Solubility of Salol in Pure Alcohols from (283.15 to 308.15) K

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The solubility of salol in methanol, ethanol, 1-propanol, 2-propanol, 1-butanol, 2-butanol, and 2-methyl-1-propanol was determined in the temperature range from (283.15 to 308.15) K by a static analytical method. The concentrations of the investigated salol in saturated solution were analyzed by UV spectrometry. A second-degree polynomial was proposed for correlating the experimental data, and it exhibited good agreement.

Introduction

The chemical structure of salol ($C_{13}H_{10}O_3$, CAS registry no. 118-55-8), also known as phenyl salicylate or phenyl 2-hydroxybenzoate, involved in this study is shown in Figure 1. Salol, which commonly appears as a white powder with an aromatic aroma, has been extensively used in the manufacturing of plastics and suntan oils and had been used medicinally as an analgesic, an antipyretic, or a coating for pills in which the medicine is intended for enteric release.[1,2] In industry, salol is crystallized from solution as a final step.[3−6] Therefore, crystallization is a key step in many respects, and it determines the yield and quality of the target product. To determine proper solvents and to design an optimized production process, it is necessary to know the solubility of salol in different solvents.

Limited data are available on the solubility and temperature dependence of the solubility of salol.[2,7−9] The aim of this article is to explore the solubility of salol in seven solvents, that is, methanol, ethanol, 1-propanol, 2-propanol, 1-butanol, 2-butanol, and 2-methyl-1-propanol in the temperature range of (283.15 to 308.15) K.

Experimental Section

Chemicals. Methanol, ethanol, 1-propanol, 2-propanol, 1-butanol, 2-butanol, and 2-methyl-1-propanol were purchased from Tianjin Kewei Chemical Reagent. All above solvents were refluxed over freshly activated CaO for 2 h and then fractionally distilled. Liquids were stored over freshly activated molecular sieves of type 4A. Analysis, using the Karl Fischer technique, showed that the water content in each of the solvents was less than 0.02 mass %. The purities of the solvents were determined in our laboratory by gas chromatography: for methanol, 99.92 mass %; for ethanol, 99.90 mass %; for 1-propanol, 99.95 mass %; for 2-propanol, 99.94 mass %; for 1-butanol, 99.98 mass %; for 2-butanol, 99.95 mass %; and for 2-methyl-1-propanol, 99.93 mass %. Salol, obtained from Hangzhou Chiral Medicine Chemicals, underwent purified recrystallization from ethanol solution two times, followed by sublimation at 310 K under reduced pressure. The obtained sample was kept in a desiccator with dry silica gel. The sample was repurified by sublimation every half a month to use as fresh a sample as possible. The purity of the sample was determined to be 0.9995 in the mole fraction by a differential scanning calorimeter (Mettler DSC30).

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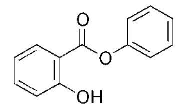

Figure 1. Structure of the salol molecule.

Apparatus and Procedures. The experimental solubility of salol in alcohol solvents in the temperature range from (283.15 to 308.15) K was measured by a static analytical method that was described in our previous work[10,11] and is briefly explained here. The experimental saturated solutions were prepared by excess solute, salol, in glass vessels containing the solvent. Solubilities were determined by equilibrating the solute with solvent in a water jacketed vessel with magnetic stirring in a constant temperature water bath (± 0.05 K) for at least 3 days. Attainment of equilibrium was verified by both repetitive measurement after a minimum of 3 additional days and approaching equilibrium from supersaturation by pre-equilibrating the solutions at a higher temperature. The actual temperature in the glass vessel was monitored by a mercury thermometer with an uncertainty of 0.05 K. The fluid between the internal and external glass tube can be exchanged by pressing or relaxing the gas bag at the top of the glass tube. Portions of salol-saturated solutions were transferred by syringe from the internal glass tube to volumetric flasks to determine the amounts of samples diluted quantitatively with solvent mixtures using a spectrophotometer (Shimadzu UV-160A). Syringes (10 mL) and needles were preheated when necessary to prevent nucleation inside the syringes during sampling. The mole fractions of the dilute solutions were determined from absorbance versus concentration calibration curves derived from the measured absorbance of solutions of known concentrations.

Results and Discussion

UV spectrometry was chosen to determine the concentration of a saturated solution of salol in the solvents. To check the reliability of the experimental method, known masses of salol were completely dissolved in ethanol, and the concentrations of solution were measured by a spectrometer (Shimadzu UV-160A). The average relative uncertainty was 2.7 % ($N = 6$).

