DENSITIES, REFRACTIVE INDICES, SPEEDS OF SOUND AND SHEAR VISCOSITIES OF DIETHYLENE GLYCOL DIMETHYL ETHER–METHYL SALICYLATE AT TEMPERATURES FROM 298.15 TO 318.15 K

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Densities, refractive indices, speeds of sound and viscosities of the diethylene glycol dimethyl ether–methyl salicylate system were measured as a function of mole fraction at 298.15, 303.15, 308.15, 313.15 and 318.15 K. The results are fitted by a power series equation involving both the temperature and mole fraction variables. The basic physical data of the mixtures are further used to calculate the excess molar volume V^E, changes in isentropic compressibility $\Delta\beta$, changes in refractivity ΔR and changes in viscosity $\Delta\eta$. The results are fitted by the Redlich–Kister polynomial relation. The isobaric thermal expansion coefficients of the mixtures are also determined from density measurements. The data are compared with those obtained from equations derived by differentiation of the Lorentz–Lorenz and Eykman relations. Refractive indices of the mixture are used to test the validity of mixing relations. The changes in isobaric thermal expansion coefficients $\Delta\alpha$ of the mixtures were examined. Viscosity data were tested in terms of the McAllister, Heric and Auslaender relations.

As part of our ongoing program of studies on binary liquid mixtures[1–5], we present here some new experimental data on density ρ, refractive index n, speed of sound u and viscosity η, for the diethylene glycol dimethyl ether–methyl salicylate mixture at temperatures from 298.15 to 318.15 K. The isentropic compressibility β was calculated from the density and speed-of-sound data. This system was selected owing to its importance in chemical engineering design processes and polymer processing industries. Moreover, such data for these mixtures are not available.

In the theoretical analysis, the experimental results are fitted by a power series equation. The results of isobaric thermal expansion coefficients of the mixtures are calculated from the density results. The data are compared with those obtained from the Lorentz–Lorenz[6] and Eykman[7] mixing rules for refractive indices. In addition, the excess molar volume V^E, changes in isentropic compressibility $\Delta\beta$, changes in refractivity, ΔR and changes in viscosity $\Delta\eta$ of the mixtures are calculated. The refractive index results in conjunction with the densities are used to test the validity of the mixing rules. The McAllister, Heric and Auslaender equations are tested for the binary viscosity data.

EXPERIMENTAL

Diethylene glycol dimethyl ether (B.D.H., England) was used as received, methyl salicylate (Oversea Chinese Chem. Factory, Shanghai, China) was purified by recommended methods[8,9]. The purity of methyl salicylate was proved by the constancy of its boiling temperature during final distillation and also by its density and refractive index data at 298.15 K which agreed reasonably with published values[8]. The gas chromatographic tests of the solvents showed a purity of 99+ mole %.

Mixtures were prepared from the liquids in specially designed ground-glass air-tight bottles and weighted on a single-pan Mettler balance (Model AE-240, Switzerland) with an accuracy of ±0.01 mg. Evaporation of solvents from the mixtures was negligible: no changes in physical properties of the mixtures were observed over a period of 2 – 3 days. The possible error in the mole fractions is estimated to be around 0.0001.

Densities of pure liquids and their binary mixtures over the composition range of 0.1 – 0.9 at 0.1 mole fraction increments were measured pycnometrically. The procedure was as reported earlier[1–5]. The densities at 298.15, 303.15, 308.15, 313.15 and 318.15 K are considered significant to four digits. Averages of triplicate measurements were used; they were reproducible to within ±0.0001 g cm^{-3}.

Refractive indices for the sodium-D line were measured with a thermostatted Abbe refractometer (Bellingham and Stanley Ltd., London) with an error of less than 0.0001 units; the data were rounded to the fourth place (see Table I). The refractometer was calibrated with a test glass of known refractive index, supplied with the instrument.

The speeds of sound were measured by using a variable path single crystal interferometer (Model M-84, Mittal Enterprises, India) following the procedure[1–5]. 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 Cannon Fenske viscometers (size 100 and 150) supplied by Industrial Research Glassware Ltd., N.Y., U.S.A.. 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 to within ±0.01 s. The calibration methods of the viscometers and experimental details were as in refs[1–5]. The results are accurate to ±0.001 mPa s. The viscosities of pure liquids agreed well with published data[8].

