

THERMODYNAMIC FUNCTIONS OF THE TRANSFER OF AMINO BENZOIC ACIDS FROM WATER TO WATER–ACETONE MIXTURES AT 25 °C

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(Received 17 December 1987)

ABSTRACT

Free energies (ΔG_1^\ominus) and entropies (ΔS_1^\ominus) of transfer of *o*-, *m*-, and *p*-aminobenzoic acids from water to water–acetone mixtures have been determined from solubility measurements at five temperatures (20–40 °C). It is found that the specific solute–solvent interactions through dispersion forces play a major role on the nature of ΔG_1^\ominus -composition profiles in the region of water-rich composition. However, in higher acetone concentration the hydrogen bonding interactions between the solvent molecules and the aminobenzoic acids as well as between the solvent molecules themselves were also considered. All these interactions have been proposed to interpret the ΔS_1^\ominus -composition profiles and are discussed.

INTRODUCTION

The thermodynamic quantities, specifically the Gibbs free energies of transfer, play an important role in many areas of chemistry, such as the estimation of solubilities, distribution ratios, complex formation constants, electrochemical potentials, etc. The ultimate goal of a treatment of these Gibbs free energies of transfer would be the ability to predict them from known solvent and ion properties. This problem could be solved by considering the sum of the contributions to the Gibbs free energy of solvation from various interactions between the ions or the molecules and the surrounding solvents and from changes in the interactions among the solvent molecules themselves [1–5]. Different models have been employed to approach solution of the problem. Such models consist of some or all of the following

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steps: the formation of a cavity in the solvent of the appropriate size, the introduction of the molecule or the ion and its interaction with a first coordination shell of solvent, electrical interactions with the solvent beyond the first coordination shell, and a rearrangement of the solvent to accommodate the foreign particle.

In this work we have studied the thermodynamic transfer parameters of *o*-, *m*-, and *p*-aminobenzoic acids from water to water–acetone mixtures. Saturated solubilities of these acids in water and in water–acetone solutions were measured at five equidistant temperatures ranging from 20 to 40 °C and the free energies ΔG_t^\ominus and entropies ΔS_t^\ominus of transfer from water to the mixed solvents were obtained therefrom.

EXPERIMENTAL

Merck analytical grade *o*-, *m*-, and *p*-aminobenzoic acids as well as acetone spectroscopic grade were used. Bidistilled water was used for preparing all solvent mixtures. The mixed solvents were prepared by mixing weighed quantities of acetone and water.

The saturated solutions of the compounds in water and in the water–acetone solutions were prepared by dissolving the required amounts of solid acid in the corresponding solvents using closed test tubes saturated with nitrogen gas. The solutions were shaken vigorously in a thermostatted water-bath for one week at the desired temperature followed by another day without shaking to reach the necessary equilibrium. The solubilities of the acids in each of the solutions investigated were determined gravimetrically by taking 2 ml of the saturated solution and evaporating to dryness using small aluminium discs heated by infrared lamp. The errors in measuring solubilities were about 2%.

RESULTS

The free energies of solutions ΔG_s^\ominus were calculated from the molar solubilities K_{sp} of the acids investigated in water and in water–acetone solutions using the equation

$$\Delta G_s^\ominus = -RT \ln K_{sp} \quad (1)$$

and fitted by the method of least squares to an equation of the form

$$\Delta G_s^\ominus = a_s + b_s T + C_s T \ln T \quad (2)$$

where T is the absolute temperature. The values of the coefficients a_s , b_s

TABLE 1

Coefficients of eq. (2) and free energies and entropies of transfer of aminobenzoic acids from water to water–acetone solution at 25 °C

