Standard Potentials of Silver-Silver Chloride Electrode in Diethylene Glycol-Water Mixtures at Different Temperatures and Related Thermodynamic Quantities

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Electromotive force measurements of cells of the type Pt, H_2 (g, 1 atm)/HCl (*m*) diethylene glycol(*x*)-water(*y*)/AgCl-Ag were carried out at five temperatures in the temperature range 5-45°C in 20, 40, 60, and 80 wt % diethylene glycol-water mixtures to evaluate the standard potentials of the Ag-AgCl electrode in the above mixtures, the primary medium effects, the mean molal activity coefficients in the concentration range 0.01-0.1 mol Kg^{-1}, and the various thermodynamic quantities for the transfer of HCl from water to these media. The standard molal potential, $_sE_m{}^\circ$, in all the solvent mixtures was expressed as a function of temperature. The significance of the various thermodynamic quantities associated with the transfer process is discussed both in relation to the acid-base nature of the solvent mixtures and also the structural effects of these solvent mixtures on the transfer process. The standard molar Gibbs free energy of transfer, $\Delta G_{t(c)}{}^\circ$, was a linear function of log ϕ_w (ϕ_w = volume fraction of water) in the various mixtures and from the slope, *n;* i.e., the number of water molecules coordinated to HCl evaluated was 2.0.

Electromotive force measurements on galvanic cells involving hydrogen, silver-silver halide electrodes have been extensively used (*1*) in recent years to determine the thermodynamics of hydrogen halides in aqueous and nonaqueous media. Such studies further offer a method of understanding the medium effects associated with the transfer of these electrolytes from water to any solvent and under suitable conditions can also be employed (*17*) for the estimation of transfer free energies of single ions. Measurements of this type on the cell:

Pt, H_2 (g, 1 atm)/HCl (*m*) diethylene
glycol(*x*)-water(*y*)/AgCl-Ag (1)

in amphiprotic and mixed aqueous amphiprotic media (*13, 15, 19, 20, 22*) have been widely reported, including glycols and their aqueous mixtures (*21*), but no emf data on the above cell in diethylene glycol and its aqueous mixtures are available. Because glycolic media have found (*16*) considerable application in nonaqueous acid-base titrations and also in understanding the physicochemical behavior of strongly acidic and basic solutions in amphiprotic solvents (*3, 12*), we have undertaken comprehensive emf measurements in this solvent and its aqueous mixtures. The present work deals with the results on the cell (Equation 1) in 20, 40, 60, and 80 wt % of diethylene glycol-water mixtures at different temperatures ranging from 5° to 45°C.

Experimental

Diethylene glycol (L.R., British Drug House) was treated with a sufficient amount of freshly heated calcium oxide, shaken well, and left overnight to remove any traces of water. The sample was subjected to a preliminary distillation. The distillate was again treated as above, the final sample repeatedly distilled under vacuum with a 45-cm long fractionating column, and the middle fraction boiling at 120°C under 10-mm pressure was collected and stored out of contact with air. Gas chromatographic analysis of the final product for the presence of ethylene glycol with SE 30 at 160°C and for water with Porapak Q at 90°C showed that the amounts of these constituents are less than 50 and 100 ppm, respectively. This had $n^{27.5}D$ 1.4445 and d^{25} of 1.115 g ml^{-1} in agreement with the literature value (*18*). Double-distilled water over an all-glass apparatus was used in the preparation of the solvent mixtures.

A stock solution of hydrochloric acid (about 0.3*M*) in the desired solvent was prepared as described earlier (*12*). These solutions retained constant strength throughout the experiment and were appropriately diluted to give the acid of the desired concentration. The experimental solutions were analyzed before and after the experiment according to the earlier procedure (*12*) with an accuracy of ±0.05%; no significant change in concentration was observed. The various solvent compositions were prepared by weight and were accurate within ±0.02%.

The Ag-AgCl electrodes were of the thermal-electrolytic type and had asymmetry potentials less than ±0.05 mV three days after preparation. The hydrogen electrodes were lightly coated with platinum black before each measurement according to the method of Hills and Ives (*11*). The observed bias potentials were less than ±0.05 mV. All measurements were made with a pair of hydrogen electrodes and four Ag-AgCl electrodes. Electrolytically generated hydrogen purified in the usual manner (*11*) served as the source of hydrogen and was passed into a pear-shaped vessel containing the experimental solution and electrodes. The cells were thermostated at each temperature with an accuracy of ±0.05°C.

