Excess Molar Volumes and Viscosity Deviations of Binary Mixtures of 2,4,6-Trimethyl-1,3,5-trioxane + Ethanol, 1-Propanol, and 1-Butanol at (298.15, 303.15, and 308.15) K

Nilesh N. Wankhede, Machhindra K. Lande, and Balasaheb R. Arbad*

Department of Chemistry, Dr. Babasaheb Ambedkar Marathwada University, Aurangabad 431004, India

Densities and viscosities of binary mixtures of 2,4,6-trimethyl-1,3,5-trioxane + ethanol, 1-propanol, and 1-butanol have been measured at (298.15, 303.15, and 308.15) K. From these measurements, excess molar volumes (V^E) and viscosity deviations ($\delta\eta$) were calculated. These results were fitted to the Redlich−Kister polynomial. The results were discussed in terms of molecular interactions.

Introduction

In recent years, there has been increasing interest in the study of thermodynamic properties of solution-phase drugs.[1−3] Excess thermodynamic properties are important parameters for understanding molecular interactions. The use of 2,4,6-trimethyl-1,3,5-trioxane as a liquid drug has caused increased interest in understanding molecular interactions with other solvents. Alcohols are highly applicable in the pharmaceutical industry. Because the physiochemical parameters of the above-mentioned system do not exist in the literature, we have undertaken a study of the measurement of physical properties of binary mixtures of 2,4,6-trimethyl-1,3,5-trioxane with ethanol, 1-propanol, and 1-butanol. We report excess molar volumes and viscosity deviations for binary mixtures of 2,4,6-trimethyl-1,3,5-trioxane with the above-mentioned alcohols at 298.15, 303.15, and 308.15 K.

Experimental Section

Materials. 2,4,6-Trimethyl-1,3,5-trioxane (Merck, ≥98%) was used as such without further purification. All of the alcohols (Qualigens, AR grade) were dried by refluxing with fused calcium oxide for 5 h and distilled at atmospheric pressure.[4] The middle fraction collected was stored over 4-Å molecular sieves. Comparing the observed densities with those reported in the literature,[5,6] we checked the purity of purified chemicals. The measured values are included in Table 1 along with the literature values.

Measurements. The binary liquid mixtures were prepared by mixing known masses of pure liquids in airtight-stoppered bottles to minimize evaporation losses. All mass measurements were performed on a Mettler one-pan balance (E-Mettler, Zurich), which can read up to the fifth decimal place with an accuracy of ±0.05 mg. The uncertainty in the mole fractions of the mixtures was estimated to be $\pm 5 \times 10^{-5}$.

The densities of pure components and their mixtures were measured using a single-arm capillary pycnometer having a bulb volume of approximately 5 cm^3 and a capillary bore with an internal diameter of 0.75 mm. The uncertainty in the density measurements was found to be $\pm 5 \times 10^{-5}$ g·cm^{-3}.

* Corresponding author. E-mail: abr_chem@yahoo.co.in.

Table 1. Comparison of Experimental and Literature Values of Density (ρ) for Pure Compounds at 298.15 K

	ρ/g·cm^{-3}	
compound	exptl	lit
ethanol	0.78506	0.78493[6]
		0.78509[5]
1-propanol	0.79960	0.7996[6]
1-butanol	0.80584	0.80575[6]

Viscosity measurements were performed using Schott Gerate (AVS 350) viscosity-measuring equipment with a series of Ubbelhode viscometers. The experimental uncertainty in the viscosity measurements was ±0.002 mPa·s. The experimental technique for density and viscosity measurements was the same as that used previously.[7] For all of the measurements, temperature was controlled by circulating the water through an ultra thermostat Julabo F-25 (made in Germany), which has a temperature precision of ±0.02 °C.

Results

Table 2 lists the experimental values of densities ρ and viscosities η of the binary mixtures of 2,4,6-trimethyl-1,3,5-trioxane + *n*-alcohols at 298.15, 303.15, and 308.15 K.

