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Molar Volumes, Molar Refractions, and Isentropic Compressibilities of (Ethanol + Methanol + 2-Methoxy-2-methylpropane) and (Ethanol + Methanol + 2-Methoxy-2-methylbutane) at 298.15 K

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Excess molar volumes (V^E) and deviations in molar refractions (ΔR) and the isentropic compressibility ($\Delta\kappa_s$) were determined for the systems ethanol + methanol + 2-methoxy-2-methylpropane and ethanol + methanol + 2-methoxy-2-methylbutane at 298.15 K and atmospheric pressure. For both systems, these results were satisfactorily correlated by the Redlich−Kister polynomial. Several empirical equations allowing prediction of the results for the ternary systems from the V^E, ΔR, and $\Delta\kappa_s$ of their constituent binary subsystems were also examined. The Kohler equation gives the best predictions of V^E, while the equations of Radojkovic *et al.* and of Jacob and Fitzner give the best predictions of ΔR and $\Delta\kappa_s$.

Introduction

Determination of the effects of mixing on thermodynamic properties is of importance in chemical engineering. Moreover, since these effects arise through molecular interactions, knowledge of them is central to the study of the thermodynamics of solutions.

The systems ethanol + methanol + 2-methoxy-2-methylpropane (MTBE) and ethanol + methanol + 2-methoxy-2-methylbutane (TAME) are of interest because the ethers are efficient and economic alternatives to the gasoline additive tetraethyl lead, which is now considered a harmful pollutant. In this work, we determined the excess molar volumes of the above two systems and also the deviations of their molar refractions and isentropic compressibilities from the mole fraction or volume fraction average, respectively, of these properties of the pure components. These parameters were estimated from the densities and refractive indices of the systems at 298.15 K and atmospheric pressure and from the speed of sound. To our knowledge, data for the above mixtures are not available in the literature.

Determination of the thermodynamic properties of mixtures becomes more tedious as the number of components increases. In this work we evaluated several empirical equations allowing prediction of the properties of ternary systems from the corresponding properties of their constituent binary subsystems (Scatchard *et al.*, 1952; Tsao and Smith, 1953; Kohler, 1960; Toop, 1965; Colinet, 1967; Jacob and Fitzner, 1977; Radojkovic *et al.*, 1977; Rastogi *et al.*, 1977).

Experimental Section

Materials. Methanol and ethanol were supplied by Merck and had nominal purities >99.7 and >99.8 mass %, respectively; 2-methoxy-2-methylpropane (MTBE) was supplied by Aldrich with nominal purity >99.8 mass %, and 2-methoxy-2-methylbutane (TAME) was supplied by Fluka with nominal purity >98.9 mass %. Water contents of the ethanol, methanol, MTBE, and TAME (determined with a Metrohm 737 KF coulometer) were 0.08, 0.03, 0.03, and 0.02 mass %, respectively.

Apparatus and Procedure. The mixtures were prepared by mass using a Mettler AE 240 balance that measured to within ±0.0001 g. The densities and speeds of sound of the mixtures were measured to within ±0.0001 g·cm^{-3} and ±1 m·s^{-1}, respectively, in an Anton Paar DSA-48 Densimeter and Sound Analyzer calibrated with air and water. Refractive indices were measured to within ±0.0001 in an ATAGO RX-1000 refractometer. A Hetotherm thermostat was used to maintain the temperature at (298.15 ± 0.02) K.

Table 1. Densities ρ and Refractive Indices n_D of the Pure Components, and Speeds of Sound u through Them, at 298.15 K and Atmospheric Pressure

	ρ/g·cm^{-3}		n_D		u/m·s^{-1}	
component	exptl	lit.	exptl	lit.	exptl	lit.
ethanol	0.7851	0.784 93[a]	1.3592	1.359 41[a]	1143	1145[d]
methanol	0.7866	0.786 37[a]	1.3264	1.326 52[a]	1102	1102[b]
MTBE	0.7356	0.735 28[c]	1.3666	1.366 30[c]	1037	g
TAME	0.7658	0.765 77[e]	1.3858	1.385 80[e]	1115	1115[b]

[a] Riddick *et al.*, 1986. [b] Arce *et al.*, 1996. [c] Daubert and Danner, 1989. [d] Amanabhavi, 1993. [e] Linek, 1987. [g] Not found.

Table 1 lists the densities, speeds of sound, and refractive indices measured for the pure components, together with published values for these parameters (Aminabhavi *et al.*, 1993; Arce *et al.*, 1996; Daubert and Danner, 1989; Linek, 1987; Riddick *et al.*, 1986).

Results

Table 2 lists the densities, speeds of sound, and refractive indices measured for the binary and ternary systems. Included in Table 2 are the corresponding excess molar volumes (V^E), which were calculated using the expression

$$V^E = V - \sum_i x_i V_i \tag{1}$$

where V is the molar volume of the mixture and V_i and x_i are the molar volume and mole fraction respectively, of component i; the molar refractions (R), which were calculated using the Lorentz−Lorenz equation

$$R = \frac{n_D^2 - 1}{n_D^2 + 2} V \tag{2}$$

and the deviations of these values from a mole fraction average of the molar refraction of the pure components

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Table 2. Densities ρ, Speeds of Sound u, Isentropic Compressibilities κ_s, Refractive Indices n_D, Excess Molar Volumes V^E, and Deviations $\Delta\kappa_s$ and ΔR for Mixtures of Ethanol (1) + Methanol (2) + MTBE (3) and Ethanol (1) + Methanol (2) + TAME (3) at 298.15 K and Atmospheric Pressure