The solubilities of salol in methanol, ethanol, 1-propanol, 2-propanol, 1-butanol, 2-butanol, and 2-methyl-1-propanol reported in Table 1 represent an average of three measurements with a reproducibility of better than 97 %. From the results, we

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Table 1. Solubility of Salol in Alcohol Solvents in the Temperature Range of (283.15 to 308.15) K

	x_1						
T/K	methanol	ethanol	1-propanol	2-propanol	1-butanol	2-butanol	2-methyl-1-propanol
283.15	0.01621	0.02265	0.02715	0.01689	0.03369	0.03813	0.01854
288.15	0.02514	0.03609	0.04295	0.02733	0.05111	0.06020	0.02877
293.15	0.04590	0.06470	0.07557	0.04870	0.09082	0.1048	0.05165
298.15	0.09459	0.1272[a]	0.1520	0.1009	0.1817	0.2011	0.1115
303.15	0.2740	0.2893	0.3298	0.2751	0.3404	0.3976	0.2787
308.15	0.6939	0.7150	0.7180	0.7019	0.7495	0.7520	0.7086

[a] 0.104 from literature.[7]

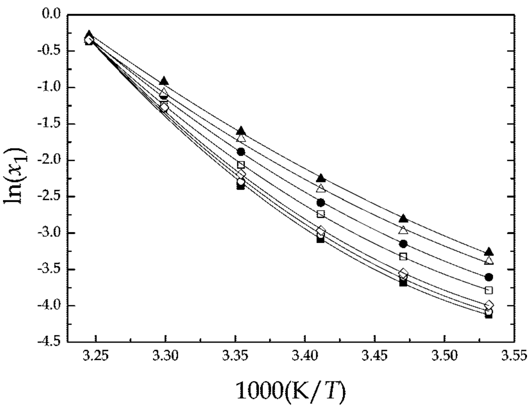

Figure 2. van't Hoff plot of salol in alcohol solvents from (283.15 to 308.15) K: ■, methanol; □, ethanol; ●, 1-propanol; ○, 2-propanol; △, 1-butanol; ▲, 2-butanol; ◇, 2-methyl-1-propanol. The line is the best fit of the experimental data calculated with the second-degree polynomials eq 1.

Table 2. Regression Curve Coefficients in Equation 1 for Salol Solubility in Seven Alcohol Solvents between (283.15 and 308.15) K

solvent	a	$10^{-5}b$	$10^{-7}c$	rmsd	R^2
methanol	356.66	−1.9893	2.7400	0.0122	0.9981
ethanol	275.29	−1.5194	2.0648	0.0013	0.9999
1-propanol	229.14	−1.2508	1.6756	0.0081	0.9996
2-propanol	350.49	−1.9563	2.6970	0.0092	0.9987
1-butanol	184.17	−0.9922	1.3055	0.0136	0.9987
2-butanol	159.45	−0.8474	1.0945	0.0104	0.9990
2-methyl-1-propanol	322.10	−1.7888	2.4505	0.0063	0.9996

can see that the solubilities of salol in alcohol solvents increase as the temperature increases.

A second-degree polynomial as follows was proposed to correlate the experimental data

$$\ln x_1 = a + {}^{b}\!/_{T} + {}^{c}\!/_{T^2} \qquad (1)$$

where x_1 and T are the mole fraction of the solute and the absolute temperature, respectively, and a, b, and c are regression curve coefficients. The coefficient values of a, b, and c are given in Table 2 with the root-mean-square deviation of solubility (rmsd). The rmsd is defined as the following

$$\text{rmsd} = \left[\frac{1}{N}\sum_{j}^{N}\left(x_{1,j} - x_{1,j}^{\text{calcd}}\right)^2\right]^{1/2} \qquad (2)$$

where N is the number of experimental points, $x_{1,j}^{\text{calcd}}$ is the solubility calculated from eq 1, and $x_{1,j}$ is the experimental value of solubility.

Figure 2 depicts the solubility of salol as obtained in a van't Hoff plot. The curves displayed in Figure 2 are nonlinear and well correlated with the second-degree polynomials for their respective solvents. Fits of R^2 between 0.9981 and 0.9999 were obtained in all solvents.

Conclusions

The solubilities of salol in methanol, ethanol, 1-propanol, 2-propanol, 1-butanol, 2-butanol, and 2-methyl-1-propanol were measured in the temperature range from (283.15 to 308.15) K by a static analytical method. The molar solubility decreases in the order 2-butanol > 1-butanol > 1-propanol > ethanol > 2-methanol-1-propanol > 2-propanol > methanol. A second-degree polynomial was employed in correlating the experimental data with good agreement. The experimental solubility and correlation equation in this work can be used as essential models in the manufacturing and purifying processes of salol in industry.

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