

w mass of the polymer on the column
 ρ density of the polymer
 χ_{12} Flory-Huggins interaction parameter

Registry No. C28, 630-02-4; C32, 544-85-4; C36, 630-06-8; PPI, 9003-07-0; PIB, 9003-27-4; PVE, 9003-17-2; NC3, 74-98-6; NC4, 106-97-8; NC5, 109-66-0; NC6, 110-54-3; NC7, 142-82-5; NC8, 111-65-9; NC9, 111-84-2; C10, 124-18-5; C11, 1120-21-4; CC5, 287-92-3; CC6, 110-82-7; CC7, 291-64-5; CC8, 292-64-8; CHX, 110-83-8; CHD, 29797-09-9; BNZ, 71-43-2; TOL, 108-88-3; EBZ, 100-41-4; CL1, 74-87-3; CL2, 75-09-2; CL3, 67-66-3; CL4, 56-23-5; BCL, 109-69-3; PCL, 543-59-9; CLH, 25495-90-3; CLO, 57214-71-8; D11, 75-34-3; D12, 107-06-2; MCH, 71-55-6; TCE, 79-01-6; CLB, 108-90-7; ACT, 67-64-1; MEK, 78-93-3; THF, 109-99-9; DOX, 123-91-1; MAC, 79-20-9; EAC, 141-78-6; PAC, 109-60-4; BAC, 123-86-4; EOH, 64-17-5; POH, 71-23-8; BOH, 71-36-3; AOH, 71-41-0.

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Excess Volumes of Binary and Ternary Mixtures of Water, Methanol, and Ethylene Glycol

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The excess molar volumes of mixtures of water + methanol, water + ethylene glycol, methanol + ethylene glycol, and water + methanol + ethylene glycol have been measured at 283.15, 293.15, and 303.15 K by using a vibrating tube densimeter. The excess volumes are all negative over the entire composition range.

Introduction

Polyester polymer is produced commercially in a two-step polymerization process, i.e., monomer formation by ester interchange of DMT (dimethyl terephthalate) with glycol or esterification of TA (terephthalic acid) with glycol, followed by polycondensation by removing excess glycol. In the DMT or TA process, methanol and water are produced as byproducts. However, the volumetric properties are very limited even for the binary mixtures composed of water, methanol, and ethylene glycol: water + methanol (1-3), water + ethylene glycol (4), and methanol + ethylene glycol (5). No experimental excess volume data for a ternary system, water + methanol +

Table I. Densities ρ of Pure Substances at 283.15, 293.15, and 303.15 K

substances	T/K	ρ /(g cm ⁻³)	
		this work	lit.
methanol	283.15	0.800 266	0.800 7 ^a
	293.15	0.790 004	0.791 29 ^a
	303.15	0.782 374	0.781 96 ^a
ethylene glycol	283.15	1.119 292	1.120 6 ^b
	293.15	1.112 020	1.113 5 ^b
	303.15	1.105 825	1.106 35 ^b

^aReference 6. ^bReference 7.

ethylene glycol, have been reported in the literature.

The purpose of this investigation is therefore to measure the excess volumes for three binary systems and one ternary system formed by water, methanol, and ethylene glycol at 283.15, 293.15, and 303.15 K.

Experimental Section

The methanol and ethylene glycol were supplied by Aldrich (purity better than 99%) and stored over Linde Type 3A mo-

Table II. Experimental Densities ρ and Excess Molar Volumes V^E for Water (1) + Methanol (2), Water (1) + Ethylene Glycol (2), and Methanol (1) + Ethylene Glycol (2) Mixtures at 283.15 K

