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Densities and Viscosities of the Binary Mixtures of Chloroethylenes with Some Aliphatic Alcohols

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Densities and viscosities of the binary mixtures of tetrachloroethylene with methanol and of trichloroethylene with ethanol, 2-propanol, and isobutanol were measured at 303.15, 313.15, and 323.15 K. The measurements were used to compute the excess volumes (V^E) and deviations in viscosity ($\Delta\eta$). The excess volumes and deviations in viscosity were represented by a Redlich and Kister expression.

Introduction

The present work on the densities and viscosities of the binary mixtures of tetrachloroethylene with methanol and of trichloroethylene with ethanol, 2-propanol, and isobutanol is a continuation of our recent work[1] on the densities and viscosities of the binary mixtures of anisole or methyl *tert*-butyl ether with benzene, chlorobenzene, benzonitrile, and nitrobenzene. The objective of this work is to understand the type and nature of interactions between different types of molecules in solution. Our literature survey does not reveal any experimental data on the densities and viscosities of the mixtures chosen for the present study.

Experimental Section

Materials. Spectropic grade methanol (SD's Fine Chemicals, Boisar, India) was distilled twice fractionally after drying over silica gel. The middle fraction of the second distillation was stored in amber colored bottles for use in the experiments. Anhydrous ethanol (Aldrich Chemical Co., Gillingham, England) was dried over silica gel and distilled twice, fractionally. The middle fraction of the second distillation was stored in amber colored bottles for use in the experiments. LR grade 2-propanol (Ranbaxy Laboratories, SAS Nagar, Punjab, India) was purified by first treating with aqueous sodium hydroxide, followed by preliminary distillation. After copper chloride was added for stabilization, the alcohol was fractionally distilled twice and the middle fraction of the second distillation was stored in amber colored bottles for use in the experiments. Extrapure AR grade isobutanol (SISCO Research Laboratories, Bombay, India) was dried over silica gel and fractionally distilled twice. The middle fraction of the second distillation was stored in amber colored bottles for use in the experiments. LR grade trichloroethylene (Ranbaxy Laboratories) was treated with potassium carbonate solution and washed with water. After the sample was dried over potassium carbonate and calcium chloride, it was fractionally distilled twice and the middle fraction of the second distillation was used in the experiments. AR grade tetrachloroethylene (SD's Fine Chemicals) was distilled twice fractionally after drying over anhydrous sodium sulfate. The middle fraction of the second distillation was collected into amber colored bottles for use in the experiments. A packed column of length equal to 30 theoretical plates was used for the fractional distillations of all the pure liquids used in the present study. The distillation of the pure liquids was carried out only a few hours before the actual measurements of the density and viscosity were carried out, and sufficient care was taken to avoid oxidation, absorption of moisture, and so forth, during the intervening period. On the basis of the comparison of the refractive index and density with the literature[2] data, presented in Table 1, and the observation of no significant second peaks in the gas chromatograms, the pure liquids used in this study are at least 99.9% pure.

Table 1. Comparison of the Refractive Indices (n_D) and Densities (ρ) of the Pure Liquids with the Literature Data of Riddick et al.[2] at 298.15 K

	n_D		ρ/kg·m^{-3}	
liquid	this work	lit.	this work	lit.
methanol	1.3265	1.326 52	786.4	786.37
ethanol	1.3594	1.359 41	784.9	784.93
2-propanol	1.3752	1.375 20	781.3	781.26
isobutanol	1.3939	1.393 89	797.8	797.80
trichloroethylene	1.4750[a]	1.475 00[a]	1451.4[b]	1451.40[b]
tetrachloroethylene	1.5032	1.503 20	1614.3	1614.32

[a] At 297.75 K [b] At 303.15 K.

Methods

Preparation of Mixtures. Airtight stoppered bottles were used for the preparation of the mixtures. First, the mass of the dry bottle was determined. The more volatile component of the mixture was introduced into the bottle, and its mass was recorded. Subsequently, the other component was introduced and the mass of the bottle along with the two pure components was determined. The contents were well mixed by applying rotary motion before use in the experiments. The composition of the mixture was determined from the masses of the two components and checked by gas chromatography before use in the experiments.

