Measurement and correlation of solid-liquid equilibrium data for nitroguanidine in water and organic solvents from 298.15 K to 338.15 K

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Abstract: Nitroguanidine(NQ) is a high-energy and low-sensitivity explosive and solid-liquid equilibrium data are significant for study on crystallization of NQ. The solubilities of NQ in water, dimethyl sulfoxide, N, N-dimethylformamide, 1,4-butyrolactone and dimethyl sulfoxide + water, N, N-dimethylformamide + water were measured by dynamic laser monitoring within a temperature range from 298.15 K to 338.15 K. The experimental data were correlated by modified Apelblat equation, λh equation, CNIBS/R-K model, and Jouyban-Acree model. The results show that the four thermodynamic models can all be used to predict solubility with high accuracy. Accrding to the Akaike's information criterion (AIC), the better models for correlating the solubility of NQ are judged. Additionally, the dissolution enthalpy, entropy and Gibbs free energy were calculated by the van't Hoff equation.

Key words: nitroguanidine (NQ); solubility; correlation models; thermodynamic properties

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0 Introduction

Nitroguanidine (NQ) is a high-energy and low-sensitivity explosive, and it is widely used as a propellant and composite explosives charge[1]. However, NQ crystal from the production is in the form of long, thin needles, which leads to a very low bulk density. Thus, it is necessary to improve crystal technology to obtain spherulitic NQ particles.

The solid-liquid phase equilibrium data are a key element in the crystallization process in respect of the choice of the best solvent medium, the initially dosage of solute and the terminal holdings of solute in the solvent, and the operation curve of process. In addition, the mathematical expression of phase equilibrium data is the essential basis for the study on the crystallization dynamics and process simulation. Though several research reports on the solubility of NQ have been published[2-5], the solid-liquid equilibrium data of NQ in water and organic solvents have not been systematically reported in the literatures.

In recent years, the measurement and prediction of solid-liquid equilibrium data have received more attention. Some analysis or dynamic methods have also been established[6-7]. Many prediction models suitable for single solvent and cosolvent have been proposed, too[8-9]. In present study, a laser dynamic method was used for the measurement of solubility of NQ in water, N, N-dimethylformamide (DMF), dimethyl sulfoxide (DMSO), 1, 4-butyrolactone (GBL), binary solvent of (DMSO + water) and (DMF + water), within a temperature range from 298.15 K to 338.15 K at atmospheric pressure. The solubility data were correlated by the modified Apelblat model, λh model, CNIBS/R-K model and Jouyban-Acree model. The predicted value were compared with the experiment values. Furthermore, the thermodynamic parameters of NQ were calculated according to van't Hoff equation and Gibbs equation.

1 Experiment

1.1 Materials and apparatus

The crude NQ was supplied by Liaoning Qingyang Chemical (Group) Co. Ltd., China, subsequently recrystallized in water, and the purity was analyzed by HPLC, 99%. All solvents were analytic reagent grade, supplied by Guangdong Xilong Chemical Co. Ltd, China, and the distilled water was self-made.

The solubility measurement device consists of a crystallizer, a temperature controlling device, and a

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laser monitoring system. The laser monitoring system was manufactured by Department of Physics, Peking University, China.

1.2 Solubility measurement

The solubility was measured by the laser dynamic method[10]. All experiments were done three replications, and the average values were used to calculate the solubility.

The mole fraction solubility (x_1) of NQ in a solvent is calculated by

$$x_1 = \frac{m_1/M_1}{m_1/M_1 + \sum_{i=2}^{n}(m_i/M_i)}, \quad (1)$$

where x_1 represents the mole fraction solubility of NQ in solvents; m_1 and M_1 mean the mass and molar mass of NQ, respectively; m_i and M_i ($i=2,3$) mean the mass and molar mass of solvents, respectively. When $n=2$, the solvent is single; and $n=3$, the solvent is binary mixture.

