SOLUBILITY OF CAFFEINE IN WATER, ETHYL ACETATE, ETHANOL, CARBON TETRACHLORIDE, METHANOL, CHLOROFORM, DICHLOROMETHANE, AND ACETONE BETWEEN 298 AND 323 K

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***Abstract*— The solubility of caffeine in water, ethyl acetate, ethanol, carbon tetrachloride, methanol, chloroform, dichloromethane and acetone were measured by a gravimetrical method from (298 to 323) K and the solubility data was correlated against temperature. The solubility of caffeine in chloroform and dichloromethane was high compared with other solvents**

***Keywords*— Caffeine; Solubility; Solvents; Correlation.**

I. INTRODUCTION

Caffeine is an alkaloid, or nitrogen-containing substance, with the chemical formula $C_8H_{10}N_4O_2$. It belongs to the group of chemicals known as methylxanthines, which also includes the closely related chemicals theophylline and theobromine. In its pure form, caffeine occurs as odorless, white, fleecy masses, glistening needles or powder. As with all methylxanthines, caffeine has low solubility and is therefore often combined with a wide variety of compounds to form complexes, such as the double salt sodium benzoate, for purposes of enhanced solubility in consumer goods like soft drinks. Early investigators (Gürü and İçen, 2004) indicate that caffeine is a central nervous system (CNS) stimulant, having the effect of temporarily warding off drowsiness, restoring alertness and muscle relaxant properties. Beverages containing caffeine, such as coffee, tea, soft drinks and energy drinks enjoy great popularity. Caffeine is the world's most widely consumed psychoactive substance. It is found in the leaves and beans of the coffee plant, in tea, yerba mate, and guarana berries, and in small quantities in cocoa, the kola nut and the Yaupon Holly. Overall, caffeine is found in the beans, leaves, and fruit of over 60 plants, where it acts as a natural pesticide that paralyzes and kills certain insects feeding upon them. Generally, caffeine is extracted from plants such as cacao, tea and coffee. The method is based on extraction from the filtrates of water-plant systems by means of solvents. Caffeine extraction is an important industrial process and can be performed using a number of different solvents. Recent results (El-Din and Abu-Raiia, 1995; Treybal, 1968) showed that the extraction processes depend upon the plants and solvents selected. So it is necessary to know the solubility data of caffeine in water and organic solvents (such as ethyl acetate, ethanol, carbon tetrachloride, methanol, chloroform, dichloromethane and acetone etc). In this study, the solubilities of caffeine in water, ethyl acetate, ethanol, carbon tetrachloride, methanol, chloroform, dichloromethane and acetone have been measured from (298 to 323) K at atmospheric pressure by a gravimetrical method and the solubility data was correlated against temperature. The experimental solubility of caffeine in water, ethanol and ethyl acetate was compared with literature data which were reported earlier (Bustamante *et al.*, 2002).

II. METHODS

Caffeine with mass fraction purity of > 98.5 % (Merck, Darmstadt, Germany) was used as obtained. The organic solvents, ethyl acetate, ethanol, carbon tetrachloride, methanol, chloroform, dichloromethane and acetone were of analytical purity grade and were purchased from Merck (Darmstadt, Germany) and re-distilled deionized water was used. All the chemicals were used without further purification.

The solubilities of caffeine in water, ethyl acetate, ethanol, carbon tetrachloride, methanol, chloroform, dichloromethane and acetone were measured by the gravimetric method which reported by early investigator (Zhu, 2001). For each measurement, an excess of known mass of caffeine was added to a known mass of solvent. Then, the equilibrium cell was heated to the required temperature with continuous stirring. To ensure equilibrium, undissolved solid and solution were allowed to settle for 48 h before sampling. For each measurement, an excess amount of caffeine was added to a known mass of solvent. Then, the equilibrium cell was heated to the required temperature with continuous stirring. After 48 h, the stirring was stopped and the solution was kept still for 48 h. Then, the excess solid could be observed in the lower part of the equilibrium cell. The sample of the upper part of the solution was withdrawn with a suitable warmed pipette to another weighed vial. The vial was closed tightly and weighed to determine the mass of the sample. Then, the vial was placed in an oven to evaporate the solvent. After the evaporation of the solvent, the vial was dried for another 5 h and reweighed to determine the mass of the solid. Thus, the solid concentration of the sample could be determined. All the solubility experiments were conducted six times to check the reproducibility.

III. CONCLUSIONS

The mole fraction solubility x of caffeine in water, ethyl acetate, ethanol, carbon tetrachloride, methanol, chloroform, dichloromethane and acetone were measured from (298 to 323) K and are summarized in Table 1.

As shown in Fig. 1 the mole fraction solubility x of caffeine was correlated as a function of temperature as follows

$$\mathrm{Ln}x = A + B\,(T/\mathrm{K}) \quad (1)$$

The parameters A and B for the solvents and root mean square deviations are listed in Table 2. The root mean square deviations (σ) is defined as:

$$\sigma = \left[\frac{\sum_{i=1}^{n} (x_{ci} - x_i)^2}{n-1} \right]^{\frac{1}{2}} \quad (2)$$

where, x_{ci} and x_i are calculated and experimental mole fraction solubility, respectively, and n is the number of experimental points. The root mean square deviations of calculated solubility in respect of experimental solubility are reported in Table 2.