Acetone mole fraction	a (kJ mol ⁻¹)	b (kJ mol ⁻¹ K ⁻¹)	c (kJ mol ⁻¹ K ⁻¹)	ΔG_t^\ominus (kJ mol ⁻¹)	ΔS_t^\ominus (J K ⁻¹ mol ⁻¹)
<i>o</i> -Aminobenzoic					
0.0	928.48	-19.5392	2.8869	-	-
0.1	626.89	-13.3051	1.9665	-6.58	-68.96
0.2	560.77	-12.1336	1.7991	-7.59	-120.00
0.3	-186.99	4.1965	-0.6276	-12.84	-183.62
0.4	-25.49	0.7920	-0.1252	-9.00	-157.41
0.5	321.78	-6.8080	1.0041	-9.28	-120.96
0.6	183.13	-3.7211	0.5439	-9.20	-126.92
0.7	78.60	-1.4644	0.2092	-9.59	-140.64
0.8	-10.12	0.5021	-0.0837	-9.56	-145.42
0.9	-26.52	0.7950	-0.1255	-9.64	-158.35
1.0	82.30	-1.7154	0.2510	-9.72	-169.60
<i>m</i> -Aminobenzoic					
0.0	496.42	-10.4601	1.5480	-	-
0.1	894.76	-18.9540	2.8031	-2.23	88.51
0.2	734.72	-15.5645	2.3012	-4.31	59.37
0.3	505.48	-10.7529	1.5899	-6.95	12.11
0.4	489.38	-10.4600	1.5481	-7.17	-0.51
0.5	351.95	-7.6065	1.1279	-7.62	-39.93
0.6	206.32	-4.2677	0.6276	-7.44	-27.53
0.7	81.37	-1.4641	0.2092	-7.16	-29.38
0.8	-56.25	-1.6200	-0.2510	-7.15	-30.14
0.9	154.47	-3.1380	0.4602	-7.12	-36.35
1.0	-22.31	0.7949	-0.1255	-5.89	-46.47
<i>p</i> -Aminobenzoic					
0.0	-581.54	13.1796	-1.9665	-	-
0.1	488.49	-10.2089	1.5062	-4.05	129.97
0.2	25.55	-0.0837	0.0000	-6.81	92.47
0.3	96.61	-1.7554	0.2510	-7.76	83.07
0.4	169.10	-3.4308	0.5021	-8.24	76.71
0.5	-171.96	3.8910	-0.5858	-10.15	41.22
0.6	63.70	-1.1715	0.1674	-8.60	59.09
0.7	172.83	-3.6819	0.5439	-8.37	72.50
0.8	294.43	-6.2342	0.9205	-8.01	77.83
0.9	113.27	-2.0502	0.2929	-7.82	97.25
1.0	-268.02	6.6196	-1.0041	-7.48	114.23

and C_s are given in Table 1. The free energies ΔG_t^\ominus and entropies ΔS_t^\ominus of transfer at 25 °C were calculated using the equations

$$\Delta G_t^\ominus = (a_s - a_w) + (b_s - b_w)T_0 + (C_s - C_w)T_0 \ln T_0 \quad (3)$$

$$\Delta S_t^\ominus = -[(b_s - b_w) + (C_s - C_w) + (C_s - C_w) \ln T_0] \quad (4)$$

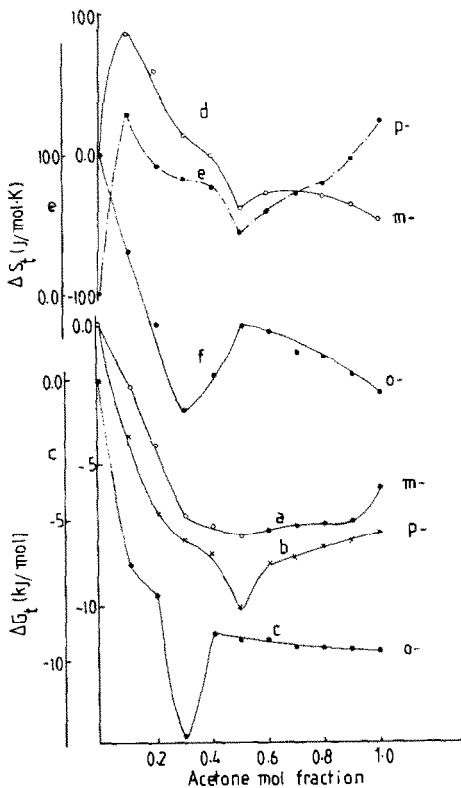


Fig. 1. Variation of ΔG_1^\ominus and ΔS_1^\ominus of aminobenzoic acids at 25°C with acetone mole fraction.