x_1	$\rho/$ (g cm ⁻³)	$V^E/$ (cm ³ mol ⁻¹)	x_1	$\rho/$ (g cm ⁻³)	$V^E/$ (cm ³ mol ⁻¹)
Water (1) + Methanol (2)					
0.0714	0.811 769	-0.2331	0.6726	0.929 369	-0.9070
0.1205	0.820 429	-0.3877	0.7023	0.935 530	-0.8549
0.1677	0.829 056	-0.5314	0.7276	0.940 722	-0.8059
0.2274	0.840 178	-0.6959	0.7600	0.947 249	-0.7340
0.2681	0.847 835	-0.7755	0.7837	0.951 941	-0.6704
0.3098	0.855 739	-0.8498	0.8063	0.956 363	-0.6076
0.3539	0.864 192	-0.9161	0.8364	0.962 194	-0.5135
0.3983	0.872 839	-0.9560	0.8567	0.966 101	-0.4525
0.4330	0.879 684	-0.9881	0.8778	0.970 230	-0.3750
0.4807	0.889 282	-1.0108	0.9024	0.975 180	-0.2960
0.5116	0.895 612	-1.0109	0.9233	0.979 607	-0.2175
0.5431	0.902 139	-1.0089	0.9430	0.984 063	-0.1517
0.5835	0.910 602	-0.9930	0.9660	0.989 762	-0.0826
0.6115	0.916 508	-0.9681	0.9829	0.994 427	-0.0383
0.6408	0.922 687	-0.9412			
Water (1) + Ethylene Glycol (2)					
0.1260	1.117 045	-0.1455	0.8013	1.064 481	-0.3113
0.2119	1.115 004	-0.2240	0.8210	1.060 030	-0.2804
0.2805	1.112 778	-0.2750	0.8382	1.055 851	-0.2647
0.3614	1.109 414	-0.3320	0.8596	1.050 204	-0.2357
0.4154	1.106 707	-0.3564	0.8744	1.046 007	-0.2164
0.4631	1.103 978	-0.3773	0.8890	1.041 593	-0.1942
0.5171	1.100 426	-0.3989	0.9075	1.035 672	-0.1574
0.5615	1.097 047	-0.4091	0.9204	1.031 314	-0.1328
0.5956	1.094 086	-0.4150	0.9329	1.026 850	-0.1122
0.6364	1.090 027	-0.4074	0.9471	1.021 589	-0.0822
0.6697	1.086 199	-0.4061	0.9584	1.017 189	-0.0644
0.6968	1.082 665	-0.3877	0.9681	1.013 299	-0.0430
0.7303	1.077 700	-0.3731	0.9814	1.007 800	-0.0177
0.7535	1.073 819	-0.3548	0.9917	1.003 361	-0.0023
0.7744	1.069 977	-0.3350			
Methanol (1) + Ethylene Glycol (2)					
0.0767	1.104 329	-0.1590	0.6827	0.940 781	-0.7517
0.1303	1.093 975	-0.2898	0.7200	0.926 618	-0.7166
0.1776	1.084 486	-0.4032	0.7433	0.917 447	-0.6704
0.2414	1.070 816	-0.5272	0.7761	0.904 168	-0.6185
0.2851	1.060 797	-0.6139	0.7976	0.895 184	-0.5693
0.3249	1.051 139	-0.6846	0.8198	0.885 674	-0.5130
0.3737	1.038 572	-0.7410	0.8465	0.873 925	-0.4685
0.4180	1.026 511	-0.7838	0.8660	0.865 137	-0.4281
0.4534	1.016 427	-0.7905	0.8851	0.856 346	-0.3703
0.5013	1.002 117	-0.8043	0.9123	0.843 580	-0.2975
0.5320	0.992 541	-0.8018	0.9298	0.835 190	-0.2423
0.5665	0.981 421	-0.7991	0.9456	0.827 460	-0.1852
0.6042	0.968 775	-0.7921	0.9682	0.826 329	-0.1091
0.6325	0.958 965	-0.7803	0.9842	0.808 288	-0.0373
0.6590	0.949 486	-0.7677			

lecular sieve to exclude atmospheric moisture. Further purification was not necessary since no secondary peaks were found from gas-chromatographic analysis. Water was double distilled and degassed before use. Density measurements were carried out with an Anton Paar DMA 60/512 vibrating-tube densimeter with an accuracy of $\pm 1 \times 10^{-5}$ g cm⁻³. The instrument was calibrated for each temperature with redistilled water and dry air at atmospheric pressure. The measuring cell was thermostated by using a Haake F3 digital circulator, the temperature being controlled within ± 0.01 K. The U-shaped sample tube was equipped with valves at the entry (top) and at the exit (bottom). After the sample was injected in this tube, the valve at the bottom was closed, and the sample was pressurized from the top. The pressure was then released to atmospheric pressure. The valve at the top was closed to stop evaporation during the experiment. This procedure ensured a bubble-free sample inside the tube.

