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Densities, Refractive Indices, Speeds of Sound, and Viscosities of Diethylene Glycol Dimethyl Ether + Butyl Acetate at 298.15, 303.15, 308.15, 313.15, and 318.15 K

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Densities, viscosities, refractive indices and speeds of sound of the diethylene glycol dimethyl ether + butyl acetate system are measured as a function of mole fraction at 298.15, 303.15, 308.15, 313.15, and 318.15 K. These results are expressed as a power series equation for temperature and mixture composition dependences, and values of the computed coefficients are given. The isobaric thermal expansion coefficients for the mixtures are estimated from density measurements. These data are compared with those obtained from equations derived by the differentiation of Lorentz–Lorenz and Eykman relationships. The refractive indices of the mixtures are also used to test the validity of the mixing rules at different temperatures. Furthermore, attempts are made to estimate the changes in isobaric thermal expansion coefficients of the mixtures.

Introduction

In continuation of our ongoing program of studies on binary liquid mixtures (*1–5*), we present here some new experimental data on the density ρ, refractive index n_D, speed of sound u, and viscosity η for the system diethylene glycol dimethyl ether + butyl acetate in the temperature range from 298.15 to 318.15 K. The isentropic compressibility β has been calculated from density and speed of sound data. This system is particularly chosen in view of its importance in chemical engineering design processes and polymer processing industries. Moreover, such data for this system are not available in the literature.

In the theoretical analysis, the experimental results are fitted to the power series equation involving temperature and mixture composition to estimate the coefficients and standard errors. The results of isobaric thermal expansion coefficients of the mixtures have been calculated from the density results. These data are compared with those obtained from the refractive index mixing rules of Lorentz–Lorenz (*6*) and Eykman (*7*). Furthermore, the refractive index data in conjunction with mixture densities are used to test the validity of the mixing rules. Attempts are also made to calculate the changes in isobaric thermal expansion coefficients and excess molar volumes of the mixtures.

Experimental Section

Materials. Diethylene glycol dimethyl ether (BDH, England) was used directly, and butyl acetate (Sisco Chemicals, India) was purified by the recommended methods (*8, 9*). The purity of butyl acetate was ascertained by the constancy of its boiling temperature during final distillation and also by comparing its density and refractive index at 298.15 K which agreed reasonably with the literature values (*8*). The gas chromatographic tests of the solvents showed a purity of 99+ mol %.

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) to an accuracy of ±0.05 mg. Preferential evaporation losses of solvents from the mixtures were kept to a minimum as evidenced by a repeated measurement of 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 ±0.0002.

Measurements. Densities ρ of the pure liquids and their binary mixtures in the composition range 0.1–0.9 at 0.1 mole fraction increments were measured by using a pycnometer having a bulb volume of about 10 cm^3 and a capillary with an internal diameter of 1 mm. The procedural details are given in our earlier papers (*1–5*). The 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 reproducible within ±0.0001 g cm^{-3}.

Refractive indices n_D for the sodium-D line were measured with a thermostated Abbe refractometer (Bellingham and Stanley Ltd., London) with an error of ±0.0001 unit (see Table I). Water was circulated into the instrument through a thermostatically controlled bath. The refractometer was calibrated by using the glass test piece of known refractive index supplied with the instrument.

Viscosities η were measured with a Cannon Fenske viscometer (size 75, ASTM D 445) supplied by the Industrial Research Glassware Ltd., New Jersey. An electronic stopwatch with a precision of ±0.01 s was used for the flow time measurements. 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 (*1–5*). Viscosities are accurate to ±0.001 mPa s, and the viscosities of pure liquids are of acceptable accuracy as evidenced by good agreement of our data with the literature (*8*).

The speeds of sound u were measured by using a variable-path single-crystal interferometer (Mittal Enterprises, New Dehli, Model M-84) as per the earlier published procedure (*1–5*). The speeds of sound data are accurate to ±2 ms^{-1}.

The isentropic compressibilities were calculated as $\beta = 1/u^2\rho$.

