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Thermodynamics of Transfer of Hydrogen Halides (HCl, HBr) in Glycerol–Dimethylformamide Mixtures from Electromotive Force Measurements

D. Muralimohan Rao and C. Kalidas*

Department of Chemistry, Indian Institute of Technology, Madras 600 036, India

The standard potentials of Ag–AgX (X = Cl^- or Br^-) electrodes in glycerol–dimethylformamide (Gly–DMF) mixtures in different solvent compositions (up to 60 wt % DMF for Ag–AgCl and 40 wt % DMF for Ag–AgBr electrodes) have been determined at three different temperatures from 25–35 °C by emf measurements with the cell Pt,H_2 (g, 1 atm)|HCl (*m*),DMF(x)–Gly(y)|AgX–Ag. The primary medium effects and the mean molal activity coefficients in the concentration ranges 0.01–0.02 mol kg^{-1} at 25 °C have been evaluated. The standard molal potentials, ${}_sE^\circ{}_m$, have been expressed as a function of temperature. The thermodynamic parameters for the transfer of HCl and HBr from glycerol to glycerol–DMF mixtures have been evaluated from emf data at 25 °C on the mole fraction scale. The significance of the various thermodynamic quantities associated with the transfer process is discussed.

Introduction

The thermodynamics of transfer of hydrogen halides in mixed and nonaqueous solvents in cells without liquid junctions has received considerable attention in recent years. The results have been mainly interpreted in terms of ion–solvent and solvent–solvent interactions by using suitable extrathermodynamic assumptions. Most of the data available in the literature from experiments employing Ag–AgCl and Ag–AgBr electrodes has been confined to mixed amphiprotic solvents (*1–8*). Some reports from studies using the same electrodes are also available on mixed aqueous aprotic solvents such as H_2O–DMSO (*9*), water–acetonitrile (*10*), and water–acetone (*11*). However, only a few data are available on these electrodes in isodielectric media such as ethylene glycol–acetonitrile (*12*), methanol–acetonitrile (*13*), methanol–propylene glycol (*14*a,b), ethylene glycol–diethylene glycol (*15*), and ethylene glycol–dimethylformamide (*16*). The use of such isodielectric solvent mixtures provides the possibility of eliminating electrostatic effects so that the chemical effects of the solvent mixtures on ion–solvent interactions can be examined. Hence, in the present study, which is in continuation of our earlier work (*17*, *18*) in mixed solvents containing dimethylformamide (DMF), we report the standard potentials of Ag–AgCl and Ag–AgBr electrodes in the nearly isodielectric mixtures of glycerol–DMF at three different temperatures. The various thermodynamic parameters associated with the transfer of HCl and HBr have been evaluated, and the significance of the various thermodynamic parameters is discussed.

Table I. Physical Constants and Other Data of Glycerol–Dimethylformamide Mixtures at Various Temperatures[a]

wt % DMF		25 °C	30 °C	35 °C	M_{xy}
10	D	42	40.6	39.3	89.68
	A'	1.3017	1.3358	1.3686	
	$B' \times 10^{-8}$	0.4494	0.4533	0.4570	
	d_0	1.2205	1.2175	1.2131	
20	D	41.7	40.2	39.0	87.47
	A'	1.3157	1.3558	1.3845	
	$B' \times 10^{-8}$	0.4510	0.4556	0.4587	
	d_0	1.1853	1.1824	1.1789	
40	D	41.2	40.0	38.7	
	A'	1.3397	1.3660	1.4006	83.37
	$B' \times 10^{-8}$	0.4537	0.4567	0.4605	
	d_0	1.1176	1.1149	1.1101	
60	D	40.3	39.3	38.4	79.64
	A'	1.3849	1.4026	1.4170	
	$B' \times 10^{-8}$	0.4588	0.4607	0.4623	
	d_0	1.0556	1.0524	1.0479	

[a] D = dielectric constant, A' and B' = Debye–Hückel constants, M_{xy} = mean molecular weight.

