of Britton (*2*) and Khripin (*3*) are included (Figure 1), there is an overall change in log K_{sp} from −6.22 to −6.38 from high to low potassium concentrations, respectively. In our analysis, we have ignored the effects of the ternary interaction parameters $\theta_{K^+-Al^{3+}}$ and $\psi_{K^+-Al^{3+}-SO_4^{2-}}$, setting them to zero in our calculations. We tried to derive values for these parameters by performing a regression analysis on the solubility data. However, we found that only 40% of the total variation can be explained by invoking these parameters and therefore do not recommend this approach. It is possible that the slight systematic variation observed in the solubility product may be due to uncertainties in the binary interaction parameters for K_2SO_4 or $Al_2(SO_4)_3$ that are recorded in Table I. One possible explanation is that the K_2SO_4 interaction parameters are applied to inappropriate solution concentration conditions in this study. The K_2SO_4 parameters were determined by Pitzer and Mayorga (*6*) from analysis of isopiestic data up to concentrations of 0.7 *m*, i.e. saturation with respect to arcanite (K_2SO_4). No C^ϕ parameter could be derived by these authors at such low concentrations. In this study, however, the parameters are applied to calculate solubility products at sulfate concentrations as high as 3 *m* at the low K_2SO_4 mole fraction end of Figure 1.

At this time, no conclusion can be drawn as to the cause of the trend in the solubility products and no recommendation is made to add or adjust any parameters in Table I that describe equilibria in mixed $K_2SO_4 + Al_2(SO_4)_3$ solutions. In modeling aluminum potassium sulfate dodecahydrate solubility in mixed salt solutions, we recommend using an average log K_{sp} of −6.3 ± 0.1 for 25 °C. From the standard chemical potentials ($\mu°/RT$) of H_2O, K^+, Al^{3+}, and SO_4^{2-} listed in Reardon (*1*), a $\mu°/RT$ value of −2074.62 ± 0.23 for $KAl(SO_4)_2 \cdot 12H_2O$ is derived, only slightly and not significantly different than the value recommended in this reference.

Conclusions

A marked trend in the solubility product of $KAl(SO_4)_2 \cdot 12H_2O$ with decreasing mole fraction of potassium in solution has been observed for previously published solubility data. This trend is noted for the solubility measurements of two independent studies when the Pitzer ion interaction model is used to calculate ion activity coefficients. The experimental results of this study show that the calculated solubility products are very consistent and do not vary substantively with potassium concentration. In examining the experimental techniques used in previous studies, it appears that the method used to evaluate the potassium content of the solution is the reason for this disparity. Previous authors determined the concentration of Al^{3+} and SO_4^{2-} analytically and then found the concentration of K^+ by charge balance difference. This method can produce large uncertainties in the estimation of potassium content when the concentrations of Al^{3+} and SO_4^{2-} are large compared to K^+.

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Partial Molar Volumes of Ethylene Glycol and Water in Their Mixtures

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The densities of ethylene glycol (EG)–water (W) mixtures were measured over the whole composition range at 5, 15, 25, 35, and 45 °C. The apparent and partial molar volumes and partial molar thermal expansions were evaluated for both components. The limiting partial molar volumes of EG and W are smaller than the molar volumes of pure EG and W, respectively, at all temperatures. A characteristic minimum or maximum was observed in the partial molar volume or thermal expansion of EG vs composition curve at low mole fraction. Mostly the volumetric behavior of EG–W mixtures exhibits a minor deviation from ideality compared to monohydric alcohol–water mixtures.

Introduction

In the previous papers, we reported the partial molar volumes of some alcohols V_A and of water V_W in their solutions (1–3). At low mole fraction X of alcohol the V_A vs X curve passes through a sharp minimum, as has been well-known for a number of aqueous solutions of nonelectrolytes. In the alcohol-rich region, on the other hand, a similar minimum was found for the V_W vs X curve in *tert*-butyl alcohol, but not in the other alcohol solutions. These peculiarities of the volumetric behavior appear to be observed in the aqueous mixtures of nonelectrolytes with a polar group. Little anomaly has been observed in the partial molar volume for the mixtures of water with hydrophobic compounds such as benzene or alkylbenzenes (*4*). In this paper we present the density data for the mixtures of water with ethylene glycol, which is bifunctional

Table I. Densities of Pure Ethylene Glycol

	ρ/(g cm^{-3})			
t/°C	this work	lit.		
5	1.124 265			
15	1.117 244	1.117 10[a]	1.116 93[b]	
25	1.110 212	1.110 0[a]	1.109 97[b]	1.109 89[c]
35	1.103 164	1.102 68[b]		
45	1.096 021			

[a] Reference 7. [b] Reference 8. [c] Reference 9.

