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Volumetric properties of MES, MOPS, MOPSO, and MOBS in water and in aqueous electrolyte solutions

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ABSTRACT

4-Morpholineethanesulfonic acid (MES), 4-morpholinepropanesulfonic acid (MOPS), 3-morpholino-2-hydroxypropanesulfonic acid (MOPSO), and 4-(*N*-morpholino)butanesulfonic acid (MOBS), are useful for pH control as standard buffers in the physiological region of 5.5–6.7 for MES, 6.5–7.9 for MOPS, 6.2–7.6 for MOPSO, and 6.9–8.3 for MOBS, respectively. On the basis of density measurements at 298.15 K, the apparent molar volumes, V_ϕ, of the above-mentioned buffers in water and in (0.05, 0.16, and 0.25) mol kg^{-1} aqueous solutions of NaCl, KCl, KBr, and CH_3COOK have been calculated. The partial molar volumes at infinite dilution, V_ϕ^o, obtained from V_ϕ, have been used to calculate the volume of transfer, $\Delta_{tr}V_\phi^o$, from water to aqueous electrolyte solutions. It was found that both V_ϕ^o and $\Delta_{tr}V_\phi^o$ vary linearly with increasing the number of carbon atoms in the alkyl group side chain of the zwitterionic buffers. These linear correlations have been utilized to estimate the contributions of the zwitterionic end group (morpholinium ion, $-SO_3^-$) and $-CH_2-$ group to V_ϕ^o and $\Delta_{tr}V_\phi^o$. The values of V_ϕ^o and $\Delta_{tr}V_\phi^o$ for some functional group contributions of the zwittierionic buffers with salts have also been reported.

1. Introduction

The pH is extremely important in biochemical reactions, to the proper metabolism and functioning of animals and plants. We can control the pH of the system at a predetermined level by the addition of buffer substances. Around 40 years ago, Good et al. [1–3] proposed 20 well-known buffers. These buffers have now become the predominant buffer system used in the study of pH-dependent phenomena for biochemical studies. Most of these buffer substances were zwitterionic species, containing both positive and negative ionizable groups. Zwitterionic buffers comparable with amino acids, show significant advantages over conventional buffers: insignificant penetration through a biological membrane, maximum buffer capacity at the physiological pH range 6.0–8.50, and no enzyme substrate or enzyme inhibitor properties [4]. Many exploratory experiments have failed, many reaction rates have been depressed, and many processes have been distorted because of the imperfections of the buffers employed. For instance, there are difficulties [5] when using many of these buffers with the Lowry method [6] in protein assays. It was observed that all of Good's buffers containing ethanolamine moieties cause interferences with this method [7]. Among the Good's zwitterionic buffers, only 4-Morpholineethanesulfonic acid (MES), 4-morpholinepropanesulfonic acid (MOPS), and 1,4-piperazinediethanesulfonic acid (PIPES) exhibit no interference when used with the bicinchoninic acid (BCA) method [8,9].

Good et al. [1] emphasized that the buffer should produce a minimum of salt effects. If the system to be studied requires salts, suitable ions can be added. If the system is adversely affected by salts, ionic buffers create problems. Recent works conducted in this laboratory have been directed towards studying the interactions of a series of ionic salts with biological buffer substances, such as *N*-[tris(hydroxymethyl)methyl]-3-aminopropanesulfonic acid (TAPS) and *N*-[tris(hydroxymethyl)methyl]-3-amino-2-hydroxy propanesulfonic acid (TAPSO) [10] and tris(hydroxymethyl)aminomethane (TRIS) and tris[hydroxymethyl]-4-amino-butanesulfonic acid (TABS) [11]. In the present study, we investigated the interactions of MES, MOPS, 3-morpholino-2-hydroxypropanesulfonic acid (MOPSO) and MOBS with ionic salts of NaCl, KCl, KBr, and CH_3COOK. These zwitterionic pH buffers have been used in various types of chemistry studies (e.g., [12–25]). These compounds are structurally related and contain at least a morpholine group and differ in the length of the alkly group side chain: the *N*-(morpholino)-alkane-sulfonic acids, containing ethyl (MES), propyl (MOPS), or butyl (MOBS). While, 3-(*N*-morpholino)-2-hydroxypropanesulfonic acid (MOPSO) is similar to MOPS in molecular structures except that MOPSO has a –OH group replacing a hydrogen on the β carbon nearby the sulfonic group. It is the purpose of the present study to investigate the ionic interactions from volumetric investigations of MES,

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MOPS, MOPSO, and MOBS in aqueous solutions of NaCl, KCl, KBr, and CH_3COOK. The densities of these zwitterionic buffers in water and in aqueous solutions of (0.05, 0.16, and 0.25) mol kg^{-1} of the above-mentioned salts have been measured at 298.15 K. Based on these data, the apparent molar volumes, V_ϕ, the partial molar volume at infinite dilution, V_ϕ^o, and transfer volumes at infinite dilution, $\Delta_{tr}V_\phi^o$ have been calculated. In addition, the apparent molar volumes and transfer volumes at infinite dilution for the zwitterionic group (morpholinium ion, $-SO_3^-$), ($-CH_2-$), ($-CH_2CH_2-$), and (–OH) groups of the zwitterionic buffers with salts have also been estimated.

2. Experimental

The zwitterionic buffers MES (mass fraction purity > 0.99), MOPS (mass fraction purity > 0.995), MOPSO (mass fraction purity > 0.99), and MOBS (mass fraction purity >0.99) were obtained from Sigma Chemical Co. (USA). 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 solutions was obtained from NANO pure-Ultra pure water system that was distilled and deionized with resistance of 18.3 MΩ.

Densities (ρ) were determined at atmospheric pressure by using Anton Paar DMA 4500 digital vibrating U-tube densimeter. By measuring the damping of the U-tube's oscillation caused by the viscosity of the filled-in sample, the DMA 4500 automatically corrects viscosity related errors. The densimeter is equipped with an internal temperature control unit, which can regulate the temperature of the measuring tube to within ±0.03 K over a temperature range of (273.15–363.15) K. Accuracy of our densities is about $\pm 5 \times 10^{-5}$ g cm^{-3}. The densimeter was calibrated with dry air and degassed distilled water periodically at 293.15 K, and then we measured the density of water at several temperatures (288.15–353.15) K and compared to values provided by Bettin et al. [26]. The calibration check is considered acceptable if it comes within 5×10^{-5} g cm^{-3} of literature values. Where necessary, a recalibration procedure is performed at (313.15 and 333.15) K. All the solutions were prepared by molality and by weight using an electronic balance (R&D Model GR-200) with a precision of ±0.1 mg.

3. Results and discussion

The apparent molar volumes, V_ϕ, of the zwitterionic buffers in water and in aqueous electrolyte solutions were calculated from the measured densities using the following equation [27]:

$$V_\phi = \left(\frac{M}{\rho}\right) - \left[\frac{10^3(\rho - \rho_o)}{(m\rho\rho_o)}\right], \quad (1)$$

where M and m are, respectively, the molar mass and molality of the zwitterionic buffers, and ρ and ρ_o are the densities of solution and the solvent, respectively. In the calculation for the molar mass of MES, MOPS, MOPSO, and MOBS (195.20, 209.26, 225.27, and 223.30) g mol^{-1} were used, respectively. The solution densities and the calculated apparent molar volumes for the zwitterionic buffers are reported in Tables 1–4. In general, the uncertainty of V_ϕ is estimated to be better than 0.1 cm^3 mol^{-1}. The apparent molar volume data for buffers in water and aqueous electrolyte solutions (Figs. 1–4) increase with concentration.

The concentration dependences of the calculated apparent molar volumes were found to be well represented by a linear equation

$$V_\phi = V_\phi^o + S_v m, \quad (2)$$

where V_ϕ^o is the apparent molar volume of the zwitterionic buffers at infinite dilution which has the same meaning as the standard partial molar volume, and S_v is a calculated slope. The values of V_ϕ^o and S_v were obtained by fitting Eq. (2) to the relevant sets of apparent molar volume data using a weighted least squares analysis procedure. The evaluated values of V_ϕ^o and S_v, together with their standard errors, correlation coefficients (r) and standard deviations of fit (SD) for Eq. (2), are presented in Tables 5–8.

