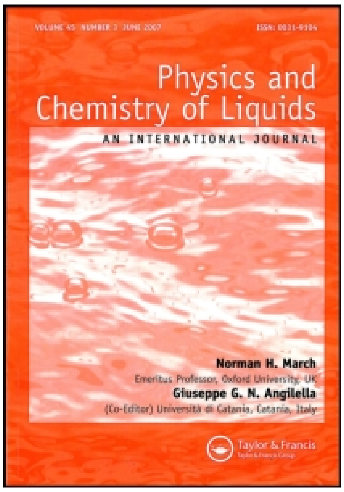

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Densities and excess molar volumes of formic acid, acetic acid and propionic acid in pure water and in water + Surf Excel solutions at different temperatures

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Densities and excess molar volumes of formic acid, acetic acid and propionic acid in pure water and in water + Surf Excel solutions at different temperatures

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Densities, ρ of the systems formic acid, acetic acid and propionic acid in water and in 0.05% and 0.1% Surf Excel (SE) solutions in water were measured at temperatures 303.15, 308.15, 313.15, 318.15 and 323.15 K respectively covering the whole composition range. Excess molar volumes, V_m^E for the systems were found to be negative and their values were found to increase with chain length of carboxylic acid. Densities and excess molar volumes have been plotted against mole fraction of the solutes (X_2). All these properties have been expressed satisfactorily by appropriate polynomials. No appreciable change of the densities and excess molar volumes were observed by the addition of surfactant (0.05% and 0.1%) to the studied systems. An attempt has been made to explain V_m^E in terms of hydrophobic hydration and hydrophilic effect of the solutes. An explanation of V_m^E in terms of hydrophobic hydration and hydrophilic effect of the solutes is offered.

Keywords: Excess molar volumes; Formic, acetic and propionic acids; Surfactants

1. Introduction

Surfactant molecules in water solution at low concentration exist in monomeric form and behave like normal electrolytes or non-polar molecules. However, on increasing the concentration of the surfactant an abrupt change in several physico-chemical properties of the solution such as osmotic pressure, electrical conductance, surface tension, viscosity, molar volume etc. is observed. This behavior of surfactant solution is ascribed to the formation of multi-molecular aggregates, called micelles. Micelle formation is a typical hydrophobic process [1]. In water medium, surfactant molecules with their long hydrophobic tails undergo hydrophobic hydration. The concentration at which the micelle first appears is referred to as the critical micelle concentration (CMC). Above this concentration micelles are in dynamic equilibrium with the

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Table 1. Densities, $\rho \times 10^3$ (kg m^{-3}), excess molar volumes, $V_m^E \times 10^6$ (m^3 mol^{-1}), of formic acid in H_2O, 0.05% H_2O + SE and 0.1% H_2O + SE systems (303.15, 308.15, 313.15, 318.15 and 323.15) K.

T/K	303.15		308.15		313.15		318.15		323.15	
X_2	ρ	V_m^E	ρ	V_m^E	ρ	V_m^E	ρ	V_m^E	ρ	V_m^E
Water + Formic acid system										
0.0000	0.995670	0.0000	0.994060	0.0000	0.992240	0.0000	0.990250	0.0000	0.988070	0.0000
0.1203	1.055888	−0.2429	1.052344	−0.2232	1.049262	−0.2156	1.045574	−0.1985	1.042032	−0.1871
0.2738	1.105991	−0.3389	1.102617	−0.3408	1.098197	−0.3231	1.093824	−0.3076	1.089121	−0.2872
0.3908	1.135801	−0.4002	1.131094	−0.3859	1.125906	−0.3621	1.120910	−0.3435	1.115615	−0.3190
0.4821	1.154080	−0.3961	1.148269	−0.3802	1.143113	−0.3649	1.137629	−0.3419	1.132431	−0.3264
0.5883	1.167456	−0.2986	1.165146	−0.3633	1.159809	−0.3521	1.153613	−0.3185	1.148251	−0.3064
0.6476	1.174809	−0.2545	1.172908	−0.3373	1.166824	−0.3109	1.160986	−0.2902	1.155289	−0.2728
0.7078	1.181962	−0.2167	1.179757	−0.2992	1.174164	−0.2901	1.167245	−0.2434	1.161290	−0.2225
0.7787	1.187960	−0.1232	1.186244	−0.2289	1.180222	−0.2117	1.174069	−0.1900	1.167808	−0.1639
1.0000	1.208973	0.0000	1.203002	0.0000	1.197080	0.0000	1.191230	0.0000	1.185442	0.0000
0.05% SE + Formic acid system										
0.0000	0.995692	0.0000	0.994367	0.0000	0.992556	0.0000	0.990415	0.0000	0.988142	0.0000
0.1204	1.056255	−0.2490	1.052665	−0.2239	1.049262	−0.2100	1.045574	−0.1953	1.042147	−0.1875
0.2746	1.107486	−0.3657	1.103155	−0.3440	1.098197	−0.3147	1.093953	−0.3042	1.089509	−0.2905
0.3886	1.135779	−0.4097	1.130896	−0.3881	1.125511	−0.3596	1.120076	−0.3324	1.115219	−0.3190
0.4829	1.153982	−0.4061	1.148556	−0.3807	1.143135	−0.3590	1.137806	−0.3419	1.132519	−0.3246
0.5884	1.171111	−0.3903	1.165398	−0.3670	1.159509	−0.3434	1.154095	−0.3293	1.148366	−0.3084
0.6459	1.178511	−0.3573	1.172908	−0.3416	1.166760	−0.3134	1.161029	−0.2964	1.155521	−0.2849
0.7090	1.185939	−0.3196	1.179889	−0.2969	1.173923	−0.2776	1.167794	−0.2535	1.161817	−0.2326
1.0000	1.208973	0.0000	1.203002	0.0000	1.197080	0.0000	1.191230	0.0000	1.185442	0.0000
0.1%SE + Formic acid system										
0.0000	0.995862	0.0000	0.994528	0.0000	0.992988	0.0000	0.991011	0.0000	0.988850	0.0000
0.1204	1.056416	−0.2494	1.053125	−0.2301	1.049814	−0.2136	1.046171	−0.1970	1.042492	−0.1828
0.2742	1.107701	−0.3702	1.102918	−0.3389	1.098692	−0.3216	1.094319	−0.3062	1.089379	−0.2803
0.3889	1.135845	−0.4079	1.120808	−0.3830	1.125533	−0.3539	1.120537	−0.3350	1.115308	−0.3117
0.4820	1.154075	−0.4105	1.148689	−0.3862	1.143399	−0.3651	1.137519	−0.3324	1.132409	−0.3189
0.5864	1.170835	−0.3894	1.164964	−0.3626	1.159165	−0.3373	1.153636	−0.3206	1.147929	−0.2992
0.6469	1.178533	−0.3530	1.172649	−0.3301	1.166502	−0.3000	1.161007	−0.2883	1.155048	−0.2639
0.7104	1.186092	−0.3178	1.180065	−0.2957	1.173923	−0.2702	1.167882	−0.2479	1.162081	−0.2313
1.0000	1.208973	0.0000	1.203002	0.0000	1.197080	0.0000	1.191230	0.0000	1.185442	0.0000

