Standard Potentials of Ag-AgCl Electrode in Methanol-Propylene Glycol Solvent System at Different Temperatures and Related Thermodynamic Quantities

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Standard potentials of the Ag-AgCl electrode were determined in a series of approximately isodielectric media formed by mixing methanol (MeOH) and propylene glycol (PG) at seven temperatures (5-35°C) from the emf measurements of the cell; Pt, H_2(g, 1 atm)/HCl(m), solvent/AgCl-Ag. These values were utilized to evaluate the thermodynamic quantities, $\Delta G_t°$, $\Delta S_t°$, and $\Delta H_t°$, accompanying the transfer of 1 mole of HCl from the standard state in methanol to the standard state in other solvents. The variation of $\Delta S_t°$ with solvent composition was examined in light of the effects of preferential solvation of H^+ and Cl^- by MeOH and PG, respectively, and that of the structural features of the solvents.

In a preceding paper (*11*) in this series, the standard potentials ($_sE°$) of the Ag-AgCl and Ag-AgBr electrodes in a series of approximately "isodielectric" media comprising methanol (MeOH, D_s = 32.63) and propylene glycol (PG, D_s = 31.0) were reported at a single temperature, 25°C. These values and related thermodynamic quantities were useful in understanding the behavior of HCl and HBr in these solvents and also in undertaking studies of proton transfer equilibria of some weak organic acids (*12*, *13*), as well as of the thermodynamic behavior of some alkali metal halides (*14*) in these solvents from the emf measurements of galvanic cells comprising these electrodes.

The free energy function is, in most cases, less discriminating than either the entropy or enthalpy function, since many of the effects relating structural aspects of solvents are associated with the corresponding effects on the entropy function (*2*, *5*, *6*, *15*). Hence, as a prerequisite to an understanding of the important structural contributions of these "isodielectric" solvents, as would be reflected in the enthalpy or entropy function of some of the systems, we determined $_sE°$ values of the AgCl-Ag electrode in these solvents at seven temperatures ranging from 5° to 35°C with an interval of 5°, which are reported in this paper.

The method of determination of $_sE°$ values of the AgCl-Ag electrode in MeOH-PG mixtures containing 10, 20, 50, 70, and 90 wt % PG is similar to that described earlier (*11*). A cell of type A: Pt, H_2(g, 1 atm)/HCl(m), solvent/AgCl-Ag, was used.

Experimental

The general experimental details, including the preparation of solvents, cell solutions, electrodes, and the measurement of densities of the solvents, have been described (*11*). The procedure for recording the emf's of cell A containing different molalities of HCl at different temperatures is also exactly similar to that described earlier (*16*). However, one important operation was incorporated in these measurements. Since one component of the solvent mixtures is appreciably volatile at the experimental temperatures, before allowing the H_2 gas to enter into the cell, the purified gas was presaturated by passing it first through the particular solvent and then through a series of six bubblers containing the same solution as present in the cell.

The temperature of the cell and the bubblers was the same. This was particularly necessary to avoid the change of composition of solvent in the cell vessel and of concentration of HCl, and hence to have a stable emf at equilibrium. The readings were recorded at intervals of 15 min till three successive readings were constant within ±0.2 mV. A period of 4-5 hr was necessary to reach equilibrium at 5°. After recording the emf's at 5°, the temperature of the bath was raised to the next higher temperature, and readings were recorded at equilibrium at that temperature. In this way, emf measurements were made at higher temperatures.

Results

The values of the emf in each solvent at different temperatures were corrected for 1-atm H_2 pressure. The vapor pressures of the solvents at different temperatures (Table I) were computed in a manner described earlier (*11*), the vapor pressure of PG in this temperature range being negligibly small (*4*). The emf values and corresponding molalities (m) of HCl are presented in Table II.

