Buffers and Ionic Salts: Densities and Solubilities of Aqueous and Electrolyte Solutions of Tris(hydroxymethyl)aminomethane and *N*-Tris[hydroxymethyl]-4-amino-butanesulfonic Acid†

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The densities of aqueous solutions of tris(hydroxymethyl)aminomethane (TRIS) and tris[hydroxymethyl]-4-amino-butanesulfonic acid (TABS), useful biological buffers within the pH range of 7.0 to 9.0 for TRIS and 8.2 to 9.5 for TABS, have been measured by a high-precision vibrating-tube digital densitometer in aqueous and in aqueous electrolyte solutions from (298.15 to 328.15) K under atmospheric pressure. This study was undertaken to investigate the interactions between these compounds and electrolytes of potassium acetate (KAc), potassium bromide (KBr), potassium chloride (KCl), and sodium chloride (NaCl). In this series of measurements, the aqueous samples were prepared with various concentrations of the buffers, up to saturated conditions, and over salt concentrations from (1 to 4) mol·dm^{-3}. The experimental densities were correlated as a function of the concentration of the buffers and ionic salts. The solubilities of buffers at 298.15 K in aqueous and in aqueous electrolyte solutions have also been determined from the experimental results of density measurements. It was found that the solubilities of TRIS and TABS in aqueous solution decrease with increasing concentration of salts (salting-out effect). The solubility data were further used to estimate the apparent free energy of transfer ($\Delta G'_{tr}$) of buffers from water to aqueous electrolyte solutions. The contribution of TABS residue ($-CH_2CH_2CH_2CH_2SO_3^-$) from water to aqueous electrolyte solutions was predicted from the $\Delta G'_{tr}$ results. The measured densities served to evaluate the apparent molar volumes, $V_\phi(m, T)$, and fitted them to an equation that describes the surface (V_ϕ against T against m). The apparent molar volumes of buffers at infinite dilution (V_ϕ^o) have been determined from the solubility data. The trends of transfer volumes ($\Delta_{tr}V_\phi^o$) have been interpreted in terms of solute−cosolute interactions on the basis of a cosphere overlap model.

Introduction

Buffers are ubiquitous components in most in vitro reaction systems because many biological and chemical systems involve acid−base equilibria and therefore depend critically on the pH of the solution. Buffers covering the pH range between 6 and 9 are especially required for biological and environmental studies. Many early buffers were not suitable for biological applications because they may not be inert enough, thus interfering with the system under study. The recent extension of the number of buffers covering the physiological pH range now makes it possible to assess much more effectively the suitability of possible buffer systems.

N-Tris[hydroxymethyl]-4-amino-butanesulfonic acid (TABS) is a zwitterionic buffer which gives good activity of four enzymes with optimum pH values in the alkaline range: β-galactosidase, esterase, phosphodiesterase, and alkaline phosphatase.[1] In biological systems where effects of K^+ and Na^+ may be important, buffers lacking these ions may be desirable; such buffers may comprise amines including tris(hydroxymethyl)aminomethane (TRIS)[2] and its derivatives and the zwitterionic "Good" buffers provided by Good and his associates.[3,4] TRIS-buffer is extensively used in biochemistry and molecular biology.[5] In biochemistry, TRIS is widely used as a component of buffer solutions, such as in TRIS-borate-EDTA (TBE) and TRIS-acetate-EDTA (TAE) buffers, especially for solutions of nucleic acids. TRIS salts are used in protein crystallization at various pH values.[6−9] Currently, most researchers use TRIS-buffer as an extender for canine semen preservation.[10,11] Canine semen can be the most efficiently frozen with an extender constituted by TRIS-buffer.[12] TRIS has been utilized in studies of double stranded complexes of peptide nucleic acids (PNA) and their cDNA sequences.[13]

TRIS buffers have been widely used to define seawater's pH values. Early workers[14] used TRIS buffers in natural seawater as secondary pH standards. TRIS buffers in synthetic seawater are now used as primary buffers to define seawater pH scales[15−18] either directly for subsequent calibration of electrometric pH measurements[19,20] or indirectly by using them to define the pK of indicator dyes for seawater pH measurements.[21−23]

Although TRIS has been a major biochemical buffer for many years, partly because it is relatively inexpensive and readily available in a highly purified form, it has disadvantages. These include its reactivity as a primary amine and its appreciable solubility in organic solvents which leads to its accumulation in the biological phases of reaction systems. Thus, TRIS buffer displaces the electron transport, and phosphorylation, pH unit when compared with a number of other buffers. It also inhibits isocitrate dehydrogenase of pea mitochondria, whereas 4-(2-hydroxyethyl)piperazine-1-ethanesulfonic acid (HEPES) does not. The TBE and TAE buffers form complexes with DNA.[24−27]

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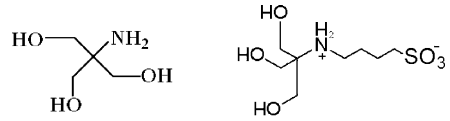
Scheme 1



DNA molecules also form extensive complexes with histidine molecules in isoelectric histidine buffers.[28] The complexes can be dissociated by adding monovalent salts such as NaCl or KBr to the solution, indicating that the complexes are stabilized by electrostatic interactions. Divalent cations are less effective than monovalent cations in dissociating the complexes. DNA−TRIS interactions also influence the rate of cleavage of plasmid pBR322 by the restriction enzyme EcoRV.[29]

With the aim to contribute to the knowledge of the interactions of these buffers (Scheme 1) with electrolytes, the present work reports the interactions between four selected salts (KAc, KBr, KCl, and NaCl) and two biological buffers of TRIS and TABS, via density measurements, which were measured by a high-precision vibrating-tube digital densitometer. We have determined the solubility of TRIS and TABS in water and in aqueous electrolyte solutions at 298.15 K from the results of the density measurement. In addition, these data can be used to study the apparent free energy of transfer of these buffers from water to aqueous electrolyte solutions at 298.15 K. We calculated the apparent molar volumes, $V_\phi(m, T)$, from the solubility data.

Experimental Section

Materials. TRIS (mass fraction purity > 0.999) and TABS (mass fraction purity > 0.99) were purchased from Sigma Chemical Co. (USA). The salts, potassium chloride (KCl, mass fraction purity 0.9999+) and potassium acetate (KAc, mass fraction purity 0.9998+), were purchased from Aldrich Chemical Co. (USA). Potassium bromide (KBr, mass fraction purity 0.995+) and sodium chloride (NaCl, mass fraction purity 0.995+) were obtained from Arcos Organics (USA). All the purchased materials were used without further purification. Water used for making the aqueous and aqueous electrolyte solutions was obtained from the NANO pure-Ultra pure water system that was distilled and deionized with resistance of 18.3 MΩ. All the aqueous solution samples were prepared gravimetrically.

Density Measurements. Densities were measured with an Anton Paar DMA-4500 vibrating-tube densitometer, Austria, with an uncertainty of $\pm 5 \cdot 10^{-5}$ g·cm^{-3}. For this kind of instrument, the sample fills a vibrating tube. Usually, it is assumed that the densitometer behaves as an oscillator without damping. This is true for low-viscosity samples, but for high-viscosity ones the damping contribution is significant, a fact that makes the "measured" density higher than the real one.[30] Therefore, corrections for high-viscosity samples are needed for this kind of densitometer. There are some studies that deal with this problem, in which different procedures are proposed to make such corrections.[31] The main advantage of the DMA-4500 densitometer is its ability to carry out this correction automatically, without any prior information about the viscosity of the sample. The densitometer is equipped with an internal temperature control unit, which can regulate the temperature of the measuring tube to within ± 0.03 K in a temperature range of (273.15 to 363.15) K. The instrument was calibrated with air and degassed distilled water.

Solubility Measurements. Solubilities of TRIS and TABS were measured at 298.15 K from the density measurements, following the procedure of Nozaki and Tanford.[32−34] The detailed procedure used in this work has been delineated in our earlier articles.[35,36] Briefly, at least nine sample vials were prepared for each investigated system. To each of the sample vials containing a fixed amount of solvent (water or aqueous electrolyte solutions) was added weighed amounts of a buffer compound to provide a series of mixtures with increasing composition of buffer mass. Of the nine vials, four to six contained low enough weights of buffer such that unsaturated solutions resulted. The remaining vials contained sufficient buffer weights to produce saturated solutions, and each of the vials was then sealed with a Teflon-coated screw cap. The vials were completely in a thermostatic shaker equipped with a water bath (BT-350R, Yih-Der, Taiwan) at $T = 298.15$ K for (36 to 48) h, and the supernatant of saturated solutions was removed through a syringe and filtered by a 0.22 μm disposal filter (Millipore, Millex-GS) before performing the density measurements. In the present study, (0, 1, 2, and 4) mol·dm^{-3} of KAc, KBr, KCl, or NaCl aqueous solutions were chosen as solvents. Since the densities of liquid samples will remain constant as the amounts of added buffers are greater than their solubility limit, the saturated solubility can be determined by the composition where density levels off on a plot of density against the original amount of buffer added in the solvent. The uncertainty of the solubility limit is lower than ± 0.8 %. The concentration of buffer in the samples, in units of (g of buffer/100 g of solvent), is calculated from eq 1.

$$\text{composition } g_{\text{buffer}}/100\ g_{\text{solvent}} = \left(\frac{\text{weight}_{\text{buffer}}\,(g)}{\text{weight}_{\text{solvent}}\,(g)}\right) \cdot 100 \tag{1}$$

The solubility limits expressed as (g of buffer/100 g of solvent) are converted to the more appropriate units of molarity (moles of buffer/liter of solution) and molality (moles of buffers/kg of solvent) using eqs 2 and 3, respectively.[37]

$$\text{molality} = \frac{W_B}{M_B}\frac{1000}{W_{sv}} \tag{2}$$

$$\text{molarity} = \frac{W_B \rho^*}{M_B(W_B + W_{sv})} \tag{3}$$

where W_B is the weight of buffer in grams; $W_{sv} = 100$ g of solvent; M_B is the buffer molecular weight; and ρ^* is the density (g·L^{-1}) of the saturated solution at the solubility limit determined experimentally. To check the reliability of the experimental procedure used in the present study, we measured the solubility limits (S_B) of TRIS buffer in water at $T = 298.15$ K ($S = 5.76$ mol·kg^{-1}), which agree fairly well with the values 5.780 mol·kg^{-1} and 5.766 mol·kg^{-1} reported by Bates et al.[38] and El-Harakany et al.,[39] respectively.

