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Solubility and solution thermodynamics of rhein in eight pure solvents from (288.15 to 313.15) K

*Yan Cheng,^a Daijie Wang,^a Zhe Zhang,^b Zhenhua Wang^{*a}*

^aShandong Analysis and Test Center, Shandong Academy of Sciences, 250014 Jinan, China

^bCollege of Chemical Engineering, University of Jinan, 250014 Jinan, China

*Corresponding author: Zhenhua Wang, Shandong Analysis and Test Center, Shandong Academy of Sciences, Keyuan Road, Shandong Province, China; Fax: 86-531-82964889; Tel: 86-531-82605345; E-mail:chengyan99@163.com

ABSTRACT: Data on solid + liquid equilibrium of rhein in solvents can provide essential support for the design of extraction, precipitation, or crystallization processes in the industry. In this study the solubility of rhein in eight different solvents namely water, 1,2-dichloroethane, glycol, ethanol, methanol, ethyl acetate, 1-propanol, and 1-butanol was measured over temperature range from (288.15 to 313.15) K under atmospheric pressure using a UV spectrophotometric method. The experimental result shows that 1-butanol, 1-propanol and ethyl acetate could be suitable solvents for industrial production of rhein. Two commonly used thermodynamic equations, including the modified Apelblat equation, and λh equation were applied to correlate the experimental solubility data. It was found that the two equations can satisfactorily correlate the solubilities of rhein in the eight solvents under different temperatures.

The dissolution enthalpy and entropy were obtained from the experimental values. The dissolution process of rhein in eight solvents within studied temperature range was endothermic, and the driving mechanism is the entropy.

Keywords: rhein; solubility; modified Apelblat equation; λh equation

1. Introduction

Rhein (1,8-dihydroxy-3-carboxy anthraquinone, CAS: 478-43-3) is an important member of the anthraquinone family which derived from the *Rheum palmatum* L, *Polygonum multiflorum* Thunb, *Cassia angustifolia* Vahl, and *Ruta graveolens* L, and they are all excellent herbs.¹ The chemical structure of rhein is shown in Fig. 1. Rhein has many well-established effects on the gastrointestinal tract and it has been proved as a potential antitumor agent as well as an effective substance in treatment of diabetic nephropathy, so rhein is a very useful medicine.^{2,3}

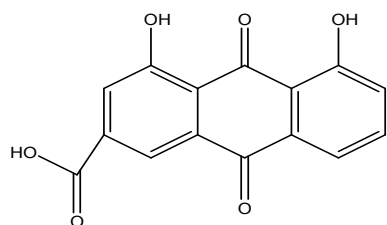


Fig. 1 Chemical structure of rhein.

Based on these peculiar and promising properties of rhein, some researchers have recently proposed an original procedure for the total chemical synthesis instead of the high-cost semi-synthetic route.⁴ Moreover, much attention has been focused on the extraction directly from natural plants,⁵ such as *Rheum palmatum* L. rhizome, and so forth. In order to increase the extraction yield of rhein in plants, many extracting technologies including thin-layer chromatographic-densitometric method,⁶ and subzero-temperature liquid-liquid extraction⁷ have been developed. No matter which process was adopted for the preparation of rhein, the crude

product cannot be utilized in clinic or as a food additive before purification. Crystallization process played a crucial role that determined the quality of the final product. Through finding an optimal solvent we can obtain the high-purity rhein by crystallization. So, the solubility of compounds in solvents is obviously one of the most important factors in the determination of proper solvents and optimization of crystallization processes.⁸⁻¹⁴ Aghanouri and Sun found that Hansen solubility parameters can satisfactorily predict solvent systems that are likely to dissolve significant amount of the plant proteins.¹⁵ Mu and his researchers have detailedly studied the dissolution behavior of chitosan and the dynamic process of radioactive iodine in ionic liquids.^{16,17} Wei and his colleagues have investigated the solubility properties and spectral characterization of sulfur dioxide in ethylene glycol derivatives.¹⁸ Therefore, researches on the solubility of solid compounds were necessary. Petralito and Travagli have found that the solubility of rhein could be enhanced by the host-guest interaction between rhein and cyclodextrins.¹⁹ To the best of our knowledge, the solubility data of rhein in water, 1,2-dichloroethane, glycol, ethanol, methanol, ethyl acetate, 1-propanol, and 1-butanol have not been reported in the literature.