Measurement of Density. The densities of the pure liquids as well as mixtures were determined by using a specially designed pycnometer, similar to the one described by Dahiya et al.[3] and described in an earlier publication.[1]

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Table 2. Densities (ρ) of the Binary Mixtures of Chloroethylenes with Some Aliphatic Alcohols

	$T = 303.15$ K		$T = 313.15$ K		$T = 323.15$ K	
	ρ	V^E	ρ	V^E	ρ	V^E
x_1	$kg \cdot m^{-3}$	$cm^3 \cdot mol^{-1}$	$kg \cdot m^{-3}$	$cm^3 \cdot mol^{-1}$	$kg \cdot m^{-3}$	$cm^3 \cdot mol^{-1}$
Methanol (1) + Trichloroethylene (2)						
1.0000	790.0	0.00	776.0	0.00	766.0	0.00
0.9006	872.0	13.95	857.0	14.22	847.0	14.51
0.7514	895.0	16.88	878.0	17.42	868.0	17.71
0.6044	1115.0	10.94	1098.0	11.17	1088.0	11.29
0.4560	1237.0	10.22	1219.0	10.42	1209.0	10.54
0.2970	1366.0	7.85	1348.0	4.11	1338.0	8.04
0.1436	1492.0	4.27	1437.0	4.29	1463.0	4.32
0.0000	1610.0	0.00	1590.0	0.00	1580.0	0.00
Ethanol (1) + Trichloroethylene (2)						
1.0000	779.0	0.00	769.0	0.00	759.0	0.00
0.9000	847.3	0.74	836.3	0.76	832.4	0.06
0.7500	949.7	1.38	937.3	1.40	925.0	1.42
0.6000	1052.2	1.59	1038.2	1.62	1024.6	1.06
0.4500	1154.6	1.49	1139.2	1.64	1124.6	1.54
0.3000	1257.1	1.16	1240.1	1.19	1223.8	1.21
0.1500	1359.5	0.66	1341.1	0.66	1323.4	0.67
0.0000	1462.0	0.00	1442.0	0.00	1423.0	0.00
2-Propanol (1) + Trichloroethylene (2)						
1.0000	776.0	0.00	766.0	0.00	756.0	0.00
0.9000	844.6	6.52	833.6	0.35	822.7	0.94
0.7500	947.5	6.50	935.0	1.72	922.7	1.74
0.6000	1050.4	5.69	1036.4	1.98	1022.8	2.00
0.4500	1153.3	4.63	1137.8	1.86	1122.8	1.89
0.3000	1256.2	3.30	1239.2	1.45	1222.9	1.47
0.1500	1359.1	1.73	1340.6	0.82	1272.9	0.48
0.0000	1462.0	0.00	1442.0	0.00	1423.0	0.00
Isobutanol (1) + Trichloroethylene (2)						
1.0000	792.0	0.00	782.0	0.00	772.0	0.00
0.9000	859.0	−0.27	848.0	−0.26	837.1	−0.41
0.7500	959.0	−0.47	947.0	−0.48	934.7	−0.48
0.6000	1060.0	−0.61	1046.0	−0.56	1032.4	−0.56
0.4500	1160.5	−0.60	1145.0	0.53	1130.0	−0.52
0.3000	1261.0	−0.49	1244.0	−0.47	1227.7	−0.40
0.1500	1361.5	−0.34	1343.0	0.36	1325.3	−0.22
0.0000	1460.0	0.00	1442.0	0.00	1423.0	0.00

Table 3. Viscosities (η) of the Binary Mixtures of Chloroethylenes with Some Aliphatic Alcohols

