Activity Coefficients and Relative Partial Molal Enthalpies of Substituted Anilines in Aqueous Perchloric Acid Solutions

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Activity coefficients and relative partial molal enthalpies have been deduced from measurements of the solubilities of 2,4-dinitroaniline, 2,6-dichloro-4-nitroaniline, and 2,4-dichloro-6-nitroaniline in aqueous perchloric acid at four temperatures. The results are discussed in relation to the Hammett acidity function H_0 for aqueous perchloric acid and enthalpies of protonation of Hammett bases as a function of perchloric acid concentration.

THE variation of Hammett acidity function H_0 with the concentration of a strong acid in water is formally related in accordance with equation (1) to the activity of

$$H_0 = -\log_{10}(a_{\mathrm{H}^+}y_{\mathrm{B}}/y_{\mathrm{BH}^+}) \qquad (1)$$

hydrogen ions a_{H^+} and the activity coefficients y_{B} and y_{BH^+} of base B and protonated base BH^+, respectively.[1] The separate determination of variations of activity coefficient with acid concentration therefore provides insight into acidity function behaviour.[2-5] An alternative approach has been to relate acidity functions with water activities [6] and to interpret the correlations in terms of either the numbers of water molecules solvating the proton,[7,8] or the differences between the numbers of water molecules solvating BH^+ and B plus the proton.[6,9-11] However, it is unlikely that the complexity of solvation phenomena in concentrated electrolyte solutions can be adequately represented by simple relationships involving water activities.[4] Studies of activity coefficient behaviour of individual species involved in the protonation equilibria are likely to be more informative.[2-5]

Enthalpies of dissociation of the conjugate acids of amines [12] and amides [13] in aqueous perchloric acid have been reported as a function of acid concentration. Despite general consistency with conclusions drawn from theories in which acidity functions are correlated with water activities, the results further emphasized the desirability of detailed knowledge of activity coefficient behaviour. Differences between the enthalpy changes ΔH and ΔH^0 for dissociation in solutions of finite acid concentration and in water, respectively,[12] are related, in accordance with equation (2), to the partial molar

$$\Delta H - \Delta H^0 = \bar{L}_{\mathrm{B}} + \bar{L}_{\mathrm{H}^+} - \bar{L}_{\mathrm{BH}^+} \qquad (2)$$

enthalpies of transfer $\bar{L}_{\mathrm{H}^+}$,$\bar{L}_{\mathrm{B}}$, and $\bar{L}_{\mathrm{BH}^+}$ of the proton, B, and BH^+ from water to solution in aqueous acid. Partial molar enthalpies of transfer may be evaluated from the variation of activity coefficients with temperature.[14] The present paper reports measurements of the solubilities of 2,4-dinitroaniline, 2,6-dichloro-4-nitroaniline, and 2,4-dichloro-6-nitroaniline in aqueous perchloric acid solutions at 288, 298, 308, and 318 K. Hence y_{B} [equation (1)] and $\bar{L}_{\mathrm{B}}$ [equation (2)] values have been deduced as a function of perchloric acid concentration.

EXPERIMENTAL

Perchloric acid solutions, estimated volumetrically, were prepared by dilution of AnalaR aqueous 71—73 w/w % perchloric acid with water. Substituted anilines were recrystallized to constant m.p. from water.

Saturated solutions of the amines in water or aqueous perchloric acid were prepared either by rotation in a water thermostat (288 and 298 K) or shaking in an air thermostat (308 and 318 K) of tubes containing excess solid amine with acid solution for *ca.* 18 h. Solutions were subsequently filtered at the particular temperature under investigation, diluted with acid solution at the same concentration as that in the saturated solution,[3-5] and estimated using a Unicam SP 8000 spectrophotometer.

RESULTS

Values of $\log_{10}y_{\mathrm{B}}$ [equation (1)] were deduced from the measured absorbance data at 347 nm for 2,4-dinitroaniline, 368 nm for 2,6-dichloro-4-nitroaniline, and 418 nm for 2,4-dichloro-6-nitroaniline. Equation (3) was applicable [5] where S_{w} and S_{A} are the solubilities of amine in water and

$$\log_{10}y_{\mathrm{B}} = \log_{10}(S_{\mathrm{w}}/S_{\mathrm{A}}) = \log_{10}(A_{\mathrm{w}}/A_{\mathrm{A}}) \qquad (3)$$

acid solution, respectively, and A_{w} and A_{A} are the corresponding experimental absorbance values. The y_{B} data are therefore referred to a standard state $y_{\mathrm{B}} = 1$ for the saturated solution of base in water, and to the molar concentration scale. The results are given in Table 1.

