Solubilities of 1,1′-Di(2-carboxyethyl)-2,2′-biimidazole in Water + Acetic Acid from (292.3 to 355.1) K

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The solubilities of 1,1′-di(2-carboxyethyl)-2,2′-biimidazole in water (1) + acetic acid (2) solvent mixtures were determined in the temperature range from (292.3 to 355.1) K and mass fraction w_1 from 0.8 to 1.0. The solubility data were well correlated with an empirical equation.

Introduction

Compounds containing the 2,2′-biimidazole moiety have been the focus of several investigations due to their biological activity as cardiotonics,[1] antiprotozoals, and enzyme active-site models.[2] In addition to its physiological activity, the aromatic biheterocyclic structure has also been incorporated into a variety of polymer[3] and macrocyclic[4] systems in an attempt to imbue polymers with thermal stability, conductivity, and metal-ion binding selectivity.[4−6] 1,1′-Di(2-carboxyethyl)-2,2′-biimidazole (Figure 1), also known as 3,3′-(2,2′-biimidazole-1,1′-diyl) dipropionic acid, is a new and important starting material for the preparation of polymer systems, which is in turn used to make many commercial materials having a variety of utilities because acylation of primary amines or hydrazine with diesters or diacids proceeds with excellent yields.[7]

The title compound ($C_{12}H_{14}N_4O_4$) has been obtained by the reaction of biimidazole and acrylonitrile in *N*,*N*-dimethylformamide at 373.15 K, then via oxidation in water. As a new good starting material for producing polymer systems, it is necessary to pursue its solubility in different solvents optimizing the reaction, especially in aqueous organic solvents. Aqueous acetic acid solvents were chosen because of the proper solubility effect of acetic acid to 1,1′-di(2-carboxyethyl)-2,2′-biimidazole. In this work, the solubilities of 1,1′-di(2-carboxyethyl)-2,2′-biimidazole in water (1) + acetic acid (2) were determined in the temperature range from (292.3 to 355.1) K and mass fraction w_1 from 0.8 to 1.0. The experimental solubility data were correlated with an empirical equation.

Experimental

Chemicals. 1,1′-Di(2-carboxyethyl)-2,2′-biimidazole was prepared and purified by repetitive recrystallization (mass fraction > 0.950). Water and glacial acetic acid were obtained from Hangzhou Chemical Reagent Co. and had a mass fraction purity greater than 0.990.

Apparatus and Procedure. Solubilities were measured by the static analytical method. Enough solute and solvent were placed in a jacketed glass bottle. The temperature was maintained to within ± 0.2 K of the desired temperature with a thermoelectric controlling system. Continuous stirring was carried out for several hours with a magnetic bar. The attainment of solid−liquid equilibrium was verified by repetitive measurements until the results were reproducible to within 0.5 %.[8] The compositions of saturated solutions were determined, when $w_1 = 1.0$, by titration with standard sodium hydroxide solution using phenolphthalein as an indicator, when $w_1 = 0.8$ and 0.9, by UV spectrophotometry. To verify the uncertainties of the measurements, additional experiments under the same situations were done in which the solubilities of benzoic acid in water were determined. The experimental values differed from the literature value by less than 1 %.[9] In this work, the estimated uncertainties in the solubility were less than 0.003 mol·L^{-1}. The measured solubilities (s) of 1,1′-di(2-carboxyethyl)-2,2′-biimidazole in water (1) + acetic acid (2) in the temperature range from (292.3 to 355.1) K and solvent composition range (w_1 from 0.8 to 1.0) are listed in Table 1.

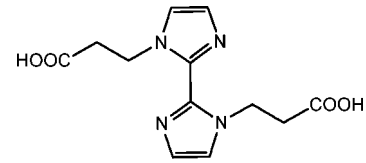

Figure 1. Structure of 1,1′-di(2-carboxyethyl)-2,2′-biimidazole.

Table 1. Solubilities of 1,1′-Di(2-carboxyethyl)-2,2′-biimidazole in Water (1) + Acetic Acid (2) in the Temperature Range from (292.3 to 355.1) K[a]

