Korean J. Chem. Eng., **23**(6), 1034-1036 (2006)

Solubility of piperonal in different pure solvents and binary isopropanol+water solvent mixtures

Shui Wang† and Dongxiu Chen*

College of Chemical Engineering, Beijing University of Chemical Technology, Beijing, China, 100029
*YiBin JianZhong Perfume Co., Ltd, 644000, China
(*Received 9 January 2006 • accepted 27 June 2006*)

Abstract–Using a laser monitoring observation technique, the solubilities of piperonal in different pure solvents and binary isopropanol+water solvent mixtures were determined by synthetic method from 273.15 K to 293.15 K. Results of these measurements were correlated by Apelbat equation and the combined nearly ideal binary solvent (CNIBS)/Redlich-Kister equation. The results find that Apelbat equation and the combined ideal binary solvent (CNIBS)/Redlich-Kister equation provided accurate mathematical representations of the experimental data, respectively.

Key words: Piperonal, Laser Monitoring Observation Technique, Solubilities, (CNIBS)/Redlich-Kister Equation

INTRODUCTION

Piperonal (heliotropin, piperonylaldehyde, 3,4-(methylenedioxy) benzaldehyde) is a known compound which occurs in various flower oils and types of vanilla. It can be prepared synthetically and, because of its sweetish, heliotropic-like odor, is used in perfumery, in particular for the perfuming of soap [He and Sun, 1995]. It is also used as a shying intensifier in electroplating process or berberine in pharmaceutics etc. Its chemical structure is shown in Fig. 1.

In practical crystallization, solubilities of piperonal in solvents are needed. Up to now, few solubilities of piperonal in organic solvents have been reported in the literature. In this work, we report solubilities of piperonal in different pure solvents and binary isopropanol+water solvent mixtures in the temperature range from 273.15 K to 293.15 K at atmospheric pressure.

EXPERIMENTAL SECTION

1. Materials

Piperonal used during the solubility measurement had a purity of 0.998 (mass fraction), and it was purchased from YiBin JianZhong Perfume Co., Ltd. Other reagents were analytical research grade reagents from Shanghai Chemical Reagent Co., while deionized Milli-Q water was used to prepare all solutions.

2. Apparatus and Procedure

Solubilities were measured by a synthetic method [Nyvlt, 1997; Roberts et al., 1994; Jiang et al., 2000]. The apparatus for solubility measurement was the same as described in literature [Li et al., 2001a, b]. The laser monitoring system consisted of a laser generator, a photoelectric transformer, and a light intensity display. A semiconductor laser device with power of 5 mW emitting a steady laser beam with wavelength of 650 nm was used to determine the solubility of solute in binary solvents mixture at a known temperature. The solubility apparatus consisted of a jacketed glass vessel maintained at a desired temperature by water circulated from a water bath with a thermoelectric controller (type 501, China). The jacket temperature could be maintained within ±0.05 K of the required temperature. Continuous stirring was achieved with a magnetic stir bar. A condenser was connected with the vessels to prevent the solvents from evaporating. A mercury-in-glass thermometer was inserted into the inner chambers of the vessels for the measurement of the temperature. The thermometer had an uncertainty of ±0.05 K.

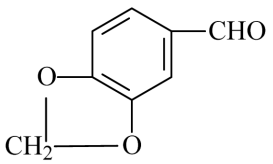

Fig. 1. Structure of piperonal.

An analytical balance (type TG332A, China) with an uncertainty of ±0.0001 g was used during the measurement. A predetermined excess mass of piperonal and solvent of known mass were placed in the jacketed vessel. The contents of the vessel were stirred continuously at a constant temperature, and the solvent was added to the vessel simultaneously. When the last portion of solute just disappeared, the intensity of the laser beam penetrating the vessel reached the maximum, and the solvent mass consumed in the measurement was recorded. Together with the mass of solute, the solubility would be obtained. To verify the uncertainty of the measurement, one other experiment was done in which the solubility of benzoic acid in water was determined. Compared with the literature data [Stephen and Stephen, 1963], the deviation of the solubility was <1%. The same solubility experiment was conducted three times. The uncertainty of the experimental solubility values is about ±0.5%. The uncertainty in the solubility values due to uncertainties in temperature measurements, weighing procedure, and instabilities of the water bath is estimated to be ±0.5%.

