NOTE

Quantitative Assessment of Acid–Base Properties of Chloride Doped Polypyrrole by Inverse Gas Chromatography

INTRODUCTION

Fowkes and many other workers[1] have emphasized that acid–base interactions play a fundamental role in adhesion, solubility, and mixing of polymers. Several methods have been developed to study acid–base interactions of materials.[1] While microcalorimetry is a direct method to determine heats of acid–base interactions, ΔH^{AB}, other methods such as FTIR, NMR, and inverse gas chromatography (IGC) are nevertheless interesting and are currently applied to study such phenomena.

Fowkes[1] suggested the use of Drago's famous four parameter equation[2] to quantitatively assess acid–base properties of polymers:

$$-\Delta H^{AB} = E_A E_B + C_A C_B \qquad (1)$$

where E and C are the susceptibility of an acid (A) or a base (B) to undergo an electrostatic and a covalent interaction, respectively. Drago established E and C parameters for many acids and bases and thus could predict the heat of acid–base complexation for almost 1600 adducts with a precision of 0.4–0.8 kJ/mol. However E and C parameters were not available for complex materials. Over the last two decades, Fowkes[1] has determined E and C parameters for polymers, silica, glass, and metal oxides using the measurements of the heats of adsorption of well characterized probes. Following these determinations, Fowkes predicted the acid–base interaction between complex materials (e.g., silica and PMMA).

Conducting polymers constitute a novel class of materials that have many potential uses.[3] Among the conducting polymers offered to the materials scientist, polypyrrole (PPy) is interesting because of its electrical conductivity and good stability. It can be synthesized either by electrochemistry, by chemical oxidation or by chemical vapour deposition. PPy-based composites were also reported in the literature.[3] Recently, in order to understand the adhesion properties of chloride doped polypyrrole (PPyCl), we have studied its dispersive and acid–base properties by IGC[4] according to the method of Saint–Flour and Papirer.[5] In this method, the acid–base interactions

are described by I_{sp}, the so-called specific interaction parameter of the probe molecule:

$$I_{sp} = \Delta G_{ADS} - \Delta G^d \qquad (2)$$

where ΔG_{ADS} and ΔG^d are the free enthalpy of adsorption and its dispersive contribution.

We[4] showed that I_{sp} values are positive for all acidic and basic probes. This indicates a specific interaction of PPyCl with both acids and bases, suggesting that PPyCl behaves amphoterically. This behaviour might explain the good mechanical properties of PPyCl/polyurethane composites.[3] However, I_{sp} values increased with temperature yielding a positive ΔH^{AB} that is contrary to the general knowledge that acid–base interactions are exothermic. Although the method of Saint–Flour and Papirer is interesting to rapidly evaluate acid–base properties of materials, it has limitations[6] and remains at best semiquantitative.

We revise our IGC data[4] in light of the recent work of Tiburcio and Manson.[7] These authors have determined Drago's E_A and C_A parameters for untreated and base-treated glass beads by IGC. Their determination relied mainly on the following assumption:

$$\Delta H^{AB} = \Delta H_{ADS} - \Delta H^d = \Delta H_{ADS} - \Delta H_{vap} \qquad (3)$$

where ΔH_{ADS}, ΔH^d, and ΔH_{vap} are the heat of adsorption, the dispersive contribution to ΔH_{ADS}, and the heat of vaporization of the injected probe, respectively. In addition, Tiburcio and Manson[7] have modified Arnett's method[8] to evaluate ΔH^{AB} from experimental values of ΔH_{ADS}:

$$\Delta H^{AB} = (\Delta H_{exp} - \Delta H^d)_{probe} - (\Delta H_{exp} - \Delta H^d)_{model} \qquad (4)$$

where the model compound must be neutral and have a size comparable to that of the "polar" probe. Applying Turbicio and Manson's[7] modifications to Arnett's[8] equation, one determines ΔH^{AB} as follows:

$$\Delta H^{AB} = (\Delta H_{ADS} - \Delta H_{vap})_{probe}$$

$$- (\Delta H_{ADS} - \Delta H_{vap})_{model}. \qquad (5)$$

Turbicio and Manson[7] pointed out that ΔH^d in eq. (3) can be overestimated if a self-associated probe is used.