Excess molar volumes V^E were calculated from the measured densities ρ by using the relation

$$V^E = \frac{x_1M_1 + x_2M_2}{\rho} - \frac{x_1M_1}{\rho_1} - \frac{x_2M_2}{\rho_2} \quad (1)$$

where ρ is the density of the mixture and M_1, x_1, ρ_1 and M_2, x_2, ρ_2 are the molecular weight, mole fraction, and density of pure 2,4,6-trimethyl-1,3,5-trioxane and *n*-alcohols, respectively. The calculated values of V^E are reported in Table 2.

Dynamic viscosities η of binary mixtures of 2,4,6-trimethyl-1,3,5-trioxane + *n*-alcohols at different temperatures were calculated by using densities and flow times with eq 2

$$\eta = K\rho t \quad (2)$$

where K is the viscometer constant ($K = 0.005$, as given by the manufacturer) and ρ and t are the density and flow time of the mixture, respectively. The viscosity deviations

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Table 2. Densities (ρ), Viscosities (η), Excess Molar Volumes (V^E), and Viscosity Deviations ($\delta\eta$) for the Binary Mixtures for 2,4,6-Trimethyl-1,3,5-trioxane (1) + *n*-Alcohols (2) at (298.15, 303.15, and 308.15) K

x_1	ρ / g·cm^{-3}	η / mPa·s	V^E / cm^3·mol^{-1}	$\delta\eta$ / mPa·s	x_1	ρ / g·cm^{-3}	η / mPa·s	V^E / cm^3·mol^{-1}	$\delta\eta$ / mPa·s	x_1	ρ / g·cm^{-3}	η / mPa·s	V^E / cm^3·mol^{-1}	$\delta\eta$ / mPa·s
2,4,6-Trimethyl-1,3,5-trioxane (1) + Ethanol (2)														
T = 298.15 K														
0.0000	0.78506	1.083	0.000	0.000	0.3433	0.90045	1.003	−0.457	−0.088	0.8003	0.97054	1.033	−0.276	−0.069
0.0372	0.80248	1.071	−0.074	−0.012	0.4485	0.92204	0.994	−0.495	−0.100	0.8452	0.97498	1.048	−0.220	−0.056
0.0801	0.82065	1.059	−0.152	−0.026	0.5823	0.94405	0.995	−0.475	−0.102	0.8932	0.97938	1.065	−0.149	−0.039
0.1299	0.83952	1.045	−0.233	−0.041	0.6816	0.95734	1.006	−0.410	−0.093	0.9446	0.98390	1.088	−0.085	−0.018
0.1885	0.85912	1.031	−0.314	−0.057	0.7582	0.96615	1.022	−0.330	−0.079	1.0000	0.98835	1.107	0.000	0.000
0.2589	0.87957	1.016	−0.392	−0.073										
T = 303.15 K														
0.0000	0.78074	0.990	0.000	0.000	0.3433	0.89577	0.912	−0.499	−0.082	0.8003	0.96515	0.939	−0.301	−0.060
0.0372	0.79821	0.979	−0.088	−0.012	0.4485	0.91727	0.903	−0.545	−0.092	0.8452	0.96945	0.951	−0.232	−0.048
0.0801	0.81630	0.966	−0.169	−0.025	0.5823	0.93904	0.904	−0.518	−0.092	0.8932	0.97380	0.967	−0.159	−0.033
0.1299	0.83519	0.952	−0.263	−0.040	0.6816	0.95218	0.915	−0.451	−0.083	0.9446	0.97826	0.986	−0.092	−0.014
0.1885	0.85468	0.938	−0.347	−0.054	0.7582	0.96083	0.929	−0.360	−0.070	1.0000	0.98264	1.001	0.000	0.000
0.2589	0.87501	0.924	−0.429	−0.069										
T = 308.15 K														
0.0000	0.77648	0.895	0.000	0.000	0.3433	0.89094	0.835	−0.547	−0.064	0.8003	0.95944	0.857	−0.341	−0.047
0.0372	0.79384	0.886	−0.091	−0.009	0.4485	0.91216	0.828	−0.589	−0.072	0.8452	0.96360	0.868	−0.259	−0.037
0.0801	0.81197	0.876	−0.189	−0.019	0.5823	0.93374	0.829	−0.570	−0.073	0.8932	0.96786	0.881	−0.181	−0.025
0.1299	0.83081	0.866	−0.294	−0.030	0.6816	0.94676	0.837	−0.506	−0.066	0.9446	0.97213	0.897	−0.095	−0.010
0.1885	0.85028	0.855	−0.393	−0.042	0.7582	0.95525	0.849	−0.408	−0.055	1.0000	0.97644	0.907	0.000	0.000
0.2589	0.87045	0.844	−0.480	−0.053										
2,4,6-Trimethyl-1,3,5-trioxane (1) + 1-Propanol (2)														