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Table II. Densities and Apparent Molar Volumes for Aqueous Solutions of Ethylene Glycol at 5, 15, 25, 35, and 45 °C

wt % of EG	$10^3(\rho - \rho_W)$/ (g cm^{-3})	$V\phi_{EG}$/ (cm^3 mol^{-1})	$V\phi_W$/ (cm^3 mol^{-1})	wt % of EG	$10^3(\rho - \rho_W)$/ (g cm^{-3})	$V\phi_{EG}$/ (cm^3 mol^{-1})	$V\phi_W$/ (cm^3 mol^{-1})	wt % of EG	$10^3(\rho - \rho_W)$/ (g cm^{-3})	$V\phi_{EG}$/ (cm^3 mol^{-1})	$V\phi_W$/ (cm^3 mol^{-1})
At 5 °C											
0.1938	0.260	53.744	18.015	2.9011	3.935	53.684	18.002	28.083	41.011	53.363	17.807
0.4122	0.553	53.748	18.014	3.863	5.254	53.672	17.998	31.167	45.664	53.373	17.775
0.6156	0.825	53.759	18.013	4.965	6.788	53.641	17.992	34.050	49.993	53.391	17.743
0.8831	1.188	53.729	18.012	6.436	8.859	53.602	17.984	37.071	54.488	53.418	17.710
1.0846	1.459	53.732	18.011	8.592	11.930	53.553	17.971	40.166	59.037	53.455	17.674
1.3156	1.771	53.729	18.010	10.887	15.249	53.507	17.955	43.146	63.349	53.499	17.639
1.5845	2.137	53.716	18.009	13.815	19.539	53.459	17.934	46.137	67.599	53.551	17.604
1.8452	2.491	53.711	18.007	16.749	23.897	53.420	17.911	48.752	71.001	53.598	17.574
2.0913	2.827	53.703	18.006	19.606	28.184	53.392	17.887	51.092	74.452	53.652	17.544
2.3472	3.176	53.698	18.005	22.397	32.396	53.373	17.862	53.273	77.383	53.701	17.517
2.6423	3.579	53.693	18.004	25.466	37.047	53.363	17.833				
At 15 °C											
0.1861	0.236	54.241	18.031	2.9269	3.752	54.183	18.019	29.307	40.223	53.920	17.835
0.3754	0.476	54.243	18.030	4.139	5.336	54.150	18.014	32.272	44.412	53.931	17.807
0.6459	0.820	54.236	18.029	5.541	7.186	54.118	18.007	35.538	48.996	53.952	17.775
0.8693	1.104	54.236	18.028	7.465	9.751	54.080	17.997	38.512	53.133	53.979	17.745
1.0722	1.362	54.236	18.027	9.364	12.311	54.048	17.986	41.488	57.226	54.012	17.714
1.3220	1.682	54.226	18.026	12.244	16.243	54.007	17.969	44.279	61.011	54.049	17.684
1.5898	2.025	54.220	18.025	14.745	19.697	53.978	17.952	47.113	64.796	54.093	17.653
1.8084	2.306	54.213	18.024	17.926	24.137	53.949	17.929	49.493	67.925	54.133	17.627
2.0475	2.614	54.206	18.023	20.870	28.279	53.930	17.907	51.774	70.874	54.176	17.602
2.3001	2.940	54.199	18.022	23.741	32.338	53.920	17.884	53.418	72.967	54.208	17.583
2.5639	3.282	54.190	18.021	26.600	36.390	53.916	17.859				
At 25 °C											
0.1754	0.212	54.707	18.068	2.9382	3.620	54.587	18.057	30.118	39.209	54.431	17.884
0.4140	0.503	54.670	18.067	3.906	4.816	54.590	18.053	33.176	43.285	54.445	17.858
0.6553	0.799	54.645	18.066	5.130	6.348	54.575	18.047	36.313	47.441	54.465	17.830
0.8921	1.089	54.639	18.065	7.084	8.814	54.552	18.038	39.116	51.124	54.490	17.804
1.1391	1.391	54.638	18.064	9.285	11.627	54.524	18.027	42.195	55.129	54.522	17.775
