

Calculation and refinement of thermodynamic parameters from thermometric titrations. II. The neutralization enthalpies of phenols in hydro-alcoholic media

R. Forteza *, A. Caro, J.M. Estela, V. Cerdà

Department of Chemistry, University of the Balearic Islands, E-07071 Palma de Mallorca, Spain

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Abstract

Several monoprotic and polyprotic phenols were analysed by thermometric titration in a 50:50 v/v methanol/water medium. The performance of various methods for the calculation and refinement of thermodynamic parameters from thermometric titration data in the determination of the neutralization enthalpies of several phenols in hydro-alcoholic media is compared in terms of precision and the influence of the medium on the titration errors.

Keywords: Hydro-alcoholic media; Neutralization enthalpies; Phenols; Thermometric titration

1. Introduction

Thermometric titrations are widely used for the determination of inorganic acids, carboxylic acids and phenols in both aqueous and non-aqueous media [1–6]; moreover, they allow the alkalimetric titration of even very weak acids [1]. In addition, they provide precise ΔH , ΔG (pK_a) and ΔS values for ionization processes in an expeditious manner.

Non-aqueous and mixed solvents offer well-known advantages in the titration of acids and bases. Were the enthalpy of the reaction not so adversely affected by the nature of the solvent, it could make rather a useful measurement parameter in thermometric titrations since fairly low heat capacities result in steep slopes in the titration graphs. This effect was investigated in earlier papers, where the influence of the

* Corresponding author.

medium on the thermometric titration of carboxylic acids [7] and amines [8] was discussed.

Phenols have been determined thermometrically by several authors. Paris and Vial [9] determined phenol and some of its homologues by thermometric titration, after brominating to increase the acidity. Also, Vaughan and Swithenbank [10] used the acetone indicator reaction to determine phenolic hydroxyl groups using KOH in isopropyl alcohol as titrant. Alkyl phenols have been quantified by a direct-injection enthalpimetric method involving acetylation and the use of a perchloric acid-catalysed reaction [11]. Godinho et al. [12] and Celeste et al. [13] determined polyhydroxyphenolic compounds by alkalimetric and redox titration, respectively.

This paper compares the results provided by various computational methods for the determination of the neutralization enthalpies of phenols in 50:50 v/v methanol/water. The influence of the medium on the quality of the analytical results in terms of accuracy and precision, and the values of the thermodynamic parameters obtained is also discussed.

2. Experimental

2.1. Apparatus

The titration system used was described in detail elsewhere [14]. The measuring bridge used a miniature thermistor ($R_T = 100 \text{ k}\Omega$, 25°C) as temperature sensor and a Houston Instruments Omniscrite Recorder with an input impedance of $1 \text{ M}\Omega$ throughout the sensitivity range. A Crison 5-ml autoburette was also used.

2.2. Heat capacity of the cell

All titrations involved using a sample volume of 50.0 ml. The heat capacity of the system was determined under the same experimental conditions by applying a known amount of heat with the aid of an electrical calibration system. It was found to be $0.1743 \pm 0.0046 \text{ kJ } ^\circ\text{C}^{-1}$ for 50:50 v/v MeOH/H₂O.

2.3. Reagents

A KOH solution in 50:50 v/v MeOH/H₂O was made and subsequently standardized with potassium hydrogen phthalate. Organic phenols of the best available quality were also used. Analytical or HPLC grade reagents were employed throughout.

2.4. Procedure

All KOH titrations were carried out by placing the phenol (in 50:50 v/v MeOH/H₂O) in the thermometric cell and adding the reagent at a constant rate once the sample had reached thermal equilibrium. Excess titrant was added in all instances. In this way, three individual samples of each phenol were titrated with 0.42116 M KOH in 50:50 v/v MeOH/H₂O at 20°C .

3. Computational and refinement methods

The computational methods used were intended to provide approximate neutralization enthalpies that would subsequently be used as starting values for the refinement programme.

3.1. Calculation of parameters for monoprotic phenols

3.1.1. The overall heat capacity (ohc) method

This method originated from the classical calorimetric method and involves measuring the overall temperature change (determined on the enthalpigram) during the titration of n moles of the compound concerned, on the assumption of reaction completion. The associated equation is

$$\Delta H = -\frac{Q}{n} = -\frac{c\Delta T}{n} \quad (1)$$

where Q is the evolved heat and c is the heat capacity of the cell and its contents. With very weak acids or bases, reaction completion is only accomplished if a large enough excess of titrant is added, which requires graphical extrapolation and hence results in decreased accuracy and precision.

3.1.2. The point-by-point heat capacity (pbphc) method

This method allows one to use all the points in the experimental enthalpigram to calculate ΔH_N . For each point in the titration curve considered, defined by its coordinates ΔV_i and ΔT_p , one must determine the fraction of compound that is actually neutralized from the acid dissociation constant or the dissolved proton concentration.

The general equation for a monoprotic acid, considering the mass, charge and heat balances, and the expression of the dissociation constant, is

$$\frac{1}{h} = -\frac{1}{K_a} - \Delta H \frac{C_a V_0^2}{c \Delta T_i V_T h} \quad (2)$$

which corresponds to a straight line such that

$$Y_i = -\frac{1}{h}$$

and

$$X_i = \frac{C_a V_0^2}{c \Delta T_i V_T h} \quad (3)$$

where C_a and C_b are the analytical concentrations of titrand and titrant, respectively, c the heat capacity of the cell and its contents, ΔT_i the temperature change after adding $(V_T - V_0)$ ml of titrant, V_T the overall volume of the solution contained in the cell at different times during the titration, and V_0 the initial volume of the titrand solution.

The straight line obtained can be fitted to experimental data by the Gauss–Newton method in order to calculate K_a from the intercept and ΔH from the slope.

The only difficulty in calculating X_i and Y_i lies in determining the proton concentration h at each point. However, such a concentration can be most readily determined by performing a potentiometric titration in parallel with the thermometric titration. Alternatively, it can be calculated by solving the Brønsted equation for a monoprotic acid

$$h^3 + \left(K_a + \frac{C_b(V_T - V_0)}{V_T} \right) h^2 + \left(\frac{C_b(V_T - V_0) - C_a V_0}{V_T} K_a - K_w \right) h - K_a K_w = 0 \quad (4)$$

This can be accomplished, among other ways, by using the Newton–Raphson iterative method.

