Chin. J. Chem. Eng., **15**(1) 110—114 (2007)

Measurement and Correlation for Solubility of Adipic Acid in Several Solvents

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Abstract Using a laser detecting system, solubility data were measured for adipic acid dissolved in six pure solvents, namely, cyclohexanone, cyclohexanol, acetic acid, *N*,*N*-dimethylformamide, *N*,*N*-dimethylacetamide, and dimethylsulfoxide at the temperature range from 293.15K to 353.15K. All these data were regressed by λh , NRTL, Wilson, and the modified Wilson models. For the study of six, λh , NRTL, and the modified Wilson models were found to provide an accurate mathematical representation of the experimental results, with overall average absolute relative deviations between measured and calculated values as 1.74%, 2.06%, and 3.06%, respectively. The results showed that the λh model is the most suitable for description of the solid-liquid equilibrium containing adipic acid.
Keywords solid-liquid equilibrium, solubility, adipic acid, modeling

1 INTRODUCTION

Adipic acid is a valuable raw material used in the production of nylon-66, fibers, lubricants, plasticizers, and food additives, as well as in the production of intermediates for pharmaceuticals, insecticides, and bactericides. Conventionally, it is manufactured by the oxidation of cyclohexanone/cyclohexanol, by the hydrogenation of phenol or, more commonly, by the oxidation of cyclohexane[1,2]. The crude products of oxidation reaction contain a series of impurities, and must be purified. Recrystallization is one of the purification methods, but the solubilities of adipic acid are nearly unavailable, except in water and ethanol[3—5]. Furthermore, it is also needed to separate the small quantity of adipic acid from the acidic washing water of the air-oxidation by-products of cyclohexane[6—8]. Therefore, the solubilities of adipic acid in six pure solvents were measured in this study. The results could be employed in the design and optimization of purification processes of adipic acid.

2 EXPERIMENTAL

2.1 Materials

All materials used in experiments were obtained from commercial sources and were used without any additional purification. The purity of materials was given in Table 1.

2.2 Apparatus and procedure

The solubility was measured by synthetic method. The experimental apparatus were shown in Fig.1. A jacket solubility cell of 50cm^3, with a temperature controlled at ±0.01K by a thermostat, was used to determine the solubility of adipic acid. The solubility

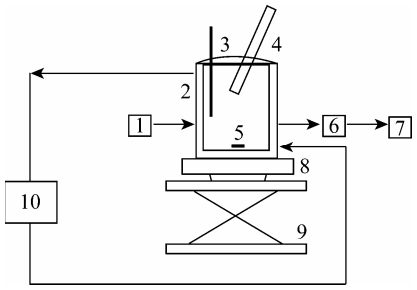

Figure 1 Schematic diagram of experimental apparatus
1—laser emitter; 2—solubility cell; 3—thermometer; 4—condenser; 5—stirring spin; 6—photoelectric transformer; 7—galvanometer; 8—magnetic stirring system; 9—trestle table; 10—thermostat

Table 1 Purity of the applied materials

Compound	Purity, %	Manufacturing plant	Compound	Purity, %	Manufacturing plant
adipic acid	99.8	Tianjin Guangfu Finechemical Plant	*N*,*N*-dimethylformamide (DMF)	99.5	The First Chemical Reagent Plant of Tianjin
cyclohexanone	99.5	The First Chemical Reagent Plant of Tianjin	*N*,*N*-dimethylacetamide (DMAC)	99.5	The First Chemical Reagent Plant of Tianjin
cyclohexanol	98.0	The First Chemical Reagent Plant of Tianjin	dimethylsulfoxide (DMSO)	99.5	The First Chemical Reagent Plant of Tianjin
acetic acid	99.5	Kewei Company of Tianjin University			

Received 2005-12-21, accepted 2006-06-02.
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cell can let laser beam to pass through it, and the power of laser was converted into electrical signal and detected by galvanometer. The use of a condenser to prevent the evaporation of the organic solvent is necessary. The thermometer used in the experiment was checked in Tianjin Metering Institute, and the uncertainty in temperature during measurement is ±0.05K. The temperature range for the solubility measurement in various solvents was approximately from 293.15K to 353.15K.

