

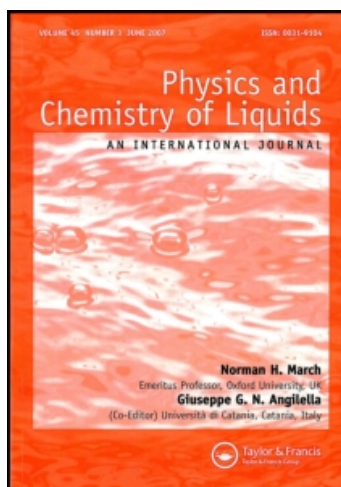
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Publisher *Taylor & Francis*

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## Physics and Chemistry of Liquids

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713646857>

### Densities and excess molar volumes of Methanol, Ethanol and *N*-Propanol in pure Water and in Water + Surf Excel solutions at different temperatures

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**To cite this Article** Kabir, M. H. , Motin, M. A. and Huque, M. E.(2004) 'Densities and excess molar volumes of Methanol, Ethanol and *N*-Propanol in pure Water and in Water + Surf Excel solutions at different temperatures', *Physics and Chemistry of Liquids*, 42: 3, 279 – 290

**To link to this Article:** DOI: 10.1080/0031910042000205346

**URL:** <http://dx.doi.org/10.1080/0031910042000205346>

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# DENSITIES AND EXCESS MOLAR VOLUMES OF METHANOL, ETHANOL AND *n*-PROPANOL IN PURE WATER AND IN WATER + SURF EXCEL SOLUTIONS AT DIFFERENT TEMPERATURES

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(Received 10 January 2004)

Densities,  $\rho$  of the systems Methanol, Ethanol and *n*-Propanol in water and in 0.05 and 0.1% Surf Excel (SE) solutions in water were measured at temperatures from 303.15 to 323.15 K covering the whole composition range. Excess molar volumes,  $V_m^E$  for the systems were found to be negative and large in magnitude. 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 explanation of  $V_m^E$  in terms of hydrophobic hydration and hydrophilic effect of the solutes is offered.

**Keywords:** Excess molar volumes; Methanol; Ethanol; *n*-Propanol; 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, an increase of concentration of the surfactant can cause an abrupt change in several physico-chemical properties of the solution such as osmotic pressure, electrical conductance, surface tension, viscosity, molar volume etc. This behaviour 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 monomeric form of the surfactant in the bulk phase. Surfactants in water solutions generally

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form spherical micelles just above the CMC and associate further to form rod-like micelles at higher concentrations [2].

Interactions between water and alcohols are extremely complex. Both alcohols and water are self-associated liquids through H-bonding. Alcohols possess hydrophilic OH group as well as hydrophobic group. The mode of interaction of these two groups towards water is completely different. The hydrophilic OH group of an alcohol forms 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-alcohol interaction is of considerable 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 the water rich region of aqueous alcohol solutions. Recently, we reported the volumetric and viscometric properties of carbohydrates in water+SE [3] and electrolytes in water+SDS [4] solutions. Here we report the effect of some simple alcohols on the structure of water and water+SE systems. Micelle forming molecules SE may force water to be in a certain structural form in the water+SE system. The perturbations of this forced structure in water+SE system by some alcohols are expected to be appreciable compared with the perturbation caused by these alcohols in the water system alone. The knowledge of interactions of simple smaller hydrophobic molecules with water and with water+surfactant solvent systems may be sometimes useful to interpret many complex systems [7]. The data are also useful for the design of mixing, storage and process equipment.

## 2. EXPERIMENTAL

### Materials

The chemicals used were procured from Aldrich chemical co. with the quoted purities: Methanol (99.5%), Ethanol (99.0%) and *n*-Propanol (99.5%). Surf Excel, a commercial detergent powder, was procured from local market at Rajshahi, Bangladesh. These chemicals were used without any further purification.

### 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  $\pm 0.0001$  g was used for the mass determination. The reproducibility of the density measurements was  $\pm 0.1\%$ , and the uncertainty was estimated to be  $\pm 0.2\%$ .

### Determination of Excess Molar Volume

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

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

where  $X_1$ ,  $M_1$  and  $\rho_1$  are the mole fraction, molar mass and density of component 1 (solvent);  $X_2$ ,  $M_2$  and  $\rho_2$  are the corresponding values of component 2 (organic solutes); and  $\rho_{\text{mix}}$  is the density of the mixture, respectively. The excess molar volumes were fitted to a Redlich–Kister polynomial equation of the form,

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

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

### 3. RESULTS AND DISCUSSION

Densities of Methanol, Ethanol and  $n$ -Propanol in water and 0.05 and 0.1% SE solutions in water were determined at temperatures of 303.15, 308.15, 313.15, 318.15 and 323.15 with an interval of 5 K. The densities of the pure components are shown in Table I together with the literature values for only 313.15 and 323.15 K, wherever possible for comparison. The agreement between the measured results and literature results has been found to be satisfactory.