Results and Discussion

The measured experimental densities (ρ) for the aqueous electrolyte solutions at several temperatures are shown in a previous paper.[40] It was found that the densities of the electrolyte solutions increase with increasing unity of molarity of salt and decrease with temperature, and the salt effects on density increment follow the order of KBr > KAc ≈ KCl > NaCl. Tables 1 and 2 present the densities and concentrations of buffers in

Table 1. Experimental Densities (ρ) for Ternary Systems of (Water + TRIS + Ionic Salts) from (298.15 to 328.15) K under Atmospheric Pressure

	ρ/g·cm^{-3}							ρ/g·cm^{-3}					
m/mol·kg^{-1}	298.15 K	303.15 K	310.15 K	318.15 K	323.15 K	328.15 K	m/mol·kg^{-1}	298.15 K	303.15 K	310.15 K	318.15 K	323.15 K	328.15 K
TRIS in water													
1.6667	1.04381	1.04204	1.03930	1.03579	1.03340	1.03082	4.2711	1.08634	1.08419	1.08098	1.07702	1.07440	1.07163
2.2940	1.05388	1.05201	1.04914	1.04551	1.04301	1.03997	4.9084	1.09803	1.09581	1.09251	1.08846	1.08580	1.08304
2.9454	1.06501	1.06304	1.06005	1.05629	1.05379	1.05116	5.5861	1.10697	1.10468	1.10129	1.09718	1.09446	1.09167
3.6602	1.07708	1.07501	1.07188	1.06802	1.06543	1.06267							
TRIS in 1 mol·dm^{-3} KAc													
0.9840	1.06677	1.06500	1.06226	1.05875	1.05636	1.05373	2.8430	1.10064	1.09857	1.09544	1.09158	1.08899	1.08623
1.6204	1.07811	1.07624	1.07337	1.06974	1.06724	1.06393	3.4415	1.11146	1.10931	1.10610	1.10214	1.09952	1.09675
2.2115	1.08915	1.08718	1.08419	1.08043	1.07793	1.07530	4.0688	1.12209	1.11987	1.11657	1.11252	1.10986	1.10710
TRIS in 2 mol·dm^{-3} KAc													
0.2196	1.09419	1.09223	1.08928	1.08561	1.08316	1.08060	2.3262	1.12899	1.12671	1.12341	1.11934	1.11669	1.11385
0.3343	1.09571	1.09373	1.09074	1.08704	1.08457	1.08201	3.0279	1.13974	1.13737	1.13391	1.12975	1.12704	1.12425
0.9881	1.10690	1.10501	1.10203	1.09819	1.09565	1.09302	3.3614	1.14554	1.14315	1.13962	1.13545	1.13271	1.12990
1.4875	1.11515	1.11298	1.10976	1.10584	1.10324	1.10056							
TRIS in 4 mol·dm^{-3} KAc													
0.0991	1.17399	1.17161	1.16804	1.16385	1.16111	1.15826	0.8428	1.18286	1.18056	1.17715	1.17249	1.16988	1.16664
0.1527	1.17471	1.17235	1.16888	1.16471	1.16200	1.15922	1.3976	1.18944	1.18692	1.18324	1.17889	1.17607	1.17320
0.1998	1.17529	1.17291	1.16943	1.16528	1.16257	1.15978	2.0043	1.19631	1.19373	1.18999	1.18557	1.18273	1.17983
0.3178	1.17680	1.17415	1.17071	1.16659	1.16391	1.16115							
TRIS in 1 mol·dm^{-3} KBr													
0.2295	1.08968	1.08779	1.08487	1.08117	1.07570	1.07211	2.1479	1.11934	1.11724	1.11407	1.11016	1.10516	1.10195
0.3368	1.09126	1.08936	1.08642	1.08274	1.07725	1.07366	3.0329	1.13242	1.13032	1.12715	1.12324	1.12064	1.11793
0.9477	1.10197	1.09996	1.09692	1.09311	1.08789	1.08439	3.9417	1.14685	1.14447	1.14098	1.13674	1.13199	1.12912
1.5816	1.11063	1.10853	1.10536	1.10135	1.09605	1.09264							
TRIS in 2 mol·dm^{-3} KBr													
0.2163	1.16771	1.16549	1.16220	1.15812	1.15520	1.14990	2.0117	1.18821	1.18599	1.18205	1.17817	1.17527	1.17071
0.2873	1.16851	1.16599	1.16271	1.15866	1.15569	1.15019	2.8207	1.19711	1.19458	1.19091	1.18651	1.18364	1.17903
0.8486	1.17522	1.17291	1.16945	1.16527	1.16252	1.15734	3.6693	1.20647	1.20345	1.19982	1.19490	1.19245	1.18642
1.4273	1.18123	1.17889	1.17577	1.17204	1.16915	1.16423							
TRIS in 4 mol·dm^{-3} KBr													
0.9122	1.31253	1.30998	1.30612	1.30165	1.29882	1.29544	2.1339	1.31835	1.31603	1.31281	1.30874	1.30614	1.30336
1.1317	1.31359	1.31093	1.30698	1.30262	1.29955	1.29662	2.3766	1.31951	1.31723	1.31393	1.30986	1.30721	1.30437
1.9440	1.31760	1.31524	1.31208	1.30816	1.30557	1.30284							
TRIS in 1 mol·dm^{-3} KCl													
0.1577	1.04712	1.04538	1.04268	1.03923	1.03690	1.03446	2.2131	1.08429	1.08267	1.08021	1.07710	1.07374	1.07107
0.2443	1.04920	1.04750	1.04479	1.04133	1.03899	1.03653	3.1410	1.09890	1.09734	1.09501	1.09135	1.08918	1.08546
0.3195	1.05064	1.04887	1.04612	1.04266	1.04030	1.03781	4.0829	1.11764	1.11557	1.11198	1.10788	1.10601	1.10192
0.9708	1.06149	1.05971	1.05706	1.05364	1.05144	1.04908	4.8539	1.12991	1.12754	1.12408	1.11993	1.11722	1.11441
1.6122	1.07310	1.07112	1.06835	1.06513	1.06285	1.05987							
TRIS in 2 mol·dm^{-3} KCl													
0.3071	1.09402	1.09204	1.08904	1.08536	1.08291	1.08036	2.2123	1.12307	1.12104	1.11738	1.11425	1.11146	1.10884
0.9072	1.10288	1.10104	1.09822	1.09469	1.09215	1.08961	3.0073	1.13567	1.13391	1.12930	1.12629	1.12314	1.12046
1.5676	1.11375	1.11179	1.10837	1.10490	1.10264	1.10032	4.1506	1.15283	1.15040	1.14688	1.14267	1.13992	1.13712
TRIS in 4 mol·dm^{-3} KCl													
0.2476	1.16432	1.16206	1.15881	1.15484	1.15229	1.14963	1.2737	1.18555	1.18327	1.17997	1.17590	1.17325	1.17041
0.4681	1.16958	1.16735	1.16411	1.16021	1.15764	1.15501	1.8582	1.19745	1.19519	1.19192	1.18689	1.18431	1.18189
0.7231	1.17464	1.17228	1.16906	1.16522	1.16268	1.16005	2.1521	1.20305	1.20066	1.19713	1.19296	1.19022	1.18741
1.0509	1.18057	1.17840	1.17518	1.17126	1.16866	1.16598	2.3906	1.20657	1.20460	1.20069	1.19714	1.19372	1.19133
TRIS in 1 mol·dm^{-3} NaCl													
0.3558	1.05004	1.04821	1.04537	1.04183	1.03943	1.03581	2.8488	1.09409	1.09189	1.08864	1.08472	1.08213	1.07895
0.9658	1.06086	1.05892	1.05597	1.05232	1.04988	1.04624	3.4654	1.10512	1.10277	1.09952	1.09558	1.09296	1.08983
1.5841	1.07209	1.07006	1.06701	1.06329	1.06077	1.05741	4.0928	1.11522	1.11319	1.10977	1.10578	1.10310	1.10011
2.2173	1.08370	1.08159	1.07843	1.07454	1.07199	1.06872	4.7375	1.12708	1.12470	1.12120	1.11701	1.11427	1.11144
TRIS in 2 mol·dm^{-3} NaCl													
0.3087	1.08606	1.08395	1.08081	1.07702	1.07454	1.07191	2.7505	1.12333	1.12096	1.11748	1.11327	1.11056	1.10778
0.9312	1.09557	1.09338	1.09015	1.08622	1.08362	1.08096	3.3589	1.13281	1.13041	1.12687	1.12263	1.11989	1.11708
1.5371	1.10560	1.10335	1.10002	1.09593	1.09329	1.09060	3.9764	1.14210	1.13964	1.13602	1.13173	1.12895	1.12611
2.1438	1.11442	1.11211	1.10871	1.10453	1.10185	1.09913	4.4486	1.14893	1.14641	1.14275	1.13856	1.13577	1.13292
TRIS in 4 mol·dm^{-3} NaCl													
0.1767	1.15190	1.14933	1.14574	1.14150	1.13874	1.13591	2.0101	1.17503	1.17275	1.16938	1.16532	1.16267	1.15991
0.3335	1.15341	1.15091	1.14738	1.14319	1.14047	1.13772	2.5722	1.18198	1.17961	1.17621	1.17212	1.16944	1.16666
0.8981	1.16150	1.15906	1.15561	1.15136	1.14868	1.14601	3.1608	1.18890	1.18666	1.18314	1.17900	1.17627	1.17345
1.4364	1.16825	1.16581	1.16246	1.15853	1.15601	1.15332	3.4340	1.19226	1.18978	1.18618	1.18196	1.17919	1.17635

water or in aqueous electrolyte solutions (m) at (298.15, 303.15, 310.15, 318.15, 323.15, and 328.15) K at atmospheric pressure, where the concentration of the last sample in each system is very close to the solubility limit. It can be noted from the tabulated values that the densities increase with increasing buffer composition and decrease with temperature.