The dissolving process of adipic acid was observed by a laser detecting system[9]. The predetermined adipic acid and the solvent were placed into the solubility cell, and heated very gradually. The power of the laser that passed through the sample increased as the solid decreased. When the last piece of solid disappeared, the laser power reached the largest value, so the corresponding temperature was determined, that is the solubility of adipic acid at given composition can be obtained. To assure the accuracy of the measurement, each sample was weighed by an analytical BS 224 S balance with the precision of 10^{-4}g, and the possible error in the mole fraction is estimated to be around ±0.0001. The increasing rate of temperature was controlled, especially near the solid-liquid equilibrium temperature, by less than 0.1K·10min^{-1}.

To confirm the reliability of the experimental apparatus, solubilities of adipic acid in water were measured and compared with those in the published reports[3]. Fig.2 shows that the experimental data are in excellent accord with those in the published reports.

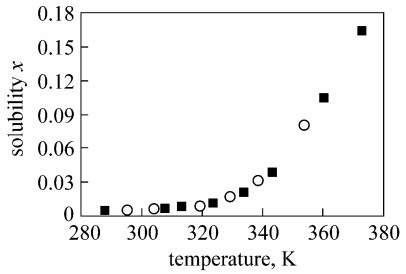

Figure 2 Solubility of adipic acid in water
○ experimental solubility values;
■ solubility values in published reports[3]

3 RESULTS AND DISCUSSION

3.1 Experimental results

With cyclohexanone, cyclohexanol, acetic acid, DMF, DMAC, DMSO as solvents, respectively, the solubilities of adipic acid in these solvents were measured in this study and listed in Table 2, where x is the mole fraction of adipic acid.

Comparing the solubility of adipic acid in six different solvents, it is obvious that DMSO has the highest dissolving capacity, and the cyclohexanone has the lowest. The solubility of adipic acid in DMSO, DMAC, and DMF is around 20 times as much as that in cyclohexanone, cyclohexanol, and acetic acid. The solubility of adipic acid in the six pure solvents rise slowly with the increase of temperature, so all the six solvents may be unsuitable for the recrystallization of adipic acid by cooling.

The difference of the solubilities of adipic acid in the six solvents arises mainly from structure. The smaller solubilities of adipic acid in cyclohexanone and cyclohexanol are probably attributable to the incompatible structures, adipic acid being with chain structure while cyclohexanone and cyclohexanol with ring structure. The self-association of acetic acid makes the decrease of its solvation ability, so the solubility of adipic acid in acetic acid is smaller than that in other solvents except in cyclohexanone and cyclohexanol.

3.2 Correlation with various models

The equation for the description of solid-liquid

Table 2 Experimental solubilities of adipic acid in various solvents

Cyclohexanone		Cyclohexanol		Acetic acid		DMF		DMAC		DMSO	
T, K	x	T, K	x	T, K	x	T, K	x	T, K	x	T, K	x
292.75	0.0104	298.80	0.0017	297.93	0.0197	290.80	0.2417	294.55	0.2939	292.95	0.3132
294.55	0.0110	301.35	0.0107	302.70	0.0246	295.05	0.2482	301.09	0.3005	296.15	0.3176
297.23	0.0140	306.43	0.0183	306.65	0.0280	301.25	0.2560	306.05	0.3094	299.35	0.3226
298.75	0.0148	308.75	0.0268	311.67	0.0337	304.45	0.2621	311.70	0.3180	301.35	0.3247
302.35	0.0163	311.95	0.0387	315.20	0.0386	307.27	0.2666	313.35	0.3204	305.45	0.3320
304.09	0.0172	317.65	0.0541	319.33	0.0442	311.10	0.2752	317.43	0.3259	309.85	0.3398
312.55	0.0240	322.90	0.0677	323.49	0.0512	316.75	0.2860	321.45	0.3312	314.47	0.3472
318.40	0.0343	329.45	0.0851	326.57	0.0568	323.85	0.3001	325.05	0.3391	320.25	0.3575
327.55	0.0452	334.75	0.0989	329.30	0.0622	329.35	0.3130	329.09	0.3488	324.95	0.3646
339.05	0.0678	340.10	0.1138	332.85	0.0694	335.25	0.3245	332.80	0.3571	328.95	0.3733
349.85	0.1020	344.90	0.1298	335.77	0.0800			336.73	0.3659	334.70	0.3838
355.15	0.1283	352.47	0.1551	339.55	0.0902						
				344.53	0.1016						
				347.65	0.1119						

equilibrium is based on the equality of chemical potentials between components in all the coexisting phases. In our study, a solid-solid transition does not occur, so the equation just mentioned reduces to a simple form[10]:

$$\ln(\gamma x) = -\frac{\Delta_m H}{R}\left(\frac{1}{T}-\frac{1}{T_m}\right) \quad (1)$$

where, $\Delta_m H$ is the molar enthalpy of fusion of solute at the normal melting temperature of solute T_m, T is the absolute temperature, R is the universal gas constant, x is the mole fraction, and γ is the activity coefficient. The normal melting temperature T_m and the fusion enthalpy $\Delta_m H$ for the solute adipic acid used in the calculation are 426.15K and 34850J·mol^{-1}[11], respectively. For the solubility calculation, the activity coefficient must be considered in the single or mixed solvents for the solute-solvent interaction. Hence, to calculate solubility as shown in Eq.(1), an activity coefficient model must be selected.