Experimental Section

The emf measurements have been made in the composition range 10–60 wt % DMF (for HCl) and 10–40 wt % DMF (for HBr) at 25, 30, and 35 °C with the cell

$$\text{Pt,H}_2\text{ (g, 1 atm)|HX (}m\text{), DMF (x)–Gly (y)|AgX–Ag} \quad (1)$$

$$X = Cl^- \text{ or } Br^-$$

Glycerol (Merck) was purified by heating it to 100 °C to remove traces of moisture, and then it was distilled under reduced pressure. The purification of other solvents and preparation of experimental solutions have been described earlier (*17*). In the case of HBr, the gas was generated by the dropwise addition of liquid bromine to tetralin and this gas was passed through traps containing tetralin and a solvent mixture and then finally absorbed in the solvent mixture to get the required strength of HBr. The Ag–AgX electrodes were of thermal electrolytic type (*19*) and had bias potentials less than 0.05 mV 3 days after the electrolysis. The hydrogen electrodes were prepared in accordance with the method of Hills and Ives (*20*). Other experimental details such as temperature control, the determination of dielectric constants, and densities of solvent mixtures at various temperatures have been described earlier (*17*). The

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Table II. Electromotive Force Data of the Cell from 25 to 35 °C in Various Glycerol–DMF Mixtures

(a) For HCl

m_{HCl}, mol kg^{-1}	E, V 25 °C	30 °C	35 °C
	x = 10 wt % DMF		
0.012 03	0.318 40	0.317 09	0.315 20
0.014 10	0.311 37	0.309 37	0.307 23
0.016 11	0.304 37	0.303 17	0.302 47
0.018 09	0.299 68	0.297 88	0.295 99
0.020 03	0.295 38	0.293 65	0.291 80
	x = 20 wt % DMF		
0.012 77	0.323 46	0.323 04	0.322 45
0.014 07	0.319 13	0.318 23	0.317 18
0.015 93	0.313 60	0.312 23	0.311 74
0.018 24	0.306 76	0.306 04	0.305 80
0.023 96	0.294 06	0.294 02	0.293 04
	x = 40 wt % DMF		
0.010 47	0.344 78	0.344 70	0.343 55
0.012 23	0.338 10	0.337 71	0.336 30
0.014 48	0.330 83	0.329 50	0.328 62
0.016 10	0.325 26	0.323 66	0.323 16
0.018 09	0.319 46	0.318 65	0.318 10
0.023 90	0.306 85	0.305 67	0.305 15
	x = 60 wt % DMF		
0.006 98	0.350 05	0.346 67	0.344 34
0.008 41	0.343 22	0.338 81	0.336 42
0.010 55	0.333 42	0.328 81	0.326 25
0.012 12	0.327 41	0.322 65	0.320 65
0.014 32	0.321 32	0.317 12	0.313 64
0.016 12	0.316 42	0.313 20	0.310 06

(b) For HBr

m_{HBr}, mol kg^{-1}	E, V 25 °C	30 °C	35 °C
	x = 10 wt % DMF		
0.010 33	0.197 45	0.197 20	0.196 97
0.014 32	0.181 68	0.181 08	0.179 67
0.015 40	0.179 74	0.178 07	0.176 49
0.016 13	0.176 75	0.175 75	0.174 38
0.018 35	0.169 78	0.168 59	0.167 35
0.020 41	0.165 43	0.164 07	0.162 81
	x = 20 wt % DMF		
0.009 18	0.224 69	0.224 29	0.223 62
0.014 05	0.204 78	0.203 99	0.203 43
0.015 88	0.199 21	0.198 22	0.196 85
0.017 67	0.194 45	0.193 30	0.192 14
0.021 02	0.186 53	0.185 77	0.183 71
	x = 40 wt % DMF		
0.010 24	0.238 25	0.236 75	0.235 21
0.012 29	0.230 53	0.228 25	0.226 51
0.014 24	0.223 65	0.222 23	0.219 62
0.016 20	0.218 27	0.216 45	0.213 73
0.020 04	0.208 55	0.205 84	0.203 86
0.022 40	0.203 71	0.201 30	0.198 55