1.3799	1.688	54.627	18.063	12.334	15.575	54.489	18.011	45.008	58.738	54.557	17.748
1.6233	1.989	54.617	18.062	15.242	19.385	54.463	17.993	47.672	62.112	54.594	17.721
1.9006	2.332	54.609	18.061	18.374	23.528	54.441	17.973	50.383	65.491	54.636	17.694
2.1619	2.656	54.602	18.060	21.251	27.351	54.431	17.953	52.853	68.520	54.678	17.669
2.4227	2.980	54.595	18.059	24.209	31.303	54.425	17.931				
2.6807	3.300	54.591	18.058	27.250	35.372	54.425	17.907				
At 35 °C											
0.2598	0.303	55.117	18.122	2.8119	3.336	55.013	18.113	29.032	36.236	54.876	17.958
0.4530	0.530	55.096	18.122	3.852	4.590	54.991	18.108	32.138	40.191	54.890	17.934
0.6537	0.765	55.096	18.121	5.089	6.090	54.970	18.103	34.959	43.767	54.908	17.912
0.9094	1.067	55.078	18.120	7.292	8.787	54.937	18.093	38.129	47.756	54.934	17.885
1.0758	1.263	55.075	18.119	9.613	11.650	54.917	18.082	41.340	51.763	54.965	17.857
1.2978	1.527	55.061	18.119	12.164	14.828	54.896	18.068	44.362	55.488	54.999	17.831
1.5145	1.785	55.050	18.118	14.697	18.006	54.882	18.054	47.241	58.989	55.036	17.804
1.7619	2.081	55.037	18.117	17.316	21.305	54.874	18.039	49.913	62.190	55.075	17.779
2.0210	2.389	55.033	18.116	20.070	24.801	54.867	18.021	52.709	65.486	55.119	17.753
2.2947	2.716	55.026	18.115	23.170	28.751	54.865	18.001	55.123	68.284	55.159	17.730
2.5161	2.982	55.019	18.114	26.135	32.538	54.868	17.980				
At 45 °C											
0.3099	0.350	55.534	18.192	2.9114	3.349	55.424	18.183	27.899	33.547	55.319	18.046
0.5129	0.579	55.541	18.191	3.876	4.472	55.411	18.179	31.138	37.513	55.334	18.023
0.6755	0.763	55.537	18.191	5.116	5.929	55.389	18.174	34.340	41.419	55.353	17.999
0.8815	1.000	55.508	18.190	6.855	7.987	55.365	18.166	37.765	45.561	55.381	17.973
1.1114	1.263	55.497	18.189	8.634	10.108	55.346	18.158	40.860	49.272	55.410	17.948
1.3667	1.554	55.495	18.188	10.818	12.725	55.330	18.147	43.760	52.716	55.441	17.925
1.5675	1.786	55.482	18.188	13.345	15.764	55.321	18.135	46.525	55.967	55.474	17.901
1.8360	2.094	55.477	18.187	16.148	19.165	55.311	18.119	48.919	58.746	55.506	17.880
2.0573	2.352	55.462	18.186	19.126	22.802	55.305	18.102	51.489	61.688	55.542	17.858
2.3003	2.633	55.455	18.185	21.998	26.317	55.305	18.085	53.972	64.484	55.581	17.836
2.6055	2.992	55.434	18.184	25.059	30.061	55.312	18.065				

and more hydrophilic than monohydric alcohols.

Experimental Section

Ethylene glycol (Merck) was stored over molecule sieve 4A and used without further purification. The water content, determined by the Karl-Fischer method, was less then 0.015%. The densities of pure ethylene glycol are given in Table I. Water was distilled by using a quartz still and degassed before using.