Results and Discussion

The densities of pure methanol and ethylene glycol are given in Table I. The excess volumes for the three binary systems,

Table III. Experimental Densities ρ and Excess Molar Volumes V^E for Water (1) + Methanol (2), Water (1) + Ethylene Glycol (2), and Methanol (1) + Ethylene Glycol (2) Mixtures at 293.15 K

x_1	$\rho/$ (g cm ⁻³)	$V^E/$ (cm ³ mol ⁻¹)	x_1	$\rho/$ (g cm ⁻³)	$V^E/$ (cm ³ mol ⁻¹)
Water (1) + Methanol (2)					
0.0714	0.801 917	-0.2547	0.6726	0.922 171	-0.8939
0.1205	0.810 597	-0.3957	0.7023	0.928 648	-0.8476
0.1677	0.819 179	-0.5318	0.7276	0.934 137	-0.8020
0.2274	0.830 265	-0.6852	0.7600	0.941 090	-0.7325
0.2681	0.837 953	-0.7727	0.7837	0.946 129	-0.6757
0.3098	0.845 948	-0.8489	0.8063	0.950 915	-0.6084
0.3539	0.854 567	-0.9090	0.8364	0.957 283	-0.5192
0.3983	0.863 444	-0.9618	0.8567	0.961 582	-0.4547
0.4330	0.870 504	-0.9842	0.8778	0.966 148	-0.3833
0.4807	0.880 438	-1.0068	0.9024	0.971 632	-0.3046
0.5116	0.887 004	-1.0069	0.9233	0.976 529	-0.2272
0.5431	0.893 780	-1.0118	0.9430	0.981 427	-0.1583
0.5835	0.902 580	-0.9926	0.9660	0.987 625	-0.0844
0.6115	0.908 729	-0.9720	0.9829	0.992 628	-0.0260
0.6408	0.915 176	-0.9370			
Water (1) + Ethylene Glycol (2)					
0.1260	1.109 285	-0.1168	0.8013	1.059 420	-0.2842
0.2119	1.107 467	-0.1872	0.8210	1.055 222	-0.2671
0.2805	1.105 381	-0.2424	0.8382	1.051 267	-0.2405
0.3614	1.102 064	-0.2886	0.8596	1.045 910	-0.2175
0.4154	1.099 351	-0.3163	0.8744	1.041 922	-0.2028
0.4631	1.096 629	-0.3397	0.8890	1.037 722	-0.1788
0.5171	1.093 143	-0.3528	0.9075	1.032 089	-0.1421
0.5615	1.089 891	-0.3548	0.9204	1.027 944	-0.1235
0.5956	1.087 084	-0.3595	0.9329	1.023 704	-0.0960
0.6364	1.083 278	-0.3555	0.9471	1.018 718	-0.0784
0.6697	1.079 711	-0.3515	0.9584	1.014 561	-0.0603
0.6968	1.076 426	-0.3485	0.9681	1.010 896	-0.0227
0.7303	1.071 804	-0.3395	0.9814	1.005 738	-0.0244
0.7535	1.068 183	-0.3218	0.9917	1.001 599	-0.0230
0.7744	1.064 586	-0.3017			
Methanol (1) + Ethylene Glycol (2)					
0.0767	1.098 108	-0.2131	0.6827	0.931 214	-0.7769
0.1303	1.087 528	-0.3491	0.7200	0.916 955	-0.7294
0.1776	1.077 554	-0.4472	0.7433	0.907 718	-0.6877
0.2414	1.063 121	-0.5756	0.7761	0.894 347	-0.6234
0.2851	1.052 629	-0.6399	0.7976	0.885 303	-0.5843
0.3249	1.042 614	-0.6850	0.8198	0.875 732	-0.5231
0.3747	1.029 717	-0.7444	0.8465	0.863 918	-0.4731
0.4180	1.017 454	-0.7734	0.8660	0.855 087	-0.4212
0.4534	1.007 261	-0.7896	0.8851	0.846 259	-0.3759
0.5013	0.992 854	-0.8032	0.9123	0.833 447	-0.2908
0.5320	0.983 232	-0.8098	0.9298	0.825 031	-0.2501
0.5665	0.972 066	-0.8071	0.9456	0.817 280	-0.1967
0.6042	0.959 365	-0.8058	0.9682	0.806 119	-0.1211
0.6325	0.949 506	-0.7990	0.9842	0.798 054	-0.0543
0.6590	0.939 973	-0.7887			