monomeric form of the surfactant in the bulk phase. Surfactants in water solutions generally form spherical micelles just above the CMC and associate further to form rod-like micelles at higher concentration [2].

Although limited volumetric and viscometric results on binary systems of carboxylic acids [3,4] are available, no data are yet available for ternary systems of carboxylic acids–surfactant systems.

Interactions between water and carboxylic acids are extremely complex. Both acids and water are self-associated liquids through H-bonding. Carboxylic acids possess hydrophilic –COOH group as well as hydrophobic group (except formic acid). The mode of interaction of these two groups toward water is completely different. The hydrophilic –COOH group of an acid forms an H-bond with water through hydrophilic interactions and disrupts normal water structure, while the alkyl group promotes the structure of water molecules surrounding this group through hydrophobic hydration. A better understanding of water–acid interaction is of vital importance in the field of solution chemistry, as it can provide important information regarding hydrophilic and hydrophobic interactions. It is believed that both these effects, hydrophilic and hydrophobic, take place in water-rich regions of aqueous acid solutions.

Table 2. Densities, $\rho \times 10^3$ (kg m^{-3}), excess molar volumes, $V_m^E \times 10^6$ (m^3 mol^{-1}), of acetic acid in H_2O, 0.05% H_2O + SE and 0.1% H_2O + SE systems at (303.15, 308.15, 313.15, 318.15 and 323.15) K.

T/K	303.15		308.15		313.15		318.15		323.15	
X_2	ρ	V_m^E	ρ	V_m^E	ρ	V_m^E	ρ	V_m^E	ρ	V_m^E
Water + Acetic acid system										
0.0000	0.995670	0.0000	0.994060	0.0000	0.992240	0.0000	0.990250	0.0000	0.988070	0.0000
0.0950	1.027496	−0.4447	1.024919	−0.4465	1.021723	−0.4420	1.018413	−0.4340	1.014823	−0.4252
0.2385	1.049718	−0.8482	1.045519	−0.8364	1.041319	−0.8351	1.037251	−0.8303	1.033135	−0.8317
0.3675	1.058574	−1.0701	1.053716	−1.0556	1.048851	−1.0551	1.044392	−1.0544	1.039131	−1.0386
0.4823	1.059781	−1.1101	1.054717	−1.0995	1.049788	−1.1084	1.044928	−1.1081	1.039330	−1.0905
0.6393	1.059194	−1.0918	1.053695	−1.0772	1.048458	−1.0952	1.043262	−1.0906	1.037638	−1.0825
0.7332	1.055249	−1.9207	1.049780	−0.9121	1.044181	−0.9225	1.039253	−0.9346	1.034211	−0.9578
0.8471	1.051104	−1.7047	1.045302	−0.6857	1.039692	−0.7039	1.034464	−0.7078	1.028393	−0.6871
1.0000	1.039103	0.0000	1.033621	0.0000	1.027567	0.0000	1.022221	0.0000	1.016518	0.0000
0.05% SE + Acetic acid system										
0.0000	0.995692	0.0000	0.994367	0.0000	0.992556	0.0000	0.990415	0.0000	0.988142	0.0000
0.0950	1.028277	−0.4607	1.024850	−0.4401	1.021677	−0.4358	1.018271	−0.4283	1.015007	−0.4279
0.2386	1.050149	−0.8588	1.045541	−0.8326	1.041233	−0.8285	1.036906	−0.8189	1.033178	−0.8319
0.3679	1.058882	−1.0791	1.053848	−1.0560	1.048961	−1.0549	1.043853	−1.0360	1.038956	−1.0325
0.4821	1.060245	−1.1256	1.054739	−1.0974	1.049457	−1.0969	1.044500	−1.0915	1.039506	−1.0959
0.6382	1.058922	−1.0808	1.053677	−1.0744	1.048366	−1.0892	1.042954	−1.0766	1.037551	−1.0781
0.7348	1.054819	−0.9014	1.049694	−0.9067	1.044159	−0.9200	1.038864	−0.9164	1.034082	−0.9519
0.8508	1.050972	−0.6971	1.045324	−0.6850	1.039362	−0.6861	1.033774	−0.6723	1.028174	−0.6756
1.0000	1.039103	0.0000	1.033621	0.0000	1.027567	0.0000	1.022221	0.0000	1.016518	0.0000
0.1%SE + Acetic acid system										
0.0000	0.995862	0.0000	0.994528	0.0000	0.992988	0.0000	0.991011	0.0000	0.988850	0.0000
0.0954	1.028369	−0.4593	1.024919	−0.4384	1.021838	−0.4317	1.018547	−0.4239	1.014915	−0.4140
0.2386	1.049675	−0.8444	1.045541	−0.8304	1.041082	−0.8186	1.036819	−0.8084	1.032748	−0.8106
0.3681	1.058640	−1.0698	1.053958	−1.0576	1.048961	−1.0499	1.043810	−1.0278	1.038912	−1.0230
0.4848	1.059980	−1.1151	1.054828	−1.0993	1.049744	−1.1034	1.044522	−1.0874	1.039219	−1.0801
0.6405	1.059198	−1.0908	1.053976	−1.0857	1.048504	−1.0925	1.042839	−1.0684	1.037574	−1.0750
0.7388	1.055228	−0.9181	1.049888	−0.9143	1.044181	−0.9190	1.038821	−0.9119	1.033910	−0.9413
0.8564	1.054044	−0.6693	1.045368	−0.6855	1.039384	−0.6852	1.033554	−0.6590	1.027976	−0.6634
1.0000	1.039103	0.0000	1.033621	0.0000	1.027567	0.0000	1.022220	0.0000	1.016518	0.0000