The apparent molar volumes at infinite dilution (V_ϕ^o) for the studied zwitterionic buffers increase with an increase of salt concentrations. From the V_ϕ^o data, the standard partial molar volumes of transfer at infinite dilution, $\Delta_{tr}V_\phi^o$, from water to aqueous electrolyte solution have been calculated using Eq. (3) and are included in Table 9.

$$\Delta_{tr}V_\phi^o = V_\phi^o(\text{buffer} + \text{ionic salt} + \text{water}) - V_\phi^o(\text{buffer} + \text{water}), \quad (3)$$

In the ternary system (buffer + salt + water), the interactions can be classified as: (i) ion-hydrophobic group interactions between ions of electrolytes (K^+, Na^+, CH_3COO^-, Br^-, Cl^-) and non-polar groups of the buffers; (ii) ion-hydrophilic group interactions among the hydrophilic groups (–O–, $)N^+H$, $-SO_3^-$ and –OH) of the buffers and the ions of the salts. In the light of cosphere overlap model [28], when two solute particles come close enough together so that their cospheres overlap, some cosphere material is displaced and this is accompanied by the change in thermodynamic parameters. The overlap of the hydration cospheres of two ionic species results in an increase in volume (positive $\Delta_{tr}V_\phi^o$ values), but that of the hydration cospheres of hydrophobic–hydrophobic groups and ion–hydrophobic groups results in a net volume decrease (negative $\Delta_{tr}V_\phi^o$ values). Therefore, the calculated $\Delta_{tr}V_\phi^o$ consist of these two opposite contributions. Since $\Delta_{tr}V_\phi^o$ values are positive for all the zwitterionic buffers studied, we suggest that the contribution of ion–hydrophilic group interactions is greater than that of ion–hydrophobic interactions. It can also be seen from Table 9 that $\Delta_{tr}V_\phi^o$ values increase with increasing salt concentration. A comparison of $\Delta_{tr}V_\phi^o$ for the zwitterionic buffers in the presence of ionic salts shows that the values decrease in the order CH_3COOK > KBr > KCl > NaCl. The investigated zwitterionic buffers follow the order of their decreasing $\Delta_{tr}V_\phi^o$ as MOPSO > MES > MOPS > MOBS. These observations are consistent with hydrophobicity of buffer substances: the more hydrophilic buffer is, the higher transfer volume it has. MOPSO has an extra hydrophilic group (–OH) in comparison with the molecular structure of MOPS, therefore, it has higher polarity and hence greater $\Delta_{tr}V_\phi^o$ values. Furthermore, the $\Delta_{tr}V_\phi^o$ of MOPSO are greater than those of MES which may be attributed that the enhancement of hydrophilic effect by attachment of a (–OH) group to MOPS structure is stronger than that of hydrophobic effect by attachment of a ($-CH_2-$) group to MES structure.

Using the principles of group additivity, the contributions of groups to V_ϕ^o or $\Delta_{tr}V_\Phi^0$ can be calculated by the difference of two V_ϕ^o or $\Delta_{tr}V_\phi^o$ values of buffers which have the same groups except one. For example, $\Delta_{tr}V_\phi^o$ ($-CH_2-$) is calculated by subtraction of $\Delta_{tr}V_\Phi^0$ (MES) from those of MOPS or by subtraction of $\Delta_{tr}V_\phi^o$ (MOPS) from those of MOBS, as illustrated in Schemes 1 and 2. Furthermore, $\Delta_{tr}V_\phi^o$ ($-CH_2CH_2-$) is obtained from the difference of $\Delta_{tr}V_\phi^o$ values between MOBS and MES, as shown in Scheme 3, while $\Delta_{tr}V_\phi^o$ of (–OH) group contribution is estimated by subtraction of $\Delta_{tr}V_\phi^o$ (MOPS) from those of MOPSO, as illustrated in Scheme 4.

Table 1
Densities (ρ) and apparent molar volumes (V_ϕ) of MES in water and in aqueous electrolyte solutions at 298.15 K.

m (mol kg^{-1})	ρ (g cm^{-3})	V_ϕ (cm^3 mol^{-1})	m (mol kg^{-1})	ρ (g cm^{-3})	V_ϕ (cm^3 mol^{-1})	m (mol kg^{-1})	ρ (g cm^{-3})	V_ϕ (cm^3 mol^{-1})	m (mol kg^{-1})	ρ (g cm^{-3})	V_ϕ (cm^3 mol^{-1})
MES in water			MES in 0.05 mol kg^{-1} NaCl			MES in 0.16 mol kg^{-1} NaCl			MES in 0.25 mol kg^{-1} NaCl		
0.0114	0.99779	129.50	0.0000	0.99912	–	0.0000	1.0036	–	0.0000	1.00722	–
0.0180	0.99822	129.68	0.0072	0.99959	129.92	0.0130	1.00444	130.24	0.0067	1.00765	130.48
0.0237	0.99859	129.79	0.0155	1.00013	129.96	0.0210	1.00495	130.50	0.0152	1.00819	130.77
0.0301	0.99901	129.69	0.0240	1.00068	130.05	0.0307	1.00556	130.86	0.0225	1.00865	130.97
0.0403	0.99967	129.79	0.0337	1.00130	130.29	0.0404	1.00617	131.01	0.0304	1.00915	130.97
0.0513	1.00038	129.85	0.0426	1.00187	130.35	0.0512	1.00684	131.25	0.0412	1.00982	131.26
0.0614	1.00103	129.89	0.0525	1.00250	130.44	0.0620	1.00750	131.54	0.0523	1.01051	131.36
0.0722	1.00172	129.96	0.0619	1.00310	130.44	0.0721	1.00813	131.53	0.0613	1.01105	131.71
0.0822	1.00235	130.10	0.0716	1.00371	130.55	0.0830	1.00879	131.74	0.0706	1.01160	132.07
0.0947	1.00314	130.19	0.0817	1.00435	130.56	0.0934	1.00942	131.87	0.0779	1.01203	132.31
			0.0922	1.00500	130.72				0.0855	1.01248	132.47
			MES in 0.05 mol kg^{-1} KCl			MES in 0.16 mol kg^{-1} KCl			MES in 0.25 mol kg^{-1} KCl		
			0.0000	0.99945	–	0.0000	1.00453	–	0.0000	1.00866	–
			0.0166	1.00053	129.99	0.0160	1.00556	130.20	0.0196	1.00991	130.61
			0.0244	1.00103	130.28	0.0233	1.00602	130.75	0.0252	1.01026	130.84
			0.0337	1.00163	130.26	0.0314	1.00654	130.62	0.0314	1.01066	130.66
			0.0422	1.00217	130.43	0.0404	1.00711	130.70	0.0403	1.01121	131.00
			0.0503	1.00269	130.40	0.0513	1.00780	130.73	0.0520	1.01194	131.10
			0.0576	1.00315	130.52	0.0585	1.00824	130.99	0.0592	1.01238	131.28
			0.0655	1.00365	130.57	0.0653	1.00866	131.10	0.0695	1.01302	131.30
			0.0713	1.00401	130.69	0.0726	1.00910	131.34	0.0756	1.01339	131.41
			0.0777	1.00441	130.75	0.0783	1.00945	131.41	0.0828	1.01383	131.48
			0.0849	1.00486	130.81	0.0844	1.00982	131.51	0.0908	1.01432	131.52
			0.0932	1.00537	130.94	0.0908	1.01021	131.58			
			MES in 0.05 mol kg^{-1} KBr			MES in 0.16 mol kg^{-1} KBr			MES in 0.25 mol kg^{-1} KBr		
			0.0000	1.00125	–	0.0000	1.01047	–	0.0000	1.01789	–
			0.0097	1.00188	130.38	0.0176	1.01159	130.86	0.0173	1.01898	130.89
			0.0314	1.00327	130.56	0.0308	1.01242	130.92	0.0377	1.02024	131.30
			0.0207	1.00258	130.81	0.0241	1.01200	130.80	0.0305	1.01980	131.12
			0.0375	1.00364	131.07	0.0392	1.01294	131.15	0.0443	1.02064	131.50
			0.0454	1.00414	131.08	0.0488	1.01353	131.37	0.0500	1.02098	131.72
			0.0539	1.00465	131.59	0.0570	1.01403	131.55	0.0566	1.02138	131.80
			0.0608	1.00507	131.78	0.0649	1.01450	131.84	0.0639	1.02182	131.90
			0.0681	1.00552	131.85	0.0728	1.01497	132.05	0.0712	1.02225	132.10
			0.0758	1.00596	132.35	0.0794	1.01536	132.22	0.0786	1.02269	132.20
			0.0821	1.00633	132.56	0.0867	1.01580	132.27	0.0852	1.02306	132.53
			0.0890	1.00674	132.70						
			MES in 0.05 mol kg^{-1} KAc			MES in 0.16 mol kg^{-1} KAc			MES in 0.25 mol kg^{-1} KAc		
			0.0000	0.99946	–	0.0000	1.0046	–	0.0000	1.00874	–
			0.0176	1.00058	131.45	0.0102	1.00524	132.05	0.0094	1.00932	132.79
			0.0252	1.00106	131.53	0.0174	1.00569	132.09	0.0211	1.01003	133.26
			0.0341	1.00161	131.90	0.0252	1.00618	131.97	0.0276	1.01043	133.11
			0.0417	1.00208	132.06	0.0343	1.00674	132.20	0.0369	1.01099	133.29
			0.0516	1.00268	132.41	0.0422	1.00722	132.44	0.0427	1.01133	133.56
			0.0579	1.00306	132.58	0.0491	1.00764	132.56	0.0491	1.01171	133.67
			0.0639	1.00342	132.74	0.0567	1.00809	132.86	0.0563	1.01213	133.85
			0.0707	1.00382	132.99	0.0658	1.00863	133.09	0.0643	1.01258	134.31
			0.0783	1.00427	133.17	0.0746	1.00915	133.27	0.0740	1.01313	134.62
			0.0859	1.00471	133.42	0.0956	1.01038	133.63	0.0817	1.01356	134.89
									0.0893	1.01398	135.14