Partial molar enthalpies of transfer $\bar{L}_{\mathrm{B}}$ [equation (2)] of amines from water to aqueous perchloric acid were calculated *via* equation (4) by least-squares analyses of linear

$$(\mathrm{d}\ln y_{\mathrm{B}}/\mathrm{d}T) = -(\bar{L}_{\mathrm{B}}/RT^2) \qquad (4)$$

plots of $\log y_{\mathrm{B}}$ against reciprocal temperature. Values of y_{B} were taken at constant molality of perchloric acid from smooth curves drawn through the experimental data as a function of acid concentration. High correlation coefficients for the $\log y_{\mathrm{B}}$ against $(1/T)$ plots, and the regular increases in the resulting $\bar{L}_{\mathrm{B}}$ values as a function of acid concentration (Table 2) suggest that the data are reliable.

DISCUSSION

Present activity coefficient data for three amines in aqueous perchloric acid at 298 K are compared in Figure 1 with the results of previous measurements by Essig and Marinsky [3] and Yates *et al.*[4] The agreement is good and confirms that 2,4-dichloro-6-nitroaniline and 2,6-dichloro-4-nitroaniline show similar activity coefficient behaviour, whereas 2,4-dinitroaniline is salted-in to a greater extent than the other bases with increasing perchloric acid concentration.

2,4-Dinitroaniline is also salted-in by transfer from water to aqueous sulphuric acid solutions.[5] In contrast the two mononitroanilines were salted-out in sulphuric acid up to 35 wt %, but in accordance with the results for aqueous perchloric acid were salted-in to a lesser extent than 2,4-dinitroaniline at higher acid concentrations.

TABLE 1

Values of $\log_{10}y_B$ as a function of perchloric acid concentration (C/mol dm^{-3}) for three amine bases at four temperatures

288 K		298 K		308 K		318 K	
C	$-\log y_B$	C	$-\log y_B$	C	$-\log y_B$	C	$-\log y_B$
(a) 2,6-Dichloro-4-nitroaniline							
0.70	0.173	0.50	0.120	0.75	0.199	0.57	0.153
1.25	0.285	1.25	0.290	1.17	0.288	1.20	0.299
1.82	0.377	1.65	0.354	1.75	0.402	2.05	0.445
2.42	0.476	2.19	0.433	2.50	0.507	2.75	0.558
3.01	0.542	2.92	0.549	3.45	0.644	3.40	0.663
3.68	0.624	3.65	0.638	3.75	0.697	3.90	0.721
4.13	0.673	4.14	0.716	3.90	0.710	4.13	0.747
4.85	0.752	4.90	0.782	4.50	0.773	4.75	0.764
5.44	0.805	5.50	0.838	5.01	0.809	5.20	0.863
5.90	0.834	6.06	0.901	5.92	0.920	5.65	0.915
6.61	0.911	6.35	0.916	6.40	0.981	6.54	1.022
7.50	1.010	6.88	0.997	6.75	1.012	7.01	1.070
(b) 2,4-Dichloro-6-nitroaniline							
0.50	0.130	0.64	0.161	0.61	0.181	0.57	0.170
1.05	0.258	1.50	0.330	1.20	0.312	1.15	0.282
1.75	0.381	1.76	0.426	1.78	0.438	1.70	0.444
2.25	0.480	2.19	0.506	2.39	0.552	2.33	0.564
2.80	0.564	2.92	0.612	3.01	0.656	2.75	0.638
3.55	0.663	3.51	0.689	4.10	0.759	3.63	0.761
4.11	0.721	4.14	0.758	4.82	0.864	4.25	0.835
4.80	0.800	4.84	0.842	5.15	0.889	4.75	0.882
5.44	0.860	5.30	0.890	5.92	0.992	5.35	0.950
6.55	0.954	6.06	0.942	6.40	1.002	5.90	1.004
7.40	1.029	6.40	0.994	7.10	1.073	6.40	1.052
		7.25	1.050			6.74	1.092
(c) 2,4-Dinitroaniline							
1.18	0.474	1.28	0.432	1.60	0.516	1.17	0.508
1.82	0.592	1.76	0.567	2.01	0.650	1.78	0.651
2.42	0.727	2.19	0.698	2.89	0.830	2.50	0.799
3.02	0.839	2.92	0.824	3.51	0.972	3.02	0.869
3.68	0.982	3.51	0.990	4.17	1.111	3.48	1.018
4.13	1.041	4.14	1.061	5.33	1.321	4.14	1.126
4.85	1.162	4.84	1.170	6.25	1.436	5.00	1.340
5.44	1.238	5.34	1.251	7.01	1.597	5.25	1.402
5.90	1.310	6.06	1.389			6.35	1.552
		6.44	1.424				
		7.12	1.563				