Recently, we reported the volumetric and viscometric properties of different surfactant systems like alcohols in water + SE [5], carbohydrates in water + SE [6] and electrolytes in water + SDS [7] solutions. Here we report the effect of some simple acids on the structure of water and water + SE systems. Micelle forming molecules SE may force water to be in certain structural form in the water + SE system. The perturbations of this forced structure in the water + SE system by some acids are expected to be more appreciable than the perturbation caused by these acids in the water system alone. The knowledge of interactions of simple smaller hydrophobic molecules with water and with water + surfactant solvent systems may be useful sometimes to interpret many complex systems [8]. The data are also useful for the design of mixing, storage and process equipment.

2. Experimental

2.1. *Materials*

The chemicals used were procured from BDH Chemical Co., England with the quoted purities: formic acid (95.5%), acetic acid (99.0%) and propionic

Table 3. Densities, $\rho \times 10^3$ (kg m^{-3}), excess molar volumes, $V_m^E \times 10^6$ (m^3 mol^{-1}), of *n*-propionic acid in H_2O, 0.05% $H_2O + SE$ and 0.1% $H_2O + SE$ systems at (303.15, 308.15, 313.15, 318.15 and 323.15) K.

T/K	303.15		308.15		313.15		318.15		323.15	
X_2	ρ	V_m^E	ρ	V_m^E	ρ	V_m^E	ρ	V_m^E	ρ	V_m^E
Water + Propionic acid system										
0.0000	0.995670	0.0000	0.994060	0.0000	0.992240	0.0000	0.990250	0.0000	0.988070	0.0000
0.0416	1.006552	−0.2340	1.004115	−0.2308	1.001448	−0.2257	0.998667	−0.2207	0.995703	−0.2168
0.0748	1.011838	−0.3812	1.009125	−0.3800	1.005746	−0.3673	1.002625	−0.3624	0.999010	−0.3522
0.1155	1.015731	−0.5241	1.012479	−0.5201	1.008501	−0.5012	1.004655	−0.4869	1.001032	−0.4848
0.1928	1.017210	−0.6771	1.013497	−0.6764	1.009223	−0.6613	1.004925	−0.6461	1.000508	−0.6363
0.3125	1.016920	−0.8500	1.012528	−0.8471	1.007724	−0.8299	1.002896	−0.8108	0.998506	−0.8195
0.4203	1.014205	−0.9034	1.009577	−0.9053	1.004498	−0.8876	0.999742	−0.8806	0.994987	−0.8892
0.6859	1.004205	−0.7193	0.999539	−0.7394	0.994311	−0.7327	0.988757	−0.7007	0.984080	−0.7423
1.0000	0.991219	0.0000	0.985795	0.0000	0.980481	0.0000	0.975296	0.0000	0.969705	0.0000
0.05% SE + Propionic acid system										
0.0000	0.995692	0.0000	0.994367	0.0000	0.992556	0.0000	0.990415	0.0000	0.988142	0.0000
0.0416	1.006851	−0.2403	1.004368	−0.2306	1.001563	−0.2225	0.998736	−0.2192	0.995932	−0.2202
0.0757	1.012483	−0.3959	1.009448	−0.3833	1.006112	−0.3716	1.002905	−0.3675	0.999290	−0.3590
0.1169	1.016105	−0.5347	1.012171	−0.5101	1.008742	−0.5045	1.004743	−0.4891	1.001142	−0.5433
0.1951	1.018521	−0.7170	1.014478	−0.7033	1.009862	−0.6790	1.005644	−0.6687	1.001164	−0.6590
0.6856	1.005876	−0.7842	1.000947	−0.8174	0.996406	−0.8499	0.990510	−0.8004	0.985304	−0.8127
1.0000	0.991219	0.0000	0.985795	0.0000	0.980481	0.0000	0.975296	0.0000	0.969705	0.0000
0.1%SE + Propionic acid system										
0.0000	0.995862	0.0000	0.994528	0.0000	0.992988	0.0000	0.991011	0.0000	0.988850	0.0000
0.0409	1.006506	−0.2297	1.004092	−0.2213	1.001425	−0.2111	0.998529	−0.2034	0.995634	−0.2003
0.0752	1.012117	−0.3845	1.009211	−0.3747	1.004832	−0.3573	1.002776	−0.3536	0.999250	−0.3451
0.1149	1.015423	−0.5129	1.012303	−0.5074	1.008171	−0.4800	1.004721	−0.4550	1.001054	−0.4713
0.1947	1.017518	−0.6859	1.012563	−0.6746	1.009333	−0.6569	1.006182	−0.6745	1.001907	−0.6691
0.3093	1.016702	−0.8353	1.012246	−0.8262	1.007424	−0.8044	1.004218	−0.8416	0.999355	−0.8332
0.4170	1.014193	−0.8964	1.009557	−0.8946	1.004437	−0.8719	1.000725	−0.9076	0.995828	−0.9101
0.6821	1.005219	−0.7635	0.999885	−0.7532	0.994667	−0.7447	0.989773	−0.7506	0.984373	−0.7500
1.0000	0.991219	0.0000	0.985795	0.0000	0.980481	0.0000	0.975296	0.0000	0.969705	0.0000

