

Solubility of N-ethylcarbazole in ethanol+petroleum ether mixtures at various temperatures

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Abstract—The solubility of N-ethylcarbazole in (ethanol+petroleum ether) binary solvent mixtures was measured with the temperature changing from 280.15 K to 316.15 K. The experimental data matched the solvent/Redlich-Kister (CNIBS/R-K) equation and the Jouyban-Acree equation. Computational results showed the CNIBS/R-K equation was more suitable than the Jouyban-Acree equation. The solution process in the thermodynamic properties, including the Gibbs energy, enthalpy, and entropy, was calculated by the van't Hoff analysis.

Keywords: N-ethylcarbazole, Solubility, Binary Solvent Mixtures, Thermodynamic Properties

INTRODUCTION

As an important chemical intermediates, carbazole and its derivatives are widely used in dye, medicine, pesticide, spices and macromolecule [1,2]. N-ethylcarbazole is a kind of carbazole derivatives synthesized by carbazole and diethyl sulfate. N-ethylcarbazole is widely used for synthesizing dyes such as sulfur vat blue GNX and Permanent violet RL. Permanent violet RL is recognized as the best purple pigment by now, widely used in plastics, coatings, printing, printing ink and leather coloring agent [3,4]. In terms of pharmaceutical intermediates, N-ethylcarbazole is mainly used for sulfa antibiotics, hemolytic streptococcus, pneumococcus and meningococcal infection. As a coal tar extraction, the price of N-ethylcarbazole keeps rising with the price increase of coal tar. The research of the chemical and physical properties of N-ethylcarbazole appears increasingly important. The studies on the solubility of N-ethylcarbazole in different solvents are more important, because they are guidelines for choosing the suitable solvent and are beneficial to the optimization of the crystallization process.

In this work, the solubility of N-ethylcarbazole in (ethanol+petroleum ether) binary solvent mixtures was measured from 280.15 K to 316.15 K at atmospheric pressure (101.3 kPa). Ethanol and petroleum ether were selected as binary solvent mixtures since they are inexpensive, and easily removed from the solution. The experimental data were calculated by the solvent/Redlich-Kister (CNIBS/R-K) equation and the Jouyban-Acree equation, the Jouyban-Acree model is one of the most accurate models developed in recent years [5]. All the two equations proven the accuracy of the experimental data. In addition, the thermodynamic properties of the dissolution process such as Gibbs energy, enthalpy, and entropy were calculated by the van't Hoff equation and the Gibbs equation. The results indicated that the dissolution process was endothermic.

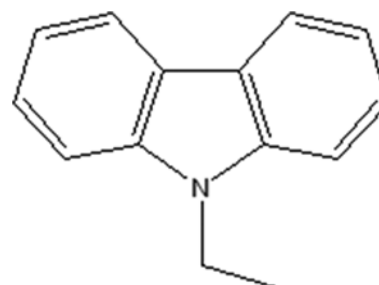


Fig. 1. Chemical structure of N-ethylcarbazole.

EXPERIMENTAL

1. Materials and Apparatus

N-ethylcarbazole ($C_{14}H_{13}N$, FW195.2597, CASRN:86-28-2, Fig. 1) was purchased from Aladdin Industrial Corporation with a mass fraction purity >97%. Its purity was measured by high performance liquid chromatography (HPLC type Agilent 1260 Infinity LC, Agilent Technologies). Ethanol and petroleum ether were supplied by Shanghai Shenbo Chemical Co., Ltd., China. All the solvents were used without further purification and more details about the purity of solvents are listed in Table 1. Analytical balance (model: BSA224S) was provided by Sartorius Scientific Instruments (Beijing) CO., Ltd. with the uncertainty of ± 0.0001 g. The Smart water-circulator thermostatic bath (model: DC-2006) was provided by Ningbo Scientz

Table 1. Provenance and purity of the materials used

Solvent	Source	Mass fraction purity	Molar mass (g·mol ⁻¹)
N-ethylcarbazole	Aladdin	≥0.970	195.26
Ethanol	Shenbo chemicals	≥0.990	46.07
Petroleum ether	Shenbo chemicals	≥0.997	195.34

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Biotechnology CO., Ltd. with the uncertainty of ± 0.01 K.

