Asian Journal of Chemistry; Vol. 27, No. 7 (2015), 2536-2538

ASIAN JOURNAL OF CHEMISTRY

http://dx.doi.org/10.14233/ajchem.2015.17997

Kinetic and Thermodynamic Properties of Biochanin A in Dimethyl Sulfoxide

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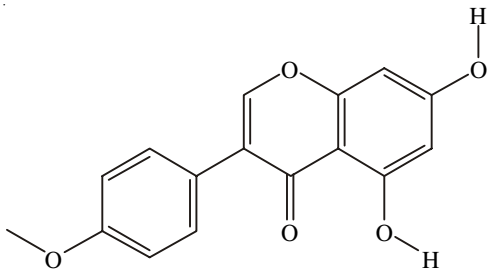
Received: 13 May 2014; *Accepted*: 21 July 2014; *Published online*: 30 March 2015; AJC-17074

In this paper, we measured the dissolution enthalpies of biochanin A in DMSO using a RD496-2000 Calvet microcalorimeter at 298.15 K under atmospheric pressure and the results show that the dissolution process possessed an endothermic behaviour. A series of thermodynamics functions and half-life period were obtained from thermodynamic and kinetic calculations. This work not only provides a simple method to determine the half-life period of a drug but also offers a theoretical guide for the clinical application of biochanin A.

Keywords: Biochanin A, Microcalorimetry, Kinetics, Thermodynamics.

INTRODUCTION

Biochanin A are flavonoids, most commonly found in legumes, especially in soyabeans or in red clover. The research for biochanin A always focus on antitumor, antioxidation[1-4], anti HIV[5] and involved in the immune regulation[6]. The molecular structure is shown as follows:



Owing to the unique property of biochanin A, much attention are drawn from the medical community. Thus it is necessary to study the solution performance and the kinetic and thermodynamic properties of biochanin A.

EXPERIMENTAL

Biochanin A was purchased from Baoji Fangsheng Biological Development Co., Ltd. (purity: > 99 %). DMSO was analytical grade.

Equipment and conditions: The experiment was performed using a RD496-2000 Calvet microcalorimeter (Mianyang CAEP Thermal Analysis Instrument Company, China). The microcalorimeter was calibrated by the Joule effect and its sensitivity was (64.28 ± 0.04) μV mW^{-1} at 298.15 K. The enthalpy of dissolution of KCl (spectrum purity) in distilled water (*ca.* 20 mg/2.000 g) measured at 298.15 K was 17.535 kJ mol^{-1}, which was in excellent accordance with the literature value of 17.545 kJ mol^{-1} [7], showing that the device for measuring the enthalpy used in this work was reliable.

Experimental methods: The proper amount of biochanin A (4.39, 14.60, 20.86, 25.10 and 29.96 mg) was dissolved in 1.50 mL of DMSO at 298.15 K under atmospheric pressure. The value of enthalpy changing of the process was detected by the RD496-2000 calvet microcalorimeter.

RESULTS AND DISCUSSION

Thermochemical behaviour of biochanin A dissolution in DMSO: It was found that the dissolution process of biochanin A in DMSO is an endothermic process. The thermodynamic parameters were calculated through the RD496-2000 micro-calorimeter measurements.

Dissolution curve: A certain amount of biochanin A was dissolved in DMSO at 298.15 K. Five concentration gradients were carried out in this experiment. The curve describing the entire dissolution process of biochanin A in DMSO is shown in Fig. 1.

Molar enthalpy: Table-1 shows the experimental data obtained from the typical thermogram curve of the dissolution process with different amount of biochanin A in 1.50 mL DMSO.

It is observed that the solvent concentration has little influence on the molar enthalpy ($\Delta_{sol}H_m$) at 298.15 K and the average value of $\Delta_{sol}H_m$ represents the molar enthalpy of infinite diluted in DMSO at 298.15 K[8]. Fig. 2 display the heat effect versus the amount of biochanin A in DMSO, where the linear relationship can be clearly seen.

