Chinese J. Chem. Eng., **14**(6) 780—783 (2006)

Experimental Measurement and Correlation of the Solubility of Methyl-acetyl-naphthalene in *n*-Heptane, *n*-Octane, and *n*-Dodecane

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Abstract The solubilities of 2-methyl-6-acetylnaphthalene (2,6-MAN) and 2-methyl-7-acetylnaphthalene (2,7-MAN) in *n*-heptane, *n*-octane, and *n*-dodecane were measured, respectively, from 273.15 to 319.15K using an analytical method. On the basis of the thermodynamics theory of solid-liquid equilibrium, a model was derived to relate the solubilities with temperature. Using the least square method, the parameters of the model, the fusion enthalpies $\Delta_{fus}H$ and the Margules equation coefficients A_{12} and A_{21} of 2,6-MAN and 2,7-MAN in *n*-heptane, *n*-octane, and *n*-dodecane—were obtained by regressing the experimental data. The average deviation of the model was 1.70%.
Keywords 2-methyl-6-acetylnaphthalene, 2-methyl-7-acetylnaphthalene, solubility, analytical method

1 INTRODUCTION

2-Methyl-6-acetylnaphthalene (2,6-MAN) is a type of white or pale yellow, powdery crystal, with a melting point of 332.15K. It is an important intermediate[1] used for producing 2,6-naphthalene dicarboxylic acid (2,6-NDA), which has very extensive applications in not only the light, electronic, and defense industries, but in many other areas. In particular, 2,6-NDA is an important monomer of liquid crystal polyester material (LCP) and polyethylene naphthalene-2,6-dicarboxylate (PEN). PEN is a new thermoplastic polyester with high performance. After replacing the benzene ring with a naphthalene double ring, the intensity, stability resistance, thermostability, chemical environmental resistance, hydrolytic resistance, and gas retardance are superior to those of polyethylene terephthalate (PET) and polybutylene terephthalate (PBT)[2], so its application and development have progressed rapidly in recent years. 2,6-MAN is mainly prepared from 2-methylnaphthalene by acylation using organic solvent as the medium[3]. Because the reaction produces two byproducts 2,7-MAN and 2,1-MAN[4], which have almost the same boiling points as 2,6-MAN, it is very difficult to separate them using distillation. By recrystallization, a highly purified 2,6-MAN compound can be obtained from such an isomer mixture. In this isomer mixture, the content of 2,1-MAN is much lower than that in 2,7-MAN. Therefore, the solubility data of 2,6-MAN and 2,7-MAN in different solvents are significant. However, the correlative data are scarce in literature.

In this study, the solubilities of 2,6-MAN and 2,7-MAN in *n*-heptane, *n*-octane, and *n*-dodecane were measured at different temperatures using the analytical method. The solubility model including the enthalpy of fusion $\Delta_{fus}H$ and the Margules equation coefficients A_{12} and A_{21} was derived.

2 EXPERIMENTAL

2.1 Materials

2,6-MAN, which was prepared in the lab was recrystallized before use. Its purity, which was determined by gas chromatography (GC), was higher than 99.0%. The melting point was 332.15—333.15K. In the laboratory, the 2,7-MAN, which was prepared was recrystallized before use. Its purity, which was determined by GC, was higher than 98.0%. The melting point was 319.15—321.15K.

The *n*-heptane, *n*-octane, and *n*-dodecane, and the analytical reagents, were purchased from the Shanghai Chemistry Reagent Company, China.

2.2 Method

The methods of measuring the solubility of a solid in a liquid mixture can be classified as analytical and synthetic[5,6]. The advantage of the analytical method lies in the fact that it is a reliable method, with a possibility of measuring a large number of samples simultaneously. The disadvantage is that it is tedious and time-consuming[7]. The synthetic method[8—10] involves weighing or measuring the individual components to obtain a system with a known composition. The state in which the solid phase just disintegrates is then determined by this system. The disappearance of the solid phase can be achieved either by a change in the temperature or by the addition of a known amount of solvent[11]. In this study, the analytical method was used to determine the solubility data of MAN in different solvents.

2.3 Procedure

2.3.1 *Determining standard studying curve*

A series of standard samples whose mass concentration was 1%—5% were confected by *n*-heptane, *n*-octane, and *n*-dodecane as solvents. These standard

Received 2005-10-31, accepted 2006-06-12.
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samples were analyzed by GC under consistent operating conditions. After obtaining the corresponding assay value, the functional relation of the assay value, and the real value of the sample, the standard studying curves were established.