acid (99.5%). Surf Excel, a commercial detergent powder, was procured from local market at Rajshahi, Bangladesh. These chemicals were used without any further purification.

2.2. *Density measurements*

Densities were measured by using 5 mL bicapillary pycnometers. The volumes of the pycnometers were calibrated with deionized and doubly distilled water at 303.15, 308.15, 313.15, 318.15 and 323.15 K. The densities of solutions in water and water + SE solutions were determined from the mass of the solution in the pycnometer after reaching thermal equilibrium with a water bath at the studied temperatures. A Mettler PM −200 electronic balance with an accuracy of ±0.0001g was used for the mass determination. The reproducibility of the density measurements was ±0.1%, and the uncertainty was estimated to be ±0.2%.

2.3. *Determination of excess molar volume*

The excess molar volumes, V_m^E were calculated using the following equation:

$$V_m^E/\mathrm{m^3mol^{-1}} = (X_1M_1 + X_2M_2)/\rho_{\mathrm{mix}} - (X_1M_1/\rho_1 + X_2M_2/\rho_2) \qquad (1)$$

Table 4. Coefficient, a_i, of Redlich–Kister equation (2) expressing $V_m^E \times 10^6$ in $m^3\,mol^{-1}$ and standard deviation, σ for the formic acid systems.

Systems	T/K	a_0	a_1	a_2	a_3	σ
Water + Formic acid system	303.15	−1.4736	0.8097	0.5047	0.8967	0.0193
	308.15	−1.5376	0.1900	−0.1472	0.7765	0.0044
	313.15	−1.4651	0.1375	−0.0809	0.9549	0.0071
	318.15	−1.3650	0.2880	0.0021	0.6532	0.0027
	323.15	−1.3013	0.2082	0.2363	1.0157	0.0031
0.05% SE + Formic acid system	303.15	−1.6316	0.1922	−0.2997	0.8786	0.0049
	308.15	−1.5427	0.2084	−0.2159	0.6489	0.0049
	313.15	−1.4412	0.1538	−0.1000	0.7997	0.0045
	318.15	−1.3729	0.1381	0.0722	0.9658	0.0036
	323.15	−1.3082	0.1571	0.1462	1.0125	0.0039
0.1% SE + Formic acid system	303.15	−1.6323	0.2315	−0.3121	0.8086	0.0039
	308.15	−1.5315	0.1951	−0.1790	0.8335	0.0052
	313.15	−1.4304	0.2365	−0.0947	0.7715	0.0058
	318.15	−1.3427	0.2334	−0.0919	0.6792	0.0037
	323.15	−1.2639	0.1997	0.0611	0.7763	0.0035

Table 5. Coefficient, a_i, of Redlich–Kister equation (2) expressing $V_m^E \times 10^6$ in $m^3\,mol^{-1}$ and standard deviation, σ for the acetic acid systems.

Systems	T/K	a_0	a_1	a_2	a_3	σ
Water + Acetic acid system	303.15	−4.2678	−1.7410	−10.9264	−9.5904	0.1966
	308.15	−4.4405	−0.1543	−1.2646	−0.1219	0.0214
	313.15	−4.4740	−0.2432	−1.2832	−0.1686	0.0241
	318.15	−4.4726	−0.2574	−1.2879	−0.3090	0.0194
	323.15	−4.4414	−0.4087	−1.2707	0.0504	0.0105
0.05% SE + Acetic acid system	303.15	−4.4943	0.0925	−1.4075	−0.6015	0.0279
	308.15	−4.4265	−0.0953	−1.3128	−0.4186	0.0232
	313.15	−4.4508	−0.2367	−1.2563	−0.2171	0.0229
	318.15	−4.4124	−0.3001	−1.1658	−0.0593	0.0175
	323.15	−4.4336	−0.4056	−1.2813	0.0755	0.0059
0.1% SE + Acetic acid system	303.15	−4.4968	−0.1914	−1.3288	−0.0613	0.0225
	308.15	−4.4440	−0.1721	−1.3922	−0.4979	0.0246
	313.15	−4.4547	−0.2945	−1.2821	−0.3561	0.0245
	318.15	−4.3854	−0.3330	−1.1888	−0.1406	0.0163
	323.15	−4.3902	−0.4643	−1.2573	−0.0795	0.0105