The densities of the binary and ternary systems are shown in Tables II–IV at different temperatures. The corresponding  $V_m^E$  data are also presented in Tables II–IV. For  $V_m^E$  the fitting coefficients ( $a_i$ ) are shown in Tables V–VII along with standard deviations. Figure 1 shows the plots of densities as a function of mole fraction of Methanol, Ethanol and  $n$ -Propanol in water systems. It shows continuous decrease in density at the same rate on addition of Methanol (dotted–dashed line). For Ethanol (dotted line) and  $n$ -propanol (solid line) in water show a little different variation. In the later case the decrease in density is found to be rapid on addition of solute. The decrement is continuous until the pure state is reached, but at a slower rate. In the pure state the density of alcohol has been found to be in the order of,



TABLE I Densities,  $\rho \times 10^3$  ( $\text{kg m}^{-3}$ ), of pure liquids at different temperatures

Compounds	T/K				
	303.15	308.15	313.15	318.15	323.15
Methanol	0.781266	0.778325	0.773944 0.772347 <sup>a</sup> 0.7725 <sup>b</sup>	0.769285	0.763559 0.762761 <sup>a</sup> 0.7628 <sup>b</sup>
Ethanol	0.798255	0.794517	0.780157 0.772457 <sup>a</sup> 0.77245 <sup>b</sup>	0.785760	0.771336 0.763373 <sup>a</sup> 0.7633 <sup>b</sup>
$n$ -Propanol	0.801745	0.797499	0.793515 0.787598 <sup>a</sup> 0.7875 <sup>b</sup>	0.789183	0.784714 0.778630 <sup>a</sup> 0.7785 <sup>b</sup>

<sup>a</sup>From literature of [5]; <sup>b</sup>From literature of [6].

TABLE II Densities,  $\rho \times 10^3$  ( $\text{kg m}^{-3}$ ), excess molar volumes,  $V_m^E \times 10^6$  ( $\text{m}^3 \text{mol}^{-1}$ ) of methanol in  $\text{H}_2\text{O}$ , 0.05% aqueous SE and 0.1% aqueous SE systems at 303.15, 308.15, 313.15, 318.15 and 323.15 K

$T/\text{K}$	303.15		308.15		313.15		318.15		323.15	
	$\rho$	$V_m^E$	$\rho$	$V_m^E$	$\rho$	$V_m^E$	$\rho$	$V_m^E$	$\rho$	$V_m^E$
<i>Water + methanol systems</i>										
0.0000	0.995670	0.0000	0.994060	0.0000	0.992240	0.0000	0.990250	0.0000	0.988070	0.0000
0.0597	0.978114	-0.1876	0.976368	-0.1900	0.974392	-0.1959	0.972099	-0.1996	0.969665	-0.2074
0.1280	0.961345	-0.4205	0.959474	-0.4257	0.957046	-0.4320	0.954444	-0.4396	0.951674	-0.4542