For solid-liquid equilibrium, many models[12] of activity coefficient can be used, such as Wilson, NRTL, UNIQUAC, UNIFAC, and so on. Wilson and NRTL models were selected in this study. The Wilson model is a widely used semi-empirical model, suitable for nonpolar as well as polar systems. The NRTL model has the advantage of having the third adjustable parameter α that allows its use in fitting the phase behavior of highly nonideal systems, though sometimes α is set to a fixed value.

In this article, the λh model[13] was also selected to fit the experimental data. It is proposed for the correlation of solid-liquid equilibrium directly, and it is widely accepted to be capable of dealing with strong polarity systems, which involve strong interaction between molecules. The λh model could fit the experimental data well for many systems with only two parameters, λ and h. The λh model is expressed as follows:

$$\ln\left[1+\frac{\lambda(1-x)}{x}\right] = \lambda h\left(\frac{1}{T}-\frac{1}{T_m}\right) \quad (2)$$

Besides the three models, an attempt was also made to correlate the experimental solubility data by the modified Wilson model. Parameters in Wilson model[12], $g_{12}-g_{11}$, and $g_{21}-g_{22}$, are generally considered to be only dependent on the composition, but independent of temperature. To describe accurately the activity coefficient, the parameters, $g_{12}-g_{11}$, and $g_{21}-g_{22}$, were expressed by the following temperature dependent functions:

$$g_{12}-g_{11} = A+\frac{B}{T} \quad (3)$$

$$g_{21}-g_{22} = C+\frac{D}{T} \quad (4)$$

where A, B, C and D were parameters of Eqs.(3) and (4). T was the absolute temperature. Because of these improvements, it was named m-Wilson model.

The parameters A, B, C, and D were estimated by correlating the experimental data. The optimum algorithm employed the Nelder-Mead method[14], in which the objective function was the average absolute relative deviation (E) between the experimental and calculated mole fraction of adipic acid.

$$E = \frac{1}{N}\times\sum\left|\frac{x_{exp}-x_{cal}}{x_{exp}}\right|\times 100\% \quad (5)$$

The results of the correlation with λh, NRTL, Wilson, and m-Wilson models are shown in Table 3, Figs.3 to 6. The respective parameters are shown in Table 4.

Table 3 The comparison of the correlation results for the solubility of adipic acid in six solvents

Solvents	E, %			
	λh model	NRTL model	Wilson model	m-Wilson model
cyclohexanone	3.78	3.25	3.78	3.63
cyclohexanol	4.76	3.66	6.47	4.59
acetic acid	0.97	1.50	1.88	1.09
DMF	0.28	1.26	9.55	1.47
DMAC	0.27	1.36	11.74	2.67
DMSO	0.38	1.30	14.13	4.91
total average deviation, %	1.74	2.06	7.93	3.06

For the six binary systems, the calculation results exhibit that λh model has the smallest absolute relative deviation of 1.74%, Wilson model has the largest value of 7.93%, and NRTL and m-Wilson models give the medium deviation value of 2.06% and 3.06%,

Table 4 Parameters from different models for six binary systems

Solvents	λh model		NRTL model			Wilson model		m-Wilson model			
	λ	h	$g_{12}-g_{22}$	$g_{21}-g_{11}$	α_{12}	$g_{12}-g_{11}$	$g_{21}-g_{22}$	A	B	C	D
cyclohexanone	0.8083	5061.54	1097.93	2230.77	0.03165	−1614.23	3307.65	1237.71	−5518.37	2425.58	7180.60
cyclohexanol	1.7701	2563.86	2509.23	10995.9	0.7936	32051.9	−3548.89	27492.6	−1454.38	−3816.46	7812.42
acetic acid	0.6807	5149.57	1663.86	3287.74	0.3087	−4764.98	11401.13	31.3609	25309.74	335.76	−25765.82
DMF	−0.1473	3854.79	19596.26	11431.08	0.07021	−2805.41	−12715.55	1255.78	−91290.41	9808.57	111446.5
DMAC	−0.2671	3733.92	37424.27	33432.66	0.02919	−3786.48	−11884.05	−1779.81	−151102.1	−8628.89	155220.7
DMSO	−0.3057	3396.47	28745.02	18119.84	0.05155	−5941.91	−10788.80	−4460.73	−51930.66	−72835.64	83342.19