	$T = 293.15$ K		$T = 303.15$ K		$T = 313.15$ K	
	η	$\Delta\eta$	η	$\Delta\eta$	η	$\Delta\eta$
x_1	mPa·s	mPa·s	mPa·s	mPa·s	mPa·s	mPa·s
Methanol (!) + Tetrachloroethane (2)						
1.0000	0.5000	0.0000	0.4850	0.0000	0.4750	0.0000
0.9006	0.5350	0.0052	0.5120	0.0016	0.4970	0.0016
0.7514	0.5850	0.0104	0.5520	0.0036	0.5290	0.0031
0.6044	0.6390	0.0203	0.5900	0.0042	0.5610	0.0049
0.4560	0.6830	0.0200	0.6300	0.0062	0.5920	0.0055
0.2974	0.7210	0.0102	0.6670	0.0047	0.6220	0.0029
0.1436	0.7620	0.0050	0.7050	0.0015	0.6515	0.0008
0.0000	0.8000	0.0000	0.7400	0.0000	0.6800	0.0000
Ethanol (1) + Trichloroethane (2)						
1.0000	1.0000	0.0000	0.9000	0.0000	0.7890	0.0000
0.9000	0.9601	0.0029	0.8581	0.0050	0.7593	0.0019
0.7500	0.9003	0.0073	0.8177	0.0097	0.7193	0.0092
0.6000	0.8344	0.0056	0.7650	0.0122	0.6692	0.0066
0.4500	0.7685	0.0041	0.7071	0.0095	0.6186	0.0033
0.3000	0.7027	0.0023	0.6477	0.0053	0.5690	0.0013
0.1500	0.6368	0.0006	0.5900	0.0028	0.5210	0.0005
0.0000	0.5720	0.0000	0.5320	0.0000	0.4730	0.0000
2-Propanol (1) + Trichloroethylene (2)						
1.0000	1.7000	0.0000	1.4000	0.0000	1.0000	0.0000
0.9000	1.5961	−0.0089	1.3221	0.0089	0.9562	0.0089
0.7500	1.4283	−0.0103	1.1903	0.0073	0.8775	0.0092
0.6000	1.2574	−0.0086	1.0584	0.0056	0.7948	0.0056
0.4500	1.0835	−0.0039	0.9265	0.0039	0.7141	0.0039
0.3000	0.9127	0.0023	0.7947	0.0023	0.6334	0.0023
0.1500	0.7418	0.0006	0.6628	0.0006	0.5527	0.0006
0.0000	0.5720	0.0000	0.5320	0.0000	0.4730	0.0000
Isobutanol (1) + Trichloroethylene (2)						
1.0000	2.7500	0.0000	2.1000	0.0000	1.6500	0.0000
0.9000	2.5411	0.0089	1.9521	0.0089	1.5417	0.0089
0.7500	2.2127	0.0074	1.7153	0.0073	1.3650	0.0072
0.6000	1.8844	0.0056	1.4784	0.0056	1.1848	0.0056
0.4500	1.5560	0.0039	1.2417	0.0041	1.0066	0.0039
0.3000	1.2277	0.0023	1.0047	0.0023	0.8284	0.0023
0.1500	0.8993	0.0006	0.7678	0.0006	0.6502	0.0006
0.0000	0.5720	0.0000	0.5320	0.0000	0.4730	0.0000

It consists of a small bulb of 25 mL, attached to a fine capillary of 1 mm bore, through a standard joint. The levels up to each of the markings were calibrated with the mass of HPLC grade benzene. The level of liquid (or liquid mixture) in the capillary was read by means of a traveling microscope (least count of 0.001 cm) after the apparatus was kept immersed in a thermostat maintained within ±0.05 K of the desired temperature. The mass of the dried apparatus, along with the Teflon cap, was recorded first. Subsequently, the sample (pure liquid or the mixture to be studied) was introduced into the apparatus by means of a hypodermic syringe, taking care that no air bubbles were entrapped. The apparatus was then capped and its mass was determined on a precision balance (Sartorius RC 210P) precise to within $\pm 10^{-5}$ g. The apparatus was then immersed in the thermostat and maintained at the desired temperature until the level of the liquid in the capillary remained constant for at least 30 min. From the steady level, the volume of the sample was noted from the calibration data. The densities are accurate to within ±0.5 $kg \cdot m^{-3}$, and the mole fractions reported are within ±0.0001 units.