In this work, the solubility of rhein in water, 1,2-dichloroethane, glycol, ethanol, methanol, ethyl acetate, 1-propanol, and 1-butanol was measured in the temperature range 288.15–313.15 K. The experimental solubility data were correlated with the modified Apelblat equation,²⁰⁻²² and λh equation.²³ Comparison and discussion of the solubility and two equations were carried out. In addition, the thermodynamic properties of the system were then calculated based on the experimental data.

2. Experimental section

2.1 Reagents and Apparatus. Rhein ($C_{15}H_8O_6$) was supplied by Shanghai Yuanye Bio-technology Co., Ltd., China, and the purity of the rhein was higher than 0.998. Deionized water was prepared from Elga Purelab water system (Elga, England). All the materials used in this work were of high purity (Table S1†) and the empirical parameters of solvent polarity normalized E_T^N values were adopted from the literature.²⁴ Absorbance analysis was performed by UV-vis spectrophotometer (TU-1810, Beijing Purkinje General Instrument Co., Ltd., Beijing, China).

The X-ray powder diffraction (XRPD) patterns of rhein were collected in air on a PANalytical Empyrean at room temperature using Cu KR radiation of wavelength 0.154 060 nm, a tube voltage of 40 kV, and a tube current of 40 mA. Diffraction data were recorded at 2θ values between 3° and 90° at an interval of 0.026° and a continuous scanning speed of 5 deg/min was employed. The XRPD pattern of the rhein powders is illustrated in Fig. S1† and a characteristic peak at 27.6° is observed.

2.2 Solubility Measurements. The solubility experiments of rhein were carried out using the isothermal shake-flask method. For each measurement, an excess amount of rhein was added to a 35 mL of the eight solvents with their temperatures ranging from 288.15 to 313.15 K at around 5 K increments. The apparatus and procedure for the solubility measurements adopted in this work have already been fully described in our previous work.²¹ During our experiments, each solubility value is an average of at least three parallel measurements at the same solvent for each temperature. The measuring relative uncertainty of the experimental solubility value was within 2 %.

The external calibration curve was obtained in methanol and used for quantification of rhein in different solvents. The rhein solution in 231 nm, 259 nm and 288 nm has UV adsorptions, and the maximum absorption wavelength was at 231 nm. The solubility of rhein in the studied five organic solvents is high, so we choose the 288 nm as the detection wavelength. The mole fraction solubility of rhein could be obtained using eq 1.

$$x_1 = \frac{m_1 / M_1}{m_1 / M_1 + m_2 / M_2} \quad (1)$$

where m_1 and m_2 represent mass of the solute and solvent, respectively. M_1 and M_2 represent the molecular weight of solute and solvent.

3. Results and discussion

3.1 Solubility data. The solubility data of rhein in water, 1,2-dichloroethane, glycol, ethanol, methanol, ethyl acetate, 1-propanol, and 1-butanol at different temperatures are listed in Table 1. The relative deviation (RD), and the relative average deviation (RAD) are given in Table 1. The RD is defined by eq 2.

$$RD = \frac{|x_i^{\text{cal}} - x_i^{\text{exp}}|}{x_i^{\text{exp}}} \quad (2)$$

The RAD is defined as

$$RAD = \frac{\sum_{i=1}^n \frac{|x_i^{\text{cal}} - x_i^{\text{exp}}|}{x_i^{\text{exp}}}}{n} \times 100\% \quad (3)$$

where n is the number of measured points, x_i^{cal} stands for the calculated solubility, and x_i^{exp} stands for experimental solubility values.

As shown in Table 1, the experimental solubility of rhein increased with the temperature increase. The solubility of rhein in different solvents was in the following order: 1-butanol,

1-propanol and ethyl acetate > ethanol, methanol > ethanol > glycol > 1,2-dichloroethane > water. The solubility in 1-butanol, 1-propanol and ethyl acetate was higher than the one in the

Table 1 Solubilities (x_1) of rhein in water, 1,2-dichloroethane, glycol, ethanol, methanol, 1-propanol, ethyl acetate, and 1-butanol from (288.15 to 313.15) k at pressure $p = 0.1$ MPa.