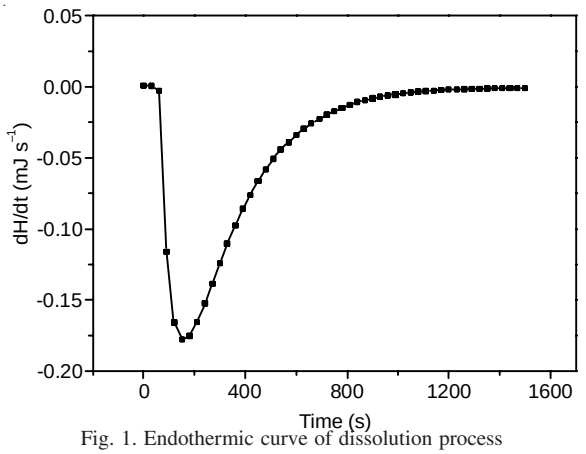


Fig. 1. Endothermic curve of dissolution process

TABLE-1
DISSOLUTION ENTHALPHY OF BIOCHANIN A IN 1.50 mL DMSO

m (mg)	10^6n (mol)	Q (mJ)	$\Delta_{sol}H_m$ (kJ mol)
4.39	15.44	-172.92	-11.20
14.60	51.36	-503.06	-9.79
20.86	73.38	-761.80	-10.38
25.10	88.30	-909.87	-10.30
29.96	105.39	-1017.20	-9.65
Average	–	–	-10.27

Note: n is the amount of biochanin A, Q is the heat effect of the process and $\Delta_{sol}H_m$ is the molar enthalpy.

Based on the linear equations, we have calculated that the molar enthalpy for the process is -9.7 kJ mol^{-1}, which is consistent with the measured values.

Kinetics of dissolution process: The kinetic equation[9] describing the dissolution of biochanin A in DMSO is

$$\frac{d\alpha}{dt} = kf(\alpha) \quad (1)$$

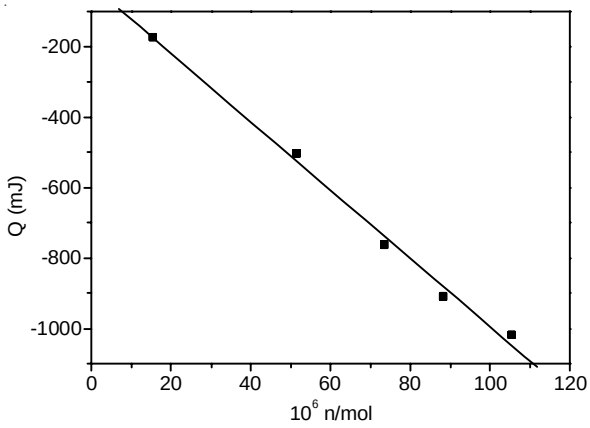


Fig. 2. Linear relationship between the heat effect (Q) and the amount of biochanin A (n) in dissolution process

And the selected model function describing the process is,

$$f(\alpha) = (1-\alpha)^n \quad (2)$$

Combining eqns. 1 and 2 and substituting $\alpha = \frac{H_t}{H_o}$ into the equation lead to a logarithmic converter:

$$\ln\left[\frac{1}{H_o}\left(\frac{dH}{dt}\right)_j\right] = \ln k + n\ln\left[1-\left(\frac{H_t}{H_o}\right)t\right], \; i = 1, 2, ..., L \quad (3)$$

In these equations, α is the conversion degree; $f(\alpha)$ is the kinetic function; H_t represents the heat at time t; H_0 is the heat of the whole process; k is the rate at which biochanin A is dissolved in DMSO; n is the reaction order and L is the counting index. By substituting the original data from Table-2, $(dH/dt)_i(H_t/H_0)_i$, H_0, i = 1, 2, …, L, into the kinetic eqn. 3, we obtained the values of n and ln k as listed in Table-3. Substituting the values of n and k into eqn. 1, we obtained that the

