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Potentiometric Determination of the Apparent Dissociation Constants of 3-(Cyclohexylamino)-1-propanesulfonic Acid and 3-(Cyclohexylamino)-2-hydroxy-1-propanesulfonic Acid in Various Hydroorganic Media

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The apparent dissociation constants of 3-(cyclohexylamino)-1-propanesulfonic acid (CAPS) and 3-(cyclohexylamino)-2-hydroxy-1-propanesulfonic acid (CAPSO) were determined at (25.00 ± 0.10) °C and $I = 0.1$ mol dm^{-3} KNO_3 by potentiometric pH titration in pure water and different hydroorganic solvent media. The organic solvents used were methanol, ethanol, *N*,*N*-dimethylformamide, dimethyl sulfoxide, acetonitrile, acetone, and dioxane. Initial estimates of the apparent dissociation constant values of the two zwitterionic amino propanesulfonic acid buffers studied have been refined with the ESAB2M computer program. pK_{a2}* values change with an increase in the concentration of organic solvent. The results obtained are discussed in terms of average macroscopic properties of the mixed solvents and the possible variation in microheterogenity of the solvation shells around the solute.

Introduction

The choice of alternative buffers had greatly increased with the commercial availability of zwitterionic amino acids and zwitterionic N-substituted aminosulfonic acids prepared by Good and co-workers (Good et al., 1966; Ferguson et al., 1980). Organic buffers suitable for use in biochemistry now include 3-(cyclohexylamino)-1-propanesulfonic acid (CAPS) and 3-(cyclohexylamino)-2-hydroxy-1-propanesulfonic acid (CAPSO). Zwitterionic N-substituted amino propane sulfonic acids show significant advantages over conventional buffers: insignificant penetration through biological membranes, maximum water solubility, no complex formation with biological samples, and no enzyme substrate or enzyme inhibitor properties. Though studies on the dissociation constants of acids and bases in various hydroorganic media have been extensively investigated, relatively little work has been done to determine the apparent dissociation constants of the biologically important zwitterionic buffers (Roy et al., 1984; Azab, 1993; Azab et al., 1993, 1994). CAPS and CAPSO are potentially useful zwitterionic buffers for use in biochemistry because of their low toxicity. In this paper we determine the apparent second stage dissociation constants of the biologically important zwitterionic buffers CAPS and CAPSO by potentiometric pH titrations in pure water and various water + ethanol, water + methanol, water + dimethylformamide, water + dimethyl sulfoxide, water + acetonitrile, water + acetone and water + dioxane mixtures containing different mass fractions of the organic solvent ranging between 0 and 0.55. The dependence of the apparent dissociation constant values on the composition of the solvent mixtures has been investigated in order to examine solvent−solute interactions.

Experimental Section

Chemicals. Reagent grade 3-(cyclohexylamino)-1-propanesulfonic acid (CAPS) and 3-(cyclohexylamino)-2-hydroxy-1-propanesulfonic acid (CAPSO) were from Sigma Chemical Co., St. Louis, MO. We determine by potentiometric pH titrations the molecular weight of CAPS and CAPSO to verify/determine the purity, especially for acidic/basic contaminants. The purity averaged 99.5% for the two compounds, with a standard deviation of 0.05%. The solvents used, methanol, ethanol, *N*,*N*-dimethylformamide, dimethyl sulfoxide, acetonitrile, acetone, and dioxane were from Merck AG, Darmstadt, Germany. A CO_2-free solution of potassium hydroxide (Merk AG) was prepared and standardized against multiple samples of primary-standard potassium hydrogenphthalate (Merck AG) under CO_2-free conditions. The molarity of HNO_3 (p.a.) was determined by titration with standard KOH (Merck AG) solutions. KNO_3 was from Merck AG, Darmstadt, FRG. The exact concentration of the stock solutions of the ligands (buffers) was determined by titration. Generally, dilute solutions were prepared by appropriate dilution of the stock using deionized water, which was in addition distilled. Hydroorganic solvent mixtures containing different mass fractions of the organic solvents were prepared by mixing weighed quantities of water and cosolvent.