2.3.2 *Measuring solubility*

The solvent and excess solute were added to a vessel with a condenser and a stirrer, and a mercury thermometer calibrated a fluctuating temperature of ±0.05K. The vessel was placed inside the thermostatic water, the temperature of which had reached a fixed value. Following this, the mixture was stirred vigorously for 1h, and the stirring was stopped when it reached the required temperature. After 15min, 2—3ml of clear liquid was added into the sampling vial with the help of a pipette. The sample was weighed by an analytical balance with an accuracy of ±0.0001g. When the required temperature was higher than the room temperature, the pipette had to be warmed up to the required temperature, and 2—5g of accurately weighed solvents were added to the sampling vial again, to ensure that 2,6-MAN and 2,7-MAN dissolved completely at room temperature. By changing the temperature of the thermostatic water, and repeating the above procedures, a series of samples were obtained at different temperatures. All samples were analyzed by GC and chromatographic assay values of all samples were obtained. Based on the above standard studying curves and diluted multiples, the real concentrations of all the samples could be obtained.

2.4 Solubility model

The behavior of solid solubility under different conditions is very evaluated using a proper thermodynamic model. On the basis of the thermodynamics theory of solid–liquid equilibrium, the solubility equation is[12]:

$$\ln \gamma_2 x_2 = \frac{\Delta_{\text{fus}} H}{R}\left(\frac{1}{T_{\text{m}}} - \frac{1}{T}\right) \quad (1)$$

where x_2 is the mole fraction solubility of the solute in the solvent, γ_2 is the liquid-phase activity coefficient of the solute, and T_{m} is the melting point temperature.

In Eq.(1), the activity coefficient γ_2 is the function of molar concentration x_2, which can be described by the Margules equation[12]:

$$\ln \gamma_2 = (1 - x_2)^2 \left[A_{21} + 2(A_{12} - A_{21})x_2\right] \quad (2)$$

where A_{12} and A_{21} are the Margules equation coefficients of the solute in the solvent.

Substituting Eq.(2) in Eq.(1), we obtain:

$$\ln x_2 + (1 - x_2)^2 \left[A_{21} + 2(A_{12} - A_{21})x_2\right] = \frac{\Delta_{\text{fus}} H}{R}\left(\frac{1}{T_{\text{m}}} - \frac{1}{T}\right) \quad (3)$$

Eq.(3) is used to describe the variation of the solubility with temperature.

3 RESULTS AND DISCUSSION

3.1 Experimental results

The solubilities of 2,6-MAN and 2,7-MAN in *n*-heptane, *n*-octane, and *n*-dodecane were measured from 273.15 to 319.15K respectively. The results are shown in Tables 1—6.

Table 1 Solubility data of 2, 6-MAN in *n*-heptane and error analysis

T, K	S, g·(100g)$^{-1}$	$X_{\text{exp}}\times10^2$	$X_{\text{cal}}\times10^2$	E, %
273.15	1.7418	0.9384	0.8463	9.81
277.15	1.9319	1.0398	1.0482	−0.81
279.15	2.1285	1.1444	1.1650	−1.80
282.15	2.4280	1.3032	1.3633	−4.61
285.15	2.8229	1.5120	1.5933	−5.37
288.15	3.3117	1.7692	1.8602	−5.14
291.15	4.0731	2.1672	2.1707	−0.16
294.15	4.8609	2.5756	2.5331	1.65
297.15	5.5468	2.9283	2.9578	−1.00
299.65	6.5778	3.4538	3.3689	2.46
303.15	8.2302	4.2843	4.0530	5.40
306.15	9.3583	4.8431	4.7670	1.57
309.15	11.0353	5.6618	5.6371	0.44
311.15	12.3510	6.2943	6.3305	−0.58
313.15	14.1700	7.1550	7.1425	0.17
316.15	17.1202	8.5178	8.6672	−1.75
319.15	21.6348	10.5275	10.7737	−2.34

