Korean J. Chem. Eng., **24**(1), 113-115 (2007)

SHORT COMMUNICATION

Solubilities of solanesol in acetonitrile, ethanol and n-hexane from 285 to 310 K

Jiang-Chu Liu†, Dian-Qing Li*, Rong-Qi Zhou and Fei Hao

Department of Chemical Engineering, Tsinghua University, Beijing, China 100084
*Research Institute of Applied Chemistry, Beijing University of Chemical Engineering, Beijing, China 100029

(*Received 4 April 2006 • accepted 14 August 2006*)

Abstract−Using a laser monitoring observation technique, we measured the solubilities of solanesol in acetonitrile, ethyl alcohol and n-hexane by a synthetic method at temperatures ranging from 285 to 310 K at atmospheric pressure. Empirical equations were proposed and the calculated results show good agreement with the experimental solubilities.

Key words: Solubility, Solanesol, Acetonitrile, Ethanol, n-Hexane

INTRODUCTION

As a kind of natural polyprenol, solanesol is abundant in tobacco and tomato leaves. With a formula of $C_{45}H_{74}O$, it has a molecular weight of 631.1. The structure of solanesol molecule is shown in Fig. 1. Under room temperature, solanesol is a kind of white or light yellow solid. Commonly, solanesol is used as starting material in synthesis of high-value bio-chemicals such as Vitamin-K analogues and Co-enzyme Q10 [Lipshutz et al., 2005]. Solanesol itself is a kind of antioxidant and can be used as medicine. Generally, solanesol is extracted from tobacco leaves and purified by various means. During the extraction and purification of solanesol, it is necessary to know its solubilities in commonly used solvents. In the research of our lab, we use acetonitrile, ethyl alcohol and n-hexane in the purification of solanesol. So, it is important to know the solubilities of solanesol in these solvents. On the other hand, the solubility of solanesol is seldom reported in the literature. Thus, in this work, the solubilities of solanesol in acetonitrile, ethyl alcohol and n-hexane were carefully determined by us in the temperature range from 285 to 310 K at atmospheric pressure.

EXPERIMENTAL SECTION

1. Chemicals

Acetonitrile used in solubility measurement was obtained from Tianjin Siyou Biomedical Technology Developing Co., and had a purity of 0.999 in mass fraction. Ethyl alcohol and n-hexane were obtained from Beijing Xiandai Dongfang Fine Chemicals Co., and had purities of 0.997 and 0.990 in mass fraction, respectively. Acetonitrile and isopropyl used in HPLC analysis were from Sigma Co., which were both of HPLC grade. Solanesol standard used in HPLC calibration was obtained from Shanghai Usea Biotech Co. and had a purity of 0.997 in mass fraction. Solanesol used in solubility measurement had a mass fraction of 0.995, which was obtained by purifying the industrial product that had a stated mass fraction of 0.9476. The industrial solanesol was obtained from Shanghai Wison Chemical Engineering Co. First, the industrial solanesol was solved in ethyl alcohol at 303 K and filtrated to remove mechanical impurity. Then, the solanesol solution was dried and re-crystallizations were carried out in ethyl alcohol and acetonitrile, respectively. The purity of the refined solanesol was determined by HPLC with the mobile phase of acetonitrile and isopropyl (6 : 4).

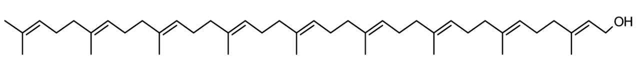

Fig. 1. Structure of solanesol molecule.

†To whom correspondence should be addressed.
E-mail: liujc02@mails.tsinghua.edu.cn

2. Apparatus and Procedure

HPLC analysis was carried out on an Agilent 1100 Chemical Workstation and the column used was a Zorbax C18 column. Solubilities were measured by a synthetic method [Roberts et al., 1994; Apelblat and Manzurola, 1999] with a laser monitoring system. In this system a laser beam was used to determine the dissolution temperature of a solid-liquid mixture of known composition [Li et al., 2001, 2002]. The laser monitoring system consisted of a laser generator, a photoelectric transformer, and a light intensity display. The solubility apparatus consisted of a jacketed glass vessel maintained at a desired temperature by water circulated from a water bath with a Beckmann thermometer. The jacket temperature could be maintained within 0.02 K of the required temperature. The internal volume of the jacketed glass vessel is approximately 20 cm^3. Continuous stirring was achieved with a magnetic stir bar. A mercury-in-glass thermometer, which had a measurement range from (271.15 to 325.15) K, was inserted into the inner chamber of the vessel for the measurement of the temperature. All of the thermometers had an accuracy of ±0.05 K. Solid-liquid mixtures were prepared by mass using an analytical balance (type TG332A, China). The balance had a range of measurement up to 20 g, with an accuracy of ±0.00001 g. Predetermined amounts of solanesol and a solvent were weighed and deposited into the jacketed vessel. Then, the contents of the vessel were heated very slowly at rates less than 2 $K \cdot h^{-1}$ with continuous stirring. When the last portion of solute just disappeared, the intensity of the laser beam penetrating the vessel reached a maximum, and the temperature was recorded as the liquid's temperature. Some of the solubility experiments were conducted two or three times to check the reproducibility. It should be pointed out that the experiment showed that a liquid-solid equilibrium is hard to reach when the solvent is acetonitrile. In this case, then, the heating rate should be less than 1 $K\cdot h^{-1}$.