RESULTS AND DISCUSSION

Experimental values of ρ, n, u, η and β of the two title substances and their binary mixtures at 298.15, 303.15, 308.15, 313.15 and 318.15 K are given in Table I. The combined effect of temperature and composition on the density, viscosity, refractive index, speed of sound and isentropic compressibility of the mixtures was fitted by the relation[10]

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

where Y is ρ, n, u, η or β. This equation, whose coefficients and standard errors are listed in Table II, fits the experimental data within the average experimental uncertainty over the temperature range of $298.15 \leq T(\mathrm{K}) \leq 318.15$ and entire composition region ($0 \leq x_1 \leq 1$).

TABLE I
Density ρ, refractive index *n*, speed of sound *u*, viscosity η and isentropic compressibility β of diethylene glycol dimethyl ether (1)–methyl salicylate (2) mixture; x_1 is the mole fraction of diethylene glycol dimethyl ether

x_1	298.15 K	303.15 K	308.15 K	313.15 K	318.15 K
			ρ, kg m^{-3}		
0.0000	1 178.2	1 172.9	1 167.9	1 162.9	1 157.9
0.1028	1 152.0	1 146.8	1 141.8	1 136.7	1 131.8
0.2002	1 127.4	1 122.3	1 117.4	1 112.2	1 107.2
0.2981	1 103.4	1 098.3	1 093.2	1 088.3	1 083.2
0.4011	1 078.3	1 073.2	1 068.2	1 063.1	1 058.1
0.5013	1 054.3	1 049.3	1 044.2	1 039.1	1 034.1
0.6014	1 030.8	1 025.7	1 020.6	1 015.6	1 010.4
0.6973	1 008.5	1 003.3	998.3	993.3	998.2
0.7972	985.5	980.5	975.4	970.4	965.2
0.9292	955.5	950.6	945.6	940.6	935.6
1.0000	939.6	934.6	929.5	924.4	919.3
			n		
0.0000	1.5350	1.5329	1.5307	1.5286	1.5264
0.1028	1.5213	1.5190	1.5167	1.5144	1.5121
0.2002	1.5087	1.5064	1.5040	1.5017	1.4996
0.2981	1.4959	1.4937	1.4913	1.4890	1.4869
0.4011	1.4825	1.4803	1.4779	1.4755	1.4734
0.5013	1.4694	1.4672	1.4650	1.4626	1.4605
0.6014	1.4565	1.4544	1.4522	1.4498	1.4476
0.6973	1.4444	1.4422	1.4402	1.4377	1.4358
0.7972	1.4321	1.4297	1.4278	1.4253	1.4233
0.9292	1.4164	1.4140	1.4119	1.4094	1.4075
1.0000	1.4074	1.4055	1.4034	1.4009	1.3992
			u, m s^{-1}		
0.0000	1 413	1 393	1 373	1 354	1 335
0.1028	1 397	1 379	1 360	1 345	1 327
0.2002	1 384	1 364	1 348	1 330	1 315
0.2981	1 367	1 348	1 332	1 315	1 298
0.4011	1 354	1 335	1 323	1 302	1 286
0.5013	1 343	1 323	1 311	1 291	1 273
0.6014	1 330	1 309	1 297	1 278	1 260
0.6973	1 316	1 295	1 284	1 264	1 250
0.7972	1 306	1 285	1 266	1 255	1 237
0.9292	1 295	1 273	1 256	1 238	1 221
1.0000	1 288	1 265	1 246	1 225	1 209

TABLE I
(*Continued*)

x_1	298.15 K	303.15 K	308.15 K	313.15 K	318.15 K
			η, mPa s		
0.0000	2.717	2.379	2.088	1.854	1.654
0.1028	2.391	2.108	1.870	1.669	1.494
0.2002	2.134	1.897	1.691	1.518	1.365
0.2981	1.924	1.719	1.538	1.387	1.252
0.4011	1.731	1.555	1.397	1.264	1.149
0.5013	1.567	1.415	1.276	1.160	1.058
0.6014	1.442	1.309	1.194	1.094	1.006
0.6973	1.314	1.199	1.097	1.008	0.930
0.7972	1.194	1.095	1.004	0.925	0.855
0.9292	1.056	0.975	0.902	0.838	0.779
1.0000	0.973	0.904	0.839	0.781	0.728
			β, TPa^{-1}		
0.0000	425	439	454	469	485
0.1028	445	458	474	487	502
0.2002	463	479	493	508	522
0.2981	485	501	516	531	548
0.4011	506	523	535	555	572
0.5013	526	545	557	577	597
0.6014	548	569	583	603	623
0.6973	572	595	608	630	648
0.7972	595	618	640	655	677
0.9292	625	649	670	694	717
1.0000	642	668	693	721	744