Table 2
Densities (ρ) and apparent molar volumes (V_ϕ) of MOPS in water and in aqueous electrolyte solutions at 298.15 K.

m (mol kg^{-1})	ρ (g cm^{-3})	V_ϕ (cm^3 mol^{-1})	m (mol kg^{-1})	ρ (g cm^{-3})	V_ϕ (cm^3 mol^{-1})	m (mol kg^{-1})	ρ (g cm^{-3})	V_ϕ (cm^3 mol^{-1})	m (mol kg^{-1})	ρ (g cm^{-3})	V_ϕ (cm^3 mol^{-1})
MOPS in water			MOPS in 0.05 mol kg^{-1} NaCl			MOPS in 0.16 mol kg^{-1} NaCl			MOPS in 0.25 mol kg^{-1} NaCl		
0.0077	0.99753	145.79	0.0000	0.99912	–	0.0000	1.0036	–	0.0000	1.00722	–
0.0172	0.99813	145.97	0.0178	1.00024	146.25	0.0098	1.00421	146.62	0.0201	1.00846	146.77
0.0292	0.99888	146.22	0.0233	1.00058	146.46	0.0194	1.00480	146.92	0.0314	1.00914	147.21
0.0386	0.99946	146.46	0.0294	1.00096	146.48	0.0253	1.00516	147.06	0.0387	1.00958	147.30
0.0496	1.00014	146.55	0.0379	1.00148	146.72	0.0318	1.00556	147.03	0.0477	1.01011	147.61
0.0556	1.00050	146.77	0.0482	1.00211	146.86	0.0394	1.00602	147.17	0.0553	1.01056	147.74
0.0611	1.00084	146.76	0.0550	1.00252	147.02	0.0482	1.00654	147.52	0.0636	1.01104	147.99
0.0668	1.00119	146.78	0.0606	1.00285	147.24	0.0570	1.00706	147.73	0.0701	1.01142	148.08
0.0736	1.00159	147.02	0.0659	1.00319	146.98	0.0668	1.00763	148.02	0.0762	1.01177	148.23
0.0812	1.00205	147.08	0.0721	1.00355	147.24	0.0731	1.00799	148.24	0.0812	1.01206	148.29
0.0869	1.00239	147.16	0.0787	1.00394	147.38	0.0797	1.00836	148.49	0.0851	1.01228	148.40
						0.0857	1.00870	148.67			
			MOPS in 0.05 mol kg^{-1} KCl			MOPS in 0.16 mol kg^{-1} KCl			MOPS in 0.25 mol kg^{-1} KCl		
			0.0000	0.99945	–	0.0000	1.00453	–	0.0000	1.00866	–
			0.0051	0.99977	146.21	0.0100	1.00515	146.74	0.0093	1.00924	146.26
			0.0108	1.00013	146.33	0.0149	1.00546	146.39	0.0139	1.00951	147.14
			0.0130	1.00027	146.26	0.0192	1.00572	146.69	0.0188	1.00981	147.26
			0.0198	1.00069	146.39	0.0233	1.00596	147.25	0.0252	1.01019	147.59
			0.0248	1.00100	146.49	0.0334	1.00658	147.21	0.0323	1.01061	147.80
			0.0322	1.00145	146.95	0.0399	1.00697	147.41	0.0361	1.01084	147.83
			0.0379	1.00180	146.94	0.0469	1.00739	147.49	0.0477	1.01152	148.16
			0.0476	1.00238	147.32	0.0549	1.00786	147.74	0.0563	1.01200	148.66
			0.0567	1.00294	147.27	0.0662	1.00851	148.14	0.0658	1.01255	148.77
			0.0657	1.00347	147.51	0.0758	1.00907	148.28	0.0736	1.01299	149.01
			0.0763	1.00410	147.64						
			MOPS in 0.05 mol kg^{-1} KBr			MOPS in 0.16 mol kg^{-1} KBr			MOPS in 0.25 mol kg^{-1} KBr		
			0.0000	1.00125	–	0.0000	1.01047	–	0.0000	1.01789	–
			0.0104	1.00190	146.44	0.0098	1.01107	146.87	0.0114	1.01858	147.03
			0.0151	1.00219	146.96	0.0150	1.01139	146.91	0.0156	1.01883	147.16
			0.0199	1.00248	147.31	0.0207	1.01172	147.69	0.0203	1.01910	147.78
			0.0262	1.00286	147.58	0.0257	1.01201	148.21	0.0165	1.01887	148.27
			0.0329	1.00325	148.03	0.0315	1.01236	148.06	0.0316	1.01975	148.42
			0.0396	1.00365	148.15	0.0389	1.01278	148.53	0.0356	1.01998	148.59
			0.0481	1.00414	148.59	0.0482	1.01331	148.92	0.0461	1.02056	149.30
			0.0589	1.00474	149.36	0.0567	1.01377	149.62	0.0551	1.02103	150.14
			0.0692	1.00531	149.85	0.0649	1.01423	149.79	0.0621	1.02139	150.69
			0.0770	1.00572	150.41	0.0759	1.01480	150.59	0.0684	1.02173	150.84
			0.0861	1.00622	150.68	0.0820	1.01513	150.76	0.0823	1.02245	151.40
			MOPS in 0.05 mol kg^{-1} KAc			MOPS in 0.16 mol kg^{-1} KAc			MOPS in 0.25 mol kg^{-1} KAc		
			0.0000	0.99946	–	0.0000	1.0046	–	0.0000	1.00874	–
			0.0191	1.00065	146.83	0.0129	1.00539	147.51	0.0174	1.00978	148.55
			0.0260	1.00107	147.15	0.0195	1.00579	147.66	0.0228	1.01010	148.63
			0.0344	1.00158	147.37	0.0253	1.00614	147.76	0.0284	1.01043	148.72
			0.0449	1.00222	147.43	0.0317	1.00652	148.00	0.0341	1.01076	148.93
			0.0555	1.00285	147.72	0.0397	1.00700	148.05	0.0414	1.01119	148.93
			0.0684	1.00362	147.87	0.0502	1.00762	148.25	0.0497	1.01167	149.08
			0.0764	1.00409	148.02	0.0592	1.00815	148.36	0.0580	1.01215	149.16
			0.0844	1.00455	148.24	0.0685	1.00869	148.53	0.0677	1.01269	149.52
						0.0754	1.00909	148.63	0.0742	1.01305	149.72
						0.0828	1.00952	148.70	0.0807	1.01341	149.88
						0.0904	1.00994	148.98	0.0868	1.01376	149.86

Table 3
Densities (ρ) and apparent molar volumes (V_ϕ) of MOPSO in water and in aqueous electrolyte solutions at 298.15 K.