0.2086	0.942634	-0.6595	0.940198	-0.6575	0.937354	-0.6648	0.934363	-0.6746	0.931224	-0.6959
0.3041	0.921021	-0.8727	0.918355	-0.8700	0.915268	-0.8822	0.911530	-0.8840	0.907826	-0.9072
0.4203	0.894432	-0.9946	0.891060	-0.9756	0.887637	-0.9893	0.883687	-0.9955	0.879717	-1.0280
0.5657	0.862748	-0.9815	0.859633	-0.9728	0.855363	-0.9685	0.851173	-0.9768	0.846996	-1.0206
0.7522	0.827090	-0.7960	0.823714	-0.7783	0.819224	-0.7718	0.814594	-0.7712	0.810141	-0.8239
1.0000	0.781266	0.0000	0.778325	0.0000	0.773944	0.0000	0.769285	0.0000	0.763559	-0.0000
<i>0.05% Aqueous SE + methanol systems</i>										
0.0000	0.995692	0.0000	0.994367	0.0000	0.992556	0.0000	0.990415	0.0000	0.988142	0.0000
0.0601	0.978160	-0.1660	0.976598	-0.1640	0.974668	-0.1639	0.972100	-0.1697	0.969711	-0.1848
0.1134	0.961495	-0.3324	0.959711	-0.3328	0.957110	-0.3437	0.954616	-0.3506	0.95206	-0.3713
0.2101	0.942920	-0.6680	0.940572	-0.6653	0.937530	-0.6769	0.934450	-0.6869	0.931839	-0.6940
0.3059	0.921175	-0.8903	0.918642	-0.8877	0.915732	-0.9048	0.911751	-0.9024	0.908025	-0.9266
0.4425	0.894938	-1.0103	0.887290	-1.0191	0.883385	-1.0250	0.879619	-1.0355	0.875327	-1.0620
0.5700	0.863265	-1.0279	0.859827	-1.0062	0.855578	-1.0030	0.851302	-1.0102	0.847061	-1.0526
0.7551	0.827266	-0.8206	0.823824	-0.7990	0.819378	-0.7947	0.814792	-0.7970	0.809372	-0.8081
1.0000	0.781266	0.0000	0.778325	0.0000	0.773944	0.0000	0.769285	0.0000	0.763559	0.0000
<i>0.1% Aqueous SE + methanol systems</i>										
0.0000	0.995862	0.0000	0.994528	0.0000	0.992988	0.0000	0.991011	0.0000	0.988850	0.0000
0.0597	0.979037	-0.2054	0.977831	-0.2108	0.976066	-0.2163	0.973914	-0.2463	0.971547	-0.2514
0.1280	0.963726	-0.4709	0.961969	-0.4717	0.959706	-0.4775	0.957355	-0.4905	0.954586	-0.5050
0.2098	0.945278	-0.7310	0.943289	-0.7334	0.940550	-0.7399	0.937523	-0.7215	0.934342	-0.7500
0.3070	0.921479	-0.9068	0.918873	-0.9004	0.916031	-0.9160	0.911766	-0.9041	0.907858	-0.9422
0.4235	0.894150	-1.0091	0.891610	-1.0106	0.888038	-1.0175	0.884249	-1.0490	0.880397	-1.0657
0.5698	0.862441	-0.9978	0.859079	-0.9772	0.855432	-0.9931	0.852356	-1.0218	0.848182	-1.0867
0.7557	0.827864	-0.8492	0.824467	-0.8290	0.819978	-0.8220	0.813830	-0.7567	0.809919	-0.8326
1.0000	0.781266	0.0000	0.778325	0.0000	0.773944	0.0000	0.769587	0.0000	0.763559	0.0000