where $T_0 = 298.15$ K and the subscript w indicates quantities for water and the subscript s indicates quantities for solution (water–acetone). The uncertainties in ΔG_1^\ominus and ΔS_1^\ominus values are calculated by Please's method [6]. The data showed 2% maximum uncertainty in ΔG_1^\ominus values and 5% in ΔS_1^\ominus values. The ΔG_1^\ominus and ΔS_1^\ominus values calculated according to eqns. (3) and (4) are listed in Table 1. The effect of solvent composition on the thermodynamic transfer parameters (ΔG_1^\ominus and ΔS_1^\ominus) of the compounds investigated is shown in Fig 1. The following trends are apparent from an overall view of Fig. 1:

- (i) The ΔG_1^\ominus values of the acids investigated pass through minima at 0.5 acetone mole fraction for *m*-amino and *p*-aminobenzoic acids and at 0.3 acetone mole fraction for *o*-aminobenzoic acid;
- (ii) ΔS_1^\ominus -solvent composition profiles show different maxima and minima. Generally, 0.5 acetone mole fraction was found to be the common position where the maximum or the minimum values in ΔS_1^\ominus for each of the acids investigated appeared.

DISCUSSION

The aminobenzoic acids investigated can be regarded as having the zwitterionic form $\text{H}_3\text{N}^+ \text{---} \text{C}_6\text{H}_4 \text{---} \text{COO}^-$, here written as $\text{H}_3\text{N}^+ \text{---} \text{B} \text{---} \text{COO}^-$. Therefore, the observed behaviour of the thermodynamic transfer quantities may be discussed by considering the solvation of the hydrocarbon nucleus (B) as well as the charged ends ($-\text{COO}^-$, $-\text{NH}_3^+$) relative to their solvation in pure water.

The hydrophobic effect of the aromatic nucleus of *o*-, *m*-, and *p*-aminobenzoic acids is the key to understanding the problem [7,8]. It is reported [9] that the water molecules surrounded a hydrophobic solute through the formation of a hydrogen-bonded network among themselves. Such highly ordered arrangement of a water molecule "skin" contributes appreciably to the ΔS_1^\ominus values of the solute.

The molecules of aminobenzoic acids investigated can be represented by $\text{B}(\text{X}_1, \text{X}_2)$ where B is the hydrophobic part while X_1 and X_2 are the hydrophilic groups which can interact with the solvents through hydrogen bonds.

In our investigation system if we represent the co-solvent molecule (acetone) as RZ (R = hydrophobic part, Z = hydrophilic part), then the solvated state of the aminobenzoic molecule in pure water and in mixed water-acetone can be represented by the model shown in Fig. 2.

In pure solvent (Fig. 2(A)) the aminobenzoic molecule is surrounded by a hydrophobically created skin in the solvent. X_1 , X_2 groups form hydrogen bonds with solvent molecules (water) at the skin surface. However, in the

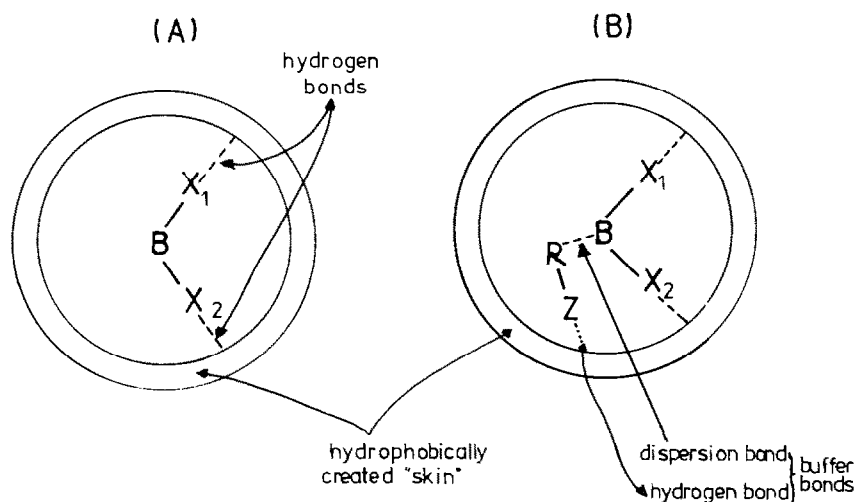


Fig. 2. Aminobenzoic molecule in water (A), and in mixed water-acetone solution (B).

aqueous–acetone solutions (Fig. 2(B)) other interactions appear due to a dispersion interaction between B and R as well as hydrogen bonded interactions between Z and the skin surface [5].