The emf's of the cell were measured at 5°, 15°, 25°, 35°, and 45°C with an OSAW VP 71120 vernier-type potentiometer (Oriental Science Apparatus Workshops, Ambala, India) capable of reading within ±0.01 mV, in conjunction with a Keithley 602 solid-state electrometer as null detector; a Weston standard cell was used for calibration. The cells normally reached equilibrium 8 hr after the start of hydrogen bubbling in all these mixtures. Constancy of emf values to ±0.05 mV over a period of half an hour was considered as an adequate criterion of equilibrium. The emf value recorded initially at 25°C was redetermined when increasing the temperature of the thermostat from 5° to 45°C and finally again at the end. All the values agreed within ±0.05 mV. As a final check of the experimental set up, the standard electrode potential of the Ag-AgCl electrode in water at 30°C was determined and found to be 0.21920 V in agreement with 0.21910 V reported previously (*10*).

The dielectric constants of the aqueous mixtures from 15° to 45°C were determined with a DK 03 Dekameter (Wissenchaftliche Technische Werkstatten, West Germany), and the value at 5°C was obtained by interpolation.

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Table I. Physical Constants and Other Data of Diethylene Glycol-Water Mixtures[a]

Diethylene-glycol, wt %		5°C	15°C	25°C	35°C	45°C	M_{xy}
20	D	75.30	73.75	71.50	68.50	65.25	
	A'	0.6016	0.5884	0.5859	0.5944	0.6098	21.59
	$B' \times 10^{-8}$	0.3474	0.3449	0.3444	0.3461	0.3490	
	D	70.10	66.90	63.75	61.00	58.10	
40	A'	0.6699	0.6836	0.6960	0.7074	0.7254	26.95
	$B' \times 10^{-8}$	0.3601	0.3625	0.3648	0.3667	0.3698	
	D	59.90	57.60	54.90	52.40	50.00	
60	A'	0.8480	0.8527	0.8700	0.8886	0.9086	35.88
	$B' \times 10^{-8}$	0.3895	0.3903	0.3929	0.3958	0.3987	
	D	47.90	46.00	44.00	42.25	40.25	
80	A'	1.1860	1.1940	1.2130	1.2280	1.2600	53.53
	$B' \times 10^{-8}$	0.4357	0.4367	0.4390	0.4408	0.4444	

[a] D = dielectric constant. A' and B' = Deybe-Hückel constants on molality scale. M_{xy} = mean mol wt.

Table II. Emf Data of Cell (Equation 1) (Corrected for 1 atm Pressure of H_2) from 5° to 45°C in Volts in Various Diethylene Glycol-Water Mixtures (X = Wt % Diethylene Glycol; m = Molality)

m_{HCl}	5°C	15°C	25°C	35°C	45°C
			$X = 20$		
0.00568	0.46848	0.47205	0.47492	0.47684	0.47740
0.01150	0.43580	0.43878	0.44072	0.44112	0.44176
0.02289	0.40530	0.40668	0.40752	0.40716	0.40652
0.04924	0.37191	0.37210	0.37154	0.37030	0.36844
0.06653	0.35783	0.35773	0.35646	0.35462	0.35260
0.07923	0.34846	0.34858	0.34761	0.34572	0.34319
0.08516	0.34676	0.34629	0.34466	0.34285	0.34056
0.1183	0.33130	0.33045	0.32842	0.32605	0.32336
			$X = 40$		
0.00961	0.43605	0.43878	0.44006	0.44045	0.43979
0.01877	0.40676	0.40767	0.40763	0.40727	0.40595
0.03361	0.37920	0.37926	0.37842	0.37690	0.37476
0.04846	0.36468	0.36418	0.36226	0.36098	0.35831
0.06825	0.35025	0.34883	0.34716	0.34469	0.34156
0.09166	0.33624	0.33448	0.33226	0.33022	0.32409
0.09543	0.33421	0.33257	0.33049	0.32853	0.32401
			$X = 60$		
0.01834	0.39208	0.38974	0.38765	0.38499	0.38145
0.02447	0.38009	0.37740	0.37384	0.37023	0.36580
0.03580	0.36266	0.35993	0.35682	0.35263	0.34866
0.04678	0.34904	0.34697	0.34378	0.33977	0.33450
0.06227	0.34140	0.33788	0.33429	0.33960	0.32657
0.06945	0.33543	0.33208	0.32980	0.32530	0.32057
0.09260	0.32356	0.31945	0.31549	0.31050	0.30507
			$X = 80$		
0.00529	0.41625	0.41250	0.40879	0.40527	0.40035
0.00567	0.41357	0.41022	0.40670	0.40235	0.39768
0.01119	0.38067	0.37619	0.37197	0.36645	0.36036
0.02225	0.35571	0.35075	0.34520	0.33990	0.33393
0.04003	0.33060	0.32484	0.31878	0.31290	0.30605
0.04721	0.32338	0.31754	0.31142	0.30481	0.29783
0.05400	0.31813	0.31171	0.30530	0.29857	0.29137
0.08736	0.29748	0.28970	0.28282	0.27542	0.26778