2. Methods

The solubility of N-ethylcarbazole in (ethanol+petroleum ether) binary solvent mixtures was measured from 280.15 K to 316.15 K at atmospheric pressure by the method similar to that described in our previous work [6,7]. Excess mass of N-ethylcarbazole and 8 ml binary solvent mixtures were added into a 10 ml glass test tube, maintained in a Smart water-circulator thermostatic bath. A continuous stirring rate of 80 rpm was taken at least for 6 hours to ensure the solution reaching equilibrium, then turned off the stirrer stand for 6 hours to ensure the suspended solid phase settle down. After that, transferred 1 ml supernatant by a pipette gun into a 5 ml beaker with cover, the empty beaker and the total weight was measured by balance immediately. Finally, we put the beaker into a dryer oven for seven days until the weight of the beaker did not change and recorded the measurement result. All the solubility experiment was repeated three times to obtain the mean value.

RESULTS AND DISCUSSION

1. Solubility Data

The molar fraction solubility are listed in Table 1 as function of initial mole fraction of ethanol in the solvent mixture and temperature.

Table 2. Mole fraction solubility (x_1) of N-ethylcarbazole in ethanol (2)+petroleum ether binary solvent mixtures at the temperature range from (280.15-316.15) K under atmospheric pressure^a

$100x_1^b$	x_2^b	$100(x_1 - x_1^{cal})/x_1$ (Eq. (4))	$100(x_1 - x_1^{cal})/x_1$ (Eq. (12))
T=280.15 K			
3.001	0.000	0.003	10.639
2.881	0.320	-0.014	23.348
2.684	0.515	0.018	18.193
2.361	0.645	0.140	26.556
2.021	0.739	-0.114	33.653
1.699	0.809	-0.571	43.396
1.424	0.864	0.429	50.873
1.191	0.908	0.214	57.878
1.021	0.944	0.284	63.003
0.872	0.974	1.388	66.663
0.744	1.000	-2.254	66.623
T=284.15 K			
3.872	0.000	0.005	11.253
3.622	0.320	-0.024	17.725
3.505	0.515	-0.046	11.542
3.023	0.645	0.463	15.455
2.575	0.739	0.070	19.321
2.152	0.809	-0.831	36.469
1.825	0.864	0.663	45.503
1.535	0.908	1.772	51.743
1.275	0.944	1.506	56.054
1.077	0.974	2.423	59.939
0.853	1.000	-3.778	59.336

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

where m_1 , m_2 , represent the mass of the solute, ethanol, petroleum ether, M_1 , M_2 , represent the molecular weight of the solute, ethanol, petroleum ether, respectively.

From Table 2 and Fig. 2, it can be observed that the solubility of N-ethylcarbazole in (ethanol+petroleum ether) binary solvent mixtures is a function of temperature and solvent composition. The solubility of N-ethylcarbazole in (ethanol+petroleum ether) binary solvent mixtures increases with the increasing temperature. The solubility was relatively high in petroleum ether but low in ethanol, while it increased with increasing petroleum ether content at constant temperature. From here we could use ethanol as effective anti-