m (mol kg^{-1})	ρ (g cm^{-3})	V_ϕ (cm^3·mol^{-1})	m (mol kg^{-1})	ρ (g cm^{-3})	V_ϕ (cm^3·mol^{-1})	m (mol kg^{-1})	ρ (g cm^{-3})	V_ϕ (cm^3·mol^{-1})	m (mol kg^{-1})	ρ (g cm^{-3})	V_ϕ (cm^3·mol^{-1})
MOPSO in water			MOPSO in 0.05 mol kg^{-1} NaCl			MOPSO in 0.16 mol kg^{-1} NaCl			MOPSO in 0.25 mol kg^{-1} NaCl		
0.0126	0.99804	146.20	0.0000	0.99912	–	0.0000	1.0036	–	0.0000	1.00722	–
0.0178	0.99845	146.01	0.0144	1.00025	146.48	0.0109	1.00445	146.68	0.0119	1.00814	147.41
0.0228	0.99884	146.33	0.0171	1.00046	146.91	0.0174	1.00495	147.16	0.0181	1.00861	147.93
0.0270	0.99917	146.23	0.0222	1.00085	147.20	0.0227	1.00535	147.65	0.0249	1.00912	148.18
0.0360	0.99987	146.38	0.0290	1.00137	147.36	0.0289	1.00582	147.95	0.0288	1.00940	148.75
0.0450	1.00057	146.50	0.0372	1.00199	147.79	0.0349	1.00627	148.19	0.0363	1.00995	149.10
0.0519	1.00110	146.69	0.0461	1.00266	147.98	0.0430	1.00688	148.22	0.0432	1.01044	149.75
0.0630	1.00195	146.83	0.0531	1.00318	148.20	0.0530	1.00762	148.60	0.0524	1.01110	150.13
0.0706	1.00253	146.89	0.0616	1.00381	148.45	0.0619	1.00828	148.75	0.0610	1.01170	150.58
0.0771	1.00303	146.94	0.0707	1.00448	148.70	0.0700	1.00886	149.08	0.0701	1.01233	151.01
			0.0787	1.00507	148.80	0.0798	1.00956	149.42	0.0819	1.01312	151.78
			MOPSO in 0.05 mol kg^{-1} KCl			MOPSO in 0.16 mol kg^{-1} KCl			MOPSO in 0.25 mol kg^{-1} KCl		
			0.0000	0.99945	–	0.0000	1.00453	–	0.0000	1.00866	–
			0.0101	1.00024	146.90	0.0119	1.00545	147.19	0.0097	1.00941	147.61
			0.0135	1.00050	147.17	0.0170	1.00584	147.66	0.0134	1.00969	147.82
			0.0182	1.00086	147.44	0.0206	1.00612	147.46	0.0197	1.01017	147.95
			0.0255	1.00143	147.35	0.0241	1.00638	147.82	0.0230	1.01041	148.13
			0.0296	1.00174	147.57	0.0306	1.00686	148.37	0.0299	1.01093	148.45
			0.0341	1.00208	147.78	0.0360	1.00727	148.35	0.0349	1.01129	148.81
			0.0434	1.00277	148.31	0.0456	1.00798	148.83	0.0426	1.01184	149.55
			0.0506	1.00330	148.64	0.0552	1.00867	149.34	0.0517	1.01248	150.10
			0.0606	1.00403	149.01	0.0657	1.00942	149.78	0.0609	1.01313	150.54
			0.0696	1.00468	149.44	0.0717	1.00984	150.03	0.0705	1.01379	151.03
			0.0808	1.00548	149.83	0.0785	1.01031	150.38	0.0784	1.01432	151.52
			MOPSO in 0.05 mol kg^{-1} KBr			MOPSO in 0.16 mol kg^{-1} KBr			MOPSO in 0.25 mol kg^{-1} KBr		
			0.0000	1.00125	–	0.0000	1.01047	–	0.0000	1.01789	–
			0.0123	1.00220	147.70	0.0139	1.01154	147.29	0.0111	1.01873	148.05
			0.0180	1.00264	147.83	0.0200	1.01199	148.31	0.0176	1.01922	148.30
			0.0228	1.00301	147.88	0.0232	1.01222	148.76	0.0237	1.01967	148.60
			0.0304	1.00358	148.28	0.0286	1.01262	148.95	0.0277	1.01996	148.92
			0.0366	1.00404	148.54	0.0342	1.01304	149.05	0.0368	1.02061	149.57
			0.0451	1.00466	149.10	0.0440	1.01374	149.68	0.0407	1.02089	149.73
			0.0532	1.00521	150.11	0.0547	1.01450	150.23	0.0513	1.02162	150.57
			0.0619	1.00582	150.64	0.0630	1.01504	151.26	0.0594	1.02216	151.24
			0.0726	1.00659	150.78	0.0698	1.01550	151.56	0.0687	1.02277	152.00
			0.0777	1.00695	150.91	0.0777	1.01604	151.89	0.0774	1.02333	152.62
			MOPSO in 0.05 mol kg^{-1} KAc			MOPSO in 0.16 mol kg^{-1} KAc			MOPSO in 0.25 mol kg^{-1} KAc		
			0.0000	0.99946	–	0.0000	1.0046	–	0.0000	1.00874	–
			0.0182	1.00086	148.18	0.0163	1.00584	148.68	0.0174	1.01004	149.70
			0.0261	1.00145	148.77	0.0224	1.00629	149.23	0.0229	1.01044	150.11
			0.0313	1.00184	148.92	0.0283	1.00672	149.70	0.0291	1.01089	150.39
			0.0377	1.00233	148.75	0.0351	1.00723	149.60	0.0343	1.01127	150.45
			0.0447	1.00283	149.41	0.0432	1.00781	150.13	0.0402	1.01169	150.76
			0.0504	1.00325	149.54	0.0491	1.00822	150.64	0.0462	1.01212	150.91
			0.0561	1.00364	150.17	0.0553	1.00866	150.88	0.0531	1.01260	151.30
			0.0624	1.00410	150.25	0.0618	1.00911	151.25	0.0618	1.01319	151.88
			0.0689	1.00456	150.52	0.0678	1.00953	151.45	0.0689	1.01367	152.26
			0.0754	1.00500	151.00	0.0743	1.00999	151.54	0.0746	1.01406	152.43
			0.0822	1.00549	151.04	0.0804	1.01041	151.76	0.0812	1.01449	152.86

Table 4
Densities (ρ) and apparent molar volumes (V_ϕ) of MOBS in water and in aqueous electrolyte solutions at 298.15 K.

m (mol kg^{-1})	ρ (g cm^{-3})	V_ϕ (cm^3 mol^{-1})	m (mol kg^{-1})	ρ (g cm^{-3})	V_ϕ (cm^3 mol^{-1})	m (mol kg^{-1})	ρ (g cm^{-3})	V_ϕ (cm^3 mol^{-1})	m (mol kg^{-1})	ρ (g cm^{-3})	V_ϕ (cm^3 mol^{-1})
MOBS in water			MOBS in 0.05 mol kg^{-1} NaCl			MOBS in 0.16 mol kg^{-1} NaCl			MOBS in 0.25 mol kg^{-1} NaCl		
0.0134	0.99789	160.25	0.0000	0.99912	–	0.0000	1.0036	–	0.0000	1.00722	–
0.0201	0.99830	160.70	0.0134	0.99996	160.52	0.0063	1.00399	160.72	0.0211	1.00851	161.23
0.0282	0.99880	160.90	0.0198	1.00036	160.56	0.0154	1.00455	160.96	0.0274	1.00889	161.35
0.0365	0.99931	161.03	0.0273	1.00082	160.84	0.0272	1.00528	160.91	0.0345	1.00932	161.36
0.0456	0.99987	161.08	0.0359	1.00135	160.91	0.0321	1.00558	160.94	0.0437	1.00986	161.73
0.0540	1.00038	161.20	0.0460	1.00197	160.97	0.0388	1.00599	160.96	0.0490	1.01017	161.88
0.0636	1.00096	161.33	0.0538	1.00244	161.14	0.0452	1.00637	161.21	0.0545	1.01049	162.03
0.0702	1.00135	161.50	0.0638	1.00305	161.16	0.0509	1.00672	161.14	0.0604	1.01084	162.04
0.0768	1.00174	161.64	0.0689	1.00336	161.17	0.0569	1.00707	161.39	0.0657	1.01115	162.10
0.0827	1.00209	161.72	0.0749	1.00372	161.23	0.0647	1.00754	161.41	0.0714	1.01147	162.34
			0.0800	1.00402	161.35	0.0700	1.00786	161.39	0.0762	1.01175	162.37
						0.0762	1.00822	161.56			
						0.0827	1.0086	161.67			
			MOBS in 0.05 mol kg^{-1} KCl			MOBS in 0.16 mol kg^{-1} KCl			MOBS in 0.25 mol kg^{-1} KCl		
			0.0000	0.99945	–	0.0000	1.00453	–	0.0000	1.00866	–
			0.0174	1.00053	160.96	0.0139	1.00539	161.06	0.0142	1.00952	161.63
			0.0277	1.00115	161.73	0.0266	1.00614	161.97	0.0208	1.00992	161.64
			0.0333	1.00149	161.76	0.0334	1.00655	162.03	0.0276	1.01032	162.00
			0.0397	1.00187	162.01	0.0410	1.00699	162.44	0.0357	1.01080	162.12
			0.0455	1.00222	162.03	0.0474	1.00738	162.25	0.0438	1.01127	162.39
			0.0509	1.00253	162.35	0.0523	1.00764	162.86	0.0500	1.01163	162.52
			0.0571	1.00289	162.55	0.0583	1.00798	163.09	0.0563	1.01198	162.89
			0.0633	1.00324	162.87	0.0637	1.00829	163.19	0.0642	1.01240	163.52
			0.0686	1.00354	163.07	0.0696	1.00862	163.39	0.0694	1.01270	163.51
			0.0748	1.00390	163.14	0.0749	1.00891	163.63	0.0759	1.01305	163.82
			0.0811	1.00424	163.51	0.0812	1.00925	163.92	0.0823	1.01340	164.00
			MOBS in 0.05 mol kg^{-1} KBr			MOBS in 0.1 mol kg^{-1} KBr			MOBS in 0.25 mol kg^{-1} KBr		
			0.0000	1.00125	–	0.0000	1.01047	–	0.0000	1.01789	–
			0.0110	1.00193	161.25	0.0126	1.01124	161.01	0.0143	1.01875	161.19
			0.0165	1.00227	161.19	0.0195	1.01165	161.53	0.0202	1.01909	161.85
			0.0221	1.00260	161.87	0.0242	1.01193	161.67	0.0273	1.01951	161.84
			0.0283	1.00298	161.76	0.0314	1.01235	162.05	0.0331	1.01983	162.50
			0.0339	1.00332	161.78	0.0415	1.01294	162.30	0.0390	1.02016	162.84
			0.0410	1.00373	162.28	0.0478	1.01330	162.55	0.0463	1.02058	162.87
			0.0489	1.00420	162.37	0.0550	1.01371	162.77	0.0533	1.02096	163.29
			0.0573	1.00467	162.93	0.0615	1.01408	162.92	0.0622	1.02146	163.41
			0.0651	1.00511	163.31	0.0674	1.01442	162.95	0.0686	1.02181	163.59
			0.0737	1.00556	163.98	0.0738	1.01476	163.36	0.0743	1.02211	163.88
			0.0824	1.00603	164.37	0.0793	1.01505	163.68	0.0803	1.02243	164.08
			MOBS in 0.05 mol kg^{-1} KAc			MOBS in 0.16 mol kg^{-1} KAc			MOBS in 0.25 mol kg^{-1} KAc		
			0.0000	0.99946	–	0.0000	1.0046	–	0.0000	1.00874	–
			0.0214	1.00079	160.99	0.0216	1.00591	161.97	0.0226	1.01009	162.44
			0.0287	1.00123	161.40	0.0287	1.00633	162.27	0.0297	1.01050	162.84
			0.0368	1.00172	161.58	0.0364	1.00678	162.58	0.0352	1.01082	162.96
			0.0454	1.00224	161.67	0.0463	1.00736	162.76	0.0414	1.01117	163.29
			0.0511	1.00258	161.79	0.0520	1.00769	162.90	0.0479	1.01153	163.67
			0.0569	1.00292	161.99	0.0588	1.00807	163.24	0.0538	1.01187	163.68
			0.0629	1.00328	162.00	0.0649	1.00842	163.33	0.0600	1.01221	163.97
			0.0694	1.00366	162.16	0.0719	1.00881	163.57	0.0673	1.01262	164.08
			0.0764	1.00407	162.27	0.0782	1.00916	163.75	0.0748	1.01303	164.30
			0.0845	1.00455	162.29	0.0854	1.00956	163.92	0.0835	1.01351	164.45