All solutions were prepared by successive addition of a stock solution or a pure component to a known quantity of another component up to about 50 wt %. The addition was carried out by weight in a mixing chamber connected to the density measuring cell with a Teflon tube and a flow pump.

Densities of the solutions were measured relative to densities of the pure solvents with an oscillating-tube densimeter (Anton Paar, DMA 60) operated in a phase locked loop mode using two measuring cells (DMA 601). Details of the apparatus and procedure have been described elsewhere (*5*). The temperature of the cells were maintained within ±0.002 °C by using a quartz temperature controller. The densimeter was calibrated at each temperature with water (*6*) and dry air.

Results and Discussion

The density differences between solutions and pure solvent at various temperatures are given in Table II for water-rich regions and in Table III for glycol-rich regions. The apparent molar volume $V\phi_2$ of component 2 in a mixture of components 1 and 2 is given by

$$V\phi_2 = X_1M_1(\rho_1 - \rho)/X_2\rho_1\rho + M_2/\rho \qquad (1)$$

where X and M are the mole fraction and the molar mass of

Table III. Densities and Apparent Molar Volumes for Ethylene Glycol Solutions of Water at 5, 15, 25, 35, and 45 °C

wt % of W	$10^3(\rho - \rho_{EG})$/ (g cm^{-3})	$V\phi_W$/ (cm^3 mol^{-1})	$V\phi_{EG}$/ (cm^3 mol^{-1})	wt % of W	$10^3(\rho - \rho_{EG})$/ (g cm^{-3})	$V\phi_W$/ (cm^3 mol^{-1})	$V\phi_{EG}$/ (cm^3 mol^{-1})	wt % of W	$10^3(\rho - \rho_{EG})$/ (g cm^{-3})	$V\phi_W$/ (cm^3 mol^{-1})	$V\phi_{EG}$/ (cm^3 mol^{-1})
					At 5 °C						
0.1436	-0.105	17.066	55.203	3.667	-2.611	17.041	55.080	28.449	-24.759	17.292	54.217
0.2795	-0.203	17.059	55.198	4.865	-3.469	17.043	55.036	31.138	-27.725	17.325	54.132
0.4805	-0.348	17.056	55.192	5.876	-4.225	17.052	55.000	34.428	-31.489	17.365	54.031
0.6631	-0.478	17.052	55.185	7.121	-5.162	17.062	54.956	37.462	-35.106	17.402	53.942
0.8422	-0.605	17.048	55.179	8.670	-6.360	17.075	54.900	40.680	-39.086	17.443	53.854
1.0474	-0.752	17.048	55.172	9.777	-7.231	17.085	54.860	44.085	-43.437	17.485	53.765
1.2604	-0.903	17.046	55.165	11.267	-8.432	17.099	54.806	47.190	-47.529	17.523	53.690
1.4420	-1.033	17.046	55.159	12.982	-9.848	17.115	54.744	50.961	-52.650	17.569	53.607
1.6327	-1.169	17.045	55.152	14.972	-11.555	17.135	54.673	54.207	-57.178	17.608	53.544
1.7992	-1.289	17.046	55.146	17.278	-13.606	17.160	54.592	57.291	-61.573	17.644	53.492
1.9601	-1.405	17.047	55.141	20.346	-16.482	17.196	54.486	60.216	-65.815	17.678	53.449
2.1419	-1.536	17.047	55.135	22.686	-18.772	17.223	54.406				
2.799	-1.992	17.040	55.111	25.850	-21.996	17.261	54.301				
					At 15 °C						
0.2817	-0.198	17.139	55.546	3.284	-2.313	17.143	55.451	22.844	-18.551	17.316	54.825
0.4889	-0.346	17.146	55.540	4.049	-2.857	17.146	55.426	25.544	-21.214	17.346	54.745
0.6260	-0.447	17.155	55.536	4.778	-3.379	17.148	55.402	28.495	-24.240	17.379	54.660
0.7747	-0.553	17.155	55.531	5.626	-3.993	17.152	55.374	31.439	-27.383	17.413	54.578
0.9716	-0.693	17.155	55.525	6.726	-4.802	17.159	55.338	35.044	-31.381	17.454	54.482
1.1387	-0.811	17.153	55.520	7.889	-5.676	17.168	55.300	38.619	-35.510	17.495	54.392
1.3040	-0.926	17.150	55.514	9.389	-6.825	17.180	55.251	41.711	-39.205	17.530	54.320
