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Determination and Correlation of Solubility in Binary System Ethanol-Water of 3,4-Bis(3-nitrofurazan-4-yl)furoxan

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Abstract: The solubility data of 3,4-bis(3-nitrofurazan-4-yl)furoxan (DNTF) in binary system ethanol-water at temperatures ranging from 298.15 to 338.15 K were determined by using a laser monitoring system under atmospheric pressure. The van't Hoff plot, modified Apelblat equation, R-K model and Jouyban-Acree model were adopted to fit the experimental solubility data. Since the correlation coefficients (R^2) of the four correlation equations are greater than 0.99 and the Root-mean-square deviations (RMSD) are close to 0, four correlation equations can be adopted to correlate the solubility data. The standard enthalpy of dissolution, standard entropy of dissolution and the Gibbs free energy were calculated based on the experimental solubility data, from which we conclude that the dissolution of DNTF is an endothermic and non-spontaneous process.

Key words: 3,4-bis(3-nitrofurazan-4-yl)furoxan; solubility; correlation; thermodynamic properties

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1 Introduction

3,4-Bis(3-nitrofurazan-4-yl)furoxan (DNTF, Fig. 1) is a novel energetic material with high density, high energy and simple synthesis technology. Further study shows that its detonation performance is more superior than octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX) but close to 1,2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane (CL-20)[1]. Since it was synthesized, researchers mainly focused on its synthesis[2], crystal structure[3] and comprehensive performance[4-6].

Solution crystallization process is an important and traditional way to enhance the purity and morphology of solid products. What's more, the solubility is an extremely significant thermodynamic data for crystallization and calculation other thermodynamic parameters. Besides, solubility can affect the capacity of the crystallization process, as well as its ability to reject undesired compounds and minimize loss in the mother liquor. Ethanol is the most widely used organic solvent because of inexpensive, non-toxic and environmental-friendly. Moreover, the solubility of DNTF is moderate and obviously changes with temperature and concentration in ethanol. Therefore, ethanol can be used as the solvent for crystallizing DNTF and it's necessary to study the solubility of DNTF in binary system ethanol-water.

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In this work, the solubility of DNTF in six different concentration ethanol solvents at 298.15-338.15 K is measured. Four common correlation equations are adopted to correlate the experimental values. The standard enthalpy of dissolution, standard entropy of dissolution and standard Gibbs free energy are calculated according to the experimental data.

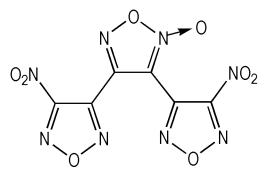

Fig.1 Chemical structure of DNTF

2 Experimental

2.1 Chemical Materials

DNTF sample was provided by Xi'an Modern Chemistry Research Institute. It was purified by recrystallization in alcohol and its mass fraction purity, measured by High Performance Liquid Chromatography, was greater than 0.995. Ethanol of analytical reagent grade was purchased from local reagent factory without further purification whose mass fraction purity was no less than 0.995. Deionized water was made by a Millipore Mili-Q Plus water system.

2.2 Single Crystal Structure Determination

The transparent single crystal of DNTF was cultivated from binary system ethanol-water and was characterized by using

the single crystal X-ray diffraction analysis, the molecular structure was shown in Fig. 2. The results show that the crystal is orthorhombic with and the crystal parameters are same with reference [3].

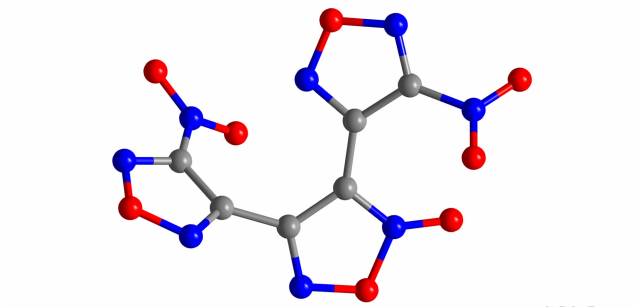

Fig. 2 The molecular structure of DNTF

2.3 Powder DNTF Crystal Structure Determination

Since the solubility may change with the crystal structure, it's necessary to confirm the crystal structure before the measurement of its solubility. The DNTF single crystal and DNTF powder used to measure the solubility were identified by powder X-ray diffraction (PXRD) which was carried out by using CuK_α radiation (1.54 Å) within 2θ range of 5° to 50° on Rigaku D/max-2500 (Rigaku, Japan) at a scanning rate of 1 step · s^{-1}. The result of PXRD was shown in Fig. 3 which illustrate clearly that the crystallinity and the crystal form of the powder DNTF used to measure the solubility are the same with the single crystal cultivated from binary system ethanol-water.

