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Densities, Refractive Indices, Speeds of Sound, and Shear Viscosities of Diethylene Glycol Dimethyl Ether with Ethyl Acetate, Methyl Benzoate, Ethyl Benzoate, and Diethyl Succinate in the Temperature Range from 298.15 to 318.15 K

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Densities, refractive indices, speeds of sound, and shear viscosities for the mixtures of diethylene glycol dimethyl ether with ethyl acetate, methyl benzoate, ethyl benzoate, or diethyl succinate are measured as a function of mole fraction at temperatures of 298.15, 303.15, 308.15, 313.15, and 318.15 K. The values of these properties are fitted to a power series equation involving both temperature and the mole fraction of the mixture. The experimental values of the mixtures and pure liquids are also used to calculate excess molar volume V^E, changes in isentropic compressibility $\Delta\beta$, changes in refractivity ΔR, and changes in viscosity $\Delta\eta$ for the mixing process. These results are fitted to the Redlich–Kister polynomial relation to estimate the binary coefficients. The specific acoustic impedance factor of the liquids has been calculated to see a possible match of their values with that of sea water, and the potential applications of these liquids as sonar transducer fill fluids have been investigated. The refractive index and density values of the mixtures are used to test the accuracy of the available refractive index mixing relationships in predicting the binary refractive index data. Viscosity results are also analyzed by using the viscosity equations of McAllister, Heric, and Auslaender.

Introduction

As a part of an ongoing program of research by Aminabhavi and coworkers (*1–6*) concerning the physicochemical studies on binary liquid mixtures, we present here some new and useful experimental data on density ρ, refractive index n, speed of sound u, and viscosity η, for the mixtures of diethylene glycol dimethyl ether with ethyl acetate, methyl benzoate, ethyl benzoate, or diethyl succinate in the temperature interval of 298.15–318.15 K. The isentropic compressibility, β, has been calculated from density and speed of sound results. The reason for selecting diethylene glycol dimethyl ether (also called dimethyldiglycol or simply diglyme) is that many of the polyalkyl ether glycols have been used as transducer fill fluids in underwater Navy research (*7*). These fill fluids exhibit an acoustical match with sea water in terms of density, speed of sound, and specific acoustic impedance to avoid loss of energy associated with the reflection of the sound wave. This prompted us to undertake a detailed investigation of the important physical property data on mixtures of diglyme with structurally different esters. The particular esters were chosen in view of their importance in polymer processing industries as plasticizers. To the best of our knowledge, such binary data for the chosen mixtures have not been previously studied. Moreover, from a fundamental viewpoint, it would be interesting to know the behavior of diglyme in an environment of ester molecules.

The experimental results of this study have been used to calculate mixing properties such as excess molar volume V^E, changes in isentropic compressibility $\Delta\beta$, changes in refractivity ΔR, and viscosity deviations from a mole fraction average $\Delta\eta$, of the mixtures. An attempt was also made to analyze the refractive index and density results to test the accuracy of the available mixing rules in predicting the binary refractive index values. Totally, nine different refractive index mixing relations proposed by Arago and Biot (*8*), Dale and Gladstone (*9*), Lorentz and Lorenz (*10, 11*), Eykman (*12*), Weiner (*13*), Heller (*14*), Newton (*15*), Oster (*16*), and Eyring and John (*17*) are used for the analysis. The viscosity equations of McAllister (*18*), Heric (*19*), and Auslaender (*20*) have been used to calculate the binary viscosity data in order to test their accuracies in predicting the binary viscosities (*21*). The specific acoustic impedance values of the liquids have been calculated from the speed of sound and density data in order to see any possible match of these liquids with sea water.

Experimental Section

Materials. Diethylene glycol dimethyl ether (BDH, England), methyl benzoate (Naarden, Holland), and diethyl succinate (Riedel, Germany) were used directly as received. Ethyl acetate (Fischer, Madras) and ethyl benzoate (CDH, New Delhi) were purified by the recommended methods (*22, 23*). The purities of ethyl acetate and ethyl benzoate were ascertained by the constancy of their boiling temperature during final distillation and also from their density, viscosity, and refractive index values at 298.15 K which agreed with the literature values (see Table 1). Gas chromatographic analyses were made using a flame ionization detector (Nucon series, model 5700/5765, with fused silica columns) having a sensitivity better than 10^{-8} g of fatty acid/μL of solvent. The GLC purity analysis for each liquid is also included in Table 1.

Mixtures were prepared by mixing the appropriate volumes of liquids in specially designed ground-glass air-tight bottles and weighed in a single-pan Mettler balance (Switzerland, model AE-240) to an accuracy of ±0.01 mg. Preferential evaporation losses of solvents from the mixtures were kept to a minimum as evidenced by a repeated measurement of

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Table 1. Comparison of Experimental Densities (ρ), Viscosities (η), and Refractive Indices^a (n) of Pure Liquids with Literature Values at 298.15 K

	ρ/(g·cm^{-3})		η/(mPa·s)		n	
liquid (mol % purity)	exptl	lit. (ref)	exptl	lit. (ref)	exptl	lit. (ref)
diglyme (99.4)	0.9396	0.9384 (*22*)	0.973	0.989 (*22*)	1.4074	1.4058 (*22*)
ethyl acetate (99.2)	0.8939	0.8942 (*34*)	0.430	0.429 (*34*)	1.3714	1.3701 (*35*)
methyl benzoate (99.3)	1.0788^b	1.0790 (*22*)	1.638^b	1.673^b (*22*)	1.5152	1.5146 (*22*)
ethyl benzoate (99.5)	1.0373^b	1.0384 (*36*)	1.751^b	1.751^b (*22*)	1.5046	1.5035 (*22*)
diethyl succinate (99.1)	1.0353	1.0358^d (*25*)	2.466	2.461 (*25*)	1.4196	1.4200^c (*25*)

^{a} Values apply to the sodium D line. ^{b} Values compared at 303.15 K. ^{c} Values available at 293.15 K. ^{d} Values interpolated from ref 25.

the physical properties over an interval of 2–3 days, during which time no changes in the physical properties were observed. The possible error in the mole fractions is estimated to be around ±0.0001.

Measurements. Densities of pure liquids and binary mixtures in the composition range 0.1–0.9 mole fraction were measured at 0.1 mole fraction increments using a pycnometer having a bulb volume of 15 cm^3 and a capillary with an internal diameter of 1 mm. The procedural details are the same as given earlier (*1–6*). Densities at 298.15, 303.15, 308.15, 313.15, and 318.15 K are considered significant to four figures. An average of triplicate measurements was taken into account, and these were generally reproducible within ±0.0002 g cm^{-3}.

Refractive indices for the sodium D line were measured with a thermostated Abbe refractometer (Bellingham and Stanley Ltd., London) with an error of less than 0.0001 unit. Water was circulated into the instrument through a thermostatically controlled bath. The refractometer was frequently calibrated by using the glass test piece of known refractive index supplied with the instrument. The sample mixtures were directly injected into the prism assembly of the instrument using an air-tight hypodermic syringe, and the refractive index values were noted after the solutions attained the proper temperature of the refractometer. This procedure was repeated at least three times, and the average of these values was taken for the calculation of refractive index data.

The speed of sound values were obtained by using a variable-path single-crystal interferometer (Mittal Enterprises, New Delhi, model M-84) as per the earlier published procedure (*1–6*). The speed of sound data are accurate to ±2 m s^{-1}. The isentropic compressibilities were calculated as $\beta = 1/u^2\rho$.

Viscosities were measured with a Cannon Fenske viscometer (sizes 100 and 150) supplied by the Industrial Research Glassware Ltd., New Jersey. An electronic stop watch with a precision of ±0.01 s was used to measure the flow times. Triplicate measurements of flow times were reproducible within ±0.01 s. The calibration methods of the viscometers and the experimental details are the same as given earlier (*1–6*). Viscosities are accurate to ±0.001 mPa·s.

During the measurements, the mixtures were transferred to the pycnometer, viscometer, or ultrasonic cell in a controlled atmosphere, taking extreme care to avoid external contamination. In all property measurements, an INSREF, model 016 AP, thermostat was used at a constant temperature control of ±0.01 K at the desired temperature as checked by means of a calibrated (1968 temperature scale) thermometer. Most of the physical property data of pure components of this study are of acceptable quality as evidenced by agreement of these data with the literature values (see Table 1). The results of binary mixtures compiled in Table 2 are the averages of at least three independent measurements for each composition.