This is indeed the case for almost all polar probes. Fowkes[1] has determined ΔH_{vap}^d, the dispersive contribution to ΔH_{vap} for some usual solvents such as those used in the present work. We suggest, therefore, that eqs. (3) and (5) be modified as follows:

$$\Delta H^{AB} = \Delta H_{ADS} - \Delta H_{vap}^d \qquad (6)$$

and

$$\Delta H^{AB} = (\Delta H_{ADS} - \Delta H^d)_{\text{probe}}$$
$$- (\Delta H_{ADS} - \Delta H_{vap}^d)_{\text{model}}. \qquad (7)$$

EXPERIMENTAL

The full details of the synthesis, surface analysis by X-ray photoelectron spectroscopy and IGC measurements were reported elsewhere.[4]

RESULTS AND DISCUSSION

ΔH^{AB} values have been calculated by six methods.

Method 1: based on eq. (3) as in Tiburcio and Manson's[7] work and abbreviated TM.

Methods 2 and 3: based on Arnett's[8] method and modified by Turbicio and Manson[7] as shown in eqs. (4) and (5). We call these methods ATM1 and ATM2, respectively, for reasons outlined below.

Method 4: based on eq. (6) as we suggested above. We abbreviate it PLC for Pigois–Landureau and Chehimi.

Methods 5 and 6: based on eq. (7) and abbreviated APLC1 and APLC2, respectively. These are modifications we have made to Arnett's[8] method. APLC denotes Arnett, Pigois–Landureau, and Chehimi.

In ATM1 and APLC1, the model compound is neutral and of similar size to the probe as suggested by Turbicio and Manson.[7] In methods ATM2 and APLC2, we suggest that the model (neutral) and the polar probes have similar values of $a(\gamma_L^d)^{1/2}$. a and γ_L^d are the surface area and the dispersive contribution to the surface tension of the probe, respectively. Our choice of $a(\gamma_L^d)^{1/2}$ to compare the polar probe and the neutral model one, was inspired by the IGC method of Schultz et al.[9] for estimating the dispersive component of the free enthalpy of adsorption. The surface area (a) and $a(\gamma_L^d)^{1/2}$ values are reported in Table I.

Estimation of ΔH^{AB}

ΔH_{ADS}, ΔH_{vap}, ΔH_{vap}^d, and ΔH^{AB} are reported in Table II for n-pentane (C_5), n-hexane (C_6), carbon tetrachloride (CCl_4), chloroform $(CHCl_3)$, $tert$-butyl alcohol (t-BuOH), tetrahydrofuran (THF), and ethyl acetate (EtAc). One

Table I a and $a(Y_L^d)^{1/2}$ of the Molecular Probes

Probes	a^a	$a(Y_L^d)^{1/2\,b}$
C_5	45.5	186
C_6	51.5	221
CCl_4	46	238
$CHCl_3$	44	224
t-BuOH	—	—
THF	45	213
EtAc	48	213

[a] a in Å^2.[9]
[b] $a(Y_L^d)^{1/2}$ in $\text{Å}^2 \text{ mJ}^{1/2} \text{ m}^{-1}$.[9]

can note that the ΔH_{ADS} values are very close to ΔH_{vap} for C_5 and C_6 since these probes interact only by dispersive forces. However CCl_4, which is expected to behave in this way, has ΔH_{ADS} smaller than ΔH_{vap} and ΔH_{vap}^d. The polar probes have, on the contrary, ΔH_{ADS} exceeding their ΔH_{vap} by an amount in the range of 8.9–15.2 kJ/mol, and exceeding ΔH_{vap}^d by 14.1–22.7 kJ/mol. Thus, both the TM and PC approximations show that PPyCl is an amphoteric species, demonstrated elsewhere[4] by means of the I_{sp} values. The difference in ΔH^{AB} on going from TM to PC is greater for the most self-associated probes. ΔH^{AB}(PC) $- \Delta H^{AB}$(TM) are 1, 5.4, and 7.5 kJ/mol for $CHCl_3$, EtAc, and THF, respectively. This trend parallels the percentages of self-association (%SA)[1]: 1.6%, 18%, and 27%. This point has been qualitatively raised by Turbicio and Manson.[7] On the other hand, Fowkes[1] has advised IGC users: "In future IGC studies of the acid-base surface properties of . . . materials, it is recommended that the acidic or basic probes be chosen from those which have minimal acid–base self-association. . . ."

