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Note

Thermodynamics of the dissociation of *trans*-cinnamic acid in water-dioxane mixtures at different temperatures

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INTRODUCTION

In continuation of our study on the thermodynamics of electrodes and electrolyte systems in mixed aqueous media[1, 2] (water + dioxane), we now report the dissociation constant of *trans*-cinnamic acid in water +10, +20, +30, and +40 mass% of dioxane over the temperature range 15 to 35 °C using cells of the type

$$\text{Pt, } H_2/\text{HCi}(m_1),\ \text{NaCi}(m_2),\ \text{NaCl}(m_3)/\text{AgCl–Ag} \qquad \text{(A)}$$

where HCi stands for *trans*-cinnamic acid.

Standard thermodynamic quantities, such as ΔG^0, ΔH^0, ΔS^0, and ΔC_p^0, for the transfer of HCi from the aqueous standard state to the standard state in the mixed solvents, have been evaluated.

EXPERIMENTAL

Trans-cinnamic acid, sodium cinnamate and sodium chloride were the same samples used in the previous studies[3, 4]. Dioxane was purified as described earlier[1, 2]. Silver–silver chloride and hydrogen electrodes were prepared according to the methods available in the literature[5, 6]. Purification of hydrogen has been described earlier[7]. The solvent mixtures of various mass percentages were prepared as described in our earlier articles[1, 2]. Stock solutions of acid and sodium salts were prepared by dissolving the appropriate weighed amounts of acid and sodium salts in known weights of water + dioxane mixtures of various compositions. Solutions for e.m.f. measurements were prepared from stock solutions by the method of double dilution. The cell vessels were of an all-glass type of the design recommended by Daniels et al.[8]. The cell measurements were carried out with electrodes set up as described earlier[9]. All measurements were made in water thermostats maintained at appropriate temperatures varying within ±0.1 °C.

RESULTS AND DISCUSSION

A summary of e.m.f. data, e.m.f. values corrected to 1 atm, at different temperatures for various water + dioxane mixtures are shown in Table 1.

TABLE 1

SUMMARY OF E.M.F. DATA OF CELL(A) AT DIFFERENT TEMPERATURES IN VARIOUS WATER + DIOXANE MIXTURES

$10^3 m_1$ (mole kg^{-1})	$10^3 m_2$ (mole kg^{-1})	$10^2 m_3$ (mole kg^{-1})	E^a (V)				
			15°C	20°C	25°C	30°C	35°C
Water + 10 mass % dioxane							
0.451	2.062	1.038	0.6369	0.6409			0.6516
0.451	2.062	1.557	0.6263	0.6306	0.6340	0.6379	0.6409
0.451	2.062	2.076	0.6199	0.6239			0.6334
0.451	2.062	2.595		0.6163	0.6198	0.6235	0.6257
0.451	2.062	3.114	0.6089	0.6141	0.6156	0.6198	0.6231
0.451	2.062	4.152	0.6015	0.6057	0.6091	0.6115	0.6142
0.451	2.062	4.671	0.5972	0.6007	0.6039	0.6074	0.6099
0.451	2.062	5.190	0.5957	0.5986		0.6061	0.6093
0.451	2.062	6.228	0.5909	0.5937	0.5958	0.6002	0.6026
0.451	2.062	6.747			0.5940	0.5980	
0.451	2.062	7.266		0.5920		0.5981	0.6003
0.451	2.062	8.304	0.5838		0.5898		
Water + 20 mass % dioxane							
0.333	2.497	1.123			0.6501	0.6529	0.6556
0.333	2.497	2.246	0.6270	0.6302			
0.333	2.497	2.807	0.6216	0.6239	0.6263	0.6295	
0.333	2.497	3.369			0.6218		0.6270
0.333	2.497	3.957	0.6137	0.6155	0.6179		0.6213
0.333	2.497	4.492					0.6180
0.333	2.497	5.615				0.6111	0.6122
0.333	2.497	6.176	0.6036	0.6047	0.6063	0.6098	0.6105
0.333	2.497	7.299	0.5989				
0.333	2.497	8.422		0.5970	0.5982	0.6009	
Water + 30 mass % dioxane							
0.496	2.913	1.118	0.6595	0.6637	0.6673		0.6733
0.496	2.913	1.677	0.5491	0.6530	0.6561		0.6546
0.496	2.913	2.236	0.6418	0.6460	0.6489	0.6525	
0.496	2.913	2.795	0.6368	0.6404	0.6432	0.6464	0.6498
0.496	2.913	3.354			0.6378	0.6408	0.6443
0.496	2.913	5.031	0.6203	0.6254		0.6317	0.6344
0.496	2.913	5.590		0.6220	0.6256		0.6315
0.496	2.913	6.708	0.6130	0.6172	0.6201	0.6231	0.6259
0.496	2.913	7.826	0.6099	0.6139	0.6169	0.6202	0.6221
0.496	2.913	8.944		0.6098	0.6125	0.6158	0.6186
Water + 40 mass % dioxane							
0.433	2.307	1.328		0.6678			
0.433	2.307	1.992		0.6570	0.6602	0.6629	
0.433	2.307	2.656	0.6463	0.6502	0.6532	0.6549	0.6572
0.433	2.307	3.984	0.6374	0.6405	0.6427	0.6455	0.6478
0.433	2.307	4.648			0.6382	0.6407	0.6432

