

Measurement and Correlation for Solubility of Dimethyl-2,6-naphthalene Dicarboxylate in Organic Solvents

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Abstract Solubility of dimethyl-2,6-naphthalene dicarboxylate in acetic acid, *N,N*-dimethylformamide, *N,N*-dimethyl acetamide, dimethyl sulphoxide, and *N*-methyl-2-ketopyrrolidine were determined using a dynamic method. The measured systems were correlated by UNIFAC group contribution method. A new main group (aromatic ester, ACCOO) was defined to express the activity coefficients of the aromatic ester. New interaction parameters of the ACCOO group were expressed as the first-order function of temperature and were determined from the experimental data. The calculated results for the new interaction parameters were satisfactory. The measured systems were also correlated with the Wilson and λ - h models, and the results were compared with those of the UNIFAC model.

Keywords solid-liquid equilibrium, solubility, dimethyl-2,6-naphthalene dicarboxylate, UNIFAC group contribution method, activity coefficient

1 INTRODUCTION

Dimethyl-2,6-naphthalene dicarboxylate (DM-2,6-NDC) is a monomer used for producing polyethylene 2,6-naphthalate (PEN). PEN can be used in many fields, such as chemical engineering, light industry, and electronic industry[1,2]. Fibers and films made from PEN have considerably improved strength and superior thermal properties relative to polyethylene terephthalate. PEN can be obtained by condensing DM-2,6-NDC with ethylene glycol, and DM-2,6-NDC is prepared by the esterification of 2,6-naphthalene dicarboxylic acid with methanol[3,4]. However, to date, because of problems in the purification process[5], only a quantity of several thousand tons of PEN per year could be produced in USA and Japan[6,7]. To prepare high-quality PEN suitable for commercial use, it is necessary to start with purified DM-2,6-NDC. Purified DM-2,6-NDC must be light in color, substantially free of organic and inorganic impurities, and low in particulate matter. Recrystallization is one step in the purification process of crude DM-2,6-NDC. For the design and optimization of the recrystallization process, reliable solubility data are required. But the solubility data of DM-2,6-NDC are not easily available in the literature. Therefore, the solubilities of DM-2,6-NDC in five organic solvents are determined in this study. The UNIFAC group contribution method is used to correlate the experimental data, and the group interaction parameters of the ester group linked to the aromatic ring are determined by correlating the experimental data.

2 EXPERIMENTAL

2.1 Materials

DM-2,6-NDC was commercially obtained from the Mitsubishi Gas Chemical Corporation of Japan. According to the document sent with the DM-2,6-NDC sample, the purification of DM-2,6-NDC was 100%, and its melting point was 191.5°C, which coincided with the result of the determination in the current study. All other materials used in the experiment were

analytical reagent, with purity higher than 99% and were used without further purification.

2.2 Procedure and apparatus

The solubility was determined using the dynamic method. A predetermined sample was heated very slowly [it was less than $0.1\text{K}\cdot(10\text{min})^{-1}$, close to the solid-liquid equilibrium temperature]. The solid in the solution (sample) dissolved with an increase in temperature, and the temperature at which the last piece of the solid dissolved was the solid-liquid equilibrium temperature of the sample.

The experimental apparatus has been described in detail earlier[8]. It includes a titanium solid-liquid equilibrium cell, a laser detecting system, a temperature controlling and measurement system, and a magnetic stirring system. Two small quartz glass columns installed at the two sides of the titanium cell to allow the laser beam to go through the cell. The power of the laser beam is detected by the galvanometer and then converted into an electrical signal, which increases as the solid dissolves. When the last piece of solid dissolves, the laser power reaches the greatest value, and the temperature corresponding to the greatest value of the galvanometer is the solid-liquid equilibrium temperature of the sample. The thermocouple used in the experiment was calibrated in the Tianjin Metrology Institute(Tianjin, China), and the accuracy of the thermocouple was $\pm 0.01^\circ\text{C}$.

The solubility of benzoic acid in water measured using this apparatus agreed well with the data in the literature[9], and therefore the reliability of the experimental apparatus was verified.