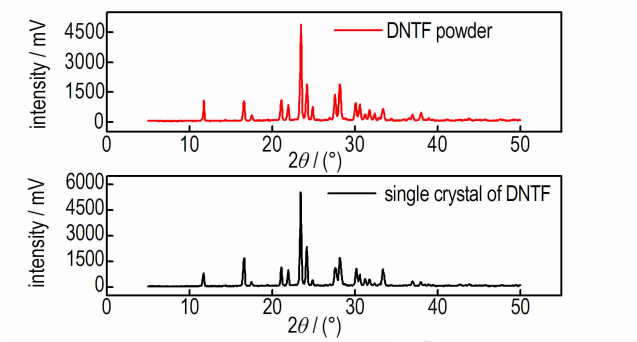

Fig. 3 Powder X-ray diffraction of DNTF

2.3 Experimental Procedures

The laser monitoring system (Fig. 4), the same method with Shi et al[7], was used to detect the phase transformation point at a constant temperature. The procedure of solubility measurement is same with Lan et al[8]. The solubility of DNTF in binary system ethanol-water within 298.15–338.15 K expressed by mole fraction was calculated by equation (1), the initial mole fraction composition of the binary solvent mixtures was defined by equation (2):

$$x_1 = \frac{m_1/M_1}{m_1/M_1 + m_2/M_2 + m_3/M_3} \quad (1)$$

$$x_2 = \frac{m_2/M_2}{m_2/M_2 + m_3/M_3} \quad (2)$$

where x_1 is the solubility (solid-liquid equilibria) of DNTF in mole fraction; x_2 is the solute-free mole fraction of ethanol in the binary liquid solvents, m_1, m_2, m_3 are the mass of DNTF, ethanol, water, respectively, M_1, M_2, M_3 are the molecular mass of DNTF, ethanol, water, respectively.

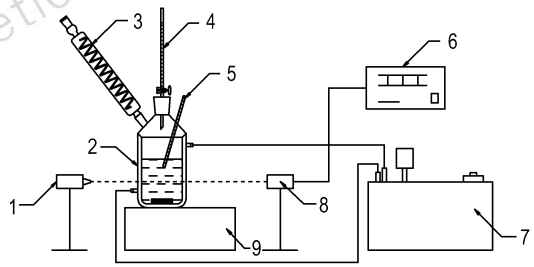

Fig. 4 Flow diagrams of experiment
1—laser generator, 2—glass vessel, 3—condenser pipe, 4—burette, 5—mercury thermometer, 6—digital display, 7—thermostatic bath, 8—photoelectric switch, 9—magnetic stirrer

3 Results and discussion

3.1 Measured Solubility

Solubility values of DNTF measured in different concentrationbinary system ethanol-water at temperatures ranging from 298.15 K to 338.15 K are listed in Table 1.

3.2 Correlation of Solubility Data

Since solid-liquid equilibrium is usually not available, correlation and prediction schemes are frequently utilized. The van't Hoff plot, modified Apelblat equation, R-K model and Jouyban-Acree model are adopted to correlate the experimental values. Root-mean-square deviation (RMSD) is used to evaluate the fitting results of the correlation equation. The RMSD is defined as:

$$\mathrm{RMSD} = \left[\frac{1}{N}\sum_{i=1}^{N}(x_{ci}-x_{1i})^2\right]^{1/2} \quad (3)$$

where N represents the total number of experimental points, x_{1i} is the experimental data, x_{ci} is the calculated values.