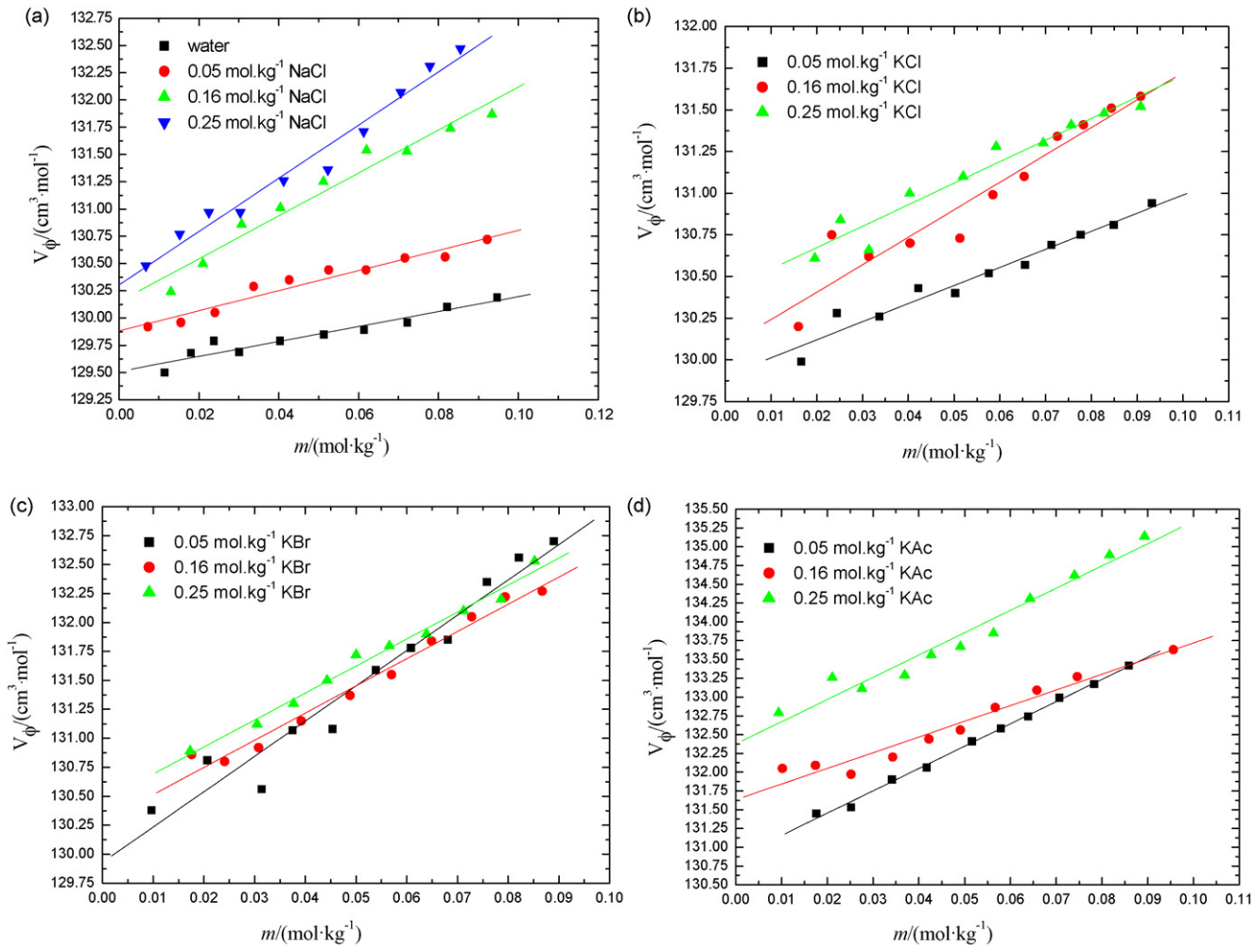


Fig. 1. Apparent molar volume (V_ϕ) as a function of molality (m) of MES in water and aqueous electrolyte solutions: (a) NaCl, (b) KCl, (c) KBr, and (d) KAc. Dashed lines are correlated results from Eq. (2).

The contribution of the above-mentioned groups to the partial molar volume (V_ϕ^o) and transfer volumes ($\Delta_{tr}V_\phi^o$) of buffers at infinite dilution, are listed in Table 10. The tabulated values show that V_ϕ^o of (–CH_2–) group determined via Scheme 1 are different from those via Scheme 2, indicating that V_ϕ^o (–CH_2–) values are sensitive to the nature of neighboring groups. It should also be noted that the extremely low V_ϕ^o (–OH) in water and in aqueous electrolyte solutions, which causes a considerable decrease in

Table 5
Volumetric parameters from Eq. (2) of MES in water and aqueous electrolyte solution at T = 298.15 K.

m (mol kg^{-1})	V_ϕ^o (cm^3 mol^{-1})	r	S_v	SD
NaCl				
0.00	129.51 ± 0.04	0.959	6.87 ± 0.71	0.06
0.05	129.88 ± 0.04	0.974	9.22 ± 0.76	0.07
0.16	130.15 ± 0.09	0.980	19.68 ± 1.52	0.12
0.25	130.30 ± 0.07	0.987	24.41 ± 1.40	0.12
KCl				
0.05	129.90 ± 0.05	0.979	10.86 ± 0.75	0.06
0.16	130.08 ± 0.10	0.958	16.48 ± 1.64	0.13
0.25	130.42 ± 0.07	0.970	12.91 ± 1.14	0.09
KBr				
0.05	129.92 ± 0.13	0.976	30.49 ± 2.26	0.18
0.16	130.29 ± 0.07	0.990	23.48 ± 1.20	0.09
0.25	130.45 ± 0.06	0.993	23.30 ± 0.98	0.06
KAc				
0.05	130.87 ± 0.04	0.998	29.69 ± 0.63	0.04
0.16	131.63 ± 0.09	0.976	20.90 ± 1.64	0.13
0.25	132.35 ± 0.11	0.981	29.63 ± 1.93	0.16

Table 6
Volumetric parameters from Eq. (2) of MOPS in water and aqueous electrolyte solution at T = 298.15 K.

m (mol kg^{-1})	V_ϕ^o (cm^3 mol^{-1})	r	S_v	SD
NaCl				
0.00	145.71 ± 040	0.992	17.21 ± 0.74	0.06
0.05	146.03 ± 0.08	0.970	17.42 ± 1.54	0.10
0.16	146.29 ± 0.07	0.990	26.59 ± 1.62	0.10
0.25	146.39 ± 0.06	0.994	24.09 ± 0.93	0.06
KCl				
0.05	146.06 ± 0.06	0.978	22.05 ± 1.58	0.12
0.16	146.33 ± 0.12	0.961	26.50 ± 2.69	0.18
0.25	146.48 ± 0.16	0.964	36.56 ± 3.58	0.24
KBr				
0.05	146.09 ± 0.08	0.996	54.53 ± 1.56	0.13
0.16	146.43 ± 0.12	0.990	53.87 ± 2.55	0.20
0.25	146.55 ± 0.19	0.981	61.99 ± 4.14	0.32
KAc				
0.05	146.59 ± 0.07	0.986	19.31 ± 1.31	0.08
0.16	147.34 ± 0.04	0.993	17.44 ± 0.67	0.06
0.25	148.16 ± 0.06	0.987	20.02 ± 1.09	0.08