Procedure. pH potentiometric measurements were made on solutions in a double-walled glass vessel at (25 ± 0.1) °C with a commercial Fisher combined electrode. A Fisher Accumet pH/ion meter Model 825 MP was used. The instrument was calibrated against standard buffers of pH 4.00 (phthalate buffer) and 9.20 (borate buffer). The instrument was rechecked after each experiment. The electrode system was calibrated in aqueous medium in terms of hydrogen ion concentration instead of activities. Thus, all the constants determined in this work are concentration constants. Calibration of the electrode system was done in the working medium by the MAGEC program (May and Wiliams, 1985) using the data of titration of nitric acid with potassium hydroxide, both of known concentration, under the same temperature and medium condition, $I = 0.1$ mol dm^{-3} (KNO_3). During the MAGEC calculation the calibration parameters (standard potential of the cell and value of ionic product of the medium) have been refined. Additionally the calibration procedure has been used to test the Nernstian response of the potentiometric cell. The temperature was controlled by a Fisher Scientific Isotemp Refrigerated Circulator Model 9000 water thermostat, and it was maintained

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within ±0.1 °C. Purified nitrogen was bubbled through the solution to maintain an inert atmosphere. Efficient stirring of the solution was achieved with a magnetic stirrer. All test solutions (1×10^{-3} mol dm^{-3} zwitterionic buffer ligand + 4×10^{-3} mol dm^{-3} HNO_3) were prepared in a constant ionic medium, 0.1 mol dm^{-3} KNO_3, by mixing the appropriate amounts of ligand, nitric acid, potassium nitrate, and the proportion of the different organic solvents studied. At each mixture, at least four titrations were performed. The concentration of free hydrogen ion, C_{H^+}, at each point of the titration was calculated from the measured emf, E, of the cell RE/TS/GE (RE and GE denote the reference and glass electrodes, respectively, and TS is the test solution) using the Nernst equation

$$E = E° + Q \log C_{H^+} \qquad (1)$$

where $E°$ is a constant that includes the standard potential of the glass electrode.

It is to be assumed that the activity coefficient is constant, an assumption usually justified by performing the experiments with a medium of high ionic strength (0.1 mol dm^{-3} KNO_3). Values for K_w for water in water + organic solvent systems have been taken from the literatures (Bates, 1964; Woolly and Hepler, 1972; Woolley et al., 1970; Gutbezahl and Grunwald, 1953; Harned and Fallon, 1939). The pH meter readings have been corrected in accordance with the method described by Douheret (Douheret, 1967, 1968). This was carried out to account for the difference in basicity, relative permittivity, and ion activity in partially aqueous solutions relative to pure solvent. The protonation constants were then determined by use of the Bjerrum function (Bjerrum, 1921)

$$\bar{n} = (H_T - h + K_w/h)/A_T = (\beta_1 h + 2\beta_2 h^2)/(1+\beta_1 h + \beta_2 h^2) \qquad (2)$$

which is calculated from the experimental quantities, h, the total concentration of titratable hydrogen ion H_T and the total reagent concentration A_T. The pK_{a2} values were determined from the overall protonation constants calculated by the linearization method of Irving and Rossotti (1953). Initial estimates of pK_{a2} values were refined with the ESAB2M computer program (de Stefano et al., 1987) by minimizing the error squares sum

$$U_v = \sum_i W_i (V_i - V_{calcd,i})^2 \qquad (3)$$

where V_i and $V_{calcd,i}$ are experimental and calculated values of the titrant for every point i of the titration curve. The weight is calculated by

$$1/W_i = S_i^2 = S_V^2 + (\delta V_i/\delta E_i)^2 \cdot S_E^2 \qquad (4)$$

where S_i, S_V, S_E are estimated variance and estimates of standard deviation in titrant volume and potential, respectively. Titrant volume, $V_{calcd,i}$, can be calculated from an explicit equation (Arena et al.,1979; Rigano et al., 1984). The program ESAB2M minimizes eq 3 by using the Gauss–Newton nonlinear least-squares method (Dixon, 1972). Our calculation has been performed with a Gaussian error in V of $S_V = 0.005$. In our potentiometric pH titrations, we put $E° = 0$ (formal potential of the electrodic couple) in the input instructions, since the program reads in pH in this case.