where X_1, M_1 and ρ_1 are the mole fraction, molar mass and density of component 1 (pure or mixed solvent), X_2, M_2 and ρ_2 are the corresponding values of component 2 (organic solutes), and ρ_{mix} is the density of the mixture, respectively. The excess molar volumes were fitted to a Redlich–Kister polynomial equation of the form

$$V_m^E/m^3\,mol^{-1} = X_1 X_2 \sum_{i=0}^{n} a_i (1 - 2X_1)^i \tag{2}$$

where a_i is the ith fitting coefficient. Using $n = 3$, four a_i coefficients and the standard deviation σ were obtained through the least squares method.

Table 6. Coefficient, a_i, of Redlich–Kister equation (2) expressing $V_m^E \times 10^6$ in $m^3 mol^{-1}$ and standard deviation, σ for the propionic acid systems.

Systems	T/K	a_0	a_1	a_2	a_3	σ
Water + *n*-Propionic acid system	303.15	−3.6594	0.3819	0.2731	2.7718	0.0094
	308.15	−3.6785	0.2678	0.0936	2.6300	0.0081
	313.15	−3.6095	0.2394	−0.0060	2.3693	0.0067
	318.15	−3.5893	0.2474	0.6590	3.0104	0.0049
	323.15	−3.6562	0.0640	0.3781	2.6512	0.0088
0.05% SE + *n*-Propionic acid system	303.15	−3.8159	0.1963	−0.1824	2.4710	0.0020
	308.15	−4.5537	−0.0651	3.5682	5.6825	0.0049
	313.15	−3.5381	−0.3338	−2.2772	0.6132	0.0024
	318.15	−4.0611	−0.1833	1.5431	3.8843	0.0053
	323.15	0.5091	0.0328	−24.1444	−18.9285	0.0147
0.1% SE + *n*-Propionic acid system	303.15	−3.6493	0.1586	−0.3241	2.3653	0.0042
	308.15	−3.6426	0.1658	−0.0782	2.4698	0.0047
	313.15	−3.5439	0.1648	−0.3197	1.9071	0.0025
	318.15	−3.6501	0.4752	−0.2591	1.0525	0.0117
	323.15	−3.6654	0.4051	−0.0659	1.3996	0.0027

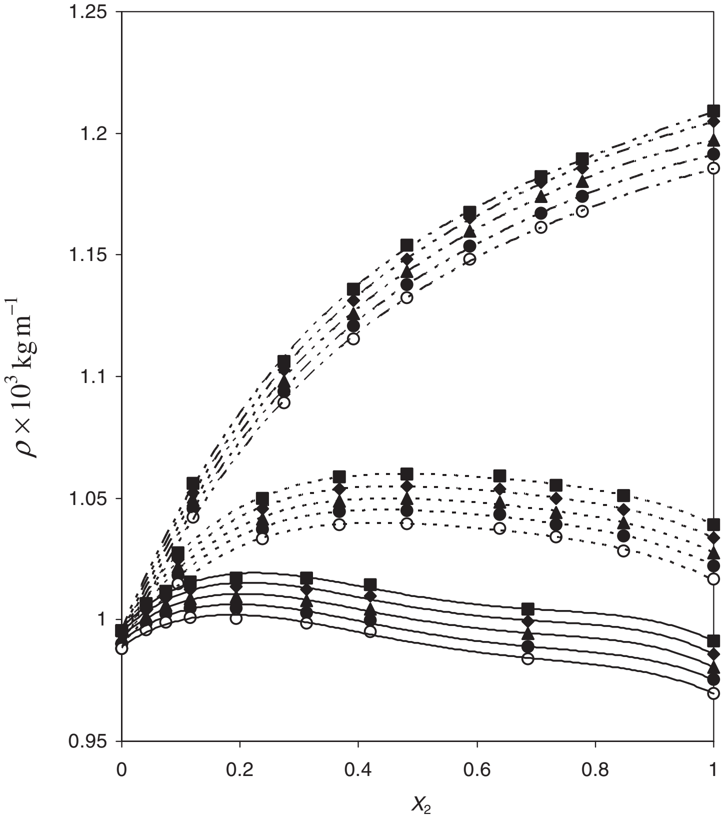

Figure 1. Plots of density (ρ) *versus* X_2 of formic acid (dashed–dotted line), acetic acid (dotted line) and propionic acid (solid line) in water systems at ■, 303.15 K; ◆, 308.15 K; ▲, 313.15 K; ●, 318.15 K; ○, 323.15 K.

