THERMODYNAMIC BEHAVIOUR OF HYDROCHLORIC ACID IN PROPYLENE GLYCOL AND ITS AQUEOUS MIXTURES FROM ELECTROMOTIVE FORCE MEASUREMENTS

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ABSTRACT

The standard potentials of the silver–silver chloride electrode in pure propylene glycol (PG) and in nineteen PG + water solvent mixtures, covering the whole range of solvent composition, were determined from electromotive force measurements of cells of the type: Pt, H_2 (gas, 1 atm): HCl (m) in solvent: AgCl, Ag, at twelve different temperatures from 0 to 55°C at 5°C intervals. The molality, m, of HCl ranged from 0.001 to 0.1 mole kg^{-1}. The standard EMF was determined by an extrapolation method making use of the extended terms of the Debye–Hückel theory. The temperature variation of the standard EMF was used to calculate the standard thermodynamic functions for the cell reaction and the standard thermodynamic quantities for the transfer of HCl from water to the respective solvents. The results are discussed both in terms of the acid–base behaviour of the solvents and also their structural effects on the transfer process.

INTRODUCTION

Electrochemical studies, used in recent years to determine the thermodynamics of hydrogen halides in aqueous and non-aqueous media, offer a method of understanding the medium effects associated with the transfer of these electrolytes from water to any solvent. The thermodynamic behaviour of hydrochloric acid in pure or mixed solvents has long been a subject of interest. However, few electrochemical studies have been made in propylene glycol (PG) or its aqueous mixtures. The EMF measurements on HCl solutions in PG [1,2], performed at nine temperatures from 5 to 45°C, were used to determine the standard potentials of the Ag–AgCl electrode, the activity coefficients and the relative partial molal enthalpies of HCl, in PG, and the medium effects of PG on HCl. Similar EMF measurements have been made on hydrochloric acid solutions in two aqueous solvents [3]

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containing 10 and 20 wt.% PG, at 25°C, where the standard potentials of the Ag–AgCl electrode and the activity coefficients of HCl in these solvents were derived. This study [3] was restricted to one temperature only. But, to understand more clearly the proton transfer equilibria as well as ionic processes in general in any solvent, evaluation of the energetics involved should be of prime importance. However, no electrochemical thermodynamic transfer functions for HCl have so far been reported in PG + water mixtures.

Thus, in continuation of our studies on this subject [4–6], We have now undertaken measurements of the E.M.F. of the cell

Pt, H_2(gas, 1 atm): HCl (m) in solvent: AgCl, Ag   (A)
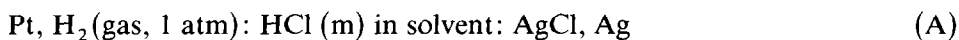
in nineteen PG + water solvent mixtures as well as in pure PG at twelve different temperatures from 0 to 55°C at 5°C intervals. This wide range of temperature is sufficient to yield better accuracy in the calculation of the thermodynamic properties that are dependent on the temperature coefficient of the EMF. The results have been utilized to derive the standard EMF of cell (A), which is the standard potential of the Ag–AgCl electrode, the thermodynamic functions for the cell reaction and the thermodynamic quantities for the transfer of HCl from water to the respective solvents. We can thus obtain a comprehensive understanding of the thermodynamic behaviour of HCl in these media and of the properties and structure of the solvents.

EXPERIMENTAL

PG was of B.D.H. AnalaR quality and was further purified as described earlier [2]. The characterstic properties of the product agreed well with those reported elsewhere [1,3] for pure PG. Because of the hygroscopic nature of glycols [1,7], the distilled glycol was kept in an atmosphere of dry argon, redistilled freshly and used within a few hours. Care was always taken during all the operations to avoid exposure of the solvents and solutions to the atmosphere as far as practicable. Redistilled deionized water, having a specific conductance of 0.7×10^{-6} Ω^{-1} cm^{-1}, was generally used in preparing the solutions. The cell solutions were prepared by weight dilution of the stock solution with solvent, and the PG content of all the solutions reported was accurate to ± 0.03 wt.%. All the solutions were freshly prepared before taking measurements.