RESULTS AND DISCUSSION

The solubility data of piperonal in pure water, isopropanol, acetone, trichloromethane, and ethanol at different temperature are pre-

†To whom correspondence should be addressed.
E-mail: lantianxia2005@sohu.com

Table 1. Mole fraction solubility x of piperonal in pure solvents

T/K	Water		Isopropyl alcohol		Acetone		Trichloromethane		Ethanol	
	$10^3\,x^{exptl}$	$10^3\,x^{calcd}$	x^{exptl}	x^{calcd}	x^{exptl}	x^{calcd}	x^{exptl}	x^{calcd}	x^{exptl}	x^{calcd}
273.15	0.1180	0.1174	0.0174	0.0174	0.0521	0.0517	0.4275	0.4288	0.0056	0.0055
278.15	0.1530	0.1568	0.0227	0.0229	0.0655	0.0666	0.4766	0.4739	0.0143	0.0154
283.15	0.2200	0.2110	0.0332	0.0321	0.0876	0.0873	0.5308	0.5309	0.0396	0.0364
288.15	0.2770	0.2858	0.0461	0.0476	0.1176	0.1160	0.5984	0.6023	0.0697	0.0722
293.15	0.3930	0.3895	0.0753	0.0744	0.1551	0.1563	0.6934	0.6913	0.1228	0.1224

Table 2. Parameters of Eq. (1) for solubility of piperonal in pure solvents

Solvent	A	B	C	10^2rmsd
Water	−359.7900	10876.6796	55.4223	0.0006
Isopropyl alcohol	−1461.6755	57138.8874	222.5373	0.0928
Acetone	−504.5606	17614.2129	77.9164	0.1042
Trichloromethane	−353.2008	13385.8860	54.0726	0.2385
Ethanol	3084.5553	−142038.8072	−458.0663	0.1917

sented in Table 1. The temperature dependence of piperonal solubility in pure solvents is described by the modified Apelblat equation which is a semi-empirical equation [Liu and Fu, 2004]:

$$\ln x = A + \frac{B}{T/K} + C\ln(T/K) \tag{1}$$

where x is the mole fraction solubility of piperonal, T is the absolute temperature, and A, B, and C are the dimensionless parameters. The calculated solubility values of piperonal are also given in Table 1. The values of parameters A, B, and C and the root-mean-square deviations (RMSDs) are listed in Table 2. The RMSD is defined as

$$\mathrm{RMSD} = \left[\frac{1}{n}\sum_{i=1}^{n}(x_i^{calcd} - x_i^{exptl})^2\right]^{1/2} \tag{2}$$

Where n is the number of experimental points, x_i^{calcd} represents the solubility calculated from Eq. (1), and x_i^{exptl} represents the experimental solubility values.

The solubility data of piperonal in binary isopropanol+water solvent mixtures in the temperature range from 273.15 K to 293.15 K are presented in Table 3. The solubility data in binary isopropanol+water solvent mixtures are described by the CNIBS/Redlich-Kister model.

Acree and co-workers [Acree, 1992; Acree et al., 1991; Acree and Zvaigzne, 1991] suggested the CNIBS/Redlich-Kister model,

$$\ln x_A = x_B^o \ln(x_A)_B + x_C^o \ln(x_A)_C + x_B^o x_C^o \sum_{i=0}^{N} S_i (x_B^o - x_C^o)^i \tag{3}$$

as a possible mathematical representation for describing how experiment isothermal solubility of a crystalline solute dissolved in a binary solvent mixture varies with binary solvent composition. S_i is the model constant and N can be equal to 0, 1, 2 and 3, respectively. Depending on the values of N, four equations can be obtained from Eq. (3). x_B^o and x_C^o refer to the initial mole fraction composition of the binary solvent calculated as if solute (A) were not present. $(x_A)_i$ is the saturated mole fraction solubility of the solute in pure solvent i.