Results and Discussion

Empirical Fittings. The experimental results of ρ, η, n_D, u, and β of the two pure liquids and their nine binary mixtures at the five temperatures are given in Table I. The variation of these properties with temperature T was studied by using

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Table I. Experimental Densities ρ, Viscosities η, Refractive Indices n_D, Speeds of Sound u, and Isentropic Compressibilities β for Diethylene Glycol Dimethyl Ether (1) + Butyl Acetate (2)

x_1	$\rho/(g\ cm^{-3})$	$\eta/(mPa\ s)$	n_D	$u/(m\ s^{-1})$	β/TPa^{-1}	x_1	$\rho/(g\ cm^{-3})$	$\eta/(mPa\ s)$	n_D	$u/(m\ s^{-1})$	β/TPa^{-1}
298.15 K											
0.0000	0.8759	0.679	1.3929	1201	792.18	0.5960	0.9150	0.852	1.4010	1252	697.02
0.0984	0.8824	0.706	1.3955	1209	775.61	0.6999	0.9216	0.884	1.4023	1261	682.17
0.1972	0.8892	0.734	1.3972	1217	759.28	0.8241	0.9292	0.924	1.4048	1272	664.76
0.3029	0.8962	0.764	1.3978	1226	742.33	0.8975	0.9334	0.948	1.4056	1278	655.53
0.4013	0.9022	0.791	1.3994	1235	727.16	1.0000	0.9396	0.973	1.4074	1288	641.97
0.4999	0.9089	0.822	1.3996	1244	710.52						
303.15 K											
0.0000	0.8705	0.634	1.3911	1178	828.58	0.5960	0.9097	0.791	1.3991	1231	725.27
0.0984	0.8770	0.659	1.3934	1187	808.84	0.6999	0.9165	0.820	1.4003	1241	709.05
0.1972	0.8840	0.684	1.3949	1196	790.99	0.8241	0.9239	0.856	1.4025	1252	690.14
0.3029	0.8910	0.712	1.3959	1205	773.19	0.8975	0.9284	0.878	1.4034	1258	680.37
0.4013	0.8970	0.736	1.3970	1215	755.80	1.0000	0.9346	0.904	1.4055	1265	668.23
0.4999	0.9036	0.764	1.3973	1223	739.69						
308.15 K											
0.0000	0.8653	0.594	1.3890	1157	863.90	0.5960	0.9046	0.737	1.3968	1211	754.35
0.0984	0.8719	0.616	1.3910	1166	843.62	0.6999	0.9114	0.763	1.3982	1219	737.89
0.1972	0.8788	0.639	1.3924	1174	825.65	0.8241	0.9190	0.796	1.4003	1231	718.55
0.3029	0.8858	0.664	1.3934	1183	806.37	0.8975	0.9235	0.816	1.4016	1238	707.01
0.4013	0.8919	0.686	1.3947	1192	788.73	1.0000	0.9295	0.839	1.4034	1246	693.31
0.4999	0.8985	0.714	1.3951	1202	770.97						
313.15 K											
0.0000	0.8600	0.557	1.3864	1136	910.57	0.5960	0.8994	0.690	1.3944	1190	784.85
0.0984	0.8667	0.578	1.3888	1149	874.30	0.6999	0.9063	0.712	1.3955	1199	767.30
0.1972	0.8738	0.599	1.3901	1157	854.93	0.8241	0.9139	0.742	1.3979	1212	744.79
0.3029	0.8806	0.622	1.3915	1165	837.00	0.8975	0.9183	0.759	1.3995	1219	733.47
0.4013	0.8867	0.641	1.3926	1171	821.90	1.0000	0.9244	0.781	1.4009	1225	720.45
0.4999	0.8933	0.665	1.3930	1181	803.09						
318.15 K											
0.0000	0.8548	0.524	1.3841	1113	943.90	0.5960	0.8943	0.642	1.3919	1169	818.52
0.0984	0.8619	0.542	1.3865	1122	921.26	0.6999	0.9011	0.665	1.3935	1176	802.05
0.1972	0.8691	0.562	1.3879	1135	893.15	0.8241	0.9089	0.692	1.3958	1193	773.73
0.3029	0.8755	0.583	1.3892	1143	874.55	0.8975	0.9132	0.709	1.3970	1199	761.64
0.4013	0.8816	0.601	1.3901	1151	856.23	1.0000	0.9197	0.728	1.3992	1209	744.05
0.4999	0.8876	0.622	1.3094	1158	840.45						