Equation (1) may be written in the form (5) where α,

$$-H_0 = \log_{10}(\alpha C) + \log_{10}y_B + \log_{10}(y_{H^+}/y_{BH^+}) \quad (5)$$

deduced as before,[12] represents the fraction of perchloric acid dissociated at concentration C. The relative contributions of the terms in equation (5) to the Hammett acidity function [12] are shown in Figure 2. At very low acid concentrations H_0 is positive and is primarily determined by the value of $\log_{10}C$, since $\alpha = 1$ and the combined activity coefficient terms in equation (5) approximate to zero. In the acid concentration range studied here, however, $(y_B y_{H^+}/y_{HB^+}) > 1$ and the negative contribution of $\log_{10}y_B$ [Figure 2(c) or (e)] to $-H_0$ is counteracted by a larger positive contribution from $\log_{10}(y_H/y_{BH^+})$ [Figure 2(d) or (f)]. Estimates of y_{BH^+} have suggested [3,4] that $y_{BH^+} > 1$ and hence it follows that $y_{H^+} > 1$ with $y_{H^+} > y_{BH^+}$. The increasing positive values of $-H_0$ with increasing acid concentration are therefore governed by positive contributions from $\log_{10}(\alpha C)$ and $\log_{10}y_{H^+}$, which combined give $\log_{10}a_{H^+}$ [equation (1)] and which are partially compensated by negative contributions from $\log_{10}y_B$ and $-\log_{10}y_{BH^+}$. More detailed analyses of activity coefficient contributions to acidity function behaviour of Hammett bases in perchloric acid solutions have been reported elsewhere.[3,4] However, it is appropriate here to consider the activity coefficient data in terms of the Gibbs free energies of transfer of B, H$^+$, and BH$^+$ from water to aqueous perchloric acid solutions. An assessment of the relative contributions of enthalpy and entropy effects to the free energy data can then be made.

The chemical potentials of B, H$^+$, and BH$^+$ are given

TABLE 2

Partial molar enthalpies of transfer (L_B/kJ mol^{-1}) of three aniline bases from water to aqueous perchloric acid at concentration m/mol kg^{-1}

m	(a) 2,6-Cl_2-4-NO_2 L_B	(b) 2,4-Cl_2-6-NO_2 L_B	(c) 2,4-$(NO_2)_2$ L_B
1.05	1.21	0.87	
1.60	1.75	1.75	1.46
2.20	2.51	2.72	2.63
2.81	2.91	3.96	3.47
3.48	3.21	4.08	3.22
4.15	3.96	4.47	4.72
4.87	5.06	4.67	5.23
5.62	5.25	5.25	8.15
6.41	5.51	5.44	8.15
7.25	5.93	5.62	9.33
8.12	6.35	6.35	10.21
9.05	6.69	7.12	10.21
10.00	7.03	7.99	