Measurement of Viscosity. A Hoppler type falling ball viscometer with the provision to maintain the temperature to within ±0.05 K of the required value by connection to a circulating type thermostat was used for the present set of experiments. During the experiments, care was taken to avoid entrainment of any air bubbles or particulate matter in the apparatus. Care was also taken to avoid parallax error. The time measurements were accurate to within ±0.05 s. On the basis of our studies on several pure liquids, the viscosity measurements of this study are expected to be within ±0.2% of their true values.

Results and Discussion

The measured values of density (ρ) and viscosity (η) along with the values of excess volumes (V^E) and deviations in viscosity ($\Delta\eta$) calculated as described below are presented in Tables 2 and 3. The excess volumes are calculated from the mixture density data from the relation

$$V^E = V - (x_1 V_1 + x_2 V_2) \qquad (1)$$

where V is the molar volume of the mixture, defined as

$$V = (x_1 M_1 + x_2 M_2)/\rho \qquad (2)$$

M_1 and M_2 are the molecular masses of the pure components 1 and 2, x_1 and x_2 are the mole fractions of the components 1 and 2, ρ is the density of the mixture, and V_1 and V_2 are the molar volumes of the pure components calculated from

$$V_i = M_i/\rho_i \qquad (3)$$

where the subscript i represents component i.