Table 2. Experimental Densities (ρ) for Ternary Systems of (Water + TABS + Ionic Salts) from (298.15 to 328.15) K under Atmospheric Pressure

	ρ/g·cm^{-3}							ρ/g·cm^{-3}					
m/mol·kg^{-1}	298.15 K	303.15 K	310.15 K	318.15 K	323.15 K	328.15 K	m/mol·kg^{-1}	298.15 K	303.15 K	310.15 K	318.15 K	323.15 K	328.15 K
TABS in water													
0.9378	1.06723	1.06548	1.06276	1.05929	1.05690	1.05408	4.7956	1.21848	1.21610	1.21271	1.20868	1.20607	1.20341
1.5515	1.10073	1.09886	1.09593	1.09231	1.08987	1.08699	5.1539	1.22857	1.22617	1.22274	1.21868	1.21606	1.21341
2.4874	1.14355	1.14142	1.13829	1.13448	1.13199	1.12940	5.5488	1.23588	1.23346	1.22998	1.22589	1.22325	1.22058
4.0801	1.20045	1.19812	1.19476	1.19076	1.18817	1.18552							
TABS in 1 mol·dm^{-3} KAc													
1.1092	1.12206	1.12010	1.11713	1.11347	1.11109	1.10851	3.7151	1.21598	1.21361	1.21019	1.20615	1.20360	1.20100
1.7143	1.14657	1.14452	1.14141	1.13766	1.13525	1.13276	4.7178	1.24059	1.23821	1.23473	1.23068	1.22811	1.22550
2.0187	1.15785	1.15567	1.15245	1.14858	1.14612	1.14358	5.1065	1.25037	1.24796	1.24446	1.24038	1.23780	1.23519
2.2756	1.17032	1.16810	1.16484	1.16093	1.15844	1.15585	5.4501	1.25915	1.25675	1.25325	1.24916	1.24659	1.24399
3.0564	1.19219	1.18988	1.18650	1.18249	1.17996	1.17736							
TABS in 2 mol·dm^{-3} KAc													
0.7450	1.13161	1.12952	1.12641	1.12265	1.12019	1.11762	2.7415	1.21859	1.21617	1.21271	1.20862	1.20605	1.20345
1.0801	1.15114	1.14898	1.14577	1.14189	1.13939	1.13682	3.3739	1.23890	1.23647	1.23297	1.22885	1.22627	1.22366
1.2927	1.16047	1.15820	1.15488	1.15093	1.14841	1.14583	3.8714	1.25068	1.24825	1.24473	1.24061	1.23803	1.23543
1.4913	1.16858	1.16626	1.16288	1.15886	1.15632	1.15373	4.4438	1.26346	1.26102	1.25749	1.25338	1.25079	1.24818
1.9129	1.19190	1.18952	1.18608	1.18202	1.17947	1.17687							
TABS in 4 mol·dm^{-3} KAc													
0.6829	1.21338	1.21108	1.20781	1.20392	1.20128	1.19858	2.8255	1.27024	1.26778	1.26422	1.26004	1.25742	1.25477
1.0999	1.22747	1.22513	1.22179	1.21786	1.21530	1.21267	3.2752	1.27866	1.27619	1.27263	1.26844	1.26581	1.26317
1.4753	1.24102	1.23862	1.23513	1.23102	1.22844	1.22580	3.9265	1.29247	1.28999	1.28642	1.28220	1.27957	1.27692
1.9887	1.25370	1.25126	1.24773	1.24358	1.24098	1.23834							
TABS in 1 mol·dm^{-3} KBr													
1.1889	1.15588	1.15374	1.15056	1.14665	1.14179	1.13852	3.0462	1.22242	1.22006	1.21661	1.21250	1.20802	1.20487
1.7909	1.18184	1.17957	1.17632	1.17233	1.16762	1.16433	3.7081	1.24616	1.24373	1.24020	1.23604	1.23201	1.22917
2.3552	1.20564	1.20333	1.19994	1.19588	1.19125	1.18805	4.4738	1.26247	1.25999	1.25644	1.25225	1.24855	1.24601
TABS in 2 mol·dm^{-3} KBr													
0.9366	1.21327	1.21091	1.20743	1.20324	1.20051	1.19570	3.3510	1.28887	1.28631	1.28263	1.27830	1.27553	1.27171
1.6871	1.24056	1.23812	1.23459	1.23036	1.22761	1.22281	4.3871	1.30863	1.30603	1.30232	1.29796	1.29519	1.29173
2.2775	1.26190	1.25940	1.25580	1.25151	1.24875	1.24463	4.7318	1.31658	1.31399	1.31026	1.30591	1.30313	1.29972
TABS in 4 mol·dm^{-3} KBr													
0.9627	1.34809	1.34532	1.34130	1.33659	1.33357	1.33050	3.0140	1.38224	1.37944	1.37549	1.37087	1.36795	1.36498
1.4267	1.35806	1.35529	1.35130	1.34662	1.34363	1.34058	3.6440	1.38836	1.38557	1.38163	1.37705	1.37415	1.37121
2.0066	1.36916	1.36638	1.36240	1.35774	1.35478	1.35176	3.9499	1.39202	1.38926	1.38533	1.38077	1.37788	1.37495
TABS in 1 mol·dm^{-3} KCl													
1.2651	1.12671	1.12465	1.12159	1.11783	1.11535	1.11279	4.2165	1.23456	1.23215	1.22868	1.22457	1.22194	1.21924
1.8927	1.15517	1.15302	1.14982	1.14597	1.14346	1.14087	4.8710	1.24851	1.24604	1.24253	1.23839	1.23574	1.23304
2.5873	1.18334	1.18106	1.17775	1.17378	1.17122	1.16858	5.1605	1.25704	1.25456	1.25099	1.24684	1.24417	1.24146
3.6148	1.21224	1.20992	1.20657	1.20256	1.19997	1.19728							
TABS in 2 mol·dm^{-3} KCl													
1.0008	1.15228	1.15010	1.14690	1.14305	1.14050	1.13783	3.8344	1.25191	1.24944	1.24591	1.24176	1.23912	1.23642
1.6902	1.18011	1.17786	1.17456	1.17059	1.16800	1.16533	4.5115	1.26747	1.26496	1.26141	1.25723	1.25457	1.25187
2.4232	1.21122	1.20886	1.20545	1.20141	1.19880	1.19612	4.8158	1.27547	1.27295	1.26936	1.26515	1.26248	1.25977
3.1228	1.22805	1.22564	1.22217	1.21806	1.21543	1.21274							
TABS in 4 mol·dm^{-3} KCl													
0.9914	1.22309	1.22070	1.21758	1.21367	1.21104	1.20835	3.5939	1.29727	1.29472	1.29107	1.28681	1.28410	1.28136
1.5752	1.24408	1.24165	1.23822	1.23421	1.23156	1.22884	4.0249	1.30334	1.30078	1.29713	1.29286	1.29014	1.28741
2.2794	1.26458	1.26209	1.25851	1.25432	1.25165	1.24892	4.3125	1.31044	1.30787	1.30421	1.29991	1.29719	1.29445
2.9153	1.27913	1.27660	1.27298	1.26875	1.26606	1.26333							
TABS in 1 mol·dm^{-3} NaCl													
0.9211	1.10131	1.09928	1.09624	1.09250	1.09004	1.08665	3.8585	1.21922	1.21681	1.21334	1.20922	1.20657	1.20387
1.6553	1.13636	1.13427	1.13112	1.12734	1.12485	1.12154	4.6879	1.23761	1.23514	1.23162	1.22746	1.22480	1.22209
2.0066	1.15171	1.14955	1.14631	1.14244	1.13991	1.13681	5.3560	1.25373	1.25124	1.24766	1.24347	1.24080	1.23807
2.4096	1.17021	1.16794	1.16460	1.16062	1.15805	1.15502							
TABS in 2 mol·dm^{-3} NaCl													
1.0194	1.14059	1.13834	1.13503	1.13105	1.12846	1.12579	3.6141	1.23717	1.23467	1.23109	1.22689	1.22420	1.22147
1.7625	1.17423	1.17192	1.16852	1.16446	1.16183	1.15912	4.4423	1.25480	1.25228	1.24867	1.24444	1.24176	1.23901
2.1442	1.19101	1.18863	1.18517	1.18107	1.17840	1.17566	4.7936	1.26412	1.26158	1.25795	1.25370	1.25101	1.24825
2.7734	1.20850	1.20607	1.20256	1.19843	1.19575	1.19303	5.1034	1.27340	1.27084	1.26721	1.26297	1.26028	1.25753
TABS in 4 mol·dm^{-3} NaCl													
0.9452	1.19929	1.19675	1.19311	1.18878	1.18601	1.18320	3.9740	1.28951	1.28687	1.28309	1.27869	1.27591	1.27309
1.5200	1.22123	1.21866	1.21498	1.21063	1.20787	1.20506	4.3066	1.29594	1.29329	1.28953	1.28514	1.28235	1.27952
1.8185	1.23381	1.23121	1.22749	1.22313	1.22036	1.21754	4.7905	1.30356	1.30090	1.29713	1.29274	1.28995	1.28714
2.2643	1.24507	1.24245	1.23870	1.23433	1.23156	1.22873	0.9452	1.19929	1.19675	1.19311	1.18878	1.18601	1.18320
3.1003	1.27045	1.26781	1.26404	1.25966	1.25688	1.25406							