The Dekameter was initially checked at 30°C with methanol and water as standard liquids. The dielectric constants are accurate within ±0.2%. The vapor pressure and density of all the solvent mixtures were obtained from the data of Gallant (*8*). The physical constant data of the solvent mixtures are presented in Table I.

Results and Discussion

The emf data of the cell (Equation 1) in the various solvent mixtures, corrected to a partial pressure of 1 atm of hydrogen, are given in Table II. The standard molal potentials ${}_sE_m{}^\circ$ of the cell in all the solvent mixtures were determined by extrapolating the function

$$E_o' = E + 2\,k \log m - 2\,kA'm^{1/2}/(1 + aB'm^{1/2}) - 2\,k \log (1 + 0.002\,mM_{xy}) = {}_sE_m{}^\circ - 2\,kbm \quad (2)$$

to zero molality. Such a plot, which is representative of the general trend, is shown for 40 wt % diethylene glycol-water mixture in Figure 1. In the above equations,

$$k = 2.303\,RT/F \quad (3)$$

m is the molality of HCl, A' and B' are the Debye-Hückel constants on the molality scale, a is the ion-size parameter, b is the coefficient occurring in the activity coefficient expression as a function of molality, and M_{xy} is the mean molecular weight of the mixed solvent given by

$$M_{xy} = 100/(x/M_x + y/M_y) \quad (4)$$

where x and y represent the weight percentages of diethylene glycol and water, and M_x and M_y are the corresponding molecular weights. In determining ${}_sE_m{}^\circ$, a = 5 Å was used as this was found to give good linear plots with the least slope. Other values of a = 4, 6, 7 Å were employed, and no change in ${}_sE_m{}^\circ$ was observed. Table III gives the ${}_sE_m{}^\circ$ values at all temperatures and also ${}_sE_c{}^\circ$ and ${}_sE_N{}^\circ$, i.e., the ${}_sE^\circ$ on molarity and mole fraction scales at 25°C calculated from (*10*)

$$ {}_sE_N{}^\circ = {}_sE_m{}^\circ - 2\,k \log (1000/M_{xy}) \quad (5)$$

and

$$ {}_sE_c{}^\circ = {}_sE_m{}^\circ + 2\,k \log d_0 \quad (6)$$

where d_0 is the density of the solvent. The standard error in $E_m{}^\circ$ is about ±0.25 mV in all the mixtures at different temperatures. ${}_sE_m{}^\circ$, expressed as a function of temperature by Equation 7 where t is the temperature in Celsius scale, is tabulated in Table IV.

$$ {}_sE_m{}^\circ = E_{m\cdot 25}{}^\circ + b\,(t - 25) + c\,(t - 25)^2 \quad (7)$$

The stoichiometric mean activity coefficients of hydrochloric acid ${}_s\gamma_\pm$ referred to a value of unity at infinite dilution in the given solvent calculated from the equation

$$\log {}_s\gamma_\pm = ({}_sE_m{}^\circ - E)/2\,k - \log m \quad (8)$$

in various solvent mixtures at 25°C at rounded molalities are recorded in Table V. This table also contains the pri-