Results and Discussion

***Empirical* Fittings.** Experimental values of ρ, n, u, η, and β at 298.15, 303.15, 308.15, 313.15, and 318.15 K were fitted to eq 1 to calculate simultaneously the property Y (=ρ, n, u, η, and β) under consideration for any values of T and

$$Y(T,x_1) = \{[a_0 \exp(a_1 T)](b_0 + b_1 x_1 + b_2 x_1^2 + b_3 x_1^3)\}^{1/2} \tag{1}$$

x_1 of the mixture (*26*). This equation, whose coefficients and standard errors are listed in Table 3, fits the experimental data within the average uncertainty of experimental errors for the temperature range of $298.15 \leq T/\text{K} \leq 318.15$ and composition range of $0 \leq x_1 \leq 1$.

Excess Quantities. Experimental density values of the binary mixtures are used to calculate the excess molar volume, V^E, as

$$V^E = V_m - V_1 x_1 - V_2 x_2 \tag{2}$$

where V_m is the molar volume of the mixture and V_i that of the pure components; x_i represents the mole fraction of the ith component. For all mixtures, the values of V^E are negative, indicating possible hydrogen-bond-type interactions between diglyme and ester molecules. However, the extent of these interactions varies depending on the nature of the ester molecule and also the experimental temperature.

Figure 1 displays the dependence of V^E on x_1 for all the mixtures at 298.15 K. It is observed that mixtures of diglyme with aromatic esters, viz., methyl benzoate and ethyl benzoate, exhibit large volume contractions; i.e., at 298.15 K, the V^E values at equimolar compositions of these mixture are −0.318 and −0.245 cm^3·mol^{-1}, respectively. The interactions in these mixtures may be classified as weak dipole–induced dipole type forces resulting from the polarization of ester molecules by the dipoles of the surrounding diglyme molecules. This effect can be superimposed upon the dipole–dipole interactions and thus lead to a slight increase in the attraction, giving negative V^E. However, in the case of mixtures of diglyme with aliphatic esters, viz., ethyl acetate and diethyl succinate, volume contractions are comparatively smaller and these values are −0.163 and −0.157 cm^3·mol^{-1}, respectively. Moreover, the nature of the V^E vs x_1 curves varies identically in these mixtures, but this pattern is not observed for the mixtures of diglyme with aromatic esters.

The effect of temperature on excess molar volume is depicted, respectively, in Figures 2 and 3 for mixtures of diglyme with ethyl acetate or methyl benzoate, as a typical member of the class of aliphatic and aromatic esters. A considerable amount of volume contraction is observed for the diglyme + ethyl acetate mixture from 298.15 to 318.15 K; thus, the decrease in the values of V^E for this mixture from 298.15 to 318.15 K is 0.095 cm^3·mol^{-1} (see Figure 2). Similarly, in the case of the diglyme + diethyl succinate mixture, the increase in volume contraction is 0.105 cm^3·mol^{-1}, and this dependence is not displayed graphically to avoid the overcrowding of the curves. On the other hand, for the diglyme + methyl benzoate mixture as shown in Figure 3, the change in V^E is quite small, i.e., 0.048 cm^3·mol^{-1}. Similarly, in the case of the diglyme + ethyl benzoate mixture, the change in the values of V^E is 0.039 cm^3·mol^{-1}. These observations suggest that, with a rise in temperature of the mixtures, the specific

Table 2. Experimental Densities (ρ), Vicosities (η), Refractive Indices (n), and Speeds of Sound (u) of Binary Mixtures at Different Temperatures

x_1	$\rho/(g\cdot cm^{-3})$	$\eta/(mPa\cdot s)$	n	$u/(m\cdot s^{-1})$	x_1	$\rho/(g\cdot cm^{-3})$	$\eta/(mPa\cdot s)$	n	$u/(m\cdot s^{-1})$
Diethylene Glycol Dimethyl Ether (1) + Ethyl Acetate (2)									
T = 298.15 K									
0.0000	0.8939	0.430	1.3714	1145	0.6005	0.9264	0.748	1.3972	1238
0.1016	0.9008	0.477	1.3771	1162	0.6994	0.9303	0.815	1.4002	1252
0.2005	0.9069	0.527	1.3820	1180	0.8013	0.9337	0.867	1.4032	1264
0.3016	0.9125	0.579	1.3863	1196	0.8999	0.9368	0.920	1.4052	1276
0.4007	0.9175	0.633	1.3902	1211	1.0000	0.9396	0.973	1.4074	1288
0.4999	0.9221	0.690	1.3939	1225					
T = 303.15 K									
0.0000	0.8878	0.407	1.3690	1123	0.6005	0.9211	0.698	1.3950	1218
0.1016	0.8947	0.451	1.3746	1143	0.6994	0.9250	0.750	1.3980	1231
0.2005	0.9010	0.497	1.3797	1160	0.8013	0.9286	0.807	1.4014	1243
0.3016	0.9068	0.546	1.3842	1176	0.8999	0.9317	0.854	1.4033	1255
0.4007	0.9120	0.594	1.3883	1191	1.0000	0.9346	0.904	1.4055	1265
0.4999	0.9167	0.645	1.3918	1205					
T = 308.15 K									
0.0000	0.8814	0.387	1.3662	1098	0.6005	0.9158	0.653	1.3929	1199
0.1016	0.8888	0.428	1.3722	1121	0.6994	0.9198	0.706	1.3960	1212
0.2005	0.8952	0.469	1.3771	1139	0.8013	0.9235	0.748	1.3988	1224
0.3016	0.9012	0.513	1.3818	1156	0.8999	0.9267	0.794	1.4012	1235
0.4007	0.9064	0.558	1.3858	1171	1.0000	0.9295	0.839	1.4034	1246
0.4999	0.9112	0.604	1.3895	1185					
T = 313.15 K									
0.0000	0.8751	0.368	1.3637	1075	0.6005	0.9104	0.612	1.3906	1180
0.1016	0.8827	0.406	1.3697	1100	0.6994	0.9145	0.659	1.3936	1192
0.2005	0.8893	0.445	1.3747	1119	0.8013	0.9183	0.700	1.3964	1203
0.3016	0.8954	0.485	1.3793	1136	0.8999	0.9216	0.740	1.3949	1215
0.4007	0.9008	0.526	1.3834	1151	1.0000	0.9244	0.781	1.4009	1225
0.4999	0.9059	0.569	1.3874	1166					
T = 318.15 K									
0.0000	0.8687	0.350	1.3612	1053	0.6005	0.9052	0.575	1.3888	1161
0.1016	0.9767	0.385	1.3671	1077	0.6994	0.9093	0.616	1.3918	1173
0.2005	0.8835	0.421	1.3726	1095	0.8013	0.9133	0.653	1.3947	1185
0.3016	0.8898	0.459	1.3773	1113	0.8999	0.9165	0.689	1.3970	1197
0.4007	0.8954	0.496	1.3815	1130	1.0000	0.9193	0.728	1.3992	1209
0.4999	0.9005	0.535	1.3852	1146					
Diethylene Glycol Dimethyl Ether (1) + Methyl Benzoate (2)									
T = 298.15 K									
0.0000	1.0837	1.810	1.5152	1408	0.5990	0.9953	1.286	1.4494	1336
0.1017	1.0679	1.707	1.5042	1400	0.6958	0.9816	1.209	1.4393	1324
0.1985	1.0533	1.622	1.4931	1388	0.7991	0.9673	1.129	1.4287	1310
0.3026	1.0380	1.532	1.4816	1373	0.8979	0.9536	1.055	1.4184	1296
0.3989	1.0239	1.448	1.4709	1360	1.0000	0.9396	0.973	1.4074	1288
0.4978	1.0098	1.367	1.4603	1348					
T = 303.15 K									
0.0000	1.0788	1.638	1.5126	1392	0.5990	0.9904	1.173	1.4471	1320
0.1017	1.0630	1.542	1.5020	1384	0.6958	0.9768	1.105	1.4370	1309
0.1985	1.0484	1.467	1.4908	1372	0.7991	0.9623	1.036	1.4264	1294
0.3026	1.0329	1.389	1.4793	1357	0.8979	0.9487	0.971	1.4165	1280
0.3989	1.0190	1.317	1.4690	1344	1.0000	0.9346	0.904	1.4055	1265
0.4978	1.0048	1.245	1.4579	1332					
T = 308.15 K									
0.0000	1.0739	1.491	1.5101	1372	0.5990	0.9854	1.073	1.4447	1300
0.1017	1.0581	1.401	1.4998	1364	0.6958	0.9718	1.014	1.4346	1289
0.1985	1.0435	1.334	1.4886	1352	0.7991	0.9574	0.953	1.4241	1274
0.3026	1.0281	1.264	1.4770	1337	0.8979	0.9437	0.894	1.4141	1261
0.3989	1.0140	1.200	1.4669	1325	1.0000	0.9295	0.839	1.4034	1246
0.4978	0.9999	1.137	1.4557	1312					
T = 313.15 K									
0.0000	1.0690	1.365	1.5073	1352	0.5990	0.9804	0.987	1.4423	1280
0.1017	1.0533	1.279	1.4975	1344	0.6958	0.9668	0.934	1.4323	1268
0.1985	1.0386	1.218	1.4862	1332	0.7991	0.9524	0.879	1.4218	1254
0.3026	1.0232	1.155	1.4745	1317	0.8979	0.9387	0.828	1.4118	1240
0.3989	1.0092	1.100	1.4638	1304	1.0000	0.9244	0.781	1.4009	1225
0.4978	0.9949	1.044	1.4531	1292					
T = 318.15 K									
0.0000	1.0641	1.253	1.5048	1334	0.5990	0.9754	0.911	1.4403	1261
0.1017	1.0483	1.169	1.4952	1326	0.6958	0.9618	0.862	1.4302	1250
0.1985	1.0337	1.116	1.4841	1314	0.7991	0.9474	0.814	1.4196	1236
0.3026	1.0182	1.061	1.4724	1300	0.8979	0.9336	0.768	1.4094	1222
0.3989	1.0042	1.012	1.4618	1287	1.0000	0.9193	0.728	1.3992	1209
0.4978	0.9899	0.962	1.4510	1275					