x_1	x_2	ρ/g·cm^{-3}	u/m·s^{-1}	κ_s/TPa^{-1}	n_D	V^E/cm^3·mol^{-1}	$\Delta\kappa_s$/TPa^{-1}	ΔR/cm^3·mol^{-1}	x_1	x_2	ρ/g·cm^{-3}	u/m·s^{-1}	κ_s/TPa^{-1}	n_D	V^E/cm^3·mol^{-1}	$\Delta\kappa_s$/TPa^{-1}	ΔR/cm^3·mol^{-1}
Ethanol + Methanol + MTBE																	
0.0523	0.9477	0.7865	1106	1040	1.3288	0.001	0	0.004	0.1907	0.7627	0.7823	1110	1037	1.3393	−0.122	−16	−0.045
0.1248	0.8752	0.7863	1109	1033	1.3321	0.003	0	0.007	0.1324	0.8352	0.7835	1109	1039	1.3358	−0.088	−11	−0.043
0.1631	0.8369	0.7862	1111	1030	1.3337	0.003	0	0.008	0.0683	0.9150	0.7850	1107	1040	1.3321	−0.048	−6	−0.031
0.2146	0.7854	0.7861	1114	1025	1.3358	0.004	0	0.009	0.6978	0.0000	0.7662	1107	1066	1.3644	−0.423	−44	−0.021
0.2621	0.7379	0.7860	1116	1021	1.3376	0.005	0	0.008	0.5644	0.1912	0.7692	1108	1059	1.3605	−0.409	−44	−0.024
0.3114	0.6886	0.7859	1118	1017	1.3394	0.005	0	0.008	0.4935	0.2928	0.7709	1109	1055	1.3578	−0.389	−43	−0.035
0.3500	0.6500	0.7859	1120	1014	1.3408	0.006	0	0.007	0.4228	0.3941	0.7727	1109	1052	1.3549	−0.360	−40	−0.040
0.4096	0.5904	0.7858	1123	1010	1.3428	0.006	0	0.006	0.3585	0.4862	0.7745	1109	1050	1.3521	−0.326	−38	−0.040
0.4567	0.5433	0.7857	1125	1006	1.3444	0.006	0	0.005	0.2696	0.6136	0.7770	1109	1047	1.3475	−0.266	−32	−0.039
0.4974	0.5026	0.7856	1126	1003	1.3457	0.006	0	0.004	0.1917	0.7253	0.7794	1108	1046	1.3426	−0.203	−24	−0.042
0.5357	0.4643	0.7856	1128	1001	1.3469	0.006	0	0.004	0.1239	0.8224	0.7818	1106	1045	1.3376	−0.139	−17	−0.045
0.6073	0.3927	0.7855	1131	996	1.3490	0.006	0	0.003	0.1074	0.8462	0.7824	1106	1045	1.3363	−0.122	−15	−0.044
0.6508	0.3492	0.7854	1132	993	1.3503	0.006	0	0.003	0.0613	0.9122	0.7841	1105	1044	1.3327	−0.072	−8	−0.036
0.6990	0.3010	0.7854	1134	990	1.3517	0.005	0	0.003	0.5955	0.0000	0.7609	1095	1095	1.3654	−0.477	−46	−0.023
0.7371	0.2629	0.7853	1135	988	1.3527	0.005	0	0.003	0.5116	0.1410	0.7635	1098	1087	1.3627	−0.475	−48	−0.024
0.7938	0.2062	0.7853	1137	985	1.3543	0.004	0	0.003	0.4789	0.1958	0.7645	1099	1083	1.3615	−0.470	−48	−0.025
0.8346	0.1654	0.7852	1139	982	1.3553	0.003	0	0.003	0.4139	0.3050	0.7668	1101	1076	1.3589	−0.453	−48	−0.025
0.8854	0.1146	0.7852	1140	980	1.3566	0.003	0	0.002	0.3507	0.4110	0.7692	1102	1070	1.3559	−0.425	−46	−0.025
0.9435	0.0565	0.7851	1142	977	1.3580	0.001	0	0.002	0.2971	0.5011	0.7713	1104	1065	1.3530	−0.392	−44	−0.025
0.0709	0.0000	0.7384	1044	1242	1.3667	−0.110	−11	−0.004	0.2470	0.5852	0.7735	1104	1060	1.3499	−0.352	−41	−0.025
0.1130	0.0000	0.7399	1048	1229	1.3667	−0.176	−17	−0.006	0.1674	0.7189	0.7772	1105	1054	1.3440	−0.269	−32	−0.023
0.1571	0.0000	0.7416	1053	1217	1.3668	−0.243	−22	−0.008	0.1271	0.7866	0.7793	1105	1051	1.3406	−0.216	−27	−0.021
0.2085	0.0000	0.7437	1058	1202	1.3668	−0.313	−28	−0.011	0.0734	0.8767	0.7822	1105	1047	1.3353	−0.135	−17	−0.015
0.2599	0.0000	0.7458	1062	1188	1.3668	−0.373	−32	−0.013	0.4965	0.0000	0.7561	1085	1124	1.3659	−0.496	−45	−0.022
0.2903	0.0000	0.7471	1065	1180	1.3667	−0.404	−35	−0.015	0.4207	0.1527	0.7594	1089	1111	1.3632	−0.527	−49	−0.033
0.3627	0.0000	0.7501	1072	1160	1.3666	−0.459	−40	−0.018	0.3742	0.2463	0.7616	1092	1102	1.3614	−0.526	−51	−0.033
0.4095	0.0000	0.7522	1076	1148	1.3665	−0.481	−42	−0.019	0.3274	0.3406	0.7639	1094	1093	1.3592	−0.513	−52	−0.035
0.4570	0.0000	0.7543	1081	1135	1.3662	−0.493	−44	−0.021	0.2994	0.3969	0.7654	1096	1088	1.3577	−0.499	−52	−0.037
0.5033	0.0000	0.7564	1085	1122	1.3660	−0.496	−45	−0.022	0.2482	0.5001	0.7682	1098	1080	1.3544	−0.461	−50	−0.045
0.5674	0.0000	0.7595	1092	1104	1.3656	−0.486	−46	−0.022	0.2023	0.5926	0.7710	1100	1072	1.3508	−0.414	−47	−0.055
0.6088	0.0000	0.7615	1097	1092	1.3653	−0.472	−46	−0.023	0.1482	0.7014	0.7746	1101	1064	1.3459	−0.339	−40	−0.064
0.6582	0.0000	0.7641	1102	1077	1.3648	−0.448	−45	−0.022	0.0902	0.8183	0.7789	1102	1057	1.3396	−0.233	−27	−0.063
0.7018	0.0000	0.7664	1107	1064	1.3644	−0.420	−44	−0.021	0.0546	0.8900	0.7818	1103	1052	1.3354	−0.152	−18	−0.050
0.7449	0.0000	0.7689	1112	1051	1.3639	−0.386	−42	−0.020	0.3966	0.0000	0.7516	1075	1152	1.3665	−0.476	−42	−0.019
0.7934	0.0000	0.7717	1118	1036	1.3633	−0.340	−38	−0.018	0.3347	0.1560	0.7553	1080	1135	1.3638	−0.533	−48	−0.031
0.8758	0.0000	0.7769	1129	1011	1.3620	−0.239	−28	−0.012	0.3044	0.2324	0.7573	1083	1127	1.3624	−0.549	−50	−0.033
