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Thermodynamics of the Second Dissociation Constants (pK₂) of Piperazine-N,N′-bis-2-hydroxypropanesulfonic Acid (POPSO Sesquisodium Salt) and Associated Thermodynamic Functions from (278.15 to 328.15) K

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Abstract

The second acidic dissociation constants of protonated piperazine-N,N′-bis-2-hydroxypropane-sulfonic acid (POPSO sesquisodium salt) have been determined at 12 different temperatures from (278.15 to 328.15) K including 310.15 K. Electromotive-force measurement technique was used employing hydrogen-silver chloride cells without liquid junction. The results of pK₂ are given by the equation: $pK_2 = -1041.77/T + 51.0459 - 6.97646\ln T$. The uncertainty of the fit is ±0.0008. At 289.15 K, pK₂ = 7.8029; whereas, at 310.15 K (body temperature), pK₂ = 7.6862. Thus, the buffer solutions of POPSO and its sodium salt are useful for pH control in the physiological pH region of (7.0 to 8.5). The changes of Gibbs free energy (ΔG°), enthalpy (ΔH°), entropy (ΔS°) and heat capacity ΔCp° were computed from the temperature derivative of the pK₂ for the dissociation of the zwitterionic acid $POPSO^{\pm-3} = POPSO^{-4} + H^+$ in the standard state. At 298.15 K, these results are compared with those of similar components, which are the derivatives of the parent compounds TAURINE, PIPERAZINE and MORPHOLINE.

Keywords

pH, Buffer Compound, Liquid Junction, Thermodynamic Functions, Activity Coefficients,

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Electromotive-Force, pK$_2$

1. Introduction

Piperazine-N,N′-bis-2-hydroxypropanesulfonic acid (POPSO sesquisodium salt) is a water soluble solid of considerable interest as a physiological buffer [1] for the control of pH between (7.0 and 8.5). Very recently, we have reported the values of the second dissociation constant (pK$_2$) of 2,2-bis(hydroxymethyl)-2,2′,2″-nitrilotriethanol (BIS-TRIS) [2], N-(2-acetamino)-iminodiacetic acid monosodium (ADA) [3] and monosodium 1,4-piperazinediethanesulfonate [4] from (278.15 to 328.15) K. Hetzer *et al.* [5] have determined pK$_2$ values of PIPERAZINE, the parent compound of (POPSO), from (273.15 to 323.15) K. Thiel *et al.* [6] did not provide any pK$_2$ value for (POPSO) but they did study the effect of pH on the variation of enzyme activity and growth of bacterial strain with some zwitterionic buffers including Good Buffer (POPSO) [1] [7]. Goldberg *et al.* [8], in their comprehensive review article, reported that no accurate thermodynamic data of pK$_2$ and related thermodynamic quantities for POPSO sesquisodium salt are available in literature. They also recommended (POPSO) buffer for use in the physiological pH range of 7.0 - 8.5.

We have now studied to report the values of the second thermodynamic dissociation constants of (POPSO) and the associated thermodynamic functions from (278.15 to 328.15) K. The dissociation process of POPSO sesquisodium salt is represented by

$$\text{POPSO}^{\pm-3} \underset{}{\overset{K_2}{\rightleftharpoons}} \text{H}^+ + \text{POPSO}^{-4} \tag{1}$$

where K$_2$ is the thermodynamic equilibrium constant. The structure of POPSO sesquisodium salt is given below:
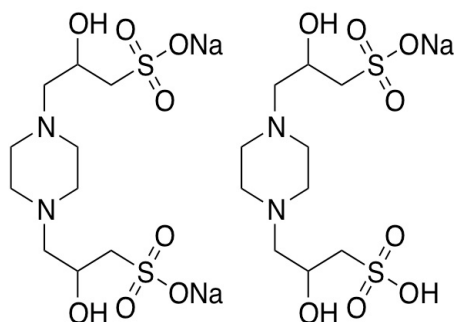
The pK$_2$ value of (PIPERAZINE) [5] is 9.731 and for (PIPES) it is 7.140 [4]. From the preliminary titration of POPSO sesquisodium salt with NaOH [1], the approximate pK$_2$ value of (POPSO) at 298.15 K is 7.785; whereas, our value from a comprehensive study is 7.803.

