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Standard Potentials of Silver–Silver Bromide Electrode in Propylene Glycol–Water Mixtures at Different Temperatures and the Related Thermodynamic Quantities

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Standard electrode potentials of the silver–silver bromide electrode were determined in the temperature range 15–45 °C in 20–90 wt % propylene glycol–water mixtures by emf measurements of the cell Pt,H_2(g, 1 atm)/HBr(m),propylene glycol (x)–water (y)/AgBr–Ag. The standard molal potential, ${}_sE^\circ{}_m$, in the various solvent mixtures has been expressed as a function of temperature. The primary medium effect, the mean molal activity coefficient, and the various thermodynamic parameters for the transfer of the HBr from water to these solvent mixtures at 25 °C have been reported. The variation of the thermodynamic parameters with solvent composition has been discussed. The number of water molecules coordinated to HBr, n, was calculated from the slope of the linear plot observed between $\Delta G_t{}^\circ{}_c$ and $-RT \ln \phi_w$ (ϕ_w = volume fraction of water).

Introduction

In continuation of our earlier investigations (1–4) on electrolyte–solvent interactions in mixed aqueous amphiprotic solvents, the present work deals with the determination of standard potentials of the silver–silver bromide electrode in propylene glycol–water mixtures of varying composition which have been utilized for the evaluation of the thermodynamic parameters governing the transfer of hydrogen bromide and of hydrogen and bromide ions from water to the mixed solvents (aquo-organic mixtures). Although such measurements on galvanic cells involving hydrogen and silver–silver bromide electrodes have been reported in a few amphiprotic solvent–water mixtures (4–7), no data are available in propylene glycol–water mixtures. It may be pointed out that such studies are useful, not only to elucidate the nature of the electrolyte–solvent interactions but also for an understanding of ion solvation in mixed solvents employing suitable extrathermodynamic assumptions (16). The emf data of the following cell

Pt,H_2(g, 1 atm)/HBr(m),propylene glycol (x)–water (y)/AgBr–Ag (1)

in the composition range 20–90 wt % propylene glycol–water mixtures and in the temperature range 15–45 °C were reported.

Experimental Section

The purification of the solvents and the preparation of the silver–silver bromide and hydrogen electrodes are similar to those described earlier (4, 8). The stock solutions of aqueous HBr were prepared from triple-distilled water over an all-glass apparatus and HBr (BDH) which was freshly distilled twice before use. All solutions were prepared by weight. The molality of HBr in the experimental solution was determined by titration against aqueous sodium hydroxide which was previously standardized with a standard solution of potassium hydrogen phthalate. The experimental setup and the procedure used for the emf measurements are identical with those given earlier (1). All measurements were made with a pair of hydrogen electrodes and two pairs of Ag–AgBr electrodes. The cells were thermostated at each temperature with an accuracy of ±0.1 °C. The silver–silver bromide electrodes were found to be stable over the entire temperature range, and constancy of the cell emf within ±0.05 mV over a period of 30 min was considered as an adequate criterion of equilibrium in the emf measurements. The physical constants of the aqueous mixtures at various temperatures have been reported earlier (19).

Results and Discussion

The emf data of cell 1 in the various solvent mixtures, corrected to a partial pressure of 1 atm of hydrogen, are given in Table I. The standard molal potentials, ${}_sE^\circ{}_m$, of the cell in the various solvent mixtures were determined by extrapolation of the function

$$E^{\circ\prime} = E + 2k \log m - 2kA'c^{1/2}/(1 + aB'c^{1/2}) - 2k \log (1 + 0.002mM_{xy}) = {}_sE^\circ{}_m - 2kbm \qquad (2)$$

to zero molality. Such a plot in 20 wt % propylene glycol, which is typical of the results in these mixtures, is shown in Figure 1. In eq 2

$$k = RT \ln 10/F \qquad (3)$$

m and c are the molality and molarity of HBr, respectively, A' and B' are the Debye–Hückel constants on the molality scale, a is the ion size parameter (Å), b is the coefficient occurring in the expression for activity coefficient as a function of molality, and M_{xy} is the mean molecular weight of the solvent. In the determination of ${}_sE^\circ{}_m$, a = 5 Å was used in all compositions. Table II gives the ${}_sE^\circ{}_m$ values at the various temperatures and also ${}_sE^\circ{}_c$ and ${}_sE^\circ{}_N$, i.e., the ${}_sE^\circ$ values on the molar and mole fraction scale at 25 °C calculated from