Table 2. Continued

$100x_1^b$	x_2^b	$100(x_1 - x_1^{cal})/x_1$ (Eq. (4))	$100(x_1 - x_1^{cal})/x_1$ (Eq. (12))
T=288.15 K			
4.992	0.000	0.002	12.399
4.612	0.320	-0.027	9.582
4.238	0.515	0.125	3.651
3.672	0.645	-0.163	10.256
3.163	0.739	-0.016	20.264
2.657	0.809	0.041	28.583
2.186	0.864	-0.082	36.993
1.794	0.908	0.513	42.777
1.451	0.944	-0.055	44.465
1.179	0.974	-0.373	47.052
0.969	1.000	-0.206	48.520
T=292.15 K			
6.289	0.000	-0.002	12.105
5.932	0.320	0.024	4.885
5.137	0.515	-0.099	-6.179
4.402	0.645	0.052	-0.609
3.761	0.739	0.170	9.496
3.152	0.809	0.048	16.759
2.6	0.864	-0.300	25.091
2.139	0.908	-0.262	29.827
1.763	0.944	0.051	37.698
1.456	0.974	0.158	43.678
1.212	1.000	0.412	37.772
T=296.15 K			
7.73	0.000	0.001	10.170
7.023	0.320	-0.009	-3.307
6.653	0.515	0.033	-8.573
5.775	0.645	-0.021	-2.091
4.845	0.739	-0.041	5.279
3.963	0.809	0.003	13.587
3.199	0.864	0.006	1.902
2.577	0.908	0.050	25.975
2.088	0.944	0.350	29.074
1.689	0.974	-0.296	28.443
1.39	1.000	-0.223	24.145

Table 2. Continued

$100x_1^b$	x_2^b	$100(x_1-x_1^{cal})/x_1$ (Eq. (4))	$100(x_1-x_1^{cal})/x_1$ (Eq. (12))
T=300.15 K			
9.48	0.000	0.003	8.554
9.063	0.320	-0.035	-1.270
8.493	0.515	0.174	-10.222
7.355	0.645	-0.326	-10.097
6.24	0.739	0.245	2.626
5.087	0.809	0.187	5.687
4.018	0.864	-0.836	8.689
3.195	0.908	-0.182	11.702
2.586	0.944	2.313	15.114
2.015	0.974	0.616	18.070
1.549	1.000	-3.253	7.036
T=304.15 K			
11.599	0.000	0.003	7.223
10.641	0.320	-0.031	-3.251
9.683	0.515	0.115	-12.153
8.725	0.645	-0.090	-10.954
7.767	0.739	-0.146	-6.501
6.809	0.809	0.021	-2.014
5.851	0.864	0.200	1.450
4.893	0.908	0.359	3.841
3.935	0.944	-0.348	4.549
2.977	0.974	0.905	6.458
2.019	1.000	-1.575	4.353
T=308.15 K			
14.714	0.000	-0.001	2.627
13.543	0.320	0.007	-2.099
12.371	0.515	-0.025	-15.163
11.2	0.645	0.063	-14.940
10.028	0.739	-0.020	-11.659
8.857	0.809	-0.062	-8.678
7.686	0.864	0.020	-5.543
6.514	0.908	0.008	-2.104
5.343	0.944	-0.010	-3.832
4.171	0.974	-0.016	-4.959
3.042	1.000	0.014	80.477

solvent in the crystallization process.

2. Data Correction

In this work, the CNIBS/Redlich-Kister model was used to describe the relationship of the experimental isothermal mole fraction solubility and binary solvent compositions [8,9]. The model is presented in Eq. (2):

$$\ln x_1 = x_2 \ln(x_1)_2 + x_3 \ln(x_1)_3 + x_2 x_3 \sum_{i=0}^N S_i (x_2 - x_3)^i \quad (2)$$

where x_2 and x_3 represent the initial mole fraction composition of the (ethanol+petroleum ether) binary solvent. S_i is the model constant, $(x_1)_i$ is the saturated mole fraction solubility of the solute in pure solvent i . N can be equal to 0, 1, 2 and 3. When $N=2$ and $x_3=1-x_2$, Eq. (2) can be written as Eq. (3):