The electrodes were prepared essentially as described elsewhere [4–6], and were preserved over the respective solvents when not in use. The experimental set-up and the general procedure used for the EMF measurements were identical to those given previously [4–6]. In the preparation of non-aqueous or PG-rich stock solutions of HCl, care was taken to keep the vessel

containing the solvent in a freezing mixture, to arrest the rise in temperature of the resulting solutions due to the heat evolved on dissolution of HCl gas in the solvents [1]. It was expected that this would slow the rate of probable side reactions such as the formation of chlorohydrin, especially at appreciably higher concentrations [1]. The molality of HCl solutions ranged from 0.001 to 0.1 mole kg^{-1}. The acid concentration was accurate to $\pm 0.03\%$. The EMF measurements were made with three hydrogen electrodes and three silver–silver chloride electrodes for each solution. The cells were thermostated at each temperature with an accuracy of $\pm 0.01°C$. The silver–silver chloride electrodes, which functioned smoothly with good reproducibility in the solvents, were found to be stable over the entire range of temperature, and constancy of the cell EMF to ± 0.1 mV over a period of $\frac{1}{2}$ h was considered as an adequate criterion of equilibrium in the EMF measurements. As a precaution, a given cell was never measured over the entire temperature range. Three series of results were made at each acid concentration. The first was from 0 to 20°C, the second from 15 to 40°C and the third from 35 to 55°C. As new solutions were prepared for the measurements in each, the results serve as an excellent means of checking the reproducibility of the procedure. The EMF values were generally reproducible to $\pm$ 0.2 mV for different solutions. Equilibrium was usually established within 1–2 h for cells containing water-rich solvents at higher temperatures but a relatively longer time, 3–4 h, was required for the PG-rich solvents cells and especially at lower temperatures. The cell measurements were made in triplicate, and the mean values of these observations recorded. The triplicate results generally agreed within $\pm$ 0.2 mV. The observed values of EMF were corrected in the usual way to a hydrogen pressure of 1 atm. The physical properties of the solvents over the temperature range 0–55°C were derived from the previous data [1,3,7,8].

RESULTS AND DISCUSSION

Standard electrode potential

The standard potentials of the Ag–AgCl electrode in PG and its aqueous mixtures have been determined at each temperature by the usual extrapolation technique, making use of the extended terms of the Debye–Hückel theory, and the procedure is essentially the same as that used in our previous determinations [4–6]. The least-squares values of the standard potential E_m^0 (molality scale) of the Ag–AgCl electrode found in this investigation are summarized in Table 1, for each solvent, along with the values for water as the solvent [4–6]. The ion-size parameters that gave a satisfactory linear extrapolation were in the range 0.41–0.53 nm depending on both temperature and solvent composition. A deviation of $\pm$ 0.05 mV in E_m^0 was seen

TABLE 1

Standard molal potentials, E_m^0, of the silver–silver chloride electrode in propylene glycol + water solvent mixtures at 0–55°C