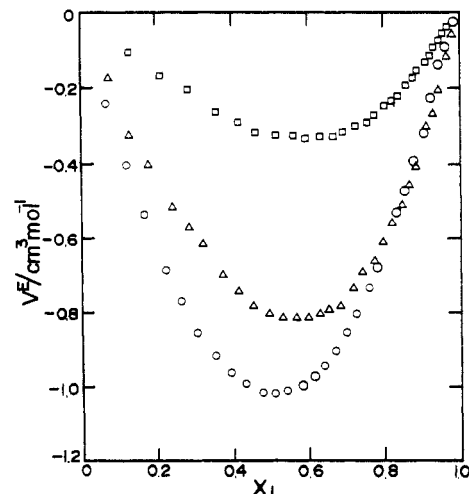


Figure 1. Excess molar volumes V^E of three binary systems as a function of the mole fraction x_1 at 293.15 K: (O) water (1) + methanol (2); (□) water (1) + ethylene glycol (2); (Δ) methanol (1) + ethylene glycol (2).

Table IV. Experimental Densities ρ and Excess Molar Volumes V^E for Water (1) + Methanol (2), Water (1) + Ethylene Glycol (2), and Methanol (1) + Ethylene Glycol (2) Mixtures at 303.15 K

x_1	$\rho/$ (g cm ⁻³)	$V^E/$ (cm ³ mol ⁻¹)	x_1	$\rho/$ (g cm ⁻³)	$V^E/$ (cm ³ mol ⁻¹)	x_1	$\rho/$ (g cm ⁻³)	$V^E/$ (cm ³ mol ⁻¹)	x_1	$\rho/$ (g cm ⁻³)	$V^E/$ (cm ³ mol ⁻¹)
Water (1) + Methanol (2)											
0.0714	0.794 146	-0.2450	0.4330	0.863 620	-0.9953	0.6726	0.916 561	-0.9034	0.8567	0.957 566	-0.4683
0.1205	0.802 958	-0.4059	0.4807	0.873 659	-1.0193	0.7023	0.923 312	-0.8553	0.8778	0.962 274	-0.3952
0.1677	0.811 721	-0.5410	0.5116	0.880 326	-1.0181	0.7276	0.929 040	-0.8085	0.9024	0.967 923	-0.3187
0.2274	0.823 023	-0.6936	0.5431	0.887 240	-1.0172	0.7600	0.936 295	-0.7372	0.9233	0.972 971	-0.2270
0.2681	0.830 823	-0.7751	0.5835	0.896 268	-0.9950	0.7837	0.941 545	-0.6798	0.9430	0.978 038	-0.1373
0.3098	0.838 901	-0.8582	0.6115	0.902 611	-0.9746	0.8063	0.946 522	-0.6185	0.9660	0.984 489	-0.0910
0.3539	0.847 580	-0.9192	0.6408	0.909 289	-0.9453	0.8364	0.953 123	-0.5306	0.9829	0.989 741	-0.0324
0.3983	0.856 510	-0.9654									
Water (1) + Ethylene Glycol (2)											
0.1260	1.103 143	-0.1077	0.5956	1.081 236	-0.3312	0.8013	1.053 891	-0.2496	0.9204	1.024 393	-0.1128
0.2119	1.100 881	-0.1700	0.6364	1.077 389	-0.3306	0.8210	1.049 907	-0.2384	0.9329	1.020 407	-0.0931
0.2805	1.098 693	-0.2074	0.6697	1.073 783	-0.3280	0.8382	1.046 181	-0.2194	0.9471	1.015 687	-0.0753
0.3614	1.095 573	-0.2629	0.6968	1.070 481	-0.3155	0.8596	1.041 165	-0.1929	0.9584	1.011 716	-0.0531
0.4154	1.093 092	-0.2915	0.7303	1.065 888	-0.2999	0.8744	1.037 442	-0.1756	0.9681	1.008 185	-0.0401
0.4631	1.090 570	-0.3149	0.7535	1.062 335	-0.2889	0.8890	1.033 528	-0.1586	0.9814	1.003 153	-0.0189
0.5171	1.087 245	-0.3259	0.7744	1.058 844	-0.2752	0.9075	1.028 272	-0.1318	0.9917	0.999 054	-0.0054
0.5615	1.084 048	-0.3314									
Methanol (1) + Ethylene Glycol (2)											
0.0767	1.091 149	-0.1755	0.4534	0.999 548	-0.7832	0.6827	0.923 851	-0.7815	0.8660	0.847 862	-0.4581
0.1303	1.080 106	-0.3249	0.5013	0.985 249	-0.8045	0.7200	0.909 622	-0.7293	0.8851	0.839 034	-0.4069
0.1776	1.069 833	-0.4068	0.5320	0.975 688	-0.8154	0.7433	0.900 404	-0.6925	0.9123	0.826 203	-0.3074
0.2414	1.055 175	-0.5197	0.5665	0.964 580	-0.8183	0.7761	0.887 059	-0.6577	0.9298	0.817 758	-0.2665
0.2851	1.044 638	-0.5746	0.6042	0.951 929	-0.8163	0.7976	0.878 034	-0.6129	0.9456	0.809 964	-0.2081
0.3249	1.034 641	-0.6222	0.6325	0.942 100	-0.8062	0.8198	0.868 482	-0.5572	0.9682	0.798 709	-0.1202
0.3737	1.021 821	-0.7047	0.6590	0.932 592	-0.7979	0.8465	0.856 685	-0.5071	0.9842	0.790 548	-0.0614
0.4180	1.009 656	-0.7481									