Table 2 (Continued)

x_1	$\rho/(\mathrm{g{\cdot}cm^{-3}})$	$\eta/(\mathrm{mPa{\cdot}s})$	n	$u/(\mathrm{m{\cdot}s^{-1}})$	x_1	$\rho/(\mathrm{g{\cdot}cm^{-3}})$	$\eta/(\mathrm{mPa{\cdot}s})$	n	$u/(\mathrm{m{\cdot}s^{-1}})$
Diethylene Glycol Dimethyl Ether (1) + Ethyl Benzoate (2)									
T = 298.15 K									
0.0000	1.0421	1.936	1.5046	1378	0.6032	0.9822	1.301	1.4478	1326
0.1021	1.0323	1.805	1.4954	1362	0.7035	0.9720	1.216	1.4379	1313
0.2028	1.0225	1.694	1.4862	1358	0.8017	0.9616	1.134	1.4277	1305
0.3004	1.0128	1.590	1.4771	1350	0.9022	0.9508	1.056	1.4178	1295
0.4044	1.0024	1.485	1.4672	1342	1.0000	0.9396	0.973	1.4074	1288
0.5041	0.9924	1.389	1.4576	1336					
T = 303.15 K									
0.0000	1.0373	1.751	1.5023		0.6032	0.9773	1.189	1.4455	
0.1021	1.0274	1.629	1.4930		0.7035	0.9669	1.111	1.4355	
0.2028	1.0176	1.533	1.4838		0.8017	0.9566	1.039	1.4256	
0.3004	1.0079	1.442	1.4747		0.9022	0.9458	0.967	1.4157	
0.4044	0.9974	1.350	1.4649		1.0000	0.9346	0.904	1.4055	
0.5041	0.9874	1.266	1.4552						
T = 308.15 K									
0.0000	1.0325	1.591	1.5001		0.6032	0.9724	1.088	1.4433	
0.1021	1.0227	1.476	1.4908		0.7035	0.9620	1.020	1.4333	
0.2028	1.0128	1.390	1.4815		0.8017	0.9516	0.957	1.4236	
0.3004	1.0031	1.311	1.4725		0.9022	0.9407	0.895	1.4135	
0.4044	0.9926	1.231	1.4626		1.0000	0.9295	0.839	1.4034	
0.5041	0.9825	1.157	1.4530						
T = 313.15 K									
0.0000	1.0277	1.453	1.4977		0.6032	0.9676	1.000	1.4409	
0.1021	1.0179	1.342	1.4884		0.7035	0.9571	0.940	1.4309	
0.2028	1.0081	1.268	1.4792		0.8017	0.9467	0.883	1.4212	
0.3004	0.9984	1.198	1.4701		0.9022	0.9358	0.829	1.4111	
0.4044	0.9878	1.126	1.4602		1.0000	0.9244	0.781	1.4009	
0.5041	0.9777	1.062	1.4505						
T = 318.15 K									
0.0000	1.0229	1.332	1.4955		0.6032	0.9626	0.922	1.4386	
0.1021	1.0131	1.228	1.4861		0.7035	0.9521	0.868	1.4288	
0.2028	1.0033	1.161	1.4768		0.8017	0.9418	0.818	1.4192	
0.3004	0.9935	1.098	1.4677		0.9022	0.9309	0.770	1.4093	
0.4044	0.9830	1.035	1.4579		1.0000	0.9193	0.728	1.3992	
0.5041	0.9727	0.976	1.4482						
Diethylene Glycol Dimethyl Ether (1) + Diethyl Succinate (2)									
T = 298.15 K									
0.0000	1.0353	2.466	1.4196	1320	0.6024	0.9825	1.412	1.4134	1301
0.1002	1.0273	2.198	1.4187	1316	0.7034	0.9723	1.296	1.4120	1298
0.2023	1.0189	2.009	1.4177	1310	0.8010	0.9620	1.187	1.4106	1296
0.3012	1.0104	1.843	1.4167	1305	0.9025	0.9508	1.077	1.4090	1290
0.4033	1.0013	1.681	1.4157	1305	1.0000	0.9396	0.973	1.4074	1288
0.5032	0.9920	1.535	1.4146	1304					
T = 303.15 K									
0.0000	1.0299	2.196	1.4173	1302	0.6024	0.9774	1.283	1.4111	1283
0.1002	1.0220	1.951	1.4165	1298	0.7034	0.9673	1.184	1.4098	1278
0.2023	1.0137	1.792	1.4155	1294	0.8010	0.9570	1.086	1.4086	1267
0.3012	1.0052	1.650	1.4146	1290	0.9025	0.9459	0.994	1.4070	1270
0.4033	0.9962	1.513	1.4135	1288	1.0000	0.9346	0.904	1.4055	1265
0.5032	0.9870	1.386	1.4123	1286					
T = 308.15 K									
0.0000	1.0246	1.973	1.4152	1276	0.6024	0.9724	1.163	1.4090	1261
0.1002	1.0169	1.737	1.4144	1269	0.7034	0.9622	1.082	1.4077	1257
0.2023	1.0085	1.599	1.4134	1265	0.8010	0.9520	0.997	1.4063	1255
0.3012	1.0001	1.476	1.4125	1265	0.9025	0.9409	0.920	1.4049	1249
0.4033	0.9911	1.355	1.4113	1263	1.0000	0.9295	0.839	1.4034	1246
0.5032	0.9819	1.251	1.4101	1262					
T = 313.15 K									
0.0000	1.0189	1.779	1.4133	1263	0.6024	0.9673	1.061	1.4069	1242
0.1002	1.0115	1.559	1.4126	1255	0.7034	0.9573	0.989	1.4055	1239
0.2023	1.0032	1.438	1.4116	1254	0.8010	0.9471	0.919	1.4041	1234
0.3012	0.9949	1.330	1.4104	1251	0.9025	0.9360	0.852	1.4026	1230
0.4033	0.9859	1.229	1.4093	1249	1.0000	0.9244	0.781	1.4009	1225
0.5032	0.9768	1.139	1.4081	1247					
T = 318.15 K									
0.0000	1.0140	1.615	1.4115	1242	0.6024	0.9624	0.969	1.4047	1222
0.1002	1.0067	1.406	1.4107	1242	0.7034	0.9523	0.908	1.4033	1219
0.2023	0.9984	1.299	1.4096	1239	0.8010	0.9421	0.849	1.4021	1217
0.3012	0.9900	1.206	1.4084	1232	0.9025	0.9310	0.792	1.4007	1212
0.4033	0.9811	1.115	1.4072	1230	1.0000	0.9193	0.728	1.3992	1209
0.5032	0.9719	1.034	1.4060	1225					