Proton concentrations were calculated using $pK_w = 14.74$ for a 50:50 MeOH/H₂O medium [15, 16] and the pK_a values for the different phenols, whether obtained from the literature [17] or calculated from the Hammett equation, namely $pK_a = 9.92 - 2.3 \Sigma \sigma$ [18], where σ is a constant that includes the effects of ring substituents on pK_a . The pK_a values thus obtained were extrapolated to a 50:50 MeOH/H₂O medium on the basis of published data [17, 19].

In applying the equations obtained at each point along the titration curve, the effect of dilution was taken into account, in terms not only of the analytical concentrations of titrand and titrant (C_a and C_b), but also of the heat capacity of the system.

By using various statistical criteria [20], we calculated the precision achieved: the calculated slopes and intercepts were accurate at a 95% confidence level. This method is a variant of the entropic titrations reported by Izatt et al. [21].

3.2. Calculation of parameters for diprotic phenols

3.2.1. The overall heat capacity (ohc) method

The ohc method allowed ΔH_T , ΔH_1 and ΔH_2 for several diprotic phenols to be calculated in much the same way as for monoprotic phenols above.

3.2.2. The point-by-point heat capacity (pbphc) method

With diprotic phenols, the mass, charge and heat balances (including ΔH_1 and ΔH_2 , the enthalpies of neutralization of the two protons), in addition to the expressions for the successive dissociation constants, lead to the following general equation

$$\frac{c V_T \Delta T (h^2 + K_1 h + K_1 K_2)}{V_0^2 C_a K_1 h} = \Delta H_1 + \Delta H_T \frac{K_2}{h} \quad (5)$$

which gives rise to a straight line such that

$$X_i = \frac{K_2}{h}$$

and

$$Y_i = -\frac{c V_T \Delta T_i (h^2 + K_1 h + K_1 K_2)}{V_0^2 C_a K_1 h} \quad (6)$$

This can be fitted to the experimental points by using the Gauss–Newton method in order to obtain ΔH_1 and ΔH_T from the intercept and slope, respectively.

The h values needed to calculate X_i and Y_i can be obtained by applying the Newton–Raphson method to the equation

$$h^4 + \left(\frac{C_b(V_T - V_0)}{V_T} + K_1 \right) h^3 + \left(\frac{C_b(V_T - V_0) - C_a V_0 K_1 + K_1 K_2 - K_w}{V_T} \right) h^2 + \left(\frac{C_b(V_T - V_0) - 2C_a V_0 K_1 K_2 - K_1 K_w}{V_T} \right) h - K_1 K_2 K_w = 0 \quad (7)$$

3.3. Software

The enthalpies of neutralization of monoprotic and diprotic pehnols were calculated with the aid of two computer programs, CAPUA&BI and CAPUACDI, which were written in QuickBasic and compiled for faster execution on IBM and PC-compatible computers. Both programs use the point-by-point heat capacity method. Data are input as the lengths of Y and X coordinates measured directly on the graph paper. From such data and the values of the required parameters (initial concentrations of sample and titrant, pK_a , initial sample volume, pK_w , Y and X scale transformation coefficients to ΔT and ml, respectively, the number of experimental points, etc.), the two programs create the data files used by the program for refinement of thermodynamic parameters (MINITERM). Tables 1 and 2 list typical results provided by the two programs. (The software used in this work can be obtained from SCIWARE, Banco de Programas, Departamento de Química, Universitat de les Illes Balears, E-07071 Palma de Mallorca, Spain.)

3.4. Refinement of parameters

MINITERM [22] uses the overall enthalpies and the logarithms of the overall stability constants as unknown parameters

$$U = \sum_i (\Delta T_{\text{meas},j} - \Delta T_{\text{calc},i})^2 = \sum_i \left(\Delta T_{\text{meas},i} + \left(\Delta H_M[M] + \Delta H_L[L] + \sum_j \Delta H_j B_j [M]^{q_j} [L]^{p_j} [H^+]^{r_j} \right) \frac{V_0}{C_0} \times 1000 \right)^2 \quad (8)$$

It calculates the values that result in the minimal non-weighted sum of the squared residuals (U) of the measured (ΔT_{meas}) and calculated (ΔT_{calc}) temperature increments, in addition to the probable errors. Σ_i and Σ_j denote the summations of all (q, p, r)

Table 1

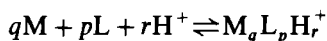
Result file created by the program CAPUA&BI for the determination of the neutralization enthalpy of 4,6-dinitro-*o*-cresol using the point-by-point heat capacity method

V_T	T	pH	$[H^+]$	X	Y	D
50.236	0.01560	5.0647	0.862E-05	0.497E+05	0.116E+06	-0.374E+05
50.266	0.01860	5.1462	0.714E-05	0.503E+05	0.140E+06	-0.173E+05
50.295	0.01980	5.2250	0.596E-05	0.566E+05	0.168E+06	-0.323E+05
50.332	0.02280	5.3215	0.477E-05	0.613E+05	0.210E+06	-0.227E+05
50.369	0.02580	5.4181	0.382E-05	0.676E+05	0.262E+06	-0.134E+05
50.413	0.02880	5.5377	0.290E-05	0.797E+05	0.345E+06	-0.125E+05
50.443	0.03060	5.6219	0.239E-05	0.910E+05	0.419E+06	-0.156E+05
50.472	0.03360	5.7119	0.194E-05	0.102E+06	0.515E+06	0.669E+04
50.516	0.03660	5.8647	0.137E-05	0.133E+06	0.732E+06	0.134E+05
50.553	0.03930	6.0195	0.956E-06	0.177E+06	0.105E+07	0.297E+05
50.575	0.04080	6.1334	0.736E-06	0.221E+06	0.136E+07	0.413E+05
50.605	0.04260	6.3312	0.466E-06	0.334E+06	0.214E+07	0.603E+05
50.664	0.04500	8.9009	0.126E-08	0.117E+09	0.796E+09	-0.194E+03

Run 3: $[KOH] = 0.42116 M$; $C_s = 0.0055909 M$ 50:50 MeOH/H₂O; initial heat capacity = 0.04165 kcal °C⁻¹; $V_0 = 50 ml$; $pK_a = 5.32$; $K_a = 5.43E-06$, $pK_a = 5.3$; $\Delta H = -6.80 \pm 0.03 kcal mol^{-1}$; $r = 1.0000$; $U = 1.0283E+10$; $\sigma = 3.0574E+04$; $rsd = 0.0457$.

complex species and experimental points, respectively, ΔH_M and ΔH_L are the apparent dilution enthalpies of the complex species (in cal mol⁻¹), V_0 the initial volume (ml) and C_0 the initial heat capacity (in cal °C⁻¹).