Table 2 Solubility data of 2, 6-MAN in *n*-octane and error analysis

T, K	S, g·(100g)$^{-1}$	$X_{\text{exp}}\times10^2$	$X_{\text{cal}}\times10^2$	E, %
273.15	1.4568	0.8951	0.8488	5.17
277.65	1.7143	1.0517	1.0764	−2.35
283.15	2.2798	1.3938	1.4315	−2.7
287.15	2.8218	1.7195	1.7571	−2.19
291.15	3.4812	2.1128	2.1548	−1.99
293.15	3.9409	2.3851	2.3863	−0.05
297.15	4.8087	2.8951	2.9293	−1.18
301.15	6.2154	3.7106	3.6061	2.82
303.15	7.0136	4.1673	4.0084	3.81
306.65	8.2487	4.8654	4.8453	0.41
311.15	10.7176	6.2310	6.2659	−0.56
314.15	13.1803	7.5546	7.5407	0.18
316.15	15.1861	8.6053	8.6158	−0.12
319.15	19.0414	10.5592	10.78249	−2.11

Table 3 Solubility data of 2, 6-MAN in *n*-dodecane and error analysis

T, K	S, g·(100g)$^{-1}$	$X_{exp}\times10^2$	$X_{cal}\times10^2$	E, %
273.15	0.9563	0.8764	0.8641	1.40
279.65	1.3388	1.2226	1.2092	1.10
283.15	1.5984	1.4560	1.4458	0.70
288.15	2.0751	1.8823	1.8643	0.96
291.15	2.4366	2.2030	2.1722	1.40
293.65	2.8222	2.5428	2.4692	2.89
296.65	3.2426	2.9106	2.8846	0.89
299.15	3.7957	3.3902	3.2906	2.94
301.65	4.1549	3.6991	3.7642	−1.76
305.15	5.2158	4.6002	4.5757	0.53
308.15	6.1143	5.3503	5.4614	−2.08
311.15	7.9256	6.8270	6.6108	3.17

Table 4 Solubility data of 2, 7-MAN in *n*-heptane and error analysis

T, K	S, g·(100g)$^{-1}$	$X_{exp}\times10^2$	$X_{cal}\times10^2$	E, %
273.15	2.1432	0.01152	0.01133	1.70
275.15	2.3027	0.01237	0.01257	−1.62
277.15	2.5636	0.01375	0.01395	−1.47
279.15	2.9303	0.01569	0.01550	1.20
282.15	3.4041	0.01818	0.01818	0.01
286.15	4.2875	0.02279	0.02260	0.81
289.15	5.0673	0.02682	0.02679	0.10
291.15	5.6314	0.02972	0.03016	−1.48
293.15	6.5421	0.03436	0.03412	0.68

Table 5 Solubility data of 2, 7-MAN in *n*-octane and error analysis

T, K	S, g·(100g)$^{-1}$	$X_{exp}\times10^2$	$X_{cal}\times10^2$	E, %
273.15	1.8563	0.0114	0.0113	0.56
276.15	2.1278	0.0130	0.0132	−1.07
279.15	2.4956	0.0152	0.0153	−0.38
281.15	2.8162	0.0172	0.0169	1.50
284.15	3.1945	0.0194	0.0196	−1.14
287.15	3.8127	0.0231	0.0228	1.09
289.15	4.2013	0.0254	0.0253	0.44
292.15	4.8423	0.0291	0.0295	−1.13
295.15	5.7234	0.0343	0.0345	−0.64
297.15	6.4881	0.0387	0.0384	0.71

Table 6 Solubility data of 2, 7-MAN in *n*-dodecane and error analysis

T, K	S, g·(100g)$^{-1}$	$X_{exp}\times10^2$	$X_{cal}\times10^2$	E, %
273.15	1.4265	0.0130	0.0125	3.76
275.15	1.4856	0.0135	0.0139	−2.43
278.15	1.7365	0.0158	0.0162	−2.40
281.15	2.1542	0.0195	0.0189	3.38
283.15	2.2615	0.0205	0.0209	−2.12
286.15	2.6463	0.0239	0.0244	−2.35
289.15	3.1917	0.0287	0.0286	0.07
292.15	3.7985	0.0339	0.0337	0.66
295.15	4.6267	0.0410	0.0399	2.72
297.15	5.1472	0.0454	0.0449	1.20
300.15	6.0015	0.0526	0.0541	−2.98

3.2 Model regression results

In the solubility model [Eq.(2)], the model parameters ($\Delta_{fus}H$ and A_{12} and A_{21}) were obtained by the least square method (as shown in Tables 7—8). The comparison between the calculated solubility data and the experimental data are shown in Tables 1—6 and Figs.1—2. Tables 1—6 and Figs.1—2, show that the correlation coefficients (R^2) of the model for the six groups of experimental data exceed 0.99. The average deviation of the model is 1.70%.