3.2.1 van't Hoff plot

Assuming the solution is an ideal solution (γ = 1), then the solubility of DNTF can be correlated by the van't Hoff plot[9-10] which reflects the relationship between the mole fraction of a solute and the temperature when the solvent effect is considered. The van't Hoff plot can be described as follows:

$$\ln x_1 = A + B/T \quad (4)$$

Table 1 Experimental mole fraction solubility values x_{1i} and calculated solubility values x_{ci} of DNTF in binary system ethanol-water at temperature T and pressure p=0.1 MPa[1)]

x_2	T / K	$10^3 x_{1i}$	x_2	T / K	$10^3 x_{1i}$	x_2	T / K	$10^3 x_{1i}$
	298.1500	8.1235		298.1500	4.0155		298.1500	1.9221
	303.1500	9.3626		303.1500	4.7642		303.1500	2.3859
	308.1500	10.9555		308.1500	5.7368		308.1500	2.9937
	313.1500	12.8627		313.1500	7.0041		313.1500	3.7940
1.0000	318.1500	15.2488	0.8544	318.1500	8.6617	0.7354	318.1500	4.8531
	323.1500	18.4692		323.1500	10.8404		323.1500	6.2611
	328.1500	22.2804		328.1500	13.7188		328.1500	8.1419
	333.1500	27.2617		333.1500	17.5420		333.1500	10.6657
	338.1500	33.4828		338.1500	22.6478		338.1500	14.0668
	298.1500	1.0967		298.1500	0.6947		298.1500	0.3078
	303.1500	1.3607		303.1500	0.8757		303.1500	0.4560
	308.1500	1.7170		308.1500	1.1189		308.1500	0.6612
	313.1500	2.2006		313.1500	1.4477		313.1500	0.9398
0.6363	318.1500	2.8618	0.5526	318.1500	1.8950	0.4808	318.1500	1.3107
	323.1500	3.7724		323.1500	2.5074		323.1500	1.7955
	328.1500	5.0356		328.1500	3.3510		328.1500	2.4181
	333.1500	6.8010		333.1500	4.5203		333.1500	3.2045
	338.1500	9.2856		338.1500	6.1502		338.1500	4.1820

Note: 1) The standard uncertainty u are $u(T)$=0.1 K, $u(p)$=0.02 MPa, $u_r(x)$=0.3%.

where T is the absolute temperature of experiment, A and B are the model parameters. Table 2 lists the model parameters values of A, B, the correlation coefficient of fitting results and RMSD. Fig. 5 is the fitting curves correlated by equation (4), which graphically illustrates the function between $\ln x_1$ and $1/T$. From Fig. 5 we can clearly see that it is a linear relationship between $\ln x_1$ and $1/T$, the RMSD of the correlation results are acceptable. So the ideal equation can be used to correlate the solubility of DNTF in binary system ethanol-water well.

Table 2 Model parameters, correlation coefficient and RMSD of van't Hoff plot

x_2	A	B	R^2	10^3×RMSD
1.0000	7.0971	−3571.6462	0.9897	0.8996
0.8544	9.0229	−4361.5616	0.9890	0.7332
0.7354	10.4990	−5017.9904	0.9936	0.3905
0.6363	11.1451	−5385.6756	0.9901	0.3354
0.5526	11.0772	−5497.9764	0.9926	0.1969
0.4808	14.0042	−6575.3102	0.9992	0.0564

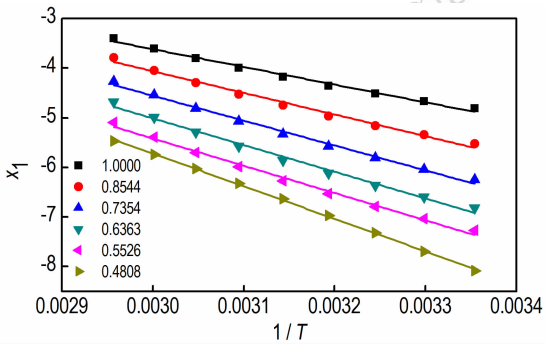

Fig. 5 Solubility of DNTF in ethanol-water binary system correlated with different temperatures. The points represent the experimental data. Curves are calculated according to Eq. (4) using the van't Hoff plot

3.2.2 Modified Apelblat Equation

The modified Apelblat equation[11-13] deduced from the Clausius-Clapeyron equation is a semiempirical equation, which has been widely used in correlation the experimental solubility values. The equation can be expressed as:

$$\ln x_1 = A + B/T + C\ln T \quad (5)$$

where A, B and C are the model parameters. Table 3 lists the model parameter values of A, B, C, R^2 and the RMSD. The experimental solubility values of DNTF in ethanol-water binary system at different temperatures and the solubility curve fitted by the modified Apelblat equation are shown in Fig. 6. It is clear that modified Apelblat equation demonstrates good consistency with the experimental values at different temperatures. Besides, the correlation coefficient of each concentration ethanol is close to 1 and the RMSD is micro, so the modified Apelblat equation can correlate the solubility of DNTF in binary system ethanol-water at different temperatures precisely.