Table V. Experimental Densities ρ and Excess Molar Volumes V^E for Water (1) + Methanol (2) + Ethylene Glycol (3) at 283.15, 293.15, and 303.15 K

x_1	x_2	$\rho/$ (g cm ⁻³)	$V^E/$ (cm ³ mol ⁻¹)	x_1	x_2	$\rho/$ (g cm ⁻³)	$V^E/$ (cm ³ mol ⁻¹)
$T = 283.15$ K							
0.0880	0.8868	0.827 877	-0.3630	0.6103	0.2570	0.989 772	-0.8967
0.4410	0.5376	0.892 810	-0.9791	0.7163	0.1593	1.008 407	-0.6699
0.7802	0.2023	0.961 860	-0.6485	0.8088	0.0745	1.025 841	-0.4381
0.9548	0.0299	0.997 980	-0.1047	0.8491	0.0359	1.033 742	-0.3011
0.0908	0.8574	0.842 035	-0.4499	0.1115	0.5660	0.964 260	-0.9058
0.1740	0.7752	0.857 105	-0.6751	0.2154	0.4770	0.979 492	-0.9792
0.3216	0.6319	0.883 135	-0.9205	0.3919	0.3263	1.006 734	-0.9821
0.4501	0.5053	0.907 810	-0.9988	0.5383	0.2016	1.030 794	-0.8598
0.5637	0.3959	0.929 618	-0.9290	0.6652	0.0938	1.051 436	-0.6247
0.6640	0.2976	0.950 122	-0.8749	0.7221	0.0457	1.060 432	-0.4791
0.7523	0.2114	0.968 121	-0.7105	0.1293	0.3550	1.032 202	-0.8542
0.8323	0.1333	0.983 099	-0.4752	0.2421	0.2697	1.046 445	-0.8507
0.9038	0.0630	0.997 253	-0.2326	0.4356	0.1224	1.071 744	-0.6814
0.9371	0.0308	1.005 268	-0.1439	0.5203	0.0577	1.082 735	-0.5314
0.1007	0.7259	0.901 433	-0.7403	0.0638	0.1369	1.090 825	-0.3989
0.1921	0.6423	0.915 842	-0.8884	0.1489	0.0824	1.099 628	-0.3799
0.3533	0.4936	0.943 090	-1.0255	0.2278	0.0372	1.106 382	-0.3318
0.4904	0.3671	0.967 736	-1.0138				
$T = 293.15$ K							
0.0880	0.8868	0.818 050	-0.3777	0.6103	0.2570	0.982 683	-0.8948
0.4410	0.5376	0.884 456	-0.9980	0.7163	0.1593	1.003 362	-0.6889
0.7802	0.2023	0.956 498	-0.6551	0.8088	0.0745	1.020 915	-0.4272
0.9548	0.0299	0.995 742	-0.1086	0.8491	0.0359	1.029 223	-0.2843
0.0908	0.8574	0.832 221	-0.4644	0.1115	0.5660	0.955 071	-0.9194
0.1740	0.7752	0.847 321	-0.6820	0.2154	0.4770	0.970 658	-0.9891
0.3216	0.6319	0.873 967	-0.9311	0.3919	0.3263	0.998 537	-0.9791
0.4501	0.5053	0.899 477	-1.0137	0.5383	0.2016	1.022 958	-0.8334
