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STANDARD POTENTIALS OF THE SILVER–SILVER IODIDE ELECTRODE AND THE THERMODYNAMIC PROPERTIES OF HYDRIODIC ACID IN PROPYLENE GLYCOL + WATER SOLVENTS

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ABSTRACT

The electromotive force of the buffered cell: Pt, H_2 (gas, 1 atm): HOAc (m_1), KOAc (m_2), KI (m_3), solvent: AgI, Ag, in propylene glycol (PG) and in 19 PG + water solvent mixtures has been measured at 5°C intervals from 0 to 55°C. The values of the standard potentials of the silver–silver iodide electrode have been determined in these solvents at the indicated temperatures. The standard potential in each solvent has been expressed as a function of temperature. The standard thermodynamic functions for the cell reaction and the standard thermodynamic quantities for the transfer of 1 mole of HI from water to the respective solvents have been evaluated. The results are interpreted in terms of the acid–base properties of the solvents as well as the preferential solvation of ions.

INTRODUCTION

Electromotive force measurements on galvanic cells involving hydrogen, silver–silver halide electrodes, with or without the buffer solutions, have been widely used in recent years [1–7] to determine the thermodynamics of hydrogen halides in aqueous and non-aqueous media. The study of the thermodynamic properties of hydriodic acid in such media has recently been a subject of interest. The standard potentials of silver–silver iodide electrodes and related thermodynamic quantities in non-aqueous propylene glycol (PG), determined from the EMF measurements of the buffered cells at 5–45°C, have been reported by Kundu et al. [3]. Despite the well-known industrial and pharmaceutical applications of the primary–secondary dihydric alcohol, PG, as a solvent [8,9], no EMF data, and thus no electrochemical thermodynamic quantities for HI, have so far been reported in aqueous mixtures of PG.

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Thus, as a part of a comprehensive study on the standard potentials of the silver–silver halide electrodes in both aqueous and non-aqueous media [6,7,10,11], the authors have undertaken to determine the standard potentials of the Ag–AgI electrode in 19 PG + water solvent mixtures as well as in non-aqueous PG at 12 different temperatures in the range 0–55°C. This wide temperature range is sufficient to yield better accuracy in the calculation of the thermodynamic properties that are dependent on the temperature coefficient of the EMF. Thus, a comprehensive understanding of the thermodynamic properties of hydriodic acid in these media can be obtained.

Measurements of the EMF of cells of the type

$$\text{Pt, } H_2(\text{gas, 1 atm}) : \text{HI } (m), \text{ solvent} : \text{AgI, Ag} \qquad \text{(I)}$$

showed a slow variation in the observed EMF with time, especially for PG-rich solvents at high temperatures. Similar observations were reported by Kundu et al. [3]. Their preliminary experiments with HI solutions in PG indicated a gradual drift in the observed EMF values. This was ascribed to the slow reaction of the acid with the solvent forming halohydrin, and also partly to the oxidation of HI [3]. Hence, the method of using cell (I) was not considered suitable.

On the other hand, EMF measurements using buffered cells of the type

$$\text{Pt, } H_2(\text{gas, 1 atm}) : \text{HOAc } (m_1), \text{ KOAc } (m_2), \text{ KI } (m_3), \text{ solvent} : \text{AgI, Ag} \qquad \text{(II)}$$

showed that these cells function better for this system than the unbuffered cells. Therefore, the EMF measurements of the buffered cells have been used for the determination of the standard potentials of the Ag–AgI electrode in PG + water solvents.

EXPERIMENTAL

Acetic acid (Merck) was further purified as described elsewhere [3]. Potassium iodide (Merck) was dried at 200°C for 2 h and kept in a vacuum desiccator before use. Redistilled deionized water which had a conductivity of $0.7 \times 10^{-6}\ \Omega^{-1}\ \text{cm}^{-1}$ was generally used in the preparation of various aqueous solutions. PG (BDH, AnalaR) was further purified as described earlier [5]. The characteristic physical properties of the product agreed well with those reported elsewhere [4] for pure PG. Because of the highly hygroscopic nature of PG [4,8,9], the distilled glycol was kept in an atmosphere of dry argon, freshly redistilled 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.

