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Note

THERMODYNAMICS OF THE TRANSFER OF (H^+SCN^-) FROM WATER TO METHANOL + WATER MIXTURES FROM THE STUDY OF SILVER–SILVER THIOCYANATE ELECTRODES

CHIDANANDA PATRA and P.K. DAS

Mayurbhanj Chemical Laboratory, Ravenshaw College, Cuttack 753003 (India)

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The Ag–AgSCN electrode was studied in water at various temperatures by Vanderzee and Smith [1] and by Lal and Prasad [2]. This electrode was studied in dioxan + water mixtures in this laboratory [3] using cell (I).

$$\mathrm{Pt, H_{2(g)}|KSCN(}m_1\mathrm{)\ HClO_4(}m_2\mathrm{)|AgSCN{-}Ag} \qquad \text{(I)}$$

In the present investigation the same cell is studied in 10, 20, 30 and 40% (w/w) methanol–water mixtures at 15, 25 and 35°C.

EXPERIMENTAL

Methanol was of BDH AnalaR quality and was purified by standard method [4]. AnalaR KSCN was recrystallized four times and a stock solution of about 1 M was made from this sample. The stock solution was diluted 10 times (w/w) and analyzed gravimetrically via AgSCN. 60% perchloric acid (E. Merck G.R.) was used as stock solution. This was diluted 10 times (w/w) and was standardized by titration against recrystallized AnalaR borax solution [5]. Cell solutions were made up as mole/kg of the solvent.

The Ag–AgSCN electrodes were prepared by thermal electrolyte method [2], electrolyzing in oxygen-free 0.2 M KSCN and 0.06 M $HClO_4$ solution for 1 h at 0.5–0.7 mA. They were washed in water and kept connected in a 'U' tube in a portion of the experimental solution to eliminate the bias potential, if any. Electrodes with bias potential more than ±0.05 mV were rejected. The electrodes are stable for more than a month unless exposed to light and air.

The other experimental details have been reported earlier [6]. The cells were found to reach equilibrium within 4 h (3 h at 35°C). Duplicate readings were taken by measuring the EMF in two cells with the same solution and readings agreeing to ±0.05 mV were considered. The densities, dielectric constants, vapour pressures and Debye–Hückel parameters for methanol + water mixtures were taken from earlier studies [7].

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RESULTS AND DISCUSSION

The EMF values of cell (I) in different methanol + water mixtures, after correction to 1 atm pressure, are reported in Table 1. For this cell

$$E = E^0_m - k \log a_{H^+} a_{SCN^-} \tag{1}$$

where E^0_m is the standard potential (molal) of the cell, a_{H^+} and a_{SCN^-} are the activities of H^+ and SCN^- ions, respectively, and k is 2.3026 RT/F.

Equation (2) is used for the activity coefficient (γ_i)

$$-\log \gamma_i = \frac{AZ_i^2 I^{1/2}}{1 + I^{1/2}} + \beta_i I \tag{2}$$

where I is the ionic strength, A is the Debye–Hückel parameter, and the $\beta_i I$ term

TABLE 1

Values of E_{cor}(V)

	m_1	m_2	15°C	25°C	35°C	15°C	25°C	35°C
	10% Methanol + water					*20% Methanol + water*		
1.	0.0005	0.0005	0.46714	0.48472	0.50217	0.47204	0.48673	0.50238
2.	0.002	0.002	0.39951	0.41508	0.40900	0.40488	0.41715	0.43023
3.	0.004	0.003	0.37280	0.38658	0.40098	0.37824	0.38999	0.40280
4.	0.006	0.004	0.35597	0.37047	0.38348	0.36094	0.37326	0.38448
5.	0.01	0.005	0.33772	0.35125	0.36462	0.34359	0.35437	0.36685
6.	0.015	0.006	0.32307	0.33705	0.34907	0.33034	0.34037	0.35183
7.	0.02	0.007	0 31198	0.32439	0.33786	0.31888	0.32955	0.34099
8	0.0225	0.008	0.30597	0.31810	0.33111	0.31232	0.32390	0.33492
9.	0.025	0.009	0.30029	0.31232	0.32620	0.30647	0.31801	0.32924
10.	0.03	0.01	0.29148	0.30523	0.31830	0.29782	0.31078	0.32316
11.	0.0325	0.011	0.28753	0.29936	0.31282	0.29475	0.30704	0.31761
12.	0.035	0.012	0.28318	0.29552	0.30830	0.29066	0.30217	0.31395
13.	0.04	0.014	0.27938	0.28759	0.30028	0.28793	0.29525	0.30630
14.	0.045	0.015	0.26998	0.28216	0.29509	0.27799	0.28966	0.30165
	30% Methanol + water					*40% Methanol + water*		
1.	0.0005	0.0005	0.47608	0.49088	0.50470	0.48106	0.49560	0.51012
2.	0.002	0.002	0.40897	0.42149	0.43353	0.41426	0.42615	0.43961
3.	0.004	0.003	0.38311	0.39435	0.40557	0.38998	0.40012	0.41171
4.	0.006	0.004	0.36591	0.37752	0.38808	0.37201	0.38300	0.39419
5.	0.01	0.005	0.34925	0.36025	0.37002	0.35411	0.36533	0.37611
6.	0.015	0.006	0.33480	0.34595	0.35518	0.34086	0.35166	0.36174
7.	0.02	0.007	0.32402	0.33536	0.34439	0.33120	0.34091	0.35067
8.	0.0225	0.008	0.31811	0.32908	0.33831	0.32562	0.33463	0.34530
9.	0.025	0.009	0.31291	0.32430	0.33277	0.31913	0.32949	0.33935
10.	0.03	0.01	0.30613	0.31670	0.32554	0.31244	0.32256	0.33241
11.	0.0325	0.011	0.30166	0.31309	0.32188	0.30824	0.31846	0.32815
12.	0.035	0.012	0.29775	0.30867	0.31748	0.30435	0.31462	0.32416
13.	0.04	0.014	0.29491	0.30174	0.31070	0.30194	0.30783	0.31685
14.	0.045	0.015	0.28620	0.29691	0.30540	0.29297	0.30283	0.31254