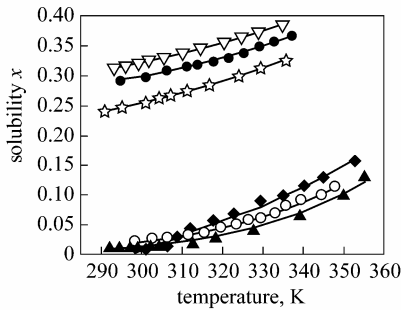

Figure 3 The correlating results of λh model
▲ adipic acid (1)+cyclohexanone; ◆ (1)+cyclohexanol; ○ (1)+acetic acid; ☆ (1)+DMF; ● (1)+DMAC; ▽ (1)+DMSO; —— calculated with λh equation; ▲, ◆, ○, ☆, ●, ▽ experimental values

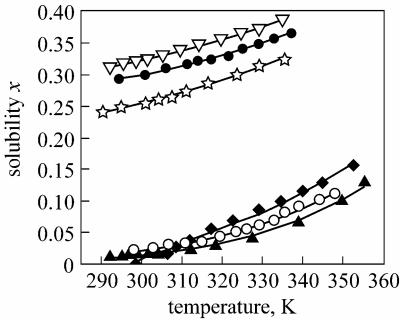

Figure 4 The correlating results of NRTL model
▲ adipic acid(1)+cyclohexanone; ◆ (1)+cyclohexanol; ○ (1)+acetic acid; ☆ (1)+DMF; ● (1)+DMAC; ▽ (1)+DMSO; —— calculated with NRTL equation; ▲, ◆, ○, ☆, ●, ▽ experimental values

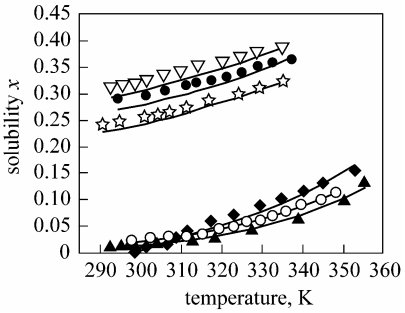

Figure 5 The correlating results of Wilson model
▲ adipic acid (1)+cyclohexanone; ◆ (1)+cyclohexanol; ○ (1)+acetic acid; ☆ (1)+DMF; ● (1)+DMAC; ▽ (1)+DMSO; —— calculated with Wilson equation; ▲, ◆, ○, ☆, ●, ▽ experimental values

respectively. It shows that λh model is more suitable for solid-liquid equilibrium systems than the other models. This conclusion coincides with the opinion of the other followers[15 — 17]. The precisions of NRTL and m-Wilson models are also acceptable for use in industry.

Comparing the results of Wilson and m-Wilson models, the latter gives much better results than the original Wilson model. It shows that the activity coefficient indeed relies on temperature.

4 CONCLUSIONS

The solubility of adipic acid in six pure solvents,

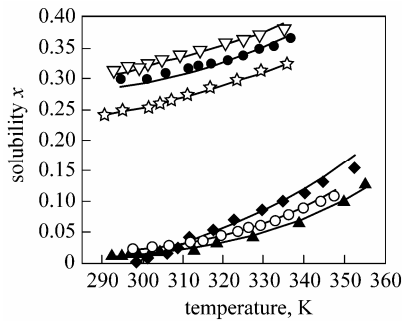

Figure 6 The correlating results of m-Wilson model
▲ adipic acid (1)+cyclohexanone; ◆ (1)+cyclohexanol; ○ (1)+acetic acid; ☆ (1)+DMF; ● (1)+DMAC; ▽ (1)+DMSO; —— calculated with m-Wilson equation; ▲, ◆, ○, ☆, ●, ▽ experimental values

namely, cyclohexanone, cyclohexanol, acetic acid, DMF, DMAC, and DMSO were measured at the range of temperature from 293.15K to 353.15K. These data not only were helpful for industry design but also formed the basis for further theoretical studies.