0.8901	0.0000	0.7778	1130	1006	1.3618	−0.217	−26	−0.011	0.2766	0.3027	0.7593	1085	1119	1.3608	−0.557	−52	−0.034
0.9436	0.0000	0.7813	1137	991	1.3607	−0.125	−15	−0.006	0.2415	0.3910	0.7619	1088	1108	1.3586	−0.553	−54	−0.035
0.0000	0.0782	0.7384	1043	1244	1.3660	−0.171	−13	−0.006	0.1932	0.5128	0.7658	1093	1094	1.3549	−0.522	−54	−0.038
0.0000	0.1265	0.7401	1047	1233	1.3655	−0.266	−20	−0.010	0.1607	0.5947	0.7687	1095	1084	1.3518	−0.482	−53	−0.041
0.0000	0.1769	0.7418	1051	1221	1.3650	−0.355	−27	−0.013	0.1178	0.7029	0.7728	1099	1072	1.3469	−0.403	−48	−0.043
0.0000	0.2224	0.7435	1054	1211	1.3644	−0.424	−33	−0.015	0.0826	0.7918	0.7765	1101	1063	1.3419	−0.312	−40	−0.040
0.0000	0.2673	0.7452	1057	1201	1.3638	−0.483	−38	−0.017	0.0449	0.8867	0.7808	1102	1055	1.3357	−0.188	−26	−0.030
0.0000	0.3116	0.7468	1060	1192	1.3630	−0.530	−42	−0.019	0.3100	0.0000	0.7479	1069	1171	1.3667	−0.421	−36	−0.015
0.0000	0.3536	0.7485	1063	1183	1.3623	−0.565	−46	−0.020	0.2733	0.1185	0.7510	1073	1157	1.3650	−0.505	−42	−0.021
0.0000	0.4067	0.7506	1066	1172	1.3612	−0.596	−50	−0.021	0.2412	0.2218	0.7538	1077	1144	1.3633	−0.555	−47	−0.026
0.0000	0.4282	0.7515	1067	1168	1.3607	−0.604	−51	−0.022	0.2130	0.3131	0.7566	1081	1132	1.3614	−0.580	−50	−0.031
0.0000	0.5172	0.7554	1073	1150	1.3583	−0.616	−55	−0.022	0.1819	0.4131	0.7598	1085	1118	1.3589	−0.585	−53	−0.035
0.0000	0.5639	0.7575	1076	1141	1.3568	−0.607	−56	−0.022	0.1480	0.5226	0.7637	1090	1103	1.3555	−0.560	−55	−0.038
0.0000	0.6060	0.7596	1078	1132	1.3553	−0.591	−56	−0.021	0.1213	0.6088	0.7670	1093	1091	1.3523	−0.515	−54	−0.038
0.0000	0.6619	0.7625	1082	1120	1.3530	−0.558	−56	−0.020	0.0930	0.7001	0.7708	1097	1079	1.3483	−0.443	−50	−0.035
0.0000	0.7090	0.7652	1085	1109	1.3508	−0.520	−55	−0.018	0.0649	0.7907	0.7750	1100	1067	1.3433	−0.344	−43	−0.029
0.0000	0.7519	0.7677	1089	1099	1.3485	−0.476	−53	−0.016	0.0328	0.8942	0.7803	1102	1056	1.3362	−0.195	−27	−0.018
0.0000	0.8388	0.7736	1095	1078	1.3428	−0.359	−46	−0.012	0.2139	0.0000	0.7440	1058	1201	1.3668	−0.320	−28	−0.011
0.0000	0.8458	0.7741	1095	1076	1.3423	−0.348	−45	−0.011	0.1838	0.1407	0.7478	1065	1180	1.3650	−0.447	−39	−0.015
0.0000	0.8905	0.7774	1098	1067	1.3385	−0.267	−36	−0.009	0.1650	0.2285	0.7504	1069	1166	1.3636	−0.507	−45	−0.019
0.0000	0.9401	0.7814	1100	1058	1.3336	−0.160	−22	−0.005	0.1450	0.3222	0.7535	1074	1151	1.3618	−0.552	−50	−0.024
0.9056	0.0000	0.7788	1132	1002	1.3615	−0.193	−23	−0.010	0.1260	0.4111	0.7566	1078	1137	1.3597	−0.573	−53	−0.027
0.7715	0.1480	0.7796	1129	1005	1.3580	−0.169	−21	−0.009	0.1048	0.5102	0.7604	1083	1122	1.3569	−0.569	−55	−0.030
0.6485	0.2839	0.7805	1127	1009	1.3545	−0.146	−19	−0.007	0.0844	0.6052	0.7644	1087	1107	1.3535	−0.535	−55	−0.031
0.5454	0.3978	0.7812	1124	1013	1.3512	−0.125	−17	−0.006	0.0653	0.6945	0.7685	1091	1093	1.3496	−0.472	−52	−0.030
0.4528	0.5000	0.7820	1121	1017	1.3479	−0.106	−15	−0.005	0.0424	0.8019	0.7741	1096	1075	1.3436	−0.354	−43	−0.024
0.3761	0.5847	0.7826	1119	1021	1.3450	−0.089	−14	−0.005	0.0233	0.8911	0.7793	1100	1061	1.3372	−0.218	−30	−0.016
0.2897	0.6800	0.7834	1116	1026	1.3414	−0.070	−11	−0.004	0.1049	0.0000	0.7396	1048	1232	1.3666	−0.163	−16	−0.005
0.2177	0.7596	0.7841	1113	1030	1.3382	−0.053	−9	−0.003	0.0909	0.1334	0.7438	1055	1207	1.3654	−0.387	−30	−0.010
0.1428	0.8423	0.7849	1110	1035	1.3345	−0.035	−6	−0.002	0.0804	0.2339	0.7472	1061	1188	1.3640	−0.508	−40	−0.017
0.0832	0.9082	0.7856	1107	1039	1.3314	−0.021	−4	−0.001	0.0711	0.3218	0.7503	1066	1172	1.3624	−0.579	−47	−0.024
0.8037	0.0000	0.7723	1119	1033	1.3633	−0.329	−37	−0.017	0.0615	0.4136	0.7538	1072	1155	1.3603	−0.618	−53	−0.031
0.6525	0.1882	0.7743	1119	1032	1.3588	−0.296	−35	−0.031	0.0526	0.4984	0.7573	1077	1139	1.3580	−0.623	−56	−0.037
0.5730	0.2870	0.7755	1118	1031	1.3564	−0.275	−34	−0.029	0.0414	0.6055	0.7620	1083	1119	1.3542	−0.585	−57	−0.041
0.4991	0.3789	0.7767	1117	1032	1.3539	−0.253	−32	−0.027	0.0315	0.6995	0.7666	1088	1102	1.3500	−0.509	−54	−0.041
0.4118	0.4876	0.7781	1116	1033	1.3505	−0.222	−28	−0.029	0.0212	0.7984	0.7721	1093	1084	1.3443	−0.387	−46	−0.035
0.3230	0.5981	0.7797	1114	1034	1.3464	−0.186	−24	−0.035	0.0104	0.9009	0.7788	1099	1063	1.3366	−0.214	−31	−0.022
0.2772	0.6551	0.7806	1113	1035	1.3441	−0.166	−22	−0.040									