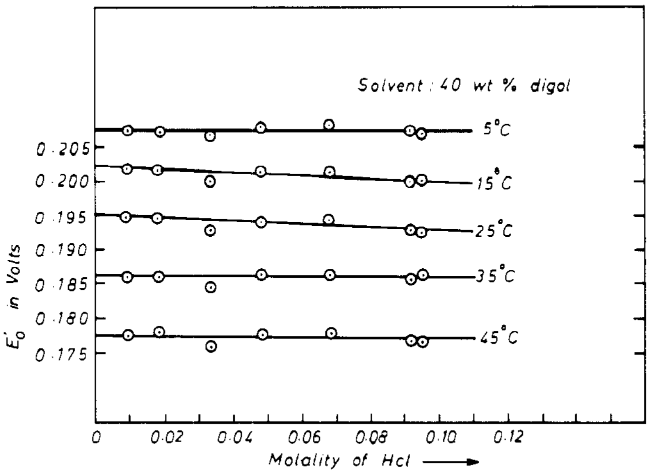

Figure 1. Extrapolation of plot of E_0' (V) (Equation 2) against molality of HCl in diethylene glycol–water mixture (40 wt % diethylene glycol) at different temperatures

Table III. $_SE_m°$ **at Different Temperatures and** $_SE_N°$ **and** $_SE_c°$ **at 25°C in Volts in Various Diethylene Glycol–Water Mixtures**

Diethylene glycol, wt %	5°C	15°C	25°C	$_SE_c°$	$_SE_N°$	35°C	45°C
0	0.2341	0.2286	0.2224	0.2223	0.0160	0.2157	0.2083
20	0.2166	0.2113	0.2053	0.2069	0.0082	0.1977	0.1894
40	0.2073	0.2023	0.1955	0.1984	0.0098	0.1863	0.1778
60	0.1903	0.1812	0.1709	0.1751	−0.0001	0.1597	0.1484
80	0.1572	0.1451	0.1326	0.1377	−0.0177	0.1193	0.1054

Table IV. Coefficients of Empirical Equation $_SE_m° = {}_SE_{m\cdot 25}° + b\,(t - 25) + c\,(t - 25)^2$

Diethylene glycol, wt %	$_SE_{m\cdot 25}°$	$-b \times 10^4$	$-c \times 10^6$	SD
0	0.2224	6.400	2.980	0.0000
20	0.2051	6.799	5.260	0.0002
40	0.1952	7.475	6.780	0.0003
60	0.1708	10.520	3.600	0.0001
80	0.1325	12.950	3.080	0.0001

Table V. Mean Activity Coefficients ($_S\gamma_\pm$) **at Rounded Molalities and Primary Medium Effect of HCl (log** $_m\gamma_\pm$**) in Various Diethylene Glycol-Water Mixtures at 25°C (x, wt % Diethylene Glycol)**[a]

	m_{HCl}						
x	0.01	0.02	0.04	0.06	0.08	0.10	log $_m\gamma_\pm$
20	0.900	0.855	0.817	0.795	0.780	0.772	0.144
40	0.883	0.850	0.815	0.780	0.757	0.747	0.228
60	0.837	0.795	0.712	0.665	0.645	0.640	0.435
80	0.822	0.745	0.655	0.630	0.612	0.607	0.759

[a] For x = 0%, see ref. *10*, p 716.

Table VI. Evaluation of θ **from Plots of ln** D **Against** T **in Range of 15–45°C**

Diethylene glycol, wt %	0[a]	20[b]	40[b]	60[b]	80[b]
θ, K^{-1}	220	221.5	217.9	218.0	227.7

[a] Ref. *19*. [b] Present work.

mary medium effect (log $_m\gamma_\pm$) of HCl at 25°C in the various media which has been calculated from

$$\log {}_m\gamma_\pm = ({}_WE_m° - {}_SE_m°)/2k \qquad (9)$$

where the subscripts W and S on $E_m°$ represent the values in water and the solvent, respectively. The primary medium effect is a measure of the free energy change associated with the transfer of 1 mole of the electrolyte from water to the given solvent at infinite dilution. For the transfer process,

$$\text{HCl (H}_2\text{O)} = \text{HCl (diethylene glycol-water mixture)} \qquad (10)$$

the standard Gibbs free energy of transfer, $\Delta G_t°$, has been evaluated in the various solvent mixtures at 25°C by the equation:

$$\Delta G_t° = F({}_wE_N° - {}_SE_N°) \qquad (11)$$

The transfer process is associated with a transfer of charged species, i.e., of H$^+$ and Cl$^-$ ions from water to the mixed solvents at infinite dilution. It is therefore plausible to expect that it consists of an electrostatic part $\Delta G_{t(\text{el})}°$, corresponding to a change in the dielectric constant of the medium and another nonelectrostatic part $\Delta G_{t(nonel)}°$, arising owing to specific chemical interactions between the ions and the solvent which depend on the basicity of the solvent. Thus,

$$\Delta G_t° = \Delta G_{t(\text{el})}° + \Delta G_{t(\text{nonel})}° \qquad (12)$$