TABLE III Densities,  $\rho \times 10^3$  ( $\text{kg m}^{-3}$ ), excess molar volumes,  $V_m^E \times 10^6$  ( $\text{m}^3 \text{mol}^{-1}$ ) of ethanol in  $\text{H}_2\text{O}$ , 0.05% aqueous SE and 0.1% aqueous SE systems at 303.15, 308.15, 313.15, 318.15 and 323.15 K

$T/\text{K}$	303.15		308.15		313.15		318.15		323.15	
	$\rho$	$V_m^E$	$\rho$	$V_m^E$	$\rho$	$V_m^E$	$\rho$	$V_m^E$	$\rho$	$V_m^E$
<i>Water + ethanol systems</i>										
0.0000	0.995670	0.0000	0.994060	0.0000	0.992240	0.0000	0.990250	0.0000	0.988070	0.0000
0.0950	0.963428	-0.3923	0.961909	-0.4109	0.959289	-0.4127	0.956196	-0.4069	0.953096	-0.3445
0.1722	0.942749	-0.6531	0.938920	-0.6553	0.935741	-0.6553	0.932085	-0.6499	0.922848	-0.5612
0.2382	0.923805	-0.7970	0.920711	-0.8037	0.916553	-0.7741	0.912908	-0.7719	0.908869	-0.7315
0.3661	0.892544	-0.9080	0.888334	-0.9058	0.884321	-0.8895	0.880237	-0.8637	0.875629	-0.8517
0.4821	0.868408	-0.8756	0.864578	-0.8608	0.861202	-0.8641	0.856614	-0.8494	0.852163	-0.8479
0.6358	0.842689	-0.7396	0.838735	-0.7223	0.834338	-0.7226	0.829955	-0.7164	0.825329	-0.6900
0.7918	0.823025	-0.5858	0.819232	-0.5805	0.814833	-0.5770	0.810202	-0.5595	0.805969	-0.5699
1.0000	0.798255	0.0000	0.794517	0.0000	0.780157	0.0000	0.785760	0.0000	0.771336	0.0000
<i>0.05% Aqueous SE + ethanol systems</i>										
0.0000	0.995692	0.0000	0.994367	0.0000	0.992596	0.0000	0.990415	0.0000	0.988242	0.0000
0.0949	0.964711	-0.4196	0.961966	-0.4061	0.959375	-0.4082	0.956312	-0.4058	0.952935	-0.3968
0.1729	0.943459	-0.7080	0.940018	-0.6861	0.936300	-0.6723	0.932688	-0.6666	0.928841	-0.6556
0.2386	0.925211	-0.8401	0.921722	-0.8223	0.917409	-0.7986	0.913940	-0.8041	0.909440	-0.7801
0.3680	0.893140	-0.9644	0.888798	-0.9047	0.884631	-0.9231	0.880369	-0.9130	0.875850	-0.8944
0.4850	0.869902	-0.9391	0.865061	-0.8990	0.861822	-0.9147	0.857327	-0.9008	0.852760	-0.8849
0.6401	0.843829	-0.8243	0.839166	-0.7699	0.834833	-0.7641	0.830213	-0.7470	0.825781	-0.7417
0.7945	0.825497	-0.6881	0.819518	-0.6118	0.815133	-0.6113	0.810598	-0.5988	0.806188	-0.5989
1.0000	0.798255	0.0000	0.794517	0.0000	0.790157	0.0000	0.785760	0.0000	0.781336	0.0000
<i>0.1% Aqueous SE + ethanol systems</i>										
0.0000	0.995862	0.0000	0.994528	0.0000	0.992988	0.0000	0.991011	0.0000	0.988850	0.0000
0.0948	0.964872	-0.4193	0.962066	-0.4045	0.959496	-0.4028	0.956610	-0.4014	0.953440	-0.3971
0.1734	0.943695	-0.7164	0.940083	-0.6904	0.936394	-0.6759	0.932946	-0.6695	0.929189	-0.6608
0.2386	0.925871	-0.8577	0.922271	-0.8368	0.918069	-0.8119	0.914467	-0.7762	0.910011	-0.7885
0.3684	0.893207	-0.9482	0.888953	-0.9117	0.884852	-0.9395	0.880391	-0.8802	0.875984	-0.8657
0.4854	0.870037	-0.9662	0.865198	-0.9071	0.861939	-0.9287	0.857482	-0.8750	0.852231	-0.8792
0.6400	0.844081	-0.8353	0.839263	-0.7732	0.834619	-0.7496	0.829911	-0.7270	0.825917	-0.7442
0.7946	0.823619	-0.6858	0.819606	-0.6770	0.815468	-0.6275	0.810744	-0.6061	0.805990	-0.5849
1.0000	0.798255	0.0000	0.794517	0.0000	0.790157	0.0000	0.785760	0.0000	0.781336	0.0000

TABLE IV Densities,  $\rho \times 10^3$  ( $\text{kg m}^{-3}$ ), excess molar volumes,  $V_m^E \times 10^6$  ( $\text{m}^3 \text{mol}^{-1}$ ) of *n*-propanol in  $\text{H}_2\text{O}$ , 0.05% aqueous SE and 0.1% aqueous SE systems at 303.15, 308.15, 313.15, 318.15 and 323.15 K