1.4579	-1.034	17.149	55.510	11.404	-8.413	17.197	55.185	44.925	-43.159	17.567	54.249
1.6104	-1.144	17.151	55.505	12.841	-9.588	17.211	55.138	48.571	-47.778	17.608	54.176
1.7640	-1.254	17.152	55.500	14.504	-10.979	17.228	55.085	52.243	-52.556	17.648	54.110
1.9607	-1.393	17.151	55.494	16.946	-13.091	17.253	55.007	55.426	-56.791	17.682	54.060
2.1759	-1.544	17.150	55.487	19.886	-15.750	17.284	54.915	58.439	-60.872	17.714	54.020
					At 25 °C						
0.1468	-0.108	17.302	55.903	3.016	-2.122	17.257	55.820	26.121	-21.379	17.446	55.149
0.4313	-0.306	17.264	55.894	4.881	-3.435	17.258	55.763	28.911	-24.172	17.476	55.076
0.6026	-0.430	17.270	55.890	5.908	-4.171	17.262	55.732	32.068	-27.450	17.509	54.997
0.7499	-0.535	17.270	55.886	6.951	-4.934	17.269	55.701	35.121	-30.731	17.542	54.925
0.9449	-0.673	17.268	55.880	7.968	-5.686	17.275	55.670	38.422	-34.401	17.577	54.850
1.1175	-0.795	17.267	55.875	9.526	-6.862	17.286	55.623	41.684	-38.140	17.612	54.781
1.2598	-0.899	17.270	55.871	11.042	-8.037	17.298	55.577	44.921	-41.958	17.645	54.718
1.4475	-1.030	17.268	55.866	12.748	-9.401	17.314	55.527	48.169	-45.885	17.679	54.659
1.6425	-1.168	17.267	55.860	15.070	-11.309	17.335	55.458	51.379	-49.852	17.711	54.607
1.8020	-1.282	17.268	55.856	17.692	-13.551	17.360	55.382	54.513	-53.804	17.743	54.561
1.9887	-1.414	17.267	55.850	20.837	-16.364	17.392	55.293	57.630	-57.800	17.773	54.522
2.1633	-1.538	17.267	55.845	23.521	-18.865	17.419	55.218				
					At 35 °C						
0.1296	-0.091	17.370	56.260	2.2228	-1.545	17.361	56.204	22.126	-17.277	17.505	55.658
0.2897	-0.201	17.357	56.256	3.412	-2.356	17.355	56.170	25.011	-19.952	17.533	55.586
0.4521	-0.311	17.349	56.252	4.368	-3.022	17.357	56.143	28.463	-23.305	17.569	55.503
0.6284	-0.432	17.348	56.247	5.574	-3.873	17.363	56.109	31.993	-26.861	17.604	55.422
0.8659	-0.593	17.345	56.240	6.985	-4.887	17.371	56.069	35.348	-30.365	17.638	55.350
1.0614	-0.741	17.364	56.236	8.682	-6.134	17.382	56.021	38.661	-33.938	17.671	55.282
1.2646	-0.879	17.360	56.230	10.144	-7.236	17.393	55.980	42.278	-37.961	17.707	55.213
1.4749	-1.023	17.358	56.224	11.923	-8.614	17.408	55.930	46.119	-42.359	17.744	55.146
1.6497	-1.144	17.358	56.219	14.598	-10.760	17.432	55.857	49.804	-46.685	17.779	55.088
1.8419	-1.280	17.360	56.214	16.930	-12.702	17.454	55.794	53.385	-50.981	17.812	55.038
2.0182	-1.404	17.361	56.210	19.582	-14.993	17.479	55.723	56.465	-54.740	17.840	55.000
					At 45 °C						
0.1202	-0.076	17.385	56.627	2.0696	-1.379	17.437	56.575	22.151	-17.100	17.613	56.061
0.3131	-0.204	17.414	56.622	2.734	-1.826	17.440	56.557	25.188	-19.874	17.642	55.991
0.4913	-0.321	17.417	56.617	3.550	-2.380	17.444	56.535	28.250	-22.774	17.671	55.923
0.6589	-0.435	17.427	56.613	4.941	-3.345	17.455	56.498	31.213	-25.673	17.700	55.859
0.8040	-0.531	17.428	56.609	7.406	-5.102	17.475	56.432	34.667	-29.162	17.733	55.789
0.9657	-0.639	17.430	56.605	8.695	-6.047	17.485	56.398	38.009	-32.648	17.764	55.725
1.1397	-0.754	17.430	56.600	10.161	-7.147	17.499	56.360	41.369	-36.249	17.796	55.664
1.3246	-0.877	17.430	56.595	11.727	-8.351	17.513	56.319	44.750	-39.957	17.826	55.607
1.4937	-0.993	17.435	56.591	14.012	-10.160	17.534	56.260	48.248	-43.891	17.858	55.554
1.6672	-1.109	17.435	56.586	16.694	-12.364	17.560	56.193	51.565	-47.693	17.887	55.507
1.8580	-1.237	17.436	56.581	19.242	-14.541	17.585	56.131	54.840	-51.513	17.915	55.466