MINITERM considers the following equilibrium



for which

$$\beta = \frac{[M_q L_p H_r^+]}{[M]^q [L]^p [H^+]^r}$$

and

$$\Delta H_j = -n_j Q_j = -\frac{n_j C_0 V_{tot} \Delta T}{V_0}$$

Because zero values for q are allowed, equilibria involving protonation of amines ($+r$, $+\log \beta^H$) or deprotonation of carboxylic acids or phenols ($-r$, $-\log \beta^H$) may be considered, i.e. only $H_r L_p$ complexes are formed.

MINITERM can deal with a maximum of 80 experimental points, measured off the titration curve, and 8 species. Therefore, the maximum number of parameters it can handle is 18 because the last two parameters are always the dilution enthalpies of the reactants M and L, in that order.

Table 2

Result file created by the program CAPUACDI for the neutralization enthalpy of gallic acid using the point-by-point heat capacity method

V_T	T	pH	$[H^+]$	X	Y	D
50.044	0.00180	4.095	8.038E-05	0.00	-3.34	3.761
50.088	0.00660	4.358	4.387E-05	0.00	-7.04	0.056
50.131	0.01020	4.545	2.849E-05	0.00	-7.50	-0.402
50.190	0.01200	4.736	1.837E-05	0.00	-6.20	0.896
50.234	0.01740	4.855	1.398E-05	0.00	-7.35	-0.247
50.277	0.02100	4.961	1.094E-05	0.00	-7.49	-0.392
50.336	0.02460	5.091	8.109E-06	0.00	-7.27	-0.172
50.380	0.02880	5.184	6.550E-06	0.00	-7.54	-0.444
50.438	0.03300	5.305	4.951E-06	0.00	-7.51	-0.405
50.482	0.03660	5.397	4.005E-06	0.00	-7.58	-0.477
50.526	0.04080	5.493	3.216E-06	0.00	-7.75	-0.651
50.584	0.04440	5.630	2.347E-06	0.00	-7.60	-0.502
50.628	0.04860	5.745	1.801E-06	0.00	-7.75	-0.649
50.672	0.05220	5.877	1.326E-06	0.00	-7.79	-0.688
50.730	0.05580	6.107	7.816E-07	0.00	-7.67	-0.610
50.818	0.06060	6.929	1.178E-07	0.00	-7.47	-0.356
50.876	0.06240	8.433	3.687E-09	0.05	-7.94	-0.257
50.920	0.06300	8.762	1.729E-09	0.12	-8.49	-0.141
50.964	0.06420	8.966	1.081E-09	0.18	-9.20	-0.097
51.022	0.06540	9.164	6.849E-10	0.29	-10.22	0.032
51.066	0.06660	9.285	5.183E-10	0.38	-11.18	0.095
51.110	0.06780	9.393	4.045E-10	0.49	-12.28	0.167
51.168	0.06900	9.524	2.991E-10	0.67	-13.96	0.362
51.212	0.07080	9.617	2.415E-10	0.83	-15.71	0.340
51.256	0.07260	9.708	1.958E-10	1.02	-17.83	0.313
51.314	0.07440	9.830	1.479E-10	1.35	-21.28	0.436
51.358	0.07680	9.924	1.190E-10	1.68	-25.05	0.213
51.402	0.07860	10.024	9.460E-11	2.11	-29.80	0.143
51.460	0.08040	10.171	6.748E-11	2.96	-38.84	0.287
51.504	0.08220	10.298	5.036E-11	3.96	-49.84	0.174
51.548	0.08400	10.449	3.555E-11	5.61	-67.94	-0.039
51.606	0.08580	10.718	1.916E-11	10.41	-119.91	-0.007
51.650	0.08700	10.999	1.002E-11	19.91	-222.92	-0.171

Run 3: $[KOH] = 0.42116$ M; $C_s = 0.00702242$ M 50:50 MeOH/H₂O; initial heat capacity, 0.04165 kcal °C⁻¹; $V_0 = 50$ ml; $pK_1 = 5.26$; $pK_2 = 9.70$; $\Delta H_1 = -7.10 \pm 0.29$ kcal mol⁻¹; $\Delta H_T = -10.83 \pm 0.07$ kcal mol⁻¹; $r = -0.9998$; $E = +7.7496E-01$.

MINITERM allows the simultaneous refinement of up to four arbitrarily chosen parameters. When $\log \beta$ and ΔH are refined simultaneously, the serial numbers of the latter parameter must always precede those of the former.

Tables 3 and 4 show the results obtained in the refinement of enthalpies from an experimental titration of a monoprotic and a diprotic phenol, respectively.

Table 3

Result file created by the program MINITERM by refining the enthalpies and pK values of 4,6-dinitro-*o*-cresol in 50:50 v/v MeOH/H₂O

mL	pH	Tot. M	Tot. L	ΔT_m	ΔT_c	<i>D</i>
0.044	4.241	0.100E+01	0.559E-02	0.00240	0.00334	-0.00094
0.074	4.445	0.100E+01	0.558E-02	0.00360	0.00513	-0.00153
0.103	4.600	0.100E+01	0.558E-02	0.00540	0.00701	-0.00161
0.118	4.666	0.100E+01	0.558E-02	0.00840	0.00796	0.00044
0.147	4.783	0.100E+01	0.557E-02	0.00960	0.00991	-0.00031
0.177	4.886	0.100E+01	0.557E-02	0.01080	0.01189	-0.00109
0.192	4.933	0.100E+01	0.557E-02	0.01260	0.01288	-0.00028
0.236	5.065	0.100E+01	0.556E-02	0.01560	0.01590	-0.00030
0.265	5.146	0.100E+01	0.556E-02	0.01860	0.01792	0.00068
0.295	5.225	0.100E+01	0.556E-02	0.01980	0.01998	-0.00018
0.332	5.321	0.100E+01	0.555E-02	0.02280	0.02256	0.00024
0.369	5.418	0.100E+01	0.555E-02	0.02580	0.02519	0.00061
0.413	5.538	0.100E+01	0.555E-02	0.02880	0.02837	0.00043
0.442	5.622	0.100E+01	0.554E-02	0.03060	0.03051	0.00009
0.472	5.712	0.100E+01	0.554E-02	0.03360	0.03266	0.00094
0.516	5.865	0.100E+01	0.553E-02	0.03660	0.03594	0.00066
0.553	6.020	0.100E+01	0.553E-02	0.03930	0.03869	0.00061
0.575	6.133	0.100E+01	0.553E-02	0.04080	0.04035	0.00045
0.605	6.331	0.100E+01	0.552E-02	0.04260	0.04259	0.00001
0.664	8.901	0.100E+01	0.552E-02	0.04500	0.04711	-0.00211
<i>Q</i> ^a	<i>P</i> ^a	<i>R</i> ^a	$\log \beta$	$\Delta H/(\text{cal mol}^{-1})$		
0	1	-1	-5.363	-7114		