In order to get very accurate and reproducible pH values required for biomedical research and the calibration of the pH meter assembly with glass electrode, highly reliable pK$_2$ values are prerequisites. The main purpose of this paper is to establish (POPSO) as a pH buffer standard for physiological use. We have undertaken to determine the pK$_2$ values of (POPSO) at 12 different temperatures in the range (278.15 to 328.15) K employing the following galvanic cell for the electromotive-force measurements (e.m.f):

$$\text{Pt}(s), \text{H}_2(g), 101.325 \text{ kPa} \big| \text{Na}_3\text{POPSO}(m_1) + \text{Na}_4\text{POPSO}(m_2) + \text{NaCl}(m_3) \big| \text{AgCl}, \text{Ag}(s) \tag{A}$$

where, for the cell A, there is no liquid junction; m_1, m_2, m_3 indicate the molalities of the respective species; and two electrodes (hydrogen gas electrode and the silver-silver chloride) are used.

2. Experimental

Materials—POPSO sesquisodium salt was obtained from Sigma-Aldrich (St. Louis, Missouri) and was used as received. Its assay was ≥98%. The molecular formula is $C_{20}H_{41}N_4Na_3O_{16}S_4$ and the molecular mass is 790.79 g/mol. It is highly soluble in water. The buffer solutions were prepared from weighted amounts of CO$_2$-free redis-

tilled water, dried samples of NaCl, POPSO sesquisodium salt, and CO_2-free standard solution of NaOH. Usually, all buffer solutions were prepared a day before the e.m.f measurements were made. Vacuum corrections were made to all masses. The ionic strength (I) range for all experimental buffer solutions was from I = 0.0354 to 0.101 mol·kg^{-1}. The uncertainty in the concentration (molality) is estimated to be within ±0.03%.

3. Methods and Results

The method of making e.m.f measurements over the temperature range was essentially the same as that used in the study of (PIPES) [4]. At 298.15 K, the standard deviation between the initial and the middle e.m.f reading was ±0.04 mV. The preparation of the thermal electrolytic type Ag-AgCl electrode, the hydrogen electrode, the design of cells [3] [4], and other experimental details have been described in previous publications [9]-[11]. The e.m.f values have been corrected, as usual, to the partial pressure of one atmosphere of dry hydrogen. These cell voltage values are listed in **Table 1**.

Table 1. Electromotive-force (e.m.f) of cell A (in volts): Pt(s); H_2(g), 1 atm|Na_3POPSO (m_1) + Na_4POPSOate (m_2) + NaCl (m_3)|AgCl(s), Ag(s).

$^a m_1$	$^a m_2$	$^a m_3$	278.15 K	283.15 K	288.15 K	293.15 K	298.15 K	303.15 K
0.001400	0.002500	0.002000	0.85947	0.86490	0.87023	0.87519	0.88000	0.88400
0.001667	0.003006	0.002500	0.85502	0.86048	0.86581	0.87070	0.87549	0.87921
0.001730	0.004000	0.003904	0.85097	0.85636	0.86167	0.86655	0.87135	0.87492
0.001833	0.004900	0.004901	0.84931	0.85470	0.86004	0.86495	0.86977	0.87316
0.002017	0.005500	0.006002	0.84510	0.85043	0.85574	0.86061	0.86537	0.86859
0.002167	0.005500	0.005996	0.84341	0.84871	0.85398	0.85884	0.86357	0.86675
0.002333	0.006000	0.006000	0.84359	0.84891	0.85423	0.85912	0.86386	0.86698
0.002667	0.006900	0.005803	0.84437	0.84973	0.85512	0.86009	0.86485	0.86786
0.003017	0.007500	0.005998	0.84247	0.84781	0.85320	0.85819	0.86292	0.86580
0.003333	0.006500	0.006498	0.83486	0.84005	0.84527	0.85007	0.85467	0.85750
0.005000	0.006000	0.006996	0.82139	0.82634	0.83135	0.83594	0.84029	0.84282
0.001667	0.005000	0.005002	0.85159	0.85702	0.86240	0.86735	0.87221	0.87570
0.002020	0.005556	0.006057	0.84500	0.85033	0.85564	0.86052	0.86528	0.86850
0.002333	0.006000	0.006503	0.84174	0.84702	0.85231	0.85717	0.86187	0.86496
0.002500	0.006500	0.006895	0.84043	0.84571	0.85100	0.85588	0.86057	0.86355
0.002750	0.006800	0.006999	0.83885	0.84411	0.84940	0.85427	0.85894	0.86184
0.002834	0.006999	0.007498	0.83710	0.84233	0.84761	0.85247	0.85711	0.85994
0.002884	0.007199	0.007705	0.83654	0.84178	0.84706	0.85192	0.85655	0.85935
0.003000	0.007500	0.008003	0.83555	0.84077	0.84605	0.85092	0.85554	0.85827
m_1	m_2	m_3	308.15 K	310.15 K	313.15 K	318.15 K	323.15 K	328.15 K
0.001400	0.002500	0.002000	0.88829	0.88983	0.89217	0.89582	0.89938	0.90257
0.001667	0.003006	0.002500	0.88356	0.88508	0.88739	0.89100	0.89448	0.89754
0.001730	0.004000	0.003904	0.87916	0.88066	0.88294	0.88648	0.89000	0.89287
0.001833	0.004900	0.004901	0.87742	0.87890	0.88117	0.88469	0.88817	0.89103
0.002017	0.005500	0.006002	0.87281	0.87426	0.87649	0.87994	0.88337	0.88612