Wt.% PG	E_m^0 (abs. volts) at.					
	0°C	5°C	10°C	15°C	20°C	25°C
0	0.23665	0.23410	0.23137	0.22853	0.22555	0.22236
5	0.23336	0.23067	0.22787	0.22501	0.22193	0.21874
10	0.22993	0.22724	0.22452	0.22152	0.21836	0.21513
15	0.22628	0.22373	0.22084	0.21789	0.21482	0.21141
20	0.22294	0.22035	0.21757	0.21448	0.21119	0.20784
25	0.21980	0.21717	0.21433	0.21119	0.20787	0.20442
30	0.21671	0.21390	0.21104	0.20782	0.20441	0.20089
35	0.21318	0.21049	0.20756	0.20430	0.20083	0.19721
40	0.20982	0.20707	0.20396	0.20075	0.19733	0.19347
45	0.20628	0.20336	0.20018	0.19692	0.19339	0.18943
50	0.20235	0.19939	0.19633	0.19283	0.18904	0.18512
55	0.19788	0.19503	0.19181	0.18835	0.18463	0.18039
60	0.19308	0.19014	0.18696	0.18331	0.17933	0.17511
65	0.18749	0.18450	0.18114	0.17756	0.17360	0.16905
70	0.18098	0.17799	0.17474	0.17090	0.16665	0.16208
75	0.17301	0.17017	0.16676	0.16292	0.15867	0.15372
80	0.16305	0.16021	0.15669	0.15274	0.14827	0.14303
85	0.14906	0.14602	0.14251	0.13823	0.13335	0.12796
90	0.12667	0.12370	0.12011	0.11561	0.11056	0.10467
95	0.08220	0.07918	0.07529	0.07067	0.06533	0.05898
100	−0.00752	−0.01067	−0.01471	−0.01965	−0.02549	−0.03229

when the value of the parameter was varied within ± 0.02 nm of the chosen value. The average standard deviation in E_m^0 is ± 0.1, ± 0.2 and ± 0.3 mV for solvents containing 5–50, 55–80 and 85–100 wt.% PG, respectively.

The values of E_m^0 (in abs. volts) obtained at twelve temperatures for each solvent were fitted by the method of least-squares to a quadratic equation of the form

$$E_m^0 = a - b(T - 298.15) - c(T - 298.15)^2 \tag{1}$$

where T is the thermodynamic temperature. The parameters a, b and c are given in Table 2, for each solvent, along with the values for water as the solvent [4–6]. Values of E_m^0 calculated by eqn. (1) and the experimental values (Table 1) generally agree within ± 0.15 mV.

The values of the standard potentials on the molar concentration (E_c^0) and mole fraction (E_N^0) scales have been computed with the help of the usual relations [4–6]. These values at 25°C are included in Table 2. Both E_c^0 and E_N^0 values decrease with increasing PG content in the solvent mixture.

Reported standard potentials of the Ag–AgCl electrode in pure PG [1,2] or its aqueous mixtures [3] and our corresponding new values are collected in

30°C	35°C	40°C	45°C	50°C	55°C
0.21907	0.21564	0.21205	0.20828	0.20443	0.20044
0.21532	0.21185	0.20823	0.20433	0.20033	0.19621
0.21163	0.20809	0.20434	0.20039	0.19621	0.19204
0.20795	0.20422	0.20043	0.19630	0.19200	0.18772
0.20417	0.20046	0.19656	0.19235	0.18809	0.18348
0.20078	0.19686	0.19269	0.18851	0.18412	0.17935
0.19717	0.19313	0.18884	0.18450	0.17979	0.17504
0.19339	0.18921	0.18496	0.18033	0.17545	0.17053
0.18954	0.18524	0.18063	0.17604	0.17110	0.16586
0.18524	0.18092	0.17617	0.17136	0.16624	0.16077
0.18091	0.17630	0.17138	0.16633	0.16085	0.15524
0.17599	0.17121	0.16609	0.16080	0.15518	0.14915
0.17042	0.16554	0.16016	0.15458	0.14869	0.14227
0.16413	0.15902	0.15337	0.14749	0.14120	0.13441
0.15707	0.15153	0.14556	0.13927	0.13242	0.12528
0.14848	0.14260	0.13618	0.12949	0.12232	0.11445
0.13745	0.13116	0.12447	0.11706	0.10909	0.10078
0.12201	0.11522	0.10786	0.09997	0.09132	0.08223
0.09824	0.09095	0.08298	0.07436	0.06497	0.05498
0.05206	0.04414	0.03561	0.02613	0.01578	0.00486
−0.04001	−0.04833	−0.05774	−0.06805	−0.07929	−0.09137