T/K	$10^4 x_1^{exp}$	100RD		$10^4 x_1^{exp}$	100RD		$10^4 x_1^{exp}$	100RD	
		Eq.(2)	Eq.(3)		Eq.(2)	Eq.(3)		Eq.(2)	Eq.(3)
	water			1,2-dichloroethane			glycol		
288.15	0.0013	7.69	7.69	0.0461	4.47	5.86	0.0743	0.13	1.34
293.15	0.0019	5.26	5.26	0.0528	1.41	1.52	0.0875	1.60	1.26
298.15	0.0024	0	0	0.0595	3.24	3.86	0.1022	3.52	3.62
303.15	0.0031	3.22	3.22	0.0697	3.83	4.59	0.1287	2.72	2.41
308.15	0.0039	2.56	0	0.0864	1.47	1.16	0.1510	2.38	2.32
313.15	0.0048	2.08	0	0.1007	0.71	1.29	0.1689	2.25	1.66
	100RAD	3.47	2.69	100RAD	2.52	3.05	100RAD	2.10	2.10
	ethanol			methanol			ethyl acetate		
288.15	0.0768	5.08	2.21	0.1095	1.55	3.29	0.1489	3.09	1.01
293.15	0.0942	3.07	2.66	0.1298	2.08	2.23	0.1725	1.68	1.51
298.15	0.1205	3.15	2.32	0.1454	2.68	3.51	0.2058	2.72	1.85
303.15	0.1452	3.65	2.41	0.1708	2.40	3.39	0.2343	2.60	1.54
308.15	0.1676	0.06	0.66	0.2085	2.06	1.58	0.2584	0.58	1.08
313.15	0.1973	1.52	0.66	0.2376	0.13	0.67	0.2925	1.02	0.2
	100RAD	2.76	1.82	100RAD	1.82	2.44	100RAD	1.95	1.20
	1-propanol			1- butanol					
288.15	0.1070	0.37	4.95	0.1433	1.88	2.86			
293.15	0.1299	5.00	3.77	0.1746	5.04	4.58			
298.15	0.1791	3.29	2.23	0.2304	0.69	1.48			
303.15	0.2134	2.30	4.26	0.2939	3.54	0.58			
308.15	0.2829	3.39	2.26	0.3541	1.41	0.54			
313.15	0.3351	1.43	0.24	0.4201	1.71	0.69			
	100RAD	2.63	2.95	100RAD	2.38	1.79			

(1) x_1 is the mole fraction of the solubility of rhein at the experimental temperature T.

(2) RD is the relative deviation, and RAD is the relative absolute deviation.

(3) The experimental pressure is 0.1 MPa.

(4) Standard uncertainties u are $u(T) = 0.10$ K, $u_r(p) = 0.05$, $u_r(x) = 0.02$.

other five solvents at studied temperature. It can be seen that the solubility values of rhein increase obviously with the decrease of the solvatochromic parameters except for

1,2-dichloroethane and ethyl acetate. The solvatochromic parameter E_T^N of ethyl acetate is 0.228, however, the solubility values of rhein in ethyl acetate is lower than those in 1-propanol and 1-butanol. 1,2-dichloroethane has high hydrophobicity and water has high hydrophilicity, so the properties of solvent remarkably influences rhein solubility. All in all, aliphatic monoalcohols and ethyl acetate solvents can dissolve more rhein than in pure water or pure 1,2-dichloroethane. Maybe the formation of hydrogen bonds between the proton H on the –OH or –COOH groups of rhein and the oxygen atom of hydroxyl groups of the aliphatic monoalcohols can promote the solubility of rhein.¹⁶ Wu and Zhang have found that the solubility of genistein increased with increasing polarity of the solvents to some extent.²²

3.2 Data correlation

Table 2 Parameters of the modified Apelblat equation for the solubility of rhein in water, 1,2-dichloroethane, glycol, ethanol, methanol, 1-propanol, ethyl acetate, and 1-butanol from (288.15 to 313.15) K.

solvent	A	B	C	R ²
water	-49.750	-1779.9	8.7194	0.994
1,2-dichloroethane	-71.441	-547.78	12.353	0.995
glycol	-86.9689	723.93	14.440	0.996
ethanol	-100.81	1632.4	16.355	0.988
methanol	-0.57907	-2885.4	1.4578	0.994
ethyl acetate	-85.601	867.34	14.216	0.999
1-propanol	-1.6997	-3559.6	2.0860	0.991
1-butanol	-4.5460	-3155.7	2.3967	0.992

(1) A, B and C are parameters of the modified Apelblat equation.