Table 3. Coefficients and Standard Errors of Eq 1

function	a_0	a_1	b_0	b_1	b_2	b_3	σ
Diethylene Glycol Dimethyl Ether (1) + Ethyl Acetate (2)							
$\rho/(\mathrm{g \cdot cm^{-3}})$	1.5041	−0.0024	1.0887	0.1821	−0.0684	0.0081	0.0007
$\eta/(\mathrm{mPa \cdot s})$	38.3568	−0.0266	14.093	25.5991	35.5707	−8.4272	0.0065
n	1.3498	−0.0007	1.6973	0.1474	−0.0693	0.0141	0.0006
$u/(\mathrm{m \cdot s^{-1}})$	4975.16	−6.6965	2065.1	440.063	−119.83	121.324	47.076
Diethylene Glycol Dimethyl Ether (1) + Methyl Benzoate (2)							
$\rho/(\mathrm{g \cdot cm^{-3}})$	1.5579	−0.0020	1.3626	−0.3958	0.0714	−0.0174	0.0004
$\eta/(\mathrm{mPa \cdot s})$	11356.9	−0.0356	11.474	−12.279	6.1062	−1.7312	0.0111
n	1.6039	−0.0006	1.7262	−0.2514	0.0058	0.0100	0.0003
$u(\mathrm{m \cdot s^{-1}})$	6349.8	−5.7625	1752.4	−281.08	−64.955	38.9712	2.0443
Diethylene Glycol Dimethyl Ether (1) + Ethyl Benzoate (2)							
$\rho/(\mathrm{g \cdot cm^{-3}})$	1.4155	−0.0020	1.3957	−0.2651	0.0140	−0.0134	0.0004
$\eta/(\mathrm{mPa \cdot s})$	10059.9	−0.0361	16.971	−21.664	13.5867	−4.2551	0.0126
n	1.5671	−0.0006	1.7496	−0.2115	−0.0071	−0.0003	0.0002
Diethylene Glycol Dimethyl Ether (1) + Diethyl Succinate (2)							
$\rho/(\mathrm{g \cdot cm^{-3}})$	1.6448	−0.0021	1.2074	−0.1799	−0.0284	−0.0054	0.0002
$\eta/(\mathrm{mPa \cdot s})$	6706.15	−0.0410	175.46	−336.03	322.163	−130.71	0.0266
n	1.4509	−0.0006	1.6595	−0.0206	−0.0062	−0.0017	0.0001
$u/(\mathrm{m \cdot s^{-1}})$	4998.67	−6.1035	2149.3	−153.57	142.508	−102.35	2.7084

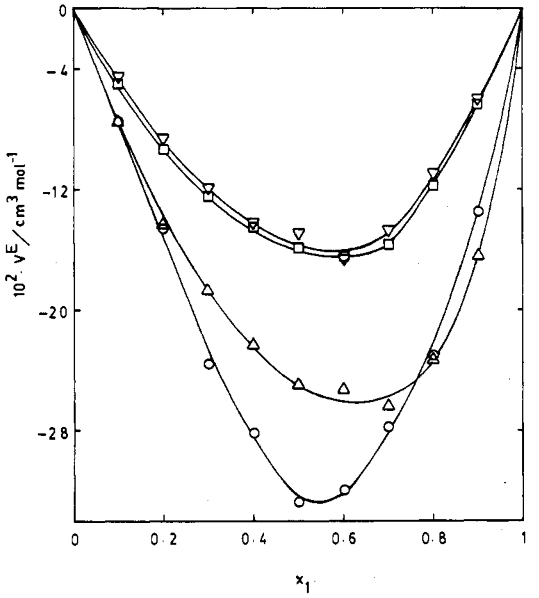

Figure 1. Comparison of excess molar volumes of different mixtures at 298.15 K. Symbols: (○) methyl benzoate, (△) ethyl benzoate, (□) ethyl acetate, and (▽) diethyl succinate.

interactions arising from induced dipole–dipole type forces tend to increase more with aliphatic esters than with aromatic esters.

Sound properties of the mixtures are important in many engineering applications and also from a fundamental viewpoint to understand the mixing process. Thus, deviations of the isentropic compressibility from a volume fraction average, $\Delta\beta$, have been calculated as (*1–6*)

$$\Delta\beta = \beta_m - \beta_1\phi_1 - \beta_2\phi_2 \tag{3}$$

where β_m is the isentropic compressibility of the mixture and β_i that of the pure components and ϕ_i is the volume fraction of the mixture defined as $\phi_i = x_iV_i/\Sigma x_iV_i$. The changes in isentropic compressibility values follow a different trend as shown in Figure 4. In the case of the diglyme + methyl benzoate mixture, a large negative $\Delta\beta$ is observed, whereas for the diglyme + ethyl acetate mixture, these values are less negative and also the dependence is not uniform. However, in the case of mixtures of diglyme with diethyl succinate or ethyl benzoate, the $\Delta\beta$ values show sigmoidal trends and exhibit both positive and negative values.

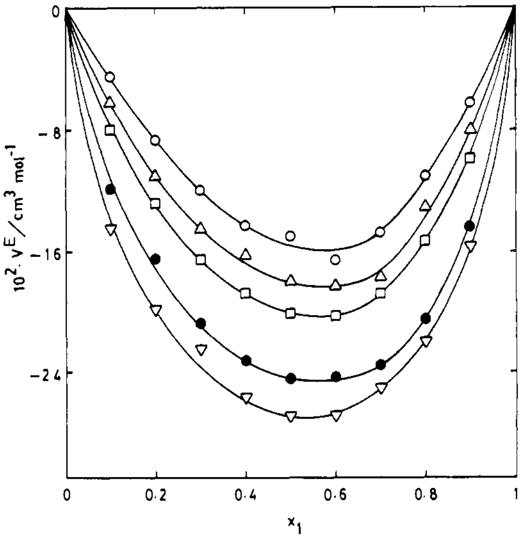

Figure 2. Effect of temperature on excess molar volume for the diethylene glycol dimethyl ether + ethyl acetate mixture. Symbols: (○) 298.15 K, (△) 303.15 K, (□) 308.15 K, (●) 313.15 K, and (▽) 318.15 K.

An interesting observation occurred when the diglyme + diethyl succinate mixture was placed in the ultrasonic cell at a frequency of 1 kHz and the experiment continued. At 308.15 K, the color of the mixture turned light blue. Upon further raising the temperature to 318.15 K, it turned dark blue, and this color remained permanent even after keeping the mixtures up to nearly 60 days. Possibly because of this anomaly, the behavior of $\Delta\beta$ vs ϕ_1 curves for this mixture is found to be far from the usual observations (see Figure 4). This effect is not an experimental artifact, since it was confirmed by repeated measurements. Also, in the case of the diglyme + ethyl benzoate mixture, another unusual effect was seen. At higher temperatures (beyond 298.15 K), the solution acquired a green color, and also an emulsion was formed after passing the ultrasonic waves at a frequency of 4 kHz. This mixture also exhibited an unusual behavior; i.e., a sigmoidal shape is observed for the dependence of $\Delta\beta$ on ϕ_1 at 298.15 K (Figure 4). A plausible explanation for the above-mentioned phenomenon is that a molecular complex might have been formed under the influence of sonic waves, causing this unusual effect; however, this needs further investigations using spectroscopic techniques.

The effect of temperature on $\Delta\beta$ is shown in Figure 5 for mixtures of diglyme with methyl benzoate where it is found

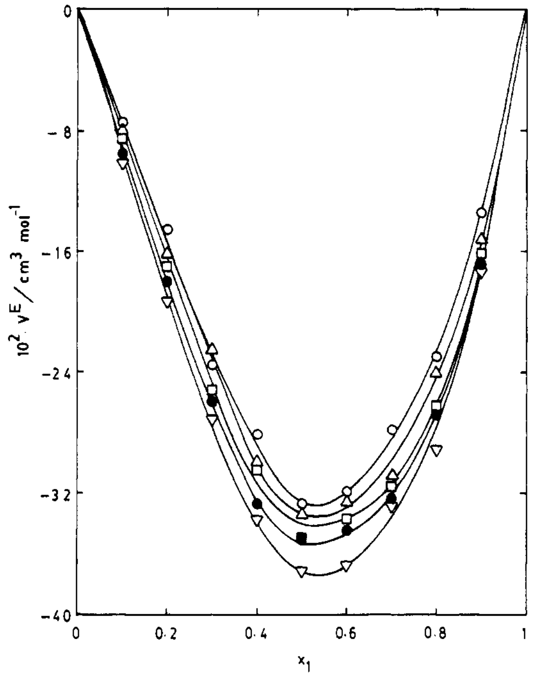

Figure 3. Effect of temperature on excess molar volume for the diethylene glycol dimethyl ether + methyl benzoate mixture at the temperatures given in Figure 2.