The excess molar volume values, V^E, of the mixtures were calculated as

$$V^E = V_m - V_1 x_1 - V_2 x_2 \ , \qquad (2)$$

where V_m is the molar volume of the mixture and V_i is the molar volume of the i-th pure component whose mole fraction in the system is x_i. The calculated V^E values are shown in Fig. 1 for all temperatures applied. The excess molar volumes of the mixtures are negative over the entire mole fraction range at any temperature. This suggests that strong specific interactions occur between the hydroxy group of methyl salicylate and the oxygen atom of the diethylene glycol dimethyl ether leading to large negative V^E values. Note that V^E becomes more negative at higher temperatures; the shapes of the curves within the temperature interval of 298.15 to 318.15 K, however, are symmetric over the entire mole fraction region of the mixtures and the minima occur near the equimolar composition at any temperature.

The changes in isentropic compressibility $\Delta\beta$ were calculated as

$$\Delta\beta = \beta_m - \beta_1\phi_1 - \beta_2\phi_2 \ , \qquad (3)$$

where β_m is the isentropic compressibility of the mixture and β_i is that of the i-th pure component; ϕ_i is the volume fraction of the mixture defined as $\varphi_i = x_iV_i/\sum x_iV_i$. The $\Delta\beta$

TABLE II
Correlation coefficients and standard errors in Eq. (*1*)

Function	a_0	a_1	b_0	b_1	b_2	b_3	σ
ρ . 10^{-3} kg m^{-3}	1.7775	–0.0019	1.3868	–0.6111	0.1201	–0.0175	0.0005
η, mPa s	525 510.0	–0.0428	4.5219	–9.5025	9.4390	–3.7706	0.0339
n	1.6414	–0.0006	1.7184	–0.2958	0.0113	0.0108	0.0002
u, m s^{-1}	5 229.8	–5.3763	1 891.8	–365.73	–3.3153	36.7027	2.6215
β, TPa^{-1}	11.77	1.288	330.1	272.6	130.5	35.3	2.61

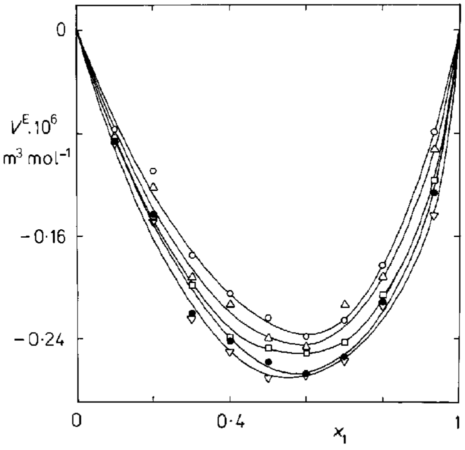

FIG. 1
Excess molar volume at 298.15 K (❍); 303.15 K (∆); 308.15 K (❑); 313.15 K (●); 318.15 K (∇)

values are shown in Fig. 2. The data are also negative over the entire mole fraction range at any temperature and follow the same trend as the V^E values. The $\Delta\beta$ values decrease with increasing temperature and their minima lie at the equimolar composition of the mixture. This is an additional evidence of the occurrence of specific interactions in the mixtures.

The changes in molar refractivity ΔR were calculated as[3–5]

$$\Delta R = R_m - R_1\phi_1 - R_2\phi_2 \ , \tag{4}$$

where R_m is the molar refractivity of the mixture and R_i is the molar refractivity of the *i*-th pure component. The molar refractivities of the mixtures and pure components were calculated from the Lorentz–Lorenz

$$\left(R_i \equiv \frac{n_i^2 - 1}{n_i^2 + 2}\,\frac{M_i}{\rho_i}\right)$$

and Eykman

$$\left(R_i \equiv \frac{n_i^2 - 1}{n_i + 0.4}\,\frac{M_i}{\rho_i}\right)$$

equations.