the components and ρ_1 and ρ are the densities of component 1 and the solution. The results for ethylene glycol $V\phi_{EG}$ and for water $V\phi_W$ in their mixtures were also summarized in Tables II and III.

For very dilute solutions the variation of $V\phi_2$ with concentration can be fitted with a linear equation

$$V\phi_2 = V_2^\infty + A_2 m \tag{2}$$

where V_2^∞ is the limiting partial molar volume and *m* is the molality of the solute. The maximum concentration of the linear region was found to be about 0.5 and 1.2 mol·kg^{-1} for EG in W and W in EG, respectively, at all temperatures studied. The parameters of eq 2, determined by the method of least squares, are summarized in Table IV and V. The values of V_{EG}^∞ or V_W^∞ are in good agreement with those from the literature. Also reported in these tables are the values of the excess limiting partial molar volume V_2^E, calculated by

$$V_2^E = V_2^\infty - V_2^* \tag{3}$$

where V_2^* is the molar volume of the pure solute. Both values of V_{EG}^E and V_W^E are negative as well as those for most aqueous mixtures, although the absolute values and their temperature dependence are less conspicuous compared to the the case for alcohol-water mixtures (*1-3*).

The partial molar volumes were evaluated over the whole composition range by using the relation

$$V_2 = V\phi_2 + X_1X_2(\partial V\phi_2/\partial X_2) \tag{4}$$

Table IV. Limiting Partial Molar Volumes of Ethylene Glycol in Water

t/°C	V_{EG}^{∞}/ (cm^3 mol^{-1})	A_{EG}/ (cm^3 kg mol^{-2})	V_{EG}^{E}/ (cm^3 mol^{-1})	ref
5	53.76	−0.15	−1.45	this work
	53.77	−0.1		10
	53.88			14
15	54.26	−0.16	−1.29	this work
	54.26			8
25	54.66	−0.15	−1.25	this work
	54.68			8
	54.63	−0.1		10
	54.63	−0.08		11
	54.60	−0.06		12
	54.60	−0.10		13
	54.6			14
35	55.10	−0.20	−1.16	this work
	55.01			8
45	55.55	−0.27	−1.08	this work
	55.43	−0.1		10
	55.38			14

Table V. Limiting Partial Molar Volumes of Water in Ethylene Glycol

t/°C	V_{W}^{∞}/ (cm^3 mol^{-1})	A_{W}/ (cm^3 kg mol^{-2})	V_{W}^{E}/ (cm^3 mol^{-1})	ref
5	17.05	−0.002	−0.97	this work
	16.98			14
15	17.15	−0.002	−0.88	this work
25	17.27	−0.002	−0.80	this work
	17.26			14
35	17.35	0.008	−0.77	this work
45	17.42	0.015	−0.77	this work
	17.40			14