Table II. Coefficients and Standard Errors of Equation 3

function	a_0	a_1	b_0	b_1	b_2	b_3	σ
$\rho/(g\ cm^{-3})$	1.2784	−0.0023	1.1835	0.1885	−0.0076	0.0015	0.0003
$\eta/(mPa\ s)$	51.9476	−0.0280	37.946	26.638	15.6451	−4.184	0.0033
n_D	1.5350	−0.0006	1.5208	0.0448	−0.0477	0.0351	0.0004
$u/(m\ s^{-1})$	6911.50	−6.8830	1615.3	251.20	1.2375	7.9172	1.9049
β/TPa^{-1}	5.4003	16.1454	957.61	−475.4	188.229	−58.25	3.6287

the following exponential relation (*10*):

$$Y = a_0 \exp(a_1 T) \qquad (1)$$

Here, Y represents ρ, η, n_D, u, or β of the mixtures; a_0 and a_1 are the parameters which could be estimated from the nonlinear least-squares method (Marquardt algorithm). Equation 1 fits the experimental values well and calculates the property Y within the limits of experimental error at each composition. The calculations of the properties at different mole fractions could be performed by using eq 2,

$$Y = \sum_{i=0}^{n} b_i x_1^{\,i} \qquad (2)$$

where the coefficients b_i for $n = 3$ were obtained by a nonlinear least-squares method at each temperature. It is observed that eq 2 calculates the property Y within the experimental error.

The effect of temperature and composition has been fitted by the following relation (*11*):

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

which calculates the property Y (=ρ, η, n_D, u, and β) for any value of T and x_1 of the binary mixture. This equation, whose coefficients and standard errors are listed in Table II, fits the experimental data within the average uncertainty of experimental errors in the range of $298.15 \le T/K \le 318.15$ and composition $0 \le x_1 \le 1$.

Mixing Rules. Following our earlier work (*12*), we have attempted to test the validity of different refractive index mixing rules as given by Arago–Biot (A–B) (*13*), Gladstone–Dale (G–D) (*14*), Lorentz–Lorenz (L–L) (*6*), Eykman (Eyk) (*7*), Weiner (WR) (*15*), Heller (HR) (*16*), Newton (NW) (*17*), Oster (OS) (*18*), and Eyring–John (E–J) (*19*) by comparing the experimental and calculated values of n_D. The results of this analysis given by the average deviations of the differences % Δn_D as calculated from eq 4, where n_D^{calcd} is the refractive index of the mixture calculated from mixing rules, are given in Table III. Among all the equations tested, the Lorentz–Lorenz relation shows the least deviation. However, each of the equations produces the experimental data well within the limits of experimental uncertainty.

$$\%\ \Delta n_D = n_D^{\,exptl} - n_D^{\,calcd} \qquad (4)$$

Isobaric Thermal Expansivity. It may be noted that, when the values of ρ are fitted to eq 1, the negative parameter a_1 coincides with the isobaric thermal expansion coefficient,

Table III. Average Percentage Difference $\%\Delta n_D$ (from Equation 4) for Different Mixing Rules

	$\%\Delta n_D \times 10^2$				
mixing rule	298.15 K	303.15 K	308.15 K	313.15 K	318.15 K
Arago–Biot	–0.294	–3.187	–4.782	–1.833	–5.054
Gladstone–Dale	–0.294	–3.186	–4.782	–1.833	–5.054
Lorentz–Lorenz	–0.161	–3.055	–4.651	–1.700	–4.911
Eykman	–0.249	–3.143	–4.738	–1.789	–5.006
Weiner	–1.209	–4.093	–5.683	–2.752	–6.053
Heller	–0.175	–3.069	–4.665	–1.714	–4.925
Newton	–0.429	–3.320	–4.915	–1.969	–5.202
Oster	–0.367	–3.258	–4.853	–1.905	–5.132
Eyring–John	–0.226	–3.119	–4.715	–1.765	–4.981

$\alpha = -(\partial \ln \rho/\partial T)$. The values of $\bar{\alpha}_1$ (average thermal expansion coefficient between 298.15 and 318.15 K) are 1.0757×10^{-3} and 1.1939×10^{-3} K^{-1} for diethylene glycol dimethyl ether and butyl acetate, respectively. However, the refractive index data of pure liquids can be fitted to temperature by the following relationship:

$$n_D = a + bT \qquad (5)$$

where b is the temperature coefficient (dn/dT), giving a value of -4.2085×10^{-4} K^{-1} for diethylene glycol dimethyl ether and -4.4623×10^{-4} K^{-1} for butyl acetate. The coefficients of linear regression for the refractive index data were around 0.999. With these data, one can proceed to calculate the isobaric thermal expansivities of diethylene glycol dimethyl ether and butyl acetate from the differentiations with respect to temperature of the Eyk and L–L relations as (*20*)

$$\alpha_{(\mathrm{Eyk})} = -\frac{n_D^2 + 0.8n_D + 1}{(n_D^2 - 1)(n_D + 0.4)}(dn_D/dT) \qquad (6)$$

$$\alpha_{(\mathrm{L-L})} = -\frac{6n_D}{(n_D^2 - 1)(n_D^2 + 2)}(dn_D/dT) \qquad (7)$$