2 Correlated models

In the last 20－30 years, many very useful semi-theoretical or empirical mathematic models describing the solute solubility in single or mixed solvent were studied[11-14]. In this paper, the solubilities of NQ in four pure solvents are correlated with temperature and composition by modified Apelblat equation and λh equation, of which the solubilities of NQ in two binary solvents are correlated by modified Apelblat equation, CNIBS/R-K equation, and Jouyban-Acree model, respectively.

2.1 Modified Apelblat equation

The modified Apelblat equation[15-16] is derived from the Clausius-Clapeyron equation, which can be used to correlate the solubility with temperature. The equation is expressed as

$$\ln x_1 = A + B/T + C\ln T, \quad (2)$$

where T represents the absolute temperature; A, B and C are model parameters.

2.2 λh equation

The λh equation was proposed by Buchowski[17-18], which used to express the relationship between the mole fraction solubility and the temperature. The equation is described as

$$\ln\left(1+\lambda\frac{1-x_1}{x_1}\right) = \lambda h\left(\frac{1}{T}-\frac{1}{T_m}\right), \quad (3)$$

where T and T_m are the system temperature and the melting temperature of the solute, respectively; λ and h are model parameters.

2.3 CNIBS/R-K equation

The CNIBS/R-K equation proposed by Acree[19] is mainly used to correlate the solubility with the composition of the binary solvent when the temperature is constant[20]. The expression is

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

where x_A is the mole fraction of solvent A in the binary mixtures; B_0, B_1, B_2, B_3 and B_4 are the model parameters.

2.4 Jouyban-Acree model

The Jouyban-Acree (J-A) model[21] is widely used for describing the effect of both temperature and solvent initial composition on solute solubility in a binary solvent system. The equation can be expressed as

$$\ln x_1 = A_1 + \frac{A_2}{T} + A_3\ln T + A_4 x_A + A_5\frac{x_A}{T} + x_6\frac{X_A^2}{T} + A_7\frac{x_A^3}{T} + A_8\frac{x_A^4}{T} + A_9 X_A\ln T, \quad (5)$$

where A_1-A_9 are model parameters.

3 Estimation of thermodynamic parameters of solution

According to the van't Hoff equation, the dissolution enthalpy, entropy and Gibbs energy can be estimated when the solubility of solute was measured[22-23]. The relationship can be expressed by

$$\ln x = -\frac{\Delta_{dis}H}{RT} + \frac{\Delta_{dis}S}{R}. \quad (6)$$

4 Results and discussion

4.1 Measured solubility

The solubility data of NQ in water, DMF, DMSO, and GBL are listed in Table 1 and Fig. 1, respectively.

As shown in Table 1, the solubilities of NQ in above solvents all increase with the temperature. The solubility order is DMSO＞DMF＞GBL＞water. A weaker temperature dependence is shown in DMF and DMSO. As the temperature increases from 298.15 K to 338.15 K, the solubility values in DMF and DMSO increase by 55% and 21%, respectively;

while increase by 696% and 597% in water and GBL, respectively.

Table 1 Experimental and calculated solubility values of NQ in pure solvents ($\times 10^{-2}$ mol/mol)

T(K)	Water			DMSO			DMF			GBL		
	x_1^{exp}	x_1^{Apel}	$x_1^{\lambda h}$	x_1^{exp}	x_1^{Apel}	$x_1^{\lambda h}$	x_1^{exp}	x_1^{Apel}	$x_1^{\lambda h}$	x_1^{exp}	x_1^{Apel}	$x_1^{\lambda h}$
298.15	0.050	0.051	0.051	20.874	20.849	20.868	8.139	8.092	8.134	0.270	0.285	0.282
303.15	0.069	0.069	0.066	21.332	21.334	21.337	8.542	8.569	8.511	0.352	0.362	0.360
308.15	0.087	0.086	0.086	21.772	21.835	21.826	9.024	9.073	9.010	0.440	0.457	0.456
313.15	0.110	0.111	0.110	22.347	22.354	22.335	9.578	9.605	9.532	0.573	0.573	0.573
318.15	0.142	0.141	0.140	22.905	22.890	22.866	10.148	10.165	10.077	0.716	0.714	0.715
323.15	0.175	0.178	0.178	23.436	23.443	23.419	10.806	10.756	10.748	0.903	0.884	0.886
328.15	0.221	0.223	0.223	24.019	24.013	23.997	11.459	11.378	11.445	1.119	1.089	1.091
333.15	0.278	0.278	0.279	24.599	24.601	24.600	12.055	12.033	12.070	1.325	1.335	1.335
338.15	0.348	0.345	0.346	25.196	25.206	25.231	12.644	12.722	12.725	1.612	1.628	1.624