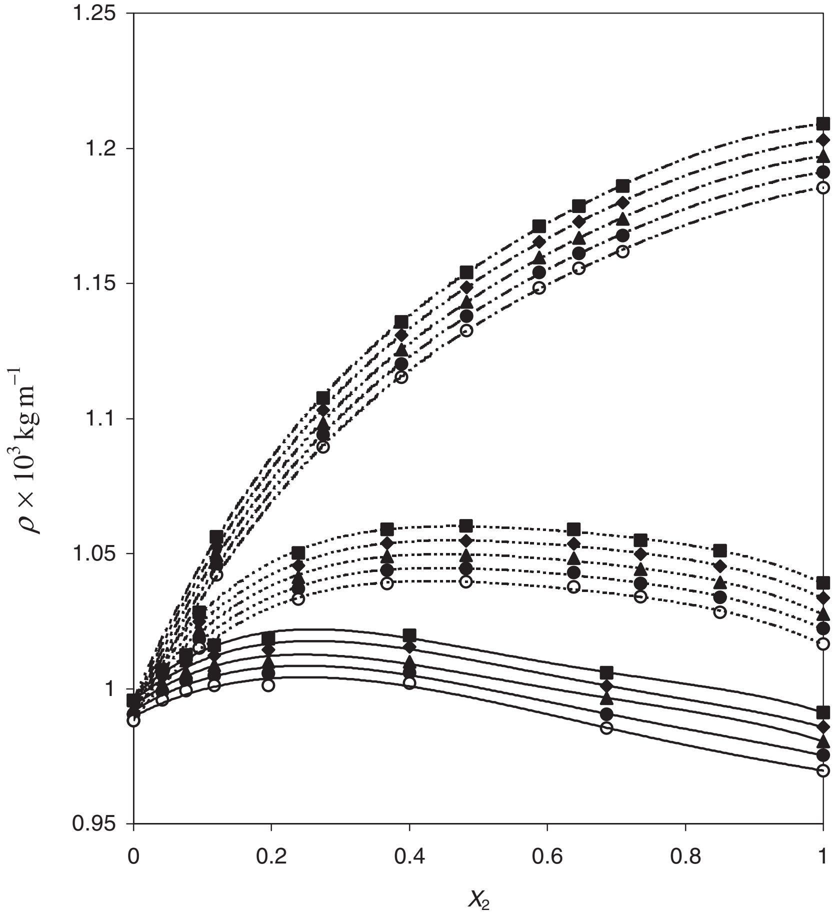

Figure 2. Plots of density (ρ) *versus* X_2 of formic acid (dashed–dotted line), acetic acid (dotted line) and propionic acid (solid line) + 0.05% SE systems at ■, 303.15 K; ◆, 308.15 K; ▲, 313.15 K; ●, 318.15 K; ○, 323.15 K.

3. Results and discussion

Densities of formic acid, acetic acid, and propionic acid in water and 0.05% and 0.1% SE solutions were determined at 303.15, 308.15, 313.15, 318.15 and 323.15 K, respectively. The densities of the binary and ternary systems have been shown in tables 1–3 at different temperatures. The corresponding V_m^E data are also presented in tables 1–3. For V_m^E the fitting coefficients (a_i) are shown in tables 4–6 along with standard deviations. Figure 1 shows the plots of densities as a function of mole fraction of formic acid, acetic acid, and propionic acid in water systems. It is seen that the density of formic acid + water system increases as formic acid is added to water (dotted–dashed line). As the concentration of formic acid increases, the rate of rise of density decreases. For acetic acid, when it is added to water the density increases initially, passing through a maxima at ~0.04 mole fraction and then declines continuously on further addition of acid (dotted line). In the case of propionic acid the shape of this system appears

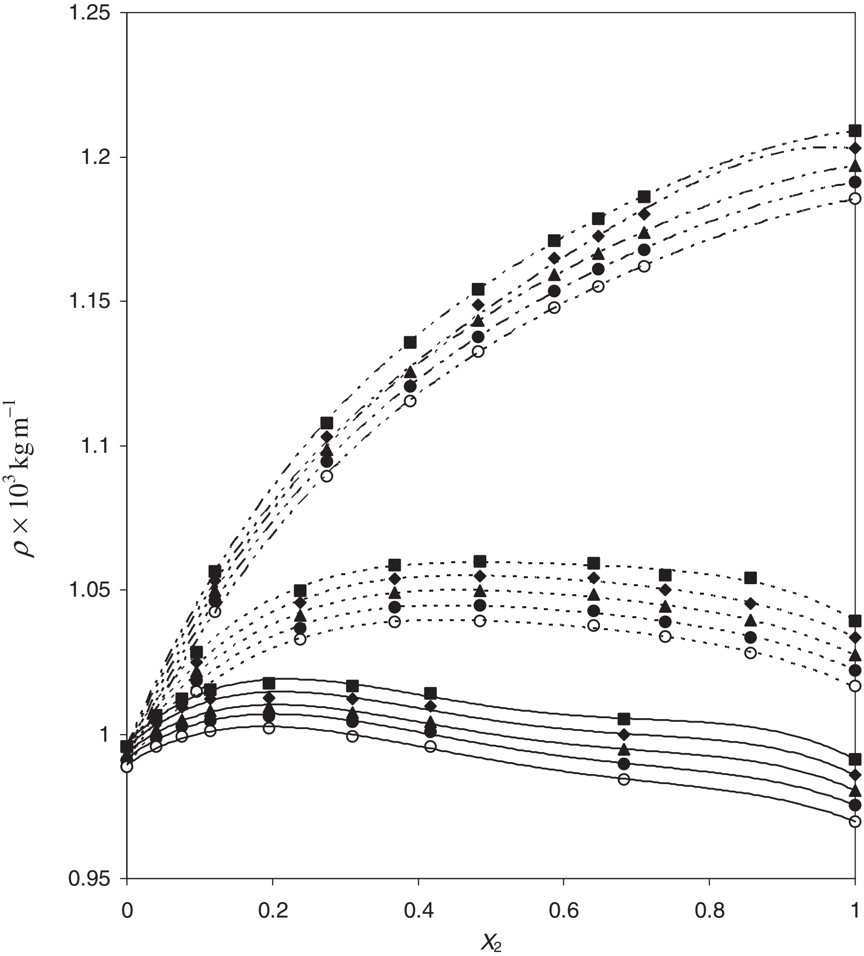

Figure 3. Plots of density (ρ) *versus* X_2 of formic acid (dashed–dotted line), acetic acid (dotted line) and propionic acid (solid line) + 0.1% SE systems at ■, 303.15 K; ◆, 308.15 K; ▲, 313.15 K; ●, 318.15 K; ○, 323.15 K.