T = 298.15 K														
0.0000	0.79960	1.943	0.000	0.000	0.1970	0.86073	1.481	−0.380	−0.297	0.7214	0.95842	1.105	−0.458	−0.235
0.0286	0.80970	1.861	−0.067	−0.058	0.3124	0.88886	1.312	−0.514	−0.370	0.8026	0.96819	1.105	−0.348	−0.168
0.0484	0.81643	1.807	−0.111	−0.096	0.4052	0.90829	1.219	−0.574	−0.385	0.8948	0.97807	1.109	−0.184	−0.086
0.0743	0.82491	1.740	−0.166	−0.140	0.5270	0.93022	1.145	−0.588	−0.358	1.0000	0.98835	1.107	0.000	0.000
0.1010	0.83329	1.676	−0.219	−0.182	0.5689	0.93694	1.129	−0.575	−0.338					
T = 303.15 K														
0.0000	0.79464	1.725	0.000	0.000	0.1970	0.85587	1.322	−0.420	−0.261	0.7214	0.95317	1.001	−0.504	−0.201
0.0286	0.80477	1.653	−0.074	−0.051	0.3124	0.88399	1.175	−0.567	−0.324	0.8026	0.96280	1.002	−0.383	−0.142
0.0484	0.81150	1.606	−0.123	−0.084	0.4052	0.90338	1.096	−0.633	−0.336	0.8948	0.97251	1.005	−0.201	−0.072
0.0743	0.82000	1.548	−0.183	−0.124	0.5270	0.92520	1.034	−0.648	−0.310	1.0000	0.98264	1.001	0.000	0.000
0.1010	0.82840	1.492	−0.242	−0.160	0.5689	0.93188	1.021	−0.634	−0.292					
T = 308.15 K														
0.0000	0.79053	1.537	0.000	0.000	0.1970	0.85132	1.187	−0.440	−0.226	0.7214	0.94775	0.915	−0.557	−0.167
0.0286	0.80059	1.474	−0.077	−0.045	0.3124	0.87922	1.061	−0.597	−0.279	0.8026	0.95727	0.915	−0.439	−0.117
0.0484	0.80728	1.433	−0.128	−0.073	0.4052	0.89844	0.994	−0.670	−0.288	0.8948	0.96687	0.915	−0.259	−0.058
0.0743	0.81572	1.383	−0.191	−0.108	0.5270	0.92007	0.942	−0.692	−0.263	1.0000	0.97644	0.907	0.000	0.000
0.1010	0.82406	1.334	−0.252	−0.139	0.5689	0.92669	0.931	−0.681	−0.247					
2,4,6-Trimethyl-1,3,5-trioxane (1) + 1-Butanol (2)														
T = 298.15														
0.0000	0.80584	2.618	0.000	0.000	0.1940	0.86102	1.756	−0.914	−0.569	0.6932	0.95621	1.193	−1.323	−0.378
0.0289	0.81471	2.460	−0.148	−0.114	0.3007	0.88693	1.471	−1.283	−0.693	0.8331	0.97207	1.184	−0.760	−0.176
0.0582	0.82346	2.311	−0.296	−0.220	0.4056	0.90958	1.302	−1.538	−0.704	0.9165	0.98010	1.143	−0.334	−0.090
0.0804	0.82994	2.204	−0.405	−0.292	0.5091	0.92891	1.219	−1.626	−0.630	1.0000	0.98835	1.107	0.000	0.000
0.0999	0.83553	2.116	−0.498	−0.351	0.6218	0.94667	1.193	−1.514	−0.486					
T = 303.15 K														
0.0000	0.80200	2.297	0.000	0.000	0.1940	0.85678	1.568	−0.930	−0.478	0.6932	0.95123	1.075	−1.370	−0.324
0.0289	0.81080	2.164	−0.151	−0.096	0.3007	0.88265	1.324	−1.323	−0.583	0.8331	0.96665	1.064	−0.774	−0.153
0.0582	0.81950	2.037	−0.300	−0.184	0.4056	0.90500	1.177	−1.572	−0.595	0.9165	0.97450	1.030	−0.336	−0.079
0.0804	0.82593	1.948	−0.411	−0.245	0.5091	0.92420	1.103	−1.669	−0.534	1.0000	0.98264	1.001	0.000	0.000
0.0999	0.83147	1.873	−0.506	−0.295	0.6218	0.94175	1.077	−1.556	−0.415					
T = 308.15 K														
0.0000	0.79820	2.032	0.000	0.000	0.1940	0.85247	1.406	−0.946	−0.408	0.6932	0.94598	0.980	−1.430	−0.272
0.0289	0.80691	1.917	−0.151	−0.082	0.3007	0.87835	1.197	−1.380	−0.497	0.8331	0.96087	0.969	−0.797	−0.126
0.0582	0.81551	1.809	−0.301	−0.157	0.4056	0.90034	1.070	−1.621	−0.505	0.9165	0.96865	0.938	−0.367	−0.063
0.0804	0.82187	1.732	−0.413	−0.209	0.5091	0.91920	1.006	−1.709	−0.453	1.0000	0.97644	0.907	0.000	0.000
0.0999	0.82735	1.668	−0.508	−0.252	0.6218	0.93655	0.983	−1.604	−0.350					