The standard potentials of the Ag-AgCl electrode ($E_m°$) were determined by extrapolation to m = 0 of the function $E°'$ defined by Equation 1 (*11*):

$$E°' = E + 2k \log m - \frac{2k S_f C^{1/2}}{1 + a_0 B C^{1/2}} - 2k \log (1 + 0.002\, m M_s) = E_m° + f(m) \quad (1)$$

where all terms have their usual significance. The values of Debye-Hückel constants S_f and B were computed from the relations $S_f = 1.824 \times 10^6/(D_s T)^{3/2}$ and $B = 50.29/(D_s T)^{1/2}$, where D_s is the dielectric constant of the solvent at the particular temperature as given in Table I. At any temperature the values of D_s at different compositions were estimated by assuming the volume fraction additivity rule suitable for ideal mixture for dielectric constants (*11*). The values so obtained are furnished in Table I.

The dielectric constants of MeOH and PG at different temperatures were computed from the temperature coefficients of the dielectric constant given in the literature (*7*). The approximate values of C (molar concentration) were calculated by equating it to md_s, where d_s is the density of the particular solvent at that temperature (Table I). The values of M_s, the molecular weight of the pure solvent or the average molecular weight of a solvent mixture, were computed from the usual relation (*8*). For computing the values of $E°'$, the value of a_0 was taken as zero. Figure 1 illustrates the typical extrapolation for $E_m°$ of the Ag-AgCl electrode in one of these solvents (50% PG). $E_m°$ values so evaluated at different temperatures are presented in Table III. The $E_m°$ values in each sol-

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vent of this system can be represented as a function of temperature as given below:

$$0\%\ \text{PG}\ (1),\ E_m{}^\circ = -0.0103 - 1.208 \times 10^{-3}(t - 25) - 4.00 \times 10^{-6}(t - 25)^2$$

$$10\%\ \text{PG},\ E_m{}^\circ = +0.0020 - 1.26 \times 10^{-3}(t - 20) - 6.80 \times 10^{-6}(t - 20)^2$$

$$20\%\ \text{PG},\ E_m{}^\circ = +0.0023 - 1.36 \times 10^{-3}(t - 20) - 4.90 \times 10^{-6}(t - 20)^2$$

$$50\%\ \text{PG},\ E_m{}^\circ = -0.0030 - 1.35 \times 10^{-3}(t - 20) - 3.61 \times 10^{-6}(t - 20)^2$$

$$70\%\ \text{PG},\ E_m{}^\circ = -0.0086 - 1.48 \times 10^{-3}(t - 20) + 4.50 \times 10^{-6}(t - 20)^2$$

$$90\%\ \text{PG},\ E_m{}^\circ = -0.0174 - 1.72 \times 10^{-3}(t - 20) + 1.14 \times 10^{-5}(t - 20)^2$$

$$100\%\ \text{PG}\ (16),\ E_m{}^\circ = -0.0323 - 1.58 \times 10^{-3}(t - 25) - 8.968 \times 10^{-7}(t - 25)^2$$

The standard potentials in molal (${}_sE_m{}^\circ$) and mole fraction (${}_sE_N{}^\circ$) scales at 25° are presented in Table IV. The subscript *s* denotes that the values are referred to the particular solvent as the reference state. The values at 25° compare fairly well with those reported earlier (*11*).

The free energy changes accompanying the transfer of 1 mole of HCl, $\Delta G_t{}^\circ$ (HCl), from the standard state in the reference solvent methanol to that in other solvents were computed at 25° with the help of Relation 2:

$$\Delta G_t{}^\circ\ (\text{HCl}) = -F({}_sE_N{}^\circ - {}_mE_N{}^\circ) \qquad (2)$$

and are presented in Table V. The subscript *m* refers to methanol as the solvent. The mole fraction scale has been used to eliminate the effect of changes in concentration (*9, 17*). The corresponding entropies, $\Delta S_t{}^\circ$ (HCl), and enthalpies, $\Delta H_t{}^\circ$ (HCl), have also been computed by the usual relations (*23*) from the constants of the $E_m{}^\circ$-temperature equation given above. The $\Delta G_t{}^\circ$ values are

Table I. Necessary Parameters for Evaluation of $E^{\circ\prime}$ of Equation 1 in MeOH-PG mixtures at Different Temperatures