Table 3 for comparison. The new values of E_m^0 are in full agreement with those obtained by Claussen and French [3] for the 10 and 20% PG solvent mixtures at 25°C, where the differences are 0.08 and 0.09 mV. Also, the E_m^0 values reported by Kundu et al. [1] for pure PG at 25, 30 and 35°C are in good agreement with those obtained in this work. Kundu et al. [1] reported that the 11 mV more negative value of E_m^0 for the Ag–AgCl electrode in PG at 30°C, than the corresponding value of Kundu and Das [2] (see Table 3), indicate that the samples of the solvents used in their previous work [2] were not dry enough though they used similar treatment for purification. Thus, the more negative values of E_m^0 obtained in this work at 5–20°C and at 40 and 50°C may be ascribed to the same reason, because of the hygroscopic nature of glycols [1,7]. Moreover, Kundu et al. [1] neglected the correction factors for converting the observed EMF values to 1 atm hydrogen pressure, since the vapour pressures of PG are relatively small at 5–45°C [1]. Furthermore, Kundu et al. [1] expressed their E_m^0 values for the Ag–AgCl electrode in PG at 5–45°C as a function of temperature by an equation similar to eqn. (1) and the standard deviation in E_m^0 [1] is ± 0.4 mV. However, the contribution of their term $c(t - 25)^2$ to the E_m^0 value is within the calculated error, and actually there [1] is a linear dependence of E_m^0 on temperature.

TABLE 2

Values of the parameters a, b and c of eqn. (1) for evaluation of E_m^0 in propylene glycol + water solvent mixtures from 0 to 55°C, and the standard potentials of the Ag–AgCl electrode on the molar concentration, E_c^0, and mole fraction, E_N^0, scales at 25°C

Wt.% PG	$10^2 a$ (V)	$10^4 b$ (V K^{-1})	$10^6 c$ (V K^{-2})	E_c^0 (abs. V)	E_N^0 (abs. V)
0	22.236	6.452	2.875	0.22221	0.01596
5	21.876	6.585	3.089	0.21878	0.01436
10	21.512	6.724	3.284	0.21534	0.01281
15	21.140	6.844	3.506	0.21183	0.01125
20	20.784	7.001	3.725	0.20848	0.00996
25	20.441	7.155	3.968	0.20527	0.00890
30	20.089	7.344	4.221	0.20196	0.00786
35	19.719	7.522	4.524	0.19846	0.00677
40	19.347	7.764	4.805	0.19492	0.00579
45	18.942	8.030	5.153	0.19103	0.00465
50	18.513	8.256	5.644	0.18688	0.00344
55	18.039	8.575	6.149	0.18225	0.00198
60	17.513	8.898	6.859	0.17708	0.00021
65	16.905	9.298	7.601	0.17105	−0.00212
70	16.208	9.677	8.619	0.16411	−0.00505
75	15.372	10.171	9.686	0.15575	−0.00902
80	14.303	10.787	10.958	0.14504	−0.01490
85	12.795	11.494	12.411	0.12991	−0.02468
90	10.467	12.342	14.032	0.10656	−0.04205
95	5.896	13.265	15.818	0.06074	−0.08107
100	−3.230	14.382	17.670	−0.03066	−0.16465

Standard thermodynamic functions for the cell reaction

For the cell reaction

$$\tfrac{1}{2} H_2(\text{gas, 1 atm}) + AgCl(s) = Ag(s) + HCl(\text{solvated}) \tag{2}$$
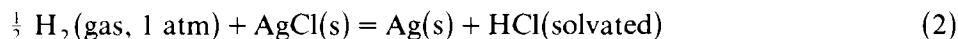
the thermodynamic functions were evaluated from the temperature variation of E_m^0 in different solvents. Thus, the standard changes of free energy (ΔG^0) were evaluated using

$$\Delta G^0 = -nFE_m^0 = -F\left[a - b(T - 298.15) - c(T - 298.15)^2\right] \tag{3}$$

The values of ΔG^0 are accurate to ± 29 J mole^{-1}. The standard changes of entropy (ΔS^0) and enthalpy (ΔH^0) for the cell reaction were computed by the usual relations [4–6] and the results are recorded in Table 4.