The electrostatic part of the standard Gibbs free energy of transfer, $\Delta G_{t(\text{el})}°$, has been calculated in all the solvent mixtures from Born's equation:

$$\Delta G_{t(\text{el})}° = (Ne^2/2)\,(1/r^+ + 1/r^-)\,(1/D_s - 1/D_w) \qquad (13)$$

with $r^+ = 2.80$ Å and $r^- = 1.81$ Å for H$^+$ and Cl$^-$ ions, respectively. D_s and D_w are the dielectric constants of the solvent and water, N is the Avogadro's number, and e is the electronic charge in the above equation. The nonelectrostatic part of the standard Gibbs free energy of transfer $\Delta G_{t(\text{nonel})}°$ was then obtained from Equation 12. The $\Delta G_t°$ values are accurate to ±10 cal. The standard entropy of transfer $\Delta S_t°$ was evaluated by using

$$\Delta S_t° = -d/dT\cdot F\,({}_wE_N° - {}_SE_N°) = F\{(b_s - b_w) + 2(c_s - c_w)\,(t - 25) + (K_w - K_s)\} \qquad (14)$$

where b_s and b_w and c_s and c_w are the coefficients from Table IV in the solvent and water, respectively, and $K_w = 2\,R/F \ln (1000/18.016) = (6.92 \times 10^{-4})$ and $K_s = 2\,R/F \ln (1000/M_{xy})$. The last term of Equation 14 arises in the conversion of $_SE_m°$ to $_SE_N°$. The electrostatic part of the standard entropy of transfer $\Delta S_{t(\text{el})}°$ can be obtained by differentiating Equation 13 with respect to temperature and multiplying by −1 to give

$$\Delta S_{t(\text{el})}° = (-Ne^2/2)\,(1/r^+ + 1/r^-)\,(1/D_s\theta_s - 1/D_w\theta_w) \qquad (15)$$

where θ is a constant given by $1/\theta = -d \ln D/dT$ and is characteristic of the medium (*9*). θ was evaluated from the plots of $\ln D$ against T (in the range 15-45°C) which are linear for all the compositions of diethylene glycol-water mixtures, and the slopes evaluated by least-squares analysis are recorded in Table VI. The nonelectrostatic part of the standard entropy of transfer, $\Delta S_{t(\text{nonel})}^\circ$, is obtained from an equation similar to Equation 12. The standard enthalpy of transfer, ΔH_t°, its electrostatic part $\Delta H_{t(\text{el})}^\circ$, and the nonelectrostatic part $\Delta H_{t(\text{nonel})}^\circ$ can be calculated from the general equation:

$$\Delta H_t^\circ = \Delta G_t^\circ + T\Delta S_t^\circ \tag{16}$$

All these thermodynamic quantities are recorded in Table VII. From this table, ΔG_t° is positive in all diethylene glycol-water mixtures and increases (except in 40 wt % diethylene glycol-water) with increasing diethylene glycol content of the medium. This suggests that hydrogen chloride is in a higher free energy state in all these mixtures, and the transfer process is not favored as the amount of diethylene glycol increases. On the contrary, $\Delta G_{t(\text{nonel})}^\circ$ is increasingly negative in all diethylene glycol-water mixtures, indicating that the transfer process is favored as far as chemical interactions are concerned; this suggests that all diethylene glycol-water mixtures are more basic than water.

According to Franks and Ives (*7*) and Feakins and Voice (*4*), the effect of ionic fields on the structure of the solvent will appear as a compensating contribution in ΔH_t° and $T\Delta S_t^\circ$. A comparison of $\Delta G_{t(\text{el})}^\circ$ and $\Delta G_{t(\text{nonel})}^\circ$ shows that $\Delta G_{t(\text{el})}^\circ$ predominates, causing an unfavorable effect on the overall transfer process. Considering ΔH_t° and ΔS_t°, Franks and Ives (*7*) have emphasized the importance of these quantities in explaining the structural effects of the solvents on the transfer process.