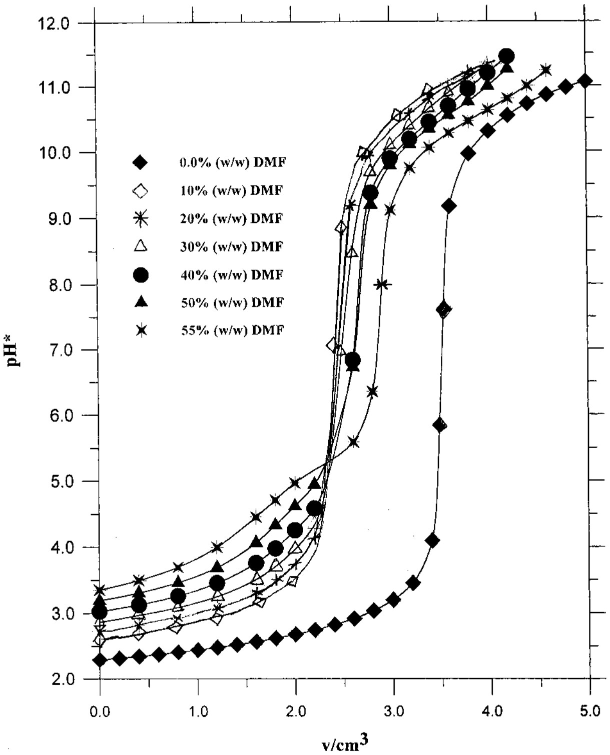
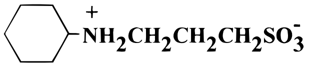


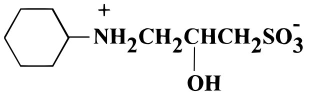
Figure 1. pH* vs volume of 0.0862 mol dm^{-3} KOH for CAPS in DMF + water mixtures at 25 °C and I = 0.1 mol dm^{-3} KNO_3.

Results and Discussion

3-(cyclohexylamino)-1-propanesulfonic acid (CAPS) and 3-(cyclohexylamino)-2-hydroxy-1-propanesulfonic acid (CAPSO) possess the following zwitterionic structures, respectively.



(CAPS)



(CAPSO)

The uncharged neutral form Z is negligible. The apparent second-stage dissociation constants of the above-mentioned zwitterionic buffers are due to the cationic group $^+NH_2$. If the above zwitterions are designated $Z^{\pm}$, the second dissociation step, the deprotonation of $^+NH_2$ group can be represented

$$Z^{\pm} \rightleftharpoons H^+ + Z^-$$

Representative titration curves from which the initial estimates of the apparent dissociation constants have been calculated are shown in Figures 1–3. The refined pK_{a2}* values of CAPS and CAPSO in different solvent mixtures are given in Tables 1 and 2. The values obtained in the present work for the apparent dissociation constant values pK_{a2} of the zwitterionic buffers studied in pure water agree with the literature data (Perrin and Dempsey, 1979). It has been observed (Scheller et al., 1980) that the presence of hydroxy groups two C atoms distant from the basic N leads to a systematic decrease of the basicity that is fairly independent of the type of amine (i.e., primary, secondary,