^a *Q*, *P* and *R* are the stoichiometric coefficients of the metal, ligand and proton, respectively.

$\Delta H_{\text{metal}} = 0.000\text{E}+00$; $\Delta H_{\text{ligand}} = 0.000\text{E}+00$; root of residuals = 0.1492E-04; SD = 0.9103E-03.

4. Results and discussion

4.1. Titration curves and errors

Figs. 1–3 show the titration curves obtained for several phenols in a 50:50 v/v MeOH/H₂O medium. As can be seen, most of the phenols, e.g. those bearing cyano, nitro and chloro substituents, gave rise to sharp end-points. However, some dimethoxy-, dimethyl- and trimethylphenols provide ill-defined end-points owing to the roundness of their titration curves. The two extremes are reflected in the data listed in Table 5; as can be seen, the good results obtained for cyano- and nitrophenols, among others, are in contrast with those yielded by 2, 3, 5- and 2, 3, 6-trimethylphenol, which can be ascribed to the shape of the thermometric curves they exhibit. However,

Table 4

Result file created by the program MINITERM by refining the enthalpies and pK values of gallic acid in 50:50 v/v MeOH/H₂O

mL	pH	Tot. M	Tot. L	ΔT_m	ΔT_c	D
0.044	4.095	0.100E+01	0.702E-02	0.00180	0.00417	-0.00237
0.088	4.358	0.100E+01	0.701E-02	0.00660	0.00722	-0.00062
0.131	4.545	0.100E+01	0.700E-02	0.01020	0.01045	-0.00025
0.190	4.736	0.100E+01	0.700E-02	0.01200	0.01483	-0.00283
0.234	4.855	0.100E+01	0.699E-02	0.01740	0.01812	-0.00072
0.277	4.961	0.100E+01	0.698E-02	0.02100	0.02139	-0.00039
0.336	5.091	0.100E+01	0.698E-02	0.02460	0.02573	-0.00113
0.380	5.184	0.100E+01	0.697E-02	0.02880	0.02897	-0.00017
0.438	5.305	0.100E+01	0.696E-02	0.03300	0.03325	-0.00025
0.482	5.397	0.100E+01	0.696E-02	0.03660	0.03644	0.00016
0.526	5.493	0.100E+01	0.695E-02	0.04080	0.03964	0.00116
0.584	5.630	0.100E+01	0.694E-02	0.04440	0.04385	0.00055
0.628	5.745	0.100E+01	0.694E-02	0.04860	0.04698	0.00162
0.672	5.877	0.100E+01	0.693E-02	0.05220	0.05007	0.00213
0.730	6.107	0.100E+01	0.692E-02	0.05580	0.05419	0.00161
0.774	6.369	0.100E+01	0.692E-02	0.05940	0.05726	0.00214
0.818	6.929	0.100E+01	0.691E-02	0.06060	0.06026	0.00034
0.876	8.433	0.100E+01	0.690E-02	0.06240	0.06251	-0.00011
0.920	8.762	0.100E+01	0.690E-02	0.06300	0.06369	-0.00069
0.964	8.966	0.100E+01	0.689E-02	0.06420	0.06488	-0.00068
1.022	9.164	0.100E+01	0.688E-02	0.06540	0.06650	-0.00110
1.066	9.285	0.100E+01	0.688E-02	0.06660	0.06774	-0.00114
1.110	9.393	0.100E+01	0.687E-02	0.06780	0.06901	-0.00121
1.168	9.524	0.100E+01	0.688E-02	0.06900	0.07074	-0.00174
1.212	9.617	0.100E+01	0.686E-02	0.07080	0.07207	-0.00127
1.256	9.708	0.100E+01	0.685E-02	0.07260	0.07343	-0.00083
1.314	9.830	0.100E+01	0.684E-02	0.07440	0.07528	-0.00088
1.358	9.924	0.100E+01	0.684E-02	0.07680	0.07670	0.00010
1.402	10.024	0.100E+01	0.683E-02	0.07860	0.07815	0.00045
1.460	10.171	0.100E+01	0.682E-02	0.08040	0.08013	0.00027
1.504	10.298	0.100E+01	0.682E-02	0.08220	0.08164	0.00056
1.548	10.449	0.100E+01	0.681E-02	0.08400	0.08314	0.00086
1.606	10.718	0.100E+01	0.680E-02	0.08580	0.08510	0.00070
1.650	10.999	0.100E+01	0.680E-02	0.08700	0.08634	0.00066
Q^a	P^a	R^a	$\log \beta$	$\Delta H/(\text{cal mol}^{-1})$		
0	1	-1	-5.241	-7409		
0	1	-2	-15.034	-10777		

^a Q , P and R are the stoichiometric coefficients of the metal, ligand and proton, respectively.

$\Delta H_{\text{metal}} = 0.000E+00$; $\Delta H_{\text{ligand}} = 0.000E+00$; root of residuals = 0.4549E-04; SD = 0.1211E-02.