	°C						
	5	10	15	20	25	30	35
10 wt % PG (M_s = 34.00)							
D_s	36.78	35.68	34.57	33.56	32.56	31.59	30.65
Vapor press (p), mm	39.08	52.66	70.04	92.70	120.9	156.4	199.6
Density (d_s), g/cc	0.8275	0.8229	0.8183	0.8138	0.8093	0.8045	0.7997
S_f	1.763	1.797	1.835	1.869	1.906	1.947	1.987
B	0.4973	0.5003	0.5040	0.5071	0.5104	0.5140	0.5175
20 wt % PG (M_s = 36.22)							
D_s	36.68	35.58	34.49	33.46	32.47	31.50	30.56
Vapor press (p), mm	36.50	49.00	64.60	85.50	110.9	142.9	183.9
Density (d_s), g/cc	0.8496	0.8448	0.8401	0.8354	0.8308	0.8265	0.8222
S_f	1.770	1.806	1.842	1.878	1.915	1.955	1.995
B	0.4979	0.5013	0.5046	0.5078	0.5112	0.5147	0.5182
50 wt % PG (M_s = 45.08)							
D_s	36.35	35.25	34.16	33.14	32.14	31.18	30.24
Vapor press (p), mm	28.40	38.10	50.60	66.50	86.30	111.2	142.9
Density (d_s), g/cc	0.9203	0.9158	0.9114	0.9075	0.9036	0.8995	0.8954
S_f	1.795	1.829	1.867	1.905	1.945	1.986	2.027
B	0.5002	0.5034	0.5069	0.5102	0.5139	0.5174	0.5210
70 wt % PG (M_s = 53.85)							
D_s	36.02	34.93	33.84	32.81	31.82	30.85	29.92
Vapor press (p), mm	20.40	27.40	36.30	47.80	61.90	79.80	102.6
Density (d_s), g/cc	0.9694	0.9654	0.9614	0.9575	0.9537	0.9498	0.9458
S_f	1.820	1.855	1.894	1.934	1.974	2.018	2.060
B	0.5025	0.5058	0.5093	0.5129	0.5164	0.5201	0.5237
90 wt % PG (M_s = 66.87)							
D_s	35.52	34.43	33.37	32.34	31.35	30.26	29.45
Vapor press (p), mm	8.40	11.30	15.00	19.50	25.60	33.20	42.50
Density (d_s), g/cc	1.0220	1.0180	1.0140	1.0100	1.0060	1.0022	0.9984
S_f	1.858	1.894	1.936	1.976	2.018	2.066	2.110
B	0.5060	0.5093	0.5130	0.5165	0.5202	0.5243	0.5279

Table II. Emf (Volt) of Cell A in MeOH-PG Mixtures from 5° to 35°C

	°C						
m_{HCl}	5	10	15	20	25	30	35
10 wt % PG							
0.00572	0.2805	0.2795	0.2780	0.2769	0.2755	0.2736	0.2716
0.01014	0.2571	0.2554	0.2536	0.2517	0.2498	0.2475	0.2453
0.01647	0.2368	0.2349	0.2330	0.2311	0.2292	0.2268	0.2243
0.02032	0.2280	0.2258	0.2240	0.2219	0.2192	0.2173	0.2145
0.02845	0.2142	0.2122	0.2102	0.2083	0.2064	0.2038	0.2013
0.03415	0.2075	0.2051	0.2028	0.2009	0.1990	0.1959	0.1929
0.04009	0.2012	0.1985	0.1968	0.1942	0.1917	0.1888	0.1860