The experimental methods and procedures, such as those employed for the preparation of hydrogen and silver–silver iodide electrodes, preparation of cell solutions of the required ionic strengths in the respective solvents, setting up of the cells and measurements of EMF, were similar to those described in previous studies [3,12]. The electrodes having bias potentials of the order of 0.1 mV were used, and these were preserved over the respective solvents and kept in the dark when not in use. The molalities of HOAc, OAc^- and I^- solutions were in the range 0.005–0.05 mole kg^{-1}. The PG content of all the solutions reported was accurate to ±0.05 wt.%. All solutions were freshly prepared before taking measurements. The EMF measurements were made with three hydrogen electrodes and three silver–silver iodide electrodes for each solution. The cells were thermostated at each temperature with an accuracy of ±0.01°C. The behaviour of the electrodes in the buffer mixtures was excellent and consistent within ±0.1 mV.

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 ±0.2 mV for different solutions. The cell measurements were made in triplicate, and the mean values of these observations recorded. The triplicates generally agreed within ±0.2 mV. The EMF data observed in the various solutions were corrected in the usual way to 1 atm hydrogen pressure. The physical properties of the solvents over the temperature range 0–55°C were derived from previous data [4,9,13].

RESULTS AND DISCUSSION

The EMF (E) of the buffered cell (II) is given [3,12] by

$$E = E_m^0 - k \log K_a - k \log(a_1 a_3/a_2) \tag{1}$$

where E_m^0 is the standard EMF of the cell, which is the standard potential of the silver–silver iodide electrode on the molal scale, K_a is the dissociation constant of acetic acid in the particular solvent at the corresponding temperature, k is $(RT \ln 10)/F$, a is the activity and the subscripts 1, 2 and 3 refer to HOAc, OAc^- and I^-, respectively. The extrapolation function E' given [3,12] by

$$\begin{aligned} E' = E - k(\mathrm{p}K_a) + k \log(m_1 m_3/m_2) &= E_m^0 - k \log(\gamma_1\gamma_3/\gamma_2) \\ &= E_m^0 + \mathrm{f}(u) \end{aligned} \tag{2}$$

was constructed for each solvent at each temperature, where the symbols have their usual significance [3,12]. The pK_a values of acetic acid in the respective solvents in the same temperature range, determined earlier [3,11],

TABLE 1

Standard molal potentials, $-E^0_{\mathrm{m}}$(V), of the silver–silver iodide electrode in propylene glycol + water solvent mixtures at 0–55°C

Wt.%	Temp. (°C)											
PG	0	5	10	15	20	25	30	35	40	45	50	55
0	0.14617	0.14714	0.14813	0.14939	0.15078	0.15235	0.15398	0.15579	0.15774	0.15984	0.16205	0.16438
5	0.14729	0.14821	0.14946	0.15068	0.15207	0.15367	0.15541	0.15724	0.15912	0.16124	0.16346	0.16596
10	0.14838	0.14933	0.15061	0.15184	0.15328	0.15491	0.15667	0.15856	0.16045	0.16262	0.16487	0.16739
15	0.14954	0.15049	0.15182	0.15307	0.15455	0.15623	0.15807	0.15994	0.16186	0.16413	0.16636	0.16895
20	0.15073	0.15177	0.15310	0.15446	0.15591	0.15762	0.15948	0.16132	0.16339	0.16568	0.16795	0.17057
25	0.15191	0.15295	0.15433	0.15562	0.15720	0.15896	0.16084	0.16283	0.16485	0.16722	0.16951	0.17219
30	0.15312	0.15417	0.15562	0.15705	0.15858	0.16039	0.16233	0.16437	0.16642	0.16879	0.17122	0.17394
35	0.15446	0.15556	0.15707	0.15846	0.16012	0.16198	0.16399	0.16600	0.16818	0.17073	0.17309	0.17592
40	0.15577	0.15695	0.15849	0.15997	0.16172	0.16360	0.16567	0.16775	0.17004	0.17258	0.17507	0.17796
45	0.15735	0.15856	0.16018	0.16169	0.16346	0.16544	0.16759	0.16976	0.17207	0.17471	0.17725	0.18022
50	0.15924	0.16052	0.16216	0.16383	0.16561	0.16769	0.16992	0.17214	0.17458	0.17733	0.17998	0.18304
55	0.16113	0.16247	0.16419	0.16594	0.16783	0.16995	0.17228	0.17457	0.17709	0.17997	0.18273	0.18589
60	0.16351	0.16493	0.16672	0.16858	0.17057	0.17279	0.17521	0.17771	0.18032	0.18329	0.18618	0.18943
65	0.16596	0.16748	0.16940	0.17129	0.17352	0.17582	0.17830	0.18107	0.18379	0.18694	0.19002	0.19341
70	0.16899	0.17064	0.17268	0.17472	0.17711	0.17957	0.18222	0.18508	0.18810	0.19145	0.19474	0.19850
75	0.17301	0.17479	0.17702	0.17928	0.18183	0.18449	0.18737	0.19059	0.19378	0.19743	0.20103	0.20499
80	0.17844	0.18056	0.18287	0.18552	0.18840	0.19136	0.19464	0.19808	0.20173	0.20572	0.20978	0.21421
85	0.18656	0.18913	0.19216	0.19517	0.19843	0.20208	0.20574	0.20977	0.21408	0.21836	0.22315	0.22782
90	0.20031	0.20374	0.20765	0.21148	0.21559	0.22002	0.22448	0.22926	0.23430	0.23932	0.24476	0.25013
95	0.22985	0.23451	0.23959	0.24457	0.24982	0.25527	0.26076	0.26648	0.27249	0.27837	0.28468	0.29084
100	0.31304	0.31962	0.32624	0.33303	0.33990	0.34669	0.35355	0.36072	0.36767	0.37488	0.38217	0.38936