TABLE 2

Values of E_m^0(V)

Temp. (°C)	Methanol (% w/w)			
	10	20	30	40
15	0.08808	0.09281	0.09643	0.10152
25	0.09246	0.09412	0.09788	0.10254
35	0.09607	0.09626	0.09858	0.10412

accounts for the Hückel effect, polarizability and ion size, etc. Equation (1), after using eqn. (2) and rearranging, becomes

$$E^0 = E + k \log m_{H^+} m_{SCN^-} - \frac{2kAI^{1/2}}{1+I^2} = E_m^0 - \beta I \qquad (3)$$

where $\beta = \beta_{H^+} + \beta_{SCN^-}$.

E_m^0 in eqn. (3) can be calculated using the experimental data (E), m_{H^+} ($=m_2$), m_{SCN^-} ($=m_1$). E_m^0 and β are obtained by linear least squares analysis and are reported in Tables 2 and 3, respectively. The average standard deviation in E_m^0 is ±0.1 mV.

For the transfer process: H^+SCN^- (in water) → H^+SCN^- (in methanol + water mixtures) the thermodynamic quantities ΔG_t^0 (standard free energy of transfer), ΔS_t^0 (standard entropy of transfer) and ΔH_t^0 (standard enthalpy of transfer) have been evaluated from the standard potential of the silver–silver thiocyanate electrode (in mole fraction scale) in water and various methanol + water mixtures using the method proposed by Feakins and Watson [8]. The data for E_m^0 in water were taken from the work of Lal and Prasad [2]. These thermodynamic quantities are reported in Table 4.

Table 4 shows the values of ΔG_t^0 to be negative for all solvent compositions in methanol + water systems. For H^+SCN^- negative ΔG_t^0 values were also obtained for dioxan + water mixtures [3]. It may be suggested that H^+SCN^- is in a higher free energy state in water than methanol + water mixtures; therefore the transfer of H^+SCN^- is favoured from water to aquo-methanol mixtures within the temperature range studied, thus indicating that the escaping tendency of H^+SCN^- is greater in pure aqueous medium than in methanol + water mixtures.

TABLE 3

Values of β

Temp. (°C)	Methanol (% w/w)			
	10	20	30	40
15	−3.34	−2.64	−1.70	−1.63
25	−2.99	−1.50	−1.03	−1.05
35	−2.20	−0.53	−0.86	−0.90

TABLE 4

Values of ΔG_t^0, ΔS_t^0 and ΔH_t^0

Temp.(°C)	Methanol (% w/w)			
	10	20	30	40
ΔG_t^0(J mole^{-1})				
15	−4.82465	−685.10087	−1270.8138	−2008.9859
25	−519.13277	−911.85962	−1518.8010	−2224.1655
35	−998.70339	−1257.3048	−1733.0157	−2531.9784
ΔS_t^0(J K^{-1} mole^{-1})				
15	53.16785	16.74156	26.48723	16.88620
25	49.69408	28.61019	23.10990	26.14958
35	46.22031	40.47886	19.73258	35.41296
ΔH_t^0(J mole^{-1})				
15	15316.021	4139.1483	6361.7460	2856.9431
25	14296.653	7618.5552	5371.6484	5572.5934
35	13244.548	11216.660	4347.7759	8380.8787

The values of ΔH_t^0 and ΔS_t^0 are positive at all the temperatures in different solvent compositions studied. The positive ΔS_t^0 values indicate that the ordering of solvent mixtures is not favoured by the pair of ions (H^+SCN^-).

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