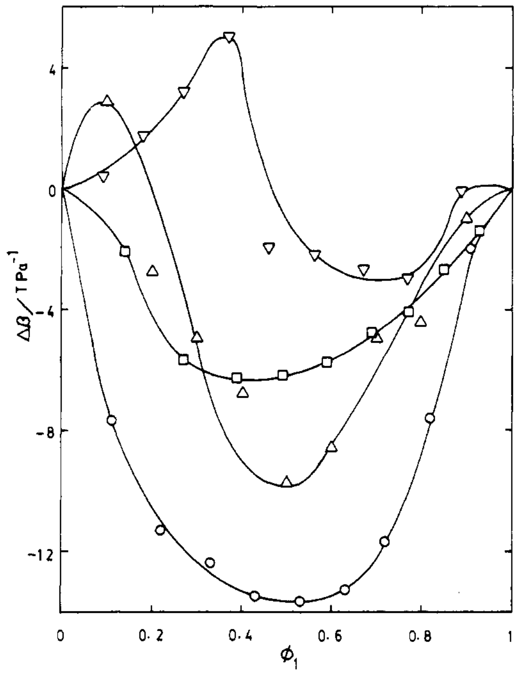

Figure 4. Comparison of changes in isentropic compressibility of different mixtures at 298.15 K. Symbols are the same as in Figure 1.

that $\Delta\beta$ decreases with an increase in temperature. A systematic trend in the decrease of $\Delta\beta$ values with an increase in temperature also occurs in other mixtures (not shown graphically to minimize the number of plots).

From the speed of sound and density results, the specific acoustic impedance factor, z, was calculated as $z = \rho u$. It is realized that the molecules which have the ability for specific intermolecular interactions such as diglyme and esters exhibit high z values. Our calculated values of z at 298.15 K for diglyme and methyl benzoate are, respectively, 1.559×10^6 and 2.148×10^6 kg·m^{-2}·s^{-1}, suggesting strong intermolecular interactions. Also, the rationale behind such a calculation was to find a match of the z value for sea water for which $z = 1.57 \times 10^6$ kg·m^{-2}.s^{-1} at 298.15 K. Indeed, our value of z for diethyl succinate at 318.15 K being 1.564×10^6 kg.m^{-2}.s^{-1} is close to that of sea water. Thus, out of the five liquids selected in this study, the z values of diglyme at 298.15 K and diethyl succinate at 318.15 K closely resemble the value for sea water (*27*). Also, these liquids, unlike castor oil, do not possess high viscosity and, hence, may serve to be possible candidates as sonar transducer fill fluids.

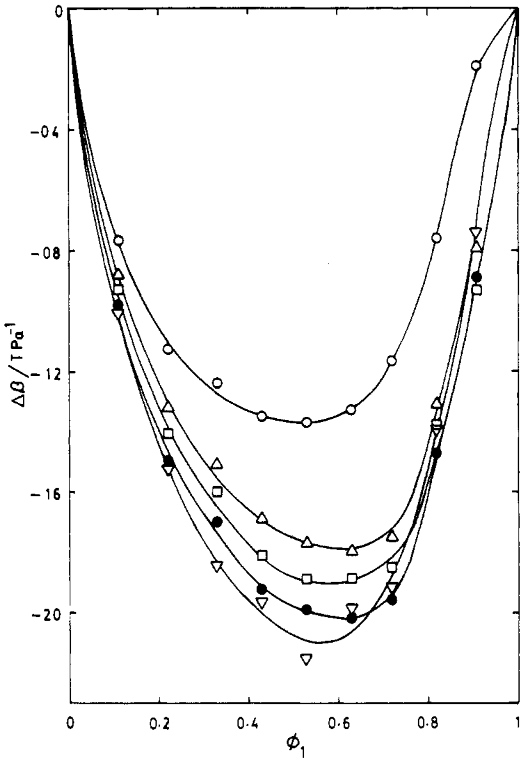

Figure 5. Effect of temperature on changes in isentropic compressibility for the diethylene glycol dimethyl ether + methyl benzoate mixture at the temperatures given in Figure 2.

The molar refractivity data were used to calculate the deviation in refractivity from a volume fraction average, ΔR, as (*1–6*)

$$\Delta R = R_m - R_1\phi_1 - R_2\phi_2 \qquad (4)$$

where R_m stands for molar refractivity of the mixture, while R_i represent those for pure liquids. In a physical sense, ΔR represents the electronic perturbation of the molecular orbitals during mixing of the pure liquids, and therefore, its sign and magnitude give indication about the mixing phenomenon. The molar refractivities of the pure solvents and their mixtures were calculated by using the Lorentz–Lorenz (*10, 11*) relation. The plots of ΔR vs volume fraction at 298.15 K are given in Figure 6. It is found that, for the diglyme + methyl benzoate mixture, ΔR exhibits a high maximum of 0.198 cm^3·mol^{-1}. In a qualitative sense, this implies that there is a greater molecular orbital perturbation during mixing of these liquids. However, in the case of mixtures of diglyme with ethyl benzoate or diethyl succinate the variation of ΔR with ϕ_1 is almost identical throughout the composition scale. For the latter mixture, ΔR values are slightly higher at higher concentrations of diglyme in the mixture. On the other hand, for the diglyme + ethyl acetate mixture the values of ΔR are negative. While the effect of temperature on ΔR is not very systematic with all the systems, mixtures of diglyme + ethyl benzoate or + diethyl succinate show a significant decrease in ΔR values with an increase in temperature. A typical behavior of the effect of temperature on ΔR is shown in Figure 7, for the diglyme + ethyl benzoate mixture.

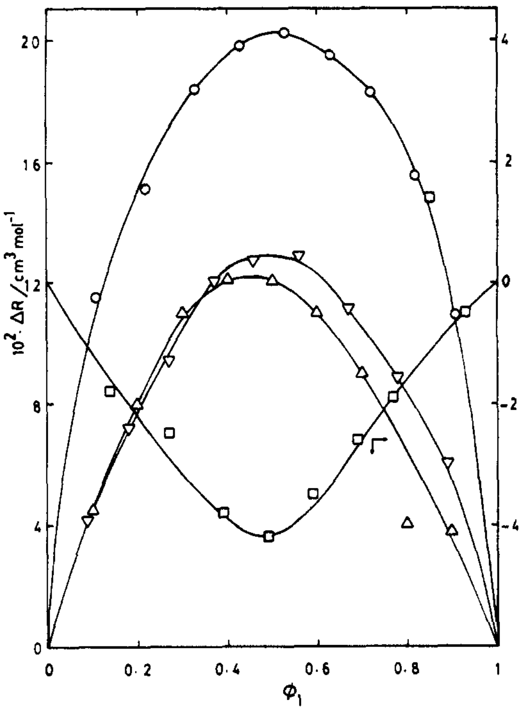

Figure 6. Comparison of changes in refractivity at 298.15 K for diethylene glycol dimethyl ether + ester mixtures as given in Figure 1.

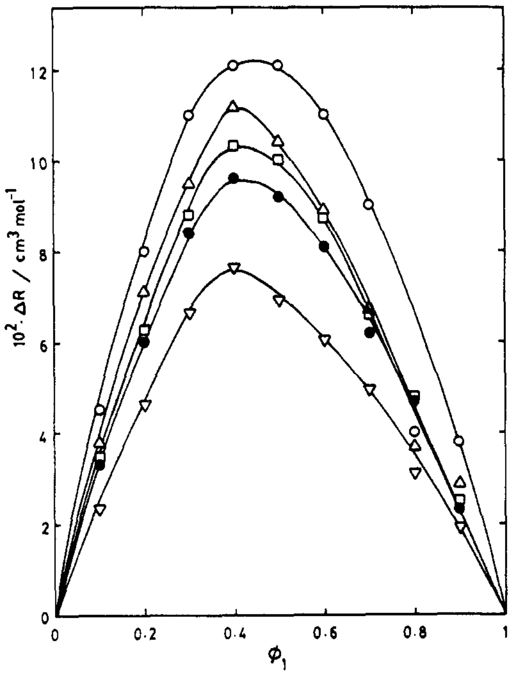

Figure 7. Effect of temperature on changes in refractivity for the diethylene glycol dimethyl ether + ethyl benzoate mixture at the temperatures given in Figure 2.