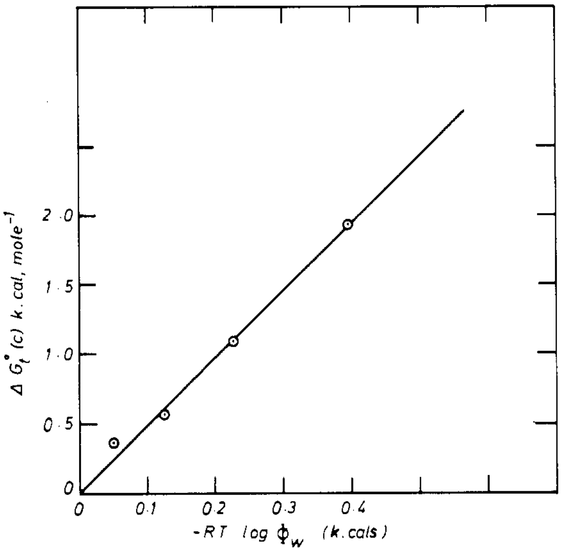

Figure 2. Extrapolation of plot of $\Delta G_{t(c)}^\circ$ against $-RT \log \phi_w$ at 25°C

ΔH_t° passes through an endothermic maximum at about 20 wt % diethylene glycol and then becomes increasingly negative (exothermic) up to 80 wt % diethylene glycol. The change in ΔH_t° is, however, overshadowed by a large decrease of $T\Delta S_t^\circ$ with increasing diethylene glycol content. This is most possibly due to the increased effect of ionic fields on the solvent molecules in media of lower dielectric constant to produce ordered structures. This is also consistent with the heat evolution on transfer, i.e., a lowering of structural enthalpy associated with structure-making ion-solvent interactions above 20 wt % diethylene glycol.

The endothermic maximum at about 20 wt % diethylene glycol is, however, due to a different reason, viz., the effect of HCl in disrupting the ordered structure in mixtures of low diethylene glycol content when transferred from water to these media. Addition of small amounts of alcohols promotes the hydrogen-bonded structure of water, and HCl is a better structure breaker in the mixed medium than in water (*7*). The changes in $\Delta H_{t(\text{nonel})}^\circ$ and $\Delta S_{t(\text{nonel})}^\circ$ with the solvent composition are generally similar after making allowance for the electrostatic contribution. However, these are affected somewhat by the values of radii chosen for the cation and anion in Equation 13.

$\Delta H_{t(\text{nonel})}^\circ$ continuously decreases up to 80 wt % diethylene glycol, changing sign from positive to negative at about 40 wt % diethylene glycol. This is in general agreement (*5*) with the variation of *B*-coefficients of viscosity of electrolytes in alcohol-water mixtures. Representing $\Delta H_{t(\text{nonel})}^\circ \approx T\Delta S_t^\circ - T\Delta S_{t(\text{el})}^\circ$ after Feakins et al. (*5*), below 40 wt % diethylene glycol, the second term predominates, whereas at higher compositions the first term primarily decides the sign of $\Delta H_{t(\text{nonel})}^\circ$. A plot of the standard molar free energy of transfer, $\Delta G_{t(c)}^\circ$ against solvent composition in terms of volume fraction of water ϕ_w in these media (Figure 2) according to the relation (*6*):

$$\Delta G_{t(c)}^\circ = -2.303\, nRT \log \phi_w$$

is linear with $n = 2.0$. This value, representing the number of water molecules coordinated to the hydrogen halide, is, however, small compared to the values (*14*) obtained in other media.

Further measurements with the other silver halide electrodes in these media have been made and will be communicated shortly.

Table VII. Thermodynamic Quantities for Transfer of HCl from Water to Various Diethylene Glycol-Water Mixtures at 25°C on Mole Fraction Scale[a]

Diethylene glycol, wt %	ΔG_t°	$\Delta G_{t(\text{el})}^\circ$	$\Delta G_{t(\text{nonel})}^\circ$	$\Delta S_t^\circ \times 10^3$	$\Delta S_{t(\text{el})}^\circ \times 10^3$	$\Delta S_{t(\text{nonel})}^\circ \times 10^3$	ΔH_t°	$\Delta H_{t(\text{el})}^\circ$	$\Delta H_{t(\text{nonel})}^\circ$
20	179	186	−7	−138	−792	654	138	−50	188
40	143	444	−301	−806	−2125	1319	−97	−189	92
60	372	826	−454	−6690	−4243	−2450	−1625	−439	−1186
80	777	1507	−730	−10710	−6313	−4390	−2416	−375	−2041

[a] ΔG_t° and ΔH_t° in cal; ΔS_t° in cal K^{-1} mol^{-1}. 4.184 J = cal.