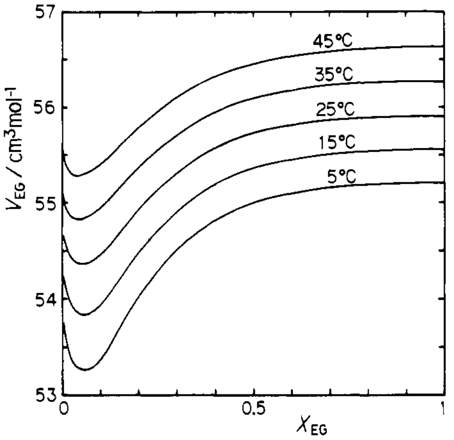

Figure 1. Partial molar volumes of ethylene glycol in ethylene glycol–water mixtures.

The $\partial V\phi_2/\partial X_2$ values were calculated by a local fitting procedure in which five consecutive values of $V\phi_2$ were represented by a quadratic equation in a certain mole fraction range. The results for V_{EG} and V_W are shown in Figures 1 and 2, respectively. The partial molar thermal expansions, $E_2 = \partial V_2/\partial T$, were also calculated for both components, and the results at 25 °C were illustrated in Figure 3. In the water-rich region the $V_{EG}(X_{EG})$ curve exhibits a sharp minimum which is more pronounced and shifts to higher mole fraction as the temperature is lowered. The $E_{EG}(X_{EG})$ curve passes through a maximum in a mole fraction range similar to the V_{EG} minimum. The existence of these extrema at low concentration is typical of the aqueous solutions of monofunctional nonelectrolytes. The depth of the extrema for ethylene glycol is, however, much lower than that for the monohydric alcohols. In the EG-rich regions, on the other hand, the $V_W(X_{EG})$ curve shows only a monotonous variation with the concentration. This is in contrast to that of the alcohol solutions; for example, the $V_W(X_W)$ curve has a minimum in *tert*-butyl alcohol (*1*), while in isopropyl alcohol (*2*) the V_W values increase abruptly with the first increase of the concentration of water.

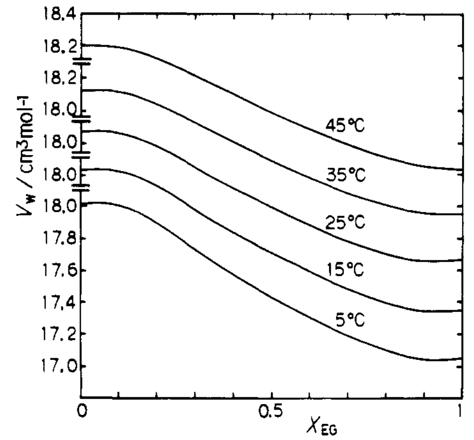

Figure 2. Partial molar volumes of water in ethylene glycol–water mixtures.

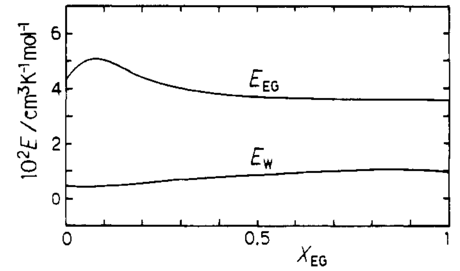

Figure 3. Partial molar thermal expansions of ethylene glycol and water in their mixtures at 25 °C.

In conclusion, the volumetric behavior of the ethylene glycol–water mixtures exhibits only a minor departure from ideality. This may result from the following two main reasons. At first, the partial molar volume is governed by the solvent compressibility, as has been demonstrated by Hamilton and Stokes (*15*) and Dack (*16*) experimentally and by French and Criss (*17*) on the basis of the scaled particle theory. The isothermal compression coefficients of water and ethylene glycol are comparable: 4.52 × 10^{-5} (*6*) and 3.72 × 10^{-5} bar^{-1} (*14*), respectively, which are about half the values for alcohols (*18*). Second, the hydrogen bonding interactions between ethylene glycol and water are essentially comparable to those in the pure components, and there exists only a weak hydrophobic interaction in the aqueous ethylene glycol solutions.

Registry No. EG, 107-21-1; water, 7732-18-5.

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