It is evident from Table 4 that while the standard free energy changes for the cell reaction, which are all negative in aqueous mixtures and positive in pure PG, increase the standard entropy changes, which are all negative, decrease with an increase in either the PG content in the solvent or the temperature of the solvent system, i.e. with a decrease in the dielectric constant of the solvent. The standard enthalpy changes are all negative and

TABLE 3

Comparison between reported values of E_m^0 and our corresponding new values in propylene glycol and its aqueous mixtures

Temp. (°C)	E_m^0 in 10% PG		E_m^0 in 20% PG		$- E_m^0$ in pure PG		
	Ref. 3	This work	Ref. 3	This work	Ref. 2	Ref. 1	This work
5						0.0015	0.01067
10						0.0089	0.01471
15						0.0166	0.01965
20						0.0244	0.02549
25	0.21505	0.21513	0.20775	0.20784		0.0323	0.03229
30					0.029	0.0402	0.04001
35						0.0483	0.04833
40						0.0561	0.05774
45						0.0638	0.06805

decrease with increasing temperature, in any solvent. At 5°C, the values of ΔH^0 increase with increasing PG content. On the other hand, while the values of ΔH^0 at 15°C increase to a maximum at around 20% PG, then decrease to a minimum at around 80% PG and thereafter increase, the values of ΔH^0 at 25–55°C decrease to minima at around 90% PG and thereafter increase, with increasing concentration of PG.

Standard thermodynamic quantities for the transfer process

The standard changes of Gibbs free energy (ΔG_t^0), enthalpy (ΔH_t^0), entropy (ΔS_t^0) and heat capacity (ΔC_p^0) for the transfer of one mole of HCl from the standard state in water to the standard states of the respective solvents

$$HCl \ (in \ water) = HCl \ (in \ respective \ PG + water \ solvents) \qquad (4)$$

were obtained from the temperature variation of standard EMF of the cell on the mole fraction scale.

$$E_N^0 = a' - b'T - c'T^2 \qquad (5)$$

The effect of the solvent on transfer Gibbs energy must be calculated on the mole fraction scale [9,10] which does not contain the change of the number of solvent molecules by different solvents. Therefore, it will eliminate Gibbs energy changes due to concentration changes in the transfer process [10]. The standard changes of Gibbs free energy can thus be represented as a function of temperature (in K) by

$$F\left({}^w E_N^0 - {}^s E_N^0 \right) = \Delta G_t^0 = A - BT + CT^2 \qquad (6)$$

The least-squares values of the parameters of eqns. (5) and (6) are given in Table 5. The standard changes of enthalpy, entropy and heat capacity for the

TABLE 4

Standard molal thermodynamic functions of the cell reaction in propylene glycol + water solvent mixtures from 5 to 55°C

Temp. (°C)	Wt.% PG										
	0	10	20	30	40	50	60	70	80	90	100
$-\Delta G^0$ (J mole^{-1})											
5	22588	21927	21261	20637	19980	19238	18350	17173	15459	11939	−1023
15	22049	21373	20693	20051	19370	18604	17690	16489	14735	11155	−1899
25	21454	20756	20054	19383	18667	17862	16897	15638	13800	10099	−3116
35	20804	20075	19342	18634	17871	17011	15973	14621	12654	8773	−4675
45	20098	19332	18559	17803	16983	16051	14916	13438	11296	7176	−6574
55	19337	18524	17704	16891	16002	14982	13726	12089	9726	5308	−8814
$-\Delta H^0$ (J mole^{-1})											
5	36817	36447	36050	35815	35658	35336	34866	33891	32645	29998	18606
15	38388	38241	38085	38121	38283	38419	38514	38600	38632	37665	28260
25	40015	40099	40193	40509	41001	41612	42494	43476	44831	45603	38256
35	41697	42020	42372	42978	43812	44914	46507	48518	51241	53812	48593
45	43434	44004	44623	45529	46716	48324	50651	53726	57863	62291	59270
55	45227	46052	46945	48161	49712	51844	54928	59101	64696	71041	70289
$-\Delta S^0$ (J K^{-1} mole^{-1})											
5	51.2	52.2	53.2	54.6	56.4	57.9	59.4	60.1	61.8	64.9	70.6
15	56.7	58.5	60.4	62.7	65.6	68.8	72.6	76.7	82.9	92.0	104.7
25	62.3	64.9	67.5	70.9	74.9	79.7	85.9	93.4	104.1	119.1	138.8
35	67.8	71.2	74.7	79.0	84.2	90.5	99.1	110.0	125.2	146.2	172.9
45	73.3	77.6	81.9	87.1	93.5	101.4	112.3	126.6	146.4	173.2	207.0
55	78.9	83.9	89.1	95.3	102.7	112.3	125.6	143.3	167.5	200.3	241.1