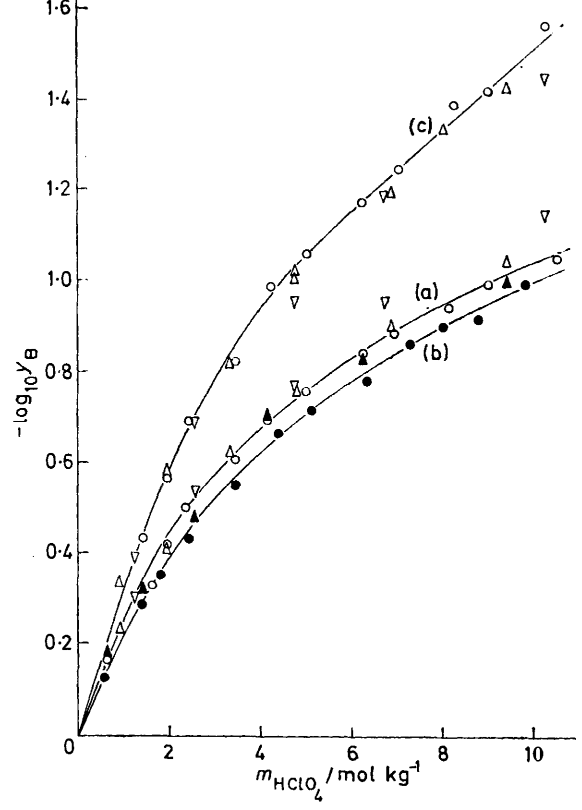

FIGURE 1 Activity coefficient data (298 K) from ○ present work, △ ref. 4, ▽ ref. 3, for (a) 2,4-dichloro-6-nitroaniline, (b) 2,6-dichloro-4-nitroaniline (shaded points), (c) 2,4-dinitroaniline in aqueous perchloric acid

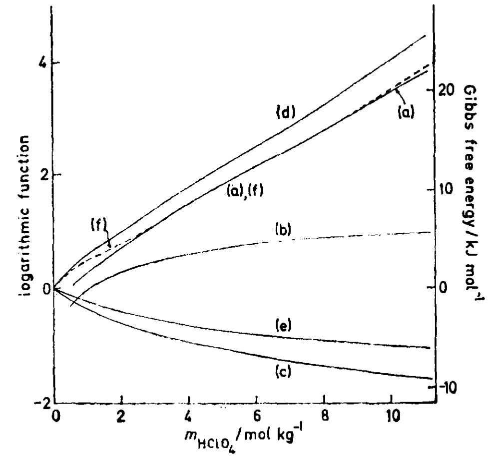

FIGURE 2 Factors contributing to the variation of $-H_0$ [curve (a)] with perchloric acid concentration: (b) $\log_{10}(\alpha C)$, (c) $\log_{10}y_B$, (d) $\log_{10}(y_{H^+}/y_{BH^+})$ for 2,4-dinitroaniline, (e) $\log_{10}y_B$, (f) $\log_{10}(y_{H^+}/y_{BH^+})$ for 2,6-dichloro-4-nitroaniline. The right hand axis gives the magnitudes of the corresponding Gibbs free-energy functions

by equations (6)—(8) in which $\mu_i{}^0(H_2O)$ and $\mu_i{}^0(HClO_4)$ are the standard chemical potentials of species i referred to standard states in water and in an aqueous perchloric acid solution, respectively, C_i is the molar concentration

$$\mu_B = \mu_B{}^0(H_2O) + RT\ln C_B y_B = \mu_B{}^0(HClO_4) + RT\ln C_B \quad (6)$$

of species i and y_i is the activity coefficient of i referred to water standard state. At equilibrium equation (9) is applicable and leads to equations (10) and (11) for the molar free-energy changes accompanying the dissociation of BH^+ at infinite dilution in aqueous perchloric acid and in water, respectively. K_{BH^+} is the acid dissociation

$$\mu_{H^+} = \mu_{H^+}{}^0(H_2O) + RT\ln C_{H^+}y_{H^+} = \mu_{H^+}{}^0(HClO_4) \quad (7)$$

$$\mu_{BH^+} = \mu_{BH^+}{}^0(H_2O) + RT\ln C_{BH^+}y_{BH^+} = \mu_{BH^+}{}^0(HClO_4) + RT\ln C_{BH^+} \quad (8)$$

$$\mu_{BH^+} = \mu_{H^+} + \mu_B \quad (9)$$

$$\Delta G = \mu_B{}^0(HClO_4) + \mu_{H^+}{}^0(HClO_4) - \mu_{BH^+}{}^0(HClO_4) = RT\ln(C_{BH^+}/C_B) \quad (10)$$