Table II. Continued

	°C						
m_{HCl}	5	10	15	20	25	30	35
			10 wt % PG				
0.05061	0.1922	0.1895	0.1869	0.1841	0.1816	0.1787	0.1758
0.06797	0.1792	0.1765	0.1738	0.1709	0.1680	0.1651	0.1622
0.07829	0.1745	0.1719	0.1693	0.1664	0.1634	0.1603	0.1573
0.08584	0.1712	0.1684	0.1656	0.1626	0.1596	0.1563	0.1531
			20 wt % PG				
0.00493	0.2873	0.2857	0.2842	0.2830	0.2804	0.2794	0.2765
0.00753	0.2682	0.2666	0.2651	0.2637	0.2619	0.2593	0.2568
0.00835	0.2646	0.2628	0.2610	0.2593	0.2575	0.2549	0.2523
0.00989	0.2573	0.2556	0.2540	0.2520	0.2500	0.2476	0.2453
0.01232	0.2483	0.2462	0.2441	0.2418	0.2395	0.2370	0.2345
0.01550	0.2386	0.2367	0.2349	0.2326	9.2313	0.2275	0.2248
0.01700	0.2360	0.2339	0.2317	0.2290	0.2263	0.2234	0.2204
0.02040	0.2280	0.2261	0.2242	0.2214	0.2187	0.2159	0.2131
0.02509	0.2190	0.2169	0.2149	0.2125	0.2090	0.2071	0.2042
0.03141	0.2110	0.2084	0.2058	0.2035	0.2013	0.1979	0.1944
0.03534	0.2054	0.2029	0.2003	0.1979	0.1955	0.1931	0.1908
0.03941	0.2011	0.1969	0.1947	0.1921	0.1896	0.1868	0.1840
0.04879	0.1919	0.1896	0.1864	0.1846	0.1811	0.1791	0.1761
0.05910	0.1834	0.1808	0.1783	0.1759	0.1725	0.1707	0.1680
0.06855	0.1772	0.1746	0.1720	0.1692	0.1665	0.1634	0.1603
0.08005	0.1700	0.1673	0.1647	0.1620	0.1593	0.1565	0.1538
0.08872	0.1656	0.1630	0.1604	0.1577	0.1550	0.1517	0.1485
			50 wt % PG				
0.00501	0.2824	0.2813	0.2802	0.2783	0.2765	0.2744	0.2724
0.00756	0.2652	0.2632	0.2622	0.2601	0.2586	0.2560	0.2538
0.01079	0.2523	0.2503	0.2482	0.2456	0.2430	0.2404	0.2378
0.01240	0.2447	0.2429	0.2411	0.2387	0.2370	0.2342	0.2317
0.01543	0.2356	0.2337	0.2318	0.2296	0.2274	0.2248	0.2223
0.02139	0.2225	0.2206	0.2188	0.2166	0.2144	0.2113	0.2083
0.02550	0.2177	0.2150	0.2124	0.2096	0.2069	0.2042	0.2015
0.03371	0.2056	0.2029	0.2003	0.1979	0.1955	0.1922	0.1890
0.04316	0.1966	0.1942	0.1909	0.1889	0.1859	0.1826	0.1783
0.04861	0.1924	0.1896	0.1869	0.1840	0.1811	0.1780	0.1750
0.06098	0.1828	0.1803	0.1779	0.1751	0.1718	0.1688	0.1658
0.07050	0.1769	0.1744	9.1719	0.1690	0.1662	0.1631	0.1600
0.08241	0.1726	0.1682	0.1654	0.1625	0.1595	0.1561	0.1528
0.09173	0.1673	0.1635	0.1619	0.1595	0.1560	0.1524	0.1488
			70 wt % PG				
0.00452	0.2859	0.2825	0.2800	0.2773	0.2752	0.2740	0.2727
0.01036	0.2502	0.2463	0.2444	0.2423	0.2405	0.2383	0.2351
0.01346	0.2407	0.2374	0.2345	0.2312	0.2288	0.2266	0.2240
0.02232	0.2191	0.2162	0.2132	0.2107	0.2083	0.2051	0.2025
0.03031	0.2072	0.2049	0.2019	0.1989	0.1960	0.1937	0.1904
0.04086	0.1950	0.1916	0.1893	0.1868	0.1841	0.1820	0.1796
0.05213	0.1848	0.1819	0.1790	0.1764	0.1738	0.1711	0.1680
0.06191	0.1772	0.1745	0.1719	0.1700	0.1677	0.1649	0.1617
0.07181	0.1712	0.1685	0.1669	0.1643	0.1617	0.1587	0.1557
0.08305	0.1652	0.1625	0.1609	0.1583	0.1557	0.1523	0.1486
			90 wt % PG				
0.00513	0.2749	0.2722	0.2681	0.2659	0.2611	0.2585	0.2560
0.01005	0.2474	0.2434	0.2396	0.2345	0.2309	0.2289	0.2258
0.01283	0.2387	0.2347	0.2292	0.2247	0.2209	0.2180	0.2151
0.02001	0.2206	0.2161	0.2116	0.2079	0.2043	0.2007	0.1973
0.02517	0.2102	0.2073	0.2019	0.1975	0.1936	0.1905	0.1874
0.03035	0.2040	0.1997	0.1945	0.1908	0.1860	0.1838	0.1800
0.03517	0.1986	0.1933	0.1885	0.1844	0.1804	0.1767	0.1729
0.04014	0.1922	0.1886	0.1826	0.1795	0.1749	0.1716	0.1685
0.04832	0.1862	0.1820	0.1758	0.1706	0.1673	0.1651	0.1610
0.05470	0.1806	0.1738	0.1710	0.1669	0.1629	0.1592	0.1556
0.06132	0.1764	0.1710	0.1660	0.1630	0.1590	0.1549	0.1508
0.07023	0.1700	0.1658	0.1617	0.1595	0.1534	0.1493	0.1453
0.08139	0.1634	0.1592	0.1550	0.1509	0.1469	0.1433	0.1400
0.09221	0.1583	0.1524	0.1490	0.1457	0.1425	0.1379	0.1333