The change in molar refractivity is due to electronic perturbations arising from the orbital mixing of the components and thus is a measure of electronic interactions between the mixing components. The ΔR_{L-L} values are positive over the entire composition region and decrease systematically with increasing temperature. However, the specific interactions suggest that stable molecular species are formed in the mixture, as indicated by the maxima in the ΔR versus ϕ_1 plots at any temperature. Only the

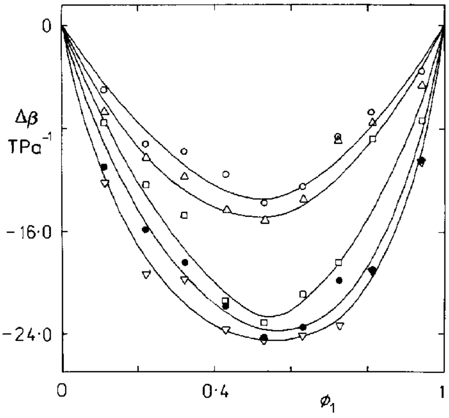

FIG. 2
Changes in isentropic compressibility. Temperatures as in Fig. 1

Lorentz–Lorenz data are shown in Fig. 3 because the Eykman relation gives identical results.

The changes in viscosity $\Delta\eta$ of the mixtures were calculated as

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

The $\Delta\eta$ versus x_1 plots are shown in Fig. 4. The $\Delta\eta$ values are negative over the entire composition region and increase monotonically with increasing temperature. The minimum in the $\Delta\eta$ versus x_1 plot, however, is observed at $x_1 \approx 0.4$ for any temperature.

Each of the functions $F = V^E$, $\Delta\beta$, ΔR and $\Delta\eta$ was fitted by the Redlich–Kister[11] relation

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

where C_i represents the mixture composition (i.e., x_i or ϕ_i). The A_i parameters were calculated by the least squares method. The standard errors σ between the calculated and experimental data were obtained as

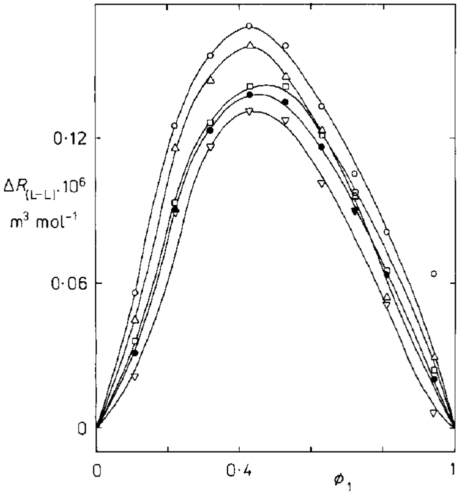

FIG. 3
Changes in refractivity (ΔR_{L-L}). Temperatures as in Fig. 1

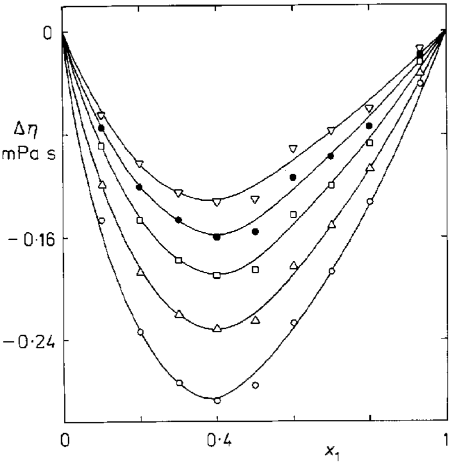

FIG. 4
Changes in viscosity. Temperatures as in Fig. 1

$$\sigma = \left[\sum_{i=1}^{n} \left\{ F_{\mathrm{expt}} - F_{\mathrm{calc}} \right\}^{2} / (n-p) \right]^{1/2} , \qquad (7)$$

where F is the excess quantity, n is the number of data points, and p is the number of estimated parameters. A summary of the error analysis is given in Table III. The smooth curves in Figs 1 – 4 correspond to the calculated values.