Note: x_1^{exp} is the experiment value of solubiliby, x_1^{Apel} and $x_1^{\lambda h}$ are calculation values of solubiliby by correlation equations

As for crystallization, too high or too low solubility is not appropriate. Therefore, the binary solvent is considered.

The solubility values of NQ in (DMSO + water) and (DMF + water) are listed in Tables 2 − 3 and Fig. 1, respectively. The moderate solubility is shown in them, all of which increases with temperature and the mole fraction of DMSO or DMF.

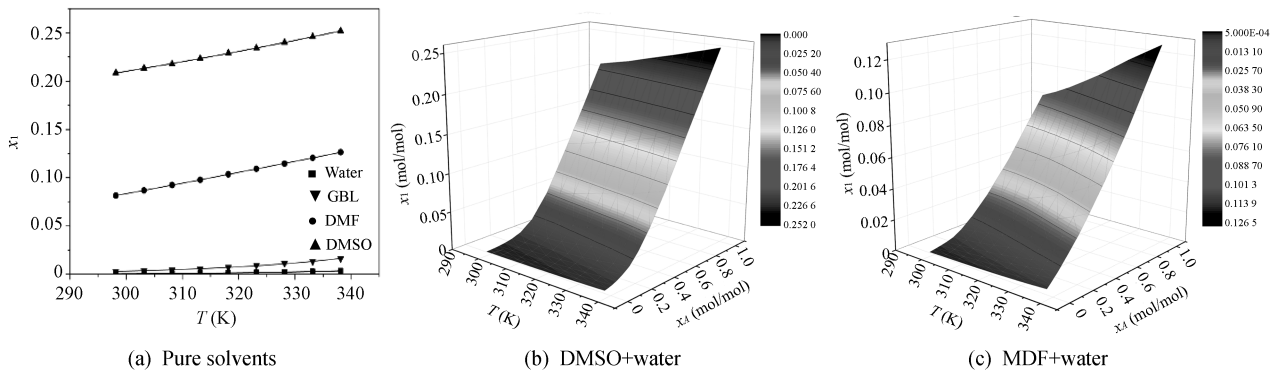
Table 2 Experimental and calculated solubility values of NQ in DMSO+water ($\times 10^{-2}$ mol/mol)