Substitution of $(1-x_C^o)$ for x_B^o in Eq. (3) with N=2, and subsequent rearrangements result in Eq. (4).

Table 3. Experimental solubility (x_A) of Piperonal in binary water (B)+isopropanol (C) solvent mixtures at the temperature range from 273.15 K to 293.15 K

x_C^o	$10^2\,x_A^{exptl}$	$10^2\,x_A^{calcd}$	x_C^o	$10^2\,x_A^{exptl}$	$10^2\,x_A^{calcd}$
	T=273.15 K			T=278.15 K	
0.0000	0.0118	0.0117	0.0000	0.0153	0.0153
0.0980	0.0719	0.0735	0.0980	0.1093	0.1083
0.2013	0.2939	0.2921	0.2013	0.4386	0.4458
0.3103	0.7916	0.7842	0.3103	1.1723	1.1631
0.3976	1.3477	1.3359	0.3976	1.8892	1.8828
0.4858	1.9151	1.9237	0.4858	2.5492	2.5497
0.5846	2.4516	2.4732	0.5846	3.0661	3.0725
0.6966	2.7928	2.8091	0.6966	3.3062	3.3205
0.8008	2.7758	2.7655	0.8008	3.2410	3.2416
0.8964	2.4341	2.4090	0.8964	2.9318	2.9217
1.0000	1.7431	1.7517	1.0000	2.3176	2.3233
	T=283.15 K			T=288.15 K	
0.0000	0.0220	0.0220	0.0000	0.0277	0.0278
0.0980	0.1793	0.1793	0.0980	0.2693	0.2681
0.2013	0.7347	0.7389	0.2013	1.1883	1.1870
0.3103	1.7844	1.7834	0.3103	2.8889	2.9016
0.3976	2.6944	2.6845	0.3976	4.2817	4.3352
0.4858	3.4677	3.4413	0.4858	5.5935	5.5160
0.5846	4.0452	4.0544	0.5846	6.5652	6.4990
0.6966	4.4547	4.4976	0.6966	7.2065	7.2719
0.8008	4.6022	4.6304	0.8008	7.3667	7.4803
0.8964	4.4037	4.3304	0.8964	6.8745	6.7540
1.0000	3.3179	3.3367	1.0000	4.6069	4.6301
	T=293.15 K			T=293.15 K	
0.0000	0.0393	0.0395	0.5846	13.5798	13.6570
0.0980	0.5206	0.5168	0.6966	15.0094	14.8132
0.2013	2.6676	2.6370	0.8008	14.5975	14.7532
0.3103	6.5133	6.6510	0.8964	12.5216	12.5669
0.3976	9.6765	9.7501	1.0000	7.5250	7.5043
0.4858	12.1988	12.0060			

Table 4. Parameters of Eq. (2) for solubility of piperonal in binary isopropyl alcohol (B)+water (C) solvent mixtures at the temperature range from 273.15 K to 293.15 K

T/K	B_0	B_1	B_2	B_3	B_4	10^4 RMSDs
273.15	−9.0541	21.857	−34.201	26.971	−9.6175	8.0832
278.15	−8.7832	23.561	−39.917	32.194	−10.817	0.7129
283.15	−8.4232	26.042	−51.814	49.458	−18.663	2.9014
288.15	−8.1896	28.446	−59.792	60.271	−23.808	6.4425
293.15	−7.8367	32.639	−72.397	75.316	−30.311	11.0239

$$\ln x_A = \ln(x_A)_B + [\ln(x_A)_C - \ln(x_A)_B + S_0 + S_1 + S_2]x_C^o + [-S_0 + 3S_1 + 5S_2]x_C^{o2} + [-2S_1 - 8S_2]x_C^{o3} + [-4S_2]x_C^{o4} \quad (4)$$

Which can be written as Eq. (5)

$$\ln x_A = B_0 + B_1 x_C^o + B_2 x_C^{o2} + B_3 x_C^{o3} + B_4 x_C^{o4} \quad (5)$$

The experimental solubility data x_A^{expl} correlated with Eq. (5) and the calculated solubilities x_A^{calc} are listed in Table 3. The values of the five dimensionless parameters B_0, B_1, B_2, B_3 and B_4 are listed in Table 4 together with the root-mean-square deviations (RMSDs).