The deviations in viscosity are calculated using the relation

$$\Delta\eta = \eta - (x_1\eta_1 + x_2\eta_2) \qquad (4)$$

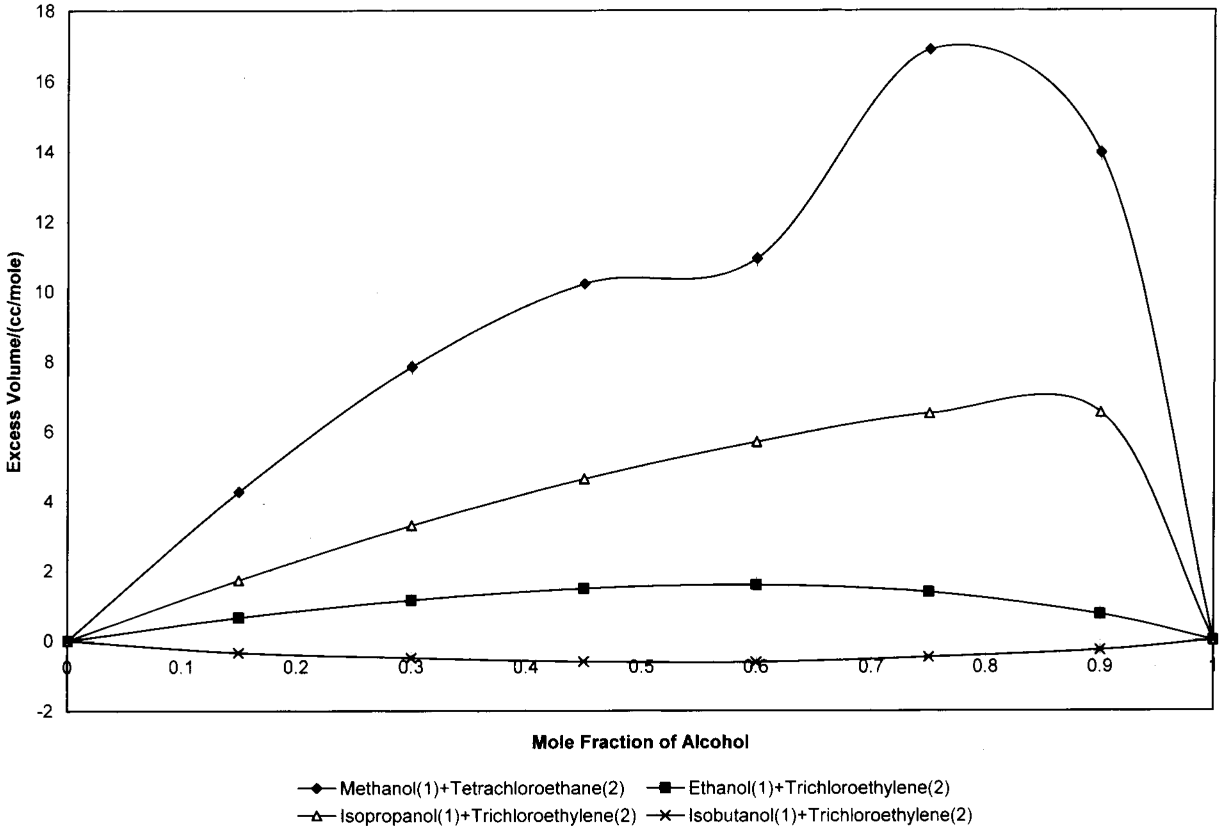

Figure 1. Excess volumes at 303.15 K.

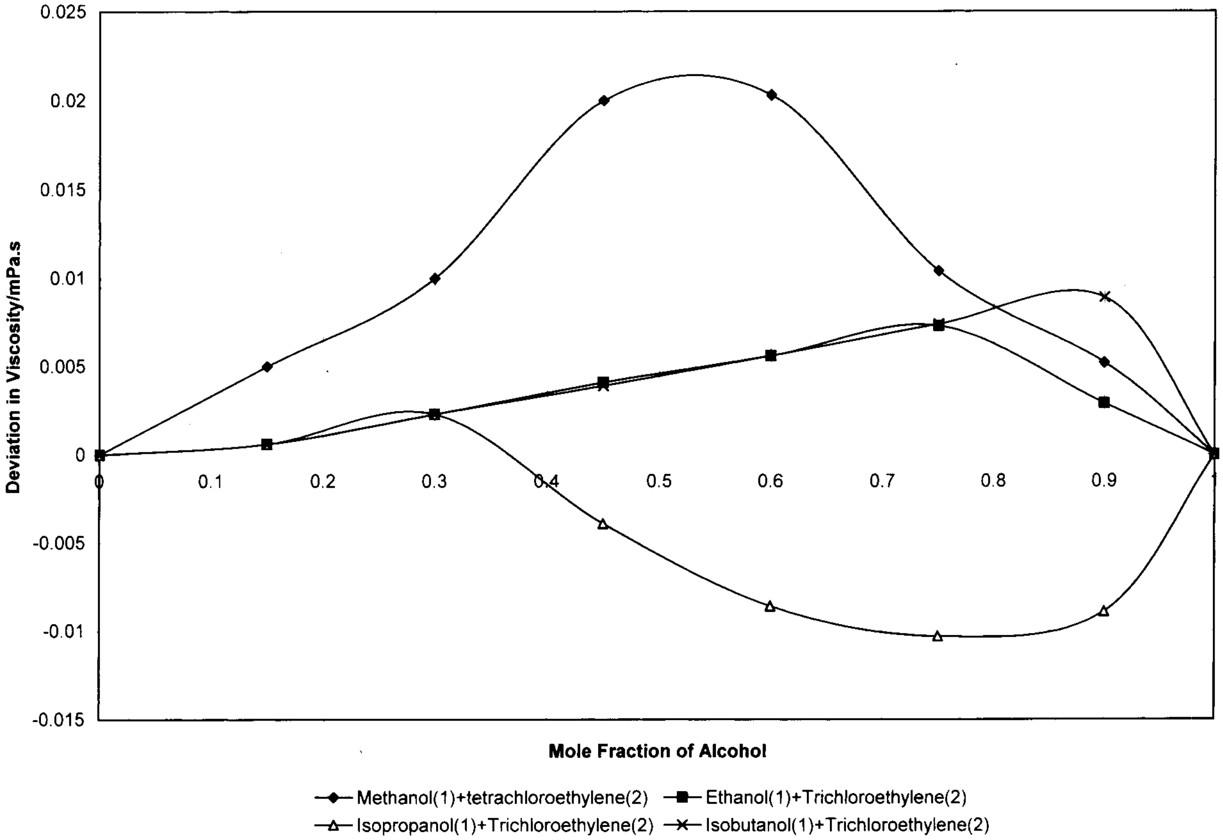

Figure 2. Deviations in viscosity at 303.15 K.

