_m S$ were calculated by Equation (23). [b] The standard uncertainty are $u(T)$ = 0.03 K, $u(p)$ = 0.3 kPa. The combined expanded uncertainties are $u_c(\Delta_m H)$ = 0.060$\Delta_m H$, $u_c(\Delta_m S)$ = 0.065$\Delta_m S$, $u_c(\Delta_m G)$ = 0.070$\Delta_m G$ (0.95 level of confidence).

Table 12. Mixing thermodynamic properties of 1,5-pentanediamine adipate dihydrate in water +DMF mixtures [a,b].

x_w	$\Delta_m H$/kJ·mol^{-1}	$\Delta_m G$/kJ·mol^{-1}	$\Delta_m S$/J·mol^{-1}·K^{-1}
	T = 278.15 K		
0.648	−23.05	−2.277	−1.024
0.741	−17.50	−1.803	1.927
0.811	−11.39	−1.397	9.279
0.866	−7.392	−1.064	11.70
0.945	−3.686	−5.551	6.710
	T = 283.15 K		
0.648	−22.87	−2.271	−0.567
0.741	−17.12	−1.797	2.989
0.811	−11.34	−1.395	9.239
0.866	−7.374	−1.064	11.56
0.945	−4.046	−5.547	5.304
	T = 288.15 K		
0.648	−22.73	−2.263	−0.359
0.741	−16.68	−1.789	4.219
0.811	−11.11	−1.389	9.652
0.866	−7.371	−1.058	11.16
0.945	−4.172	−5.560	4.818
	T = 293.15 K		
0.648	−22.52	−2.253	0.0403
0.741	−16.32	−1.782	5.112
0.811	−10.89	−1.381	9.958
0.866	−7.454	−1.055	10.58
0.945	−4.501	−5.570	3.647
	T = 298.15 K		
0.648	−22.35	−2.244	0.308
0.741	−15.67	−1.767	6.708
0.811	−10.82	−1.377	9.888
0.866	−7.546	−1.052	10.00
0.945	−4.552	−5.499	3.178
	T = 303.15 K		
0.648	−22.14	−2.239	0.819
0.741	−15.47	−1.757	6.946
0.811	−10.66	−1.364	9.832
0.866	−7.644	−1.043	9.199
0.945	−4.822	−5.145	1.065
	T = 308.15 K		
0.648	−21.69	−2.223	1.733
0.741	−15.06	−1.742	7.638
0.811	−10.65	−1.351	9.300
0.866	−7.894	−1.036	8.023
0.945	−5.467	−5.538	0.2324
	T = 313.15 K		
0.648	−21.30	−2.209	2.528
0.741	−14.67	−1.719	8.059
0.811	−10.71	−1.335	8.432
0.866	−8.115	−1.029	6.952
0.945	−5.760	−5.469	−0.9297

[a] The values of $\Delta_m G$, $\Delta_m H$ and $\Delta_m S$ were calculated by Equation (23). [b] The standard uncertainty are $u(T)$ = 0.03 K, $u(p)$ = 0.3 kPa. The combined expanded uncertainties are $u_c(\Delta_m H) = 0.060\Delta_m H$, $u_c(\Delta_m S) = 0.065\Delta_m S$, $u_c(\Delta_m G) = 0.070\Delta_m G$ (0.95 level of confidence).

5. Conclusions

In this paper, the solubility data of 1,5-pentanediamine adipate dihydrate in binary solvent mixtures (water + methanol, water + ethanol, water + DMF) were measured under atmospheric pressure at temperatures ranging from 278.15 K to 313.15 K by gravimetric method. The solubility of 1,5-pentanediamine adipate dihydrate increased with the rising

of temperature. At fixed temperature and solvent composition, the solubility order of 1,5-pentanediamine adipate dihydrate is (water + methanol) > (water + ethanol) > (water + DMF), which is consistent with the solvent polarity of methanol, ethanol and DMF. In water + methanol binary mixtures, the trend of solubility with components changes as the temperature rises, and the cut-off point is 303.15 K. Meanwhile, the cosolvency phenomenon was observed in water + ethanol system and maximum solubility values were observed when molar content of the water is about 0.8–0.9. As for water + DMF mixed solvent, a progressive increase in the initial content of organic solvent results in a decrease in its solubility. Furthermore, the solubility data were fitted by the Apelblat model, the NRTL model, the CNIBS/R–K model, and the Jouyban–Acree model. The results show satisfied fitting consistency. Finally, the mixing thermodynamic data indicate that the mixing process is spontaneous.

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