Within the temperature range of the measurements, solubility of caffeine in the solvents increased with an increase in temperature. The experimental solubility of caffeine in water, ethanol and ethyl acetate was compared with the literature data shown in Fig. 2. As can be seen, there is a satisfactory agreement between our solubilities of caffeine in water, ethanol and ethyl acetate with those reported in the literature.

Table 1. Mole Fraction Solubility of caffeine in Eight Solvents Between (293 to 323) K

T/K	10^3x	T/K	10^3x
Water			
298	2.098±0.003	313	4.367±0.065
303	2.621±0.021	318	7.916±0.009
308	3.075±0.004	323	10.151±0.034
Methanol			
298	2.004±0.008	313	4.194±0.009
303	2.683±0.005	318	5.111±0.007
308	3.409±0.009	323	5.859±0.01
Ethanol			
298	1.713±0.008	313	2.645±0.007
303	2.046±0.003	318	4.656±0.007
308	2.188±0.003	323	5.512±0.006
Carbon Tetrachloride			
298	1.564±0.002	313	3.059±0.002
303	2.094±0.004	318	3.569±0.005
308	2.602±0.003	323	4.074±0.003
Acetone			
298	4.535±0.009	313	8.468±0.023
303	5.759±0.008	318	9.946±0.01
308	6.977±0.011	323	12.322±0.012
Chloroform			
298	66.895±0.007	313	83.434±0.007
303	72.685±0.006	318	88.716±0.011
308	78.356±0.011	323	94.032±0.009
Dichloromethane			
298	36.961±0.009	313	47.379±0.003
303	40.602±0.008	318	50.548±0.007
308	44.146±0.002		
Ethyl Acetate			
298	4.046±0.002	313	5.522±0.027
303	4.459±0.006	318	7.866±0.017
308	4.836±0.024	323	9.946±0.002

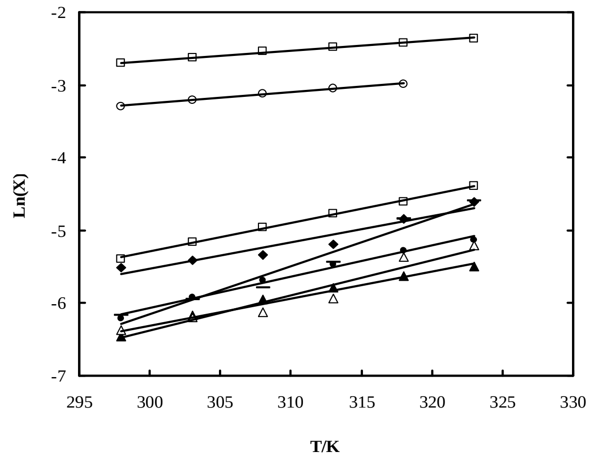

Fig. 1. Solubility x of caffeine as a function of temperature in:-, water; •, methanol; Δ, ethanol; ▲, Carbon Tetrachloride; □, Chloroform; ■, acetone; ♦, ethyl acetate; o, Dichloromethane, Solid lines are values from Eq. 1 with coefficients from Table 2.

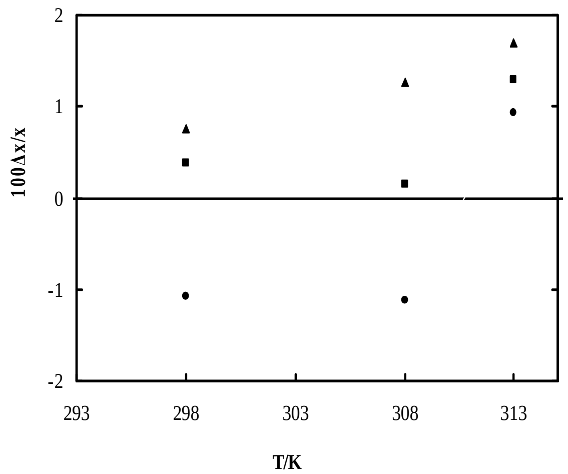

Fig. 2. Fractional deviations $\Delta x = x - x$ (lit) of caffeine solubility at various temperatures in ethyl acetate, ethanol, water obtained in this work, x, from literature values, x (lit). ♦, ethyl acetate. Δ, ethanol. ×, water.

Table 2. A and B Values and the Root-Mean-Square Deviations (σ) of the Measured Solubility from the Calculated Results

Solvent	A	B	$10^3\sigma$
Water	-25.952	0.066	0.604
Methanol	-18.932	0.0429	0.204
Ethanol	-20.947	0.0486	0.411
Carbon Tetrachloride	-17.533	0.0374	0.140
Acetone	-17.003	0.039	0.161
Chloroform	-6.717	0.0135	0.714
Dichloromethane	-7.9389	0.0156	0.439
Ethyl Acetate	-16.321	0.036	0.592

The solubility of caffeine decreases in the order of chloroform, dichloromethane, acetone, ethyl acetate, water, methanol, ethanol, and carbon tetrachloride. The solubility of caffeine in chloroform showed a higher value than those in the other solvents. Thus, chloroform is a better solvent to separate and purify caffeine from solutions.

The solubilities of caffeine as a function of temperature in water and ethanol in this work were compared with the caffeine+H2O+EtOH and ethanol–ethyl acetate system from literature. It showed that the addition of ethanol as co-solvent decreases the solubility of caffeine in the water. But the addition of ethyl acetate as co-solvent increases the solubility of caffeine in the ethanol.

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