Table 2. (Continued)

x_1	x_2	ρ/g·cm^{-3}	u/m·s^{-1}	κ_s/TPa^{-1}	n_D	V^E/cm^3·mol^{-1}	$\Delta\kappa_s$/TPa^{-1}	ΔR/cm^3·mol^{-1}
				Ethanol + Methanol + TAME				
0.9522	0.0000	0.7840	1143	977	1.3622	−0.070	−5	−0.004
0.9009	0.0000	0.7828	1142	979	1.3651	−0.136	−11	−0.007
0.8530	0.0000	0.7818	1142	981	1.3675	−0.190	−15	−0.010
0.7985	0.0000	0.7806	1141	984	1.3699	−0.241	−18	−0.013
0.7480	0.0000	0.7795	1139	988	1.3718	−0.280	−19	−0.015
0.6978	0.0000	0.7785	1138	992	1.3736	−0.311	−20	−0.017
0.6463	0.0000	0.7774	1136	996	1.3751	−0.335	−20	−0.019
0.5990	0.0000	0.7765	1135	1000	1.3765	−0.351	−21	−0.020
0.5494	0.0000	0.7755	1133	1004	1.3777	−0.361	−20	−0.020
0.5022	0.0000	0.7746	1132	1007	1.3788	−0.365	−20	−0.020
0.4565	0.0000	0.7738	1131	1010	1.3798	−0.364	−20	−0.020
0.4066	0.0000	0.7729	1130	1014	1.3807	−0.357	−19	−0.020
0.3546	0.0000	0.7720	1128	1018	1.3816	−0.343	−18	−0.019
0.3092	0.0000	0.7712	1127	1021	1.3824	−0.326	−17	−0.017
0.2565	0.0000	0.7703	1125	1025	1.3831	−0.299	−15	−0.016
0.2047	0.0000	0.7694	1123	1030	1.3838	−0.263	−13	−0.013
0.1559	0.0000	0.7685	1122	1034	1.3844	−0.220	−11	−0.011
0.1059	0.0000	0.7677	1120	1039	1.3849	−0.165	−8	−0.008
0.0583	0.0000	0.7668	1118	1044	1.3854	−0.100	−5	−0.004
0.8988	0.0000	0.7829	1142	979	1.3653	−0.139	−12	−0.007
0.7801	0.1320	0.7833	1139	985	1.3620	−0.126	−10	−0.008
0.7042	0.2165	0.7835	1136	989	1.3596	−0.117	−10	−0.009
0.6216	0.3085	0.7838	1133	993	1.3569	−0.107	−9	−0.009
0.5411	0.3980	0.7841	1130	998	1.3540	−0.095	−8	−0.008
0.4479	0.5017	0.7845	1126	1005	1.3504	−0.082	−7	−0.008
0.3446	0.6166	0.7849	1122	1013	1.3459	−0.065	−5	−0.007
0.2669	0.7030	0.7853	1118	1019	1.3422	−0.052	−4	−0.006
0.1904	0.7882	0.7856	1114	1026	1.3382	−0.038	−3	−0.004
0.1073	0.8807	0.7860	1109	1035	1.3334	−0.022	−2	−0.003
0.7970	0.0000	0.7807	1141	985	1.3701	−0.243	−18	−0.013
0.6981	0.1241	0.7813	1138	989	1.3670	−0.230	−17	−0.010
0.6224	0.2191	0.7818	1135	992	1.3644	−0.216	−16	−0.007
0.5513	0.3083	0.7823	1133	996	1.3617	−0.201	−15	−0.005
0.4883	0.3873	0.7827	1130	1000	1.3590	−0.186	−14	−0.004
0.3794	0.5239	0.7835	1126	1007	1.3538	−0.155	−12	−0.002
0.3187	0.6001	0.7839	1123	1012	1.3505	−0.135	−11	−0.001
0.2369	0.7028	0.7846	1119	1019	1.3456	−0.105	−9	−0.000
0.1707	0.7858	0.7851	1115	1025	1.3410	−0.078	−7	0.000
0.0981	0.8769	0.7857	1110	1033	1.3354	−0.047	−4	0.000
0.6984	0.0000	0.7784	1138	992	1.3735	−0.311	−20	−0.017
0.6093	0.1276	0.7793	1136	994	1.3704	−0.303	−20	−0.013
0.5432	0.2222	0.7800	1134	997	1.3678	−0.292	−19	−0.011
0.4825	0.3092	0.7806	1132	999	1.3652	−0.276	−19	−0.009
0.4268	0.3888	0.7812	1130	1002	1.3624	−0.259	−18	−0.007
0.3413	0.5113	0.7822	1127	1007	1.3576	−0.224	−16	−0.005
0.2828	0.5950	0.7828	1124	1011	1.3539	−0.195	−15	−0.004
0.2147	0.6926	0.7837	1120	1017	1.3488	−0.157	−13	−0.002
0.1436	0.7944	0.7846	1115	1025	1.3427	−0.111	−10	−0.001
0.0781	0.8882	0.7855	1110	1033	1.3360	−0.063	−6	−0.001
0.6030	0.0000	0.7766	1136	998	1.3766	−0.350	−21	−0.020
0.5284	0.1237	0.7776	1134	1000	1.3737	−0.349	−21	−0.019
0.4789	0.2058	0.7783	1133	1002	1.3714	−0.343	−20	−0.018
0.4112	0.3180	0.7793	1131	1004	1.3680	−0.325	−20	−0.017