RESULTS AND DISCUSSION

Solubility is an import physical property of a separating system. Much research has been done in the measuring of solubilities for certain separating systems [Yoo et al., 1997; Byun and Choi, 2004]. But, the solubilities of solanesol in solvents are seldom reported in literature. So, it is necessary to determine the solubilities of solanesol in commonly used separating agents.

According to the literature [Rowland, 1956], the melt point of solanesol is between 38 and 42 degrees Celsius. In this research, we found that solanesol is going to melt in these solvents when the temperature is near 38 degrees Celsius (about 311 K). For this reason, the maximum temperatures determined in this research are all below 311 K.

The experimental solubilities of solanesol in acetonitrile, ethanol and n-hexane are presented in Table 1, where T represents the absolute temperature, C represents the mass fraction, and C_c represents the calculated solubility (in term of the mass fraction). For all three solvents, solubility of solanesol increases with the increase of temperature significantly. The solubility of solanesol in acetonitrile is relatively smaller than that in ethanol and n-hexane. This could be explained by the effect of solvents. The polarity of acetonitrile is the biggest one of the three solvents; meanwhile, the polarity of solanesol is very small. So, the solubilities of solanesol in ethanol and n-hexane, which have small polarities, are relatively bigger. It is clear that when the temperature is below 293 K, the solubility in n-hexane is the biggest of the three solvents. However, with the increase of the temperature, the solubility in ethanol increases much greater than that in n-hexane. When the temperature is higher than 303 K, the solubilities in ethanol and n-hexane are both very large, especially when the temperature is approaching the melt point.

Table 1. Solubilities of solanesol in acetonitrile, ethyl alcohol and hexane

T/K	100C	$100C_c$	T/K	100C	$100C_c$
		Acetonitrile			
291.30	0.0707	0.0766	301.90	0.6280	0.6052
293.65	0.1115	0.1212	303.80	0.9349	0.8765
294.70	0.1462	0.1487	305.70	1.2261	1.2695
296.25	0.2097	0.2011	307.15	1.6456	1.6843
298.95	0.3512	0.3405	308.10	2.0232	2.0270
300.85	0.4794	0.4932	308.95	2.4283	2.3923
		Ethyl Alcohol			
285.15	0.3576	0.3220	296.65	8.0094	7.9525
286.50	0.5339	0.4692	297.65	12.3500	10.5100
287.65	0.7888	0.6466	300.15	21.3183	21.1033
289.15	0.9917	0.9823	301.70	30.5710	32.5127
290.70	1.4102	1.5135	302.30	39.1733	38.4338
291.30	1.7944	1.7891	303.10	49.4928	48.0388
292.40	2.5845	2.4313	304.10	60.1924	63.4878
293.40	3.2972	3.3132	304.55	73.3661	71.9755
294.45	4.4296	4.3061	305.50	94.4556	93.8055
		n-hexane			
284.90	3.1746	3.3239	301.00	8.4608	8.2725
288.45	3.4200	3.4996	302.45	9.9166	10.1816
290.35	3.8503	3.6676	303.30	11.3931	11.6179
292.55	4.1703	3.9733	304.25	13.3862	13.5743
295.95	4.9818	4.8584	305.15	16.2002	15.8442
298.50	5.9717	6.1205	306.30	19.5007	19.4797
299.50	6.8359	6.8431			

The solubility data were correlated with exponential equations:

$$C=C_0+ae^{bT} \tag{1}$$

Table 2. Parameters for correlation equations

Solvent	C_0	a	b	R^2	10^2RMSD
Acetonitrile	0	1.6596E-28	0.19496	0.9987	0.03
Ethanol	0	9.4751E-59	0.27884	0.9984	1.13
n-hexane	3.17474	1.0731E-28	0.21937	0.9986	0.19

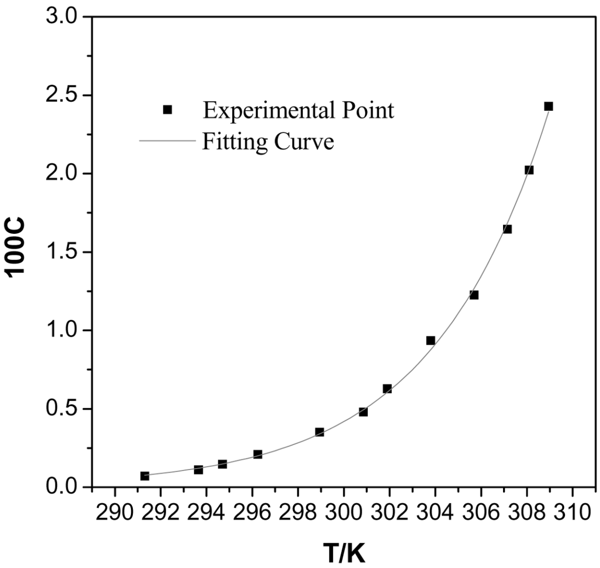

Fig. 2. Solubility of solanesol in acetonitrile.