transfer process were obtained by applying the usual thermodynamic relations [4–6] to eqn. (6). The standard transfer thermodynamic quantities calculated at 5–55°C are collected in Table 6. The values of ΔG_t^0 are accurate to $\pm$ 58 J mole^{-1}.

The standard Gibbs free energy of transfer is an index of the differences in interactions of the ions (for example, H$^+$ and Cl$^-$) and the solvent molecules in the two different media. The values of ΔG_t^0, which are all positive, increase with an increase in either the PG content in the solvent or the temperature of the solvent system. The positive values of ΔG_t^0 support the view that the transfer of HCl from water to the glycolic solvent is not favoured, i.e. water is more basic than the glycolic solvents. The increase in ΔG_t^0 with increasing PG content in the solvent suggests that the solute is strongly stabilized by solvation with water molecules. There is some evidence that the chloride ion is not strongly solvated by water [11], thus the positive and increasing values of ΔG_t^0 might indicate the proton stabilization with water molecules. Thus the transfer energies lend support to the view that the hydrogen ion interacts strongly with water molecules in preference to glycol molecules in glycolic solvents.

The transfer process of ions from water to the respective solvents includes a number of changes connected with building up and breaking down the structure [10]. Further, the structure-forming processes are exothermic and accompanied by entropy decrease and the structure-breaking processes are endothermic and leading to the entropy increase [12,13]. The values of ΔH_t^0 and ΔS_t^0 reflect contributions from the effects of the ions on the structure of the solvents while the values of ΔG_t^0 provide information in regard to the acid–base theory of ion solvation [12]. The function ΔG_t^0 is a simpler one, and may not be affected by structural factors [13].

TABLE 5

Values of the parameters a', b' and c' of eqn. (5) for evaluation of E_N^0 in propylene glycol + water solvent mixtures from 0 to 55°C, and the values of the parameters A, B and C of eqn. (6) for evaluation of thermodynamic quantities for transfer of HCl from water to propylene glycol + water media

Wt.% PG	$10^2 a'$ (V)	$-10^4 b'$ (V K^{-1})	$10^6 c'$ (V K^{-2})	$10^{-2} A$ (J mole^{-1})	B (J K^{-1} mole^{-1})	$10^2 C$ (J K^{-2} mole^{-1})
0	15.916	10.692	2.875			
10	12.367	12.858	3.284	34.240	22.228	3.946
20	8.545	15.211	3.725	71.120	46.364	8.201
30	4.463	17.826	4.221	110.500	73.160	12.987
40	−0.218	20.888	4.805	155.665	104.439	18.622
50	−7.043	25.399	5.644	221.519	149.899	26.717
60	−16.930	32.002	6.859	316.907	215.799	38.439
70	−31.557	41.718	8.619	458.042	312.066	55.421
80	−50.945	54.556	10.958	645.104	438.902	77.988
90	−77.471	71.331	14.032	901.035	604.388	107.648
100	−117.425	90.984	17.670	1286.530	798.661	142.749