3 RESULTS AND DISCUSSION

3.1 Experimental results

With DM-2,6-NDC as the solute and acetic acid, *N,N*-dimethylformamide (DMF), *N,N*-dimethylacetamide (DMA), dimethyl sulphoxide (DMSO), and

N-methyl-2-ketopyrrolidine (NMP), respectively, as solvents, the solubilities of five binary systems were

determined in this study and are listed in Tables 1, 2, and 3, in which x_1 is the mole fraction of the solute in

Table 1 Experimental solubility data and correlation result of the proposed UNIFAC model

Solute: DM-2,6-NDC				Solute: DM-2,6-NDC			
Solvent: Acetic acid				Solvent: DMF			
$T, ^\circ\text{C}$	x_1^{exp}	x_1^{cal}	$e, \%$	$T, ^\circ\text{C}$	x_1^{exp}	x_1^{cal}	$e, \%$
19.34	0.000510	0.000513	-0.52	30.16	0.002530	0.00267	-5.56
22.50	0.000621	0.000616	0.84	36.21	0.003410	0.00354	-3.91
27.20	0.000804	0.000803	0.11	44.75	0.005206	0.00521	0
33.71	0.001159	0.001146	1.15	56.50	0.008836	0.00862	2.39
38.48	0.001466	0.001473	-0.48	62.28	0.01157	0.01098	5.09
43.35	0.001902	0.001890	0.62	69.06	0.01501	0.01445	3.74
47.50	0.002321	0.002324	-0.14	76.70	0.01929	0.01948	-0.99
49.85	0.002541	0.002606	-2.58	84.81	0.02724	0.02689	1.28
56.00	0.003808	0.003501	8.06	89.58	0.03235	0.03234	0.02
60.32	0.004279	0.004271	0.18	93.45	0.03960	0.03804	3.94
64.05	0.005098	0.005058	0.79	95.23	0.04085	0.04049	0.89
70.15	0.006569	0.006617	-0.72	99.87	0.04948	0.04878	1.42
76.98	0.008330	0.008838	-6.11	104.71	0.05742	0.05856	-1.99
84.23	0.01132	0.01191	-5.18	106.51	0.06109	0.06279	-2.79
89.65	0.01430	0.01478	-3.38	108.99	0.06611	0.06901	-4.38
93.51	0.01688	0.01719	-1.88	110.23	0.06990	0.07270	-4.00
99.36	0.02173	0.02155	0.79				
102.49	0.02482	0.02427	2.20				
108.63	0.03039	0.03044	-0.17				
112.81	0.03523	0.03547	-0.69				
119.32	0.04597	0.04518	1.71				
121.56	0.04925	0.04896	0.59				
125.35	0.05643	0.05626	0.29				
127.39	0.06065	0.06065	0				

Table 2 Experimental solubility data and correlation result of the proposed UNIFAC model

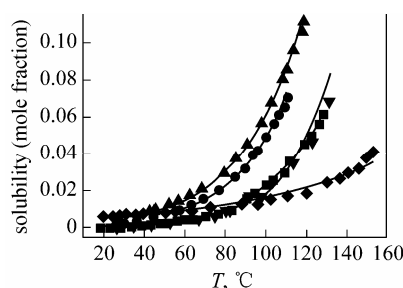
Solute: DM-2,6-NDC				Solute: DM-2,6-NDC			
Solvent: DMA				Solvent: DMSO			
$T, ^\circ\text{C}$	x_1^{exp}	x_1^{cal}	$e, \%$	$T, ^\circ\text{C}$	x_1^{exp}	x_1^{cal}	$e, \%$
25.96	0.003446	0.003642	-5.68	25.13	0.000669	0.000720	-7.69
41.90	0.007202	0.007159	0.59	34.92	0.001126	0.001187	-5.47
47.20	0.008952	0.008856	1.07	43.42	0.001794	0.001796	0
53.10	0.01116	0.01115	0.11	51.82	0.002722	0.002657	2.36
57.23	0.01290	0.01332	-3.30	67.70	0.005372	0.005359	0.24
64.12	0.01665	0.01687	-1.36	74.03	0.007256	0.007040	2.97
69.24	0.02023	0.02037	-0.71	80.20	0.009523	0.009148	3.94
79.60	0.03015	0.02975	4.50	83.51	0.01093	0.01051	3.82
85.40	0.03774	0.03647	3.36	92.04	0.01565	0.01505	3.82
91.25	0.04517	0.04461	1.24	96.73	0.01605	0.01773	-10.51
97.65	0.05727	0.05593	2.34	101.50	0.02255	0.02235	0.88
103.11	0.06736	0.06728	0.11	113.70	0.03525	0.03735	-5.96
108.56	0.08140	0.08140	0	121.66	0.04706	0.05265	-11.89
110.23	0.08554	0.08612	-0.68	131.92	0.06899	0.08351	-21.08
113.86	0.09631	0.09763	-1.37				
117.99	0.1074	0.1118	-4.09				
119.02	0.1124	0.1162	-3.44				