Table 3. Predicted Results from Equation 4 and Correlated Results from Equation 6 for Ternary Aqueous Systems

system	$10^2 \cdot a_1$ / g·cm^{-3a}	a_2 / g·cm^{-3a}	p_1[b]	p_2[b]	p_3[b]	from eq 1 AARD %[c]	from eq 3 AARD %[d]
water + TRIS	3.15602	0.708699	–	–	–	0.11	–
water + TABS	7.74654	0.661610	–	–	–	0.26	–
water + TRIS + KAc[e]	3.15602	0.708699	−0.38966	0.525332	0.743455	1.04	0.16
water + TRIS + KBr[e]	3.15602	0.708699	−1.34417	0.571821	1.052408	2.00	0.14
water + TRIS + KCl[e]	3.15602	0.708699	−0.12753	0.318879	0.543195	1.14	0.20
water + TRIS + NaCl[e]	3.15602	0.708699	−0.41331	0.524147	0.863622	1.25	0.16
water + TABS + KAc[e]	7.74654	0.661610	−2.22187	0.775811	1.045978	2.05	0.27
water + TABS + KBr[e]	7.74654	0.661610	−3.13290	0.668427	1.185392	3.74	0.18
water + TABS + KCl[e]	7.74654	0.661610	−1.80870	0.730897	1.180139	1.98	0.15
water + TABS + NaCl[e]	7.74654	0.661610	−1.17204	0.673487	1.002374	2.08	0.21

[a] Parameters in eq 4. [b] Parameters in eq 6. [c] AARD/% = $(100/N)\sum_{i=1}^{N}|\rho_i^{calc} - \rho_i^{expt}|/\rho_i^{expt}$, where N is the number of data points and $\rho^{calc} = \rho_w + a_1[m]^{a_2} + b_1[salt]^{b_2}$. [d] AARD/% = $(100/N)\sum_{i=1}^{N}|\rho_i^{calc} - \rho_i^{expt}|/\rho_i^{expt}$, where N is the number of data points and $\rho = \rho_w + a_1[m]^{a_2} + b_1[salt]^{b_2} + p_1[m/100]^{p_2}[salt/10]^{p_3}$. [e] Parameters $10^2 \cdot b_1$ and b_2 are 4.62317 and 0.946424 for the KAc-containing system; 8.21748 and 0.984256 for the KBr-containing system; 4.40501 and 0.970168 for the KCl-containing system; and 3.92698 and 0.960618 for the NaCl-containing system, resepctively.[40]

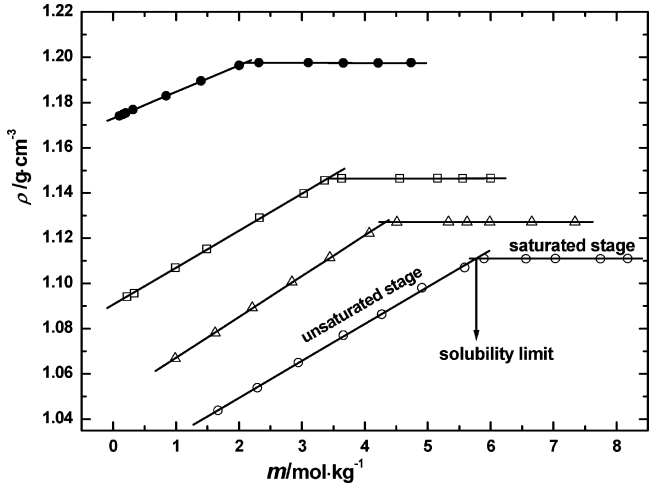


Figure 1. Representative solubility profiles of TRIS in water or KAc aqueous solutions at 298.15 K: ○, water; Δ, 1 mol·dm^{-3} KAc; □, 2 mol·dm^{-3} KAc; ●, 4 mol·dm^{-3} KAc. The symbol m is the composition of buffer in the prepared sample vials.

For the salt-free (0 mol·dm^{-3}) and the buffer-free (aqueous electrolytes) binary systems, the densities of solutions over the entire temperature range can be expressed satisfactorily by the following empirical equation[40]

$$\rho = \rho_w + a_1[m]^{a_2} + b_1[salt]^{b_2} \quad (4)$$

where ρ_w is the density of pure water; $[m]$ is the concentration of buffers (mol·kg^{-1}); and [salt] is salt concentration in [mol·dm^{-3}]. The optimal values of parameters a_1 and a_2 are reported in Table 3 for buffer-free binary systems, while b_1 and b_2 were previously reported.[40] The values of $(a_1 \times a_2)$ in eq 4 represent the density increment caused by increasing a mole of the buffer in 1 kg of solvent. It shows that the magnitude of density increment of TABS is greater than that of TRIS. The tabulated average absolute deviation (AARD) is defined as (Table 3)

$$AARD/\% = (100/N)\sum_{i=1}^{N}|\rho_i^{calc} - \rho_i^{expt}|/\rho_i^{expt} \quad (5)$$

where N is the number of data points.

It was notable that the densities of the (water + buffers + salts) ternary systems could not estimated directly from eq 4 with the determined parameters (a_1, a_2) and (b_1, b_2). The AARDs of prediction from eq 4, as presented in Table 3, are obviously greater than the experimental uncertainty. The accuracy of density calculations was significantly improved by adding an extra term into eq 4 to take the interactions between buffer and salt into account; i.e.

$$\rho = \rho_w + a_1[m]^{a_2} + b_1[salt]^{b_2} + p_1\left[\frac{m}{100}\right]^{p_2}\left[\frac{salt}{10}\right]^{p_3} \quad (6)$$

where p_1, p_2, and p_3 are model parameters whose optimal values can be obtained by fitting the above empirical model to density data for each ternary system of (water + buffer + salt). The optimized values of p_1, p_2, and p_3 together with the AARD of density correlation for each ternary system are presented in Table 3. This empirical model can correlate the density data to within about the experimental uncertainty. Similar calculated results were observed for the other temperatures as well. These results provide evidence for the existence of interactions between the buffers and ionic salts. As seen from Table 3, the values of parameter p_1 are negative for all the investigated ternary systems, indicating that the interactions between buffers and ionic salts result in density decrease or volume expansion. It was found that the values of parameters p_1, p_2, and p_3 of TABS are significantly greater than those on TRIS. This indicates that the zwitterionic TABS molecules are larger in size in solutions with higher salt concentrations. This effect can be attributed to the fact that the amino and sulfonic groups of TABS dissociate in aqueous solutions and become positively and negatively charged, respectively. The dissociation of TABS molecules in the presence of salts leads to the formation of ion pairs between the charged groups of TABS and salt ions. The formation of the ion pairs, on the one hand, increases the apparent molar volume of TABS and, on the other hand, reduces the electrostatic interactions between TABS molecules and water molecules and ions. This in turn reduces the interactions of water molecules and ions with the hydrocarbon backbone of TABS resulting in an increase in the number of water molecules attached to the amino and sulfonic groups of TABS in the form of hydration water. This effect can also be seen from the increasing values of V_ϕ^0 of TABS at higher salt concentrations (hereafter, Table 9).

The solubility of TRIS and TABS at $T = 298.15$ K in water and in aqueous electrolyte solutions was determined from the results of density measurements. As an example, Figure 1 shows the density profile of TRIS in water and in (1, 2, and 4) mol·dm^{-3} concentrations of KAc. The solubility limits, ex-

Table 4. Buffer Solubilities (S_B) and Densities (ρ^*) at Solubility Limits in Water or Ionic Salt Aqueous Solutions at $T = 298.15$ K and at Atmospheric Pressure

	S_B/mol·kg^{-1}				ρ^*/g·cm^{-3}			
solvent	0 mol·dm^{-3}	1 mol·dm^{-3}	2 mol·dm^{-3}	4 mol·dm^{-3}	0 mol·dm^{-3}	1 mol·dm^{-3}	2 mol·dm^{-3}	4 mol·dm^{-3}
				TRIS				
water	5.76[a]				1.11099			
KAc		4.35	3.40	2.11		1.12716	1.14640	1.19750
KBr		4.76	3.92	2.46		1.15906	1.20929	1.31998
KCl		4.92	4.29	2.73		1.13123	1.15505	1.21403
NaCl		4.97	4.56	3.52		1.13123	1.15078	1.19350
				TABS				
water	5.91				1.25825			
KAc		5.51	4.77	4.13		1.26499	1.28340	1.29957
KBr		5.54	5.21	4.50		1.29211	1.32772	1.39925
KCl		5.75	5.32	4.95		1.27639	1.29147	1.32565
NaCl		5.61	5.47	4.89		1.26982	1.28526	1.31216

[a] $S_B = 5.780$;[38] 5.766.[39]