Table 3 Model parameters, R^2 and RMSD of modified Apelblat equation

x_2	A	B	C	R^2	10^3×RMSD
1.0000	−157.8944	4026.4127	24.4825	0.9968	0.3975
0.8544	−189.7637	4798.7239	29.4945	0.9965	0.3065
0.7354	−224.4064	5823.4107	34.8435	0.9989	0.1098
0.6363	−100.1344	−301.2858	16.5367	0.9924	0.1978
0.5526	−114.0275	239.1465	18.5788	0.9952	0.1048
0.4808	−131.1201	606.8177	21.2693	0.9984	0.0442

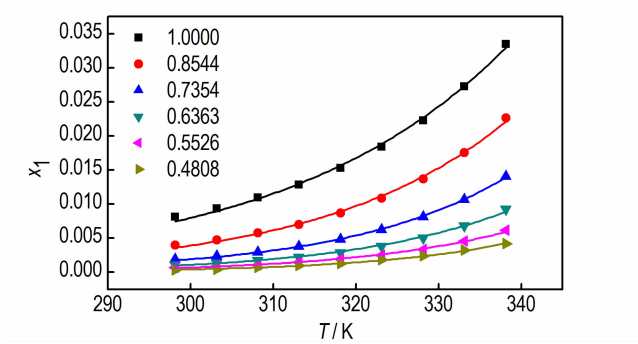

Fig. 6 Solubility of DNTF in binary system ethanol-water correlated with different temperatures. The points represent the experimental data. Curves are calculated according to Eq. (5) using the Modified Apelblat equation

3.2.3 R-K Model

The R-K model[14-15] is one of the best models used to calculate the solute solubility in binary solvents and it is expressed as follows:

$$\ln x_1 = x_2 \ln (x_1)_2 + x_3 \ln (x_1)_3 + x_2 x_3 \sum_{i=1}^{N} S_i (x_2 - x_3)^i \quad (6)$$

where x_1 is the solubility of DNTF, x_2 and x_3 stand for the initial molar fraction composition of ethanol and water in binary solvent mixtures when the solute is not added, $(x_1)_2$ and $(x_1)_3$ are the mole fraction solubility of DNTF in pure ethanol and water, respectively. S_i is the model constant and N can be 0, 1, 2 or 3[16]. For binary solvents system, substituting $N=2$ and $x_3 = 1 - x_2$ into Eq. (6) can give a simplified equation as follows.

$$\ln x_1 = B_0 + B_1 x_2 + B_2 x_2^2 + B_3 x_2^3 + B_4 x_2^4 \quad (7)$$

where B_0, B_1, B_2, B_3, and B_4 are the model parameters. The model parameters values of B_0, B_1, B_2, B_3, B_4, R^2 and the RMSD are displayed in Table 4. The solubility data calculated by the R-K equation are graphically displayed in Fig. 7 which illustrates clearly to us that the solubility values correlated by the R-K equation are in good agreement with the experimental ones. Besides, the R^2 and RMSD are acceptable, so the R-K equation can be used to correlate the solubility of DNTF in ethanol-water binary system at different concentration accurately.

Table 4 Model parameters, R^2 and RMSD of R-K equation

T/K	B_0	B_1	B_2	B_3	B_4	R^2	$10^3 \times$RMSD
298.15	−22.3169	76.8816	−157.8715	152.8098	−54.3125	0.9979	0.0558
303.15	−16.0126	37.6058	−66.7289	62.5669	−22.1021	0.9994	0.0351
308.15	−10.4332	9.1354	−9.9706	12.6271	−5.8762	0.9996	0.0348
313.15	−12.5686	23.6067	−40.9087	40.7800	−15.2629	0.9999	0.0173
318.15	−2.8862	−28.3402	64.9447	−53.5560	15.6584	0.9999	0.0338
323.15	0.8744	−47.9255	105.8041	−90.8652	28.1156	0.9998	0.0524
328.15	2.7568	−57.2875	126.1851	−110.1939	34.7344	0.9995	0.0698
333.15	−9.3064	12.4146	−17.6670	18.8874	−7.9327	1.0000	0.0259
338.15	−20.3303	76.2986	−149.6736	137.5824	−47.2722	0.9995	0.1064