0.3636	0.3971	0.7800	1129	1006	1.3652	−0.306	−20	−0.016
0.2983	0.5053	0.7810	1126	1009	1.3608	−0.272	−19	−0.014
0.2482	0.5884	0.7818	1124	1013	1.3570	−0.240	−18	−0.012
0.1867	0.6904	0.7829	1120	1018	1.3514	−0.193	−15	−0.010
0.1237	0.7949	0.7840	1116	1025	1.3446	−0.137	−12	−0.007
0.0682	0.8868	0.7851	1111	1033	1.3374	−0.079	−8	−0.004
0.4995	0.0000	0.7746	1132	1007	1.3791	−0.365	−20	−0.020
0.4316	0.1358	0.7759	1132	1006	1.3760	−0.381	−22	−0.020
0.3865	0.2262	0.7768	1131	1007	1.3736	−0.380	−22	−0.019
0.3351	0.3291	0.7779	1130	1007	1.3704	−0.368	−23	−0.018
0.2923	0.4148	0.7788	1128	1009	1.3674	−0.349	−23	−0.016
0.2432	0.5130	0.7799	1126	1011	1.3633	−0.317	−22	−0.014
0.2048	0.5900	0.7808	1124	1014	1.3596	−0.285	−20	−0.013
0.1518	0.6961	0.7821	1120	1019	1.3535	−0.229	−17	−0.010
0.1075	0.7848	0.7833	1116	1025	1.3474	−0.173	−14	−0.007
0.0596	0.8807	0.7847	1110	1034	1.3393	−0.102	−8	−0.004
0.4016	0.0000	0.7729	1130	1014	1.3811	−0.356	−19	−0.020
0.3460	0.1385	0.7744	1129	1012	1.3781	−0.393	−21	−0.020
0.3082	0.2326	0.7755	1129	1012	1.3757	−0.402	−22	−0.019
0.2749	0.3154	0.7765	1128	1012	1.3732	−0.400	−23	−0.019
0.2346	0.4158	0.7777	1127	1012	1.3697	−0.383	−24	−0.017
0.1863	0.5360	0.7792	1125	1014	1.3646	−0.345	−23	−0.015
0.1236	0.6923	0.7814	1120	1020	1.3560	−0.263	−19	−0.011
0.1125	0.7198	0.7818	1119	1021	1.3541	−0.245	−18	−0.010
0.0816	0.7969	0.7829	1116	1026	1.3483	−0.189	−15	−0.008
0.0427	0.8938	0.7846	1110	1035	1.3393	−0.106	−8	−0.004
0.3101	0.0000	0.7713	1127	1020	1.3826	−0.327	−17	−0.018
0.2718	0.1236	0.7728	1128	1018	1.3802	−0.390	−20	−0.018
0.2385	0.2308	0.7742	1128	1016	1.3776	−0.421	−22	−0.018
0.2102	0.3223	0.7754	1127	1015	1.3750	−0.431	−24	−0.017
0.1821	0.4128	0.7767	1126	1015	1.3719	−0.424	−24	−0.016
0.1507	0.5139	0.7781	1125	1016	1.3678	−0.398	−24	−0.014
0.1202	0.6125	0.7795	1123	1018	1.3629	−0.354	−23	−0.012
0.0934	0.6987	0.7809	1120	1021	1.3576	−0.300	−20	−0.010
0.0649	0.7906	0.7824	1116	1026	1.3506	−0.227	−16	−0.008
0.0158	0.9492	0.7855	1107	1039	1.3338	−0.063	−6	−0.002
0.1951	0.0000	0.7693	1124	1029	1.3842	−0.255	−13	−0.013
0.1664	0.1473	0.7714	1125	1024	1.3814	−0.370	−18	−0.015
0.1479	0.2419	0.7727	1125	1022	1.3792	−0.417	−21	−0.015
0.1310	0.3286	0.7740	1125	1020	1.3768	−0.440	−23	−0.015
0.1136	0.4177	0.7754	1125	1019	1.3739	−0.444	−24	−0.015
0.0931	0.5230	0.7771	1124	1019	1.3696	−0.425	−24	−0.013
0.0727	0.6275	0.7788	1122	1021	1.3642	−0.379	−23	−0.012
0.0580	0.7027	0.7802	1119	1023	1.3594	−0.330	−21	−0.010
0.0345	0.8231	0.7825	1114	1029	1.3495	−0.222	−16	−0.007
0.0189	0.9030	0.7842	1110	1035	1.3407	−0.131	−11	−0.004
0.1107	0.0000	0.7679	1121	1036	1.3850	−0.171	−8	−0.008
0.0943	0.1482	0.7702	1123	1030	1.3825	−0.330	−15	−0.011
0.0847	0.2352	0.7715	1124	1027	1.3806	−0.394	−18	−0.012
0.0744	0.3282	0.7730	1124	1024	1.3781	−0.437	−21	−0.012
0.0639	0.4226	0.7746	1124	1022	1.3751	−0.455	−23	−0.012
0.0548	0.5052	0.7760	1123	1021	1.3719	−0.450	−24	−0.012
0.0412	0.6279	0.7782	1121	1022	1.3658	−0.405	−23	−0.010
0.0342	0.6915	0.7794	1120	1024	1.3618	−0.365	−22	−0.009
0.0226	0.7961	0.7815	1116	1028	1.3534	−0.272	−18	−0.007
0.0114	0.8967	0.7838	1111	1034	1.3425	−0.153	−12	−0.004