$${}_sE^\circ{}_c = {}_sE^\circ{}_m + 2k \log d_0 \qquad (4)$$

$${}_sE^\circ{}_N = {}_sE^\circ{}_m - 2k \log (1000/M_{xy}) \qquad (5)$$

where d_0 is the density of the solvent. The standard error in $E^\circ{}_m$ is about ±0.2 mV in all the mixtures at different temperatures. The ${}_sE^\circ{}_m$ can be expressed as a function of temperature according to

$${}_sE^\circ{}_m = E^\circ{}_{m,25^\circ\mathrm{C}} + \mathbf{b}(t - 25) + \mathbf{c}(t - 25)^2 \qquad (6)$$

where t is the temperature in degrees Celsius and **b** and **c** are empirical coefficients. These data are summarized in Table III. The standard deviations in ${}_sE^\circ{}_m$, calculated from eq 6, were found to be within 0.2–0.3 mV. The stoichiometric mean molal activity coefficients of hydrogen bromide, ${}_s\gamma_\pm$, referred to a value of unity at infinite dilution in the particular solvent and calculated according to the equation

$$\log {}_s\gamma_\pm = ({}_sE^\circ{}_m - E)/2k - \log m \qquad (7)$$

at 25 °C in all solvent mixtures at rounded molalities of the acid, are recorded in Table IV. The primary medium effects of

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Table I. Emf Data of Cell 1, Corrected for 1-atm Pressure of H_2, from 15 to 45 °C in Various Propylene Glycol-Water Mixtures[a]

m_{HBr}, mol kg^{-1}	E, V 15 °C	25 °C	35 °C	45 °C
		x = 20 wt %		
0.003 893	0.341 88	0.347 53	0.352 29	0.356 12
0.005 924	0.322 32	0.327 09	0.330 98	0.334 27
0.008 762	0.305 60	0.309 06	0.313 34	0.316 16
0.010 04	0.298 68	0.302 68	0.305 63	0.307 80
0.010 35	0.296 43	0.300 30	0.303 49	0.305 51
0.020 85	0.269 32	0.266 72	0.268 73	0.270 12
0.036 99	0.234 47	0.235 68	0.236 24	0.235 52
0.052 75	0.220 41	0.221 82	0.222 53	0.222 29
0.067 64	0.208 71	0.209 86	0.210 33	0.210 02
		x = 40 wt %		
0.004 614	0.326 69	0.331 01	0.332 68	0.332 88
0.006 185	0.321 87	0.317 03	0.320 35	0.322 60
0.007 449	0.301 74	0.305 59	0.308 75	0.310 98
0.009 631	0.290 75	0.294 19	0.296 87	0.298 72
0.015 42	0.267 82	0.270 51	0.272 50	0.273 54
0.029 43	0.238 38	0.240 79	0.241 55	0.241 23
0.043 17	0.218 63	0.219 95	0.220 17	0.219 95
0.057 74	0.205 08	0.206 22	0.206 01	0.204 63
0.073 16	0.195 82	0.196 35	0.195 83	0.193 74
0.080 13	0.192 46	0.192 34	0.191 91	0.189 71
		x = 75 wt %		
0.004 292	0.298 29	0.298 01	0.297 23	0.296 00
0.005 832	0.284 86	0.283 00	0.282 69	0.281 03
0.007 591	0.273 59	0.272 10	0.270 37	0.268 27
0.014 47	0.245 24	0.242 81	0.240 51	0.237 27
0.021 55	0.228 53	0.225 00	0.222 39	0.218 83
0.035 27	0.206 00	0.202 89	0.199 62	0.195 33
0.043 99	0.194 51	0.190 57	0.184 91	0.177 55
0.057 01	0.183 66	0.179 48	0.175 54	0.170 45
0.072 34	0.172 90	0.168 20	0.164 21	0.159 11
		x = 90 wt %		
0.004 735	0.255 50	0.251 19	0.246 58	0.242 02
0.007 429	0.235 57	0.231 25	0.226 75	0.221 43
0.014 42	0.207 85	0.202 77	0.197 51	0.191 64
0.025 12	0.182 52	0.176 24	0.170 13	0.163 40
0.033 41	0.172 21	0.165 69	0.160 29	0.153 32
0.046 18	0.157 40	0.150 88	0.144 32	0.136 84
0.055 42	0.151 16	0.144 21	0.137 51	0.130 27
0.063 97	0.144 82	0.138 41	0.131 08	0.122 87
0.077 82	0.136 06	0.129 28	0.122 03	0.113 14