were used for evaluation of E'. The plotting of the functions E' against ionic strengths (u) of the corresponding systems resulted in straight lines, which on extrapolation to $u = 0$ by the method of least squares gave the intercepts equal to the E_m^0 values of the Ag–AgI electrode in each solvent at each temperature. The E_m^0 values in PG + water solvents as well as in non-aqueous PG are summarized in Table 1, together with the values for water as the solvent [10]. The values of E_m^0, presented in Table 1, are accurate to better than ± 0.1, ± 0.2 and ± 0.3 mV for solvents containing 5–45, 50–75 and 80–100 wt.% PG, respectively.

It is seen, from Table 1, that the E_m^0 values are all negative and decrease with an increase in either temperature or PG content in the solvent, i.e. with a decrease in dielectric constant of the medium.

The values of E_m^0 (in abs. volts) obtained at 12 different temperatures for each solvent (Table 1) were fitted by the method of least squares to a

TABLE 2

Values of the parameters a, b and c of eqn. (3) for evaluation of E_m^0 in propylene glycol + water solvent mixtures from 0 to 55°C, and the standard potentials of the Ag–AgI 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})	$-E_c^0$ (V)	$-E_N^0$ (V)
0	15.237	3.191	2.731	0.15252	0.35877
5	15.367	3.267	2.731	0.15365	0.35807
10	15.491	3.331	2.739	0.15469	0.35722
15	15.623	3.415	2.741	0.15580	0.35638
20	15.761	3.472	2.774	0.15697	0.35549
25	15.897	3.568	2.790	0.15811	0.35448
30	16.039	3.658	2.835	0.15932	0.35342
35	16.198	3.773	2.871	0.16071	0.35240
40	16.359	3.893	2.929	0.16214	0.35127
45	16.543	4.029	2.990	0.16382	0.35020
50	16.769	4.192	3.064	0.16594	0.34938
55	16.994	4.353	3.173	0.16808	0.34835
60	17.278	4.571	3.300	0.17083	0.34770
65	17.582	4.828	3.473	0.17382	0.34699
70	17.958	5.161	3.693	0.17755	0.34671
75	18.448	5.609	4.083	0.18245	0.34722
80	19.136	6.274	4.429	0.18935	0.34929
85	20.209	7.308	4.265	0.20013	0.35472
90	22.003	8.888	3.872	0.21814	0.36675
95	25.529	10.957	3.046	0.25351	0.39532
100	34.670	13.790	1.431	0.34506	0.47905