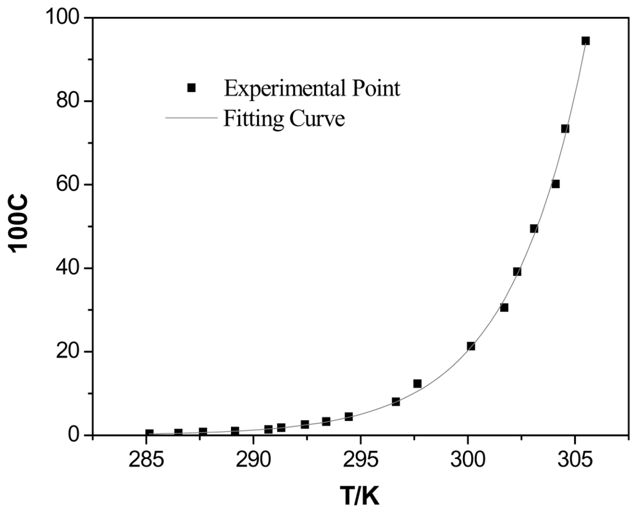

Fig. 3. Solubility of solanesol in ethanol.

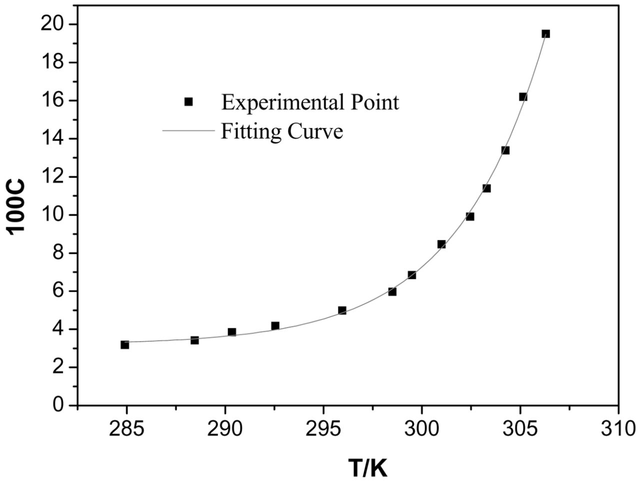

Fig. 4. Solubility of solanesol in n-hexane.

Where, a, b and C_0 are empirical constants. The values of these constants together with the values of the coefficients of determination (R^2) and the root-mean-square-deviations (RMSDs) are listed in Table 2. From Tables 1 and 2, it is clear that the calculated solubilities show good agreement with the experimental data. The experimental solubilities and correlation equations in this work can be used as essential data and empirical models to predict the solubilities of solanesol in these three solvents.

REFERENCES

Apelblat, A. and Manzurola, E., "Solubilities of o-acetylsalicylic, 4-aminosalicylic, 3,5-dinitrosalicylic, and p-toluic acid, and magnesium-DL-aspartate in water from T) (278 to 348) K," *J. Chem. Thermodyn.*, **31**, 85 (1999).

Byun, H. S. and Choi, M. Y., "Solubility in the binary and ternary system for poly(alkyl acrylate)-supercritical solvent mixtures," *Korean J. Chem. Eng*., **21**, 874 (2004).

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., Solubility of 4-methylbenzoic acid between 288 K and 370 K," *J. Chem. Eng. Data*, **46**, 234 (2001).

Li, D.-Q., Liu, D.-Z. and Wang, F.-A., "Solubilities of terephthalaldehydic, 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 (2001).

Li, D.-Q., Liu, J.-C. and Liu, D.-Z., "Solubilities of terephthalaldehydic, p-toluic, benzoic, terephthalic and isophthalic acids in N,N-dimethylformamide from 294.75 to 370.45 K," *Fluid Phase Equilibria*, **200**, 69 (2002).

Lipshutz, B. H., Lower, A. and Berl, V., "An improved synthesis of the "miracle nutrient" coenzyme Q10," *Organic Letters*, **19**(7), 4095 (2005).

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).

Rowland, L., "Flue-Cured tobacco. I. Isolation of solanesol, an unsaturated alcohol," *J. Am. Chem. Soc.*, **78**(18), 4680 (1956).

Yoo, K. P., Shin, H. Y. and Noh, M. J., "Measurement and modeling solubility of bioactive coumarin and its derivatives in supercritical carbon dioxide," *Korean J. Chem. Eng*., **14**, 341 (1997).