[a] x = weight percent of propylene glycol (g (100 g)$^{-1}$). m = molality (mol kg^{-1}).

hydrogen bromide, defined as log $_m\gamma_\pm$ in the various solvent mixtures at 25 °C calculated from

$$\log {}_m\gamma_\pm = ({}_wE°_m - {}_sE°_m)/2k \tag{8}$$

are also given in the same table. $_wE°_m$ and $_sE°_m$ in eq 8 represent the standard emf of cell 1 on the molal scale in water and solvent, respectively. The primary medium effect is a measure of the free energy change associated with the transfer of 1 mol of HBr from water to the given solvent at infinite dilution according to

$$\text{HBr(water)} = \text{HBr(propylene glycol–water mixture)} \tag{9}$$

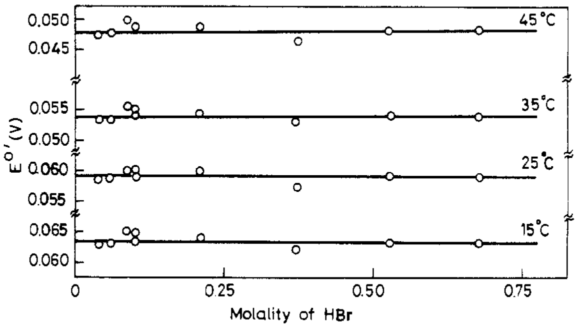

Figure 1. Extrapolation of plot of $E°'$ (V) (eq 2) against molality of HBr in propylene glycol–water mixtures (20 wt % propylene glycol) at different temperatures.

The standard free energy change, $\Delta G_t°$, for the process given by eq 9 was calculated on the mole fraction scale for the various solvent mixtures at 25 °C by using

$$\Delta G_t° = F({}_wE°_N - {}_sE°_N) \tag{10}$$

where $_wE°_N$ and $_sE°_N$ represent the standard emf's of cell 1 on the mole fraction scale. The transfer process (eq 9) is associated with the transfer of charged species, i.e., H^+ and Br^- ions, from water to the mixed solvents at infinite dilution, and it is generally agreed (*8*) that it consists of an electrostatic part, $\Delta G_t°_{el}$, and a nonelectrostatic part, $\Delta G_t°_{nonel}$. While the electrostatic-transfer free energy arises mainly due to the differences in the dielectric constants of the solvents, the nonelectrostatic part reflects the contributions of solvation and other specific ion–solvent interactions which depend on the basicity of the solvent. Thus

$$\Delta G_t° = \Delta G_t°_{el} + \Delta G_t°_{nonel} \tag{11}$$

The electrostatic contribution, $\Delta G_t°_{el}$, has been calculated in all the solvent mixtures by employing the Born equation

$$\Delta G_t°_{el} = (Ne^2/2)(1/r_{H^+} + 1/r_{Br^-})(1/D_s - 1/D_w) \tag{12}$$

using $r_{H_3O^+}$ = 2.76 Å, r_{Br^-} = 1.95 Å. $\Delta G_t°_{nonel}$ can then be obtained by using eq 11. The standard entropy of transfer, $\Delta S_t°$, was calculated from

$$\begin{aligned}\Delta S_t° &= [-(d/dt)F({}_wE°_N - {}_sE°_N)] \\ &= F[(\mathbf{b}_s - \mathbf{b}_w) + 2(\mathbf{c}_s - \mathbf{c}_w)(t - 25) + (k_w - k_s)]\end{aligned} \tag{13}$$

where $\mathbf{b}_s$ and $\mathbf{c}_s$, $\mathbf{b}_w$ and $\mathbf{c}_w$ are the coefficients from Table III for the solvent and water, respectively, and $k_w = 2R/F \ln (1000/18.016) = 6.92 \times 10^{-4}$ and $k_s = 2R/F \ln (1000/M_{xy})$. The last term in eq 13 arises in the conversion of $_sE°_m$ to $_sE°_N$. $\Delta S_t°_{el}$ can be obtained by differentiating eq 12 with respect to temperature to give

$$\Delta S_t°_{el} = -\frac{Ne^2}{2}\left(\frac{1}{r_{H^+}} + \frac{1}{r_{Br^-}}\right)\left(\frac{1}{D_s\theta_s} - \frac{1}{D_w\theta_w}\right) \tag{14}$$

where θ is a constant given by $\theta = \partial \ln D/\partial T$ and is a characteristic of the medium. θ has been evaluated from the slopes of the plots in D against temperature for the various compo-