From data listed in Tables 1-4, we can draw the following conclusions: (1) The solubility of piperonal increases with temperature increasing in five kinds of pure solvent. The solubility of piperonal in water is the lowest. The calculated solubility shows good agreement with the experimental values. (2) Water may be used as dilution in order to increase the yield of the product in crystallization process of piperonal. (3) The solubility of piperonal in binary isopropanol+water solvent mixtures is a function of temperature, and solubility increase with increase of temperature. (4) With the increase of x_C^0, the solubility of piperonal increases in binary isopropanol+water solvent mixtures; when x_C^0 is about 0.9, the solubility of piperonal reaches a maximum, then declines. The trends possibly result from the associated isopropanol-water system in binary isopropanol+water solvent mixtures. (5) The calculated solubility of piperonal in binary isopropanol+water solvent mixtures shows good agreement with the experimental values, and the experimental solubility and correlation equation in this work can be used as essential data and models in the purification process of piperonal.

REFERENCES

Acree, W. E. Jr. and Zvaigzne, A. L., "Thermodynamic properties of nonelectrolyte solutions. Part 4. Estimination and mathematical representation of solute activity coefficients and solubilities in binary solvents using the NIBS and modified wilson equation," *Thermochim. Acta*, **178**, 151 (1991).

Acree, W. E. Jr., McCargar, J. W., Zvaigzne, A. L. and Teng, L.-L., "Mathematical representation of thermodynamic properties. carbazole solubilities in binary alkane+dibutyl ether and alkane+tetrahydropyran solvent mixture," *Phys. Chem. Liq.*, **23**, 27 **(**1991).

Acree, W. E. Jr., "Mathematical representation of thermodynamic properties. Part 2. Derivation of the comined nearly ideal binary solvent (NIBS)/Redlich-Kister mathematical representation from a two-body and three-body interactional mixting model," *Thermochim. Acta*, **198**, 71 (1992).

He, J. and Sun, B. G., *Perfume chemical and technology science*, Beijing, Chemical Industry Press, 178 (1995).

Jiang, Q., Gao, G-H., Yu, Y.-X. and Qin, Y., "Solubility of sodium dimethyl isophthalate-5-sulfonate in water and in water+methanol containing sodium sulfate," *J. Chem. Eng. Data*, **45**, 292 (2000).

Li, D.-Q., Liu, D.-Z. and Wang, F.-A., "Solubilities of terephthaladehydic, p-toluic, benzoic, terephthalic, and isophthalic acids in N-methyl-2-pyrrolidone from 295.65 K to 371.35 K," *J. Chem. Eng. Data*, **46**, 172 (2001a).

Li, D.-Q., Liu, D.-Z. and Wang, F.-A., "Solubility of 4-methylbenzoic acid between 288 K and 370 K," *J. Chem. Eng. Data*, **46**, 234 (2001b).

Liu,C. W. and Fu, A. W., "Solubility of niacin in 3-picoline+water from 287.65 to 359.15 K," *J. Chem. Eng. Data*, **49**, 155 (2004).

Nyvlt, J., *Solid-liquid equilibria*, Czechoslovak Academia of Sciences: Praha (1997).

Roberts, K. L., Rousseau, R. W. and Teja, A. S., "Solubility of long-chain n-alkanes in heptane between 280 and 350 K," *J. Chem. Eng. Data*, **39**, 793 (1994).

Stephen, H. and Stephen, T., *Solubilities of inorganic and organic compounds*, Pergamon Press Oxford, Vol. 1 (1963).