The average values of α estimated between 298.15 and 318.15 K through these equations were $\bar{\alpha}_{(\mathrm{Eyk})} = 9.8541 \times 10^{-4}$ and 1.0854×10^{-3} K^{-1} and $\bar{\alpha}_{(\mathrm{L-L})} = 9.2122 \times 10^{-4}$ and 1.0194×10^{-3} K^{-1}, respectively, for diethylene glycol dimethyl ether and butyl acetate. It was observed that these values are somewhat in agreement with those obtained from density results. In order to calculate the isobaric thermal expansion coefficient α_m of the mixture, we start with the calculation of excess molar volume V^E by using

$$V_m = \sum_{i=1}^{2} x_i V_i + V^E \qquad (8)$$

where V_m is the molar volume of the mixture and V_i that of the individual components. Differentiating eq 8 with respect to T and dividing by V_m give (*21*)

$$\frac{1}{V_m}\left(\frac{\partial V_m}{\partial T}\right)_{P,x} = \frac{1}{V_m}\sum x_i\left(\frac{\partial V_i}{\partial T}\right)_{P,x_i} + \frac{1}{V_m}\left(\frac{\partial V^E}{\partial T}\right)_{P,x} \qquad (9)$$

Equation 9 can be further simplified to give an expression for α_m as

$$\alpha_m = \frac{\rho_m}{\sum(M_i x_i)}\left[\sum_i\left(\frac{M_i}{\rho_i}\right)x_i\alpha_i + \left(\frac{\partial V^E}{\partial T}\right)_{P,x}\right] \qquad (10)$$

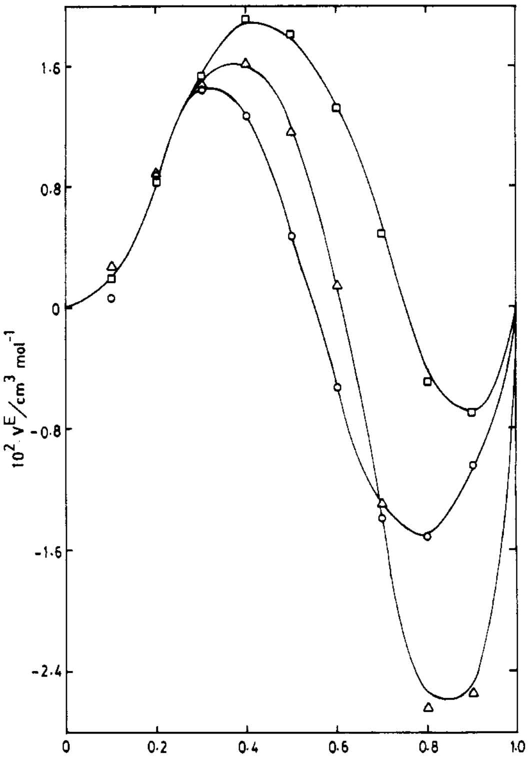

Figure 1. Dependence of the excess molar volume on the mole fraction for diethylene glycol dimethyl ether (1) + butyl acetate (2). Symbols: (○) 298.15 K; (□) 303.15 K; (△) 308.15 K.