at ~0.2 mole fraction of acid (solid line). In the pure state of acids the density has been found to follow the order:

Formic acid > Acetic acid > Propionic acid

The effect of addition of surfactant (SE) to acid systems has also been studied. Only very dilute solutions of SE (0.05% and 0.1% in water) were used for its limited solubility. Figures 2 and 3 show the plots of densities as a function of mole fraction of formic acid, acetic acid, and propionic acid in 0.05% and 0.1% SE solution systems, respectively. From these figures, it is seen that there is no appreciable change of density after adding SE to the systems. In SE systems, density increases slightly in comparison to corresponding systems without SE. This result can be explained by the fact that the concentration of SE was so little that the effect of SE on the experimental systems was negligible. It is expected that if the concentration

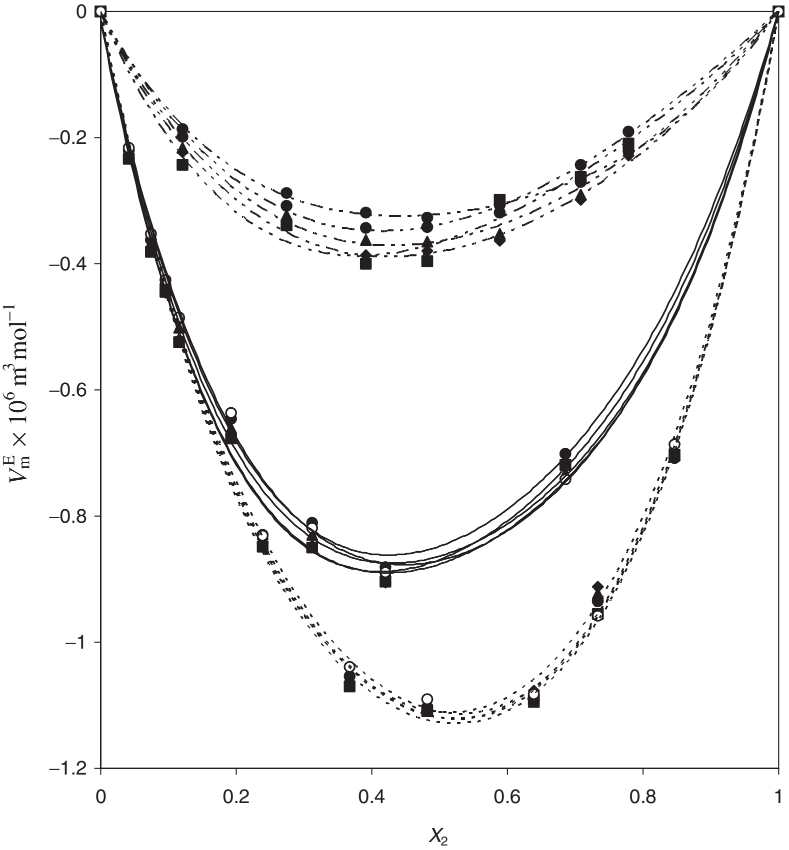

Figure 4. Plots of excess molar volume (V_m^E) *versus* X_2 for formic acid (dashed–dotted line), acetic acid (dotted line) and propionic acid (solid line) in water systems at ■, 303.15 K; ◆, 308.15 K; ▲, 313.15 K; ●, 318.15 K; ○, 323.15 K.

of SE is high enough then the density of the systems may be perturbed significantly and the effect may be observed.

Excess molar volumes, V_m^E for the systems formic acid, acetic acid, and propionic acid in water, 0.05% SE and 0.1% SE in water systems have been plotted in figures 4–6, respectively. The lines are generated by the polynomial equation (2). Examination of these figures reveals the following characteristics:

(a) V_m^E are negative and large in magnitude.
(b) Temperature effects on V_m^E are not very significant.
(c) All systems show well-defined minima.

In general, the sign of V_m^E depends upon the relative magnitude of contractive and expansive effects that arise on mixing of the components. The factors that cause contraction on mixing are:

(a) Strong specific interactions, usually a kind of chemical interaction.
(b) Strong physical interactions, such as dipole–dipole or dipole–induced dipole interactions.