Table 2. Continued

$100x_1^b$	x_2^b	$100(x_1-x_1^{cal})/x_1$ (Eq. (4))	$100(x_1-x_1^{cal})/x_1$ (Eq. (12))
T=312.15 K			
15.853	0.000	0.001	-2.799
14.668	0.320	-0.009	-32.500
13.482	0.515	0.022	-8.715
12.297	0.645	-0.031	-8.505
11.112	0.739	0.036	-0.908
9.927	0.809	-0.092	-8.768
8.741	0.864	0.083	-4.987
7.556	0.908	0.123	-5.087
6.371	0.944	-0.042	-5.790
5.185	0.974	-0.123	-12.715
4.023	1.000	-0.049	-32.868
T=316.15 K			
16.945	0.000	-0.001	-8.539
15.751	0.320	0.004	15.267
14.556	0.515	-0.018	9.736
13.362	0.645	0.035	11.249
12.167	0.739	-0.021	9.435
10.973	0.809	-0.026	5.114
9.778	0.864	0.014	-3.600
8.584	0.908	0.065	-7.573
7.389	0.944	-0.071	-90.927
6.195	0.974	0.015	-19.182
5.012	1.000	0.037	-39.211

^aExperimental uncertainty u is $u(x_1) = \pm 0.0003$, $u(T) = \pm 0.02$ K

^b x_1 denotes the mole fraction solubility of N-ethylcarbazole, x_2 denotes the initial composition of solvent mixtures, x_1^{cal} denotes the calculated solubility

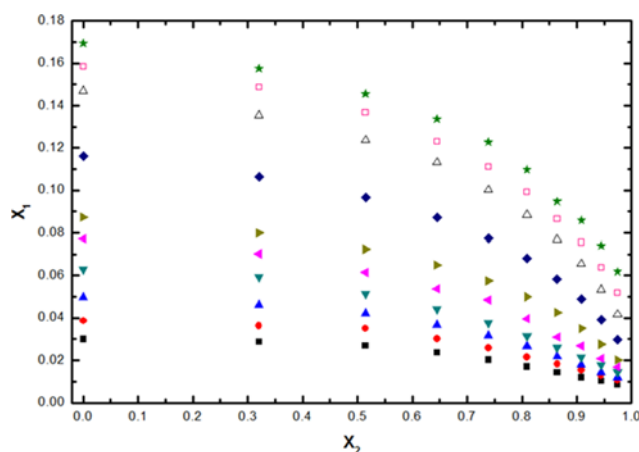


Fig. 2. Solubility of N-ethylcarbazole in ethanol+petroleum ether binary solvent mixtures: ■, 280.15 K; ●, 284.15 K; ▲, 288.15 K; ▼, 292.15 K; ◀, 296.15 K; ▶, 300.15 K; ◆, 304.15 K; △, 308.15 K; □, 312.15 K; ★, 316.15 K.

$$\ln x_1 = \ln(x_1)_3 + (\ln(x_1)_2 - \ln(x_1)_3 + S_0 - S_1 + S_2)x_2 + (-S_0 + 3S_1 - 5S_2)x_2^2 + (-2S_1 + 8S_2)x_2^3 + (-4S_2)x_2^4 \quad (3)$$

Table 3. Parameters of CNIBS/R-K equation for N-ethylcarbazole in the binary solvent as function of temperature

T/K	B ₀ ^a	B ₁ ^a	B ₂ ^a	B ₃ ^a	B ₄ ^a	MD ^a
280.15	-3.506	3.112	-13.020	17.824	-9.329	0.494
284.15	-3.251	2.359	-10.534	15.215	-8.509	1.053
288.15	-2.997	2.289	-11.631	18.090	-10.386	0.146
292.15	-2.766	2.152	-11.051	16.770	-9.522	0.143
296.15	-2.560	0.862	-5.178	8.995	-6.392	0.094
300.15	-2.356	1.970	-9.889	16.064	-9.924	0.743
304.15	-2.154	1.669	-7.758	12.412	-8.056	0.345
308.15	-1.987	-5.001	32.228	-59.056	31.435	0.022
312.15	-1.842	-2.261	10.393	-11.769	2.050	0.055
316.15	-1.696	4.647	-16.116	24.822	-15.182	0.028
					Overall	MD=0.312