Table 3 Experimental solubility data and correlation result of the proposed UNIFAC model (Solute: DM-2,6-NDC, Solvent: NMP)

$T, ^\circ\text{C}$	x_1^{exp}	x_1^{cal}	$e, \%$
20.05	0.005596	0.005650	-0.96
23.58	0.005765	0.005799	-0.59
27.33	0.006064	0.006010	0.90
30.35	0.006318	0.006210	1.71
35.62	0.006686	0.006613	1.10
38.66	0.006873	0.006873	0
43.95	0.007401	0.007384	0.23
49.74	0.008026	0.008011	0.19
55.01	0.008640	0.008640	0
63.54	0.009136	0.009727	-6.47
72.19	0.01029	0.01101	-7.00
81.08	0.01145	0.01246	-8.88
86.94	0.01251	0.01353	-8.22
95.54	0.01324	0.01513	-14.29
102.23	0.01597	0.01676	-4.99
110.21	0.01671	0.01850	-10.71
120.05	0.01948	0.02114	-8.57
131.31	0.02514	0.02511	0.14
136.77	0.02714	0.02707	0.26
141.21	0.02988	0.02906	2.75
145.68	0.03275	0.03123	4.64
150.55	0.03792	0.03441	9.25
152.62	0.03988	0.03579	10.29

the solution.

Figure 1 shows the experimental result of the five binary systems. Five kinds of symbols were used to express this result. As shown in Fig.1, the solubility data of DM-2,6-NDC in different solvents were close and showed a flat uptrend when the temperature was lower than 80°C. When the temperature was higher than 80°C, the solubility of DM-2,6-NDC in DMA and DMF increased rapidly, but its solubility in NMP still maintained a flat uptrend. This made the solubil-

**Figure 1** Solubilities of DM-2,6-NDC in acetic acid, DMF, DMA, DMSO, and NMP

- DM-2,6-NDC~acetic acid; ● DM-2,6-NDC~DMF;
- ▲ DM-2,6-NDC~DMA; ▼ DM-2,6-NDC~DMSO;
- ◆ DM-2,6-NDC~NMP; — proposed UNIFAC model

ity of DM-2,6-NDC in DMA more than five times as much as that in NMP, at a temperature of about 110°C. DMA exhibited the highest dissolution capacity difference between high temperature and low temperature among the five solvents, and it might be chosen as the solvent in the recrystallization purification process.

3.2 Solid-liquid equilibria (SLE) correlation using the UNIFAC group contribution method

An equation for the calculation of solid-liquid phase equilibria could be derived from the isofugacity criterion, that is, the fugacity of component i in the liquid phase must be equal to the fugacity of component i in the solid phase. If no solid-solid phase transition occurred in the considered temperature range, and the contributions of the heat capacities were neglected, the following equation was obtained[10]:

$$-\ln x_i \gamma_i = \Delta H_m R^{-1} (T^{-1} - T_m^{-1}) \quad (1)$$

where T is the absolute temperature of the mixture, x_i is the solubility of component i in the liquid phase, γ_i is the activity coefficient of component i in the liquid phase, and T_m is the normal melting temperature of component i . ΔH_m is the enthalpy of fusion of component i at temperature T_m . Component i is the solute, which is DM-2,6-NDC here, so T_m is 191.5°C. Because the value of ΔH_m was not available, it was estimated by the following empirical equation[11]:

$$\Delta H_m = kT_m \quad (2)$$

where k is an empirical parameter related to the properties of the solute. For an organic compound, k should be from 10 to 16. The optimum value of k was determined by the simplex method calculation[12].