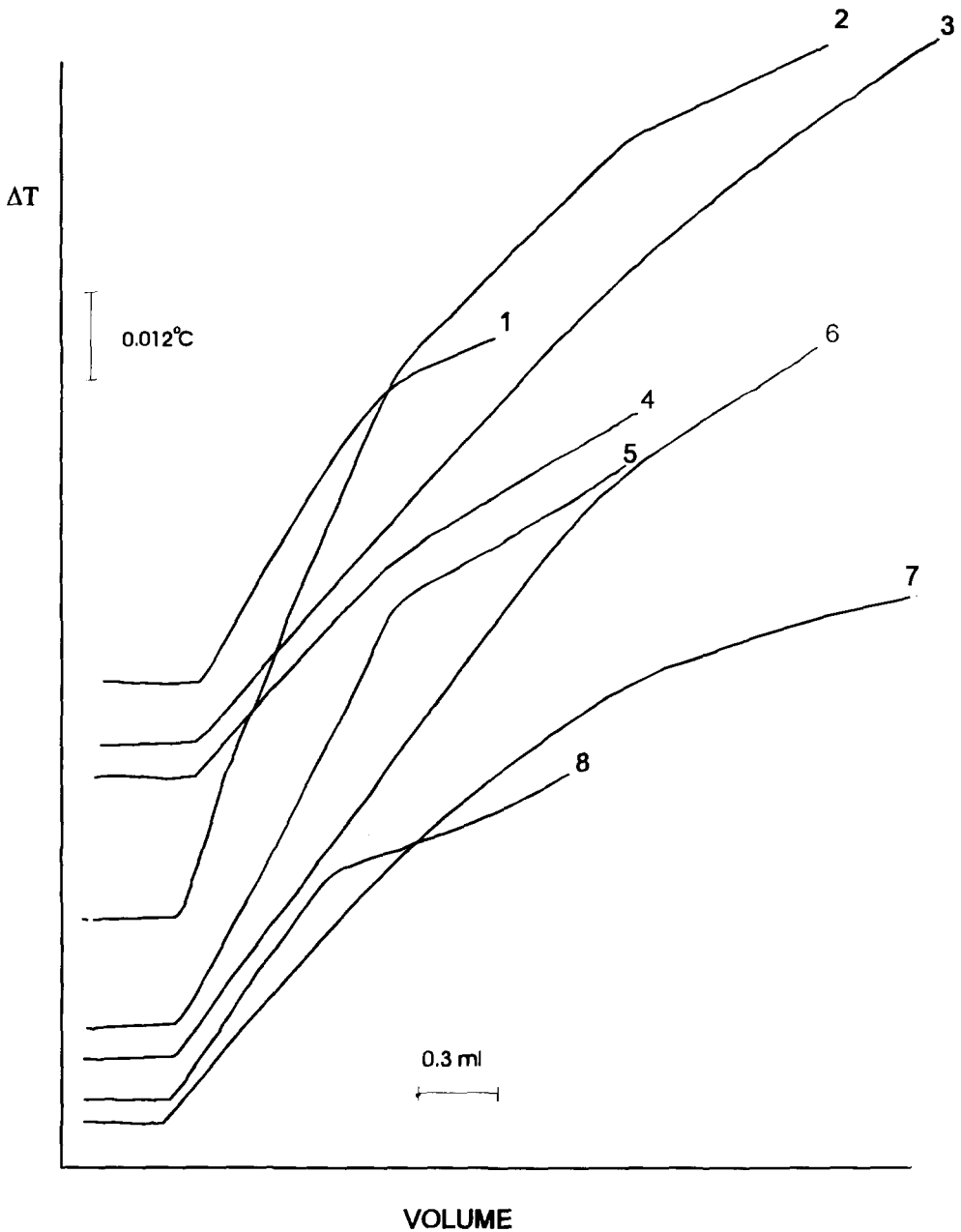


Fig. 1. Thermometric curves obtained in 50% v/v MeOH/H₂O for: (1) phenol; (2) protocatechuic acid; (3) 2,4-dimethylphenol; (4) 4-chloro-3-methylphenol; (5) 2,4,6-trichlorophenol; (6) 4-bromophenol; (7) hydroquinone; (8) 2,4-dichlorophenol. The ΔT and ΔV scales ($[\text{KOH}] = 0.42116 \text{ M}$) used are shown in the figure, except for phenol ($\Delta T = 0.060^\circ\text{C}$ and $\Delta V = 1.2 \text{ ml}$, $[\text{KOH}] = 0.84232 \text{ M}$) and 2,4-dimethylphenol ($\Delta T = 0.024^\circ\text{C}$ and $\Delta V = 0.3 \text{ ml}$, $[\text{KOH}] = 0.84232 \text{ M}$).