<i>T</i> /K	303.15		308.15		313.15		318.15		323.15	
	$\rho$	$V_m^E$	$\rho$	$V_m^E$	$\rho$	$V_m^E$	$\rho$	$V_m^E$	$\rho$	$V_m^E$
<i>Water + n-propanol systems</i>										
0.0000	0.995670	0.0000	0.994060	0.0000	0.992240	0.0000	0.990250	0.0000	0.988070	0.0000
0.0738	0.962596	-0.3214	0.959173	-0.3274	0.956462	-0.3237	0.953415	-0.3177	0.950154	-0.3108
0.1925	0.913671	-0.4876	0.910216	-0.4494	0.906194	-0.4219	0.902539	-0.4148	0.898593	-0.4037
0.3067	0.881446	-0.4547	0.877914	-0.4563	0.873896	-0.4334	0.869516	-0.4080	0.865478	-0.4029
0.4143	0.859582	-0.4133	0.855464	-0.3973	0.851210	-0.3666	0.846845	-0.3454	0.842549	-0.3353
0.5764	0.835717	-0.2607	0.831544	-0.2793	0.827525	-0.2647	0.823152	-0.2483	0.818518	-0.2246
0.6817	0.822801	-0.1888	0.819344	-0.1407	0.815228	-0.1214	0.810975	-0.1160	0.806287	-0.0896
0.8190	0.810919	-0.0510	0.806885	-0.0423	0.802662	-0.0686	0.798256	-0.0824	0.793584	-0.1070
1.0000	0.801745	0.0000	0.797499	0.0000	0.793515	0.0000	0.789183	0.0000	0.784714	0.0000
<i>0.05% Aqueous SE + n-propanol systems</i>										
0.0000	0.995692	0.0000	0.994367	0.0000	0.992556	0.0000	0.990415	0.0000	0.988142	0.0000
0.0740	0.961584	-0.3083	0.958783	-0.3160	0.956508	-0.3222	0.952818	-0.3038	0.949373	-0.2942
0.1933	0.912918	-0.4623	0.909909	-0.4442	0.906194	-0.4262	0.902130	-0.4082	0.898249	-0.4000
0.3079	0.880896	-0.4433	0.877562	-0.4494	0.873699	-0.4328	0.869252	-0.4066	0.864995	-0.3938
0.4174	0.858102	-0.3662	0.854735	-0.3835	0.850702	-0.3634	0.846139	-0.3343	0.841821	-0.3239
0.5762	0.835325	-0.2355	0.831797	-0.2911	0.827548	-0.2623	0.823290	-0.2544	0.818656	-0.2014
0.6823	0.822306	-0.1079	0.819817	-0.1753	0.815572	-0.1473	0.811427	-0.1508	0.806545	-0.1414
0.8195	0.810194	-0.0465	0.807017	-0.0502	0.802662	-0.0671	0.798542	-0.0768	0.793671	-0.0973
1.0000	0.801745	0.0000	0.797499	0.0000	0.793515	0.0000	0.789183	0.0000	0.784714	0.0000
<i>0.1% Aqueous SE + n-propanol systems</i>										
0.0000	0.995862	0.0000	0.994528	0.0000	0.992988	0.0000	0.991011	0.0000	0.988850	0.0000
0.0745	0.961653	-0.3236	0.959173	-0.3289	0.956450	-0.2972	0.952841	-0.3010	0.949611	-0.2947
0.1931	0.913801	-0.4653	0.910339	-0.4531	0.906301	-0.4211	0.902414	-0.4063	0.898399	-0.3927
0.3079	0.881138	-0.4509	0.877365	-0.4395	0.873849	-0.4334	0.869434	-0.4064	0.865095	-0.3888
0.4181	0.859030	-0.4147	0.855044	-0.4025	0.850813	-0.3699	0.846492	-0.3512	0.841953	-0.3289
0.5761	0.836820	-0.3239	0.832762	-0.3480	0.828376	-0.3093	0.823819	-0.2819	0.819299	-0.2657
0.6831	0.823383	-0.1858	0.820140	-0.2016	0.815637	-0.1542	0.811627	-0.1664	0.806760	-0.1277
0.8197	0.815786	-0.0418	0.807566	-0.0445	0.802948	-0.0442	0.798652	-0.0486	0.794242	-0.0513
1.0000	0.801745	0.0000	0.797499	0.0000	0.793515	0.0000	0.789183	-0.0000	0.784714	0.0000

TABLE V Coefficient,  $a_i$ , of Redlich–Kister Eq. (2) expressing  $V_m^E \times 10^6$  in  $\text{m}^3 \text{mol}^{-1}$  and standard deviation,  $\sigma$  for the methanol systems

Systems	$T/\text{K}$	$a_0$	$a_1$	$a_2$	$a_3$	$\sigma$
Water + methanol systems	303.15	-4.0237	0.3296	-0.5861	-2.0559	0.0018
	308.15	-3.9737	0.3371	-0.5613	-1.8259	0.0060
	313.15	-3.9886	0.4767	-0.5531	-1.9637	0.0047
	318.15	-4.0179	0.4514	-0.4915	-1.7440	0.0032
	323.15	-4.1712	0.2871	-0.6689	-1.7364	0.0028
0.05% Aqueous SE + methanol systems	303.15	-4.1513	0.2680	-0.4034	-2.5529	0.0165
	308.15	-4.1216	0.4404	-0.2929	-2.6980	0.0091
	313.15	-4.1285	0.6141	-0.3831	-2.9649	0.0083
	318.15	-4.1601	0.5600	-0.3287	-2.7065	0.0084
	323.15	-4.3091	0.3793	-0.0220	-1.9514	0.0078
0.1% Aqueous SE + methanol systems	303.15	-4.0636	0.3914	-1.5688	-2.5154	0.0115
	308.15	-4.0173	0.5163	-1.5371	-2.5334	0.0115
	313.15	-4.0747	0.5230	-1.3383	-2.2653	0.0094
	318.15	-4.2206	0.2108	-0.0494	0.0574	0.0082
	323.15	-4.3959	0.0403	-0.3552	-0.0721	0.0071

TABLE VI Coefficient,  $a_i$ , of Redlich–Kister Eq. (2) expressing  $V_m^E \times 10^6$  in  $\text{m}^3 \text{mol}^{-1}$  and standard deviation,  $\sigma$  for the Ethanol systems