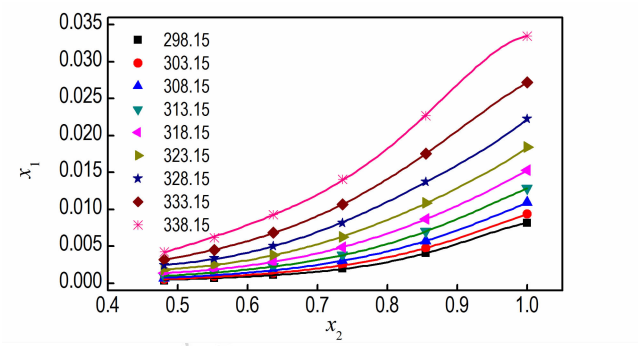

Fig. 7 Mole fraction solubility of DNTF in binary system ethanol-water at various temperatures. The points represent the experimental data. Curves are calculated according to Eq. (7) using the R-K equation

3.2.4 Jouyban-Acree Model

The Jouyban-Acree model[17-18] is also widely used to describe the solubility of DNTF in the whole temperature range by taking both composition of solution and temperature into consideration. The model is expressed as follows:

$$\ln x_1 = x_2 \ln (x_1)_2 + x_3 \ln (x_1)_3 + x_2 x_3 \sum_{i=1}^{N} J_i (x_2 - x_3)/T \quad (8)$$

where J_i is the model constant. Substitution of N=2 into Eq. (8) can give a new simplified equation as:

$$\ln x_1 = A_0 + A_1/T + A_2 \ln T + A_3 x_2 + A_4 x_2/T + A_5 (x_2)^2/T + A_6 (x_2)^3/T + A_7 (x_2)^4/T + A_8 x_2 \ln T \quad (9)$$

where A_0-A_8 are empirical model parameters, which can be obtained by least-squares analysis. The model parameters values of A_0-A_8, R^2 and the RMSD are displayed in Table 5. The three three-dimensional diagram between x_1 and x_2, T is shown in Fig. 8 which demonstrates to us that all of the experimental values are on the surface fitted by the Jouyban-Acree model, besides, the R^2 is very close to 1 and the RMSD is close to 0. Therefore, the Jouyban-Acree model is a perfect equation to correlate the experimental solubility data of DNTF in ethanol-water binary system. What's more, we can calcu-

late the solubility of DNTF in ethanol-water binary system at random temperature and concentration by the Jouyban-Acree model obtained from this study.

Table 5 Parameters of the Jouyban-Acree model for the solubility of DNTF in binary solvent system of ethanol-water binary system

parameters	value	parameters	value
A_0	−227.6819	A_6	−6594.1178
A_1	2858.2636	A_7	1615.9072
A_2	36.7655	A_8	3.9613
A_3	−40.2101	R^2	0.9995
A_4	2884.4629	10^3×RMSD	0.1687
A_5	8472.7321		

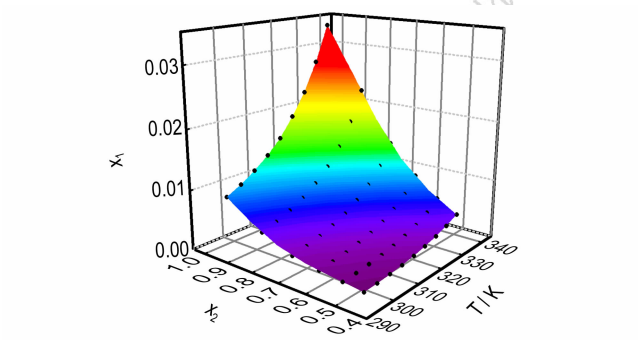

Fig. 8 Experimental mole fraction solubility of DNTF in binary system ethanol-water. The points represent the experimental data, and the surface represents the results fitted by the Jouyban-Acree model

3.3 Thermodynamic Parameters for DNTF Dissolution

Some thermodynamic properties such asthe standard enthalpy of dissolution, standard entropy of dissolution and the standard Gibbs free energy can be calculated by the solubility data measured. The function between the mole fraction solubility of DNTF and the absolute temperature can be expressed as[19]:

$$\ln x_1 = -\frac{\Delta_{dis}H^\Theta}{RT} + \frac{\Delta_{dis}S^\Theta}{R} \quad (10)$$

where R represents the gas constant (8.3145 J·K^{-1}·mol^{-1}), $\Delta_{dis}H^\Theta$ and $\Delta_{dis}S^\Theta$ are the standard enthalpy of dissolution and standard entropy of dissolution of DNTF. Assuming the $\ln x_1$ is dependent variable, $1/T$ is independent variable, so the $\ln x_1$ is linear relation with $1/T$ and we can calculate the $\Delta_{dis}H^\Theta$ from the slope and $\Delta_{dis}S^\Theta$ from the intercept of the linear equation displayed in Fig. 5. The standard Gibbs free energy of dissolution of DNTF in different solvents can be calculated as:

$$\Delta_{dis}G^\Theta = \Delta_{dis}H^\Theta - T\Delta_{dis}S^\Theta \quad (11)$$