of binary mixtures were calculated by using the relation

$$\delta\eta = \eta - \Sigma x_i \eta_i \tag{3}$$

where η is the viscosity of the mixture, η_i is the viscosity of pure component i, and x_i is the mole fraction of component i. The calculated values of $\delta\eta$ are reported in Table 2.

The calculated excess molar volumes V^E and viscosity deviations $\delta\eta$ were correlated by the Redlich−Kister polynomial[8] by using the relation

$$\Delta Y = x_1 x_2 \Sigma a_i (x_1 - x_2)^i \tag{4}$$

The coefficients in eq 4 were estimated by the least-squares fitting method, and the standard deviation was calculated

Table 3. Value of Coefficients of the Redlich−Kister Equation (Equation 4) and Standard Deviations (Equation 5) of 2,4,6-Trimethyl-1,3,5-trioxane (1) + *n*-Alcohols (2) at 298.15 K

parameter	a_0	a_1	a_2	σ
2,4,6-Trimethyl-1,3,5-trioxane (1) + Ethanol (2)				
V^E/cm^3·mol^{-1}	−1.989	0.255	0.254	0.003
$\delta\eta$/mPa·s	−0.413	−0.045	−0.042	0.001
2,4,6-Trimethyl-1,3,5-trioxane(1) + 1-Propanol (2)				
V^E/cm^3·mol^{-1}	−6.495	0.177	2.001	0.022
$\delta\eta$/mPa·s	−2.549	−1.842	0.107	0.008
2,4,6-Trimethyl-1,3,5-trioxane (1) + 1-Butanol (2)				
V^E/cm^3·mol^{-1}	−2.369	0.187	0.215	0.005
$\delta\eta$/mPa·s	−1.472	0.678	0.016	0.001

by using the relation

$$\sigma = \left[\frac{\Sigma(\Delta Y_{\text{exptl}} - \Delta Y_{\text{calcd}})^2}{D - N}\right]^{0.5} \quad (5)$$

where D and N are the number of data points and parameters, respectively.

Regression results for excess molar volumes and viscosity deviations of binary mixtures of 2,4,6-trimethyl-1,3,5-trioxane + *n*-alcohols at 298.15 K are reported in Table 3.