^aB₀, B₁, B₂, B₃, and B₄ are model constants of Eq. (4), MD is mean deviation of Eq. (13)

Eq. (3) can be further simplified as:

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

$$B_0 = \ln(x_1)_3 \quad (5)$$

$$B_1 = \ln(x_1)_2 - \ln(x_1)_3 + S_0 - S_1 + S_2 \quad (6)$$

$$B_2 = -S_0 + 3S_1 - 5S_2 \quad (7)$$

$$B_3 = -2S_1 + 8S_2 \quad (8)$$

$$B_4 = -4S_2 \quad (9)$$

where B₀, B₁, B₂, B₃, and B₄ are model constants of this model and were calculated. They are listed in Table 3. The CNIBS/R-K model can only be used to predict and describe the solubility data for different concentrations of a mixed solvent at a fixed temperature. For describe the effect of both solvent compositions and temperature on the solubility of N-ethylcarbazole, we need another model called Jouyban-Acree model as follows [10-12]:

$$\ln x_1 = x_2 \ln(x_1)_2 + x_3 \ln(x_1)_3 + x_2 x_3 \sum_{i=0}^N \frac{J_i (x_2 - x_3)^i}{T} \quad (10)$$

where J_i is the parameters of this model, T is the absolute tempera-

ture, and other symbols denote the same meaning as Eq. (2). When N=2 and x₃=1-x₂, Eq. (10) can be written as Eq. (11):

$$\ln x_1 = \ln(x_1)_3 + (\ln(x_1)_2 - \ln(x_1)_3)x_2 + \frac{(J_0 - J_1 + J_2)x_2}{T} + \frac{(-J_0 + 3J_1 - 5J_2)x_2^2}{T} + \frac{(-2J_1 + 8J_2)x_2^3}{T} + \frac{(-4J_2)x_2^4}{T} \quad (11)$$

Eq. (11) can be further simplified as:

$$T \ln x_1 = A_0 + A_1 T + A_2 T x_2 + A_3 x_2 + A_4 x_2^2 + A_5 x_2^3 + A_6 x_2^4 \quad (12)$$

where A₀, A₁, A₂, A₃, A₄, A₅, A₆ are model constants of this model and were calculated. They are listed in Table 4.

The solubility data of N-ethylcarbazole calculated by Eq. (4) and Eq. (12) are listed in Table 2. The mean deviation (MD) defined was used to evaluate the agreement between the model predictions and the experimental data:

$$MD = 100 \frac{\sum \frac{|x_1 - x_1^{cal}|}{x_1}}{N_1} \quad (13)$$

where N₁ is the number of experimental points, x₁ is the experi-

Table 4. Parameters of the Jouyban-Acree equation for N-ethylcarbazole in the binary solvent for temperature range of 280.15-316.15 K

T/K	A ₀ ^a	A ₁ ^a	A ₂ ^a	A ₃ ^a	A ₄ ^a	A ₅ ^a	A ₆ ^a	MD ^a
280.15								4.044
284.15								3.605
288.15								2.727
292.15								1.993
296.15								1.337
300.15								7.558
304.15								4.665
308.15								2.648
312.15								1.112
316.15								8.827
	-4967.44	14.1	6.64	-1858.59	170.56	-448.39	-383.63	
							Overall	MD=1.957

^aA₀^a, A₁^a, A₂^a, A₃^a, A₄^a, A₅^a and A₆^a are model constants of Eq. (12), MD is mean deviation of Eq. (13)