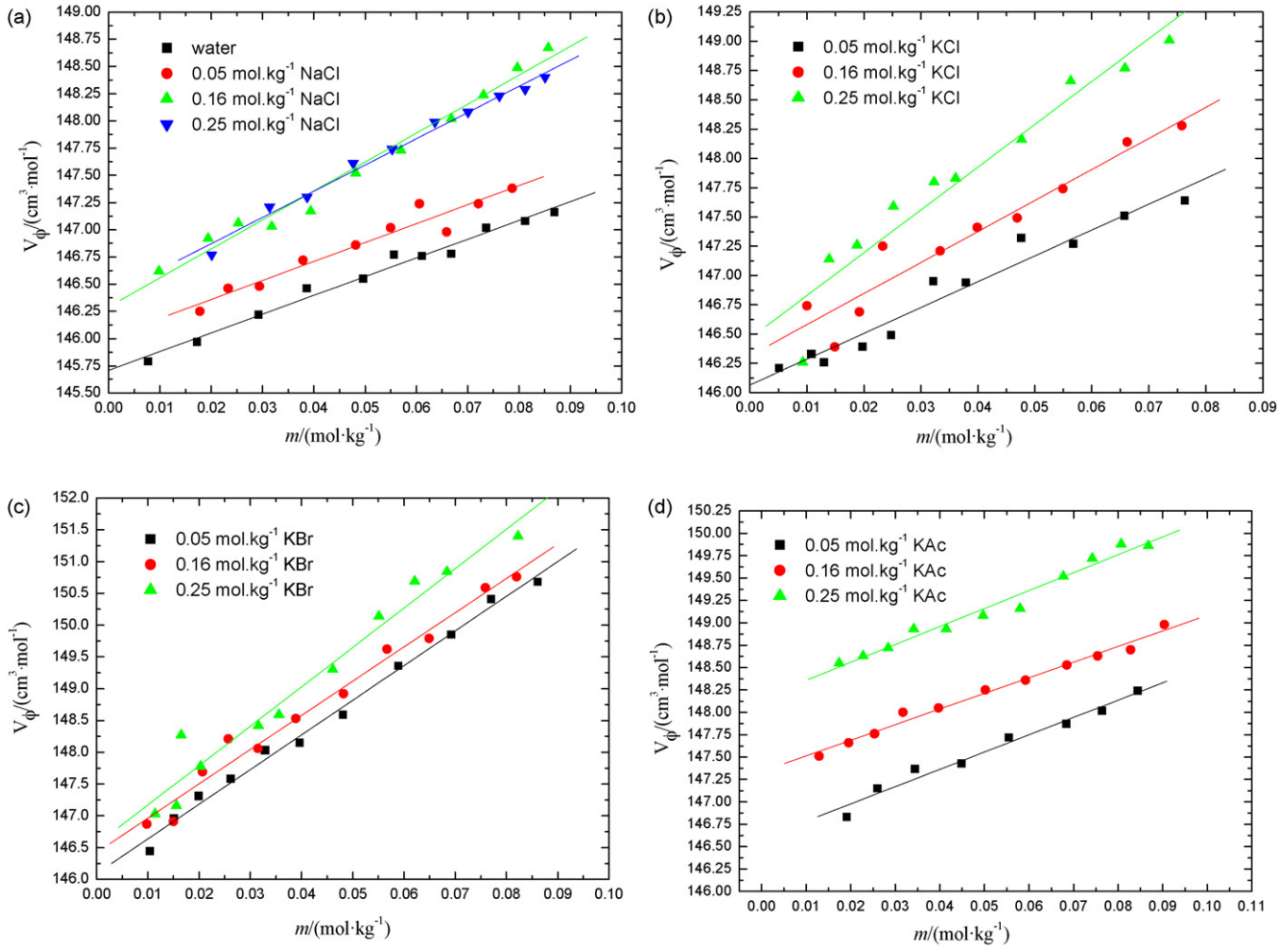


Fig. 2. Apparent molar volume (V_ϕ) as a function of molality (m) of MOPS in water and aqueous electrolyte solutions: (a) NaCl, (b) KCl, (c) KBr, and (d) KAc. Dashed lines are correlated results from Eq. (2).

the volume of MOPSO molecule. It is reasonable to rationalize the observed decrease in the volume of MOPSO molecule due to the strong intramolecular hydrogen-bonding interactions between the (–OH) group and zwitterionic centers. It can be seen from Table 10 that the contribution of non-polar parts (methylene groups) on buffer to $\Delta_{tr}V_\phi^o$ are negative (ion + hydrophobic). However, the contribution of (–OH) group to $\Delta_{tr}V_\phi^o$ is positive in the presence of all the salts.

Table 7
Volumetric parameters from Eq. (2) of MOPSO in water and aqueous electrolyte solution at T = 298.15 K.

m (mol kg^{-1})	V_ϕ^o (cm^3 mol^{-1})	r	S_v	SD
NaCl				
0.00	145.92 ± 0.06	0.969	13.71 ± 1.24	0.08
0.05	146.33 ± 0.12	0.980	33.72 ± 2.45	0.17
0.16	146.68 ± 0.14	0.972	35.33 ± 3.04	0.21
0.25	146.83 ± 0.10	0.995	61.45 ± 2.16	0.15
KCl				
0.05	146.49 ± 0.08	0.993	41.50 ± 1.66	0.12
0.16	146.71 ± 0.08	0.994	46.85 ± 1.65	0.12
0.25	146.88 ± 0.09	0.995	59.31 ± 1.89	0.14
KBr				
0.05	146.75 ± 0.19	0.981	56.17 ± 3.93	0.27
0.16	146.84 ± 0.19	0.986	66.58 ± 3.99	0.27
0.25	147.01 ± 0.09	0.997	71.17 ± 1.98	0.13
KAc				
0.05	147.37 ± 0.15	0.985	46.01 ± 2.71	0.18
0.16	148.13 ± 0.14	0.987	47.68 ± 2.62	0.18
0.25	148.88 ± 0.08	0.995	48.01 ± 1.57	0.11

Table 8
Volumetric parameters from Eq. (2) of MOBS in water and aqueous electrolyte solution at T = 298.15 K.

m (mol kg^{-1})	V_ϕ^o (cm^3 mol^{-1})	r	S_v	SD
NaCl				
0.00	160.25 ± 0.09	0.970	17.95 ± 1.59	0.12
0.05	160.43 ± 0.05	0.970	11.48 ± 1.03	0.07
0.16	160.63 ± 0.06	0.962	11.79 ± 1.06	0.09
0.25	160.75 ± 0.07	0.986	21.75 ± 1.31	0.07
KCl				
0.05	160.49 ± 0.10	0.989	36.76 ± 1.80	0.12
0.16	160.69 ± 0.13	0.984	39.60 ± 2.36	0.16
0.25	160.89 ± 0.11	0.986	37.49 ± 2.13	0.15
KBr				
0.05	160.55 ± 0.14	0.979	43.71 ± 3.01	0.23
0.16	160.78 ± 0.09	0.989	35.38 ± 1.76	0.13
0.25	160.95 ± 0.15	0.977	40.25 ± 2.92	0.21
KAc				
0.05	160.77 ± 0.09	0.973	19.54 ± 1.65	0.10
0.16	161.39 ± 0.05	0.996	30.07 ± 0.89	0.06
0.25	161.87 ± 0.12	0.983	32.88 ± 2.17	0.13