Continued

0.002167	0.005500	0.005996	0.87094	0.87238	0.87459	0.87801	0.88141	0.88413
0.002333	0.006000	0.006000	0.87120	0.87264	0.87485	0.87828	0.88171	0.88441
0.002667	0.006900	0.005803	0.87214	0.87358	0.87581	0.87926	0.88273	0.88540
0.003017	0.007500	0.005998	0.87008	0.87149	0.87371	0.87712	0.88059	0.88319
0.003333	0.006500	0.006498	0.86161	0.86298	0.86510	0.86838	0.87169	0.87419
0.005000	0.006000	0.006996	0.84671	0.84797	0.84996	0.85299	0.85607	0.85831
0.001667	0.005000	0.005002	0.87995	0.88145	0.88374	0.88730	0.89082	0.89372
0.002020	0.005556	0.006057	0.87272	0.87417	0.87639	0.87984	0.88327	0.88603
0.002333	0.006000	0.006503	0.86914	0.87056	0.87276	0.87615	0.87955	0.88221
0.002500	0.006500	0.006895	0.86775	0.86916	0.87134	0.87472	0.87811	0.88073
0.002750	0.006800	0.006999	0.86602	0.86742	0.86959	0.87293	0.87631	0.87888
0.002834	0.006999	0.007498	0.86410	0.86548	0.86763	0.87095	0.87430	0.87683
0.002884	0.007199	0.007705	0.86351	0.86487	0.86700	0.87033	0.87368	0.87617
0.003000	0.007500	0.008003	0.86243	0.86380	0.86594	0.86923	0.87258	0.87505

The general equation for calculating the thermodynamic acidic dissociation constant, pK_2, is obtained by combining the e.m.f equations (the Nernst equation for the cell) with the dissociation step (mass-law expression) of Equation (1) and with the extended form of the Debye-Hückel equation for the molal activity coefficients (γ) of all ions present in the buffer solution. The resulting equation is given below:

$$pK_2' = (E - E°)F/(RT\ln10) + \log\left(m_{POPSO^{\pm-3}} \cdot m_{Cl^-}/m_{POPSO^{-4}}\right) + \log\left(\gamma_{POPSO^{\pm-3}} \cdot \gamma_{Cl^-}/\gamma_{POPSO^{-4}}\right) \tag{2}$$

whereas the last term of Equation (2) is equal to

$$\frac{6A\sqrt{I}}{1 + Ba°\sqrt{I}} \tag{3}$$

In this equation, E is the corrected e.m.f from **Table 1**, E° is the standard electrode potential of the cell, I is the ionic strength of the buffer solution, A and B are the Debye-Hückel constants [12] and Ba° is 1.38 $kg^{1/2} \cdot mol^{-1/2}$ [12] for all experimental temperatures corresponding to an "ion-size parameter" a° of 4.2 A°.

In Equation (2), the "apparent" thermodynamic dissociation constant, pK_2', becomes equal to the true pK_2 (intercept) at an ionic strength (I) of zero from the linear plot of the following equation:

$$pK_2' = pK_2 - \beta I \tag{4}$$

in which:

$$I = 6m_1 + 10m_2 + m_3 \tag{5}$$

and β is the slope parameter. The terms m_1, m_2, m_3 correspond to the molalities of species indicated in cell A and Equation (2). The values of pK_2, together with standard deviation of the intercept and also the values β with the standard deviation of the least squares fit, are listed in **Table 2**.

In order to calculate the associated thermodynamic quantities for the dissociation process, the values of pK_2 for 12 experimental temperatures (278.15 to 328.15) K were fitted to the following Ives-Moseley equation [13]:

$$pK_2 = A/T + B + C\ln T \tag{6}$$

The resulting equation is:

$$pK_2 = -1041.77/T + 51.0459 - 6.97646\ln T \tag{7}$$

and the standard deviation of the fit is 0.0008.