where η, η_1, and η_2 are the viscosities of the mixture and pure components 1 and 2, respectively. The excess volumes (V^E) and deviations in viscosity ($\Delta\eta$) are fitted by the method of least squares to a third-order Redlich−Kister

Table 4. Parameters h_j and Standard Deviations $\sigma(V^E)$ for the Different Binary Mixtures

T/K	h_0	h_1	h_2	h_3	$\sigma(V^E)$
		Methanol + Tetrachloroethylene			
303.15	19.62	−176.6	−571.5	604.8	0.73
313.15	45.70	−100.8	60.08	208.7	1.44
323.15	19.98	178.0	−575.7	616.1	0.82
		Ethanol + Trichlorothylene			
303.15	4.952	1.040	2.988	−0.1190	0.01
313.15	3.990	−9.285	−12.84	8.893	0.04
323.15	9.157	−37.21	101.8	−77.88	0.30
		2-Propanol + Trichloroethylene			
303.15	−3.865	170.0	−44.53	388.6	0.35
313.15	10.31	−39.71	114.3	86.47	0.12
323.15	−1.285	44.04	−70.49	40.16	0.05
		Isobutanol + Trichloroethylene			
303.15	−2.957	2.619	−2.953	0.046	0.02
313.15	−3.955	9.872	−16.29	7.385	0.05
323.15	−0.4155	−12.33	29.98	−23.68	0.03

Table 5. Parameters h_j and Standard Deviations $\sigma(\eta^E)$ for Different Binary Systems

T/K	h_0	h_1	h_2	h_3	$\sigma(\Delta\eta)$
		Methanol + Tetrachloroethylene			
303.15	0.066 37	−0.3799	1.5000	1.3470	0.0005
313.15	0.009 582	0.2030	−0.3828	0.2131	0.0004
323.15	0.011 87	0.1546	−0.2360	0.1113	0.0004
		Ethanol + Trichloroethylene			
303.15	0.014 06	0.1028	0.3489	−0.2341	0.0006
313.15	0.226 1	0.4356	0.2539	−0.1845	0.0005
323.15	0.044 91	0.4083	1.0960	−0.1406	0.0010
		2-Propanol + Trichloroethylene			
303.15	−0.003 796	0.07576	−0.1624	0.2270	0.0005
313.15	−0.029 28	0.3261	−0.8097	0.6712	0.0006
323.15	−0.028 56	0.3195	−0.7939	0.6609	0.0006
		Isobutanol + Trichloroethylene			
303.15	−0.028 56	0.3195	−0.7939	0.6609	0.0006
313.15	−0.030 35	0.3349	−0.8262	0.6800	0.0006
323.15	−0.029 98	0.3326	−0.8253	0.6814	0.0006

equation (higher order does not increase the accuracy of the representation significantly)

$$V^E \quad \text{or} \quad \Delta\eta = x_1(1 - x_1)\sum_j h_j(2x_1 - 1)^j \tag{5}$$

where h_j's are the coefficients of the polynomial. The standard deviation is calculated for each set of isothermal data from

$$\sigma(V^E \text{ or } \Delta\eta) = [\{(V^E \text{ or } \Delta\eta)_{\text{exp}} - (V^E \text{ or } \Delta\eta)_{\text{cal}}\}^2/(n - 1)]^{0.5} \tag{6}$$

where n represents the number of observations in the particular set. Tables 4 and 5 summarize the polynomial coefficients and standard deviations for excess volumes (V^E) and deviations in viscosity ($\Delta\eta$), respectively. The uncertainties in the representation are within the experimental errors. The excess volumes as well as the deviations in viscosity are generally larger for the methanol (1) + tetrachloroethylene (2) system compared to the systems containing trichloroethylene. In the systems with trichloroethylene as one of the components, the excess volumes are in the order 2-propanol > ethanol > isobutanol while the deviations in viscosity are in the order 2-propanol > ethanol ≈ isobutanol. Figures 1 and 2 show the excess volumes and deviations in viscosity as a function of the mole fraction of alcohol at 303.15 K. On the whole, it is felt that there are only weak interactions for the set of systems chosen for the present study. The data and the representation are expected to be useful for design purposes.

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