correct within ±0.02 kcal, and the expected errors in $\Delta S_t°$ and $\Delta H_t°$ are ±0.2 cal deg^{-1} and ±0.14 kcal, respectively. Note that the observed magnitudes of $\Delta G_t°$ (HCl) values are slightly at variance with those reported earlier (*11*). This is because the $_sE_m°$ value of the reference solvent (MeOH) used earlier is different from the present case. The present source of data (loc. cit.) has been utilized, because it incorporates the relevant data at different temperatures.

Discussion

The variations in $\Delta G_t°$, $\Delta S_t°$, and $\Delta H_t°$ for HCl with weight % PG are shown graphically in Figure 2. As expected, the variation of $\Delta G_t°$ (HCl) is less discriminating than those for the other two functions. The values of $\Delta G_t°$ (HCl) decrease somewhat sharply at first with a distinct tendency to assume limiting values, as the proportion of PG increases (Figure 2), the corresponding variations of $\Delta S_t°$ (HCl) and $\Delta H_t°$ (HCl) being quite complex. It is presumably reasonable (*2, 5, 6, 15, 18, 19, 25*) to assume that the minima at the extreme regions and maxima at about 50–55% PG are associated with the structural aspects of the solvents, especially because (*24*) very little electrostatic contribution arising from the small difference of permittivity of the solvents is involved in those values.

It is generally believed that MeOH (*3, 10, 20–22*) and possibly PG (*15*) are associated-type liquids, but devoid of any water-like characteristic structure. But whether the addition of PG to MeOH, or vice-versa, brings in any change in the respective structures is a matter of special interest, and to obtain some insight into this matter, we may examine the observed variation in $\Delta S_t°$ (HCl) with the composition of the medium. The transfer of an ion from MeOH to any of the other solvents referred to here is expected to bring in the following structural changes (*18, 19*): (1) breaking down the structure formed by MeOH molecule around the ion concerned; (2) building up of the "characteristic" liquid structure, if any, by the released MeOH molecules; (3) breaking down of the "characteristic" liquid structure of other solvents, if any, so that the solvent molecules may be free to solvate the transferred ion; and (4) building up of the ordered structure by the solvent molecules released by process 3 around the ion. The observed $\Delta S_t°$ (HCl) should be represented by Equation 3:

$$\Delta S_t° \text{ (HCl)} = \sum_{1}^{4} \Delta S_i° \, (H^+ + \text{Cl}^-) = \Delta S_1° \, (\text{H}^+ + \text{Cl}^-) - \Delta S_2° \, (\text{H}^+ + \text{Cl}^-) + \Delta S_3° \, (H^+ + \text{Cl}^-) - \Delta S_4° \, (\text{H}^+ + \text{Cl}^-) \quad (3)$$

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 will depend on the relative magnitudes of the individual steps.