By application of the customary thermodynamic relations to the constants of Equation (7), the values of the standard changes of Gibbs energy ($\Delta G°$), enthalpy ($\Delta H°$), entropy ($\Delta S°$) and heat capacity ($\Delta Cp°$) for the dissociation of one mole of POPSO$^{\pm-3}$ in the standard state were derived. The uncertainties of these quantities were computed by the method of Please [14]. These values of the thermodynamic quantities with the standard deviations of regression are entered in **Table 3**. The estimated standard errors of these thermodynamic quantities are as follows: $\Delta G°$, 5 J·mol^{-1}; $\Delta H°$, 34 J·mol^{-1}; $\Delta S°$, 0.11 J·K^{-1}·mol^{-1}; and $\Delta Cp°$, 4 J·K^{-1}·mol^{-1}.

4. Discussion

There does not appear to be any accurate thermodynamic data in the literature for the dissociation of (POPSO). Only very preliminary data from a simple titration method [1] is available, with no mention of the ionic strength. At 298.15 K the value was reported to be 7.785 (calculated from the temperature derivative). From the precise and rigorous experimental measurements, our values of pK$_2$ at 298.15 K from **Table 2** are 7.8029 ± 0.0008. Thus, there is a significant difference between these two measurements. Also Azab *et al.* [15] reported the pK$_2$ value of (POPSO) from the simple titration of (POPSO) buffer solution against KOH. Their value is 7.60 ± 0.02. This significant difference is explained. The titration method involves ion-selective electrode with a calomel reference causing a greater uncertainty in e.m.f value due to the liquid junction potential. Our method involves precise measurement using hydrogen and Ag-AgCl electrodes without liquid junction.

Table 2. Second dissociation constant of Na$_3$POPSO from (278.15 to 328.15) K.

T/K	pK$_2$	σ (pK$_2$)^a	β	σ (β)^b
278.15	8.0363	0.0009	2.888	0.011
283.15	7.9785	0.0009	2.859	0.010
288.15	7.9192	0.0009	2.784	0.010
293.15	7.8614	0.0009	2.689	0.010
298.15	7.8029	0.0008	2.691	0.010
303.15	7.7445	0.0008	2.918	0.009
308.15	7.6862	0.0008	2.878	0.009
310.15	7.6628	0.0008	2.893	0.009
313.15	7.6277	0.0009	2.898	0.009
318.15	7.5693	0.0008	2.913	0.009
323.15	7.5113	0.0008	2.891	0.009
328.15	7.4535	0.0008	2.983	0.009

^{a}Standard deviation of pK$_2$; ^{b}Slope parameter.

Table 3. Thermodynamic quantities for the dissociation of Na$_3$POPSO from (278.15 - 328.15) K.

	278.15 K	288.15 K	298.15 K	308.15 K	318.15 K	328.15 K
$\Delta G°$	42,792 ± 4	43,688 ± 5	44,538 ± 5	45,343 ± 5	46,104 ± 5	46,824 ± 5
$\Delta H°$	17,206 ± 96	18,541 ± 62	19,877 ± 34	21,213 ± 36	22,548 ± 68	23,884 ± 107
$\Delta S°$	−92.0 ± 0.3	−87.3 ± 0.2	−82.7 ± 0.1	−78.3 ± 0.1	−74.0 ± 0.2	−69.9 ± 0.3
$\Delta Cp°$	134 ± 4	134 ± 4	134 ± 4	134 ± 4	134 ± 4	134 ± 4

Units: $\Delta G°$, $\Delta H°$, J·mol^{-1}; $\Delta S°$, $\Delta Cp°$, J·K^{-1}·mol^{-1}.

It is interesting to mention that at the human body temperature of 310.15 K, our pK_2 value is 7.6628. The pH of blood at this temperature is equal to 7.407. Thus, the (POPSO) buffer can be used as pH primary standard for physiological use. Moreover, the usefulness of (POPSO) and other Good Buffers [7] [9] [11] for pH control in the range of physiological interest, in the aggregation of peptides [16] and surface active behavior [17], have been reported.

It is interesting to compare the values of the thermodynamic quantities of some structurally related zwitterionic buffer compounds with that of (POPSO). Such a comparison of the values at 298.15 K is summarized in **Table 4**. Examples of structurally similar compounds are; N-substituted amino sulfonic acids, (TABS) [9], (MOBS)

Table 4. Comparison of the thermodynamic functions for the second acid dissociation constant of Na$_3$POPSO with structurally related compounds in water at 298.15 K.