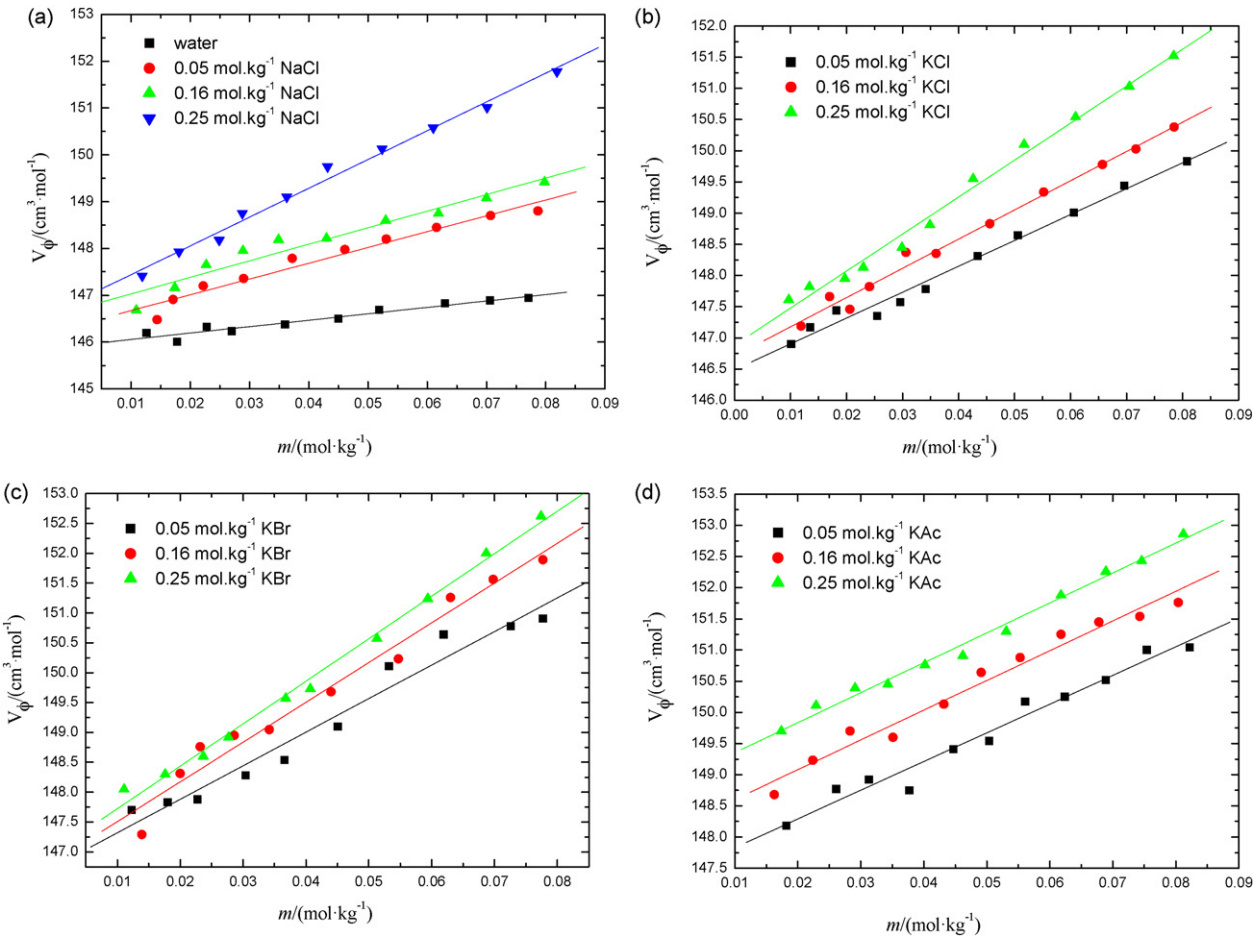


Fig. 3. Apparent molar volume (V_ϕ) as a function of molality (m) of MOPSO in water and aqueous electrolyte solutions: (a) NaCl, (b) KCl, (c) KBr, and (d) KAc. Dashed lines are correlated results from Eq. (2).

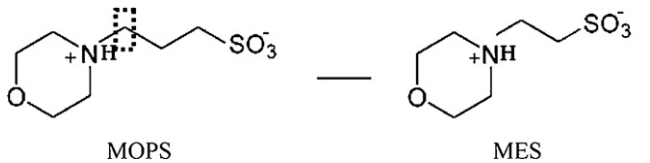
The V_ϕ^o values of MES, MOPS, and MOBS in water and in aqueous electrolyte solution vary linearly with the number of carbon atoms, n_c, in their alkyl group side chains. For example, the V_ϕ^o of the above-mentioned buffers in water are plotted in Fig. 5 as a function of n_c. Similar observations have also been reported in the literature for homologous series of α,ω-amino acids [29–37], alkylammonium halides [38,39], peptides [40] and diaminoalkane molecules [41] of varying chain length. A linear regression analysis of V_ϕ^o values versus n_c in water and in aqueous electrolyte solutions could be reasonably represented by Eq. (4):

$$V_\phi^o = V_\phi^o(\text{morpholinium ion}, -SO_3^-) + n_c V_\phi^o(-CH_2-) \quad (4)$$

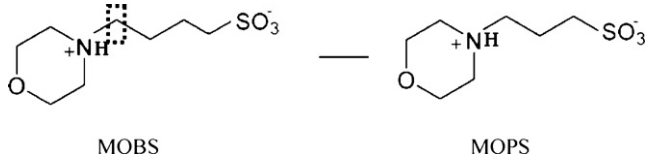
where V_ϕ^o (morpholinimum ion, $-SO_3^-$) and $V_\phi^o(-CH_2-)$ are the zwitterionic end group and methylene group contributions, respectively. The values of V_ϕ^o (morpholinimum ion, $-SO_3^-$) and $V_\phi^o(-CH_2-)$ are listed in Table 11. The $V_\phi^o(-CH_2-)$ value derived, here (15.37 $cm^3\ mol^{-1}$), agrees well with the previously reported value (15.40 $cm^3\ mol^{-1}$) [32] for homologous series of α-amino

Table 9
The transfer volumes at infinite dilution ($\Delta_{tr}V_\phi^o$) for buffers in aqueous electrolyte solutions at 298.15 K.

m (mol kg^{-1})	MES	MOPS	MOPSO	MOBS
NaCl				
0.05	0.37	0.32	0.41	0.18
0.16	0.64	0.58	0.76	0.38
0.25	0.79	0.68	0.91	0.50
KCl				
0.05	0.38	0.35	0.57	0.24
0.16	0.74	0.62	0.79	0.44
0.25	0.85	0.77	0.96	0.64
KBr				
0.05	0.41	0.38	0.83	0.30
0.16	0.78	0.72	0.92	0.53
0.25	0.91	0.84	1.09	0.70
KAc				
0.05	1.36	0.88	1.45	0.52
0.16	2.12	1.63	2.21	1.14
0.25	2.84	2.45	2.96	1.62



Scheme 1. Schematic illustration of the contribution of (–CH_2–) group of MOPS.



Scheme 2. Schematic illustration of the contribution of (–CH_2–) group of MOBS.

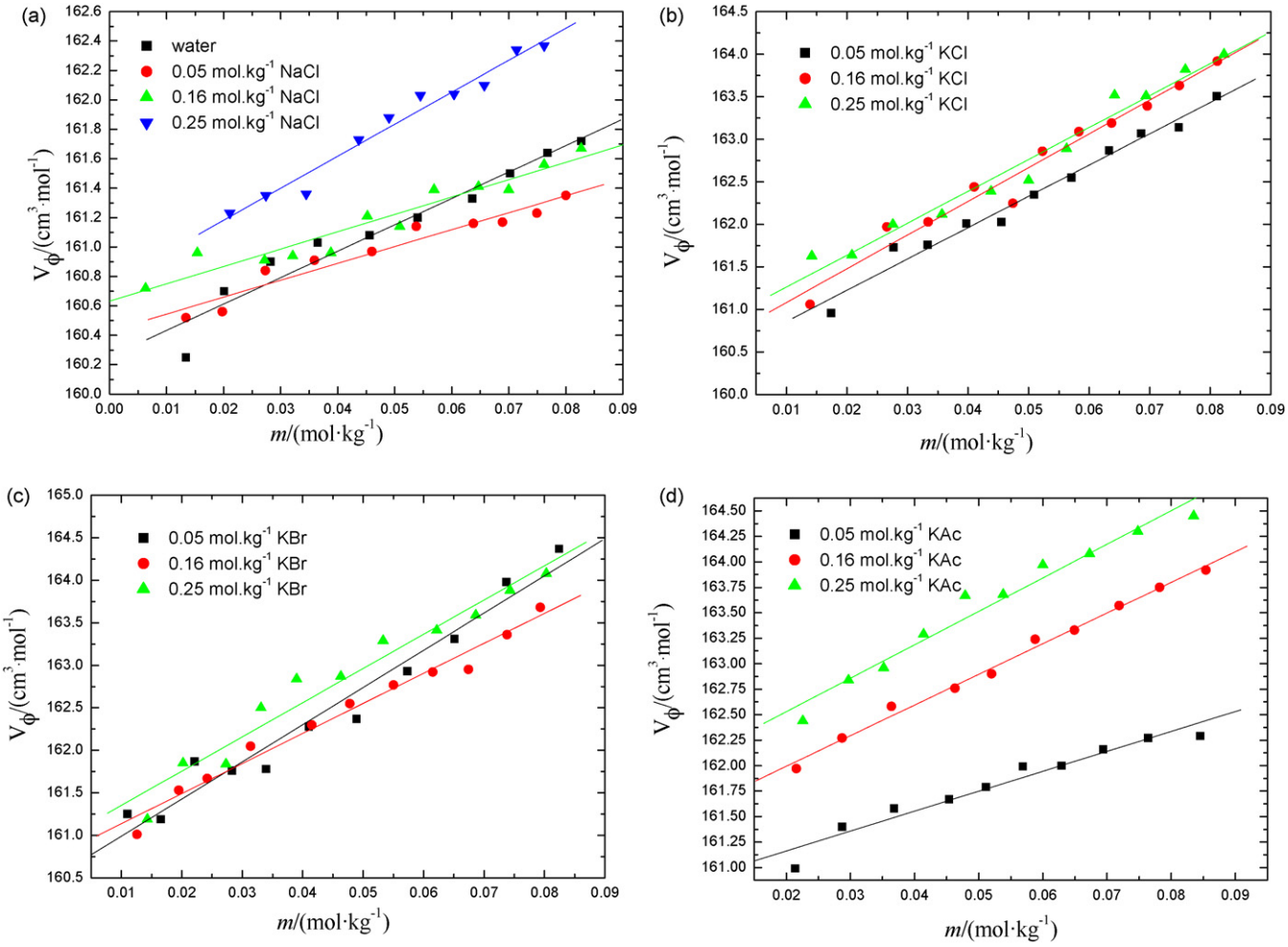
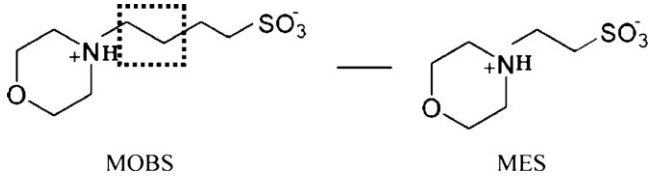