The free energy of transfer of H^+, $\Delta G_t°$ (H^+), becomes increasingly positive, while that for Cl^-, $\Delta G_t°$ (Cl^-), becomes increasingly negative as the proportion of PG increases, the magnitude of the latter being greater than the former at any solvent composition (*14*). Thus, as the glycophilicity of Cl^- exceeds the methanophilicity of H^+, it may be expected that with the increasing proportion of PG, the order around the solvated Cl^- should ex-

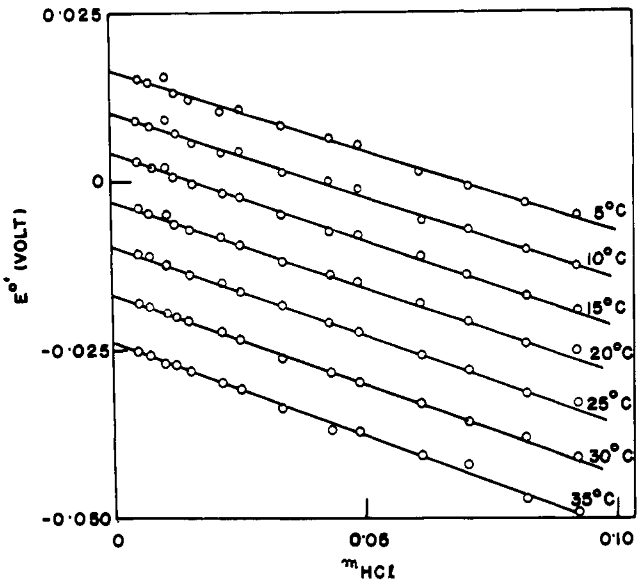

Figure 1. Extrapolation of emf data to give $E_m°$ for Ag-AgCl electrode in 50% methanol and 50% propylene glycol at different temperatures

Table IV. Standard Potentials of Ag-AgCl Electrode in MeOH-PG Mixtures at 25°C

Wt % PG	$_sE_m°$, V	$_sE_N°$, V	Wt % PG	$_sE_m°$, V	$_sE_N°$, V
0	−0.0103	−0.1871	70	−0.0160	−0.1662
10	−0.0044	−0.1781	90	−0.0260	−0.1649
20	−0.0048	−0.1741	100	−0.0323	−0.1646
50	−0.0100	−0.1693			

Table V. Free Energy, Entropy, and Enthalpy of Transfer of HCl from MeOH to MeOH-PG Mixtures at 25°C

Wt % PG	$\Delta G_t°$ (HCl), kcal mol^{-1}	$\Delta S_t°$ (HCl), cal mol^{-1} deg^{-1}	$\Delta H_t°$ (HCl), kcal mol^{-1}
10	−0.20	−2.5	−0.95
20	−0.30	−4.2	−1.55
50	−0.42	−2.8	−1.25
70	−0.48	−3.3	−1.46
90	−0.54	−6.2	−2.39
100	−0.62	−5.1	−2.04

Table III. $E_m°$ (Volt) of Ag-AgCl Electrode in MeOH-PG Mixtures at Different Temperatures

Wt % PG	°C						
	5	10	15	20	25	30	35
10	+0.0194	+0.0139	+0.0081	+0.0020	−0.0044	−0.0113	−0.0184
20	+0.0215	+0.0150	+0.0090	+0.0023	−0.0048	−0.0120	−0.0192
50	+0.0163	+0.0102	+0.0037	−0.0030	−0.0100	−0.0170	−0.0240
70	+0.0145	+0.0070	−0.0010	−0.0086	−0.0160	−0.0225	−0.0300
90	+0.0110	+0.0010	−0.0080	−0.0174	−0.0260	−0.0325	−0.0410