Table 3. Polynomial Coefficients (A_n) and Standard Deviations (σ) Obtained for the Fits of Eq 7 to the V^E, $\Delta\kappa_s$, ΔR Composition Data for the Binary Systems (for $\Delta\kappa_s$, System Compositions Were in Volume Fraction, ϕ_i)

property	A_0	A_1	A_2	A_3	A_4	σ
			Ethanol + Methanol			
V^E/cm^3·mol^{-1}	0.0249					0.001
$\Delta\kappa_s$/TPa^{-1}	−0.0607					0.2
ΔR/cm^3·mol^{-1}	−0.0171	−0.0304	0.0496			0.001
			Methanol + MTBE			
V^E/cm^3·mol^{-1}	−2.4651		−0.1678	−0.3632		0.001
$\Delta\kappa_s$/TPa^{-1}	−214.7	72.0	−86.4	130.0		0.4
ΔR/cm^3·mol^{-1}	−0.0885					0.001
			Ethanol + MTBE			
V^E/cm^3·mol^{-1}	−1.9854	0.0379		−0.5576		0.001
$\Delta\kappa_s$/TPa^{-1}	−179.4	46.5	−56.4	53.9		0.2
ΔR/cm^3·mol^{-1}	−0.0864	−0.0377				0.001
			TAME + Ethanol			
V^E/cm^3·mol^{-1}	−1.4593	−0.0471	−0.2821	−0.1467		0.001
$\Delta\kappa_s$/TPa^{-1}	−79.72	−33.84	−42.51			0.2
ΔR/cm^3·mol^{-1}	−0.0816					0.001
			TAME + Methanol			
V^E/cm^3·mol^{-1}	−1.8559	−0.1787	−0.3252	−0.2319		0.001
$\Delta\kappa_s$/TPa^{-1}	−84.6	−52.6		−62.4	−128.4	0.2
ΔR/cm^3·mol^{-1}	−0.0857					0.001

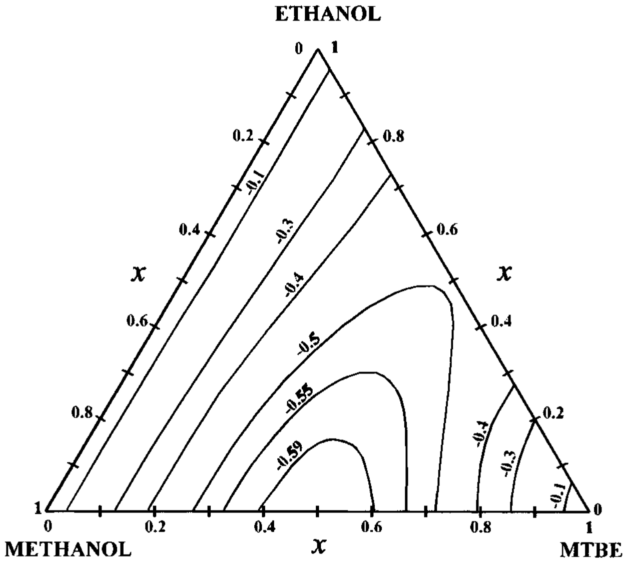

Figure 1. Excess molar volume isolines for ethanol (1) + methanol (2) + MTBE (3) at 298.15 K and atmospheric pressure (system compositions in mole fraction).

(ΔR), which were obtained from

$$\Delta R = R - \sum_i x_i R_i \tag{3}$$

where R_i is the molar refraction of pure component i.

The speeds of sound through the mixtures (u) and the corresponding densities (ρ) were used to calculate isentropic compressibilities (κ_s, Table 2) using the equation

$$\kappa_s = u^{-2}\rho^{-1} \tag{4}$$

and the deviations in isentropic compressibility ($\Delta\kappa_s$, Table 2) were obtained using the expression

$$\Delta\kappa_s = \kappa_s - \sum_i \phi_i \kappa_{si} \tag{5}$$

where κ_s and κ_{si} are the isentropic compressibilities of the mixture and component i, respectively, and ϕ_i is the volume fraction of component i in the mixture as given by

$$\phi_i = x_i V_i / \sum_j \phi_j V_j \tag{6}$$

where j refers to all components of the mixture.

For the ethanol + methanol + 2-methoxy-2-methylpropane system, Figure 1 shows excess volume isolines (system compositions in mole fractions, x_i), and Figure 2 shows isolines for the deviation in isentropic compressibility (system compositions in volume fraction, ϕ_i). These data are shown for the ethanol + methanol + 2-methoxy-2-methylbutane system in Figures 3 and 4.

Correlation

The V^E, ΔR, and $\Delta\kappa_s$ data were correlated with the composition data by means of the Redlich–Kister polynomial (1948), which for binary mixtures is

$$\Delta M = x_i x_j \sum_n A_n (x_i - x_j)^n \tag{7}$$

where ΔM is V^E or ΔR and x_i is the mole fraction of component i in the mixture, or ΔM is $\Delta\kappa_s$ and x_i is the volume fraction of component i in the mixture, A_n is the polynomial coefficient, and n is the number of the polynomial coefficient.

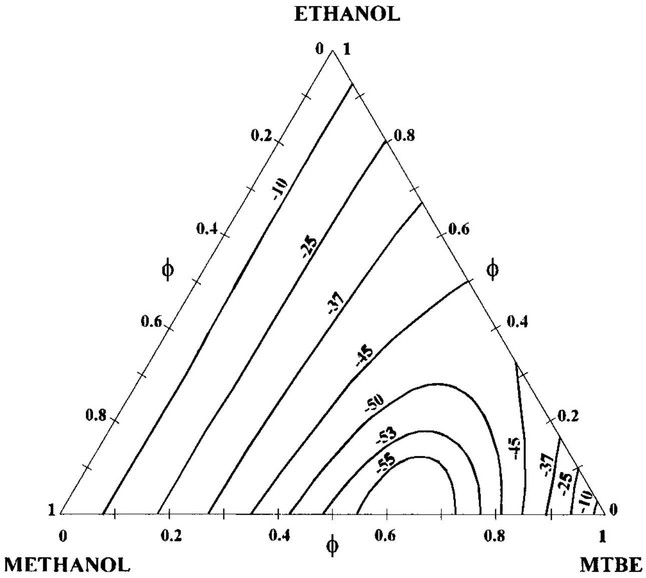

Figure 2. Isolines for the deviation in isentropic compressibility of ethanol (1) + methanol (2) + MTBE (3) mixtures at 298.15 K and atmospheric pressure (system compositions in volume fraction).