Table 5. Thermodynamic functions relative to solution process of N-ethylcarbazole in the binary solvent at mean temperature

x_2^a	$\Delta H_{soln}^o / \text{KJ} \cdot \text{mol}^{-1}{}^a$	$\Delta G_{soln}^o / \text{KJ} \cdot \text{mol}^{-1}{}^a$	$\Delta S_{soln}^o / \text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}{}^a$	$\% \xi_H^a$	$\% \xi_{TS}^a$
0.000	37.218	6.172	104.127	54.521	45.479
0.320	40.244	5.949	115.026	53.991	46.009
0.515	45.960	6.197	133.365	53.615	46.385
0.645	46.017	6.594	132.228	53.859	46.141
0.739	44.259	7.065	124.751	54.337	45.663
0.809	42.394	7.560	116.834	54.895	45.105
0.864	40.620	8.081	109.137	55.523	44.477
0.908	39.452	8.577	103.557	56.098	43.902
0.944	38.828	9.048	99.885	56.594	43.406
0.974	38.404	9.494	96.966	57.052	42.948
1.000	39.127	9.965	97.811	57.296	42.704

^a x_2 denotes the initial composition of solvent mixtures, $\Delta H_{soln}^o / \text{KJ} \cdot \text{mol}^{-1}$ denotes the standard molar enthalpy of solution, $\Delta G_{soln}^o / \text{KJ} \cdot \text{mol}^{-1}$ denotes the standard molar Gibbs energy of solution, $\Delta S_{soln}^o / \text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$ denotes the standard molar entropy of solution, $\% \xi_H$ and $\% \xi_{TS}$ denote the comparison of the relative contribution to the standard Gibbs energy by enthalpy and entropy, respectively

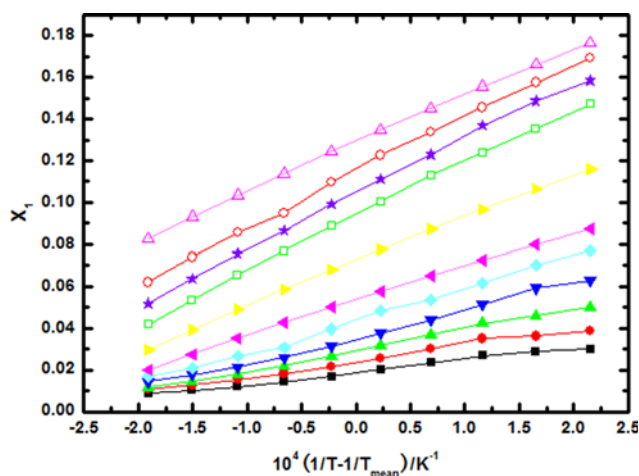


Fig. 3. Mole fraction solubility (x_1) of N-ethylcarbazole in the binary solvent against $10^4(1/T - 1/T_{mean})$ with a straight line to correlate the data: \blacksquare , $x_2=0$; \bullet , $x_2=32\%$; \blacktriangle , $x_2=51.1\%$; \blacktriangledown , $x_2=64.5\%$; \blacklozenge , $x_2=73.9\%$; \blacktriangleleft , $x_2=80.9\%$; \blacktriangleright , $x_2=86.4\%$; \square , $x_2=90.8\%$; \star , $x_2=97.4\%$; \circ , $x_2=97.4\%$; \triangle , $x_2=1$.

mental solubility, x_{1cal} is the calculated solubility. The values of MD, the parameter values of Eq. (4) and Eq. (12) were all listed in Tables 3-5.

As we can see from Table 2 and Fig. 2-3, it is clearly described that the solubility of N-ethylcarbazole in (ethanol+petroleum ether) binary solvent mixtures is a function of temperature and solvent composition. The solubility is relatively high in petroleum ether, but low in ethanol, the solubility of N-ethylcarbazole increases with the increasing petroleum ether content. The MD value for the CNIBS/R-K equation was 0.312, and for the Jouyban-Acree equation was

1.957. This result indicates that the calculated results from both of two equations shows good agreement with the experimental data. Moreover, the lower value of the overall MD showed the CNIBS/R-K equation is more suitable than the Jouyban-Acree equation in this work. The CNIBS/R-K equation can only be used for the prediction of solubility for different concentrations of a mixed solvent at constant temperature, while the Jouyban-Acree equation can be used for predicting solubility at different temperatures and different concentrations [13].