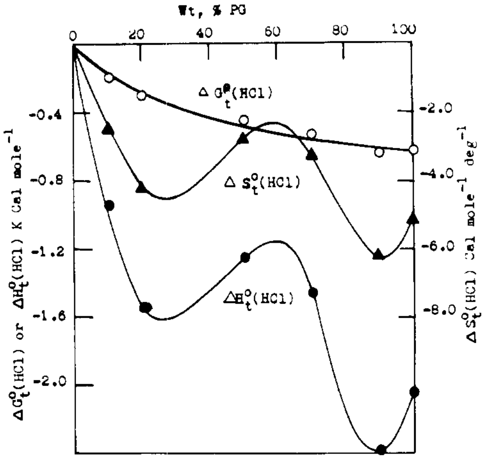

Figure 2. Variation of $\Delta G_t°$ (HCl), $\Delta S_t°$ (HCl), and $\Delta H_t°$ (HCl) with weight % PG from MeOH to MeOH–PG solvent mixtures at 25°C

ceed that around the solvated proton. As a result, $|\Delta S_4°$ ($H^+ + Cl^-$)$|$ should increase with increasing proportion of PG. But the observed variation of $\Delta G_t°$ ($H^+ + Cl^-$) suggests that $|\Delta S_4°$ ($H^+ + Cl^-$)$|$ is not likely to increase uniformly, but with a decreasing rate.

The order around an ion, including both the primary and secondary solvation zone of the ion, is greater than that around a central solvent dipole. As a result, $|\Delta S_1°$ ($H^+ + Cl^-$)$|>|\Delta S_2°$ ($H^+ + Cl^-$)$|$ and $|\Delta S_4°$ ($H^+ + Cl^-$)$| > |\Delta S_3°$ ($H^+ + Cl^-$)$|$. And as steps 1 and 2 refer to methanol, the sum [$\Delta S_1°$ ($H^+ + Cl^-$) $-$ $\Delta S_2°$ ($H^+ + Cl^-$)] should be a constant positive quantity. But since steps 3 and 4 are related to solvents other than MeOH, the sum [$\Delta S_3°$ ($H^+ + Cl^-$) $-$ $\Delta S_4°$ ($H^+ + Cl^-$)] should be a negative quantity, the magnitudes of which should, however, vary with the composition of the solvent. So, in all probability the overall value of $\Delta S_t°$ (HCl) should be dictated largely by the quantity [$\Delta S_3°$ ($H^+ + Cl^-$) $-$ $\Delta S_4°$ ($H^+ + Cl^-$)].

In the methanol-rich region the sharp fall in $\Delta S_t°$ (HCl) values leads us to suspect that it may be due, not only to a sharper decrease in the values of $-\Delta S_4°$ ($H^+ + Cl^-$), but also to less positive magnitudes of $\Delta S_3°$ ($H^+ + Cl^-$) for the mixed solvents in this region of composition. This implies that in this region there occurs a breakdown of the individual solvent structures releasing more monomeric forms of the dipoles from their respective associated forms, when PG is added to MeOH. But upon addition of more PG, the sharp increase of $\Delta S_t°$ (HCl) is possibly due to the relatively less negative magnitudes of $-\Delta S_4°$ ($H^+ + Cl^-$) combined with the increasingly positive magnitudes of $\Delta S_3°$ ($H^+ + Cl^-$). This possibly implies that in this region the solvent dipoles of both kinds form some sort of hydrogen-bonded clusters among themselves, which, however, ultimately break down with further addition of PG, as indicated by the decrease in $\Delta S_t°$ (HCl) values, resulting in a maximum at 50–60 wt % of PG.

At the extreme PG-rich region, the observed increase of $\Delta S_t°$ (HCl) resulting in a minimum perhaps arises from the less nagative magnitudes of $-\Delta S_4°$ ($H^+ + Cl^-$), as expected from the nature of variation of $\Delta G_t°$ (HCl), and partly from the more positive magnitudes of $\Delta S_3°$ ($H^+ + Cl^-$), implying a more associated nature of pure PG. The above conclusions regarding the relative structure of the mixed solvents have, however, to be substantiated by similar studies with HBr and HI.

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