T(K)	$x_A=0.027\ 4$				$x_A=0.059\ 6$				$x_A=0.098\ 0$			
	x_1^{exp}	x_1^{Apel}	x_1^{CRK}	x_1^{JA}	x_1^{exp}	x_1^{Apel}	x_1^{CRK}	x_1^{JA}	x_1^{exp}	x_1^{Apel}	x_1^{CRK}	x_1^{JA}
298.15	0.076	0.071	0.080	0.077	0.105	0.103	0.109	0.111	0.159	0.149	0.158	0.169
303.15	0.097	0.092	0.095	0.098	0.134	0.132	0.134	0.140	0.197	0.190	0.200	0.210
308.15	0.117	0.118	0.115	0.124	0.164	0.167	0.164	0.175	0.243	0.240	0.244	0.260
313.15	0.147	0.150	0.150	0.157	0.206	0.210	0.206	0.218	0.299	0.301	0.299	0.319
318.15	0.184	0.190	0.180	0.195	0.262	0.263	0.253	0.269	0.366	0.375	0.370	0.389
323.15	0.236	0.239	0.238	0.242	0.325	0.326	0.322	0.330	0.457	0.464	0.457	0.472
328.15	0.307	0.298	0.305	0.298	0.411	0.403	0.406	0.402	0.570	0.570	0.568	0.569
333.15	0.368	0.370	0.369	0.365	0.494	0.494	0.493	0.488	0.696	0.696	0.691 3	0.683
338.15	0.455	0.455	0.458	0.444	0.599	0.601	0.606	0.588	0.850	0.845	0.8410	0.814
T(K)	$x_A=0.144\ 5$				$x_A=0.202\ 2$				$x_A=0.275\ 4$			
	x_1^{exp}	x_1^{Apel}	x_1^{CRK}	x_1^{JA}	x_1^{exp}	x_1^{Apel}	x_1^{CRK}	x_1^{JA}	x_1^{exp}	x_1^{Apel}	x_1^{CRK}	x_1^{JA}
298.15	0.259	0.241	0.253	0.276	0.459	0.439	0.451	0.491	0.900	0.855	0.911	0.962
303.15	0.317	0.303	0.318	0.338	0.552	0.537	0.550	0.590	1.056	1.028	1.055	1.129
308.15	0.385	0.378	0.387	0.412	0.660	0.653	0.659	0.705	1.236	1.228	1.235	1.318
313.15	0.466	0.468	0.463	0.498	0.783	0.789	0.779	0.838	1.435	1.459	1.442	1.531
318.15	0.560	0.577	0.572	0.599	0.943	0.948	0.944	0.990	1.699	1.725	1.689	1.771
323.15	0.693	0.706	0.692	0.716	1.128	1.133	1.129	1.163	2.000	2.028	2.000	2.039
328.15	0.850	0.858	0.845	0.852	1.307	1.345	1.347	1.361	2.355	2.373	2.316	2.337
333.15	1.038	1.037	1.026	1.008	1.591	1.590	1.624	1.584	2.769	2.764	2.743	2.668
338.15	1.260	1.247	1.236	1.186	1.895	1.870	1.934	1.836	3.233	3.204	3.211	3.035
T(K)	$x_A=0.371\ 6$				$x_A=0.503\ 4$				$x_A=0.695\ 2$			
	x_1^{exp}	x_1^{Apel}	x_1^{CRK}	x_1^{JA}	x_1^{exp}	x_1^{Apel}	x_1^{CRK}	x_1^{JA}	x_1^{exp}	x_1^{Apel}	x_1^{CRK}	x_1^{JA}
298.15	2.085	1.969	2.082	2.080	5.047	5.046	5.047	4.843	10.927	10.825	10.924	10.880
303.15	2.287	2.269	2.287	2.372	5.497	5.497	5.497	5.323	11.377	11.377	11.373	11.420
308.15	2.585	2.603	2.586	2.693	5.974	5.972	5.974	5.833	11.927	11.937	11.923	11.969
313.15	2.956	2.974	2.954	3.044	6.471	6.471	6.471	6.374	12.505	12.505	12.503	12.524
318.15	3.314	3.382	3.319	3.429	7.044	6.993	7.043	6.945	12.946	13.082	12.946	13.087
323.15	3.822	3.832	3.822	3.847	7.540	7.534	7.540	7.547	13.666	13.666	13.666	13.657
328.15	4.244	4.325	4.257	4.302	8.015	8.111	8.013	8.181	14.200	14.257	14.200	14.233
333.15	4.868	4.864	4.876	4.795	8.706	8.706	8.704	8.847	14.855	14.855	14.855	14.815
338.15	5.529	5.450	5.534	5.326	9.369	9.325	9.368	9.544	15.563	15.459	15.564	15.402

Note: x_1^{Apel}, x_1^{CRK} and x_1^{JA} represent the calculation values of solubility by correlation equations

Table 3 Experimental and calculated solubility values of NQ in DMF+water ($\times 10^{-2}$ mol/mol)