T/K	s/mol·L^{-1}	s_c/mol·L^{-1}	T/K	s/mol·L^{-1}	s_c/mol·L^{-1}
		$w_1 = 0.8$			
295.2	0.0704	0.0660	333.5	0.1773	0.1841
302.5	0.0868	0.0894	340.7	0.2665	0.2581
310.2	0.0993	0.1012	347.3	0.3418	0.3516
317.3	0.1145	0.1131	355.1	0.5182	0.5195
324.6	0.1381	0.1352			
		$w_1 = 0.9$			
296.2	0.0516	0.0507	333.2	0.1380	0.1436
302.9	0.0596	0.0635	341.4	0.2060	0.1990
310.0	0.0708	0.0737	350.2	0.2700	0.2861
317.7	0.0857	0.0872	354.7	0.3542	0.3473
324.7	0.1085	0.1078			
		$w_1 = 1.0$			
293.3	0.0307	0.0307	330.6	0.0981	0.1030
303.5	0.0396	0.0394	338.0	0.1323	0.1313
310.2	0.0493	0.0496	345.5	0.1568	0.1569
317.5	0.0634	0.0644	353.6	0.1929	0.1925
323.2	0.0835	0.0801			

[a] s: Experimental solubilities. s_c: Calculated solubilities. w_1: Mass fraction of water in water (1) + acetic acid (2).

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Table 2. Curve-Fitting Parameters of 1,1′-Di(2-carboxyethyl)-2,2′-biimidazole in Water (1) + Acetic Acid (2) in the Temperature Range from (292.3 to 355.1) K

	a	b	c	d	σ
	mol·L^{-1}	mol·L^{-1}·K^{-1}	10^{-4}mol·L^{-1}·K^{-2}	10^{-7}mol·L^{-1}·K^{-3}	mol·L^{-1}
$w_1 = 0.8$	−112.4	1.0870	−35.00	37.70	0.0081
$w_1 = 0.9$	−55.82	0.5431	−17.60	19.15	0.0091
$w_1 = 1.0$	8.45	−0.0722	1.978	−1.686	0.0032

Results and Discussion

For potential practical use in industry, the temperature dependence of 1,1′-di(2-carboxyethyl)-2,2′-biimidazole solubility at fixed solvent composition in the temperature range from (292.3 to 355.1) K was correlated with the empirical equation

$$s/\text{mol}\cdot\text{L}^{-1} = a + bT + cT^2 + dT^3 \quad (1)$$

where s is the solubility of 1,1′-di(2-carboxyethyl)-2,2′-biimidazole; T is the absolute temperature; and a, b, c, and d are parameters. The calculated solubility values of 1,1′-di(2-carboxyethyl)-2,2′-biimidazole are also given in Table 1. The values of parameters a, b, c, and d and the root-mean-square deviations (rmsd) are listed in Table 2. The rmsd is defined as

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

where s_c is the solubility calculated by eq 1 and n is the number of experimental points.

The solubilities of 1,1′-di(2-carboxyethyl)-2,2′-biimidazole in water (1) + acetic acid (2) determined in this work and the values calculated with eq 1 are given in Figure 2 for comparison. As can be seen, the solubilities determined in this work obviously increase with increasing acetic acid content possibly by the protonation and increase with increasing temperature. With an increase in temperature, the discrepancies increase, especially beyond $T = 340$ K. In this work, the solubility was determined by the steady-state method; the evaporation of solvent in the vessel had unobvious effects on the solubility determination.

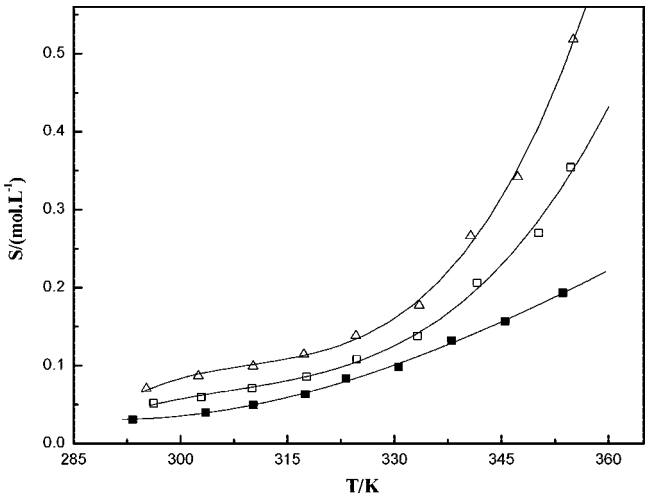

Figure 2. Solubility s of 1,1′-di(2-carboxyethl)-2,2′-biimidazole in water (1) + acetic acid (2) in the temperature range from (292.3 to 355.1) K: △, $w_1 = 0.8$; □, $w_1 = 0.9$; ■, $w_1 = 1.0$, in this work; −, calculated with eq 1.

From the data listed in Tables 1 and 2, the calculated solubilities show good agreement with the experimental values. The experimental solubility and the correlation equation in this work can be used as essential data and models in the new process development of attempting to incorporate them into a variety of polymer and macrocyclic systems.

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