Table III. ${}_{s}E^\circ_m$ at Different Temperatures and ${}_{s}E^\circ_N$ and ${}_{s}E^\circ_c$ at 25 °C in Various Glycerol–DMF Mixtures

wt % DMF	${}_{s}E^\circ_m$, V 25 °C	30 °C	35 °C	${}_{s}E^\circ_c$, V	${}_{s}E^\circ_N$, V
		For HCl			
10	0.076 50	0.070 97	0.064 18	0.086 74	−0.047 40
20	0.086 04	0.079 47	0.074 25	0.094 77	−0.039 14
40	0.098 06	0.093 45	0.086 79	0.103 77	−0.029 58
60	0.080 44	0.071 03	0.064 59	0.083 22	−0.049 54
		For HBr			
10	−0.049 62	−0.053 89	−0.058 98	−0.039 38	−0.173 52
20	−0.029 12	−0.034 34	−0.038 64	−0.020 39	−0.154 30
40	−0.011 16	−0.016 73	−0.022 70	−0.005 45	−0.138 80

Table IV. Coefficients of the Empirical Equation ${}_{s}E^\circ_m = {}_{s}E^\circ_{m,25\,°C} + b(t - 25) + c(t - 25)^2$

wt % DMF	${}_{s}E^\circ_{m,25\,°C}$	$-b \times 10^4$	$-c \times 10^5$
	For HCl		
0[a]	0.020 77	10.936	5.76
10	0.076 50	9.799	2.519
20	0.086 04	14.490	−2.700
40	0.098 06	7.169	4.100
60	0.080 44	21.789	−5.939
	For HBr		
0[b]	−0.113 80	10.999	0.000
10	−0.049 62	7.719	1.640
20	−0.029 12	11.359	−1.839
40	−0.011 16	10.739	0.800

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physical constant data of solvent mixtures are reported in Table I.

Results and Discussion

The emf data of cell 1 in the various solvent mixtures are given in Table IIa,b. The standard molal potentials, ${}_{s}E^\circ_m$, of the cell in the various solvent mixtures have been determined by extrapolation of the function

$$E^{\circ\prime} = E + 2K\log m - 2KA'C^{1/2}/(1 + aB'C^{1/2}) - 2K\log(1 + 0.002mM_{xy}) = {}_{s}E^\circ_m - 2Kbm \qquad (2)$$

to zero molality. In eq 2

$$K = RT\ln(10/F) = 2.303RT/F \qquad (3)$$

m and C are the molality and molarity of the acid, respectively. A' and B' are the Debye–Hückel constants, a is the ion size parameter (Å), b is the coefficient occurring in the expression for the activity coefficient as a function of molality, and M_{xy} is the mean molecular weight of the solvent mixture. In the determination of ${}_{s}E^\circ_m$, a = 5 Å was used in all compositions. Table III gives the ${}_{s}E^\circ_m$ values at the various temperatures and also ${}_{s}E^\circ_c$ and ${}_{s}E^\circ_N$, i.e., the ${}_{s}E^\circ$ values in molar and mole fraction scales, at 25 °C calculated from

$${}_{s}E^\circ_c = {}_{s}E^\circ_m + 2K\log d_0 \qquad (4)$$

$${}_{s}E^\circ_N = {}_{s}E^\circ_m - 2K\log(1000/M_{xy}) \qquad (5)$$

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

$${}_{s}E^\circ_m = {}_{s}E^\circ_{m,25\,°C} + b(t - 25) + c(t - 25)^2 \qquad (6)$$

where t is the temperature in degrees celsius and b and c are empirical coefficients. These data are summarised in Table IV. The stoichiometric mean molal activity coefficients of the acids, ${}_{s}\gamma_\pm$, referred to a value of unity at infinite dilution in the particular solvent and calculated according to the equation