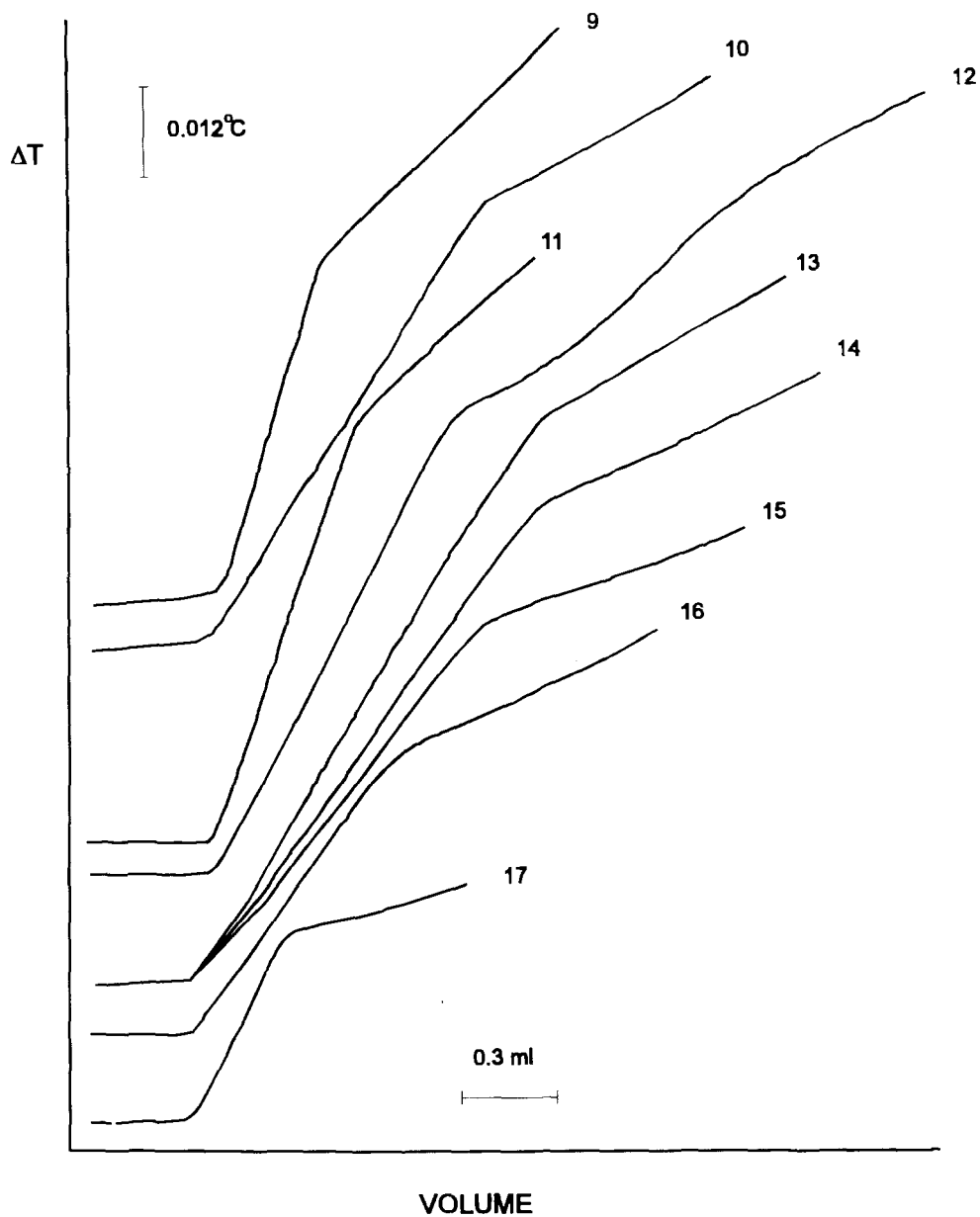


Fig. 2. Thermometric curves obtained in 50% v/v MeOH/H₂O for: (9) 4-nitrophenol; (10) 2-nitrophenol; (11) 2-chlorophenol; (12) gallic acid; (13) 2-cyanophenol; (14) 4-cyanophenol; (15) 3-cyanophenol; (16) 3-nitrophenol; (17) pentachlorophenol. The ΔT and ΔV scales ($[\text{KOH}] = 0.42116 \text{ M}$) used are shown in the figure, except for 2-chlorophenol ($\Delta T = 0.024^\circ\text{C}$ and $\Delta V = 1.2 \text{ ml}$, $[\text{KOH}] = 0.84232 \text{ M}$) and 4-nitrophenol ($\Delta T = 0.012^\circ\text{C}$ and $\Delta V = 0.3 \text{ ml}$, $[\text{KOH}] = 0.84232 \text{ M}$).

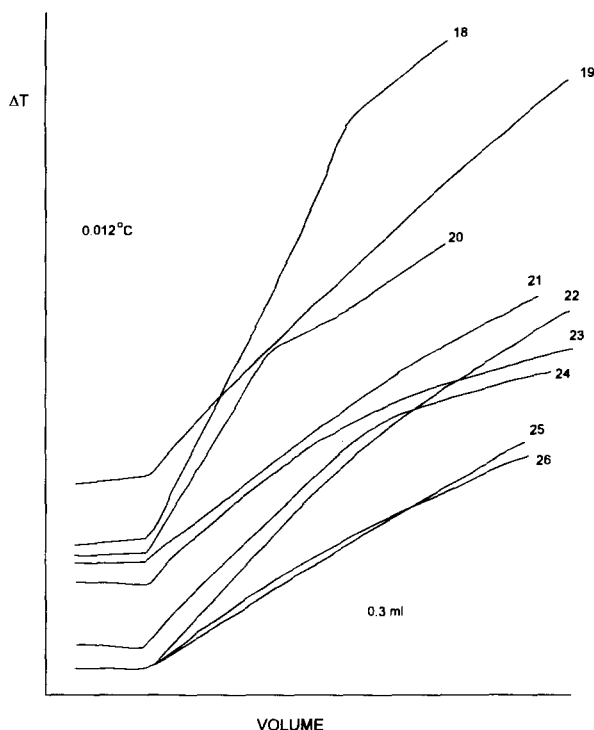


Fig. 3. Thermometric curves obtained in 50% v/v MeOH/H₂O for: (18) 2,4-dinitrophenol; (19) 2,3,5-trimethylphenol; (20) 2,4,6-dinitro-*o*-cresol; (21) 2,6-dimethylphenol; (22) resorcinol; (23) 3,4-dimethoxyphenol; (24) 3,5-dimethoxyphenol; (25) 2,3,6-trimethylphenol; (26) 2,6-dimethoxyphenol. The ΔT and ΔV scales ($[KOH] = 0.42116 M$) used are shown in the figure.

Table 5

Titration errors and precision in the determination of various phenols in 50:50 MeOH/H₂O

Compound	Sample/mmol	Found/mmol	Error %	rsd %
Phenol	2.0176	1.9800	-1.82	0.71
4-Bromophenol	0.3228	0.3399	5.29	6.47
2-Chlorophenol	0.9746	0.9948	3.60	6.94
2,4-Dichlorophenol	0.2180	0.2317	6.28	1.29
2,4,6-Trichlorophenol	0.3065	0.3190	4.08	2.92
Pentachlorophenol	0.0705	0.0753	6.77	2.39
4-Chloro-3-methylphenol	0.2980	0.2984	0.14	4.62
2-Cyanophenol	0.4554	0.4521	-0.72	1.57
3-Cyanophenol	0.3728	0.3794	1.77	2.53
4-Cyanophenol	0.4531	0.4555	0.53	1.36
2-Nitrophenol	0.3589	0.3694	2.93	2.92

Table 5 (Continued).