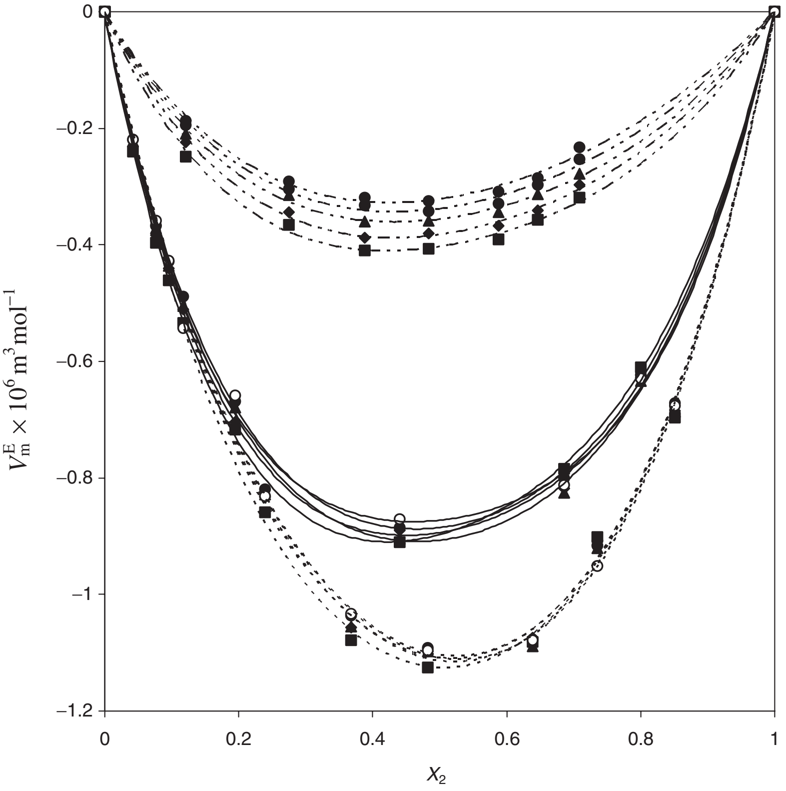

Figure 5. Plots of excess molar volume (V_m^E) *versus* X_2 for formic acid (dashed–dotted line), acetic acid (dotted line) and propionic acid (solid line) + 0.05% SE systems at ■, 303.15 K; ◆, 308.15 K; ▲, 313.15 K; ●, 318.15 K; ○, 323.15 K.

(c) Favorable geometrical fitting of component molecules.
(d) Occupation of void spaces of one component by the other. This is expected when the molecular sizes of the compounds differ by a large magnitude.
(e) Hydrophobic hydration. This is a special type of interaction, which occurs in water-rich regions when an organic solute molecule is surrounded by a network of highly ordered water molecules.

The factors that cause expansion of volume on mixing of the components are:

(a) Dissociation of one component or both of the components.
(b) Steric hindrance.
(c) Geometrical mismatch of the molecules.
(d) Formation of weaker solute–solvent bonds than solute–solute and solvent–solvent bonds.

The large negative V_m^E of the systems, a typical characteristic of hydrophobic solutes, leads to the conviction that the factors causing the volume contraction far outweigh the factor responsible for volume expansion [9]. Of the contractive factors, perhaps the hydrophobic hydration is by far the most effective one in volume reduction, as by this process the hydrophobic molecules occupy the spaces inside the so-called

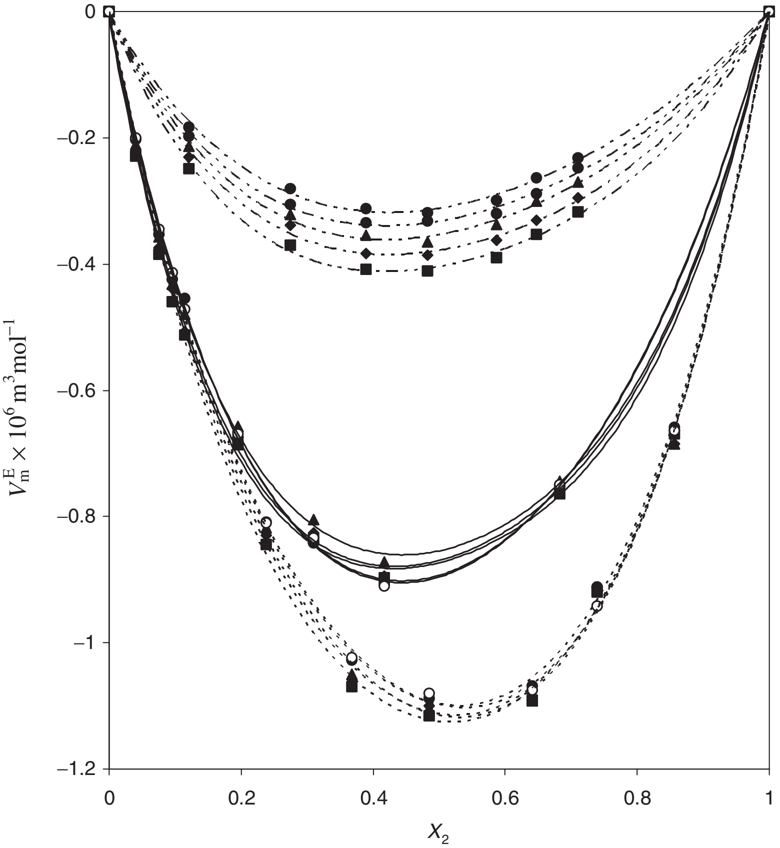

Figure 6. Plots of excess molar volume (V_m^E) *versus* X_2 for formic acid (dashed–dotted line), acetic acid (dotted line) and propionic acid (solid line) + 0.1% SE systems at ■, 303.15 K; ◆, 308.15 K; ▲, 313.15 K; ●, 318.15 K; ○, 323.15 K.

cages formed by the highly structured water molecules, and thus ensure maximum economy of volume, whereas in other cases, shrinkage takes place through strong interactions or attractive forces whose contribution to volume reduction is only relatively small.

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