T(K)	$x_A=0.025\ 3$				$x_A=0.055\ 2$				$x_A=0.091\ 0$			
	x_1^{exp}	x_1^{Apel}	x_1^{CRK}	x_1^{JA}	x_1^{exp}	x_1^{Apel}	x_1^{CRK}	x_1^{JA}	x_1^{exp}	x_1^{Apel}	x_1^{CRK}	x_1^{JA}
298.15	0.087	0.086	0.081	0.083	0.130	0.129	0.118	0.124	0.191	0.192	0.179	0.191
303.15	0.112	0.114	0.106	0.107	0.165	0.167	0.155	0.159	0.242	0.243	0.233	0.241
308.15	0.149	0.148	0.138	0.137	0.214	0.215	0.201	0.202	0.310	0.305	0.299	0.302
313.15	0.192	0.189	0.176	0.174	0.277	0.273	0.256	0.254	0.385	0.382	0.379	0.375
318.15	0.238	0.239	0.222	0.220	0.347	0.343	0.321	0.317	0.469	0.475	0.469	0.464
323.15	0.298	0.298	0.275	0.275	0.424	0.427	0.397	0.393	0.584	0.587	0.577	0.569
328.15	0.362	0.366	0.342	0.342	0.522	0.527	0.490	0.484	0.722	0.722	0.709	0.695
333.15	0.441	0.445	0.423	0.423	0.643	0.645	0.602	0.593	0.883	0.884	0.864	0.843
338.15	0.541	0.535	0.524	0.519	0.789	0.783	0.740	0.722	1.082	1.077	1.053	1.017
T(K)	$x_A=0.134\ 8$				$x_A=0.189\ 4$				$x_A=0.259\ 5$			
	x_1^{exp}	x_1^{Apel}	x_1^{CRK}	x_1^{JA}	x_1^{exp}	x_1^{Apel}	x_1^{CRK}	x_1^{JA}	x_1^{exp}	x_1^{Apel}	x_1^{CRK}	x_1^{JA}
298.15	0.273	0.276	0.281	0.299	0.412	0.413	0.456	0.472	0.744	0.750	0.764	0.750
303.15	0.356	0.350	0.357	0.371	0.520	0.520	0.564	0.576	0.898	0.893	0.904	0.897
308.15	0.438	0.440	0.453	0.458	0.649	0.647	0.694	0.699	1.072	1.058	1.071	1.069
313.15	0.553	0.549	0.567	0.562	0.804	0.799	0.850	0.845	1.247	1.249	1.267	1.269
318.15	0.679	0.679	0.692	0.686	0.975	0.977	1.020	1.017	1.463	1.468	1.488	1.502
323.15	0.831	0.834	0.844	0.832	1.173	1.186	1.226	1.218	1.707	1.719	1.754	1.772
328.15	1.012	1.016	1.027	1.004	1.431	1.428	1.475	1.453	2.001	2.007	2.074	2.084
333.15	1.220	1.231	1.239	1.206	1.712	1.706	1.756	1.725	2.338	2.333	2.431	2.443
338.15	1.494	1.480	1.494	1.442	2.023	2.024	2.092	2.041	2.712	2.704	2.853	2.856
T(K)	$x_A=0.352\ 8$				$x_A=0.483\ 1$				$x_A=0.677\ 7$			
	x_1^{exp}	x_1^{Apel}	x_1^{CRK}	x_1^{JA}	x_1^{exp}	x_1^{Apel}	x_1^{CRK}	x_1^{JA}	x_1^{exp}	x_1^{Apel}	x_1^{CRK}	x_1^{JA}
298.15	1.369	1.354	1.319	1.201	2.433	2.411	2.351	2.019	4.362	4.311	4.456	4.143
303.15	1.492	1.504	1.472	1.401	2.544	2.562	2.469	2.281	4.503	4.534	4.577	4.464
308.15	1.662	1.683	1.659	1.631	2.747	2.759	2.648	2.578	4.756	4.810	4.842	4.831
313.15	1.893	1.897	1.879	1.896	2.985	3.007	2.873	2.916	5.112	5.145	5.210	5.250
318.15	2.159	2.154	2.149	2.201	3.311	3.314	3.193	3.300	5.551	5.545	5.649	5.728
323.15	2.485	2.462	2.469	2.550	3.710	3.692	3.564	3.737	6.066	6.018	6.183	6.271
328.15	2.852	2.830	2.854	2.950	4.202	4.153	4.010	4.233	6.640	6.574	6.779	6.888
333.15	3.268	3.272	3.279	3.407	4.733	4.716	4.504	4.796	7.274	7.227	7.430	7.590
338.15	3.778	3.803	3.779	3.928	5.349	5.402	5.065	5.434	7.890	7.990	8.079	8.386