Table 5. Apparent Transfer Free Energies of TRIS, TABS, and TABS Residue Contribution from Water to Aqueous Electrolyte Solutions at $T = 298.15$ K and at Atmospheric Pressure

	$\Delta G'_{tr}$/J·mol^{-1}						$\Delta g'_{tr}$/J·mol^{-1}		
solvent	1 mol·dm^{-3}	2 mol·dm^{-3}	4 mol·dm^{-3}	1 mol·dm^{-3}	2 mol·dm^{-3}	4 mol·dm^{-3}	1 mol·dm^{-3}	2 mol·dm^{-3}	4 mol·dm^{-3}
		TRIS			TABS		TABS residue ($-CH_2CH_2CH_2CH_2SO_3^-$)		
KAc	396.42	770.20	1559.62	57.18	176.28	312.30	−339.24	−593.92	−1247.32
KBr	183.23	396.19	1019.29	−0.81	−4.01	26.39	−184.04	−400.20	−992.90
KCl	192.56	359.79	1026.99	−8.70	41.06	54.95	−201.26	−318.73	−972.04
NaCl	176.25	270.09	612.44	28.83	24.83	92.06	−147.42	−245.26	−520.38

pressed as S_B (mol·kg^{-1}), and the densities (ρ^*) of saturated solution at solubility limit were obtained at the intersection of the two fitted lines in each experiment. Table 4 summarizes the solubility limits and the corresponding densities (ρ^*) of the saturated solutions. The experimental results in Table 4 demonstrate that the solubilities of TRIS and TABS decrease with increasing concentrations of KAc, KBr, KCl, and NaCl solutions and indicate the salting-out effect is dominant. Among the series of potassium salts, the observed order of the salting-out effect is KAc > KBr > KCl. The anions exert their effects independently, which are the relative effects of CH_3COO^-, Br^-, and Cl^-. Furthermore, we found that the salting-out effect of KCl > NaCl for the TRIS buffer and NaCl ≈ KCl for TABS buffer, respectively.

The free energy of transfer of a solute from one solvent system to another can be based on the solubilities of that solute in these two solvent systems.[32,41] At the solubility limit of the biological buffer in aqueous electrolyte solutions, two phases are in equilibrium, the solid phase of the buffer and the liquid phase of solution. At equilibrium, the chemical potential of the biological buffer in the crystalline phase must be equal to the chemical potential of the biological buffer in solution. Since the chemical potential of a buffer in its crystal is invariant, regardless of the solvent with which it is in contact, and since this chemical potential is the same in both solvent systems, the chemical potential of the biological buffer at the saturation point in one solvent must equal its chemical potential at the saturation point in the second solvent,[32−34,37,43,44] eq 7.

$$\mu^o_{B,w} + RT\ln S_{B,w} + RT\ln \gamma_{B,w} = \mu^o_{B,ws} + RT\ln S_{B,ws} + RT\ln \gamma_{B,ws} \quad (7)$$

where $\mu^o_{B,w}$ and $\mu^o_{B,ws}$ are the standard chemical potentials assigned to the buffer in water and in salt solution; $S_{B,w}$ and $S_{B,ws}$ are the buffer solubilities in water and in salt solution and expressed either in molar, molal, or mole fraction units; and $\gamma_{B,w}$ and $\gamma_{B,ws}$ are the activity coefficients of the solute expressed in terms of molar, molal, or mole fraction in water and in salt solution, respectively, at the solubility limit. The transfer free energy of the biological buffer from water to salt solution is equal to the difference between the standard state chemical potentials of the buffer in each solution, eq 8.[37]

$$\Delta\mu^o = \mu^o_{B,ws} - \mu^o_{B,w} = RT\ln\left(\frac{S_{B,w}}{S_{B,ws}}\right) + RT\ln\left(\frac{\gamma_{B,w}}{\gamma_{B,ws}}\right) \quad (8)$$

According to Nozaki and Tanford's analysis,[32−34] the ratio of the activity coefficient term makes only a small contribution to ΔG_{tr}, thereby this effect of the simplification is negligible and also not much greater than the experimental uncertainty. Many researchers[32−34,42,43] have ignored the activity coefficient on the right-hand side of eq 8. We used only the first term on the right side of eq 8 and declare the quantities reported here as apparent transfer free energy ($\Delta G'_{tr}$).[32−34] The apparent transfer free energy expressed in unit of molarity is shown in eq 9.[37]

$$\Delta G'_{tr} = RT\ln\left(\frac{n_{B,w}}{n_{B,ws}}\right) + RT\ln\left(\frac{V_{S,ws}}{V_{S,w}}\right) \quad (9)$$

Here, $n_{B,w}$ and $n_{B,ws}$ represent the moles of solute soluble in 100 g of water and in 100 g of electrolyte solution and $V_{S,w}$ and $V_{S,ws}$ are the total volumes of the aqueous solution and electrolyte solution containing the saturating solute on the molarity scale. It should be noted that the transfer free energies reported by Cohn and Edsall[45] and Tanford[46] are based upon the mole fraction scale, while Robinson and Jencks[47,48] and Bolen and co-workers[49,50] used the molarity scale. Ben-Naim[51] has strongly suggested in the favor of molarity scale for obtaining transfer free energies. Therefore, we also used molarity

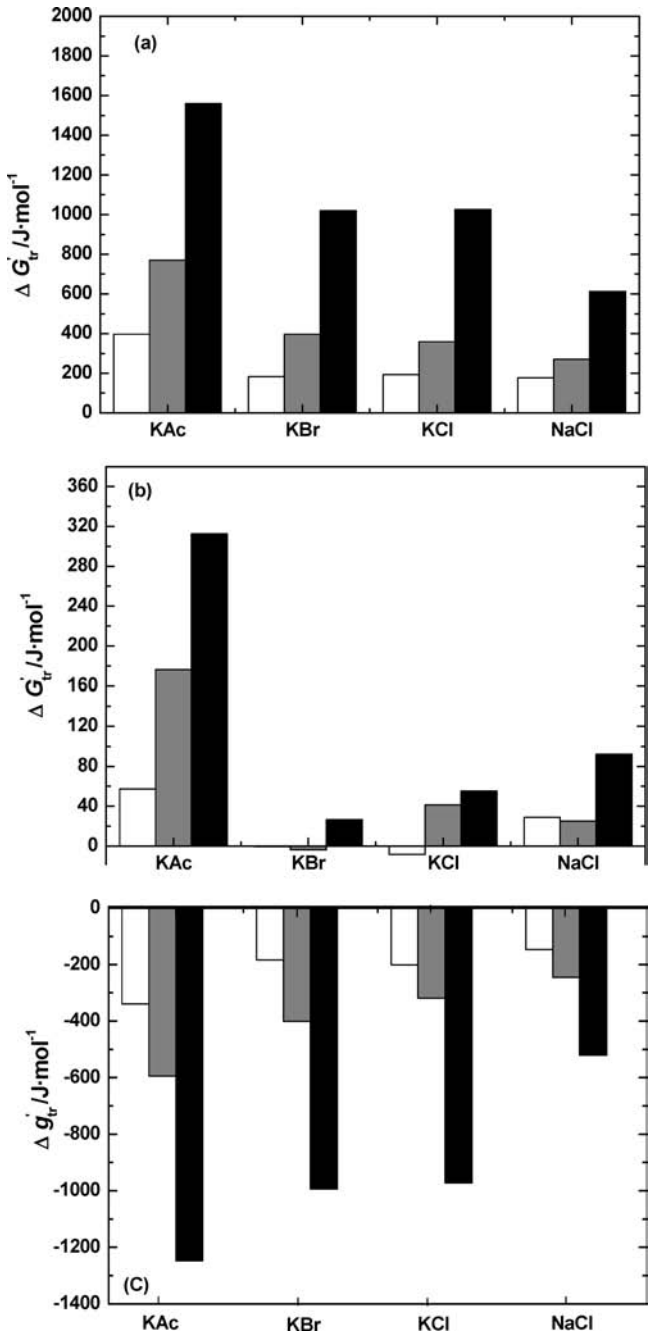
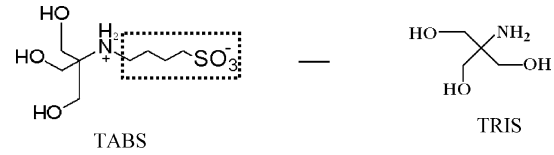


Figure 2. Display of apparent transfer free energies of (a) TRIS; (b) TABS; (c) TABS residue contribution from water to 1 M (white), 2 M (gray), and 4 M (black) of the salts at $T = 298.15$ K.

scale for calculating the transfer free energies (eq 9). The calculated $\Delta G'_{tr}$ values are reported in Table 5.

The transfer model has been a fixture in biophysical chemistry since at least the 1930s.[52] Usually, the transfer free energy is positive indicating that the interactions between the biological buffer and the salt are unfavorable. In contrast, if ΔG_{tr} has a negative sign, it indicates that the interactions are favorable. Table 5 and Figure 2 (a) illustrate the unfavorable interactions of TRIS buffer with four salts, positive values of $\Delta G'_{tr}$, and increases with increasing salt concentration. The positive $\Delta G'_{tr}$ values indicate that salt has a salting-out effect on the hydrophobic group. Interestingly, a large increase in the $\Delta G'_{tr}$ for TRIS occurred in KAc solution. It should also be noted that the interactions of TABS with salts are much less unfavorable than those on TRIS (Figure 2 (b)); the zwitterions have very

Scheme 2. Schematic Illustration of the Contribution of the TABS Side Chain



large dipole moments[53−55] and interact electrostatically with the solvent and other charged molecules in the solution.[29,56−60] Surprisingly, the negative $\Delta G'_{tr}$ values are obtained in TABS with (1 and 2) mol·dm^{-3} KBr or 1 mol·dm^{-3} KCl, favorable interactions, and this behavior is sharply reversed since these solutions exhibit a salting-out effect.