Systems	$T/\text{K}$	$a_0$	$a_1$	$a_2$	$a_3$	$\sigma$
Water + ethanol systems	303.15	-3.4418	1.5314	-1.6761	-2.1953	0.0040
	308.15	-3.3811	1.6108	-1.8752	-2.2021	0.0027
	313.15	-3.3712	1.3652	-1.7252	-1.5944	0.0095
	318.15	-3.3164	1.2826	-1.6603	-1.2640	0.0076
	323.15	-3.2753	1.4493	-1.3351	-2.7384	0.0147
0.05% Aqueous SE + ethanol systems	303.15	-3.7263	1.1466	-2.1466	-1.9763	0.0172
	308.15	-3.5222	1.3136	-1.8860	-1.7221	0.0150
	313.15	-3.5638	1.3202	-1.6447	-1.7829	0.0118
	318.15	-3.5340	1.3586	-1.5740	-1.7308	0.0196
	323.15	-3.4485	1.2988	-1.7067	-1.8278	0.0109
0.1% Aqueous SE + ethanol systems	303.15	-3.7634	1.1614	-2.1064	-1.9023	0.0193
	308.15	-3.5489	1.3994	-1.9236	-1.9497	0.0174
	313.15	-3.5774	1.6021	-1.8149	-2.6496	0.0171
	318.15	-3.3827	1.3073	-1.9788	-1.8885	0.0170
	323.15	-3.4179	1.1562	-1.6712	-1.2775	0.0169

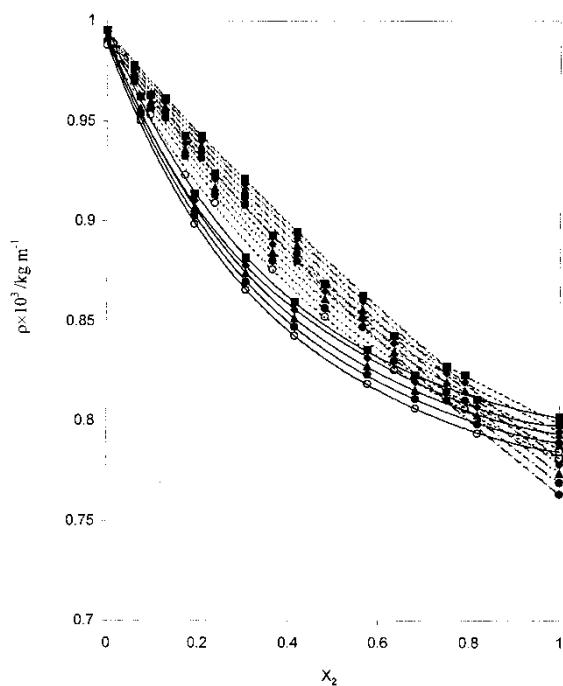
The effect of addition of surfactant (SE) to alcohol systems has also been studied. Only very dilute solutions of SE (0.05 and 0.1% in water) were used for its limited solubility. Figures 3 and 4 show the plots of densities as a function of mole fraction of Methanol, Ethanol, and *n*-Propanol in 0.05 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 of SE is high enough then the density of the systems may be perturbed significantly and the effect may be observed.

Excess molar volume,  $V_m^E$  for the systems of Methanol, Ethanol and *n*-Propanol in water, 0.05% SE and 0.1% SE in water systems have been plotted in Figures 4–6,



TABLE VII Coefficient,  $a_i$ , of Redlich–Kister Eq. (2) expressing  $V_m^E \times 10^6$  in  $\text{m}^3 \text{mol}^{-1}$  and standard deviation,  $\sigma$  for the  $n$ -propanol systems

Systems	$T/\text{K}$	$a_0$	$a_1$	$a_2$	$a_3$	$\sigma$
Water + $n$ -propanol systems	303.15	-1.3293	1.5048	-1.1625	1.9119	0.0129
	308.15	-1.3575	1.4625	-0.1093	3.0375	0.0137
	313.15	-1.2743	1.3385	0.0824	3.4459	0.0176
	318.15	-1.2033	1.2216	0.1063	3.6996	0.0124
	323.15	-1.1385	1.3755	0.2208	3.5234	0.0138
0.05% Aqueous SE + $n$ -propanol systems	303.15	-1.1459	1.8213	-1.3360	1.0758	0.0172
	308.15	-1.3989	1.1819	0.0880	3.5710	0.0103
	313.15	-1.2915	1.2191	0.0505	3.6128	0.0140
	318.15	-1.2351	1.0209	0.1628	3.8689	0.0133
	323.15	-1.0026	1.3703	-1.7579	0.8747	0.0173
0.1% Aqueous SE + $n$ -propanol systems	303.15	-1.4505	1.2063	-0.5809	2.6642	0.0156
	308.15	-1.5359	0.7988	0.3870	4.5395	0.0073
	313.15	-1.3881	1.1223	0.2705	3.3937	0.0154
	318.15	-1.3082	0.9178	0.1647	3.7520	0.0093
	323.15	-1.2037	1.0145	0.0765	3.4580	0.0137