(2) R² is the coefficient of determination.

3.2.1 Modified Apelblat Equation. The modified Apelblat equation²⁵ deduced from the Clausius-Clapeyron equation is a frequently used empirical model, which correlates the mole fraction solubility and the absolute temperature T:

$$\ln(x_1) = A + \frac{B}{T/K} + C \ln(T/K) \quad (4)$$

where x_1 is the molar fraction solubility of rhein, T is the absolute temperature, and A , B , and C are the equation parameters. The correlated values of A , B , and C together with determination coefficient R^2 are listed in Table 2.

3.2.2 λh Equation. The λh equation originally proposed by Buchowski et al. is another semi-empirical model to correlate most solid-liquid equilibrium with just two adjustable parameters.²⁶ The λh equation is described as follows:

$$\ln \left[1 + \frac{\lambda(1-x_1)}{x_1} \right] = \lambda h \left(\frac{1}{T/\text{K}} - \frac{1}{T_m/\text{K}} \right) \quad (5)$$

where x_1 presents the molar fraction solubility of rhein at the system temperature T , and T_m is the normal melting temperature of rhein of $T = 604.15$ K;²⁷ λ and h are two adjustable parameters determined from the solubility data. The correlated values of λ and h together with determination coefficient R^2 are listed in Table 3. The parameter λ is regarded as the mean association number of solute molecules which reflects the nonideality of the solution system, while h represents the enthalpy of solution. The values of λ and h are different in eight pure solvents and the large difference of values of λ and h present in water probably display the variation of dissolution enthalpy. Fig. 2 and 3 showed the measured solubility of rhein in the investigated temperature range together with calculated values for eq 4 and eq 5, respectively.

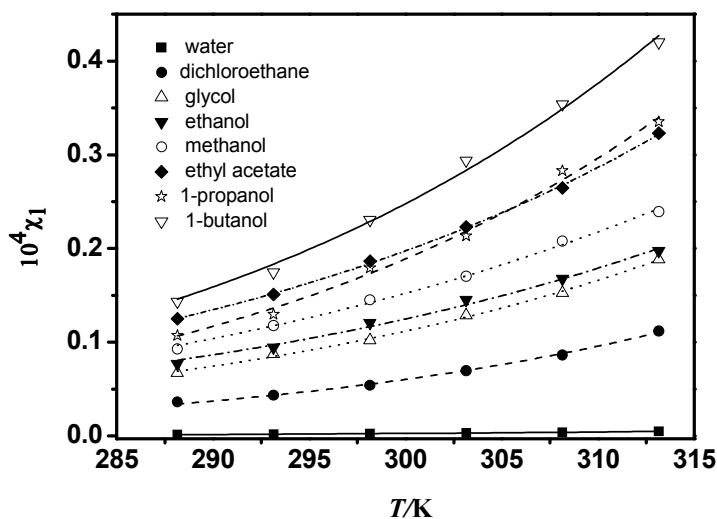


Fig. 2 Solubility of rhein (x_1) in eight solvents from (288.15 to 313.15) k: ■ water; ● 1,2-dichloroethane; △ glycol; ▼ ethanol; ○ methanol; ◆ ethyl acetate; ☆ 1-propanol; and ▽ 1-butanol. The corresponding lines were from the calculated based on eq 4.