The $\Delta G'_{tr}$ values obtained from this study can be used to shed more light on the interaction between TABS and salts, by estimating the contribution of the side chain of TABS to the transfer free energy, $\Delta g'_{tr}$, assuming additivity of the free energy of solvent interactions. The side chain contributions to the transfer free energies of TABS are obtained simply from the difference between $\Delta G'_{tr}$ of the TABS and those of TRIS at the same experimental conditions, as illustrated by Scheme 2.

Since $\Delta G'_{tr}$ is, by definition, free of solute−solute interactions, it provides information regarding solute−solvent interactions. The results in Table 5 and graphically illustrated in Figure 2 (c) reveal that the apparent transfer energy ($\Delta g'_{tr}$) contributions of TABS residue from water to aqueous electrolyte solutions (from Scheme 2) are negative and also increase with increasing salt concentration. The negative contribution indicates that the interactions between the solvent and TABS residue are favorable.

The apparent molar volumes, V_ϕ of TRIS and TABS in water and in aqueous electrolyte solution were computed from the density of the solution by using the following equation

$$V_\phi = (M/\rho) - [10^3(\rho - \rho_o)/(m\rho\rho_o)] \qquad (10)$$

where M and m are, respectively, the molar mass and molality of the biological buffers and ρ and ρ_o are the densities of solution and the solvent (water + ionic salts, or water), respectively. The values of V_ϕ at each ionic salt concentration at (298.15 to 328.15) K are summarized in Tables 6 and 7. It was found that V_ϕ values of TRIS and TABS increase with increasing temperature in the presence of all cosolutes studied. We fitted the apparent molar volumes V_ϕ to empirical function (eq 11) of m and T for each system

$$V_\phi(m,T) = v_0 + v_1T + v_2T^2 + v_3mT^5 + v_4m + v_5m^2 + \frac{v_6m}{(m^5T - 273.15)} \qquad (11)$$

In eq 11, v_i are regression coefficients given in Table 8 with average absolute deviation (AARD).

To shed more light on the interactions between the biological buffers under study and salts, we studied the partial molar volumes, V^o_ϕ, of biological buffers in water at infinite dilution from the solubility data at 298.15 K, following the procedure of Auton et al.[61]

Ford et al.[62] measured apparent molar volumes of TRIS at molalities $m \leq 0.5$ mol·kg^{-1} and at temperatures from (278.15 to 393.15) K well below the minimum $m = 1.6$ mol·kg^{-1} of our experiments. Our V^o_ϕ value (9.17 cm^3·mol^{-1}) at $T = 298.15$

Table 6. Apparent Molar Volumes V_ϕ of TRIS in Water and in Aqueous Electrolyte Solutions as a Function of Concentration of TRIS and Ionic Salts from (298.15 to 328.15) K under Atmospheric Pressure

m	V_ϕ/cm^3·mol^{-1}						m	V_ϕ/cm^3·mol^{-1}					
mol·kg^{-1}	298.15 K	303.15 K	310.15 K	318.15 K	323.15 K	328.15 K	mol·kg^{-1}	298.15 K	303.15 K	310.15 K	318.15 K	323.15 K	328.15 K
TRIS in water							TRIS in 1 mol·dm^{-3} KAc						
1.6667	89.09	89.42	89.84	90.29	90.56	90.87	0.9840	92.39	92.59	92.88	93.23	93.46	93.53
2.2940	91.37	91.70	92.12	92.58	92.89	93.54	1.6204	93.42	93.66	94.00	94.39	94.67	95.23
2.9454	92.01	92.34	92.76	93.23	93.51	93.79	2.2115	93.10	93.35	93.71	94.12	94.38	94.51
3.6602	92.11	92.43	92.86	93.32	93.61	93.92	2.8430	92.59	92.86	93.23	93.65	93.92	94.12
4.2711	92.21	92.53	92.95	93.42	93.70	93.99	3.4415	91.99	92.26	92.63	93.05	93.31	93.51
4.9084	91.53	91.85	92.26	92.72	93.00	93.27	4.0688	91.48	91.75	92.12	92.54	92.80	92.99
5.5861	91.60	91.91	92.33	92.78	93.07	93.34							
TRIS in 2 mol·dm^{-3} KAc							TRIS in 4 mol·dm^{-3} KAc						
0.2196	86.76	87.03	87.32	87.61	87.83	88.06	0.0991	0.0991	80.86	81.05	82.13	82.49	82.94
0.3343	91.04	91.32	91.69	92.07	92.34	92.56	0.1527	0.1527	85.22	85.31	85.61	85.85	86.06
0.9881	93.50	93.60	93.87	94.30	94.58	94.85	0.1998	0.1998	87.29	87.47	87.79	87.97	88.18
1.4875	93.55	93.84	94.24	94.68	94.96	95.24	0.3178	0.3178	89.58	90.40	90.60	90.76	90.89
2.3262	92.93	93.22	93.59	94.03	94.30	94.61	0.8428	0.8428	92.21	92.31	92.51	93.27	93.37
3.0279	92.49	92.78	93.17	93.60	93.87	94.14	1.3976	1.3976	92.35	92.60	92.98	93.38	93.65
3.3614	92.00	92.28	92.67	93.09	93.36	93.63	2.0043	2.0043	92.23	92.49	92.85	93.26	93.51
TRIS in 1 mol·dm^{-3} KBr							TRIS in 2 mol·dm^{-3} KBr						
0.2295	77.27	77.53	77.84	77.91	78.05	78.24	0.2163	85.17	85.30	85.42	85.65	85.93	86.20
0.3368	83.97	84.22	84.55	84.64	76.97	77.56	0.2873	87.65	89.59	88.71	88.89	89.29	90.14
0.9477	90.92	91.21	91.56	91.89	91.99	92.15	0.8486	91.90	92.14	92.51	92.89	92.96	93.20
1.5816	93.21	93.50	93.88	94.32	94.60	94.75	1.4273	92.87	93.10	92.97	93.15	93.51	93.65
2.1479	93.28	93.53	93.87	94.23	94.38	94.46	2.0117	92.61	92.77	93.28	93.48	93.69	93.73
3.0329	92.99	93.21	93.51	93.84	93.19	93.13	2.8207	92.31	92.57	92.92	93.32	93.52	93.66
3.9417	92.05	92.33	92.70	93.11	93.28	93.32	3.6693	91.82	92.19	92.50	93.02	93.10	93.68
TRIS in 4 mol·dm^{-3} KBr													
0.9122	99.16	99.18	99.35	99.47	99.53	99.91							
1.1317	97.21	97.32	97.56	97.66	97.88	97.96							
1.9440	93.65	93.68	93.63	93.64	93.68	93.73							
2.1339	93.24	93.27	93.27	93.35	93.40	93.48							
2.3766	92.74	92.77	92.81	92.92	92.99	93.10							
TRIS in 1 mol·dm^{-3} KCl							TRIS in 2 mol·dm^{-3} KCl						
0.1577	90.83	91.11	91.29	91.68	91.89	91.99	0.3071	78.58	78.75	79.01	79.23	79.42	79.56
0.2443	91.67	91.74	91.96	92.33	92.56	92.76	0.9072	90.86	90.88	90.94	91.04	91.32	91.49
0.3195	93.02	93.31	93.64	93.99	94.27	96.53	1.5676	92.14	92.28	92.77	92.90	92.97	93.00
0.9708	96.77	96.97	97.12	97.38	97.43	97.52	2.2123	92.72	92.89	93.41	93.43	93.77	93.98
1.6122	96.12	96.42	96.66	96.79	96.93	97.47	3.0073	92.24	92.30	93.09	93.12	93.55	93.77
2.2131	95.16	95.24	95.32	95.41	96.09	96.38	4.1506	91.47	91.73	92.08	92.49	92.74	92.99
3.1410	94.66	94.73	94.79	95.12	95.23	95.88							
4.0829	92.67	92.89	93.68	93.78	93.81	94.47							
4.8539	91.99	92.27	92.65	93.07	93.34	93.60							
TRIS in 4 mol·dm^{-3} KCl							TRIS in 1 mol·dm^{-3} NaCl						
0.2476	117.84	117.98	118.11	118.50	118.67	118.98	0.3558	82.10	82.34	82.68	82.98	83.15	83.38
0.4681	102.62	102.71	102.85	103.05	103.24	103.42	0.9658	91.88	92.17	92.55	92.95	93.17	93.45
0.7231	97.42	97.66	97.81	97.95	98.10	98.28	1.5841	93.16	93.45	93.83	94.22	94.48	94.57
1.0509	94.61	94.68	94.84	95.08	95.28	95.49	2.2173	93.10	93.39	93.78	94.22	94.47	94.55
1.2737	92.79	92.94	93.15	93.49	93.71	94.02	2.8488	93.11	93.40	93.78	94.20	94.45	94.53
1.8582	90.22	90.35	90.54	91.29	91.46	91.53	3.4654	92.50	92.82	93.17	93.56	93.81	93.90
2.1521	89.43	89.62	89.92	90.25	90.49	90.73	4.0928	92.13	92.33	92.71	93.09	93.35	93.41
2.3906	89.25	89.27	89.71	89.80	90.28	90.36	4.7375	91.24	91.52	91.90	92.31	92.57	92.61
TRIS in 2 mol·dm^{-3} NaCl							TRIS in 4 mol·dm^{-3} NaCl						
0.3087	82.45	82.64	82.94	83.10	83.19	83.38	0.1767	91.90	92.38	92.59	92.84	93.07	93.36
0.9312	92.34	92.60	92.95	93.34	93.62	93.85	0.3335	94.60	94.78	94.88	95.05	95.18	95.24
1.5371	93.14	93.39	93.76	94.21	94.49	94.72	0.8981	93.70	93.82	93.94	94.25	94.38	94.45
2.1438	93.58	93.84	94.20	94.66	94.93	95.17	1.4364	93.60	93.75	93.85	93.96	94.02	94.15
2.7505	93.47	93.73	94.09	94.53	94.79	95.05	2.0101	93.43	93.51	93.66	93.88	94.03	94.21
3.3589	92.95	93.20	93.56	93.98	94.24	94.49	2.5722	92.99	93.12	93.30	93.54	93.71	93.90
3.9764	92.45	92.70	93.06	93.47	93.73	93.98	3.1608	92.60	92.70	92.93	93.19	93.38	93.58
4.4486	92.09	92.35	92.71	93.08	93.33	93.58	3.4340	92.37	92.53	92.78	93.07	93.27	93.48

K for aqueous TRIS, using solubility data, is just 0.20 less than the value reported by Ford et al.[62] at that temperature. The values of apparent molar volume at infinite dilution, V_ϕ^o, are reported in Table 9. The V_ϕ^o values are higher in the case of TABS as compared to TRIS which is indicative of stronger interaction in the former case with solvent.