TABLE 3

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

Temp. (°C)	Wt.% PG 0	10	20	30	40	50	60	70	80	90	100
ΔG^0(J mole^{-1})											
5	14191	14409	14582	14879	15146	15489	15916	16473	17424	19664	30845
15	14420	14651	14837	15150	15437	15805	16261	16864	17901	20409	32134
25	14701	14946	15145	15475	15784	16180	16671	17327	18463	21229	33451
35	15036	15294	15506	15855	16188	16614	17143	17860	19111	22124	34795
45	15422	15695	15922	16290	16648	17107	17680	18465	19845	23094	36167
55	15862	16148	16391	16780	17165	17659	18280	19141	20664	24138	37567
ΔH^0(J mole^{-1})											
5	8559	8410	8242	8105	7842	7528	7191	6587	5340	−33	−4627
15	7067	6914	6726	6556	6242	5854	5388	4569	2920	−2148	−5409
25	5522	5364	5157	4952	4585	4120	3521	2480	415	−4338	−6218
35	3924	3762	3534	3294	2872	2328	1591	320	−2176	−6604	−7055
45	2274	2107	1858	1581	1102	476	−403	−1912	−4852	−8943	−7920
55	571	399	128	−187	−725	−1434	−2461	−4215	−7614	−11358	−8812
$-\Delta S^0$(J K^{-1} mole^{-1})											
5	20.2	21.6	22.8	24.4	26.3	28.6	31.4	35.5	43.4	70.8	127.5
15	25.5	26.9	28.1	29.8	31.9	34.5	37.7	42.7	52.0	78.3	130.3
25	30.8	32.1	33.5	35.3	37.6	40.4	44.1	49.8	60.5	85.8	133.1
35	36.1	37.4	38.9	40.8	43.2	46.4	50.5	56.9	69.1	93.2	135.8
45	41.3	42.7	44.2	46.2	48.9	52.3	56.8	64.0	77.6	100.7	138.6
55	46.6	48.0	49.6	51.7	54.5	58.2	63.2	71.2	86.2	108.2	141.3

quadratic equation of the form

$$E_m^0 = a - b(T - 298.15) - c(T - 298.15)^2 \quad (3)$$

where T is the thermodynamic temperature. The parameters a, b and c are recorded in Table 2, for each solvent, along with the values for water as the solvent [10]. The maximum difference between the experimental values of E_m^0 (Table 1) and those computed by eqn. (3) at the 12 temperatures is 0.13 mV for the various PG + water solvents.

The values of E_m^0, obtained by Kundu et al. [3], for the Ag–AgI electrode in the non-aqueous PG solvent are now compared with the corresponding new values obtained in the present work. These values are −0.3197, −0.3258, −0.3332, −0.3399, −0.3468, −0.3535, −0.3609, −0.3676 and −0.3749 V at 5, 10, 15, 20, 25, 30, 35, 40 and 45°C, respectively. There is an excellent agreement between eight from nine values. The differences range from 0.02 to 0.18 mV, except at 10°C where the difference is 0.44 mV. The more negative value of E_m^0 obtained in this work at 10°C indicates that the solvents used in previous studies were not dry enough [3]. This may be so in view of the highly hygroscopic nature of PG [4,8,9].

The values of the standard potentials on the molar and mole fraction scales, E_c^0 and E_N^0, respectively, were computed at 25°C with the help of the usual relations [6,7], and are also included in Table 2. It is evident from Table 2 that the values of E_c^0 and E_N^0 are all negative. The values of E_c^0 decrease, while the E_N^0 values increase to a maximum at around 70 wt.% PG and thereafter decrease, with increasing PG content in the solvent.

Standard thermodynamic functions for the cell reaction

The standard electrode potentials of cell (II) and their temperature coefficients are essentially related to the standard free energy, enthalpy and entropy changes (ΔG^0, ΔH^0 and ΔS^0) involved in the cell reaction

$$\tfrac{1}{2}\ \mathrm{H_2(gas,\ 1\ atm) + AgI\ (s) = Ag\ (s) + HI\ (solvated)} \quad (4)$$

Hence, the standard changes of free energy could be calculated from the relation

$$\Delta G^0 = -nFE_m^0 = -F\left[a - b(T - 298.15) - c(T - 298.15)^2\right] \quad (5)$$

The calculated values of ΔG^0 are accurate to ±29 J mole^{-1}. The standard thermodynamic functions of the cell were computed at 5–55°C by applying the usual thermodynamic relations [6,7] to eqn. (5) and these are recorded in Table 3, where all refer to the molal scale.

