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THE ENTHALPIES OF DILUTION OF AQUEOUS SOLUTIONS CONTAINING CATECHOL, RESORCINOL OR PYROGALLOL AT 298.15 K

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ABSTRACT

The enthalpies of dilution at 298.15 K of aqueous solutions containing catechol, resorcinol or pyrogallol have been determined. The results have been treated to obtain the homotactic enthalpic virial coefficients. The markedly different values obtained indicate that there are quite dissimilar molecular mechanisms operating in the association of the different phenols.

INTRODUCTION

We are currently involved in an investigation into the nature of the interactions which occur between proteins and naturally occurring phenolic compounds [1–4]. As part of this investigation it was necessary to determine the enthalpies of dilution of the simple phenols catechol (benzene-1,2-diol), resorcinol (benzene-1,3-diol) and pyrogallol (benzene-1,2,3-triol). The results obtained have some interest in their own right in that they allow a simple and straightforward test of a group-additivity approach [5] to the solution chemistry thermodynamics of organic molecules in aqueous systems. This approach works remarkably well for systems containing a wide range of solutes including alcohols [5–8], some sugars [5–9], amides [5,10–12], acids [13], substituted peptides [14–21] and electrolytes [22]. It is clear however that it will not be applicable in situations where steric hindrance, intramolecular interactions and cooperative effects occur [5,23]. It was considered at the outset of this present work that the phenols studied might well show some rather specific effects because of the relative positions of the hydroxyl groups on the aromatic rings and this is borne out by the experimental results obtained.

EXPERIMENTAL

The experimental procedures used for obtaining the enthalpies of dilution are given elsewhere [14]. The output from the LKB batch microcalorimeter used was modified so that the heat flow–EMF signal from the calorimeter block was fed via an amplifier, through an interface to a microprocessor which was programmed to integrate the total signal. The operating temperature of the calorimeter was (298.15 ± 0.01) K.

TABLE 1

Experimental enthalpies of dilution of resorcinol, catechol and pyrogallol solutions at 298.15 K

m_A (mol kg^{-1})	m'_A (mol kg^{-1})	10^3 n (mol)	ΔH (mJ)
Resorcinol			
0.9996	0.6208	3.766	583
0.9996	0.7630	3.760	332
0.9996	0.3748	1.863	537
0.9996	0.1889	0.999	430
0.9996	0.1346	0.641	292
0.9996	0.2106	1.085	447
0.5001	0.2456	1.075	173
0.5001	0.1108	0.592	139
0.5001	0.0989	0.335	97.1
0.5001	0.0700	0.339	102
0.1990	0.0979	0.423	36.7
0.1990	0.0696	0.335	38.8
0.1990	0.0413	0.219	32.8
Catechol			
1.0009	0.3860	2.001	−546
1.0009	0.7553	3.889	−454
1.0009	0.2043	1.044	−399
0.9886	0.6468	3.878	−439
1.0251	0.2048	0.786	−351
1.0251	0.1163	0.527	−253
0.4986	0.2422	1.017	−133
0.4986	0.0637	0.306	−61.1
0.1997	0.0980	0.411	−14.9
Pyrogallol			
0.9976	0.4775	1.896	−120
0.9976	0.6447	3.772	−106
0.9976	0.7880	3.752	−99.2
0.9976	0.7311	2.869	−91.0
0.9976	0.1908	0.954	−46.0
0.9982	0.4725	1.847	−123
0.9982	0.6479	3.796	−116
0.9982	0.3117	1.875	−96.2
0.9982	0.7211	2.855	−92.6
0.9982	0.1052	0.493	−33.3
0.4949	0.3232	1.949	−34.6
0.4949	0.3629	1.472	−33.0
0.4949	0.1633	0.981	−29.2
0.4949	0.1616	0.970	−27.8
0.5012	0.0957	0.479	−18.3

The resorcinol and pyrogallol used were of analytical reagent grade and both were dried over P_2O_5 for at least 24 h before use. Reagent grade catechol was purified by sublimation and similarly dried over P_2O_5. All of the phenols were stored under conditions which minimised any contact with light.

All of the phenols used have a tendency to undergo oxidation reactions in the presence of oxygen so as to minimise such reactions, the experiments were performed on solutions from which oxygen was removed. The calorimeter was also flushed with nitrogen prior to the dilution experiments.

RESULTS

The thermodynamic formalism used has been given in detail elsewhere [14]. The excess enthalpy per kilogram of solvent (H^{ex}) may be represented as a virial expansion in the molality (m_A) of the solute A

$$H^{ex} = h_{AA}m_A^2 + h_{AAA}m_A^3 + \dots \tag{1}$$

where the enthalpic virial coefficients (h_{AA}, h_{AAA}) represent interactions between the subscripted species. These coefficients are readily obtained from enthalpy of dilution experiments since it can be shown [14] that in the dilution of a solution containing n moles of solute from an initial molality m_A to a final molality m'_A, the enthalpy change (ΔH) is given by

$$\Delta H = n(m'_A - m_A)[h_{AA} + (m'_A + m_A)h_{AAA} + \dots] \tag{2}$$

The experimental results obtained on the three systems investigated are given in Table 1 and these were each fitted to eqn. (2) by the use of a least-squares routine. The resulting virial coefficients are presented in Table 2.