$$\log {}_{s}\gamma_\pm = ({}_{s}E^\circ_m - E)/2K - \log m \qquad (7)$$

at 25 °C in all solvent mixtures at rounded molalities of the acids are recorded in Table V. The primary medium effect of HCl and HBr, defined as log ${}_{m}\gamma_\pm$ in the various solvent mixtures at 25 °C, calculated from

$$\log {}_{m}\gamma_\pm = ({}_{G}E^\circ_m - {}_{s}E^\circ_m)/2K \qquad (8)$$

is also incorporated in the same table. ${}_{G}E^\circ_m$ and ${}_{s}E^\circ_m$ in eq 8 represent the standard emfs of the cell (1) on the molal scale in glycerol and solvent, respectively. The primary medium effect is a measure of the free energy change associated with

Table V. Mean Molal Activity Coefficient ($s\gamma_\pm$) at Rounded Molalities (m_{acid}) of Acids and Primary Medium Effects of Acids (log $m\gamma_\pm$) in Various Glycerol–DMF Mixtures at 25 °C

wt % DMF	$s\gamma_\pm$ at m_{acid} (mol kg^{-1}) 0.01	0.012	0.014	0.015	0.02	log $m\gamma_\pm$
			For HCl			
10	0.764	0.752	0.739	0.734	0.703	−0.471
20	0.804	0.776	0.761	0.755	0.738	−0.552
40	0.785	0.765	0.755	0.751	0.732	−0.653
60	0.692	0.666	0.644	0.636	0.610	−0.504
			For HBr			
10	0.790	0.782	0.774	0.768	0.747	−0.542
20	0.772	0.759	0.749	0.744	0.718	−0.716
40	0.761	0.736	0.723	0.716	0.691	−0.868

Table VI. Standard Thermodynamic Quantities for the Transfer of Halogen Acids from Glycerol to Glycerol–DMF Mixtures at 25 °C

	10 wt % DMF	20 wt % DMF	40 wt % DMF	60 wt % DMF
$\Delta G°_{tr(N)}$(HCl)	−5251	−6049	−6970	−5043
$\Delta G°_{tr(N)}$(HBr)	−6066	−7922	−9417	
$\Delta S°_{tr(N)}$(HCl)	10.55	−35.13	34.17	−107.13
$\Delta S°_{tr(N)}$(HBr)	31.23	−4.31	0.87	
$T\Delta S°_{tr(N)}$(HCl)	3144	−10469	101.83	−31925
$T\Delta S°_{tr(N)}$(HBr)	9306	−1284	259	
$\Delta H°_{tr(N)}$(HCl)	−2107	−16518	3213	−36968
$\Delta H°_{tr(N)}$(HBr)	3241	−9206	−9158	

[a] Units: $\Delta G°_{tr(N)}$, J mol^{-1}; $\Delta S°_{tr}$, J K^{-1} mol^{-1}; $\Delta H°_{tr}$, J mol^{-1}; $T\Delta S°_{tr}$, J mol^{-1}.

the transfer of 1 mol of acid from glycerol to the given solvent at infinite dilution according to

$$\text{HX(glycerol)} = \text{HX(glycerol–DMF)} \qquad (9)$$

The standard free energy change, $\Delta G°_{tr}$ for the above process was calculated on the mole fraction scale for the various solvent mixtures at 25 °C by using

$$\Delta G°_{tr} = F({}_{G}E°_{N} - {}_{s}E°_{N}) \qquad (10)$$

where ${}_{G}E°_{N}$ and ${}_{s}E°_{N}$ represent the standard emfs of the cell (1) on the mole fraction scale. In the case of these isodielectric mixtures, the free energy change, $\Delta G°_{tr}$, as given by eq 10 reflects mostly $\Delta G°_{tr(nonel)}$. The electrostatic component of free energy of transfer $\Delta G°_{tr(el)}$ is negligible due to the small difference in the dielectric constants of the solvents. The standard entropy of transfer, $\Delta S°_{tr}$, was calculated from