Table IV. Estimated Parameters of Equation 11 for the Excess Molar Volume at Different Temperatures

temp/K	$A_0 \times 10^2$	$A_1 \times 10^2$	A_2	$A_3 \times 10^2$	σ
298.15	1.893	20.040	–0.112	–19.290	0.027
303.15	7.293	6.271	–0.158	–0.116	0.030
308.15	4.650	15.630	–0.267	5.967	0.025
313.15	6.500	7.822	–0.495	–10.090	0.030
318.15	28.290	0.103	–1.224	–134.140	0.047

Table V. Isobaric Thermal Expansion Coefficients of Diethylene Glycol Dimethyl Ether (1) + Butyl Acetate (2) at 298.15 K

x_1	$\alpha_{m(\mathrm{exptl})} \times 10^4$	$\alpha_{m(\mathrm{L-L})} \times 10^4$	$\alpha_{m(\mathrm{Eyk})} \times 10^4$
0.0984	11.60	9.61	10.27
0.1972	11.33	9.59	10.25
0.3029	11.57	9.71	10.37
0.4013	11.44	9.77	10.43
0.4999	11.62	9.76	10.41
0.5960	11.16	9.66	10.31
0.6999	11.11	9.51	10.16
0.8241	10.91	9.34	9.99
0.8975	10.85	9.25	9.90

In order to calculate α_m from eq 10, the needed parameters, namely, V_m and V^E, were calculated in the routine manner from the density data (*1–5*). The results of V^E thus calculated from eq 8 have been fitted to the Redlich–Kister polynomial (*22*):

$$V^E/(\mathrm{cm}^3\,\mathrm{mol}^{-1}) = x_1 x_2 \sum_{i=0}^{3} A_i(x_2 - x_1)^i \qquad (11)$$

The estimated parameters A_i's and standard errors σ are given in Table IV. The excess molar volumes of the mixtures at 298.15, 303.15, and 308.15 K are presented in Figure 1. The V^E curves at other temperatures are not shown to avoid congestion of points. These plots show sigmoidal behavior. However, to calculate α_m from eq 10, the derivative term $(\partial V^E/\partial T)_{P,x}$ was evaluated from the temperature-dependent V^E results. Typical data of α_m from experiments are compared in Table V at 298.15 K with the calculated α_m from the Eyk and L–L mixing rules, i.e., eqs 6 and 7, respectively. It is

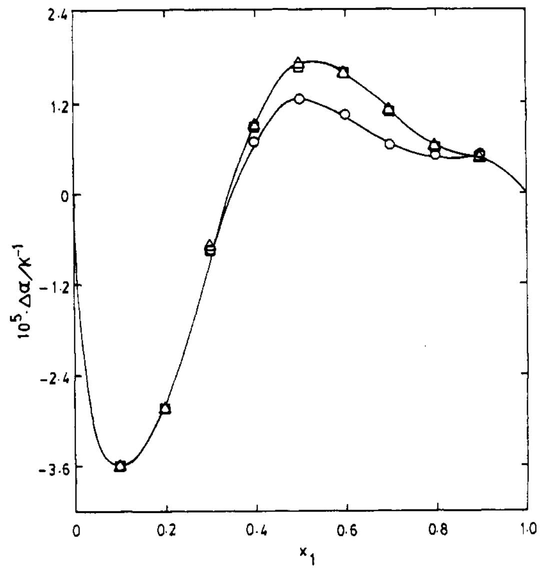

Figure 2. Dependence of changes in the isobaric thermal expansion coefficient on the mole fraction for diethylene glycol dimethyl ether (1) + butyl acetate (2). Symbols: (○) exptl; (△) L–L; (□) Eyk.

Table VI. Estimated Parameters of Changes in Isobaric Thermal Expansion Coefficients at 298.15 K

$\Delta\alpha$ relation	$A_0 \times 10^5$	$A_1 \times 10^5$	$A_2 \times 10^4$	$A_3 \times 10^4$	$\sigma \times 10^6$
exptl	5.054	-1.899	-3.411	-4.232	12.90
L–L	6.861	-5.435	-3.802	-3.611	0.28
Eyk	6.848	-5.544	-3.802	-3.609	0.29

noticed that α_m from the Eyk relation agrees somewhat more closely with the experimental α_m than α_m calculated from the L–L relation.

Further efforts were made to calculate the changes in isobaric thermal expansivity $\Delta\alpha$ for the mixtures from eq 12.

$$\Delta\alpha = \alpha_m - \alpha_1 x_1 - \alpha_2 x_2 \qquad (12)$$

The results of $\Delta\alpha_{(L-L)}$ and $\Delta\alpha_{(Eyk)}$ are compared at 298.15 K in Figure 2 with the experimental $\Delta\alpha$ data. Here again, we observe sigmoidal behavior. The estimated Redlich–Kister parameters of eq 11 for $\Delta\alpha$ are given in Table VI along with standard deviations.

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