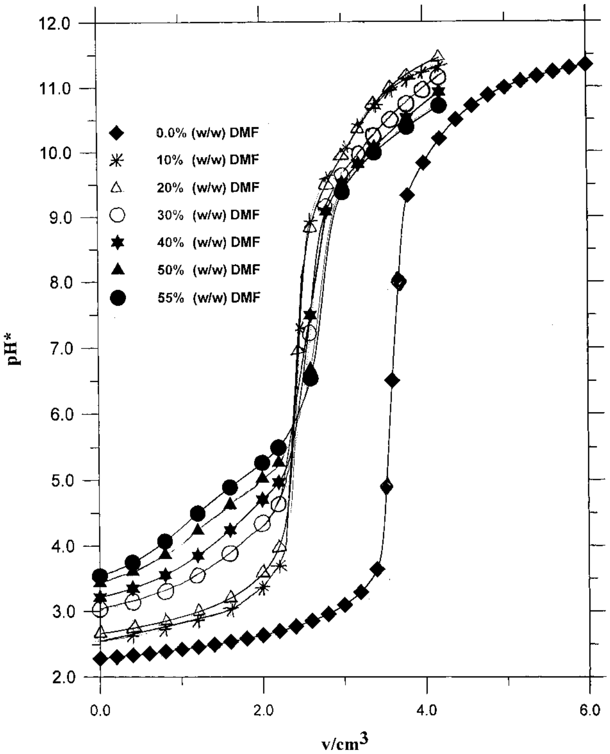


Figure 2. pH* vs volume of 0.0862 mol dm^{-3} KOH for CAPSO in DMF + water mixtures at 25 °C and I = 0.1 mol dm^{-3} KNO$_3$.

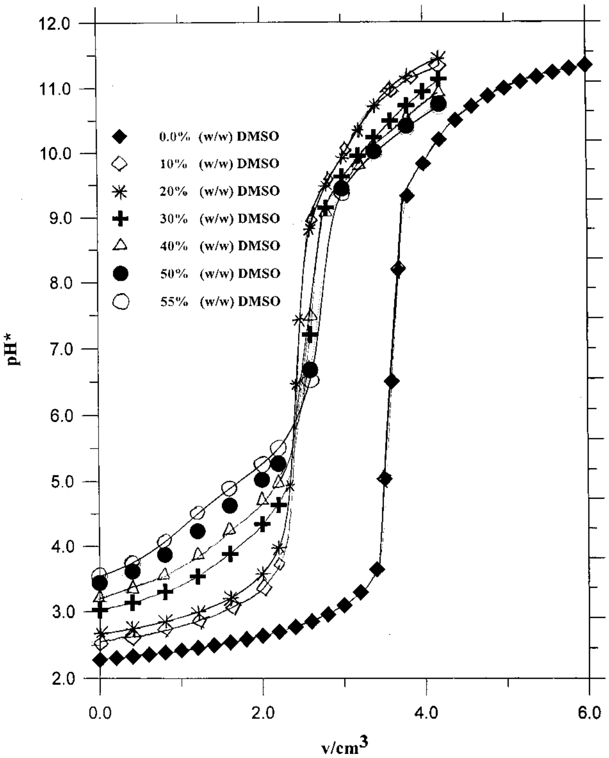


Figure 3. pH* vs volume of 0.0862 mol dm^{-3} KOH for CAPSO in DMSO + water mixtures at 25 °C and I = 0.1 mol dm^{-3} KNO$_3$.

Table 1. Refined pK_{a2}*^{a} (Apparent Dissociation Constant) Values of CAPS at Different Mass Fractions *w* for *w* Organic Solvent + (1 − *w*) Water Mixtures at 25.0 ± 0.1 °C and *I* = 0.1 mol dm^{-3} KNO$_3$