$$\Delta S°_{tr} = -(\mathrm{d}/\mathrm{d}T)F({}_{G}E°_{N} - {}_{s}E°_{N})$$
$$= F(b_s - b_G) - 2(c_s - c_G)(t - 25) + (K_G - K_s) \qquad (11)$$

where b_s, c_s, b_G, and c_G are the coefficients from Table IV for the solvent and glycerol, respectively, and

$$K_G = (2R/F)\ln(1000/92.1) = 4.112 \times 10^{-4}$$

$$K_s = (2R/F)\ln(1000/M_{xy})$$

The last term in eq 11 arises in the conversion of ${}_{s}E°_{m}$ to ${}_{s}E°_{N}$. The standard enthalpy of transfer $\Delta H°_{tr}$, was calculated from the equation

$$\Delta H°_{tr} = \Delta G°_{tr} + T\Delta S°_{tr} \qquad (12)$$

All the thermodynamic parameters on the mole fraction scale are given in Table VI. The $\Delta G°_{tr}$ values are accurate to ±20 J/mol and the expected errors in $\Delta S°_{tr}$ and $\Delta H°_{tr}$ are ±0.5 J deg^{-1} and ±150 J, respectively.

The variations in $\Delta G°_{tr}$, $\Delta S°_{tr}$ ($T\Delta S°_{tr}$), and $\Delta H°_{tr}$ for HCl and HBr are shown graphically in Figure 1. The variation of $\Delta G°_{tr}$ of HCl and HBr is less discriminating than those for the other two functions. The values of $\Delta G°_{tr}$ for HCl and HBr are increasingly negative with an increasing proportion of DMF up to 40 wt % DMF. In the case of HCl, the $\Delta G°_{tr}$ value decreases at 60 wt % DMF, the sign still being negative. As stated earlier, the value of $\Delta G°_{tr}$ depicts only the contribution due to $\Delta G°_{tr(nonel)}$ as glycerol–DMF mixtures are isodielectric. The increasingly negative values of $\Delta G°_{tr}$ with the increasing proportion of DMF indicate that all glycerol–DMF mixtures (up to 60 wt % DMF) are more basic than glycerol. This also indicates that both HCl and HBr have lower free energy in the glycerol–DMF mixtures than in glycerol.