The UNIFAC model was used to describe the activity coefficient. When the interaction parameters of vapor-liquid equilibrium in the earlier UNIFAC model[13] were used to calculate γ_1 in Eq.(1), it was found that the deviations were very large. This might be attributed to the fact that, in the earlier UNIFAC model, the ester group linked to the aromatic ring had to be separated into the AC group and COO group, and that group interaction parameters of the AC group and COO group were obtained from the phase equilibrium data that contained a few aromatic ester systems. Therefore, it was not reliable to predict aromatic ester systems using group interaction parameters of AC and COO groups in the earlier UNIFAC model.

According to the above discussion, to describe the activity coefficients of aromatic esters, it was better to determine the group interaction parameters from the data of aromatic ester systems. At the same time, a new group was introduced by defining the ACCOO group as the ester group linked to the aromatic ring. According to the experimental data that are given in Tables 1 to 3, the group interaction parameters of the ACCOO group with other groups were determined by the nonlinear minimization function (Nelder-Mead Simplex) method[12]. Other group interaction parameters needed for calculation were obtained from the earlier UNIFAC model[13], because most of them were not available in the modified UNIFAC model[14].

The objective function in the simplex method was absolute average relative deviation between the experimental and calculated mole fraction of the solute:

$$F = \frac{1}{n} \left(\sum_n \left| \frac{x_i^{\text{exp}} - x_i^{\text{cal}}}{x_i^{\text{exp}}} \right| \times 100\% \right) \quad (3)$$

where x_i is the mole fraction of the solute, and n is the number of the experimental data.

Because accuracy of the result of calculation was poor when the group interaction parameters of the ACCOO group a_{mn} were taken as constants, the a_{mn} was described as a function of temperature. Several kinds of temperature dependence were attempted to express a_{mn} , and the result showed that the first-order temperature dependence gave the smallest absolute average relative deviation F . Therefore, a_{mn} is expressed as $a_{mn} = A_{mn} + B_{mn}T$.

The group interaction parameters of the ACCOO group (A_{mn} , B_{mn}) obtained from the experimental data

are listed in Table 4. The result of calculation obtained using the proposed UNIFAC model, and correlation relative error at each experiment point is also listed in Tables 1 to 3. It was shown that the average relative deviation of the five measured systems is 3.13% (Table 5). In addition, the fusion enthalpy of DM-2,6-NDC obtained from the optimum algorithm was reasonable. The solid lines in Fig.1 show the correlation results of the proposed UNIFAC model.

3.3 Comparison with other models

To examine the accuracy of the proposed UNIFAC model, the correlation result of the proposed UNIFAC model was compared with that of the Wilson model[15,16] and the λ - h model[17]. The objective function F of the measured systems that were correlated using different models is listed in Table 5, and the parameters of the Wilson and λ - h models for five measured systems are listed in Table 6. The results of calculation showed that the Wilson model had the largest

Table 4 Interaction parameters for ACCOO group

Group		Interaction parameter (a_{mn})		Interaction parameter (a_{nm})	
m	n	A_{mn}	B_{mn}	A_{nm}	B_{nm}
ACCOO	ACH	-435.9	0.654	-94.90	-0.658
ACCOO	AC	-435.9	0.654	-94.90	-0.658
ACCOO	CH ₃	59.21	-1.099	11.78	-0.129
ACCOO	COOH	1247	0.927	535.2	-1.611
ACCOO	DMF	80.12	-0.205	-75.98	-0.746
ACCOO	CON(Me) ₂	-150.2	0.00002	-84.58	-0.652
ACCOO	DMSO	-182.3	0.236	206.3	-1.193
ACCOO	NMP	-4441	17.13	-1376	2.533
		Fusion enthalpy of DM-2,6-NDC:		29953J·mol ⁻¹	