$$\Delta G^0 = \mu_B{}^0(H_2O) + \mu_{H^+}{}^0(H_2O) - \mu_{BH^+}{}^0(H_2O) = -RT\ln K_{BH^+} \quad (11)$$

constant of BH^+ in water. But H_0 is given by equation (12) and hence $\Delta G - \Delta G^0$ is related to H_0 by equation (13). Curve (a) in Figure 2 gives the variation of $\Delta G - \Delta G^0$ with perchloric acid concentration. The magnitudes of $\Delta G - \Delta G^0$ are in accordance with the right-hand ordinate axis. The free energy of transfer $\Delta G_t(i)$ of species i from water to aqueous perchloric acid

$$H_0 = pK_{BH^+} - \log_{10}(C_{BH^+}/C_B) \quad (12)$$

$$\Delta G - \Delta G^0 = -RTH_0\ln 10 \quad (13)$$

solution is given by $\mu_i{}^0(HClO_4) - \mu_i{}^0(H_2O)$ and therefore $\Delta G - \Delta G^0$ is also given by equation (14) in which the free energies of transfer are given by equations (15)—(17).

$$\Delta G - \Delta G^0 = \Delta G_t(B) + \Delta G_t(H^+) - \Delta G_t(BH^+) \quad (14)$$

$$\Delta G_t(B) = RT\ln y_B \quad (15)$$

$$\Delta G_t(H^+) = RT\ln(\alpha C) + RT\ln y_{H^+} \quad (16)$$

$$\Delta G_t(BH^+) = RT\ln y_{BH^+} \quad (17)$$

With the units of the right-hand ordinate axis in Figure 2, curve (b) corresponds to $RT\ln(\alpha C)$ in equation (16), curves (c) and (e) represent $\Delta G_t(B)$ for 2,4-dinitroaniline and 2,6-dichloro-4-nitroaniline, respectively, and curves (d) and (f) represent the corresponding $RT\ln(y_{H^+}/y_{BH^+})$ functions which are a combination of $-\Delta G_t(BH^+)$ and the $RT\ln y_{H^+}$ contribution to $\Delta G_t(H^+)$.

The enthalpy changes ΔH and ΔH^0 [equation (2)] contributing to the Gibbs free-energy changes ΔG and ΔG^0, respectively, are related to the variation of acidity function with temperature by equation (18).[12]

$$\Delta H - \Delta H^0 = 2.303\,RT^2(\partial H_0/\partial T)_p \qquad (18)$$

Combination of equations (4), (5), and (18) leads to equation (19) which may be compared with equation (2)

$$\Delta H - \Delta H^0 = -RT^2[\mathrm{d}\ln(\alpha C)/\mathrm{d}T] + \bar{L}_B - RT^2[\mathrm{d}\ln(y_{H^+}/y_{BH^+})/\mathrm{d}T] \qquad (19)$$

in which $\bar{L}_{H^+}$ and $\bar{L}_{BH^+}$ are given by equations (20) and (21). The variation of H_0 with temperature has been

$$\bar{L}_{H^+} = -RT^2[\mathrm{d}\ln(\alpha C)/\mathrm{d}T] - RT^2(\mathrm{d}\ln y_{H^+}/\mathrm{d}T) \qquad (20)$$

$$\bar{L}_{BH^+} = -RT^2(\mathrm{d}\ln y_{BH^+}/\mathrm{d}T) \qquad (21)$$

determined and values of $\Delta H - \Delta H^0$ were calculated.[12] Values of $\mathrm{d}\ln(\alpha C)/\mathrm{d}T$ were also tabulated.[12] The present paper reports measurement of $\bar{L}_B$ for three amines in aqueous perchloric acid solutions (Table 2). Hence the separate contributions of the terms on the right-hand side of equation (19) to the variation of $\Delta H - \Delta H^0$ with perchloric acid concentration may be compared. The data are summarised in Figure 3.