In this work, we calculated change in Gibbsfree energy at 318.15 K as a mean temperature ($\Delta_{dis}G^\Theta_{mean}$).

The relative contributions from enthalpy $\%\xi_H$ and entropy $\%\xi_S$ to the standard free Gibbs energy of the solution are define by the following two equations[20]:

$$\%\xi_H = \frac{|\Delta_{dis}H^\Theta|}{|\Delta_{dis}H^\Theta| + |T\Delta_{dis}S^\Theta|} \times 100 \quad (12)$$

$$\%\xi_S = \frac{|T\Delta_{dis}S^\Theta|}{|\Delta_{dis}H^\Theta| + |T\Delta_{dis}S^\Theta|} \times 100 \quad (13)$$

The calculated enthalpy, entropy, and Gibbs energy of dissolution together with $\%\xi_H$, $\%\xi_S$ calculated under the mean temperature are displayed in Table 6. Since the values of $\Delta_{dis}H^\Theta$ are positive in all solvents, the dissolution of DNTF in binary system ethanol-water is an endothermic process. In addition, the dissolution of DNTF is a non-spontaneous process because the values of $\Delta_{dis}G^\Theta_{mean}$ are positive. Moreover, the main contributor to the standard molar Gibbs energy of dissolution is the enthalpy instead of entropy in that the $\%\xi_H$ is greater than $\%\xi_S$.

4 Conclusions

(1) The solubility values of DNTF increase with increasing the ratio of ethanol and temperature as a nonlinear function.

(2) Four correlation equations selected in this study all can be used to fit the solubility values of DNTF precisely. What's more, all of the 54 experimental values are used to correlate the parameters of Jouyban-Acree model and the correlated results are better than other three equations by comparing the R^2 and RMSD.

(3) Some important thermodynamic properties such as

Table 6 Standard enthalpy, entropy of the dissolution of DNTF in different solvents and the standard Gibbs free energy of solution at mean temperature (318.15 K)

x_2	$\Delta_{dis}H^\Theta$ /kJ·mol^{-1}	$\Delta_{dis}S^\Theta$ /J·K^{-1}·mol^{-1}	$\Delta_{dis}G^\Theta_{mean}$ /kJ·mol^{-1}	$\%\xi_H$	$\%\xi_S$	R^2
1.0000	32.1731	66.6687	10.9624	0.6027	0.3973	0.9923
0.8544	40.1884	87.1229	12.4702	0.5918	0.4082	0.9928
0.7354	45.6290	99.3142	14.0322	0.5909	0.4091	0.9961
0.6363	50.5210	110.3018	15.4285	0.5901	0.4099	0.9947
0.5526	50.8256	107.8025	16.5282	0.5971	0.4029	0.9960
0.4808	52.4800	109.7261	17.5706	0.6005	0.3995	0.9995

the standard enthalpy of dissolution, standard entropy of dissolution and standard Gibbs free energy of dissolution have been calculated.

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3,4-二硝基呋咱基氧化呋咱在乙醇-水二元体系中溶解度的测定与关联

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摘 要: 利用激光监视系统测定了3,4-二硝基呋咱基氧化呋咱(DNTF)在乙醇-水中不同温度下的溶解度,并用 van′t Hoff 方程、修正的 Apelblat 方程、R-K 方程和 Jouyban-Acree 方程对所测的溶解度数据进行拟合。四种方程的相关系数均大于0.99,且均方根偏差都接近于0,说明所选四种方程都能很好地拟合实验数据。根据所测溶解度数据,计算了 DNTF 在乙醇-水体系中的溶解熵,溶解焓和溶解的吉布斯自由能,表明 DNTF 在乙醇-水二元体系中溶解是一个吸热、非自发过程。

关键词: 3,4-二硝基呋咱基氧化呋咱(DNTF); 溶解度; 拟合; 热力学性质

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