Nomenclature

A', B' = Debye-Hückel constants on molality scale
a = ion-size parameter
m = molality of HCl
k = $2.303\,RT/F$, volt
$_sE_m^\circ$, $_sE_N^\circ$, $_sE_c^\circ$ = standard electrode potentials on molality, mole fraction, and molarity scales in solvent, volt
$_wE_m^\circ$, $_wE_N^\circ$, $_wE_c^\circ$ = standard electrode potentials on molality, mole fraction, and molarity scales in water, volt
M_{xy} = average molecular weight of the solvent (x = wt % diethylene glycol; y = wt % of water)
$_s\gamma_\pm$ = mean activity coefficient of HCl in the solvent referred to solvent standard state
ΔG_t°, ΔH_t°, ΔS_t° = free energies, enthalpies, and entropies of transfer on mole fraction scale, cal
$\Delta G_{t(c)}^\circ$ = standard Gibbs free energy of transfer on molarity scale, cal
$\Delta G_{t(\mathrm{el})}^\circ$, $\Delta H_{t(\mathrm{el})}^\circ$, $\Delta S_{t(\mathrm{el})}^\circ$ = electrostatic Gibbs free energy, enthalpy, and entropy of transfer, cal
$\Delta G_{t(\mathrm{nonel})}^\circ$, $\Delta H_{t(\mathrm{nonel})}^\circ$, $\Delta S_{t(\mathrm{nonel})}^\circ$ = nonelectrostatic (chemical) Gibbs free energy, enthalpy, and entropy of transfer, cal
$\log {}_m\gamma_\pm$ = primary medium effect
ϕ_w = volume fraction of water
K_s = $2\,R/F \ln (1000/M_{xy})$
K_w = $2\,R/F \ln (1000/18.016)$
θ = constant characteristic of the medium

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Adsorption Isotherms, Heats of Desorption, and Partial Molal Entropies for Carbon Monoxide on Linde 5A Molecular Sieve

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Adsorption parameters for individual gases on the various zeolites are sparse, despite their great utility as adsorbents (*7, 10, 11, 13, 15–17*). In particular, the published partial adsorption isotherms for CO on Linde Molecular Sieve 5A ($Ca_{4.5}Na_3[(AlO_2)_{12}(SiO_2)_{12}]\cdot nH_2O$) at 25°, 0°, and −75° and on Linde 4A ($Na_{12}[(AlO_2)_{12}(SiO_2)_{12}]\cdot nH_2O$) at 0° and −75° did not meet our needs in connection with the study of the separation of carbon isotopes by adsorption techniques. We present here adsorption isotherms for CO on Linde Sieve 5A for pressures ranging from 10^{-4} torr to several hundred torr at 77.3, 90.1, 145.0, 194.5, 230.9, and 273.2K. We also present "heat of desorption" data and partial molal entropy of the adsorbed CO derived from the adsorption isotherms.

Experimental Apparatus and Procedure

The experimental apparatus arrangement is indicated schematically in Figure 1. It contained the usual calibrated gas burets, A; a mercury manometer and its associated cathetometer, and a calibrated McLeod gage, B and C, respectively, for pressure measurement; CO supply storage, D; a cooled adsorbent vessel, E, for final purification of the CO supply; a high vacuum system, F, to provide for evacuation of the adsorption system; and the adsorbent cell, H, and its constant temperature bath, I. The gas burets, the mercury manometer, and the McLeod gage were surrounded by a shield to provide an approximately constant (measured) temperature environment for these elements.

The adsorption cell was fashioned from a 1.75-cm i.d. stainless-steel tube (0.07-cm wall) with a concentric 0.48-cm o.d. inlet tube which extended for 5.4 cm into the 5.75-cm deep cell. The inlet tube was perforated by 20 holes 0.32-cm diam to facilitate CO distribution within the cell. A 20-mesh stainless-steel screen covered the inlet tube to prevent entry of adsorbent. The ~7.4-gram samples of $^1/_{16}$-in. diam Linde Molecular Sieve 5A pellets (as supplied commercially with clay binder) occupied the annular space of the cell. Two samples of sieve were studied. The first, of 7.58-gram desorbed weight, was used for adsorption isotherms at all temperatures. The system was then modified to provide a "trap" of several grams of pure gold foil to protect the adsorbent from mercury vapor diffusing into the sample cell from the ma-

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