Viscosities of mixtures are useful in many engineering applications (*28–30*). The values of the viscosity deviations from a mole fraction average, $\Delta\eta$, for the mixtures are calculated from the viscosity values of the pure liquids and their mixtures from eq 5. The plots of $\Delta\eta$ vs x_1 at 298.15 K

$$\Delta\eta = \eta_m - \eta_1 x_1 - \eta_2 x_2 \qquad (5)$$

are displayed in Figure 8 for the binary mixtures of this study. The $\Delta\eta$ values for all the mixtures except diglyme + ethyl acetate are negative over the whole range of mixture composition and at all the temperatures. In the case of diglyme + ethyl acetate, the values of $\Delta\eta$ show a sigmoidal behavior. These data for different components of the mixtures vary in the sequence ethyl benzoate < diethyl succinate < methyl benzoate < ethyl acetate. However, this trend is quite different as observed for V^E, $\Delta\beta$, and ΔR discussed before.

The effect of temperature on $\Delta\eta$ is not the same for all mixtures. Values of $\Delta\eta$ decrease with an increase in temperature for diglyme + methyl benzoate; however, for the remaining mixtures, $\Delta\eta$ values tend to increase with temperature. The increase in $\Delta\eta$ values for the temperature interval of this study is higher (i.e., 0.046 mPa·s) for the diglyme + diethyl succinate mixture than for diglyme + ethyl acetate (0.008 mPa·s) and diglyme + methyl benzoate (0.003 mPa·s) mixtures. A typical temperature variation plot of $\Delta\eta$ vs x_1 for the diglyme + ethyl benzoate mixture is shown in

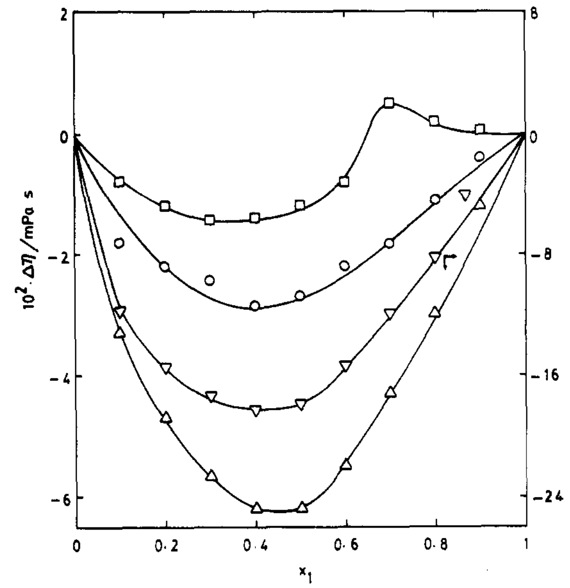

Figure 8. Comparison of changes in viscosity at 298.15 K for diethylene glycol dimethyl ether + ester mixtures as given in Figure 1.

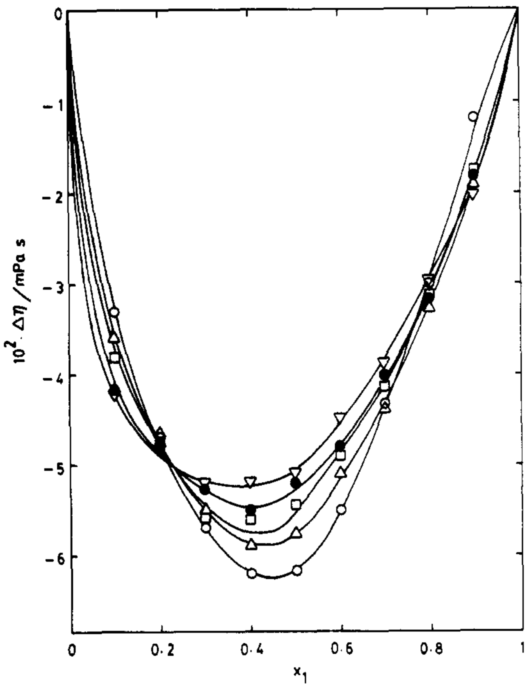

Figure 9. Effect of temperature on changes in viscosity for diethylene glycol dimethyl ether + ethyl benzoate as given in Figure 2.

Table 4. Estimated Parameters of Excess Functions for the Mixtures

function	T/K	A_0	A_1	A_2	A_3	σ	function	T/K	A_0	A_1	A_2	A_3	σ
Diethylene Glycol Dimethyl Ether (1) + Ethyl Acetate (2)													
$V^{E}/(\mathrm{cm^3\cdot mol^{-1}})$	298.15	-0.650	0.212	-0.025	-0.195	0.003	$\Delta R_{(L-L)}/(\mathrm{cm^3\cdot mol^{-1}})$	298.15	-0.160	-0.015	0.190	-0.164	0.009
	303.15	-0.694	0.161	-0.053	-0.051	0.004		303.15	-0.135	0.122	0.095	-0.502	0.015
	308.15	-0.780	0.197	-0.179	-0.086	0.005		308.15	-0.132	-0.009	0.074	-0.038	0.002
	313.15	-0.859	0.234	-0.196	-0.110	0.004		313.15	0.006	-0.941	-0.876	3.521	0.098
	318.15	-1.033	0.204	-0.403	0.009	0.005		318.15	-0.071	-0.011	-0.069	-0.115	0.004
$\Delta\eta/(\mathrm{mPa\cdot s})$	298.15	-0.042	-0.001	0.030	0.075	0.003	$\Delta\beta/\mathrm{TPa^{-1}}$	298.15	-25.744	-9.413	8.918	21.630	0.380
	303.15	-0.042	-0.048	0.027	-0.013	0.001		303.15	-39.323	-9.891	-9.601	-1.344	0.073
	308.15	-0.031	-0.070	0.018	0.060	0.002		308.15	-56.770	-13.780	-23.684	-23.565	0.180
	313.15	-0.022	-0.057	0.012	0.045	0.001		313.15	-77.286	-14.483	-26.076	-46.994	0.503
	318.15	-0.013	-0.039	-0.002	0.035	0.001		318.15	-77.283	6.886	-18.350	-69.549	0.581
Diethylene Glycol Dimethyl Ether (1) + Methyl Benzoate (2)													
$V^{E}/(\mathrm{cm^3\cdot mol^{-1}})$	298.15	-1.273	0.280	0.257	0.257	0.008	$\Delta R_{(L-L)}/(\mathrm{cm^3\cdot mol^{-1}})$	298.15	0.791	-0.048	0.567	-0.062	0.007
	303.15	-1.308	0.387	0.133	0.131	0.008		303.15	0.795	0.197	0.553	-0.251	0.010
	308.15	-1.358	0.336	0.026	0.316	0.006		308.15	0.814	0.283	0.499	-0.073	0.020
	313.15	-1.393	0.278	-0.045	0.401	0.006		313.15	0.794	0.136	0.950	0.338	0.012
	318.15	-1.463	0.317	-0.062	-0.340	0.010		318.15	0.809	0.177	0.705	0.842	0.008
$\Delta\eta/(\mathrm{mPa\cdot s})$	298.15	-0.104	-0.029	-0.013	-0.092	0.002	$\Delta\beta/\mathrm{TPa^{-1}}$	298.15	-56.041	10.392	-5.485	-64.978	0.594
	303.15	-0.106	-0.014	-0.068	-0.115	0.001		303.15	-70.702	21.283	-35.190	-30.043	0.383
	308.15	-0.117	-0.024	-0.092	-0.098	0.002		308.15	-75.178	20.671	-36.219	-29.144	0.435
	313.15	-0.120	-0.034	-0.129	-0.098	0.001		313.15	-79.591	22.083	-39.526	-30.908	0.491
	318.15	-0.114	-0.028	-0.164	-0.123	0.002		318.15	-83.876	16.257	-22.949	-36.773	-0.561
Diethylene Glycol Dimethyl Ether (1) + Ethyl Benzoate (2)													
$V^{E}/(\mathrm{cm^3\cdot mol^{-1}})$	298.15	-0.980	0.348	-0.542	0.435	0.004	$\Delta R_{(L-L)}/(\mathrm{cm^3\cdot mol^{-1}})$	298.15	0.485	0.166	-0.157	-0.098	0.009
	303.15	-0.940	0.381	-0.526	0.340	0.005		303.15	0.417	0.235	-0.148	-0.251	0.005
	308.15	-1.029	0.378	-0.594	0.295	0.005		308.15	0.397	0.150	-0.128	-0.157	0.002
	313.15	-1.116	0.339	-0.663	0.400	0.006		313.15	0.370	0.144	-0.105	-0.159	0.002
	318.15	-1.134	0.257	-0.927	0.782	0.007		318.15	0.284	0.141	-0.095	-0.191	0.002
$\Delta\eta/(\mathrm{mPa\cdot s})$	298.15	-0.244	-0.054	0.004	-0.121	0.001	$\Delta\beta/\mathrm{TPa^{-1}}$	298.15	-35.793	-0.885	59.022	37.199	0.001
	303.15	-0.225	-0.053	-0.089	-0.074	0.002							
	308.15	-0.212	-0.050	-0.120	-0.123	0.002							
	313.15	-0.203	-0.044	-0.156	-0.157	0.003							
	318.15	-0.196	-0.047	-0.161	-0.167	0.003							
Diethylene Glycol Dimethyl Ether (1) + Diethyl Succinate (2)													
$V^{E}/(\mathrm{cm^3\cdot mol^{-1}})$	298.15	-0.629	0.199	0.026	-0.138	0.005	$\Delta R_{(L-L)}/(\mathrm{cm^3\cdot mol^{-1}})$	298.15	0.512	-0.012	-0.032	0.024	0.003
	303.15	-0.724	-0.200	-0.119	-0.141	0.005		303.15	0.441	0.029	0.063	-0.051	0.006
	308.15	-0.800	0.140	-0.266	-0.007	0.003		308.15	0.403	0.036	-0.016	0.040	0.002
	313.15	-0.962	0.160	-0.654	0.082	0.008		313.15	0.378	0.005	-0.024	0.108	0.003
	318.15	-1.049	0.163	-0.835	-0.099	0.011		318.15	0.250	0.073	0.004	-0.023	0.002
$\Delta\eta/(\mathrm{mPa\cdot s})$	298.15	-0.694	-0.241	-0.203	-0.408	0.007	$\Delta\beta/\mathrm{TPa^{-1}}$	298.15	-6.745	37.171	19.423	-46.793	0.905
	303.15	-0.608	-0.227	-0.257	-0.448	0.008		303.15	-17.298	-2.613	45.692	-7.196	2.750
	308.15	-0.580	-0.261	0.295	-0.512	0.009		308.15	-17.215	31.970	34.475	6.671	0.893
	313.15	-0.533	-0.246	-0.329	-0.568	0.007		313.15	-19.347	4.682	37.787	46.310	0.949
	318.15	-0.513	-0.235	-0.317	-0.629	0.008		318.15	-10.700	14.649	-37.884	-61.112	0.935