As can be seen from Table 3 the standard free energy changes for the cell reaction are all positive and increase, while the standard entropy changes are all negative and decrease, with an increase in either the PG content in the solvent or the temperature of the medium, i.e. with a decrease in the dielectric constant of the solvent. On the other hand, the standard enthalpy changes, which decrease with increasing temperature in any solvent, appear to be positive for water-rich solvents at lower temperatures and negative for PG-rich solvents at high temperatures. At 5–35°C the values of ΔH^0 decrease, while at 45–55°C the ΔH^0 values decrease to minima at around 90 wt.% PG and thereafter increase, with increasing PG concentration in the solvent. This may be due to some structural effects which can arise from the solvent properties and/or from the solvation properties of the ions in the different solvent mixtures.

Standard thermodynamic quantities for the transfer process

Since the solvent effects on the thermodynamic properties of HI related to the present study will be best reflected in the standard free energy (ΔG_t^0), entropy (ΔS_t^0), enthalpy (ΔH_t^0) and heat capacity (ΔC_p^0) changes accompanying the transfer of 1 mole of HI from water (w) to each of the solvents (s)

$$\text{HI (in water)} = \text{HI (in respective PG + water solvents)} \qquad (6)$$

these quantities were evaluated from the temperature variation of standard EMF of the cell on the mole fraction scale.

$$E_N^0 = a' - b'T - c'T^2 \qquad (7)$$

As before [4–7,10–12], the mole fraction scale has been used, because that will eliminate effects arising from concentration changes of HI accompanying the transfer process and will reflect solvent effects more clearly, a contention that has recently been shown to be true in various non-aqueous,

TABLE 4

Values of the parameters a', b' and c' of eqn. (7) 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. (8) for evaluation of the thermodynamic quantities for transfer of HI 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	30.000	13.094	2.731			
10	29.908	13.002	2.739	−0.891	0.430	0.077
20	30.004	13.069	2.774	0.039	2.520	0.415
30	30.334	13.247	2.835	3.225	5.805	1.003
40	30.789	13.573	2.929	7.614	10.676	1.910
50	31.507	14.079	3.064	14.547	17.496	3.213
60	32.984	15.107	3.300	28.797	29.607	5.490
70	35.399	16.860	3.693	52.092	49.048	9.282
80	39.801	20.136	4.429	94.566	83.630	16.383
90	29.923	14.201	3.872	−0.741	29.992	11.009
100	6.276	−5.257	1.431	−228.900	−153.096	−12.543

and aqueous organic mixed solvents [3,4,6,7]. The standard changes of Gibbs free energy can thus be represented as a function of temperature (in K) by

$$F({}^{w}E^{0}_{N} - {}^{s}E^{0}_{N}) = \Delta G^{0}_{t} = A - BT + CT^{2} \tag{8}$$

The least-squares values of the parameters of eqns. (7) and (8) are given in Table 4. The proper choice of a function to express the thermodynamic quantity as a function of temperature has been discussed in some detail by Ives and Marsden [14]. The standard transfer thermodynamic quantities were obtained by applying the usual thermodynamic relations [6,7] to eqn. (8). The data calculated at 5–55°C are presented in Table 5. The values of ΔG^{0}_{t} are accurate to ± 58 J mole^{-1}.

It is known that the Gibbs energy of transfer is an important index of the differences in interactions of the ions (e.g. H^{+} and I^{-}) and the solvent molecules in the two different media. It is evident from Table 5 that the Gibbs free energy of transfer has negative values, which increase in magnitude as the proportion of PG increases, and after passing through minima (at around 70 and 60 wt.% PG at 5–45 and at 55°C, respectively) ultimately go over to positive values. Thus, although the transfer of HI from water to PG-rich media is non-spontaneous, the process is thermodynamically favourable so long as the extreme PG-rich region is not reached, and the spontaneity of transfer increases to a maximum at around 60–70 wt.% PG. Thus, HI appears to be in a lower Gibbs energy state and hence, more strongly stabilized in the 60–70% PG solvents, i.e. these solvents are the more basic media. On the other hand, the positive values of ΔG^{0}_{t} for the PG-rich solvents lead to the conclusion that hydriodic acid is in a lower Gibbs free energy state in water than in such solvents. In other words, the affinity of such solvents for HI is less than that of water. Water is thus more basic than the PG-rich solvents. Thus, the basicity of PG + water solvents appears to increase to a maximum at around 60–70 wt.% PG and thereafter decreases, with increasing PG concentration in the solvent. Similar behaviour was also observed by Kundu et al. [12] in their studies of HI in ethylene glycol + water solvents.