Compound	Sample/mmol	Found/mmol	Error %	rsd %
3-Nitrophenol	0.2564	0.2601	1.41	0.37
4-Nitrophenol	0.2611	0.2752	5.40	1.74
2,4-Dinitrophenol	0.4954	0.4713	-4.80	0.32
4,6-Dinitro- <i>o</i> -cresol	0.1575	0.1630	3.48	4.18
2,4-Dimethylphenol	1.6220	1.5389	-5.10	5.04
2,6-Dimethylphenol	0.4195	0.4102	-2.22	9.05
2,3,5-Trimethylphenol	0.3936	0.4349	10.50	6.57
2,3,6-Trimethylphenol	0.4856	0.4432	-8.74	5.68
2,6-Dimethoxyphenol	0.3760	0.3738	-0.58	2.65
3,4-Dimethoxyphenol	0.2978	0.3004	0.87	6.11
3,5-Dimethoxyphenol	0.2842	0.2999	5.49	4.87
Hydroquinone	0.7713	0.8212	6.50	5.84
Resorcinol	0.4110	0.4174	1.58	4.70
Gallic Acid	0.3511	0.3352 ^a	-4.54	1.38
		0.3588 ^b	2.19	1.65
Protocatechuic Acid	0.4647	0.4441 ^a	-4.43	0.90
		0.4319 ^b	-7.06	1.72

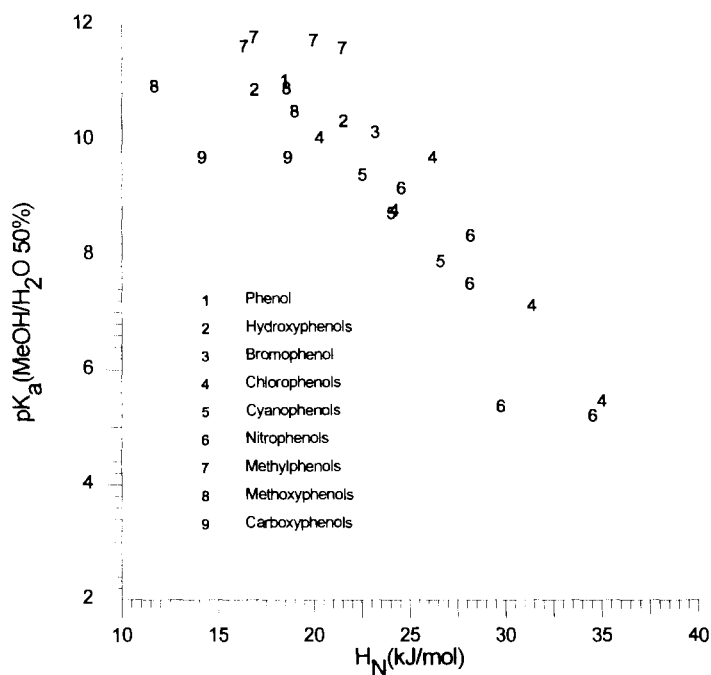
^a First equivalence point.^b Second equivalence point.Fig. 4. Plot of pK_a for several phenols against their enthalpies in 50% v/v MeOH/H₂O.

Table 6
Thermodynamic parameters of the phenols studied in 50:50 v/v MeOH/H₂O; ΔH values in kJ mol⁻¹

Sample	ohc method	pbphc method	MINITERM	pK _a
Phenol	$\Delta H = -18.41$	$\Delta H = -19.33 \pm 0.29$ $r = 0.9998$	$\Delta H = -18.41 \pm 0.21$ $pK_a = 11.03, \sigma = 4.671 \times 10^{-3}$ $U = 2.182 \times 10^{-4}$	10.96
4-Bromophenol	$\Delta H = -20.54$	$\Delta H = -23.72 \pm 0.29$ $r = 0.9999$	$\Delta H = -23.18 \pm 0.12$ $pK_a = 10.13, \sigma = 7.511 \times 10^{-4}$ $U = 7.335 \times 10^{-6}$	10.19
2-Chlorophenol	$\Delta H = -22.13$	$\Delta H = -26.82 \pm 0.67$ $r = 0.9998$	$\Delta H = -26.19 \pm 0.21$ $pK_a = 9.70, \sigma = 1.954 \times 10^{-3}$ $U = 3.054 \times 10^{-5}$	9.79
2,4-Dichlorophenol	$\Delta H = -25.06$	$\Delta H = -24.27 \pm 0.33$ $r = 0.9998$	$\Delta H = -24.18 \pm 0.16$ $pK_a = 8.78, \sigma = 3.198 \times 10^{-4}$ $U = 1.125 \times 10^{-6}$	8.89
2,4,6-Trichlorophenol	$\Delta H = -32.22$	$\Delta H = -33.01 \pm 1.13$ $r = 0.9999$	$\Delta H = -31.38 \pm 0.68$ $pK_a = 7.12, \sigma = 1.340 \times 10^{-3}$ $U = 7.183 \times 10^{-6}$	7.35
Pentachlorophenol	$\Delta H = -32.97$	$\Delta H = -35.35 \pm 2.68$ $r = 0.9985$	$\Delta H = -35.02 \pm 0.40$ $pK_a = 5.46, \sigma = 2.489 \times 10^{-4}$ $U = 2.478 \times 10^{-7}$	5.70
4-Chloro-3-methylphenol	$\Delta H = -19.00$	$\Delta H = -20.96 \pm 0.29$ $r = 0.9999$	$\Delta H = -20.25 \pm 0.20$ $pK_a = 10.04, \sigma = 6.799 \times 10^{-4}$ $U = 5.085 \times 10^{-6}$	10.27
2-Cyanophenol	$\Delta H = -26.02$	$\Delta H = -26.40 \pm 0.08$ $r = 1.0000$	$\Delta H = -26.61 \pm 0.04$ $pK_a = 7.89, \sigma = 3.368 \times 10^{-4}$ $U = 1.702 \times 10^{-6}$	7.86
3-Cyanophenol	$\Delta H = -22.43$	$\Delta H = -22.30 \pm 0.04$ $r = 1.0000$	$\Delta H = -22.51 \pm 0.04$ $pK_a = 9.39, \sigma = 3.010 \times 10^{-4}$ $U = 1.269 \times 10^{-6}$	9.36
4-Cyanophenol	$\Delta H = -23.68$	$\Delta H = -24.10 \pm 0.08$ $r = 1.0000$	$\Delta H = -24.02 \pm 0.12$ $pK_a = 8.73, \sigma = 5.058 \times 10^{-4}$ $U = 3.582 \times 10^{-6}$	8.70
2-Nitrophenol	$\Delta H = -27.95$	$\Delta H = -27.95 \pm 0.42$ $r = 0.9999$	$\Delta H = -28.16 \pm 0.12$ $pK_a = 8.34, \sigma = 4.170 \times 10^{-4}$ $U = 1.391 \times 10^{-6}$	8.28
3-Nitrophenol	$\Delta H = -24.27$	$\Delta H = -24.64 \pm 0.50$ $r = 0.9998$	$\Delta H = -24.56 \pm 0.12$ $pK_a = 9.16, \sigma = 3.878 \times 10^{-4}$ $U = 1.353 \times 10^{-6}$	9.26
4-Nitrophenol	$\Delta H = -27.86$	$\Delta H = -28.70 \pm 0.79$ $r = 0.9999$	$\Delta H = -28.12 \pm 0.38$ $pK_a = 7.50, \sigma = 7.122 \times 10^{-4}$ $U = 2.029 \times 10^{-6}$	7.72
2,4-Dinitrophenol	$\Delta H = -31.46$	$\Delta H = -34.18 \pm 0.17$ $r = 1.0000$	$\Delta H = -34.52 \pm 0.25$ $pK_a = 5.20, \sigma = 1.548 \times 10^{-3}$ $U = 3.594 \times 10^{-5}$	5.11
4,6-Dinitro- <i>o</i> -cresol	$\Delta H = -29.96$	$\Delta H = -28.45 \pm 0.01$ $r = 1.0000$	$\Delta H = -29.75 \pm 0.21$ $pK_a = 5.36, \sigma = 9.103 \times 10^{-4}$ $U = 1.492 \times 10^{-5}$ $\Delta H = -21.46 \pm 0.06$	5.32