Figure 9. The temperature variation of $\Delta\eta$ for this mixture depends on the composition of diglyme in the mixture. Around $x_1 = 0.2$, the $\Delta\eta$ dependence on temperature reverses, suggesting the presence of an isoviscous point at which the hydrodynamic behavior of the mixture remains identical for all the investigated temperatures. Such mixtures may be useful in engineering applications.

Each of the functions, $F = V^{E}$, $\Delta\beta$, ΔR, and $\Delta\eta$, discussed above have been fitted to the Redlich–Kister (31) relation

$$F = C_1C_2\sum_{i=0}^{3}A_i(C_2 - C_1)^i \qquad (6)$$

where C_i represents the mixture composition (i.e., x_i or ϕ_i depending upon the property under consideration). The binary interaction coefficients, A_i, have been estimated from a least-squares procedure. The standard errors, σ, between the calculated and the experimental values have been estimated by using

$$\sigma = [\sum_{i=1}^{m}\{F_{\mathrm{exptl}} - F_{\mathrm{calcd}}\}^2/(m - p)]^{1/2} \qquad (7)$$

where m is the number of data points and p is the number of estimated parameters. These results are presented in Table 4. It may be noted that, at equimolar compositions of the mixtures, it is the first term of eq 6 which is to be considered for the computation of excess quantities. Since the excess molar volumes of ethyl acetate and diethyl succinate are almost identical as shown in Figure 1, it is observed that the coefficient, A_0, values given in Table 4 for these two systems are somewhat comparable at all the temperatures. Also, for the diglyme + methyl benzoate mixture, the values of A_0 are more negative than for the diglyme + ethyl benzoate mixture, and this is again consistent with the V^{E} behavior of these mixtures (Figure 1). Similar patterns also exist for other mixing properties, viz., $\Delta\beta$, ΔR, and $\Delta\eta$. Additionally, all the coefficient values, A_i, given in Table 4 follow a systematic trend with the temperature.

Refractive Index Mixing Rules. There has been some interest in the literature about testing the various refractive index mixing rules from our own laboratory (*32*) and elsewhere (*33*). Along these lines, we have thought of reinvestigating the validity of different refractive index mixing rules for the present mixtures by comparing the experimental and calculated n. In this pursuit, we have used nine refractive index mixing rules which are given below:

Arago–Biot (A–B) (*8*)

$$n = n_1\phi_1 + n_2\phi_2 \qquad (8)$$

Dale–Gladstone (D–G) (*9*)

$$n - 1 = (n_1 - 1)\phi_1 + (n_2 - 1)\phi_2 \qquad (9)$$

Table 5. Average Difference in the Refractive Index from Different Mixing Relations

	$100[(n_{obsd} - n_{calcd})/n]$				
mixing rule	298.15 K	303.15 K	308.15 K	313.15 K	318.15 K
Diethylene Glycol Dimethyl Ether (1) + Ethyl Acetate (2)					
Arago–Biot	0.0952	0.1001	0.1054	0.0741	0.1295
Gladstone–Dale	0.0952	0.1001	0.1054	0.0741	0.1295
Lorentz–Lorenz	0.1033	0.1085	0.1141	0.0828	0.1385
Eykman	0.0979	0.1030	0.1084	0.0771	0.1325
Weiner	0.0451	0.0484	0.0518	0.0203	0.0731
Heller	0.1016	0.1067	0.1123	0.0810	0.1366
Newton	0.0868	0.0915	0.0964	0.0651	0.1200
Oster	0.0908	0.0956	0.1008	0.0694	0.1246
Eyring and John	0.0993	0.1045	0.1100	0.0787	0.1342
Diethylene Glycol Dimethyl Ether (1) + Methyl Benzoate (2)					
Arago–Biot	0.1776	0.1822	0.1878	0.2062	0.2015
Gladstone–Dale	0.1776	0.1822	0.1878	0.2062	0.2015
Lorentz–Lorenz	0.2553	0.2588	0.2637	0.2816	0.2757
Eykman	0.2000	0.2044	0.2099	0.2283	0.2233
Weiner	−0.3229	−0.3124	−0.3035	−0.2828	−0.2810
Heller	0.2496	0.2533	0.2584	0.2766	0.2709
Newton	0.1044	0.1098	0.1159	0.1347	0.1309
Oster	0.1335	0.1387	0.1448	0.1636	0.1596
Eyring and John	0.2141	0.2183	0.2237	0.2420	0.2368
Diethylene Glycol Dimethyl Ether (1) + Ethyl Benzoate (2)					
Arago–Biot	0.3051	0.2834	0.1103	0.1092	0.0918
Gladstone–Dale	0.3051	0.2834	0.1103	0.1092	0.0918
Lorentz–Lorenz	0.3679	0.3456	0.1724	0.1714	0.1532
Eykman	0.3234	0.3016	0.1285	0.1275	0.1100
Weiner	−0.1045	−0.1239	−0.3123	−0.3152	−0.3282
Heller	0.3635	0.3415	0.1704	0.1696	0.1516
Newton	0.2457	0.2243	0.0513	0.0499	0.0331
Oster	0.2696	0.2482	0.0752	0.0741	0.0572
Eyring and John	0.0335	0.3129	0.1398	0.1388	0.1212
Diethylene Glycol Dimethyl Ether (1) + Diethyl Succinate (2)					
Arago–Biot	0.0459	0.0394	0.0363	0.0421	0.0208
Gladstone–Dale	0.0459	0.0394	0.0336	0.0421	0.0208
Lorentz–Lorenz	0.0469	0.0403	0.0345	0.0431	0.0217
Eykman	0.0462	0.0397	0.0339	0.0424	0.0211
Weiner	0.0388	0.0328	0.0269	0.0347	0.0135
Heller	0.0469	0.0403	0.0345	0.0431	0.0217
Newton	0.0450	0.0385	0.0327	0.0411	0.0198
Oster	0.0454	0.0389	0.0331	0.0416	0.0202
Eyring and John	0.0464	0.0399	0.0341	0.0426	0.0212