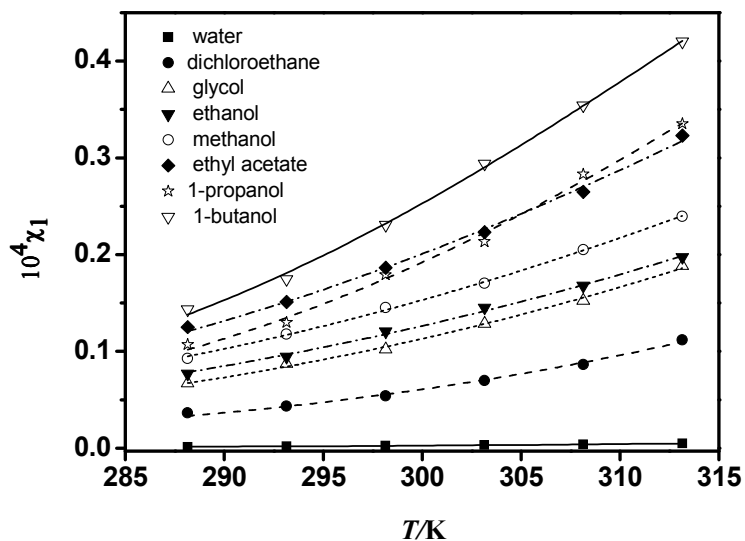


Fig. 3 Solubility of rhein (x_1) in eight solvents from (288.15 to 313.15) k: ■ water; ● 1,2-dichloroethane; △ glycol; ▼ ethanol; ○ methanol; ◆ ethyl acetate; ☆ 1-propanol; and ▽ 1-butanol. The corresponding lines were from the calculated based on eq 5.

Table 3 Parameters of the λh equation for the solubility of rhein in water, 1,2-dichloroethane, glycol, ethanol, methanol, 1-propanol, ethyl acetate, and 1-butanol from (288.15 to 313.15) k .

solvent	λ	h	R ²
water	4.4466	996.62	0.996
1,2-dichloroethane	148.96	30.974	0.993
glycol	138.81	30.023	0.996
ethanol	91.603	41.981	0.996
methanol	144.07	27.639	0.999
ethyl acetate	401.99	10.938	0.996
1-propanol	2055.4	2.6287	0.994
1-butanol	3227.0	1.6920	0.998

(1) λ and h are parameters of the λh equation.

(2) R² is the coefficient of determination.

By comparing the values of RD of eq 2 and eq 3 in Table 1, both of them have good fit for the rhein solubility data. The λh equation model is suitable for the strong polarity solvent and was widely accepted previously to fit the solid-liquid equilibria data. Therefore, the regression result of λh equation model was more accurate in water and ethanol solvents. As for the 1,2-dichloroethane system, the modified Apelblat equation indicates a better correlation for the rhein experimental solubility values. These discrepancies could be found from the comparison of the RD values shown in Table 1.

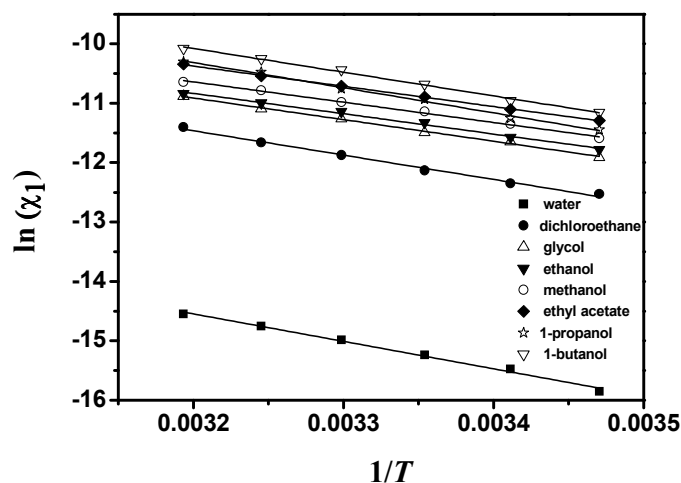


Fig. 4 Van't Hoff plots of $\ln x_1$ versus $1/T$ in different solvents: ■ water; ● 1,2-dichloroethane; △ glycol; ▼ ethanol; ○ methanol; ◆ ethyl acetate; ☆ 1-propanol; and ▽ 1-butanol. The corresponding lines were from the calculated based on eq 6.