TABLE 1 *(continued)*

$10^3 m_1$ (mole kg^{-1})	$10^3 m_2$ (mole kg^{-1})	$10^2 m_3$ (mole kg^{-1})	E^a (V)				
			15°C	20°C	25°C	30°C	35°C
0.433	2.307	5.312	0.6301	0.6324	0.6351	0.6373	0.6391
0.433	2.307	5.976	0.6258	0.6298	0.6321	0.6343	0.6359
0.433	2.307	6.640	0.6243	0.6272	0.6299		0.6349
0.433	2.307	7.968	0.6193				
0.433	2.307	8.632	0.6167	0.6198		0.6241	0.6262
0.433	2.307	9.296	0.6154	0.6185	0.6211	0.6233	0.6253
0.433	2.307	10.624					0.6215

[a] Corrected to 1 atm.

As described earlier[10], the e.m.f. of the cell (A) and the dissociation constant, K_a, of *trans*-cinnamic acid in water + dioxane mixtures are related by

$$\frac{(E - E^0)F}{2.3026\,RT} + \log \frac{m_{(\mathrm{Cl}^-)}\, m_{(\mathrm{HCi})}}{m_{(\mathrm{Ci}^-)}} = -\log K_a - \log \frac{\gamma_{(\mathrm{Cl}^-)} \times \gamma_{(\mathrm{HCi})}}{\gamma_{(\mathrm{Ci}^-)}} \qquad (1)$$

where E^0 is the standard potential of the silver–silver chloride electrode and is known[11, 12] at different temperatures in various water + dioxane mixtures, m and γ are the molalities and activity coefficients of the species designated by the subscripts. Since $m_{(\mathrm{Cl}^-)} = m_3$, $m_{(\mathrm{HCi})} = m_1 - m_{(\mathrm{H}^+)}$, and $m_{(\mathrm{Ci}^-)} = m_2 + m_{(\mathrm{H}^+)}$ the left-hand side of eqn. (1), which may be termed as the auxiliary function ($-\log K_a'$), may thus be calculated from the experimental data, if $m_{(\mathrm{H}^+)}$ is negligible compared to m_1 and m_2.

TABLE 2

VALUES OF pK_a OF *TRANS*-CINNAMIC ACID IN WATER AND WATER + DIOXANE MIXTURES AT DIFFERENT TEMPERATURES

t (°C)	pK_a				
	Water	*10%*	*20%*	*30%*	*40%*
15	4.59 ± 0.03	4.661 ± 0.006	4.760 ± 0.011	5.348 ± 0.008	5.810 ± 0.003
20	4.53 ± 0.02	4.653 ± 0.004	4.747 ± 0.003	5.338 ± 0.004	5.800 ± 0.001
25	4.50 ± 0.01	4.644 ± 0.008	4.735 ± 0.001	5.326 ± 0.002	5.792 ± 0.002
30	4.49 ± 0.02	4.635 ± 0.002	4.721 ± 0.004	5.315 ± 0.001	5.780 ± 0.001
35	4.48 ± 0.01	4.628 ± 0.004	4.707 ± 0.002	5.305 ± 0.002	5.770 ± 0.003
40	4.46 ± 0.02				
45	4.42 ± 0.02				

± denotes the standard deviation.