Table 7 Parameters of 2,6-MAN based on Eq.(2) in different solvents

Parameter	$\Delta_{fus}H$, J·mol^{-1}	A_{12}	A_{21}	R^2
n-heptane	31857	1.7699	2.3289	0.9971
n-octane	31347	1.6654	2.3690	0.9988
n-dodecane	30142	1.0814	2.4453	0.9995

Table 8 Parameters of 2, 7-MAN based on Eq.(2) in different solvents

Parameter	$\Delta_{fus}H$, J·mol^{-1}	A_{12}	A_{21}	R^2
n-heptane	27863	−0.560	2.8177	0.9989
n-octane	28600	1.4739	2.7217	0.9994
n-dodecane	28400	0.9229	2.6522	0.9971

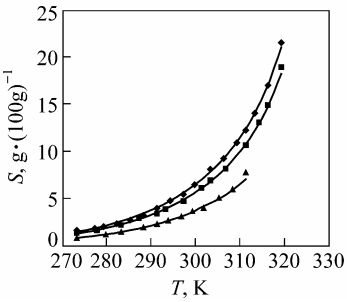

Figure 1 Comparison of real solubilities with its model value of 2,6-MAN in alkane

◆ *n*-heptane; ■ *n*-octane; ▲ *n*-dodecane

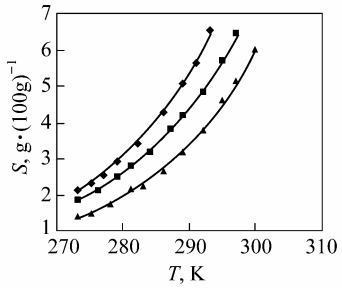

Figure 2 Comparison of real solubilities with its model value of 2,7-MAN in alkane

◆ *n*-heptane; ■ *n*-octane; ▲ *n*-dodecane

3.3 Discussion

As shown in Tables 1—6 and Figs.1—2, the solubilities of 2,6-MAN and 2,7-MAN increase with an increase in temperature; for example, at 311.15K, the solubilities of 2,6-MAN in the three solvents are 7.09, 7.36, and 8.29 times those at 273.15K, respectively. At

the same temperature and in the same solvent, the solubilities of 2,7-MAN are noticeably greater than those of 2,6-MAN, for instance, at 291.15K, in *n*-heptane, the solubilities of 2,6-MAN and 2,7-MAN are 4.0731 and 5.6314, respectively, which indicates that the alkanes can be used as solvents for the recrystallization of 2,6-MAN.

Tables 7—8 show that the enthalpies of fusion, $\Delta_{fus}H$, of 2,6-MAN and 2,7-MAN obtained by the least square linear regression method using different solvents are consistent. The average values are 31115J·mol^{-1} and 28288J·mol^{-1}, respectively; and the average deviations are 3.128% and 1.502%, respectively.

The model parameters of 2,6-MAN and 2,7-MAN in different solvents based on the average value of fusion enthalpies are listed in the Tables 9—10. The correlation coefficients (R^2) are greater than 0.99, which indicates that the model is reliable.

Table 9 Parameters of 2,6-MAN based on the average value of fusion enthalpies in different solvents

Parameter	A_{12}	A_{21}	R^2
n-heptane	1.5848	2.3821	0.9970
n-octane	1.6112	2.3852	0.9988
n-dodecane	1.4190	2.3715	0.9994

Table 10 Parameters of 2,7-MAN based on the average value of fusion enthalpies in different solvents

Parameter	A_{12}	A_{21}	R^2
n-heptane	−0.3244	2.7846	0.9989
n-octane	1.3018	2.7456	0.9994
n-dodecane	0.8787	2.6604	0.9971

4 CONCLUSIONS

(1) The solubility of 2,6-MAN and 2,7-MAN in *n*-heptane, *n*-octane, and *n*-dodecane were measured from 273.15 to 319.15K.

(2) A solubility model based on the Margules equation was established, and the enthalpies of fusion $\Delta_{fus}H$ and the Margules equation coefficients A_{12} and A_{21} of 2,6-MAN and 2,7-MAN in the alkanes, were obtained by regressing the experimental data.

NOMENCLATURE

A_{12}	Margules equation coefficient
A_{21}	Margules equation coefficient
E	$(X_{exp}-X_{cal})/X_{exp}$, %
S	solubility of solute in the solvent, g·(100g)$^{-1}$
T_m	melting point temperature, K
γ_2	liquid phase activity coefficient of solute
$\Delta_{fus}H$	enthalpy of fusion, J·mol^{-1}

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