TABLE III
Calculated parameters of excess functions for diethylene glycol dimethyl ether (1)–methyl salicylate (2) mixture at various temperatures

Function	T, K	A_0	A_1	A_2	A_3	σ
$V^E \cdot 10^6$, m^3 mol^{-1}	298.15	−0.916	0.368	−0.091	−0.161	0.008
	303.15	−0.944	0.207	−0.167	0.186	0.011
	308.15	−0.994	0.153	−0.358	0.468	0.006
	313.15	−1.046	0.133	−0.349	0.583	0.010
	318.15	−1.069	0.061	−0.418	0.836	0.013
$\Delta R_{\mathrm{L-L}} \cdot 10^6$, m^3 mol^{-1}	298.15	0.633	0.401	0.014	−0.849	0.009
	303.15	0.609	0.346	−0.266	−0.471	0.007
	308.15	0.571	0.162	−0.275	−0.295	0.003
	313.15	0.553	0.186	−0.297	−0.348	0.004
	318.15	0.528	0.191	−0.393	−0.284	0.010
$\Delta R_{\mathrm{Eyk}} \cdot 10^6$, m^3 mol^{-1}	298.15	1.056	0.992	0.036	−2.043	0.020
	303.15	0.999	0.869	−0.633	−1.173	0.016
	308.15	0.906	0.424	−0.653	−0.763	0.007
	313.15	0.859	0.482	−0.709	−0.901	0.009
	318.15	0.805	0.497	−0.936	−0.769	0.023
$\Delta\beta$, TPa^{-1}	298.15	−50.247	1.091	5.596	−9.753	1.220
	303.15	−56.387	−10.000	0.543	8.112	1.363
	308.15	−87.190	14.802	25.819	−21.351	2.635
	313.15	−90.386	17.155	−50.648	14.323	1.505
	318.15	−96.106	16.026	−66.911	0.498	1.123
$\Delta\eta$, mPa s	298.15	−1.082	−0.537	−0.113	−0.041	0.005
	303.15	−0.876	−0.431	−0.075	−0.027	0.005
	308.15	−0.714	−0.383	0.003	0.106	0.007
	313.15	−0.592	−0.336	0.014	0.115	0.008
	318.15	−0.490	−0.317	−2.473	0.125	0.008

Following an earlier suggestion[12], the validity of the refractive index mixing rules was evaluated by comparing the experimental and calculated n values. The following eight refractive index mixing rules were tested:
Gladstone–Dale (G–D)[13]:

$$n - 1 = (n_1 - 1)\,\phi_1 + (n_2 - 1)\,\phi_2\ , \tag{8}$$

Lorentz–Lorenz (L–L)[6]:

$$\frac{n^2 - 1}{n^2 + 2} = \left(\frac{n_1^2 - 1}{n_1^2 + 2}\right)\phi_1 + \left(\frac{n_2^2 - 1}{n_2^2 + 2}\right)\phi_2\ , \tag{9}$$

Eykman (Eyk)[7]:

$$\frac{n^2 - 1}{n + 0.4} = \left(\frac{n_1^2 - 1}{n_1 + 0.4}\right)\phi_1 + \left(\frac{n_2^2 - 1}{n_2 + 0.4}\right)\phi_2\ , \tag{10}$$

Weiner (WR)[14]:

$$\frac{n^2 - n_1^2}{n^2 + 2n_2^2} = \left(\frac{n_2^2 - n_1^2}{n_2^2 + 2n_1^2}\right)\phi_2\ , \tag{11}$$

Heller (HR)[15]:

$$\frac{n - n_1}{n_1} = \frac{3}{2}\left[\frac{(n_2/n_1)^2 - 1}{(n_2/n_1)^2 + 2}\right]\phi_2\ , \tag{12}$$

Newton (NW)[16]:

$$n^2 - 1 = (n_1^2 - 1)\phi_1 + (n_2^2 - 1)\phi_2\ , \tag{13}$$

Oster (OS)[17]:

$$\frac{(n^2 - 1)(2n^2 + 1)}{n^2} = \frac{(n_1^2 - 1)(2n_1^2 + 1)}{n_1^2}\,\phi_1 + \frac{(n_2^2 - 1)(2n_2^2 + 1)}{n_2^2}\,\phi_2 \quad \text{and} \tag{14}$$

Eyring–John (E–J)[18]:

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

In the equations, ϕ_i is the volume fraction of the i-th component of the mixture, n_i is the refractive index of the i-th pure component, and n is the refractive index of the mixture. The results of this analysis are given in Table IV, along with the average deviations of the difference $(\%\Delta n)_{av}$ between the experimental and calculated refractive indices. Each of these equations reproduces the experimental refractive indices within the limits of experimental uncertainty. The applicability of Eq. (*11*) at the marginal concentrations is poorer in comparison with the remaining equations, as evidenced by the larger standard deviations.