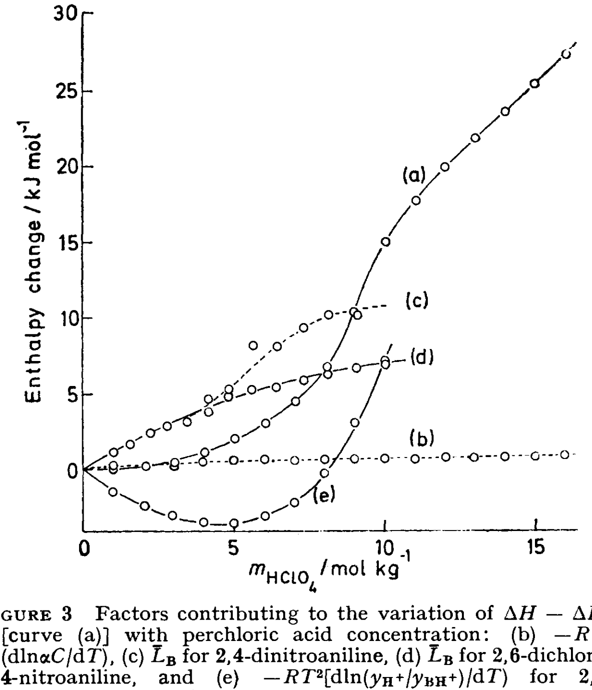

FIGURE 3 Factors contributing to the variation of $\Delta H - \Delta H^0$ [curve (a)] with perchloric acid concentration: (b) $-RT^2(\mathrm{d}\ln\alpha C/\mathrm{d}T)$, (c) $\bar{L}_B$ for 2,4-dinitroaniline, (d) $\bar{L}_B$ for 2,6-dichloro-4-nitroaniline, and (e) $-RT^2[\mathrm{d}\ln(y_{H^+}/y_{BH^+})/\mathrm{d}T)$ for 2,6-dichloro-4-nitroaniline

At perchloric acid concentrations less than *ca.* 3 mol kg⁻¹ $\Delta H - \Delta H^0$ was largely determined by the ' ideal ' concentration term in equation (20) [Figure 3(b)]. The almost exact cancellation between $\bar{L}_B$ [Figure 2(c) and (d)] and $-RT^2[\mathrm{d}\ln(y_{H^+}/y_{BH^+})/\mathrm{d}T]$ [Figure 2(e)] shows that $(y_B y_{H^+}/y_{BH^+})$ had a negligibly small temperature coefficient for $C < 3$ mol kg⁻¹. Despite this the analysis of contributions to $-H_0$ (Figure 2) shows that $(y_B y_{H^+}/y_{BH^+})$ deviates sufficiently from unity to make an appreciable contribution to $-H_0$ which increased more rapidly than $\log(\alpha C)$ with increasing $HClO_4$ concentration [equation (5)]. At higher perchloric acid concentrations the temperature coefficient of $(y_B y_{H^+}/y_{BH^+})$ became significant and the variation of (αC) with temperature made only a small contribution to the total magnitude of $\Delta H - \Delta H^0$. Variations in $\Delta H - \Delta H^0$ with changing acid concentration were influenced by the appearance of a minimum in $-RT^2[\mathrm{d}\ln(y_{H^+}/y_{BH^+})/\mathrm{d}T]$ at C *ca.* 4.5 mol kg⁻¹. The relative partial molal enthalpies of water $\bar{L}_w$ in aqueous perchloric acid solutions change sign at approximately the same acid concentration.[12] It is therefore possible that the minimum in Figure 3(e) might be related to differences between the numbers of water molecules solvating the proton and BH^+ in aqueous perchloric acid solutions. It has previously been shown that the relationship between variations in $\Delta H - \Delta H^0$ and $\bar{L}_w$ with perchloric acid concentration are consistent with theories which ascribe acidity function behaviour to changes in solvation which accompany the protonation of B to give BH^+.[12] The enthalpy data suggest that solvation effects involving charged species (H^+ and BH^+) are more important than solvation effects for neutral solutes (B) in this context. This conclusion is consistent with the free-energy data. Estimated[2,4] values of y_{H^+} and y_{HB^+} deviate more from unity than do values of y_B at the same perchloric acid concentrations and these deviations may be related to the hydration numbers of the solute species in concentrated electrolyte solutions.[15]