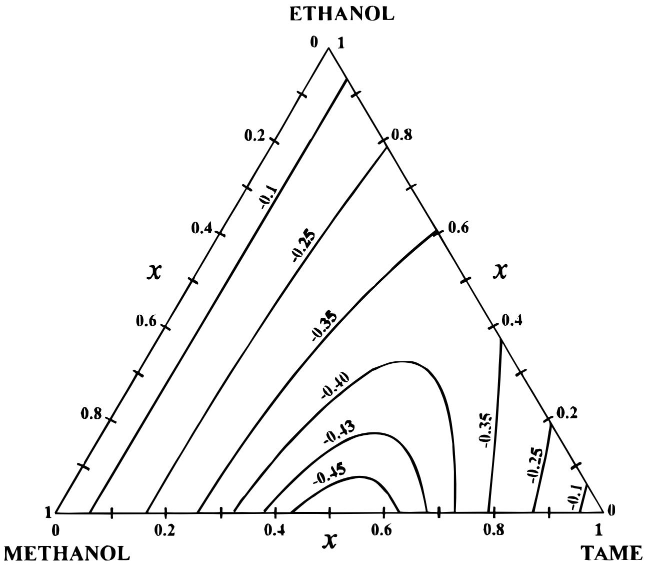

Figure 3. Excess molar volume isolines for ethanol (1) + methanol (2) + TAME (3) at 298.15 K and atmospheric pressure (system compositions in mole fraction).

For ternary systems the corresponding equation is

$$\Delta M_{123} = \Delta M_{12} + \Delta M_{32} + \Delta M_{31} + x_1 x_2 x_3 (A + B(x_1 - x_2) + C(x_3 - x_2) + D(x_3 - x_1) + E(x_1 - x_2)^2 + F(x_3 - x_2)^2 + G(x_3 - x_1)^2 + ... \tag{8}$$

where ΔM_{123} is V^E, $\Delta\kappa_s$, or ΔR, x_i is the mole fraction or volume fraction of component i, according to the parameter being correlated (as previously indicated), and ΔM_{ij} is the value of the Redlich–Kister coefficient for the same property, as obtained by fitting the Redlich–Kister polynomial to the data for the binary system (i,j).

Equations 6 and 7 were fitted to the appropriate parameter–composition data for the binary and ternary systems by least-squares regression, applying Fisher's F-test to establish the number of coefficients. These coefficients and their mean standard deviations are listed in Table 3 for the binary systems (data for the TAME + methanol system

Table 4. Polynomial Coefficients and Standard Deviations (σ) Obtained for the Fits of Eq 8 to the V^E, $\Delta\kappa_s$, and ΔR Composition Data for the Ternary Systems Ethanol (1) + Methanol (2) + MTBE (3) and Ethanol (1) + Methanol (2) + TAME (3) (for $\Delta\kappa_s$, System Compositions Were in Volume Fraction, ϕ_i)

property	*A*	*B*	*C*	*D*	*E*	*F*	*G*	σ
			Ethanol + Methanol + MTBE					
V^E/cm^3·mol^{-1}	−0.5696	0.7923	−1.3317	−0.5394				0.006
$\Delta\kappa_s$/TPa^{-1}	89.37	−2.28	−18.24	−20.51	−86.51	506.35	78.04	0.8
ΔR/cm^3·mol^{-1}	0.1192	0.6700	−0.8571	−0.1871	−2.5023	−3.1130	1.2472	0.009
			Ethanol + Methanol + TAME					
V^E/cm^3·mol^{-1}	−0.0747	0.0925	0.8920	0.7995				0.003
$\Delta\kappa_s$/TPa^{-1}	59.49	57.66	90.09	32.43				0.6
ΔR/cm^3·mol^{-1}	0.0188	0.0004	−0.2316	−0.2312				0.009

Table 5. Standard Deviations in the Excess Molar Volumes and Deviations in Molar Refraction and Isentropic Compressibility Predicted for Ternary Mixtures at 298.15 K and Atmospheric Pressure

	Radojkovic *et al.* (eq 9)	Rastogi *et al.* (eq 10)	Jacob and Fitzner (eq 11)	Colinet (eq 12)	Toop (eq 13)	Kohler (eq 14)	Tsao and Smith (eq 15)	Scatchard *et al.* (eq 16)
			Ethanol + Methanol + MTBE					
ΔV^E_{123}/cm^3·mol^{-1}	0.061	0.148	0.049	0.246	0.029	0.017	0.078	0.203
ΔR_{123}/cm^3·mol^{-1}	0.023	0.024	0.023	0.009	0.021	0.022	0.020	0.021
$\Delta\kappa_{s123}$/TPa^{-1}	3	13	2	19	8	5	13	24
			Ethanol + Methanol + TAME					
ΔV^E_{123}/cm^3·mol^{-1}	0.009	0.102	0.031	0.177	0.033	0.01	0.070	0.170
ΔR_{123}/cm^3·mol^{-1}	0.004	0.047	0.004	0.09	0.004	0.012	0.015	0.008
$\Delta\kappa_{s123}$/TPa^{-1}	1	5	1	9	4	3	6	11

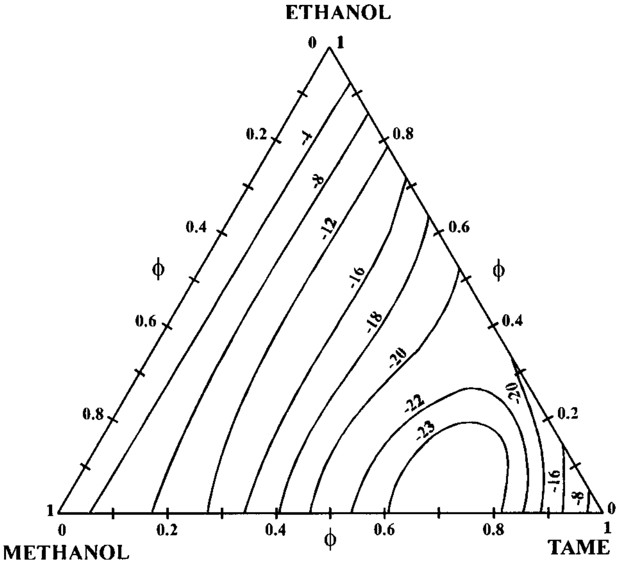

Figure 4. Isolines for the deviation in isentropic compressibility of ethanol (1) + methanol (2) + TAME (3) mixtures at 298.15 K and atmospheric pressure (system compositions in volume fractions).

were taken from Arce *et al.*, (1996)) and in Table 4 for the ternary system.