Table 5 Correlation results for different activity coefficient models

Systems	F		
	Wilson model	λ - h model	Proposed UNIFAC model
DM-2,6-NDC, acetic acid	4.81	1.71	1.63
DM-2,6-NDC,DMF	2.76	1.40	1.84
DM-2,6-NDC,DMA	1.64	1.74	1.99
DM-2,6-NDC,DMSO	5.10	2.19	5.75
DM-2,6-NDC,NMP	51.9	1.58	4.44
total average deviation	13.2	1.72	3.13

Table 6 Parameters of the Wilson model and λ - h model for five systems

Systems	Wilson model parameters		λ - h model parameters	
	$g_{12} - g_{11}$	$g_{21} - g_{22}$	λ	h
DM-2,6-NDC, acetic acid	6819.2	249.5	0.3016	16703
DM-2,6-NDC,DMF	5439	-727.1	0.5746	8256
DM-2,6-NDC,DMA	3000	432.5	0.5665	7566
DM-2,6-NDC,DMSO	6778	369.6	0.2893	17481
DM-2,6-NDC,NMP	5602	45267	0.00202	119590

average deviation of 13.2%, which was mainly attributed to the very large deviation of DM-2,6-NDC~NMP system. The λ - h model had the smallest average deviation of 1.72%. This showed that, as a model that was derived from SLE, the λ - h model was really more predominant in describing SLE, although the λ - h model did not possess a strong theoretical base and could not be used in the prediction of the solid-liquid equilibrium. This conclusion coincided with that of the previous research[8,18,19] and other reports[20,21]. The UNIFAC model had a slightly larger (3.13%) average deviation than that of the λ - h model. For DM-2,6-NDC~acetic acid, DM-2,6-NDC~DMF, and DM-2,6-NDC~DMA systems, the proposed UNIFAC model had a similar deviation as the λ - h model. The UNIFAC model had been successfully used to predict vapor-liquid equilibria (VLE), and most of the group interaction parameters were determined by the regression of vapor-liquid equilibria data collected in a large data bank. Much less attention had been paid to the SLE prediction using UNIFAC. The primary reason for the unreliable SLE prediction results might be attributed to the fact that the group interaction parameters determined by the VLE data was not suitable for SLE. But it must be pointed out that the proposed UNIFAC model could predict SLE when the group interaction parameters were available. Wilson and λ - h models do not possess the aforementioned advantage. Obviously, to obtain reliable group interaction parameters, a large amount of SLE experiment data was required.

4 CONCLUSIONS

With DM-2,6-NDC, as the solute, and acetic acid, *N,N*-dimethylformamide, *N,N*-dimethylacetamide, dimethyl sulphoxide, and *N*-methyl-2-ketopyrrolidine as the respective solvents, the solubilities of five binary systems were determined. These data provided the important basis not only for purification of DM-2,6-NDC by recrystallization, but also for the UNIFAC group contribution method.

The UNIFAC group contribution method is used in the correlation of the measured systems. New groups, the ACCOO group was introduced, and its interaction parameters were modified as a function of temperature. The interaction parameters were obtained from the regression of data of the five binary systems, and the average deviation was 3.13%. This shows that the new model is satisfactory.

Comparing the correlated results of the Wilson, the λ - h , and the proposed UNIFAC models, the λ - h model showed the best result. The deviation of the proposed UNIFAC model is close to that of the λ - h model. To improve the SLE prediction results using the UNIFAC model, a large amount of reliable SLE experimental data are needed.

NOMENCLATURE

A_{mn}, B_{mn}	coefficient in interaction parameters a_{mn} - T equation
a_{mn}	interaction parameters between m group and n group in the UNIFAC model ($a_{mn} = A_{mn} + B_{mn}T$)
e	relative error, %

F	absolute average relative deviation between experimental and calculated mole fraction of the solute
$(g_{12} - g_{11}), (g_{21} - g_{22})$	parameters in the Wilson model
ΔH_m	enthalpy of fusion of the solute at temperature T_m , J·mol ⁻¹
h	parameters in the λ - h model
n	number of experimental data
T	temperature, K
T_m	normal melting temperature of the solute, K
x_1	the concentration of the solute in the solution, mole fraction of the solute
γ_1	activity coefficient of solute in the solution
λ	parameters in λ - h model

Superscripts

cal	calculational
exp	experimental

Subscripts

i	the i th point of experiment data
m	m group
n	n group

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