The $\bar{L}_B$ values for 2,6-dichloro-4-nitroaniline and 2,4-dichloro-6-nitroaniline were similar functions of perchloric acid concentration in accordance with the corresponding similarity between the free energies of transfer [equation (15), Figure 1] for the two solutes. The transfer of the two amines from water to aqueous perchloric acid was accompanied by similar thermodynamic changes suggesting that the structural effects of varying perchloric acid concentration on solute–solvent interactions involving the amines were probably the same. The thermodynamic changes for the transfer of 2,4-dinitroaniline were of the same order of magnitude as the results for the dichloroanitroanilines but the values were enhanced. The more negative values of $\Delta G_t(B)$ for 2,4-dinitroaniline [Figure 2(c)] were matched by more positive values of $\bar{L}_B$ [Figure 3(c)] at least for concentrations of perchloric acid >5 mol kg⁻¹. Despite the opposite signs of $\Delta G_t(B)$ and $\bar{L}_B$, the overall thermodynamic functions $\Delta G - \Delta G^0$ [equation (14)] and $\Delta H - \Delta H^0$ [equation (2)] were the same sign at all perchloric acid concentrations. Solvation phenomena involving the neutral bases were apparently not the most significant factor which determined the acidity function behaviour of Hammett bases in aqueous perchloric acid solutions. This conclusion is supported by a more detailed consideration of the enthalpy and entropy contributions to $\Delta G - \Delta G^0$.

Figure 4 shows the division of the free-energy changes corresponding to the four terms in equation (5) into their enthalpy [equation (19)] and entropy contributions. The relative magnitudes of the G, H, and TS terms for the overall dissociation equilibrium $BH^+ \rightleftharpoons B + H^+$ (Figure 4a) largely reflects the corresponding comparison (Figure 4B) for the individual term [equation (5)] dependent on (y_{H^+}/y_{BH^+}). The divergences between the G, H, and TS functions for the concentration term in equation (5) (Figure 4D) are also in the same sense ($G > H > TS$) as the results for the overall equilibrium. In contrast the data corresponding to the term dependent on y_B (Figure 4C) are in the reverse sense ($TS > H > G$). The partial compensation of the positive $\log_{10}(\alpha C)$ and $\log_{10}(y_{H^+}/y_{BH^+})$ terms in equation (5) by the negative $\log_{10}y_B$ term may largely be attributed to similar compensation, but with reversal of signs, between the corresponding entropy data. The overall entropy data (Figure 4A) with varying perchloric acid concentration are primarily determined by effects involving H^+ and BH^+ with partial compensation by effects involving the neutral bases B. Differences between the partial molar entropies of transfer $\bar{S}_{H^+}$ and $\bar{S}_{BH^+}$ of H^+ and BH^+, respectively, from water to aqueous perchloric acid are sufficient to dominate the overall entropy function $(\bar{S}_B + \bar{S}_{H^+} - \bar{S}_{BH^+})$ in which $\bar{S}_B$ is the partial molar entropy of transfer of B.

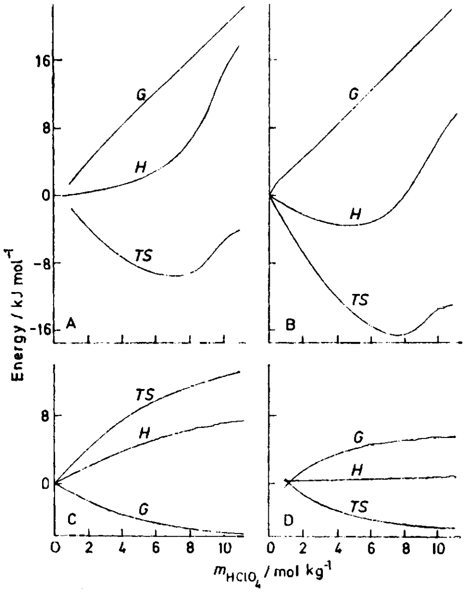

FIGURE 4 Enthalpy (H) and entropy (TS) contributions to the free energy (G) functions: (A) $-RTH_0\ln10$, (B) $RT\ln(y_{H^+}/y_{BH^+})$, (C) $RT\ln y_B$, and (D) $RT\ln(\alpha C)$. The y_B data is for 2,6-dichloro-4-nitroaniline

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