The isobaric thermal expansion coefficient α of the mixture is a useful thermodynamic quantity which can be obtained from the temperature-dependent density data as

$$\alpha = \frac{1}{\rho} \left(\frac{\partial \rho}{\partial T} \right) . \qquad (16)$$

The average α values for diethylene glycol dimethyl ether and methyl salicylate within the 298.15 to 318.15 K region are $10.8998 \ . \ 10^{-4}$ and $8.6657 \ . \ 10^{-4}$, respectively. The α values can also be calculated from temperature-dependent refractive index data by using any of the refractive index mixing rule. The following relations are derived from the Eykman and Lorentz–Lorenz equations:

TABLE IV
Average percentage difference Δn, %, from mixing relations at various temperatures

Mixing rule	298.15 K	303.15 K	308.15 K	313.15 K	318.15 K
Gladstone–Dale	0.1198	0.1011	0.0947	0.0892	0.0806
Lorentz–Lorenz	0.2279	0.2086	0.2020	0.1969	0.1873
Eykman	0.1504	0.1316	0.1253	0.1201	0.1113
Weiner	–0.5833	–0.5999	–0.6068	–0.6166	–0.6205
Heller	0.2224	0.2034	0.1971	0.1923	0.1829
Newton	0.0195	0.0010	–0.0055	–0.0116	–0.0196
Oster	0.0583	0.0400	0.0337	0.0281	0.0200
Eyring–John	0.1700	0.1511	0.1447	0.1396	0.1307

$$\alpha_{(\mathrm{Eyk})} = \frac{n^2 + 0.8\,n + 1}{(n^2 - 1)\,(n + 0.4)}\,(\mathrm{d}n/\mathrm{d}T) \tag{17}$$

$$\alpha_{(\mathrm{L-L})} = \frac{6\,n}{(n^2 - 1)\,(n^2 + 2)}\,(\mathrm{d}n/\mathrm{d}T)\ . \tag{18}$$

The average α values so calculated for the 298.15 – 318.15 K temperature region are $\overline{\alpha}_{(\mathrm{Eyk})} = 9.8541 \,.\, 10^{-4}$ and $7.6369 \,.\, 10^{-4}\ \mathrm{K}^{-1}$ and $\overline{\alpha}_{(\mathrm{L-L})} = 9.2122 \,.\, 10^{-4}$ and $6.8263 \,.\, 10^{-4}\ \mathrm{K}^{-1}$ for diethylene glycol dimethyl ether and methyl salicylate, respectively. These values are in a reasonable agreement with those obtained from the density measurements. Furthermore, the isobaric thermal expansion coefficient α can be calculated by differentiating Eq. (*2*) with respect to T and dividing the result by V_m (ref.[19]):

$$\frac{1}{V_\mathrm{m}}\left(\frac{\partial V_\mathrm{m}}{\partial T}\right)_{P,x} = \frac{1}{V_\mathrm{m}} \sum x_i \left(\frac{\partial V_i}{\partial T}\right)_{P,x_i} + \frac{1}{V_\mathrm{m}}\left(\frac{\partial V^\mathrm{E}}{\partial T}\right)_{P,x}\ . \tag{19}$$

Equation (*19*) can be simplified and rearranged to the form

$$\alpha = \frac{\rho_\mathrm{m}}{\sum (M_i x_i)}\left[\sum_i \left(\frac{M_i}{\rho_i}\right) x_i \alpha_i + \left(\frac{\partial V^\mathrm{E}}{\partial T}\right)_{P,x}\right]\ . \tag{20}$$

In order to calculate α from Eq. (*20*), the values of V_m and V^E were derived from the density data[1–5]. However, to calculate α from Eq. (*20*), the derivative $(\partial V^\mathrm{E}/\partial T)_{p,x}$ is evaluated from the temperature-dependent V^E results. Typical experimental α values at 298.15 K are compared in Table V with the data calculated from the Eykman and

TABLE V

Isobaric thermal expansivity coefficients calculated from the experimental, Lorentz–Lorenz and Eykman relations at 298.15 K; x_1 is the mole fraction of diethylene glycol dimethyl ether

x_1	$\alpha \,.\, 10^4$(exp)	$\alpha \,.\, 10^4$(L–L)	$\alpha \,.\, 10^4$(Eyk)
0.1028	8.79	6.99	7.78
0.2002	8.92	7.13	7.91
0.2981	9.12	7.31	8.07
0.4011	9.37	7.57	8.31
0.5013	9.60	7.86	8.58
0.6014	9.87	8.13	8.84
0.6973	10.04	8.33	9.03
0.7972	10.28	8.49	9.17
0.9292	10.43	8.78	9.43