The values of the transfer entropy and enthalpy reflect the complicated nature with regard to the contributions from the effects of the ions on the structure of the solvents. As can be seen from Table 5, the standard entropy (which has very small values and changes little in the water-rich solvents) and enthalpy of transfer to aqueous solvents decrease, while those for the transfer to the non-aqueous PG increase, with increasing temperature of the medium. The values of ΔH^{0}_{t} are all negative and decrease at the lower temperatures (5–35°C), whereas those at the higher temperatures (45–55°C) decrease, passing through minima at around 90 wt.% PG and thereafter increase, with increasing PG content in the solvent. At the lower temperatures (5–15°C), the values of ΔS^{0}_{t} (which are positive for the extreme region of water-rich solvents) increase to positive maxima at around 20–25% PG

TABLE 5

Standard thermodynamic quantities (mole fraction scale) for the transfer of HI 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	149	376	516	730	926	1108	1252	1130	−101	−9989
15	149	378	517	729	919	1093	1217	1038	−424	−10810
25	149	379	516	723	906	1067	1164	914	−770	−11606
35	148	379	513	714	886	1031	1091	757	−1137	−12376
45	148	378	509	702	859	983	1000	567	−1527	−13122
55	147	376	502	685	827	924	891	345	−1939	−13842
$-\Delta H_t^0$(J mole^{-1})										
5	149	317	454	717	1031	1368	1972	3219	8591	13186
15	153	341	511	825	1213	1679	2498	4146	9215	12475
25	158	365	570	937	1401	2001	3042	5107	9860	11740

35	162	390	630	1053	1596	2333	3604	6100	10528	10980
45	167	416	693	1172	1797	2677	4186	7126	11217	10194
55	172	443	758	1296	2005	3032	4786	8185	11929	9383
$-\Delta S_t^0$(J K^{-1} mole^{-1})										
5	0.0	−0.2	−0.2	0.0	0.4	0.9	2.6	7.5	31.3	83.3
15	0.0	−0.1	0.0	0.3	1.0	2.0	4.4	10.8	33.5	80.8
25	0.0	0.0	0.2	0.7	1.7	3.1	6.3	14.1	35.7	78.3
35	0.0	0.0	0.4	1.1	2.3	4.2	8.2	17.3	37.9	75.8
45	0.1	0.1	0.6	1.5	2.9	5.3	10.0	20.6	40.1	73.3
55	0.1	0.2	0.8	1.9	3.6	6.4	11.9	23.9	42.3	70.8
$-\Delta C_p^0$(J K^{-1} mole^{-1})										
5	0.4	2.3	5.6	10.6	17.9	30.5	51.6	91.1	61.2	−69.8
15	0.4	2.4	5.8	11.0	18.5	31.6	53.5	94.4	63.4	−72.3
25	0.5	2.5	6.0	11.4	19.2	32.7	55.3	97.7	65.6	−74.8
35	0.5	2.6	6.2	11.8	19.8	33.8	57.2	101.0	67.8	−77.3
45	0.5	2.6	6.4	12.2	20.4	34.9	59.1	104.2	70.0	−79.8
55	0.5	2.7	6.6	12.5	21.1	36.0	60.9	107.5	72.3	−82.3

and thereafter decrease, whereas those at the higher temperatures (25–55°C) decrease, with increasing PG concentration in the solvent.

The values of ΔH_t^0 and ΔS_t^0 could provide an insight into the solvent structure. The transfer process of ions from water to a mixed solvent includes a number of changes connected with building up and breaking down the structure [12,15]. Further, the structure-forming processes are exothermic and accompanied by a decrease in entropy, and the structure-breaking processes are endothermic and lead to an increase in entropy. The negative and decreasing values of ΔH_t^0 and ΔS_t^0 assume that ions are more effectively breaking the water structure than in the glycolic solvent. Water is therefore a more structured solvent than the PG + water solvents. On the other hand, the positive values of ΔS_t^0 for the extreme region of water-rich solvents at 5–15°C indicate that these solvents are more structured than water in this temperature range.

The values of the heat capacity (ΔC_p^0) decrease, pass through minima at around 80 wt.% PG and thereafter increase, with increasing PG content in the solvent, at any temperature. For the aqueous solvents the values of ΔC_p^0 are negative and decrease, whereas those for the non-aqueous PG solvents are positive and increase, with increasing temperature of the medium.

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