(a) Pure solvents (b) DMSO+water (c) MDF+water

Fig. 1 Solubilities for NQ in different solvents

4.2 Solubility correlation

The solubility of NQ in pure solvents is correlated by the modified Apelblat equation and λh equation, of which that in (DMSO + water), and (DMF + water) is correlated by the modified Apelblat model, CNIBS/R-K model, and the Jouyban-Acree model. The fitted model parameters are listed in Tables 4—9. The calculated solubility values are shown in Tables 1—3.

The root-mean-square deviation (δ) is calculated to evaluate the accuracy of predicted models as

$$\delta = \left(\frac{1}{N}\sum_{i=1}^{n}(x_i^{exp} - x_i^{cal})^2\right)^{\frac{1}{2}}, \qquad (7)$$

where N denotes the number of data points; x_i^{cal} represents the calculated solubility: x_i^{Apel}, $x_i^{\lambda h}$, x_i^{CRK} and x_i^{JA}.

The δ values and the square of the correlation coefficient (R^2) of these models are shown in Tables 4—7.

Table 4 Parameters, R^2 and δ of Apelblat equation in solvents

Solvents	x_A	A	B	C	$10^2\delta$	R^2	Solvents	x_A	A	B	C	$10^2\delta$	R^2
Water	—	1.83	−4 489.77	0.99	0.001 7	0.999 8	DMSO	—	−25.58	723.80	3.79	0.023 7	0.999 6
DMF	—	−40.92	841.31	6.24	0.049 5	0.999 5	GBL	—	−19.16	−3 074.33	4.14	0.015 8	0.998 3
DMSO+water	0.027 4	−7.26	−4 690.90	4.20	0.004 8	0.998 5	DMF+water	0.025 3	173.53	−12 345.60	−24.43	0.028 5	0.999 9
	0.059 6	−8.44	−4 450.04	1.30	0.003 6	0.999 5		0.055 2	76.31	−7 722.82	−10.02	0.037 2	0.999 8
	0.098 0	5.27	−4 374.59	1.98	0.005 9	0.999 4		0.091 0	−26.21	−2 730.93	5.11	0.034 2	0.999 9
	0.1445	−4.89	−4 146.64	0.33	0.011 8	0.998 7		0.134 8	33.54	−5 415.46	−3.73	0.066 6	0.999 8
	0.202 2	−6.14	−3 653.59	1.30	0.017 8	0.998 5		0.189 4	64.25	−6 646.30	−8.33	0.052 6	0.999 8
	0.275 4	−7.49	−3 331.24	3.68	0.026 1	0.998 9		0.259 5	−27.61	−1 656.80	4.96	0.077 4	0.999 9
	0.371 6	−4.02	−2 566.33	0.91	0.059 7	0.997 2		0.352 8	−284.35	10 948.77	42.71	0.163 5	0.999 7
	0.503 4	−22.31	−1 547.62	2.14	0.039 0	0.999 2		0.483 1	−374.84	15 701.84	55.89	0.282 7	0.999 6
	0.695 2	−2.51	−898.12	1.07	0.069 3	0.997 9		0.677 7	−258.51	10 673.06	38.54	0.542 3	0.999 9