3. Thermodynamic Properties of Solutions

From the above, the solution process of N-ethylcarbazole depended on both the solvent compositions and temperature, and the results could be used to elucidate the molecular mechanisms involved in the solution process [14]. Over the temperature and the solubility range under investigation, the apparent enthalpy change of solution could be related to the temperature and the solubility as following:

$$\Delta H_{soln}^o = -R \times \left(\frac{\partial \ln x_1}{\partial (1/T)} \right) \quad (14)$$

where R is the universal gas constant ($8.314 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$). The standard molar enthalpy change of solution could be related to the temperature and the solubility with the following equation based on the van't Hoff analysis [15]:

$$\Delta H_{soln}^o = -R \left(\frac{\partial \ln x}{\partial (1/T - 1/T_{mean})} \right) \quad (15)$$

The standard molar Gibbs energy of solution (ΔG_{soln}^o) can be calculated by:

$$\Delta G_{soln}^o = -RT_{mean} \times \text{intercept} = \Delta H_s - T_{mean} \Delta S_{soln}^o \quad (16)$$

where the intercept is obtained in plots of $\ln x_1$ versus $(1/T - 1/T_{mean})$ ($T_{mean} = 298.15 \text{ K}$, in the present work) [16]. The propagation of uncertainties in the thermodynamic quantities calculations was made according to the literature [17,18]. The relative contributions of the enthalpy ξ_H and ξ_{TS} to the standard free energy of solution were calculated by Eq. (17) and Eq. (18) [19,20]:

$$\% \xi_H = \frac{|\Delta H_{soln}^o|}{|\Delta H_{soln}^o| + |T \Delta S_{soln}^o|} \times 100 \quad (17)$$

$$\% \xi_{TS} = \frac{|T \Delta S_{soln}^o|}{|\Delta H_{soln}^o| + |T \Delta S_{soln}^o|} \times 100 \quad (18)$$

The data of Gibbs energy, entropy, and enthalpy were listed in Table 5 together with ξ_H and ξ_{TS} . The conclusion can be drawn from Table 5. The dissolution enthalpy is determined by the enthalpy changes in separating solvent molecules, separating solute molecules and allowing the solute and solvent to interact to form the solution. If the intermolecular forces between solute and solvent particles are weaker than other intermolecular forces, the dissolution enthalpy is positive and the solution formation is endothermic. The enthalpy and the standard Gibbs energy of N-ethylcarbazole were positive in the studied binary solvent mixtures, indicating the solution process of N-ethylcarbazole in (ethanol+petroleum ether) binary solvent mixtures was endothermic. Moreover, because val-

ues of $\% \xi_H$ were $\geq 46.38\%$, the main contributor to the standard molar Gibbs energy of solution was the enthalpy during the dissolution.

CONCLUSIONS

Solubility data of N-ethylcarbazole in (ethanol+petroleum ether) binary solvent mixtures was measured. We can draw the following conclusions: (1) The solubility of N-ethylcarbazole in (ethanol+petroleum ether) binary solvent mixtures increased with the increasing temperature, and the increasing petroleum ether content at constant temperature. (2) The calculated results from the solvent/Redlich-Kister (CNIBS/R-K) equation and the Jouyban-Acree equation showed good agreement with the experimental data, and the solvent/Redlich-Kister (CNIBS/R-K) equation was more suitable than the Jouyban-Acree equation in this work at constant temperature. (3) The experimental solubility data could be used for choosing the suitable solvent and were beneficial to the optimization of the crystallization process, while the ethanol could be used as effective anti-solvent. (4) The thermodynamic properties of the solution process, including the Gibbs energy, enthalpy, and entropy were calculated by the van't Hoff analysis, and the results indicated that the dissolution process was endothermic.

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