Lorentz–Lorenz (L–L) *(10, 11)*

$$\frac{n^2 - 1}{n^2 + 2} = \left(\frac{n_1^2 - 1}{n_1^2 + 2}\right)\phi_1 + \left(\frac{n_2^2 - 1}{n_2^2 + 2}\right)\phi_2 \qquad (10)$$

Eykman (Eyk) *(12)*

$$\frac{n^2 - 1}{n + 0.4} = \left[\frac{n_1^2 - 1}{n_1 + 0.4}\right]\phi_1 + \left[\frac{n_2^2 - 1}{n_2 + 0.4}\right]\phi_2 \qquad (11)$$

Weiner (WR) *(13)*

$$\frac{n^2 - n_1^2}{n^2 + 2n_2^2} = \left[\frac{n_2^2 - n_1^2}{n_2^2 + 2n_1^2}\right]\phi_2 \qquad (12)$$

Heller (HR) *(14)*

$$\frac{n - n_1}{n_1} = \frac{3}{2}\left[\frac{(n_2/n_1)^2 - 1}{(n_2/n_1)^2 + 2}\right]\phi_2 \qquad (13)$$

Newton (NW) *(15)*

$$n^2 - 1 = (n_1^2 - 1)\phi_1 + (n_2^2 - 1)\phi_2 \qquad (14)$$

Table 6. Values of Adjustment Parameters and Standard Deviations for Viscosity Models

equation	T/K	a (mPa·S)	b (mPa·S)	c (mPa·S)	$\sigma \times 10^2$/(mPa·S)
Diethylene Glycol Dimethyl Ether (1) + Ethyl Acetate (2)					
McAllister	298.15	0.891	0.669		0.348
	303.15	0.825	0.636		0.158
	308.15	0.776	0.602		0.309
	313.15	0.729	0.572		0.201
	318.15	0.682	0.547		0.155
Auslaender	298.15	−0.009	0.023	44.414	0.570
	303.15	−0.017	0.004	280.588	0.344
	308.15	−0.015	0.006	171.046	0.391
	313.15	−0.003	0.019	52.989	0.287
	318.15	−0.003	0.014	75.209	0.176
Heric	298.15	0.327	−0.043	0.023	0.365
	303.15	0.308	−0.014	0.024	0.144
	308.15	0.302	−0.018	0.019	0.325
	313.15	0.297	−0.012	0.013	0.212
	318.15	0.295	0.008	−0.008	0.164
Diethylene Glycol Dimethyl Ether (1) + Methyl Benzoate (2)					
McAllister	298.15	1.286	1.452		0.133
	303.15	1.172	1.323		0.185
	308.15	1.075	1.207		0.267
	313.15	0.992	1.104		0.411
	318.15	0.920	1.016		0.572
Auslaender	298.15	1.664	1.392	0.684	0.216
	303.15	1.702	1.387	0.662	0.345
	308.15	3.330	2.628	0.346	0.455
	313.15	0.073	0.029	28.220	0.194
	318.15	0.057	0.012	68.999	0.283
Heric	298.15	0.113	−0.057	0.009	0.139
	303.15	0.088	−0.044	−0.036	0.143
	308.15	0.060	−0.042	−0.065	0.145
	313.15	0.039	−0.045	−0.110	0.127
	318.15	0.026	−0.050	−0.151	0.200
Diethylene Glycol Dimethyl Ether (1) + Ethyl Benzoate (2)					
McAllister	298.15	1.307	1.526		0.180
	303.15	1.189	1.393		0.236
	308.15	1.096	1.267		0.332
	313.15	1.011	1.159		0.494
	318.15	0.939	1.063		0.550
Auslaender	298.15	0.069	0.041	19.631	0.331
	303.15	0.613	0.314	24.730	0.140
	308.15	0.049	0.017	45.712	0.109
	313.15	0.040	0.006	129.253	0.205
	318.15	0.057	0.012	59.949	0.188
Heric	298.15	0.053	−0.060	0.026	0.167
	303.15	0.035	−0.041	−0.056	0.136
	308.15	0.015	−0.051	−0.083	0.161
	313.15	−0.006	−0.053	−0.123	0.240
	318.15	−0.024	−0.064	−0.138	0.263
Diethylene Glycol Dimethyl Ether (1) + Diethyl Succinate (2)					
McAllister	298.15	1.428	1.696		0.422
	303.15	1.308	1.516		0.561
	308.15	1.208	1.335		0.714
	313.15	1.114	1.199		0.835
	318.15	1.030	1.075		0.974
Auslaender	298.15	0.080	0.025	25.738	0.604
	303.15	0.101	0.029	22.349	0.541
	308.15	0.134	0.033	19.241	0.659
	313.15	0.163	0.038	16.685	0.525
	318.15	0.145	0.025	24.600	0.660
Heric	298.15	−0.002	−0.159	−0.027	0.443
	303.15	−0.026	−0.176	−0.071	0.541
	308.15	−0.076	−0.229	−0.092	0.685
	313.15	−0.108	−0.253	−0.132	0.744
	318.15	−0.154	−0.285	−0.130	0.925

Oster (OS) *(16)*

$$\frac{(n^2 - 1)(2n^2 + 1)}{n^2} = \frac{(n_1^2 - 1)(2n_1^2 + 1)}{n_1^2}\phi_1 + \frac{(n_2^2 - 1)(2n_2^2 + 1)}{n_2^2}\phi_2 \qquad (15)$$

Eyring and John (EJ) (*17*)

$$n = n_1\phi_1^2 + 2(n_1n_2)^{1/2}\phi_1\phi_2 + n_2\phi_2^2 \qquad (16)$$

In all these equations, ϕ_i represents the volume fraction of the ith component of the mixture, n_i is the refractive index of the pure components, and n is that of the mixture. A comparison of the data expressed in terms of average percentage differences, Δn, between the experimental and calculated values for different mixing rules is given in Table 5. It should be noted that the calculated average differences between the Arago–Biot and Gladstone–Dale relations are exactly the same for all systems at all temperatures. This is expected because of similarities in the functional forms of these equations; we find that in the literature it is the Gladstone–Dale relation which is more frequently used than the Arago–Biot equation. However, most generally, the Weiner relation gives the least deviation in Δn values as compared to other mixing rules.

Viscosity Equations. In the literature of solution chemistry, a number of viscosity models have been proposed and tested over a large number of binary mixtures. Among several of these, the McAllister (*18*), Heric (*19*), and Auslaender (*20*) equations have been frequently employed. The McAllister three-body interaction model (*18*) is given as

$$\begin{aligned}\ln \lambda_m = {} & x_1^3 \ln \lambda_1 + 3x_1^2x_2 \ln a + 3x_1x_2^2 \ln b + x_2^3 \ln \lambda_2 - \\ & \ln[x_1 + x_2M_2/M_1] + 3x_1^2x_2 \ln[(2 + M_2/M_1)/3] + \\ & 3x_1x_2^2 \ln[(1 + 2M_2/M_1)/3] + x_2^3 \ln(M_2/M_1) \qquad (17)\end{aligned}$$

where λ_m ($\equiv\eta_m/\rho_m$) refers to the kinematic viscosity of the mixture and λ_1 and λ_2 are the kinematic viscosities of the pure components 1 and 2, respectively; a and b are two undetermined parameters which are characteristic of the system.

The Heric empirical relation (*19*) is

$$\begin{aligned}\ln \lambda_m = {} & x_1 \ln \lambda_1 + x_2 \ln \lambda_2 + x_1 \ln M_1 + x_2 \ln M_2 - \\ & \ln(x_1M_1 + x_2M_2) + x_1x_2[a + b(x_1 - x_2) + c(x_1 - x_2)^2] \qquad (18)\end{aligned}$$

in which M_1 and M_2 are molecular weights of components 1 and 2.

The Auslaender relation (*20*) is

$$x_1(x_1 + ax_2)(\eta_m - \eta_1) + bx_2(cx_1 + x_2)(\eta_m - \eta_2) = 0 \qquad (19)$$

In all the above equations, the coefficients a, b, and c have been calculated using the least-squares procedure and the viscosity of the mixture has been predicted.

The estimated parameters of the viscosity equations and the standard errors, σ, between the calculated and experimental values are given in Table 6. It is generally observed that the McAllister as well as Heric relation fits the experimental results better as compared to the Auslaender equation as the σ values for the latter equation are larger than others in all the systems.

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