Table 5 Parameters, R^2 and δ of λh equation in pure solvents

Solvents	λ	h	$10^2\delta$	R^2	Solvents	λ	h	$10^2\delta$	R^2
Water	0.39	12 454.45	0.001 6	0.999 7	DMSO	−0.14	3 881.46	0.027 0	0.999 6
DMF	0.13	5 024.27	0.056 1	0.998 5	GBL	1.23	3 600.10	0.014 1	0.999 0

Table 6 Parameters, R^2 and δ of CNIBS/R-K equation in binary solvents

T(K)	DMSO+water							DMF+water						
	B_0	B_1	B_2	B_3	B_4	$10^2\delta$	R^2	B_0	B_1	B_2	B_3	B_4	$10^2\delta$	R^2
298.15	−7.38	8.81	9.60	−26.57	14.25	0.005 6	1.000 0	−7.48	14.48	−21.71	19.45	−7.26	0.487 1	0.999 1
303.15	−7.27	11.28	−5.94	4.55	−6.02	0.001 4	1.000 0	−7.20	14.58	−24.98	25.07	−9.94	0.393 3	0.999 5
308.15	−7.08	11.66	−8.75	8.95	−8.26	0.000 9	1.000 0	−6.94	14.73	−28.09	30.50	−12.60	0.474 5	0.999 3
313.15	−6.77	10.02	−1.53	−5.67	1.59	0.003 1	1.000 0	−6.70	14.92	−31.14	35.85	−15.28	0.540 8	0.999 2
318.15	−6.62	11.23	−9.17	8.56	−7.27	0.006 4	1.000 0	−6.46	14.67	−31.55	36.83	−15.78	0.556 9	0.999 2
323.15	−6.29	9.34	0.21	−11.77	7.14	0.001 5	1.000 0	−6.24	14.65	−32.74	38.92	−16.82	0.687 9	0.999 2
328.15	−6.04	8.94	0.38	−12.57	8.25	0.019 3	1.000 0	−6.03	14.58	−33.48	40.20	−17.43	0.857 9	0.999 4
333.15	−5.85	9.11	−0.44	−13.25	9.742	0.014 9	1.000 0	−5.80	14.37	−33.67	40.75	−17.75	1.000 1	0.999 4
338.15	−5.62	8.64	1.51	−18.73	14.21	0.017 4	1.000 0	−5.59	14.09	−33.44	40.46	−17.59	1.273 6	0.999 3

Table 7 Parameters, R^2 and δ of Jouyban-Acree model in binary solvents

Parameters	A_1	A_2	A_3	A_4	A_5	A_6	A_7	A_8	A_9	δ	R^2
DMSO+water	−4.62	−4 595.06	46.82	−8.50	6 558.06	−1 001.20	−1 839.47	1 121.04	−6.98	0.000 7	0.999 8
DMF+water	26.16	−5 636.27	−2.59	−290.84	20 628.79	−9 493.13	10 766.59	−4 553.28	41.73	0.011 2	0.999 5

4.3 Evaluation of thermodynamic models

In order to find the optimal model for NQ, the Akaike Information Criterion (AIC)[24-25] is employed to evaluate the relative applicability of these models. The values of AIC for all models are listed in Table 8.

The result shows that the AIC of modified Apelblat equation is lower in pure solvents, which has better correlation effect, and the Jouyban-Acree model is more suitable for correlating the solubility of NQ in binary solvents.

Table 8 AIC values of two models in pure solvents and three models in binary solvents

Models	Modified Apelblat equation	λh equation	CNIBS/R-K model	Jouyban-Acree model
Pure solvents	−133.26	−124.44		
DMSO+water	−137.19		−154.96	−1 148.89
DMF+ater	−129.38		−110.75	−1 082.10

4.4 Thermodynamic parameters of solutions

According to Eq.(6), the calculated thermodynamic parameters of NQ in the above mentioned solvents are listed in Table 9. The dissolution Gibbs free energy is calculated by

$$\Delta_{dis}G = \Delta_{dis}H - T_{mean}\Delta_{dis}S, \tag{8}$$

where T_{mean} is mean temperature, 317.63 K.