0.5637	0.3959	0.922 780	-1.0158	0.6652	0.0938	1.044 037	-0.5770
0.6640	0.2976	0.943 678	-0.8899	0.7221	0.0457	1.054 322	-0.4487
0.7523	0.2114	0.961 984	-0.7052	0.1293	0.3550	1.023 351	-0.8463
0.8323	0.1333	0.978 277	-0.4722	0.2421	0.2697	1.037 684	-0.8252
0.9038	0.0630	0.993 976	-0.2345	0.4356	0.1224	1.063 825	-0.6448
0.9371	0.0308	1.002 451	-0.1414	0.5203	0.0577	1.076 148	-0.5170
0.1007	0.7259	0.892 021	-0.7640	0.0638	0.1369	1.083 614	-0.4253
0.1921	0.6423	0.906 658	-0.9081	0.1489	0.0824	1.092 343	-0.3839
0.3533	0.4936	0.934 353	-1.0331	0.2278	0.0372	1.098 943	-0.3123
0.4904	0.3671	0.959 692	-1.0147				

Table V (Continued)

x_1	x_2	$\rho/(\text{g cm}^{-3})$	$V^E/(\text{cm}^3 \text{mol}^{-1})$	x_1	x_2	$\rho/(\text{g cm}^{-3})$	$V^E/(\text{cm}^3 \text{mol}^{-1})$
$T = 303.15 \text{ K}$							
0.0880	0.8868	0.810493	-0.3807	0.6103	0.2570	0.976533	-0.8908
0.4410	0.5376	0.875986	-0.9481	0.7163	0.1593	0.996917	-0.6582
0.7802	0.2023	0.951734	-0.6636	0.8088	0.0745	1.014924	-0.3908
0.9548	0.0299	0.992671	-0.1101	0.8491	0.0359	1.024418	-0.2663
0.0908	0.8574	0.824798	-0.4744	0.1115	0.5660	0.947478	-0.9123
0.1740	0.7752	0.840082	-0.6960	0.2154	0.4770	0.963098	-0.9746
0.3216	0.6319	0.865701	-0.8945	0.3919	0.3263	0.990836	-0.9420
0.4501	0.5053	0.890301	-0.9382	0.5383	0.2016	1.015517	-0.7881
0.5637	0.3959	0.914123	-0.9510	0.6652	0.0938	1.038224	-0.5596
0.6640	0.2976	0.937087	-0.8724	0.7221	0.0457	1.048566	-0.4224
0.7523	0.2114	0.956949	-0.7115	0.1293	0.3550	1.015101	-0.7909
0.8323	0.1333	0.974025	-0.4788	0.2421	0.2697	1.029496	-0.7638
0.9038	0.0630	0.990228	-0.2342	0.4356	0.1224	1.057355	-0.6261
0.9371	0.0308	0.998512	-0.1289	0.5203	0.0577	1.069511	-0.4801
0.1007	0.7259	0.884734	-0.7792	0.0638	0.1369	1.076072	-0.3756
0.1921	0.6423	0.899692	-0.9297	0.1489	0.0824	1.084956	-0.3332
0.3533	0.4936	0.927427	-1.0394	0.2278	0.0372	1.092058	-0.2753
0.4904	0.3671	0.953243	-1.0196				