TABLE 6

Standard thermodynamic quantities (mole fraction scale) for the transfer of HCl from water to propylene glycol+water solvent mixtures at 5–55°C

Temp. (°C)	Wt.% PG									
	10	20	30	40	50	60	70	80	90	100
	$\Delta G_t^0/(J\ mole^{-1})$									
5	294	561	748	924	1127	1406	1881	2767	5277	16947
15	296	562	752	934	1141	1425	1898	2795	5329	17044
25	305	579	782	981	1209	1520	2027	2978	5597	17427
35	322	613	837	1066	1330	1693	2267	3318	6080	18095
45	346	663	919	1188	1504	1942	2617	3813	6778	19049
55	379	729	1027	1347	1731	2269	3078	4464	7691	20288
	$-\Delta H_t^0/(J\ mole^{-1})$									
5	-371	-767	-1002	-1160	-1482	-1951	-2927	-4173	-6819	-18212
15	-147	-302	-267	-105	31	126	212	244	-723	-10128
25	84	178	494	987	1597	2479	3461	4816	5588	-1759
35	323	676	1282	2116	3217	4810	6821	9545	12115	6896
45	570	1189	2095	3282	4890	7217	10292	14429	18857	15837
55	825	1719	2935	4486	6617	9702	13874	19470	25814	25062

$-\Delta S_t^0 (J\ K^{-1}\ mole^{-1})$

5	-0.3	-0.7	-0.8	-0.9	-1.3	-2.0	-3.8	-5.1	-5.5	-4.5
15	0.5	0.9	1.7	2.9	4.1	5.7	7.3	10.5	16.0	24.0
25	1.3	2.5	4.3	6.6	9.4	13.4	18.4	26.1	37.5	52.6
35	2.1	4.2	6.9	10.3	14.8	21.1	29.5	41.7	59.0	81.1
45	2.9	5.8	9.5	14.0	20.1	28.8	40.6	57.3	80.6	109.7
55	3.7	7.5	12.1	17.8	25.4	36.5	51.7	72.9	102.1	138.2

$-\Delta C_p^0 (J\ K^{-1}\ mole^{-1})$

5	22.0	45.6	72.2	103.6	148.6	213.8	308.3	433.9	598.8	794.1
15	22.7	47.3	74.8	107.3	154.0	221.5	319.4	449.4	620.4	822.7
25	23.5	48.9	77.4	111.0	159.3	229.2	330.5	465.0	641.9	851.2
35	24.3	50.5	80.0	114.8	164.7	236.9	341.6	480.6	663.4	879.8
45	25.1	52.2	82.6	118.5	170.0	244.6	352.6	496.2	685.0	908.3
55	25.9	53.8	85.2	122.2	175.3	252.3	363.7	511.8	706.5	936.9

The standard transfer enthalpy and entropy decrease with increasing temperature, in any solvent. While the values of ΔS_t^0 at 5°C are all positive, increase to a maximum at around 90% PG and thereafter decrease, the ΔS_t^0 values at 15–55°C are all negative and decrease, with increasing PG content in the solvent. At 5°C, the values of ΔH_t^0 are all positive and increase with increasing PG concentration. On the other hand, while the ΔH_t^0 values at 15°C (which are negative for 50–80% PG solvents) increase to a positive maximum at around 20% PG, then decrease to a negative minimum at around 80% PG and thereafter increase, the ΔH_t^0 values at 25–55°C (which are all negative except for pure PG at 25°C) decrease to minima at around 90% PG and thereafter increase, with increasing concentration of PG.

The negative and decreasing values of ΔH_t^0 and ΔS_t^0, at 25°C for example, assume that ions are more effectively breaking the water structure than in the mixed solvent. The water is therefore a more structured solvent than the PG + water solvents. On the other hand, the positive entropy and enthalpy of transfer of HCl from water to PG + water solvents, at 5°C for example, can be attributed to a greater structure breaking by HCl in these solvents than in water.

The heat capacity changes are all negative and decrease with increasing either temperature or PG content in the solvent.

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