The dissolution enthalpy is positive in all solvents, which means that all the dissolution processes are an endothermic process.

Table 9 Thermodynamic properties of NQ in solvents at 317.63 K

Solvents	x_A	$\Delta_{dis}H$ (kJ·mol^{-1})	$\Delta_{dis}G$ (kJ·mol^{-1})	$\Delta_{dis}S$ (J·K^{-1}·mol^{-1})	Solvents	x_A	$\Delta_{dis}H$ (kJ·mol^{-1})	$\Delta_{dis}G$ (kJ·mol^{-1})	$\Delta_{dis}S$ (J·K^{-1}·mol^{-1})
Water	—	39.95	17.40	70.99	DMSO	—	3.98	3.89	0.26
DMF	—	9.48	6.04	10.84	GBL	—	37.65	13.13	77.20
DMSO+water	0.027 4	37.91	16.59	67.14	MF+water	0.025 3	38.18	16.06	69.66
	0.059 6	36.84	15.75	66.40		0.055 2	37.78	15.07	71.51
	0.098 0	35.28	14.79	64.51		0.091 0	36.18	14.18	69.29
	0.144 5	33.15	13.65	61.41		0.134 8	35.17	13.25	69.02
	0.202 2	29.55	12.34	54.18		0.189 4	33.29	12.29	66.09
	0.275 4	26.89	10.75	50.81		0.259 5	26.87	11.18	49.39
	0.371 6	20.70	8.97	36.92		0.352 8	21.64	10.08	36.41
	0.503 4	12.85	7.05	18.27		0.483 1	16.91	8.90	25.22
	0.695 2	7.41	5.38	6.38		0.677 7	12.94	7.58	16.88

5 Conclusion

The solubilities of NQ in pure solvents (water, DMSO, DMF, GBL) and binary solvents (DMSO+water, DMF+water) are measured. The solubility order is DMSO > DMF > GBL > water. The solubilities increase with the temperature and mole fraction of DMSO or DMF. The solubilities of NQ in DMF and DMSO have a weaker temperature dependence. The solubilities of NQ in pure solvents are correlated by modified Apelblat and λh equation. The modified Apelblat equation gives the better correlate precision. The solubilities in (DMSO+water) and (DMF+water) are correlated by the modified Apelblat, CNIBS/R-K, and the Jouyban-Acree model, of which the Jouyban-Acree model is more adaptable. At 317.63 K, the dissolution enthalpy values of NQ in water, DMSO, DMF and GBL are 39.95, 3.98, 9.48 and 37.65 kJ·mol^{-1}, respectively; and the dissolution Gibbs free energy values are 17.40, 3.89, 6.04 and 13.13 kJ·mol^{-1}, respectively.

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硝基胍在水和有机溶剂中的固液相平衡数据测定与关联(298.15 K—338.15 K)

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摘 要: 硝基胍(NQ)是一种高能钝感炸药, 固液相平衡数据对于其结晶研究具有重要意义。采用激光动态法测定了硝基胍在水、二甲基亚砜(DMSO)、N, N-二甲基甲酰胺(DMF)、γ-丁内酯(GBL)、DMSO/水和DMF/水溶液中298.15 K到338.15 K温度范围内的溶解度, 并用修正的Apelblat方程、λh方程、CNIBS/R-K方程及Jouyban-Acree方程对所测溶解度数据进行了关联。对所建模型的预测结果与实验数据进行了对比, 结果表明, 上述热力学模型预测NQ溶解度的准确度较高。此外, 利用Akaike信息准则(AIC)对比了各关联模型的预测效果, 通过范特霍夫方程计算了NQ在上述溶剂中的溶解焓变、熵变及吉布斯自由能变。

关键词: 硝基胍(NQ); 溶解度; 关联模型; 热力学特性

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