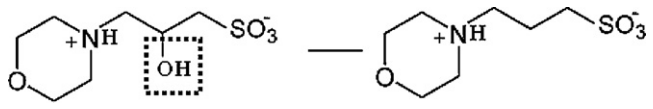
Fig. 4. Apparent molar volume (V_ϕ) as a function of molality (m) of MOBS in water and aqueous electrolyte solutions: (a) NaCl, (b) KCl, (c) KBr, and (d) KAc. Dashed lines are correlated results from Eq. (2).

acids in water. Table 11 reveals that the contribution of the zwitterionic end group to V_ϕ^o is larger than that of the (–CH_2–) group and increases with increase in the salt concentration throughout the experimental concentration range of the cosolute. Therefore, the interactions of ions with zwitterionic group of the buffers are stronger than those with (–CH_2–) group. It is interesting to note that the (–CH_2–) group is not sensitive to the salt concentration except in aqueous of CH_3COOK. Acetate ion has a hydrophobic methyl group. Its effect on the (–CH_2–) group should be different from the simple anions, additional hydrophobic-hydrophobic interactions. Thus, V_ϕ^o(–CH_2–) deceases with increasing the acetate ion concentration.

Fig. 6 is a plot of $\Delta_{tr}V_\phi^o$ versus n_c for the zwitterionic buffers in aqueous solution of CH_3COOK at 298.15 K. In light of Eq. (4), similar



Scheme 3. Schematic illustration of the contribution of (–CH_2–CH_2–) group of MOBS.



Scheme 4. Schematic illustration of the contribution of (–OH) group of MOPSO.

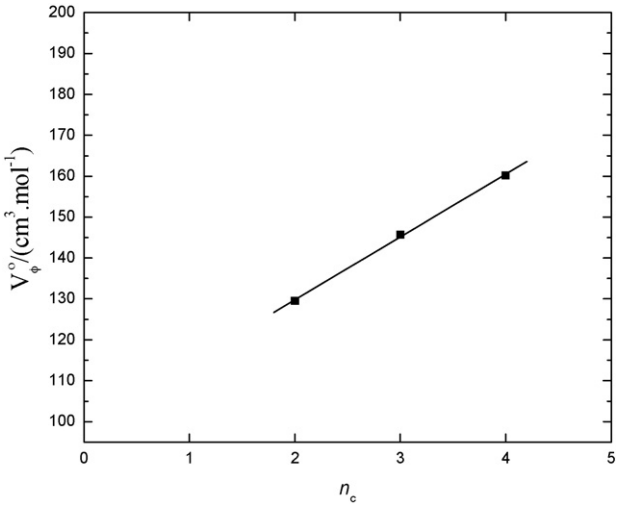


Fig. 5. The linear relationship between the partial molar volume at infinite dilution (V_ϕ^o) of the zwitterionic buffers and n_c in water at 298.15 K.

Table 10
Contributions of (–OH), (–CH_2–), and (–CH_2–CH_2–) to the partial molar volume at infinite dilution (V_ϕ^o) and transfer volumes at infinite dilution ($\Delta_{tr}V_\phi^o$) of buffers from water to aqueous electrolyte solutions at 298.15 K.

m (mol kg^{-1})	V_ϕ^o (cm^3 mol^{-1})				$\Delta_{tr}V_\phi^o$ (cm^3 mol^{-1})			
	(–CH_2–)		(–CH_2–CH_2–)	(–OH)	(–CH_2–)		(–CH_2–CH_2–)	(–OH)
	Scheme 1	Scheme 2	Scheme 3	Scheme 4	Scheme 1	Scheme 2	Scheme 3	Scheme 4
NaCl								
0.00	16.20	14.54	30.74	0.21				
0.05	16.15	14.40	30.55	0.30	−0.05	−0.14	−0.19	0.09
0.16	16.14	14.34	30.48	0.39	−0.06	−0.20	−0.26	0.18
0.25	16.09	14.36	30.45	0.44	−0.11	−0.18	−0.29	0.23
KCl								
0.05	16.16	14.43	30.59	0.43	−0.03	−0.11	−0.14	0.22
0.16	16.25	14.36	30.61	0.38	−0.12	−0.18	−0.30	0.17
0.25	16.06	14.41	30.47	0.40	−0.08	−0.13	−0.21	0.19
KBr								
0.05	16.17	14.46	30.63	0.66	−0.03	−0.08	−0.11	0.45
0.16	16.14	14.35	30.49	0.41	−0.06	−0.19	−0.25	0.20
0.25	16.10	14.40	30.50	0.46	−0.07	−0.14	−0.21	0.25
KAc								
0.05	15.72	14.18	29.90	0.78	−0.48	−0.36	−0.84	0.57
0.16	15.71	14.05	29.76	0.79	−0.49	−0.49	−0.98	0.58
0.25	15.81	13.71	29.52	0.72	−0.39	−0.83	−1.22	0.51

Table 11
Contributions of zwitterionic end group (morpholinium ion, –SO_3^-) and (–CH_2–) group to the partial molar volume at infinite dilution (V_ϕ^o) in water and in aqueous electrolyte solutions at 298.15 K.

Salt	Group	m (mol kg^{-1})			
		0	0.05	0.16	0.25
		V_ϕ^o (cm^3 mol^{-1})			
NaCl	(Morpholinium ion, SO_3^-)	99.05	99.62	99.97	100.14
	–CH_2–	15.37	15.28	15.24	15.23
KCl	(Morpholinium ion, SO_3^-)	99.05	99.60	99.79	100.22
	–CH_2–	15.37	15.30	15.31	15.23
KBr	(Morpholinium ion, SO_3^-)	99.05	99.58	100.10	100.23
	–CH_2–	15.37	15.32	15.25	15.25
KAc	(Morpholinium ion, SO_3^-)	99.05	101.23	102.15	103.18
	–CH_2–	15.37	14.95	14.88	14.76

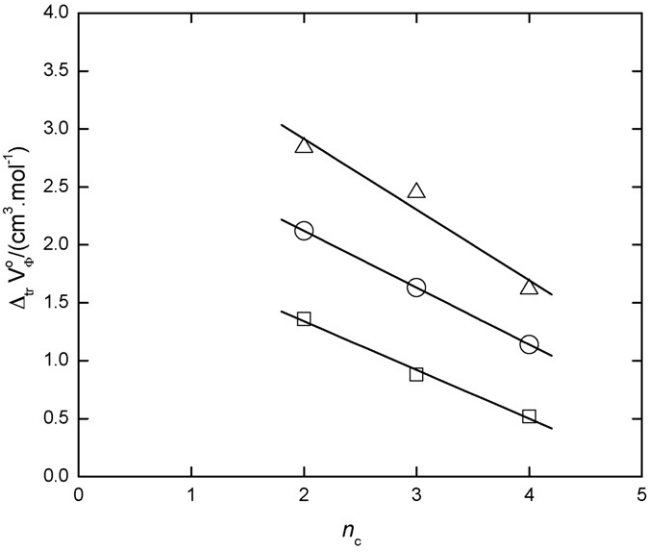


Fig. 6. Variation of the transfer volumes at infinite dilution ($\Delta_{tr}V_\phi^o$) of zwitterionic buffers as a function n_c in aqueous solutions of CH_3COOK at 298.15 K. (□) 0.05 mol kg^{-1}; (○) 0.16 mol kg^{-1}; (△) 0.25 mol kg^{-1}.

linear correlations were observed for other electrolytes as well. For brevity, the charts of other salts are not included. The intercepts and the slopes of these straight lines represent the contributions of zwitterionic end group and of (–CH_2–) group to $\Delta_{tr}V_\phi^o$, respectively. As one would expect, the contribution of (–CH_2–) group to $\Delta_{tr}V_\phi^o$ is negative and that of the zwitterionic end group is positive. These results again strengthen the dominance of the conclusions drawn from the cosphere overlap model [28].

4. Conclusion

The densities have been measured for the solutions of four zwitterionic buffers (MES, MOPS, MOPSO, and MOBS) in water and in aqueous solutions of NaCl, KCl, KBr, and CH_3COOK. Based on these density data, the apparent molar volumes V_ϕ, the apparent molar volumes at infinite dilution V_ϕ^o, and the partial molar volumes of transfer at infinite dilution $\Delta_{tr}V_\phi^o$ were calculated. Since all the values of $\Delta_{tr}V_\phi^o$ are positive, it was suggested that ion–hydrophilic interactions are much stronger than ion–hydrophobic interactions over the entire concentration range of electrolytes. The zwitterionic buffers follow the order of their decreasing $\Delta_{tr}V_\phi^o$ as MOPSO > MES > MOPS > MOBS. In addition, the group contributions calculated from V_ϕ^o confirmed that the ion-hydrophobic interactions increase with increasing length of the alkly side chains of the zwitterionic buffers.

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