Table 6 (Continued)

Sample	ohc method	pbphc method	MINITERM	pK _a
2,4-Dimethylphenol	$\Delta H = -18.41$	$\Delta H = -21.67 \pm 0.29$ $r = 0.9999$	$pK_a = 11.58, \sigma = 1.075 \times 10^{-3}$ $U = 1.272 \times 10^{-5}$ $\Delta H = -16.32 \pm 0.08$	11.52
2,6-Dimethylphenol	$\Delta H = -12.97$	$\Delta H = -16.40 \pm 0.63$ $r = 0.9987$	$pK_a = 11.62, \sigma = 4.628 \times 10^{-4}$ $U = 2.784 \times 10^{-6}$ $\Delta H = -19.96 \pm 0.12$	11.58
2,3,5-Trimethylphenol	$\Delta H = -17.53$	$\Delta H = -20.08 \pm 0.96$ $r = 0.9976$	$pK_a = 11.72, \sigma = 4.701 \times 10^{-4}$ $U = 2.873 \times 10^{-6}$ $\Delta H = -16.86 \pm 0.12$	11.67
2,3,6-Trimethylphenol	$\Delta H = -12.68$	$\Delta H = -17.86 \pm 1.34$ $r = 0.9952$	$pK_a = 11.78, \sigma = 7.032 \times 10^{-3}$ $U = 7.912 \times 10^{-6}$ $\Delta H = -11.67 \pm 0.07$	10.92
2,6-Dimethoxyphenol	$\Delta H = -10.84$	$\Delta H = -12.05 \pm 0.33$ $r = 0.9994$	$pK_a = 10.93, \sigma = 2.976 \times 10^{-4}$ $U = 1.062 \times 10^{-6}$ $\Delta H = -18.54 \pm 0.17$	10.92
3,4-Dimethoxyphenol	$\Delta H = -18.07$	$\Delta H = -19.33 \pm 0.79$ $r = 0.9985$	$pK_a = 10.89, \sigma = 6.982 \times 10^{-4}$ $U = 6.337 \times 10^{-6}$ $\Delta H = -18.99 \pm 0.12$	10.92
3,5-Dimethoxyphenol	$\Delta H = -19.12$	$\Delta H = -19.41 \pm 0.21$ $r = 0.9999$	$pK_a = 10.49, \sigma = 5.173 \times 10^{-4}$ $U = 3.211 \times 10^{-6}$ $\Delta H = -16.86 \pm 0.17$	10.43
Hydroquinone	$\Delta H = -15.61$	$\Delta H = -17.53 \pm 0.21$ $r = 0.9999$	$pK_a = 10.87, \sigma = 1.720 \times 10^{-3}$ $U = 5.030 \times 10^{-5}$ $\Delta H = -21.51 \pm 0.04$	10.85
Resorcinol	$\Delta H = -19.16$	$\Delta H = -21.63 \pm 0.12$ $r = 1.0000$	$pK_a = 10.32, \sigma = 2.240 \times 10^{-4}$ $U = 5.518 \times 10^{-7}$ $\Delta H_1 = -30.96 \pm 0.19$	10.30
Gallic Acid	$\Delta H_1 = -29.79$ $\Delta H_T = -44.10$	$\Delta H_1 = -29.71 \pm 1.21$ $\Delta H_T = -45.31 \pm 0.29$ $r = 0.9998$	$\Delta H_T = -45.10 \pm 0.29$ $pK_{a,1} = 5.24, pK_{a,2} = 9.79$ $\sigma = 1.211 \times 10^{-3}, U = 4.549 \times 10^{-5}$ $\Delta H_1 = -39.46 \pm 0.12$	5.26 9.70
Protocatechuic Acid	$\Delta H_1 = -35.98$ $\Delta H_T = -51.46$	$\Delta H_1 = -40.46 \pm 0.92$ $\Delta H_T = -54.22 \pm 1.38$ $r = 0.9990$	$\Delta H_T = -58.07 \pm 0.38$ $pK_{a,1} = 5.24, pK_{a,2} = 9.83$ $\sigma = 7.778 \times 10^{-4}, U = 1.391 \times 10^{-5}$	5.34 9.70

ohc = overall heat capacity; pbphc = point-by-point heat capacity.

some phenols provided results that were inconsistent with those expected from their titration curves, e.g. pentachlorophenol, which is scarcely soluble even in the hydroalcoholic medium used.

The thermometric titration curves obtained for hydroquinone and resorcinol show a single end-point that corresponds to the neutralization of the sole phenolic group. However, gallic and protocatechuic acids yield two end-points that correspond to the neutralization of a carboxylic and a phenolic group; none of the other hydroxyl groups appear to be titrated.

4.2. Neutralization enthalpies

Table 6 lists the neutralization enthalpies calculated by using the above-described methods together with their MINITERM-refined values. As a rule, the results provided by the different fitting methods are quite consistent, as are the calculated and refined neutralization enthalpies. Fig. 4 shows the relationship between pK_a and the enthalpies obtained for the different phenols studied in a 50:50 MeOH/H₂O medium according to the type of ring substituent.

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