Discussion

Figures 1 and 2 show that V^E and $\delta\eta$ are negative over the entire composition range for all three systems studied at 298.15 K. The V^E values at equimolar concentrations of 2,4,6-trimethyl-1,3,5-trioxane and *n*-alcohols follow the order 1-butanol < 1-propanol < ethanol. Moreover, the variation in V^E is a distinct bell shape for 1-butanol and 2,4,6-trimethyl-1,3,5-trioxane and a flat bell shape for ethanol and 1-propanol. The variation in viscosity exhibits a similar pattern, except for the 1-propanol + 2,4,6-trimethyl-1,3,5-trioxane mixture. In this case, it is bell-shaped.

The observed variations in the present investigation may be discussed in terms of several effects that may arbitrarily be divided into physical, chemical, and geometrical. The physical interactions consist mainly of dispersion forces and make a positive contribution to V^E and a negative contribution to $\delta\eta$. The chemical or specific interactions are due to charge transfer, formation of hydrogen bonds, and other complex forming interactions resulting in a negative contribution to V^E and a positive contribution to $\delta\eta$. The

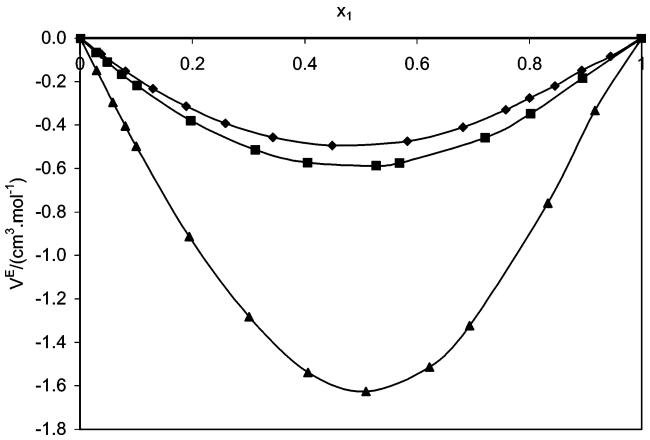

Figure 1. Variation of excess molar volumes V^E for binary mixtures of 2,4,6-trimethyl-1,3,5-trioxane with ethanol (◆), 1-propanol (■), and 1-butanol (▲) at 298.15 K.

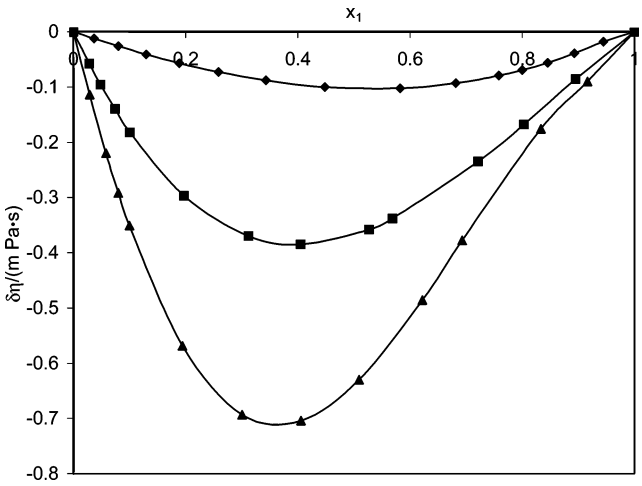

Figure 2. Variation of viscosity deviations $\delta\eta$ for binary mixtures of 2,4,6-trimethyl-1,3,5-trioxane with ethanol (◆), 1-propanol (■), and 1-butanol (▲) at 298.15 K.

structural contributions arising from the geometrical fitting of one component into other, due to differences in molar volumes[9,10] also lead to a negative contribution to V^E.

The variations of V^E and $\delta\eta$ with composition show the maximum values being at around 0.5 mole fraction. Rattan et al.[5] report a similar trend for $\delta\eta$ values for ethylbenzene and alcohol mixtures. The negative variation of V^E and $\delta\eta$ in 2,4,6-trimethyl-1,3,5-trioxane + *n*-alcohols mixtures indicates the structural contribution arising from geometrical fitting in this case. The similar size and dielectric constants and less association in 1-butanol are responsible for large negative variations. With regard to ethanol, these factors being unfavorable shows the exhibited change.

The patterns in the variation of V^E and $\delta\eta$ do not change with temperature (Figures not shown for other temperatures). Only the values are bit more negative at higher temperatures. A better interstitial accommodation is favored at higher temperatures.

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