Table 4. The slope and intercept of linear fitting of $\ln x_1$ versus $1/T$ in different solvents

solvent	Slope	Intercept	R ²
water	-4620.9	0.2376	0.9921
1,2-dichloroethane	-4105.2	1.6751	0.9932
glycol	-3637.1	0.7275	0.9964
ethanol	-3426.0	0.1304	0.9935
methanol	-3418.2	0.2985	0.9956
ethyl acetate	-3408.3	0.5338	0.9992
1-propanol	-4239.5	3.2529	0.9933
1-butanol	-3996.7	2.7131	0.9948

3.2.3 Dissolution Properties in Pure Solvents. The van't Hoff equation²⁸ for real solutions describes the relationship between the molar fraction solubility of a solute and the absolute temperature by taking the solvent effect into account, which is given as

$$\ln x_1 = -\frac{\Delta H_d}{RT} + \frac{\Delta S_d}{R} \quad (6)$$

where x_1 is the mole fraction solubility of the solute; T represents absolute temperature; and R stands for gas constant; ΔH_d represents the molar enthalpy of dissolution; ΔS_d stands for the molar entropy of dissolution.

The van't Hoff plots present in Fig. 4 can be made from the linear fit of $\ln x_1$ against $1/T$. From the slopes and the intercepts of the curves shown in Table 4, the dissolution enthalpy and entropy of rhein in eight solvents can be obtained. The molar Gibbs energy of dissolution can be calculated by the Gibbs-Helmholtz equation:

$$\Delta G_d = \Delta H_d - T\Delta S_d \quad (7)$$

Table 5. Dissolution enthalpy, entropy and molar Gibbs free energy of rhein at temperature T and pressure $p = 0.1$ MPa.

solvent	ΔH_d kJ·mol ⁻¹	ΔS_d J·mol ⁻¹ ·K ⁻¹	ΔG_d kJ·mol ⁻¹
water	38.42	1.98	37.83
1,2-dichloroethane	34.13	13.93	29.98
glycol	30.24	6.05	28.44
ethanol	28.48	1.08	28.16
methanol	28.42	2.48	27.68
ethyl acetate	28.34	4.44	27.01
1-propanol	35.25	27.04	27.18
1-butanol	33.23	22.56	26.50

(1) ΔH_d stands for the dissolution enthalpy, ΔS_d represents the dissolution entropy, and ΔG_d stands for the Gibbs energy.

(2) ΔG_d was calculated at 298.15 K.

(3) Standard uncertainties u are $u(T) = 0.10$ K, $u_r(p) = 0.05$, $u_r(x_2) = 0.01$.

The obtained dissolution entropy, enthalpy, and the Gibbs energy calculated at 298.15 K of rhein in eight pure solvents are shown in Table 5. The results show that the values of ΔH_d , ΔS_d , and ΔG_d of rhein are positive in different solvents, which imply the dissolution is an endothermic, entropy-driven, and not spontaneous process. Moreover, it can also be found that the values of ΔH_d , ΔS_d , and ΔG_d decreased with decreasing polarity of the Gibbs energy.

4. Conclusions

In this study, the solubility data of rhein in water, 1,2-dichloroethane, glycol, ethanol, methanol, ethyl acetate, 1-propanol, and 1-butanol were experimentally measured from 288.15 K to 313.15 K. The solubility increases with increasing temperature and increased in the order 1-butanol, 1-propanol and ethyl acetate > ethanol, methanol > ethanol > glycol > > water. The experiment solubility data in pure solvents were correlated with the modified Apelblat equation, and λh equation. It was found that the modified Apelblat equation could give better correlation results in ethyl acetate system and λh equation model was more accurate in water and ethanol

solvents. Finally, the dissolution enthalpy, entropy, and molar Gibbs free energy of rhein in the eight pure solvents were obtained by using van't Hoff equation and the experimental solubility data. The results indicated the dissolution process of rhein was endothermic and entropy-driving. The experimental solubility and modeling could be helpful for the purification and application of rhein.

Author information

Corresponding Author

*Tel.: +86-535-82605345. Fax: +86-535-82964889. E-mail address: chengyan99@163.com.

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Notes

The authors declare no competing financial interest.

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