Prediction

Although it would be desirable to be able to estimate the thermodynamic properties of multicomponent systems from the properties of their pure components, in practice such estimates are often inaccurate due to the effects of mixing. An attractive alternative that limits experimental work to binary mixtures is to evaluate the property changes of mixing of the multicomponent system from the properties of its constituent binary subsystems. To assess the viability of this approach for the ternary systems studied here, their V^E, ΔR, and $\Delta\kappa_s$ were predicted from these properties of their constituent binary subsystems by means of empirical equations available in the literature. The equations used were as follows.

The equation of Radojkovic *et al.* (1977)

$$\Delta M_{123} = \Delta M_{12}(x_1,x_2) + \Delta M_{23}(x_2,x_3) + \Delta M_{13}(x_1,x_3) \qquad (9)$$

in which ΔM_{ij} or ΔM_{ijk} is the excess molar volume or the deviation in the molar refraction or in the isentropic compressibility and x_i is the mole fraction or volume fraction of pure component i, as indicated above.

The equation of Rastogi *et al.* (1977)

$$\Delta M_{123} = 0.5[(x_1 + x_2)\Delta M'_{12}(x'_1,x'_2) + (x'_1 + x'_3)\Delta M'_{13}(x'_1,x'_3) + (x_2 + x_3)\Delta M'_{23}(x'_2,x'_3)] \qquad (10)$$

in which $\Delta M'_{ij}(x'_i,x'_j)$ is the excess volume or the deviation in the molar refraction or isentropic compressibility of the binary mixture and $x'_i = 1 - x'_j = x_i/(x_i + x_j)$.

The equation of Jacob and Fitzner (1977)

$$\Delta M_{123} = 4\left[\frac{x_1x_2}{(2x_1 + x_3)(2x_2 + x_3)}\Delta M'_{12}(x'_1,x'_2) + \frac{x_1x_3}{(2x_1 + x_2)(2x_3 + x_2)}\Delta M'_{13}(x'_1,x'_3)\right] + \left[4\frac{x_2x_3}{(2x_2 + x_1)(2x_3 + x_1)}\Delta M'_{23}(x'_2,x'_3)\right] \qquad (11)$$

The equation of Colinet (1967)

$$\Delta M_{123} = 0.5\left[\left(\frac{x_2}{1 - x_1}\right)\Delta M''_{12}(x_1,1-x_1) + \left(\frac{x_1}{1 - x_2}\right)\Delta M''_{12}(1-x_2,x_2) + \left(\frac{x_3}{1 - x_1}\right)\Delta M''_{13}(x_1,1-x_1)\right] + 0.5\left[\left(\frac{x_1}{1 - x_3}\right)\Delta M''_{12}(1-x_3,x_3) + \left(\frac{x_3}{1 - x_2}\right)\Delta M''_{23}(x_2,1-x_2) + \left(\frac{x_2}{1 - x_3}\right)\Delta M''_{23}(1-x_3,x_3)\right] \qquad (12)$$

The equation of Toop (1965)

$$\Delta M_{123} = \left(\frac{x_2}{1 - x_1}\right)\Delta M'_{12}(x'_1,x'_2) + \left(\frac{x_3}{1 - x_1}\right)\Delta M'_{13}(x'_1,x'_3) + (1 - x_1)^2\Delta M'_{23}(x'_2,x'_3) \qquad (13)$$

The equation of Kohler (1960)

$$\Delta M_{123} = (x_1 + x_2)^2\Delta M'_{12}(x'_1,x'_2) + (x_1 + x_3)^2(x'_1,x'_3)\Delta M'_{13} + (x_2 + x_3)^2(x'_2,x'_3)\Delta M'_{23} \quad (14)$$

The equation of Tsao and Smith (1953)

$$\Delta M_{123} = \left(\frac{x_2}{1 - x_1}\right)\Delta M'_{12}(x'_1,x'_2) + \left(\frac{x_3}{1 - x_1}\right)\Delta M'_{13}(x'_1,x'_3) + (1 - x_1)\Delta M'_{23}(x'_2,x'_3) \quad (15)$$

The equation of Scatchard *et al.* (1952)

$$\Delta M_{123} = \left(\frac{x_2}{1 - x_1}\right)\Delta M'_{12}(x'_1,x'_2) + \left(\frac{x_3}{1 - x_1}\right)\Delta M'_{13}(x'_1,x'_3) + \Delta M''_{23}(x'_2,x'_3) \quad (16)$$

For each ternary system, Table 5 lists the standard deviations in the values of V^E, ΔR, and $\Delta\kappa_s$ predicted by each equation.

Conclusions

For both the ethanol + methanol + MTBE system and the ethanol + methanol + TAME system, the excess molar volumes at 298.15 K and atmospheric pressure were negative, except for binary ethanol + methanol mixtures, which had small, positive V^E. The system containing MTBE showed the largest deviation from ideality, with minimum V^E around −0.62 $cm^3 \cdot mol^{-1}$ for mixtures with MTBE and methanol in around 0.5 mole fraction. For the system containing TAME, minimum V^E were around −0.46 $cm^3 \cdot mol^{-1}$ and also occurred for mixtures with ether and methanol in around 0.5 mole fraction.

The deviations in the molar refractions of the two systems studied were also negative except for the binary ethanol and methanol mixtures. Although the largest deviation in ΔR occurred for the system containing MTBE, these deviations were generally very small for both systems.

As occurred for V^E and ΔR, the deviations in the isentropic compressibility were negative except for methanol + ethanol mixtures, for which the components' κ_s were additive. $\Delta\kappa_s$ was again largest for the system containing MTBE, for which the minimun deviation was around −57 TPa^{-1}, as against −24 Tpa^{-1} for the system containing TAME.

The thermodynamic properties were very satisfactorily correlated by the Redlich−Kister polynomial. Most of the predictive equations examined, but especially Kohler's (1960) equation, allowed adequate prediction of V^E for the ternary systems from the data for their constituent binary subsystems. However, the predictions of ΔR and $\Delta\kappa_s$ were rather poor. The best predictions of ΔR were obtained with the equations of Toop (1965), Radojkovic *et al.* (1977), and Jacob and Fitzner (1977). The latter two equations also afforded the best predictions of $\Delta\kappa_s$, while Kohler's (1960) equation afforded somewhat poorer predictions, and the remaining equations were unsuitable for prediction of the $\Delta\kappa_s$ values for the systems studied. The equations of Scatchard *et al.* (1952), Colinet (1967), and Rastogi *et al.* (1977) were particularly unsuitable for the prediction of the V^E, ΔR, or $\Delta\kappa_s$ data for the ternary systems studied.

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