The determination of ΔH^{AB} using methods ATM1, ATM2, APLC1, and APLC2 show also that PPyCl interacts specifically with acids and bases. Both the ATM methods yield ΔH^{AB} values that are close to those obtained by the TM method. The same conclusion can be drawn from the PLC and APLC methods. However, APLC methods imply higher ΔH^{AB} values than ATM methods in the case of high %SA. In the case of the poorly self-associated $CHCl_3$, it is very interesting to note that the 12 determinations of ΔH^{AB} fall in the narrow range of 11.5–15.4 kJ/mol compared to 13.6–22.7 kJ/mol determined for THF. Now turning to the choice of the model compound, it is clear from Table II, that C_5 and C_6 yield similar ΔH^{AB} values for THF and EtAc. However, ΔH^{AB} can differ significantly in the case of $CHCl_3$ and t-BuOH when CCl_4 is chosen as the model probe instead of C_5 or C_6. This is due to the fact that $(\Delta H_{ADS} - \Delta H_{vap})$ and $(\Delta H_{ADS} - \Delta H_{vap}^d)$ are negative and not negligible for CCl_4. This is unfortunate because CCl_4 is the most appropriate neutral model for $CHCl_3$ and t-BuOH because its size and shape are similar. The use of C_6 as the model probe for $CHCl_3$ in methods ATM2 and APLC2, leads to ΔH^{AB} matching those determined by the TM and PLC methods.

Table II   Heats of Adsorption, Vaporization, and Acid–Base Interactions of the Molecular Probes

Probes	ΔH_{ADS}	ΔH_{vap}	ΔH^d_{vap}	ΔH^{AB}					
				TM	ATM1	ATM2	PLC	APLC1	APLC2
C_5	29.2[a]	27.6	27.6	1.6	0	0	1.6	0	
C_6	32.5[a]	31.9	31.9	0.6	0	0	0.6	0	0
CCl_4	30.6	32.4[b]	31.9[b]	−1.8	0	0	−1.3	0	0
$CHCl_3$	44.5	31.4	30.4[b]	13.1	11.5[c]	12.5[d]	14.1	12.5[c]	13.5[d]
				13.1	14.9[e]	14.9[e]	14.1	15.4[e]	15.4[e]
t-BuOH	52.5	43.6	—	8.9	7.3[c]	—	—	—	—
				8.9	10.7[e]	—	—	—	—
THF	46.0	30.8[b]	23.3[b]	15.2	13.6[c]	14.6[d]	22.7	21.1[c]	22.1[d]
EtAc	49.1	34.7	29.3[b]	14.4	12.8[c]	13.8[d]	19.8	18.2[c]	19.2[d]

All ΔH values are in kJ mol^{-1}.
ΔH_{vap}: from the CRC Handbook[10] except where mentioned.
ΔH^d_{vap}: from Fowkes[1] except for C_5 and C_6.
[a] By extrapolation of ΔH_{ADS} using n-heptane, n-octane, and n-nonane.[4]
[b] From Fowkes.[1]
[c] Using C_5 data.
[d] Using C_6 data.
[e] Using CCl_4 data.

Estimation of E and C Constants

The determination of E and C constants for PPyCl relies on the use of at least two probes of known E and C constants. As recommended by Drago,[2] we chose acidic or basic probes of fairly different C/E ratios. Table III reports E, C, and C/E ratios for the polar probes: t-BuOH, $CHCl_3$, THF, and EtAc. Since both Lewis acids and bases adsorb specifically on PPyCl, we determined E_B, C_B, E_A, and C_A constants for this conducting polymer. The use of eq. (1) together with the ΔH^{AB} values from Table II and Drago's constants from Table III leads to the estimation of E_B, C_B, E_A, and C_A for PPyCl. These values are reported in Table IV.