All the solubility data were correlated by λh, NRTL, Wilson, and m-Wilson models and the corresponding average absolute relative deviations of the four models were 1.74%, 2.06%, 7.93%, and 3.06%, respectively. When correlation of the solubility of adipic acid in pure solvents is required, the λh model is preferred because of its simplicity and for the best correlation results obtained. The NRTL and m-Wilson models are also valuable for the correlation of adipic acid solubility in various solvents. Furthermore, the NRTL and m-Wilson model are possible to be extended to predict the solubilities of ternary systems through the parameters of the models of the binary systems.

NOMENCLATURE

A, B, C, D	constants in the correlated $g_{12}-g_{11}$ and $g_{21}-g_{22}$ in m-Wilson model
E	average absolute relative deviation, %
$g_{12}-g_{11}$, $g_{21}-g_{22}$	parameters in Wilson mode
$g_{12}-g_{22}$, $g_{21}-g_{11}$	parameters in NRTL model
$\Delta_m H$	molar enthalpy of fusion of adipic acid, $J\cdot mol^{-1}$
h	parameter in λh model, K
N	number of experimental data
R	universal gas constant, $J\cdot mol^{-1}\cdot K^{-1}$
T	experimental temperature, K
T_m	fusion temperature, K
x	mole fraction of adipic acid
α	nonrandom parameter in NRTL model
γ	activity coefficient of adipic acid
λ	parameter in λh model

Subscripts

cal	calculated result
exp	experimental result
1	solute
2	solvent

REFERENCES

1 Davis, D.D., Kemp, D.R., Kirk-Othmer Encyclopedia of Chemical Technology, 4th ed., Vol. 1, Wiley, New York (1991).
2 Castellan, A., Bart, J.C.J., Cavallaro, S., "Industrial production and use of adipic acid", *Catal. Today*, **9**(3),

237—254(1991).
3 Stephen, H., Stephen, T., Solubilities of Inorganic and Organic Compounds (v1), Pergamon Press, New York (1963).
4 Mohan, R., Lorenz, H., Myerson, A.S., "Solubility measurement using differential scanning calorimetry", *Ind. Eng. Chem. Res.*, **41**(19), 4854—4862(2002).
5 Yi, Y.J., Hatziavramidis, D., Myerson, A. S., "Development of a small-scale automated solubility measurement apparatus", *Ind. Eng. Chem. Res.*, **44**(15), 5427—5433(2005).
6 Eniricerche, S.P.A., "Recovery of dicarboxylic acids from wastes from the production of adipic acid", Italy Pat., 1249061 (1995).
7 Inst. Ind. and Technol., "Complex compound containing acidic functional group and method of preparing adipic acid/adipate using said complex compound", CN Pat., 1426997 (2003).
8 Sutradhar, B.C., "Crystallization of adipic acid from its solution in aqueous nitric acid", USA Pat. 2005085666 (2005).
9 Ma, P.S., Xia, Q., "Determination and correlation for solubility of aromatic acid in solvents", *Chin. J. Chem. Eng.,* **9**(1), 39—44(2001).
10 Gmehling, J., Anderson, T.F., Prausnitz, J.M., "Solid-liquid equilibria using UNIFAC", *Ind. Eng. Chem. Fundam.*, **17**, 269—273(1978).
11 Dean, J. A., Lange's Handbook of Chemistry, 15th ed., McGraw-Hill, Inc, New York (1998).
12 Ma , P. S., Chemical Engineering Data, Sinopec Press, Beijing (2003). (in Chinese)
13 Buchowski, H., Ksiazcak, A., Pietrzy, K.S., "Solvent activity along saturation line and solubility of hydrogen-bonding solids", *J. Phys. Chem.*, **84**, 975—979(1980).
14 Nelder, J.A., Mead, R., "A simplex method for function minimization", *Comput. J.*, **18**, 308—313(1965).
15 Zhu, J.Q., Yu, Y.S., He, C.H., "Application of λh equation in mixed solvents", *J. Chem. Eng. Chinese Univ.,* **12**(4), 319—324(1998). (in Chinese)
16 Ma, P.S., Chen, M.M., Dong, Y., "Solid-liquid equilibria of several binary and ternary systems containing maleic anhydride", *Chin. J. Chem. Eng.*, **10**(3), 323 — 327(2002).
17 Ma, P.S., Chen, M.M., "Solid-liquid equilibrium of terephthalic acid in several solvents", *Chin. J. Chem. Eng.*, **11**(3), 334—337(2003).