The transfer of the aminobenzoic molecule from the pure water state (A) to the mixed solvent state (B) could be considered to occur by the following steps:

- (i) Rupture of the hydrogen bonds between both X_1 , X_2 and the skin surface;
- (ii) Removing the aminobenzoic molecule from the cavity;
- (iii) Rearrangement of the water molecules in the skin surface to form normal water structure;
- (iv) Creation of a suitable cavity inside the mixed solvents;
- (v) Introducing an aminobenzoic molecule into the solvent cavity;
- (vi) Formation of dispersion bonds between R and B, and hydrogen bonds between Z and the skin surface.

According to this model the change of any standard thermodynamic function (F) can be obtained from

$$\Delta F_1^\ominus = (F_s^m - F_s^w) + (F_b^w - F_b^m) + (\Delta F_{HB}^m - \Delta F_{HB}^w) + \Delta F_{BB} \quad (5)$$

where s and b signify states of solvent molecules in the “skin phase” and in the “bulk phase”, the subscripts w and m refer to pure water and mixed solvents respectively, ΔF_{HB} is the thermodynamic function of the total number of hydrogen bonds, and ΔF_{BB} is the thermodynamic function of the buffer bonds produced by acetone molecules in the cavities of mixed solvents.

In our case the analysis of ΔG_1^\ominus and ΔS_1^\ominus in terms of eqn. (5) is as follows.

Free energies of transfer

In water–acetone mixed solvents the skin phase is a more compact and more stable structure in pure water than in acetone or in a mixed solvent due to the presence of steric inhibition by R. With increasing concentration of acetone in the mixed solvent, the skin phase begins to break and becomes more loosely bound, which means that the term $(G_s^m - G_s^w)$ is a positive quantity which increases in magnitude with increasing acetone concentration. In water–acetone mixtures, compared with pure water, the strength of individual hydrogen bonds in the bulk phase increases while their total number decreases [10]. Consequently, the variation in the total interaction energy $(G_b^w - G_b^m)$ in the bulk solvent with increasing acetone concentration is small.

Due to higher polarity of water compared to acetone [11] it is expected that the positively charged $-\text{NH}_3^+$ group and the negatively charged $-\text{COO}^-$ group are more likely to be solvated by water molecules than by acetone molecules. Thus the hydrogen bonding between both the amino group and the carboxylic group with the solvent should be weakened with increasing concentration of acetone especially at higher concentrations. It means that the term $\Delta G_{\text{HB}}^{\text{m}} - \Delta G_{\text{HB}}^{\text{w}}$, which refers to hydrogen bonding interactions, is a positive quantity which increases in magnitude with increasing amounts of acetone in the solution.

With the increasing addition of acetone in the solution, dispersion interaction between R and the hydrocarbon nucleus of the aminobenzoic acid increases strongly. It causes ΔG_{BB} to have negative values which increase in magnitude as the acetone concentration in the solution is increased.