organic solvent	*w*	pK_{a2}*
methanol	0.00	10.39 ± 0.02
	0.10	10.33 ± 0.03
	0.20	10.39 ± 0.02
	0.30	10.42 ± 0.03
	0.40	10.27 ± 0.04
	0.50	10.11 ± 0.05
	0.55	10.03 ± 0.04
ethanol	0.00	10.39 ± 0.02
	0.10	10.32 ± 0.03
	0.20	10.21 ± 0.04
	0.30	10.02 ± 0.04
	0.40	9.85 ± 0.03
	0.50	9.69 ± 0.02
	0.55	9.62 ± 0.02
DMF	0.00	10.39 ± 0.02
	0.10	10.30 ± 0.03
	0.20	10.17 ± 0.04
	0.30	10.06 ± 0.05
	0.40	9.85 ± 0.05
	0.50	9.73 ± 0.05
	0.55	9.62 ± 0.04
DMSO	0.00	10.39 ± 0.02
	0.10	10.30 ± 0.04
	0.20	10.23 ± 0.03
	0.30	10.08 ± 0.03
	0.40	9.88 ± 0.04
	0.50	9.54 ± 0.02
	0.55	9.10 ± 0.03
acetonitrile	0.00	10.39 ± 0.02
	0.10	10.43 ± 0.02
	0.20	10.49 ± 0.02
	0.30	10.60 ± 0.03
	0.40	10.63 ± 0.05
	0.50	10.87 ± 0.03
acetone	0.00	10.39 ± 0.02
	0.10	10.33 ± 0.03
	0.20	10.39 ± 0.03
	0.30	10.28 ± 0.04
	0.40	10.07 ± 0.04
	0.50	9.87 ± 0.03
	0.55	9.46 ± 0.03
dioxane	0.00	10.39 ± 0.02
	0.10	10.35 ± 0.04
	0.20	10.34 ± 0.05
	0.30	10.39 ± 0.04
	0.40	10.36 ± 0.05
	0.50	10.48 ± 0.04
	0.55	10.52 ± 0.03

[a] pK_{a2}* = corrected pK_{a2} values ± uncertainties referring to statistically determined uncertainties at small 95% confidence intervals.

or tertiary). Each hydroxy group lowers the pK_a by about 0.8 log units. In agreement herewith are the apparent dissociation constants in aqueous solution (I = 0.1 mol dm^{-3} KNO$_3$; 25 °C) of CAPS (pK_{a2} = 10.39 ± 0.02) and CAPSO (9.65 ± 0.05). The results presented in Tables 1 and 2, with respect to ethanolic solution, can conveniently be discussed in terms of $\Delta G_{\text{(protonation)}}$ defined as $2.303RT(\log K^{(w)} - \log K^{(S)})$, i.e., the difference between the standard free energies of protonation in the mixed solvent and in water (Gordon 1975). Protonation of the solvent by Z$^{\pm}$ can be represented by the general equation

$$Z^{\pm} + SH \rightleftharpoons SH_2^{+} + Z^{-}$$

where Z$^{\pm}$ represents the zwitterionic form of CAPS and CAPSO, respectively, and SH denotes a molecule of solvent. Since the solutes involved in the ionization are charged, then of the two basic steps in solute−solvent interactions, i.e., charge transfer and charge separation (Gordon, 1975), only the first will be dominant. Therefore, although the difference in the permittivity between pure water and water + ethanol mixture is appreciable (78.3 vs 49.0 at 25 °C), it will have little effect on the protonation constants of the solutes. Also, the solvation in mixed ethanol + water as solvent should not differ much from that in water, since the structures of the two solvents are similar. Consequently the two effects will result in relatively small values

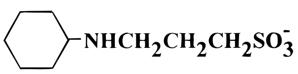
Table 2. Refined pK_{a2}*^{a} (Apparent Dissociation Constant) Values of CAPSO at Different Mass Fractions *w* for *w* Organic Solvent + (1 − *w*) Water Mixtures at 25.0 ± 0.1 °C and *I* = 0.1 mol dm^{-3} KNO_3