Table VI. Values of Parameters A_i in Equation 1 and Standard Deviations $\sigma(V^E)$, Equation 2

systems	T/K	A_0	A_1	A_2	A_3	A_4	$\sigma(V^E)$
water (1) + methanol (2)	283.15	-4.03878	-0.23679	-0.29511	0.62920	1.84874	0.0033
	293.15	-4.03091	-0.30355	-0.13290	0.85863	1.35293	0.0067
	303.15	-4.04840	-0.27803	-0.48756	0.71300	1.96629	0.0096
water (1) + ethylene glycol (2)	283.15	-1.55433	-0.65816	-0.64613	0.42829	1.02810	0.0052
	293.15	-1.36199	-0.56074	-0.90139	0.09709	1.63501	0.0083
	303.15	-1.28148	-0.59973	-0.14653	0.31161	0.35314	0.0044
methanol (1) + ethylene glycol (2)	283.15	-3.23629	-0.40929	-0.29819	-0.59744	1.15930	0.0092
	293.15	-3.25127	-0.58898	-0.51800	0.37706	0.47697	0.0091
	303.15	-3.20512	-0.97209	-0.20336	0.32431	0.02606	0.0085

Table VII. Values of Parameters B_i in Equation 3 and Standard Deviations $\sigma(V^E)$, Equation 2

system	T/K	B_0	B_1	B_2	B_3	B_4	$\sigma(V^E)$
water (1) + methanol (2) + ethylene glycol (3)	283.15	0.3312	7.2356	-35.4090	-213.3718	2548.2654	0.0061
	293.15	-0.0286	-0.8405	32.6844	87.2731	-851.1198	0.0064
	303.15	0.8536	-8.4174	-128.8976	612.7428	5536.6309	0.0039

water + methanol, water + ethylene glycol, and methanol + ethylene glycol, were measured at 283.15, 293.15, and 303.15 K. The results are given in Tables II–IV. The excess volumes of three binary systems as a function of mole fraction at 293.15 K is shown in Figure 1. The excess volumes for a ternary system, water + methanol + ethylene glycol, were also measured at the same temperatures, and the results are presented in Table V. The equation used to express the dependence of the excess volume of binary mixtures on composition is

$$V^E/(\text{cm}^3 \text{mol}^{-1}) = x_1 x_2 \sum_{i=0}^4 A_i (x_1 - x_2)^i \quad (1)$$

The values of the coefficients A_i determined by the least-squares method are included in Table VI along with their standard deviations, $\sigma(V^E)$. The values of $\sigma(V^E)$ were obtained by using the equation

$$\sigma(V^E) = [\sum (V_{\text{calcd}}^E - V_{\text{expt}}^E)^2 / (N - P)]^{1/2} \quad (2)$$

where N is the number of experimental data and P is the number of coefficients. The dependence of excess volume on mole fraction x_i for a ternary system, water (1) + methanol (2) + ethylene glycol (3), was expressed by the following equation:

$$V^E/(\text{cm}^3 \text{mol}^{-1}) = x_1 x_2 \sum_{i=0}^4 A_{i,12} (x_1 - x_2)^i + x_2 x_3 \sum_{i=0}^4 A_{i,23} (x_2 - x_3)^i + x_1 x_3 \sum_{i=0}^4 A_{i,13} (x_1 - x_3)^i + x_1 x_2 x_3 \sum_{i=0}^4 B_i (x_2 - x_3)^i x_1^i \quad (3)$$

In eq 3, the coefficients, $A_{i,12}$, $A_{i,23}$, and $A_{i,13}$, of three binary systems were taken from Table VI. The coefficients B_i of the last term in eq 3 were also determined by the least-squares method, and the results are presented in Table VII along with the standard deviations calculated by using eq 2. For all systems used in this study, the excess volumes are negative over the entire composition range.

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