TABLE 3

PARAMETERS OF EQN. (3)

Mass % dioxane	*A*	*B*	*10^3C*
0	2411.7171	−10.0149	21.5970
10	110.2445	4.4075	−0.4474
20	−224.6841	7.0311	−5.1765
30	48.5933	5.6548	−1.6503
40	−383.8246	8.9576	−6.3043

TABLE 4

STANDARD THERMODYNAMIC QUANTITIES OF THE DISSOCIATION PROCESS OF *TRANS*-CINNAMIC ACID IN WATER AND WATER + DIOXANE MIXTURES AT 25°C

Mass % dioxane	$\Delta G^0 \times 10^{-3}$ *(J mole^{-1})*	$\Delta H^0 \times 10^{-3}$ *(J mole^{-1})*	ΔS^0 *(J mole^{-1} deg^{-1})*	ΔC_p^0 *(J mole^{-1} deg^{-1})*
0	25.75	9.45	−54.70	−246.44
	25.67[a]	2.87[a]	−76.50[a]	—
10	26.50	2.87	−79.28	5.11
20	27.01	4.50	−75.55	59.07
30	30.39	3.74	−89.44	18.83
40	33.04	3.37	−99.56	71.94

[a] Ref. 3.

TABLE 5

STANDARD THERMODYNAMIC QUANTITIES[a] FOR THE TRANSFER OF *TRANS*-CINNAMIC ACID FROM WATER TO WATER + DIOXANE MIXTURES AT 25°C

Mass % dioxane	ΔG_t^0 *(J mole^{-1})*	ΔH_t^0 *(J mole^{-1})*	ΔS_t^0 *(J mole^{-1} deg^{-1})*	$\Delta C_{p_t}^0$ *(J mole^{-1} deg^{-1})*
10	742.32	−6,583.19	−24.58	251.55
20	1,258.14	−4,955.12	−20.85	305.51
30	4,633.21	−5,718.35	−34.74	265.27
40	7,285.36	−6,084.49	−44.86	318.38

[a] Molal basis.

Extrapolation of the calculated values of $-\log K_a'$ to zero ionic strength, I (here, $I = m_2 + m_3$) yields $-\log K_a$ as $\log[\gamma_{(\mathrm{Ci}^-)} \times \gamma_{(\mathrm{HCi})}/\gamma_{(\mathrm{Ci}^-)}]$ tends to zero.

The values of $-\log K_a'$ thus calculated were found to vary linearly with I and the extrapolation of the linear plot to $I = 0$ yielded the pK_a of the acid. These values are given in Table 2 along with those obtained in aqueous medium[3].

The experimental values of pK_a so obtained in both aqueous and mixed aqueous media were fitted to an empirical equation of the form

$$pK_a = A/T + B + CT \cdots \tag{2}$$

where T is the temperature in K. The values of the constants of eqn. (2) are listed in Table 3 for water and for +10, +20, +30, and +40 mass% dioxane.

By the application of the usual thermodynamic formulae[1, 2] to eqn. (2) together with its appropriate numerical constants, the thermodynamic functions ΔG^0, ΔH^0, ΔS^0 and ΔC_p^0 were evaluated. The values of these various quantities at 25°C are presented in Table 4 for water and for +10, +20, +30, and +40 mass% dioxane.

The thermodynamic quantities, ΔG_t^0, ΔH_t^0, ΔS_t^0 and $\Delta C_{p_t}^0$, for the transfer of 1 mole of HCi from water to the mixed solvents of various compositions have been derived from the usual relations[13]. These values at 25°C are listed in Table 5.

As can be seen from Table 5, the values of ΔG_t appear to be positive for all compositions of water + dioxane and increase with increase of dioxane content, supporting the view that water is more basic than the mixed solvents, and *trans*-cinnamic acid thus is more strongly stabilised by solvation with water molecules. The negative values of ΔH_t^0 and ΔS_t^0 for all compositions, suggest that the mixed solvent becomes less associated than pure water, pointing to the fact that the net amount of order created by the hydrogen and cinnamate ions formed on dissociation is more in the mixed solvent than in water. Thus, the degree of solvent orientation is more in the mixed solvent than in water medium.

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