The transfer partial molar volume of each buffer, $\Delta_{tr}V_\phi^o$, from water to aqueous electrolyte solutions is defined by

$$\Delta_{tr}V_\phi^o = V_\phi^o(\text{buffer} + \text{ionic salt} + \text{water}) - V_\phi^o(\text{buffer} + \text{water}) \quad (12)$$

The value of $\Delta_{tr}V_\phi^o$ is, by definition, free from solute−solute interactions and therefore provides information regarding solute−solvent interaction.[63] The cosphere overlap model, developed by Friedman and Krishnan,[64] can be utilized to rationalize the $\Delta_{tr}V_\phi^o$ values. According to this model, hydrophilic−ionic group interactions contribute positively, whereas hydrophilic−hydrophobic group interactions contribute negatively to the values $\Delta_{tr}V_\phi^o$.

Table 9 shows the transfer volumes $\Delta_{tr}V_\phi^o$ of TRIS and TABS from water to aqueous electrolyte solutions at T = 298.15 K. From that table, the $\Delta_{tr}V_\phi^o$ values of TABS are positive and increase with increasing salt concentrations except in 2 mol·dm^{-3} KAc, where the $\Delta_{tr}V_\phi^o$ value begins to reduce then increases again at 4 mol·dm^{-3} solution. The $\Delta_{tr}V_\phi^o$ values of TRIS are almost positive and increase with increasing salt concentrations, while they decrease in aqueous

Table 7. Apparent Molar Volumes V_ϕ of TABS in Water and in Aqueous Electrolyte Solutions as a Function of Concentration of TABS and Ionic Salts from (298.15 to 328.15) K under Atmospheric Pressure

m	V_ϕ/cm^3·mol^{-1}						m	V_ϕ/cm^3·mol^{-1}					
mol·kg^{-1}	298.15 K	303.15 K	310.15 K	318.15 K	323.15 K	328.15 K	mol·kg^{-1}	298.15 K	303.15 K	310.15 K	318.15 K	323.15 K	328.15 K
TABS in water							TABS in 1 mol·dm^{-3} KAc						
0.9378	170.75	171.30	171.98	172.67	173.12	174.56	1.1092	168.89	169.30	169.86	170.43	170.72	170.82
1.5515	172.86	173.35	174.03	174.71	175.13	176.00	1.7143	174.20	174.61	175.20	175.79	176.10	176.22
2.4874	173.34	173.85	174.50	175.17	175.55	175.92	2.0187	175.37	175.83	176.45	177.09	177.43	177.61
4.0801	172.68	173.15	173.76	174.39	174.77	175.12	2.2756	174.25	174.70	175.31	175.94	176.28	176.49
4.7956	173.16	173.61	174.19	174.81	175.18	175.54	3.0564	176.74	177.19	177.79	178.43	178.78	179.03
5.1539	172.76	173.20	173.78	174.40	174.76	175.11	3.7151	175.03	175.46	176.03	176.64	176.99	177.24
5.5488	173.26	173.70	174.28	174.90	175.27	175.62	4.7178	175.15	175.55	176.10	176.68	177.02	177.29
							5.1065	174.74	175.14	175.69	176.27	176.61	176.88
							5.4501	174.24	174.63	175.16	175.74	176.07	176.33
TABS in 2 mol·dm^{-3} KAc							TABS in 4 mol·dm^{-3} KAc						
0.7450	179.75	180.19	180.77	181.33	181.65	181.99	0.6829	168.32	168.48	168.62	168.71	168.91	169.09
1.0801	176.79	177.21	177.80	178.42	178.76	179.07	1.0999	173.87	174.11	174.41	174.68	174.88	175.06
1.2927	177.27	177.76	178.39	179.04	179.39	179.71	1.4753	174.65	174.93	175.35	175.79	176.02	176.25
1.4913	177.64	178.13	178.78	179.45	179.81	180.14	1.9887	176.89	177.20	177.64	178.13	178.40	178.66
1.9129	173.96	174.42	175.02	175.65	175.98	176.30	2.8255	178.93	179.26	179.72	180.23	180.53	180.82
2.7415	175.20	175.62	176.17	176.77	177.10	177.42	3.2752	179.26	179.58	180.04	180.56	180.87	181.16
3.3739	174.49	174.88	175.42	176.00	176.33	176.64	3.9265	178.63	178.95	179.40	179.93	180.24	180.54
3.8714	174.83	175.21	175.74	176.31	176.64	176.95							
4.4438	174.91	175.28	175.80	176.35	176.68	176.99							
TABS in 1 mol·dm^{-3} KBr							TABS in 2 mol·dm^{-3} KBr						
1.1889	171.85	172.28	172.83	173.38	173.42	173.52	0.9366	173.45	173.82	174.34	174.90	175.07	175.20
1.7909	173.41	173.86	174.38	174.94	175.07	175.28	1.6871	175.22	175.59	176.09	176.65	176.90	177.23
2.3552	172.63	173.05	173.60	174.16	173.38	173.33	2.2775	174.07	174.44	174.94	175.50	175.77	175.85
3.0462	175.22	175.63	176.18	176.75	176.24	176.31	3.3510	174.41	174.78	175.28	175.83	176.13	176.23
3.7081	173.30	173.70	174.24	174.80	174.90	175.04	4.3871	174.68	175.04	175.54	176.10	176.40	176.48
4.4738	173.99	174.39	174.91	175.47	175.54	175.62	4.7318	174.12	174.47	174.97	175.51	175.81	175.91
TABS in 4 mol·dm^{-3} KBr							TABS in 1 mol·dm^{-3} KCl						
0.9627	176.49	176.78	177.22	177.72	178.03	178.32	1.2651	171.94	172.40	172.97	173.59	173.96	174.30
1.4267	175.94	176.25	176.69	177.19	177.50	177.80	1.8927	173.47	173.91	174.49	175.10	175.46	175.80
2.0066	175.34	175.65	176.10	176.60	176.92	177.23	2.5873	173.43	173.87	174.44	175.06	175.42	175.77
3.0140	175.47	175.80	176.25	176.76	177.08	177.39	3.6148	175.18	175.59	176.13	176.72	177.08	177.44
3.6440	175.62	175.95	176.40	176.91	177.23	177.54	4.2165	173.10	173.51	174.05	174.64	175.00	175.35
3.9499	175.41	175.73	176.17	176.68	177.00	177.31	4.8710	173.66	174.07	174.60	175.19	175.55	175.90
							5.1605	173.02	173.43	173.97	174.55	174.91	175.25
TABS in 2 mol·dm^{-3} KCl							TABS in 4 mol·dm^{-3} KCl						
1.0008	167.25	167.65	168.17	168.70	169.05	169.42	0.9914	172.19	172.52	172.70	173.06	173.38	173.70
1.6902	172.74	173.13	173.65	174.23	174.60	174.95	1.5752	174.03	174.36	174.80	175.26	175.59	175.93
2.4232	171.86	172.25	172.77	173.33	173.68	174.02	2.2794	175.09	175.44	175.93	176.48	176.82	177.16
3.1228	174.41	174.80	175.33	175.91	176.26	176.61	2.9153	175.88	176.23	176.73	177.29	177.63	177.97
3.8344	172.89	173.27	173.78	174.35	174.69	175.02	3.5939	174.80	175.14	175.63	176.18	176.52	176.86
4.5115	173.09	173.47	173.97	174.53	174.87	175.21	4.0249	175.50	175.85	176.33	176.89	177.23	177.57
4.8158	172.68	173.05	173.56	174.12	174.46	174.79	4.3125	174.93	175.27	175.75	176.31	176.65	176.99
TABS in 1 mol·dm^{-3} NaCl							TRIS in 2 mol·dm^{-3} NaCl						
0.9211	172.65	173.11	173.70	174.32	174.65	174.78	1.0194	173.59	173.97	174.51	175.08	175.44	175.78
1.6553	175.57	175.97	176.53	177.10	177.43	177.14	1.7625	174.80	175.16	175.69	176.26	176.62	176.96
2.0066	175.61	176.02	176.59	177.19	177.54	177.64	2.1442	174.01	174.38	174.91	175.47	175.84	176.19
2.4096	174.38	174.81	175.39	176.01	176.36	176.46	2.7734	176.03	176.41	176.94	177.51	177.88	178.22
3.8585	173.72	174.13	174.68	175.28	175.63	175.70	3.6141	174.37	174.75	175.26	175.82	176.17	176.51
4.6879	174.59	175.00	175.53	176.13	176.48	176.60	4.4423	175.16	175.53	176.03	176.60	176.94	177.28
5.3560	174.13	174.53	175.06	175.65	176.00	176.15	4.7936	174.61	174.98	175.48	176.04	176.39	176.73
TRIS in 4 mol·dm^{-3} NaCl													
0.9452	175.77	176.09	176.54	177.10	177.43	177.75							
1.5200	176.72	177.06	177.52	178.08	178.41	178.74							
1.8185	175.56	175.90	176.37	176.92	177.25	177.58							
2.2643	176.93	177.28	177.76	178.32	178.65	179.00							
3.1003	175.64	175.98	176.46	177.00	177.33	177.66							
3.9740	175.63	175.96	176.44	176.98	177.31	177.65							
4.3066	175.59	175.93	176.39	176.93	177.27	177.60							