E_B and C_B Values

We have determined three sets of E_B and C_B values for PPyCl. It is interesting to note that the three methods gave very similar values of E_B. However, we reject the last

set because of the negative value of C_B. A negative value of C_B means endothermic acid–base interaction. The first two sets lead to values of C_B that differ by one order of magnitude. Averaged values of the two first sets are: E_B = 1.09 and C_B = 0.45, with C_B/E_B = 0.41. While C_B and C_B/E_B are very low, E_B matches the average value of 1.12 for all basic compounds studied by Drago.[2] Therefore, PPyCl behaves as a hard Lewis base and prefers to bind to hard acids of high E_A such as $CHCl_3$ or silica (E_A = 4.39, C_A = 1.14) (Fowkes[1]).

E_A and C_A Values

Table IV reports six sets of E_A and C_A values. It is interesting to note that, since the TM approximation overestimates ΔH^d, E_A and C_A are lower for the three first sets. However the three TM methods yield similar E_A values and the same C_A. From TM, ATM1, and ATM2, the averaged values are: E_A = 3.26 and C_A = 0.06, with C_A/E_A = 0.018.

The PLC, APLC1, and APLC2 methods yield higher E_A and C_A values (for the reasons outlined above) the

Table III   Drago's Parameters and C/E Ratios of the Molecular Probes

Probes	C_A/E_A	E_A	C_A	C_B/E_B	E_B	C_B
t-BuOH	0.147	2.04	0.30			
$CHCl_3$	0.053	3.02	0.16			
THF				4.37	0.98	4.27
EtAc				1.7	0.98	1.74

E_A and C_A values are in (kcal mol^{-1})$^{1/2}$.

Table IV   Drago's Parameters of PPyCl and Pyrrole

Methods	Polypyrrole			
	E_A	C_A	E_B	C_B
TM			1.03	0.08
ATM1[a]			1.14	0.81
ATM1[b]			0.94	−0.61
Average[c]			1.09	0.45
TM	3.44	0.06		
ATM1	3.04	0.06		
ATM2	3.29	0.06		
Average	3.26	0.06		
PC	4.35	0.27		
APC1	3.97	0.27		
APC2	4.2	0.27		
Average	4.17	0.27		
	Pyrrole			
Drago	2.5	0.33		

E and C values are in $(\text{kcal mol}^{-1})^{1/2}$.

[a] Method ATM1 using CCl_4 as a model probe for $CHCl_3$ and t-BuOH.

[b] Method ATM1 using C_5 as a model probe for $CHCl_3$ and t-BuOH.

[c] Average value of TM and ATM1 (CCl_4).

averages of which are: $E_A = 4.17$ and $C_A = 0.27$; with $C_A / E_A = 0.06$.

The averages of the six values of E_A and C_A for PPyCl (3.72 and 0.33, respectively) can be compared with those of pyrrole ($E_A = 2.5$, $C_A = 0.33$). We note that PPyCl has a higher E_A value whereas both C_A values are similar.

Both TM and PLC methods show that PPyCl behaves as a hard acid that prefers to bind to hard bases such as the oxygen-containing ones, e.g., poly(urethane).

CONCLUSION

A revision of our IGC work in the light of the recent developments of Turbicio and Manson[7] enabled us to quantitatively characterize the surface acid–base properties of PPyCl. For the first time we have determined E and C parameters for this conducting polymer. Since PPyCl is an amphoteric material, we thus determined E_A, C_A, E_B, and C_B values. These values show explicitly that PPyCl is a hard amphoteric material that prefers to bind to hard acids and bases. This hardness is consistent with the chemical composition of PPyCl. However, since E_A is

higher than E_B, for formulating PPyCl-based composites, PPyCl will be best mixed with Lewis bases such as polyurethane or epoxy resins. Moreover, we have shown how the determination of ΔH^{AB}, the acid–base contribution to the heat of adsorption (ΔH_{ADS}) can be affected by the degree of self association of the polar probes and thus suggested to compare ΔH_{ADS} to ΔH_{vap}^d, the dispersive contribution to the heat of vaporization, rather than the total heat of vaporization.

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