FIGURE 1 Plots of density ( $\rho$ ) versus  $X_2$  for methanol (dashed–dotted line), ethanol (dotted line) and propanol (solid line) in water systems at  $\blacksquare$ , 303.15 K;  $\blacklozenge$ , 308.15 K;  $\blacktriangle$ , 313.15 K;  $\bullet$ , 318.15 K;  $\circ$ , 323.15 K.

respectively. The lines are generated by the polynomial equation 2. Examination of these figures reveals the following characteristics:

- $V_m^E$  are negative and large in magnitude.
- Temperature effects on  $V_m^E$  are not very significant.
- All systems show well defined minima.

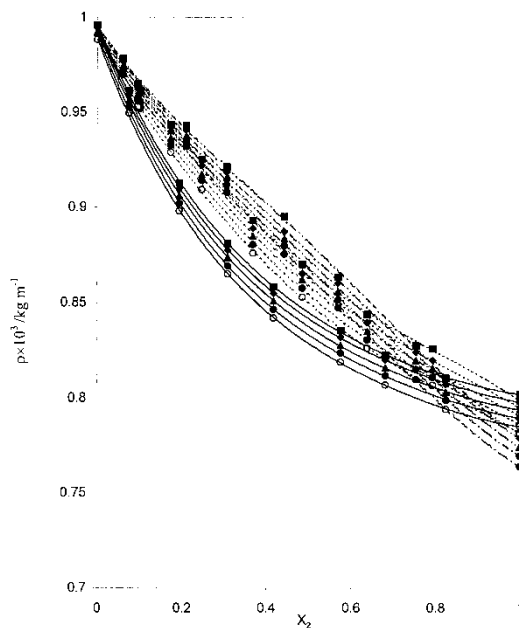


FIGURE 2 Plots of density ( $\rho$ ) versus  $X_2$  for ethanol (dashed-dotted line), ethanol (dotted line) and propanol (solid line) in 0.05% aqueous SE systems at ■, 303.15 K; ◆, 308.15 K; ▲, 313.15 K; ●, 318.15 K; ○, 323.15 K.

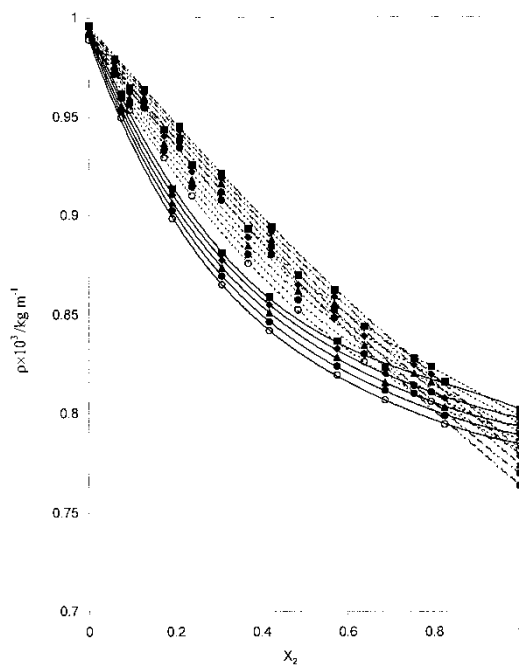


FIGURE 3 Plots of density ( $\rho$ ) versus  $X_2$  for methanol (dashed-dotted line), ethanol (dotted line) and propanol (solid line) in 0.1% aqueous SE systems at ■, 303.15 K; ◆, 308.15 K; ▲, 313.15 K; ●, 318.15 K; ○, 323.15 K.

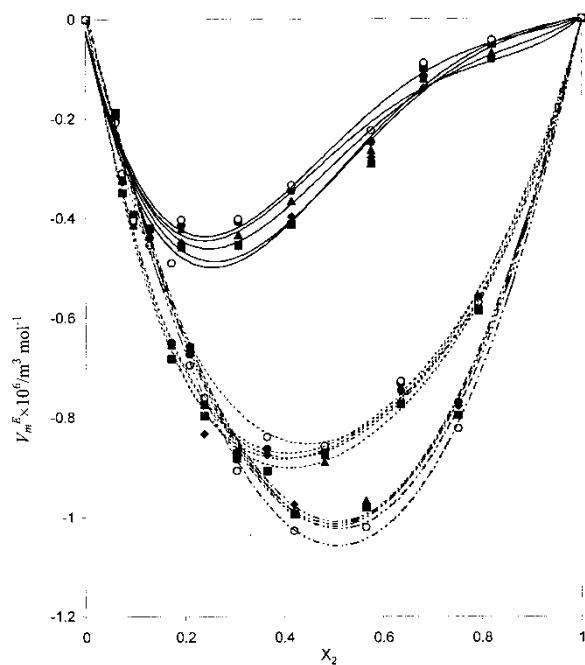


FIGURE 4 Plots of excess molar volume ( $V_m^E$ ) versus  $X_2$  for methanol (dashed-dotted line), ethanol (dotted line) and propanol (solid line) in water systems at ■, 303.15 K; ◆, 308.15 K; ▲, 313.15 K; ●, 318.15 K; ○, 323.15 K.