Table II. $_sE°_m$ at Different Temperatures and $_sE°_N$ and $_sE°_c$ at 25 °C in Various Propylene Glycol-Water Mixtures

x,[a] wt %	$_sE°_m$, V 15 °C	25 °C	35 °C	45 °C	$_sE°_c$	$_sE°_N$
0[b]	0.075 96	0.071 29	0.066 04	0.059 97	0.071 14	−0.1351
20	0.063 79	0.059 39	0.054 39	0.048 41	0.060 20	−0.1385
40	0.055 66	0.048 79	0.042 58	0.035 41	0.050 28	−0.1389
75	0.021 40	0.010 58	0.000 19	−0.011 03	0.012 62	−0.1522
90	−0.020 99	−0.035 14	−0.049 22	−0.063 51	0.033 20	−0.1819
100[c]	−0.148 90	−0.163 30	−0.178 40	−0.193 70	−0.161 60	−0.2956

[a] x = weight percent of propylene glycol. [b] From ref *8*. [c] From ref *17*.

Table III. Coefficients of the Empirical Equation ${}_sE°_m = {}_sE°_{m,25\,°C} + b(t-25) + c(t-25)^2$

x,[a] wt %	${}_sE°_{m,25\,°C}$	-10^4b	-10^6c
0	0.071 30	4.955	3.175
20	0.059 39	4.718	3.955
40	0.048 79	6.619	77.750
75	0.010 58	10.080	5.227
90	−0.035 14	14.110	46.500
100[b]	−0.163 30	14.800	1.390

[a] x = weight percent of propylene glycol. [b] From ref *17*.

sitions of propylene glycol–water mixtures.

The standard enthalpy of transfer, $\Delta H_t°$, was then calculated from the equation

$$\Delta H_t° = \Delta G_t° + T\Delta S_t° \qquad (15)$$

and the $\Delta H_t°{}_{el}$ and $\Delta H_t°{}_{nonel}$ contributions were obtained by using an equation similar to eq 11. All these thermodynamic quantities on the mole fraction scale are given in Table V. The $\Delta G_t°$ values are accurate to ±40 J and the expected errors in $\Delta S_t°$ and $\Delta H_t°$ are ±0.5 J deg^{-1} and ±160 J, respectively.

It is seen from Table V that the $\Delta G_t°$ values are positive in all propylene glycol–water mixtures and increase with the addition of propylene glycol to water, suggesting that the transfer of HBr from water to propylene glycol–water mixtures is not a favorable process. The variation of $\Delta G_t°$ with solvent composition, when examined in the light of eq 11, indicates that $\Delta G_t°{}_{el}$ becomes increasingly positive due to the decrease in dielectric constant of the medium with increasing amounts of propylene glycol, whereas $\Delta G_t°{}_{nonel}$ is negative and decreases continuously under the same conditions up to about 90 wt % propylene glycol. This indicates that the transfer process (eq 9) is favorable as far as the chemical interactions are concerned, suggesting that propylene glycol–water mixtures are more basic than water, a behavior observed in the case of other glycolic solvents (*5*, *10*). This has also been confirmed recently (*11*) on the basis of the ferrocene redox couple reference method in these media.

According to Franks and Ives (*12*) and Feakins and Voice (*9*), the effect of ionic fields on the structure of the solvent will appear as compensating contributions in $\Delta H_t°$ and $T\Delta S_t°$. A comparison of $\Delta G_t°{}_{el}$ and $\Delta G_t°{}_{nonel}$ (Table V) shows that $\Delta G_t°{}_{el}$ predominates, making the overall transfer process unfavorable.