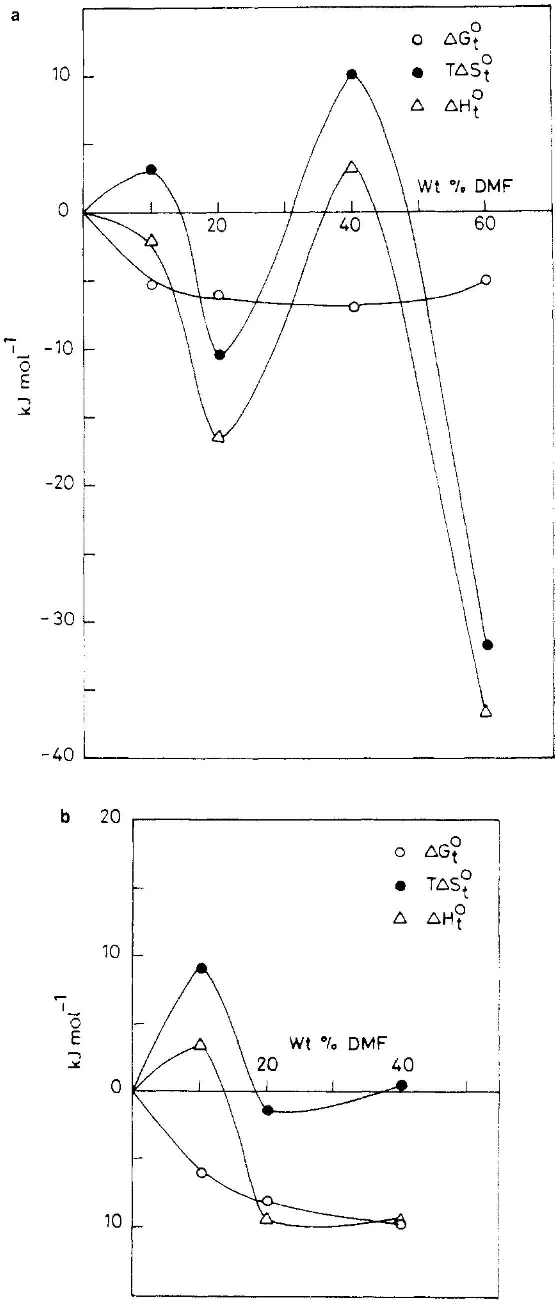

Figure 1. (a) Variation of various thermodynamic quantities (mole fraction scale) of transfer of HCl in glycerol–DMF mixtures at 25 °C. (b) Variation of various thermodynamic parameters (mole fraction scale) of transfer of HBr in glycerol–DMF mixtures at 25 °C.

Franks and Ives (*21*) suggested that the variations of $\Delta S°_{tr}$ and $\Delta H°_{tr}$ will give valuable information regarding the structural changes in the transfer process, rather than the variations of $\Delta G°_{tr}$. The transfer of an ion from glycerol to the other solvent mixtures mentioned here is expected to bring in the following structural changes (*22*): (1) breaking down the structure formed by glycerol molecules around the ion concerned, (2) building up

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the characteristic liquid structure, if any, by the released glycerol molecules, (*3*) breaking down the characteristic liquid structure of the other solvents, if any, so that the solvent molecules may be free to solvate the ion transferred, and (4) building up the ordered structure by the solvent molecules released by process 3 around the ion. The observed $\Delta S°_{\mathrm{tr(HX)}}$ may thus be represented as

$$\Delta S°_{\mathrm{tr(HX)}} = \sum_{1}^{4} \Delta S°_{i(\mathrm{H^+ + X^-})} = \Delta S°_{1(\mathrm{H^+ + X^-})} - \Delta S°_{2(\mathrm{H^+ + X^-})} + \Delta S°_{3(\mathrm{H^+ + X^-})} - \Delta S°_{4(\mathrm{H^+ + X^-})} \quad (13)$$

where $\Delta S°_i$ refers to the magnitudes of the entropy changes accompanying the respective steps indicated above. The sign and magnitude of the overall change depend on the relative magnitudes of the individual steps. In the glycerol-rich region (up to about 10 wt % DMF), the $\Delta S°_{\mathrm{tr}}$ increases may be due to a less negative magnitude of $-\Delta S°_{4(\mathrm{H^+ + X^-})}$ combined with an increasingly positive magnitude of $\Delta S°_{3(\mathrm{H^+ + X^-})}$. From 10 to 20 wt % DMF, the $\Delta S°_{\mathrm{tr}}$ decreases (the value being more negative), which indicates a decrease in the value of $-\Delta S°_{4(\mathrm{H^+ + X^-})}$ and a less positive magnitude of $\Delta S°_{3(\mathrm{H^+ + X^-})}$. This suggests that in this region there occurs a breakdown of the individual solvent structures. In the intermediate region (20-50 wt % DMF), the $\Delta S°_{\mathrm{tr}}$ values are positive, indicating an increasingly positive magnitude of $\Delta S°_{3(\mathrm{H^+ + X^-})}$ over the less negative magnitude of $-\Delta S°_{4(\mathrm{H^+ + X^-})}$. Finally, in the DMF-rich region, the $\Delta S°_{\mathrm{tr}}$ value is negative, which indicates the dominance of the negative magnitude of $-\Delta S°_{4(\mathrm{H^+ + X^-})}$ over the positive magnitude of $\Delta S°_{3(\mathrm{H^+ + X^-})}$ (This is true in the case of HCl around 60 wt % DMF). The same type of variation of $\Delta S°_{\mathrm{tr}}$ is observed for both HCl and HBr with the magnitudes in the case of HBr being somewhat smaller than those of HCl. The same trend is also observed in the case of variation of $\Delta H°_{\mathrm{tr}}$. In the case of HCl, around 40 wt % DMF an endothermic maximum is observed whereas in the case of HBr such an endothermic maximum is not noticed although the magnitude of the $\Delta H°_{\mathrm{tr}}$ decreases. It is worthwhile to mention that the variation of $\Delta S°_{\mathrm{tr}}$ with solvent composition observed in the present case is similar to that reported earlier by Kundu et al. (*14b*) in the isodielectric mixtures of methanol and propylene glycol.