DISCUSSION

It may be seen from the information given in Table 2 that resorcinol solutions are qualitatively different to solutions containing catechol or

TABLE 2

Enthalpic virial coefficients obtained from fitting the experimental results to eqn. (2)

Solute	h_{AA} (J kg mol^{-2})	h_{AAA} (J kg^2 mol^{-3})
Catechol	−800 (34) [a]	240 (23)
Resorcinol	430 (59)	–
Pyrogallol	97 (9)	–

[a] The parenthetical term is the 95% confidence limit.

pyrogallol since, not only is the enthalpic second virial coefficient of opposite sign for resorcinol but also a third virial coefficient is needed to represent adequately the experimental results.

The group-additivity principle as first proposed by Savage and Wood [5] is applicable to second virial coefficients and makes the assumption that when two solute molecules interact, they do so in such a way that each defined group on one molecule interacts with every group on the other molecule. The consequence of this is that the experimental enthalpic virial coefficient may be expressed in terms of the numbers and types of groups on the interacting molecules and appropriate enthalpic coefficients representing the interactions between the different groups. For the interaction between two molecules of the same type (i.e., homotactic interactions) the resulting expression is

$$h_{AA} = \sum_i \sum_j n_i n_j H_{ij} \tag{3}$$

In this n_i and n_j are the numbers of groups of type i and j on the A species and H_{ij} is an intensive coefficient representing the enthalpy of interaction of an ith group with a jth group.

In terms of the solutes investigated here it seems reasonable to choose as groups aromatic CH and COH groups and given this eqn. (3) becomes

$$h_{AA} = n_{CH}^2 H_{CH-CH} + 2n_{CH} n_{COH} H_{CH-COH} + n_{COH}^2 H_{COH-COH} \tag{4}$$

Using this equation the following group additivity expressions are obtained for the three phenolic systems studied:

Catechol (C)	$h_{CC} = 16H_{CH-CH} + 16H_{CH-COH} + 4H_{COH-COH}$
Resorcinol (R)	$h_{RR} = 16H_{CH-CH} + 16H_{CH-COH} + 4H_{COH-COH}$
Pyrogallol (P)	$h_{PP} = 9H_{CH-CH} + 18H_{CH-COH} + 9H_{COH-COH}$

Consequently, and irrespective of how groups are defined, if the group additivity principle applied then catechol and resorcinol would have the same enthalpic second virial coefficient. It is apparent from the information given in Table 2 that these two phenols have quite different coefficients and this clearly indicates that one or both of them is exhibiting features which lead to departures from additivity. An indication as to which the phenols is behaving unusually can be obtained by using information on group enthalpic coefficients obtained from studies on alcohols [12]. If it is assumed that an aromatic CH group is equivalent to 0.5 CH_2 groups and that an aromatic COH group is equivalent to a CHOH group, then using some recent [12] coefficients ($H_{CH_2-CH_2} = 34.5$, $H_{CH_2-CHOH} = 44.0$, $H_{CHOH-CHOH} = -13.9$ J kg mol^{-2}) we calculate that for catechol and resorcinol, group additivity leads to a value of 434 J kg mol^{-2} for the enthalpic coefficient. The experimental value for catechol is remarkably (and almost certainly coincidentally), close to this which indicates that it is resorcinol which is behaving

TABLE 3

Free energy coefficients obtained from reanalysis of the freezing temperature data of Cavallero and Indelli [24]

Solute	g_{AA} (J kg mol^{-2})	g_{AAA} (J kg^2 mol^{-3})
Catechol	−362 (19) [a]	−20 (19)
Resorcinol	−705 (15)	111 (13)
Hydroquinone	−917 (27)	538 (83)

[a] The parenthetical term is the 95% confidence limit.

anomalously. Using the same approach for pyrogallol a predicted group additivity value of 349 J kg mol^{-2} is obtained which is somewhat higher than the experimental value of 97 J kg mol^{-2}.

Further insight into the molecular features of the interactions can be obtained from the free energetic behaviour of the systems. The freezing temperature data [24] of Cavallero and Indelli for the three diols catechol, resorcinol and hydroquinone have been reanalysed using previously described [6] procedures and in Table 3 we present the free energy virial coefficients obtained from these analyses. These coefficients refer to the freezing temperature and so for catechol and resorcinol we have corrected them to 298.15 K using the Gibbs–Helmholtz equation and the experimental enthalpic coefficients assuming the heat capacity terms are negligible. These corrected second virial coefficients are given in Table 4 which also includes the enthalpic and entropic coefficients.

It is apparent from Tables 3 and 4 that the difference shown in the enthalpic coefficients of the diols is also present in the free energy coefficients although the difference is much less marked. The signs of the free energy terms are all negative which indicates a propensity for the phenols to associate but as can be seen from the enthalpic terms and more dramatically from a comparison of the entropic coefficients, the molecular mechanisms by which the molecules interact must be quite different. The coefficients for resorcinol solutions show what might be considered to be normal chemical associative behaviour which leads to exothermic enthalpy changes and negative entropy changes. In contrast the results for catechol exhibit to some

TABLE 4

Free energetic, enthalpic and entropic second virial coefficients at 298.15 K

Solute	g_{AA} (J kg mol^{-2})	h_{AA} (J kg mol^{-2})	s_{AA} (J kg mol^{-2} K^{-1})
Catechol	−404	430	2.80
Resorcinol	−697	−800	−0.35

degree the overall features usually associated with hydrophobic interactions viz an endothermic enthalpy term and a large and positive entropy term. We therefore tentatively suggest that the dominant feature of the homotactic association of resorcinol in water is direct hydrogen-bonding interaction between hydroxyl groups whereas for catechol this is either absent or subsumed by strong hydrophobic interactions between the aromatic rings. At the moment no corresponding comments can be made regarding the association of either hydroquinone or pyrogallol since enthalpic data are lacking for the former and free energetic data are not available for the latter.

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