Structure	Common name	pK_2	$\Delta H°$	$\Delta S°$	$\Delta Cp°$	Ref.
	TAURINE	9.061	41,840	−33.1	−33	[19]
	PIPERAZINE	9.731	53,390	−33.9	88	[5]
	MORPHOLINE	8.492	39,030	−31.7	48	[20]
	MES	6.270	14,602	−1.1	4	[24]
	AMPSO	9.138	43,166	−31.2	−59	[10] [18]
	DIPSO	7.576	30,192	−45.5	42	[10]
	MOBS	7.702	24,442	−61.1	74	[11]
	TABS	8.834	43,663	−23.6	39	[9]
	PIPES	7.140	11,964	−96.5	124	[4]
	Na$_3$POPSO	7.803	19,877	−82.7	134	This study

Units: $\Delta H°$, J·mol^{-1}; $\Delta S°$, $\Delta Cp°$, J·K^{-1}·mol^{-1}.

[11] and (AMPSO) [10] [18]. These are the parent compounds (TAURINE) [19], (MORPHOLINE) [20], and (PIPERAZINE) [5] [21], respectively. The value of pK_2 of (PIPES) [4] at 298.15 K is 7.1399; whereas, that for a similar structure (POPSO) from the present study is 7.8029. It is evident that lengthening of the chain has, as expected, increased the basicity (decreased the acidity) of the NH^+ group from (PIPES) to (POPSO) (this study). The enthalpy of dissociation has increased from 11,965 $J \cdot mol^{-1}$ to 19,877 $J \cdot mol^{-1}$. The increase in pK_2 is usually paralleled by the increase in $\Delta H°$. This trend is consistent with this study.

Also it indicates that there is a significant effect on the entropy of dissociation. From **Table 4**, the values of $\Delta S°$ at 298.15 K for (PIPES) [4], and (POPSO) [this investigation] are: -96.5 $J \cdot K^{-1} \cdot mol^{-1}$ and -82.7 $J \cdot K^{-1} \cdot mol^{-1}$ respectively. These values are generally in qualitative agreement. The slightly less negative value of (POPSO) is consistent with the explanation for the stabilization of the solvent structure (decreased order) in the proximity of the ions H^+, Na^+, $POPSO^{-4}$. In addition, this small change (less negative) in $\Delta S°$ (entropy of solvation of the NH^+ group) is due to the effect of the successive introduction of hydroxyl group and (MORPHOLINE) compound into the ethyl groups of monosodium POPSO.

In **Table 4**, the values of $\Delta Cp°$ at 298.15 K for (PIPES) [4] and (POPSO) [this study] are 124 $J \cdot K^{-1} \cdot mol^{-1}$ and 134 $J \cdot K^{-1} \cdot mol^{-1}$ respectively. These results (slight increase in $\Delta Cp°$ of POPSO) suggest that the substitution and the presence of an extra monosodium POPSO molecule in POPSO disodium salt apparently have two effects: 1) progressive increasing of hydrophobic characters (tending to increase $\Delta Cp°$), and 2) some changes in the solvation pattern, that is, progressively greater steric hindrance (tending to increase $\Delta Cp°$ value by exclusion of solvent) [22].

It is better to point out that the interactions of NaCl with N-substituted aminosulfonic acid (POPSO) [this study] and (MES) [23] or aminocarboxylacid (TRICINE) [24], are very complex. Thus, detailed quantitative explanations for these interactions are somewhat difficult.

5. Conclusion

For the 16 buffer solutions of **Table 1**, the largest difference between the final e.m.f reading at 298.15 K and that collected in the beginning was well within ±0.03 mV. The data is highly accurate and reproducible. The hydrogen and Ag-AgCl electrodes are reversible [25] without any complex formation with N-substituted amino acids. The results of pK_2 and related thermodynamic functions are very reliable. Unfortunately, no thermodynamic data of (POPSO) is available in the literature for the purpose of comparison. Since the value of pK_2 at 310.15 K (body temperature) of (POPSO) is 7.6628 ± 0.0008, the buffer solution of Na_3POPSO and Na_4POPSO would be a useful pH primary buffer standard for pH control in the region close to that of blood serum (pH = 7.407 at an ionic strength I = 0.16 $mol \cdot kg^{-1}$). Manuscript is under preparation, based on the new experimental data, for buffer solutions of Na_3POPSO + Na_4POPSO with and without the presence of NaCl in the physiological range of pH (7.0 to 8.5) at 12 different temperatures from (278.15 to 328.25) K.

Acknowledgements

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