TABLE VI
Values of adjustment parameters and standard deviations for viscosity models

Equation	*T*, K	*a*	*b*	*c*	$\sigma \cdot 10^2$
McAllister	298.15	1.377	1.593	–	0.38
	303.15	1.256	1.440	–	0.38
	308.15	1.148	1.303	–	0.56
	313.15	1.059	1.183	–	0.70
	318.15	0.984	1.073	–	0.76
Auslaender	298.15	3.047	1.481	0.441	0.50
	303.15	3.556	1.788	0.484	0.46
	308.15	4.913	2.568	0.288	0.68
	313.15	4.918	2.610	0.296	0.79
	318.15	4.513	2.396	0.344	0.80
Polynomial	298.15	–0.712	–0.425	–0.055	0.48
	303.15	–0.570	–0.341	–0.030	0.44
	308.15	–0.459	–0.273	0.033	0.61
	313.15	–0.377	–0.238	0.040	0.73
	318.15	–0.308	–0.225	0.022	0.76
Heric	298.15	–0.131	–0.183	0.054	0.36
	303.15	–0.124	–0.167	0.053	0.37
	308.15	–0.119	–0.154	0.083	0.52
	313.15	–0.115	–0.154	0.085	0.69
	318.15	–0.107	–0.168	0.070	0.78

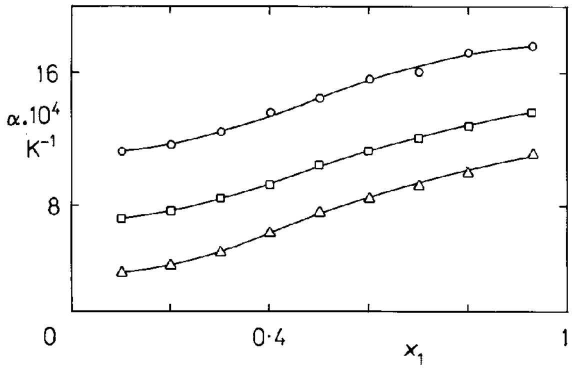

FIG. 5
Isobaric thermal expansivity from experimental measurements (❍) and from the Lorentz–Lorenz (L–L) (Δ) and Eykman (Eyk) (❑) relations

Lorentz–Lorenz mixing rules. The variation of α on x_i is shown in Fig. 5. The Eykman relation fits the experimental α values better than the Lorentz–Lorenz relation; this confirms the applicability of the Eykman relation observed earlier[20].

The hydrodynamic behavior of the solvent mixtures was studied by using the McAllister[21], Heric[22] and Auslaender[23] relations. In continuation of our earlier reseach[24], we attempted to analyze the binary viscosity data by means of those relations and also by using the polynomial relation

$$\upsilon = \upsilon_1 x_1 + \upsilon_2 x_2 + x_1 x_2 [a + b (x_1 - x_2) + c (x_1 - x_2)^2] \; . \qquad (21)$$

The calculated coefficients and the standard errors, σ, for the calculated and experimental data are given in Table VI. The McAllister and Heric relations generally fit the experimental data better than the remaining relations, as evidenced by the lower σ values.

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SYMBOLS

ρ	density, kg m^{-3}
n	refractive index
u	speed of sound, m s^{-1}
β	isentropic compressibility, TPa^{-1}
η	viscosity, mPa s
V^E	excess molar volume m^3 mol^{-1}
M	molecular weight of solvent
x	mole fraction of solvent
ϕ	volume fraction of solvent
a_i	regression coefficients in Eqs (*1*) and (*21*)
b_i	regression coefficients in Eqs (*1*) and (*21*)
c_i	regression coefficients in Eq. (*21*)
C_i	mixture composition in mole fraction or volume fraction of solvent
V	molar volume, m^3 mol^{-1}
A_i	coefficients in Eq. (*6*)
P	degree of polynomial in Eq. (*6*)
α	isobaric thermal expansion coefficient, K^{-1}
$\Delta\beta$	change in isentropic compressibility, TPa^{-1}
υ	kinematic viscosity
$\Delta\eta$	change in viscosity, mPa s
σ	standard deviation evaluated from Eqs (*1*) and (*7*)

Subscripts, superscripts

i	*i*-th component of the mixture
m	mixture properties
E	excess

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