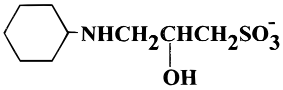
organic solvent	*w*	pK_{a2}*
methanol	0.00	9.65 ± 0.05
	0.10	9.68 ± 0.03
	0.20	9.63 ± 0.04
	0.30	9.70 ± 0.04
	0.40	9.66 ± 0.03
	0.50	9.48 ± 0.04
	0.55	9.39 ± 0.03
ethanol	0.00	9.65 ± 0.05
	0.10	9.58 ± 0.05
	0.20	9.46 ± 0.06
	0.30	9.29 ± 0.03
	0.40	9.02 ± 0.02
	0.50	8.94 ± 0.03
	0.55	8.83 ± 0.04
DMF	0.00	9.65 ± 0.05
	0.10	9.51 ± 0.02
	0.20	9.37 ± 0.02
	0.30	9.28 ± 0.03
	0.40	9.26 ± 0.02
	0.50	9.17 ± 0.03
	0.55	9.18 ± 0.04
DMSO	0.00	9.65 ± 0.05
	0.10	9.58 ± 0.02
	0.20	9.51 ± 0.03
	0.30	9.39 ± 0.02
	0.40	9.13 ± 0.04
	0.50	8.89 ± 0.05
	0.55	8.75 ± 0.04
acetonitrile	0.00	9.65 ± 0.05
	0.10	9.64 ± 0.02
	0.20	9.74 ± 0.02
	0.30	9.78 ± 0.03
	0.40	9.76 ± 0.03
	0.50	9.87 ± 0.04
	0.55	9.88 ± 0.02
acetone	0.00	9.65 ± 0.05
	0.10	9.67 ± 0.03
	0.20	9.67 ± 0.03
	0.30	9.63 ± 0.04
	0.40	9.54 ± 0.04
	0.50	9.49 ± 0.04
	0.55	9.45 ± 0.04
dioxane	0.00	9.65 ± 0.05
	0.10	9.74 ± 0.02
	0.20	9.74 ± 0.03
	0.30	9.78 ± 0.03
	0.40	9.79 ± 0.04
	0.50	9.81 ± 0.05
	0.55	9.80 ± 0.05

[a] pK_{a2}* = Corrected pK_{a2} values ± uncertainties referring to statistically determined uncertainties at small 95% confidence intervals.

of $\Delta G_{(\mathrm{protonation})}$. Accordingly with an increase in the amphiprotic ethanol solvent concentration in the aqueous medium, the change in pK_{a2}* of CAPS and CAPSO is quite small; in all cases it is decreased. The observed slight changes in pK_{a2}* of CAPS and CAPSO as the solvent is enriched in methanol can be mainly interpreted as resulting from the two following factors.

(a) The relatively high stabilization of the conjugate bases





by donor hydrogen bonds in a pure aqueous medium relative to that in the presence of methanol. This is due to the greater tendency of water molecules to serve as hydrogen bond donor as compared with other solvent molecules. Thus, an increase in the methanol proportion in the aqueous medium will result in an increase in the activity coefficient of the conjugate base, thereby causing a slight increase in the pK_{a2}* values.

(b) The greater stabilization of the proton in methanol + water mixtures relative to that in pure water through ion−solvent interaction (Bennetto et al. 1966; Tomkins, 1966). This effect will generate a low activity coefficient of the proton, therefore causing a slight decrease in pK_{a2}*.

As is evident from the results given in Tables 1 and 2, increasing the methanol concentration in the aqueous medium has different effects on the apparent dissociation constants of the zwitterionic form of CAPS and the zwitterionic form of CAPSO. With decreasing water activity the release of the proton from the amino nitrogen is rendered more difficult. In the presence of increasing concentrations of the dipolar aprotic solvents with high donicity (DMF and DMSO), deprotonation is facilitated because the solvent mixture solvates the proton more than the zwitterion. This leads to lower pK_{a2}* values in such media than that obtained in pure aqueous solution. The observed small increase in the pK_{a2}* values of CAPS and CAPSO as the solvent is enriched in dioxane may be due to the fact that the release of the proton from the amino nitrogen is rendered more difficult in the presence of this cosolvent. The observed small increase of the pK_{a2}* values of CAPS and CAPSO in the presence of varying amounts of a low basic aprotic acetonitrile solvent may be attributed to a low stabilization of the free conjugate bases of the zwitterionic buffer ligands studied by hydrogen-bonding interactions in the presence of this coorganic solvent. Acetonitrile is considered to be both a poorer acceptor as well as donor of hydrogen bonds compared to water. Also the H^+ ion becomes less stabilized in the presence of this coorganic solvent due to hydrogen ion−solvent interaction (Bates, 1964), which leads to a high activity coefficient of the proton.

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