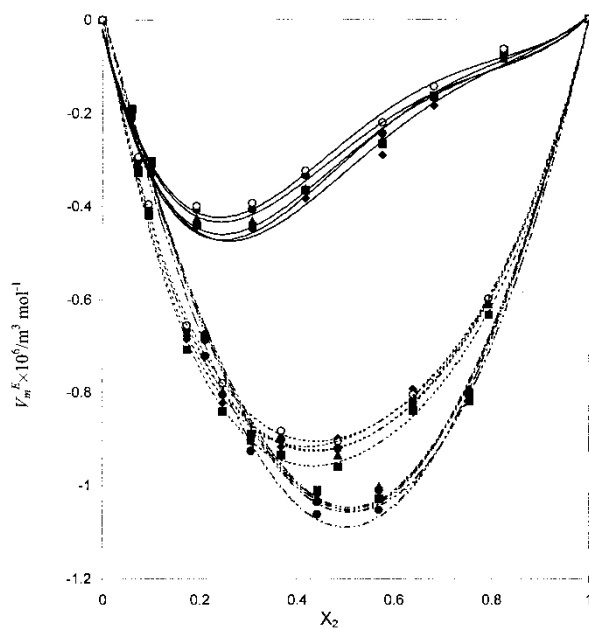


FIGURE 5 Plots of excess molar volume ( $V_m^E$ ) versus  $X_2$  for methanol (dashed-dotted line), ethanol (dotted line) and propanol (solid line) in 0.05% aqueous SE systems systems at ■, 303.15 K; ◆, 308.15 K; ▲, 313.15 K; ●, 318.15 K; ○, 323.15 K.

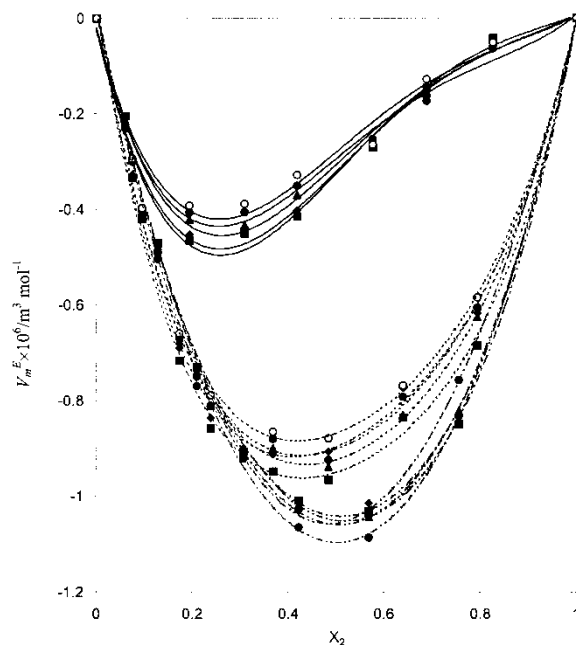


FIGURE 6 Plots of excess molar volume ( $V_m^E$ ) versus  $X_2$  for methanol (dashed–dotted line), ethanol (dotted line) and propanol (solid line) in 0.1% aqueous SE systems at ■, 303.15 K; ◆, 308.15 K; ▲, 313.15 K; ●, 318.15 K; ○, 323.15 K.

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:

- Strong specific interactions; usually a kind of chemical interaction.
- Strong physical interactions, such as dipole–dipole or dipole-induced dipole interactions.
- Favorable geometrical fitting of component molecules.
- Occupation of void spaces of one component by the other. This is expected when the molecular sizes of the compounds differ by a large amount.
- Hydrophobic hydration. This is a special type of interaction, which occurs in the water rich region 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:

- Dissociation of one component or both of the components.
- Steric hindrance.
- Geometrical mismatch of the molecules.
- Formation of weaker solute–solvent bond 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 conclusion that the factors causing the volume contraction far outweigh the factor responsible for volume expansion [8]. Of the contractive factors, 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 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.

### ***Acknowledgment***

The authors acknowledge that the Department of Chemistry, University of Rajshahi provided laboratory facilities and other relevant support for the work.

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