TABLE-2
ORIGINAL DATA OF DISSOLUTION PROCESS AT 298.15 K

m (mg)	t (s)	dH/dt (mJ s^{-1})	H_t (mJ)	H_t/H_0	H_∞ (mJ)	m (mg)	t (s)	dH/dt (mJ s^{-1})	H_t (mJ)	H_t/H_0	H_∞ (mJ)
4.39	0	-0.0224	-23.83	0.138	-172.92	20.86	200	-0.0603	-537.53	0.706	-762.00
	40	-0.0215	-38.05	0.220			240	-0.0489	-581.37	0.763	
	80	-0.0195	-51.29	0.297			280	-0.0395	-616.84	0.810	
	120	-0.0178	-63.27	0.366			320	-0.0318	-645.42	0.847	
	160	-0.0158	-74.07	0.428			360	-0.0257	-668.47	0.877	
	200	-0.0140	-83.67	0.484		25.10	0	-0.1563	-134.20	0.147	-909.87
	240	-0.0122	-92.10	0.533			40	-0.1513	-259.43	0.285	
	280	-0.0108	-99.51	0.575			80	-0.1332	-374.20	0.411	
	320	-0.0095	-106.01	0.613			120	-0.1126	-473.00	0.520	
	360	-0.0085	-111.83	0.647			160	-0.0922	-555.31	0.610	
14.60	0	-0.0834	-45.59	0.091	-502.90		200	-0.0753	-622.45	0.684	
	40	-0.091	-88.06	0.175			240	-0.0605	-676.85	0.744	
	80	-0.0899	-131.86	0.262			280	-0.0488	-720.77	0.792	
	120	-0.0849	-174.12	0.346			320	-0.0394	-756.17	0.831	
	160	-0.0783	-213.54	0.425			360	-0.0314	-784.52	0.862	
	200	-0.071	-249.59	0.496		29.96	0	-0.1778	-180.26	0.177	-1017.20
	240	-0.0638	-282.12	0.561			40	-0.1752	-265.69	0.261	
	280	-0.0568	-311.20	0.619			80	-0.1656	-348.12	0.342	
	320	-0.0503	-337.05	0.670			120	-0.1524	-424.92	0.418	
	360	-0.0445	-359.92	0.716			160	-0.1383	-495.08	0.487	
20.86	0	-0.1246	-153.46	0.201	-762.00		200	-0.124	-558.04	0.549	
	40	-0.1179	-251.68	0.330			240	-0.1103	-614.94	0.605	
	80	-0.1041	-341.21	0.448			280	-0.0973	-665.02	0.654	
	120	-0.0884	-418.66	0.550			320	-0.0861	-709.20	0.697	
	160	-0.0736	-483.76	0.635			360	-0.0761	-748.33	0.736	

TABLE-3
n AND ln k OF DISSOLUTION PROCESS AT 298.15 K

m (mg)	n	ln k (s^{-1})	R
4.39	1.12	-8.72	0.9902
14.60	0.73	-8.46	0.9933
20.86	0.91	-8.41	0.9969
25.10	1.03	-8.30	0.9937
29.96	0.94	-8.31	0.9972
Average	0.95	-8.48	–

kinetics equation of the dissolution process $\frac{d\alpha}{dt} = 10^{-3.69}(1-\alpha)^{0.95}$ that is similar to a quasi-first-order reaction of the dissolution process. So we derived the half-life period with eqn. 4 and it is 55.65 min.

$$t_{1/2} = \frac{\ln 2}{k} \quad (4)$$

Thermodynamics of biochanin A dissolved in DMSO: Based on these experimental data and calculated results, the kinetic parameters of the dissolution process were obtained through the following equation:

$$\ln\frac{k}{T} = \left(\frac{\Delta S_m^{\theta}}{R} + \ln\frac{k_B}{h}\right) - \frac{\Delta H_m^{\theta}}{RT} \quad (5)$$

Eqn. 5 can be converted into the following expression:

$$\ln\frac{kh}{k_B T} = \frac{\Delta_{sol}S_m}{R} - \frac{\Delta_{sol}H_m}{RT} \quad (6)$$

The relationship of $\Delta_{sol}H_m$ and $\Delta_{sol}S_m$ is generally defined as:

$$\Delta_{sol}G_m = \Delta_{sol}H_m - T\cdot\Delta_{sol}S_m \quad (7)$$

Therefore, we can achieve the thermodynamic parameters of the dissolution process as follows:

$\Delta_{sol}S_m$ = -349.86 J mol^{-1} K^{-1}, $\Delta_{sol}G_m$ = 94.04 kJ mol^{-1}

Conclusion

The molar enthalpy of biochanin A in DMSO was measured with the RD496-2000 type Calvet microcalorimeter at 298.15 K under atmospheric pressure. From the results it can be observed that the concentration of biochanin A has little impact on the enthalpies. Thus, the average value of $\Delta_{sol}H_m$ can represent the molar enthalpy which is -10.27 kJ mol^{-1}. The kinetic equation of dissolution process of biochanin A in DMSO at 298.15 K is $\frac{da}{dt} = 10^{-3.69}(1-a)^{0.95}$. The kinetic data shows that the dissolved order is around 1, which directly improves that the dissolution process is a simple reaction. So it is feasible to calculate the half-life period for the first-order reaction *via* dynamic methods which is $t_{1/2}$ = 55.65 min and the rate constant is $k = 2.08 \times 10^{-4}$ s^{-1}. The dissolution of biochanin A in DMSO is an endothermic process. The molar enthalpy ($\Delta_{sol}H_m$) is -10.27 kJ mol^{-1} and $\Delta_{sol}S_m$ is -349.86 J mol^{-1} K^{-1}. The negative value of the entropy of activation indicates that the dissolution process is a stable system.

ACKNOWLEDGEMENTS

This work was supported by the Phytochemistry Key Laboratory of Shaanxi Province (No. 09JS066) and the Project Foundation of Shaanxi Province (No. 2006k16-G16) in the People's Republic of China.

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