Nomenclature

${}_{s}E°_{m}$, ${}_{s}E°_{c}$, ${}_{s}E°_{N}$, standard potentials in the solvent on molality, molarity, and mole fraction scales
$E°_{m}{}'$, extrapolation function
M_{xy}, mean molar mass of solvent mixture
$s\gamma_{\pm}$, mean molal activity coefficient of solute in the solvent "s"
$m\gamma_{\pm}$, mean ionic medium effect
$\Delta G°_{\mathrm{tr}}$, $\Delta H°_{\mathrm{tr}}$, $\Delta S°_{\mathrm{tr}}$, standard free energies, enthalpies, and entropies of transfer
$\Delta G°_{\mathrm{tr(nonel)}}$, $\Delta G°_{\mathrm{tr(el)}}$, nonelectrostatic and electrostatic parts of the free energy of transfer

Registry No. DMF, 68-12-2; HCl, 7647-01-0; HBr, 10035-10-6; Ag, 7440-22-4; AgCl, 7783-90-6; AgBr, 7785-23-1; glycerol, 56-81-5.

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Excess Molar Enthalpies of Nine Binary Steam Mixtures: New and Corrected Values

Neil M. Lancaster and Christopher J. Wormald*
School of Chemistry, The University of Bristol, Bristol BS8 1TS, U.K.

Heats of mixing of binary mixtures of steam + H_2, + N_2, + CO, + CO_2, + CH_4, + C_2H_4, + C_2H_6, + C_3H_8, and + C_4H_{10} at temperatures up to 698.2 K and pressures up to 12 MPa have been reported in the literature. In some experiments, the gas flow rate was measured by condensing out the water, reducing the pressure of the gaseous component to atmospheric, and measuring the volumetric flow rate. Two corrections were overlooked in calculating the flow rate. Some gas remains dissolved in the water, and some gas is displaced from the flow system as water accumulates in the high-pressure receiver. While the dissolved gas correction is around 1%, the displacement correction is around 10% at high pressures. Previously reported heats of mixing have been recalculated, and for $0.5H_2O + 0.5H_2$ and $0.5H_2O + 0.5N_2$ some new measurements are reported.

Excess molar enthalpies H_m^E of nine binary mixtures containing steam have been measured with a high-pressure flow mixing calorimeter (*1*). The mixtures investigated are steam + nitrogen (*1*), + methane (*2*), + hydrogen (*3*), + carbon monoxide (*4*), + carbon dioxide (*4*), + ethene (*5*), + ethane (*5*), + propane (*6*), and + butane (*6*). Most of the measurements extend up to 698.2 K at pressures up to about 12 MPa and at $x = 0.5$. For some mixtures, measurements of $H_m^E(x)$ were also made over a range of composition at temperatures and pressures where it was expected that the composition dependence would be most informative. As the work progressed, improvements in both technique and data analysis were made. For measurements reported at say 698.2 K and $x = 0.50$, the actual experimental conditions under which any one measurement was made may have differed from these conditions by 1 or 2 K and by 1% or 2% in composition. Small

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