$\Delta H_t°$ (Figure 2 and Table V) passes through an endothermic maximum at about 20 wt % propylene glycol and then becomes increasingly negative (exothermic) up to 90 wt % propylene glycol. The change in $\Delta H_t°$ is similar to that in $T\Delta S_t°$. The initial increase in enthalpy and entropy of transfer may be attributed to the effect of addition of propylene glycol on the structure of water. The endothermic maximum at about 20 wt % propylene glycol is possibly due to the structure-breaking effect of HBr on the ordered structure in the solvent mixture as compared to water. This is because addition of small amounts of hydroxylic solvents are known (*12*) to promote the hydrogen-bonded structure of water and HBr is a better structure breaker in the mixed solvent than in water. The changes in $\Delta H_t°{}_{nonel}$ and $\Delta S_t°{}_{nonel}$ with the solvent composition are generally similar after making allowance for the electrostatic contribution. It must, however, be pointed out that they depend on the values of the radii chosen for the cation and anion in eq 12. An examination of $\Delta S_t°$ values (Table V) in different solvent mixtures supports the above conclusions. The positive value of $\Delta S_t°$ indicates the net structure-breaking effect of HBr at low compositions of propylene glycol. At higher compositions, $\Delta S_t°$ becomes increasingly negative, showing the net structure-making effect of the ions, which are aided by the strong ionic fields in solvents of low dielectric constant.

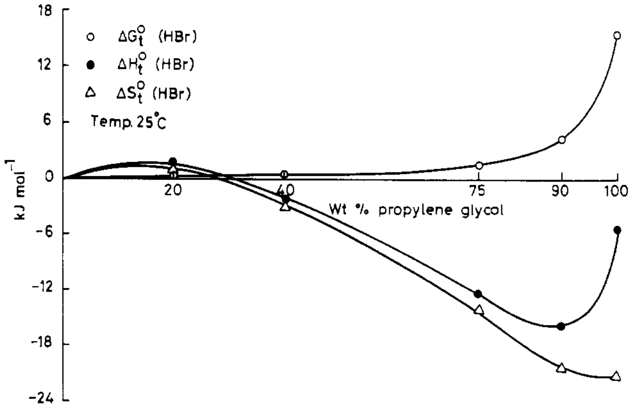

Figure 2. Variation of the various thermodynamic quantities (mole fraction scale) of transfer of HBr in propylene glycol–water mixtures.

$\Delta H_t°{}_{nonel}$ decreases continuously (Table V), indicating that the structure-making ion–solvent interactions (*13*) are predominant in media containing higher proportions of propylene glycol. This is in agreement (*13*) with the variation of *B* coefficients of viscosity of electrolytes in alcohol–water mixtures. If we represent $\Delta H_t°{}_{nonel} \approx T\Delta S_t° - T\Delta S_t°{}_{el}$ after Feakins et al. (*13*),

Table IV. Mean Molal Activity Coefficient (${}_s\gamma_\pm$) at Rounded Molalities and Primary Medium Effects of HBr (log ${}_m\gamma_\pm$) in Various Propylene Glycol-Water Mixtures at 25 °C

	m_{HBr}, mol kg^{-1}								
x,[a] wt %	0.005	0.001	0.02	0.03	0.04	0.05	0.06	0.07	log ${}_m\gamma_\pm$
20	0.937	0.886	0.853	0.833	0.818	0.805	0.796	0.788	0.101
40	0.889	0.871	0.831	0.808	0.795	0.784	0.776	0.771	0.190
75	0.863	0.783	0.722	0.695	0.678	0.664	0.653	0.644	0.513
90	0.785	0.713	0.650	0.612	0.581	0.559	0.542	0.530	0.899
100[b]	0.730	0.650	0.560	0.510	0.470	0.450			1.983

[a] x = weight percent of propylene glycol. [b] From ref *18*.

Table V. Standard Thermodynamic Quantities for the Transfer of HBr from Water to Propylene Glycol-Water Mixtures at 25 °C

x,[a] wt %	$\Delta G_t°$, J	$\Delta G_t°{}_{el}$, J	$\Delta G_t°{}_{nonel}$, J	$\Delta S_t°$, J K^{-1} mol^{-1}	$\Delta S_t°{}_{el}$, J K^{-1} mol^{-1}	$\Delta S_t°{}_{nonel}$, J K^{-1} mol^{-1}	$\Delta H_t°$, J	$\Delta H_t°{}_{el}$, J	$\Delta H_t°{}_{nonel}$, J	$T\cdot\Delta S_t°$, J mol^{-1}
20	328	713	−385	+5.0	3.8	+1.2	+1820	1 849	−29	+1 492
40	367	1952	−1585	−10.0	16.5	−26.5	−2625	6 872	−9 497	−2 992
75	1650	6122	−4472	−47.5	39.0	−86.5	−12509	17 753	−30 262	−14 159
90	4516	9452	−4936	−69.0	68.9	−137.9	−16073	30 004	−46 077	−20 589
100[b]	15488	12969	+2519	−71.0	83.1	−154.1	−5699	37 745	−43 444	−21 187