The sharp fall of values of $\Delta G_{\text{t}}^{\ominus}$ in water-rich compositions, for all aminobenzoic acids investigated, results in the predominance of ΔG_{BB} over the other term in this region. With further addition of acetone, the dispersion interactions reach saturation (constant value), while for the terms $(G_{\text{s}}^{\text{m}} - G_{\text{s}}^{\text{w}})$ and $(\Delta G_{\text{HB}}^{\text{m}} - \Delta G_{\text{HB}}^{\text{w}})$ positive values increase with increasing amounts of acetone causing an inflection in the $\Delta G_{\text{t}}^{\ominus}$ curve, as observed. The flattening curves of $\Delta G_{\text{t}}^{\ominus}$ at higher concentrations of acetone (after inflection points) in the case of *o*-amino and *m*-aminobenzoic acids are due to reaching approximate saturation values for the terms $\Delta G_{\text{BB}}, (G_{\text{s}}^{\text{m}} - G_{\text{s}}^{\text{w}})$ and $(\Delta G_{\text{HB}}^{\text{m}} - \Delta G_{\text{HB}}^{\text{w}})$ in the higher acetone concentration region. In this region the term $(G_{\text{b}}^{\text{w}} - G_{\text{b}}^{\text{m}})$ is small and has little effect on $\Delta G_{\text{t}}^{\ominus}$ curves. In contrast to the $\Delta G_{\text{t}}^{\ominus}$ behaviour of *o*- and *m*-aminobenzoic acids, *p*-aminobenzoic acid shows an increase in $\Delta G_{\text{t}}^{\ominus}$ values with increasing acetone concentration in the acetone-rich regions. This could be attributed to the higher dipole moment of the zwitterionic form of *p*-aminobenzoic acid compared to that of *o*- or *m*-aminobenzoic acids. The mixed solvents have lower dielectric constants than that of pure water. Therefore, it is expected that the electrostatic contributions to $\Delta G_{\text{t}}^{\ominus}$ in the case of *p*-aminobenzoic acid, as estimated by the Born equation [12], will be more positive than those of *o*- or *m*-aminobenzoic acids. These positive values of the electrostatic interactions indicate the increase in $\Delta G_{\text{t}}^{\ominus}$ -composition profile in *p*-aminobenzoic acid in the regions of higher acetone concentrations, as mentioned above. However, on introducing the effect of simple electrostatic solvation in our discussion, at lower acetone concentrations, we found that the essential behaviour of $\Delta G_{\text{t}}^{\ominus}$ values remains unaltered.

Entropies of transfer

As mentioned above, the skin phase is a more ordered region in pure water, than in water-acetone solutions; hence the term $(S_{\text{s}}^{\text{m}} - S_{\text{s}}^{\text{w}})$ is a

positive quantity which increases in magnitude with increasing concentration of acetone.

The addition of acetone to pure water causes the collapse of the hydrogen-bonded three-dimensional structure of pure water [10]. Therefore, the term $(S_b^w - S_b^m)$ is negative which becomes increasingly negative with increasing acetone concentration in solutions.

The term $(\Delta S_{HB}^m - \Delta S_{HB}^w)$ is obtained from the change in the configuration and disposition of the hydrogen bonds formed by $-NH_2$ and $-COOH$ groups. This term is a positive value whose magnitude increases appreciably with increasing acetone concentration. The formation of dispersion- and hydrogen-bonds between Z and the skin phase causes an ordering effect in the mixed solvents. This order increases with increasing acetone content in solutions: ΔS_{BB} is thus increasingly negative with increasing mole fraction of acetone.

The ΔS_t^\ominus -composition profile in *o*-aminobenzoic acid is quite different in water-rich compositions from that in *m*- and *p*-aminobenzoic acids. This behaviour could be attributed to the presence of internal hydrogen bonding between $-NH_2$ and $-COOH$ groups in *o*-aminobenzoic acid. Such internal hydrogen bonds cause the value of the term $(S_s^m - S_s^w)$ to be very small. Therefore, the decrease in ΔS_t^\ominus values with increasing acetone concentration for *o*-aminobenzoic acid (in water-rich composition) should be attributed to the negative values of $(S_b^w - S_b^m)$ and ΔS_{BB} . However, in the case of *m*- and *p*-aminobenzoic acids the internal hydrogen bond is absent. Therefore, the increase in ΔS_t^\ominus values on adding small amounts of acetone predominates in the term $(S_s^m - S_s^w)$, which has a positive value, at the water-rich composition. On further addition of acetone the buffer-bond terms of ΔS_{BB} and the bulk term $(S_b^w - S_b^m)$ first neutralize the skin term and then overcome it. This explains why the maximum appears in ΔS_t^\ominus -values at 0.1 acetone mole fraction.

At higher acetone concentrations, all the terms above discussed are of comparable magnitude, and the ΔS_t^\ominus values observed contain a significant contribution from each. The extremum behaviour appearing in water-acetone solutions has been also observed in other studies [13,14].

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