KCl with increasing concentration, ended by a negative value at 4 mol·dm^{-3} KCl. The $\Delta_{tr}V_\phi^o$ (H_2O aqueous KAc and NaCl) of TRIS is negative at first, then positive with an increase of molarity of salt. The positive $\Delta_{tr}V_\phi^o$ values for TRIS and TABS indicate that ion−hydrophilic interactions predominate over the ion−hydrophobic interactions. Interestingly, the transfer volumes $\Delta_{tr}V_\phi^o$ of TRIS are less than 50 % of that of TABS. It may be due to the fact that the interaction between zwitterionic end groups of TABS and ions in solvent becomes stronger.

Assuming that there is no interaction between the groups of biological buffers, the contributions of groups to the $\Delta_{tr}V_\phi^o$ are additive, as we have mentioned before. The $\Delta_{tr}V_\phi^o$ ($-CH_2CH_2CH_2CH_2SO_3^-$) approaches $\Delta_{tr}V_\phi^o$(TABS) − $\Delta_{tr}V_\phi^o$-

Table 8. Regression Parameters of Equation 9 for Apparent Molar Volumes V_ϕ and Also the Apparent Molar Volume at Infinities Dilution V_ϕ^o at 298.15 K of TRIS and TABS in Water and in Aqueous Electrolyte Solutions

system	v_0	$10^2 \cdot v_1$	$10^5 \cdot v_2$	$10^{14} \cdot v_3$	v_4	v_5	v_6	AARD/%[a]
water + TRIS	74.80	0.05699	−0.32	1.6	0.5524	−0.107	−6940	0.13
water + TRIS + 1 M KAc	88.40	−0.7710	6.32	12.4	1.2571	−0.409	−1	0.24
water + TRIS + 2 M KAc	39.12	25.2220	−30.60	−1.7	6.2647	−1.462	17	0.94
water + TRIS + 4 M KAc	156.25	−52.6147	93.81	−15.3	15.0753	−5.042	−197	1.44
water + TRIS + 1 M KBr	−808.81	590.9129	−985.29	185.5	9.5963	−2.757	−145	2.10
water + TRIS + 2 M KBr	−507.90	390.1630	−641.86	113.4	4.8421	−1.649	−401	1.22
water + TRIS + 4 M KBr	125.66	−3.6640	−10.21	102.2	−11.3883	1.494	−30	0.05
water + TRIS + 1 M KCl	306.44	−141.2780	232.38	1.7	3.1613	−0.667	2	0.91
water + TRIS + 2 M KCl	47.86	16.9087	−25.69	23.7	12.5485	−2.278	−427	0.12
water + TRIS + 4 M KCl	195.60	−43.9027	64.20	89.2	−39.1558	10.096	299	2.22
water + TRIS + 1 M NaCl	−56.91	88.0763	−139.33	21.7	7.9488	−1.435	−4	1.67
water + TRIS + 2 M NaCl	50.66	17.2222	−24.24	18.0	9.2384	−1.649	−251	1.04
water + TRIS + 4 M NaCl	187.38	−47.5780	50.83	145.0	0.8926	−1.197	−163	1.23
water + TABS	177.40	−14.9990	44.85	−22.6	0.6081	0.007	94	0.15
water + TABS + 1 M KAc	73.24	57.8460	−83.52	8.5	2.4606	−0.401	−1119	0.24
water + TABS + 2 M KAc	115.44	35.5890	−44.32	−3.5	−4.5085	0.677	−176	0.29
water + TABS + 4 M KAc	125.01	21.9910	−31.35	26.6	9.7276	−1.618	372	0.07
water + TABS + 1 M KBr	−246.26	270.0360	−437.00	43.6	1.1603	−0.339	−267	0.38
water + TABS + 2 M KBr	−94.94	169.6950	−264.00	7.1	−1.3034	0.151	104	0.19
water + TABS + 4 M KBr	146.18	14.9230	−14.72	4.1	−1.6028	0.251	−0.5	0.08
water + TABS + 1 M KCl	120.30	24.6390	−26.85	−1.6	2.6008	−0.379	−316	0.23
water + TABS + 2 M KCl	153.95	8.6404	−11.56	30.3	1.9194	−0.414	−138	0.34
water + TABS + 4 M KCl	157.62	3.8888	0.13	16.9	3.68187	−0.653	−10	0.16
water + TABS + 1 M NaCl	9.76	100.7967	−148.86	−3.5	−1.9076	0.245	272	0.18
water + TABS + 2 M NaCl	138.89	14.0916	−10.52	−2.1	2.3028	−0.347	6	0.27
water + TABS + 4 M NaCl	163.13	1.9213	9.37	−5.8	−0.5232	0.073	36	0.18

[a] AARD/% = $(100/N) \sum_{i=1}^{N} |V_{\phi,i}^{calc} - V_{\phi,i}^{expt}|/V_i^{expt}$, where N is the number of data points.

Table 9. Apparent Molar Volume at Infinite Dilution V_ϕ^o and Partial Molar Volumes $\Delta_{tr}V_\phi^o$ for TRIS and TABS in Aqueous Electrolyte Solutions at T = 298.15 K and at Atmospheric Pressure

	V_ϕ^o/cm^3·mol^{-1}				$\Delta_{tr}V_\phi^o$/cm^3·mol^{-1}		
solvent	0 mol·dm^{-3}	1 mol·dm^{-3}	2 mol·dm^{-3}	4 mol·dm^{-3}	1 mol·dm^{-3}	2 mol·dm^{-3}	4 mol·dm^{-3}
				TRIS			
water	91.17						
KAc		91.14	91.89	92.17	−0.03	0.72	1.00
KBr		91.34	91.63	92.57	0.17	0.46	1.40
KCl		91.85	91.31	88.15	0.68	0.14	−3.02
NaCl		90.95	91.94	92.23	−0.22	0.77	1.06
				TABS			
water	169.24						
KAc		172.95	171.10	177.5	3.71	1.86	8.26
KBr		171.76	173.19	174.78	2.52	3.95	5.54
KCl		171.07	171.12	173.65	1.83	1.88	4.41
NaCl		171.14	172.46	173.94	1.90	3.22	4.70

Table 10. Contribution of TABS Residue ($-CH_2CH_2CH_2CH_2SO_3^-$) to the Partial Molar Volumes of Transfer, $\Delta_{tr}V_\phi^o$, in Aqueous Electrolyte at T = 298.15 K and at Atmospheric Pressure

	$\Delta_{tr}V_\phi^o$/cm^3·mol^{-1}		
system	1 mol·dm^{-3}	2 mol·dm^{-3}	4 mol·dm^{-3}
KAc	3.74	1.14	7.26
KBr	2.35	3.49	4.14
KCl	1.15	1.74	7.43
NaCl	2.12	2.45	3.64

(TRIS) (Scheme 2). Table 10 shows the contribution of TABS residue is positive, which indicates that the ion−hydrophilic interaction between the ions salt and sulfonic group is predominate over the ion−hydrophobic interactions between the ion salt and methyl groups of TABS residue.

Conclusions

This work provides reliable density data for various binary and ternary aqueous systems that contain TRIS or TABS and electrolytes such as KAc, KBr, KCl, and NaCl from (298.15 to 328.15) K under atmospheric pressure. The experimental data were correlated satisfactorily with an empirical equation in terms of the concentrations of buffer and salts, with an augmented term to account for the interactions between buffer and electrolytes. The solubility limits of TRIS and TABS in the aqueous or the electrolyte solutions were determined at 298.15 K from the results of the density measurement. The solubilities of TABS in aqueous solution decrease with increasing concentration of salt (salting-out effect). The observed order of the salting-out effect is KAc > KBr > KCl > NaCl for TRIS and KAc > KBr > KCl ≈ NaCl for TABS, respectively. We have determined the apparent transfer free energies ($\Delta G'_{tr}$) of the biological buffers from water to aqueous electrolyte solutions based on the solubility data. The values of $\Delta G'_{tr}$ were used also to calculate the contributions of TABS residue ($-CH_2CH_2CH_2CH_2SO_3^-$) from water to aqueous electrolyte solutions. We have calculated the apparent molar volumes, $V_\phi(m, T)$, from the solubility data. The $\Delta_{tr}V_\phi^o$ values are almost positive indicating the dominance of ion−hydrophilic interactions. Also, TABS residue contributions calculated from V_ϕ^o suggest that ion−hydrophilic interaction between the ion salts and sulfonic group overwhelms the hydrophobic interactions between the ion salt and methyl groups of TABS residue.

Overall, these results provide evidence for the existence of interactions between the buffers and ionic salts, in aqueous solutions. It was found that the salt effects on TABS are greater than those on TRIS.

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