[a] x = weight percent of propylene glycol. [b] Calculated by using data from ref *17*.

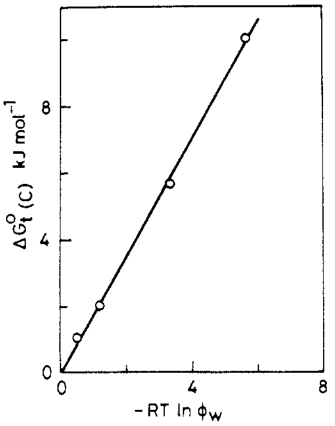

Figure 3. Plot of $\Delta G_t{}^\circ{}_c$ against $-RT \ln \phi_w$ at 25 °C.

the values of $\Delta H_t{}^\circ{}_{\text{nonel}}$ change from positive to negative at about 20% and decrease further negatively thereafter, indicating the predominantly structure-making ion-solvent interactions at higher compositions of propylene glycol. Feakins et al (*14*) have suggested a different approach to account for the variation ΔG_t° with solvent composition in terms of, ϕ_w, the volume fraction of water. A plot of the standard molar free energy of transfer, $\Delta G_t{}^\circ{}_c$, against solvent composition in terms of volume fraction of water in these media (Figure 3) according to the relation

$$\Delta G_t{}^\circ{}_c = -nRT \ln \phi_w \qquad (16)$$

is linear with $n = 1.8$. This value represents the number of water molecules coordinated to HBr and is less than the values obtained in other media as reported elsewhere (*15*).

Registry No. Ag, 7440-22-4; AgBr, 7785-23-1; HBr, 10035-10-6; propylene glycol, 57-55-6.

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Enthalpies of Combustion and Formation of Ethylene Carbonate

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Combustion calorimetry was used to determine a value for the standard enthalpy of combustion of ethylene carbonate (crystal) from which the standard enthalpy of formation was calculated; the results were $\Delta H_c^\circ(298.15\ \text{K}) = -1165.87 \pm 3.74$ kJ/mol $= -278.65 \pm 0.89$ kcal/mol and $\Delta H_f^\circ(298.15\ \text{K}) = -586.30 \pm 3.76$ kJ/mol $= -140.13 \pm 0.90$ kcal/mol. The results were obtained by burning a sample of known purity in an oxygen bomb calorimeter and correcting for trace amounts of combustibles. This compound affords a striking example of the effect of empirical formula on the standard-states correction.

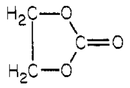
This investigation was undertaken to establish the enthalpy of formation of solid ethylene carbonate for use in reaction enthalpy-change calculations. Discordant heat-of-combustion values had appeared in the literature (*1*, *2*) which led to significantly altered results for any process designs involving the formation and subsequent reactions of this compound, and both of those studies seemed to represent conscientious work.

Reported here are the results obtained at this laboratory for measurements carefully performed of the heat of combustion of a highly purified sample of solid ethylene carbonate and a value for the enthalpy of formation derived from it.

Table I. Impurities in Ethylene Carbonate Used and Their ΔE_c° Values for Corrections

	concn, ppm	ΔE_c°, kJ/mol
benzene	215	−3263.85
n-hexane	198	−4154.63
water	6 (max)	0

Ethylene carbonate has the structural formula



Experimental Section

Apparatus and Procedure. A Parr 1241 automatic adiabatic oxygen bomb calorimeter (Parr Instrument Co., Moline, IL) was employed for the heat-of-combustion measurements. The 1108 double-valve oxygen bomb used has an internal volume of 0.342 dm^3. The fuse wire used was Parr 45C10 nickel alloy wire. Exactly 1 cm^3 (approximately 1 g) of distilled water was

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