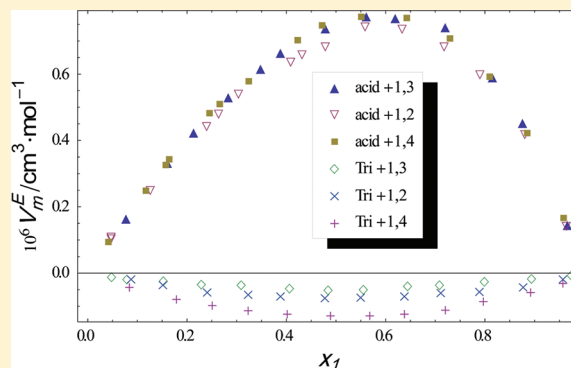


Densities, Excess Molar Volumes, Viscosity, and Refractive Indices of Binary Mixtures of Ethanoic Acid and Trichloroethylene with Dimethylbenzenes at Different Temperatures

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ABSTRACT: Liquid densities, ρ , of binary mixtures of ethanoic acid and trichloroethylene with 1,2-dimethylbenzene, 1,3-dimethylbenzene, and 1,4-dimethylbenzene were measured over the entire range of composition at (293.15, 298.15, and 303.15) K and at ambient pressure (81.5 kPa). The excess molar volumes, V_m^E , for the binary mixtures were calculated. The excess molar volumes of trichloroethylene with dimethylbenzenes are negative over the whole mole fraction range and become more negative with increasing temperature. The V_m^E values are positive for binary mixtures of ethanoic acid with dimethylbenzenes and become more positive with increasing temperature. Also, the dynamic viscosity, η , and refractive indices, n_D , were measured at 298.15 K. The excess molar volume and viscosity were compared with some values of literature at different temperatures and pressures.



INTRODUCTION

Experimental thermodynamic and transport properties of liquid mixtures are an important source of information for the characterization of the intermolecular interactions between components and can be used to test and to improve thermodynamic models. From a practical point of view, the data are useful for the design of mixing, storage, and process equipment.¹ Dimethylbenzenes are used as raw material in the plastics industry to make synthetic fibers and soft plastic for aircrafts and vehicles.² The present work is the rest of a large amount of studies on the thermodynamic characterization of liquid mixtures.

This paper reports the densities, ρ , and excess molar volume, V_m^E , of ethanoic acid (1) or trichloroethylene (1) + 1,3-dimethylbenzene (2), 1,2-dimethylbenzene (2), or 1,4-dimethylbenzene (2) at temperatures of (293.15, 298.15, and 303.15) K and at ambient pressure. Also, the dynamic viscosity, η , and refractive indices, n_D , were reported. The excess molar volume and viscosity were compared with some values of literature at different temperatures and pressures.

EXPERIMENTAL SECTION

Materials. The 1,2-dimethylbenzene, 1,3-dimethylbenzene, 1,4-dimethylbenzene, ethanoic acid, and trichloroethylene were high purity grade reagents from Merck. All of the samples were degassed by heating and cooling just before use. The purity grade, densities, refractive indices, and viscosities of pure components are given in Table 1 and compared with literature data,^{3–11} and they are in good agreement.

Measurements. The mixtures were prepared by mass using a Mettler AB 204-N balance just before use. The uncertainty in the mass measurements was $\pm 1 \cdot 10^{-7}$ kg. The conversion to molar mass was based on the relative atomic mass table of 1996 issued by the International Union of Pure and Applied Chemistry (IUPAC).¹² The average uncertainty in the mole fraction is about $\pm 1 \cdot 10^{-4}$. The density of the pure components and the mixtures was measured by means of an Anton Paar DMA 4500 oscillating U-tube densimeter with automatic viscosity correction. The temperature was adjusted to ± 0.01 K with a solid state thermostat in the cell. The instrument was calibrated with dry air and bidistilled freshly degassed water once a day. The uncertainty in the density was $\pm 1 \cdot 10^{-2}$ kg·m⁻³. The refractive indices of the pure components and the mixtures were measured at 298.15 K by using a thermostatted Abbe refractometer which their uncertainty is less than $\pm 2 \cdot 10^{-4}$ units. Water was circulated into the prism of the refractometer by a circulation pump connected to an external thermostatted water bath. The temperature of the sample was controlled to ± 0.1 K.

The viscosity of the pure components and the mixtures were measured with an Ubbelohde viscometer. The viscosity was determined according to eq 1:

$$\eta = \rho\nu = \rho(kt - c/t) \quad (1)$$

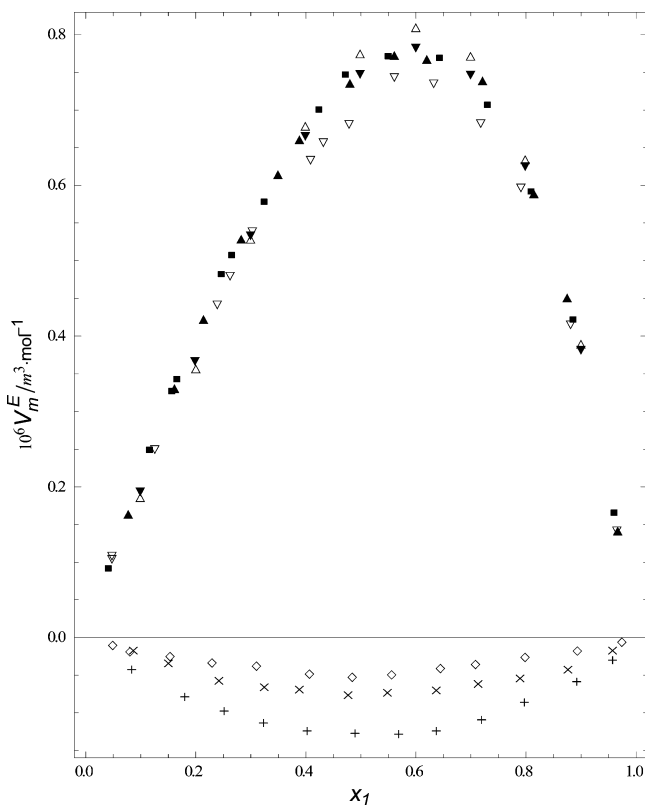
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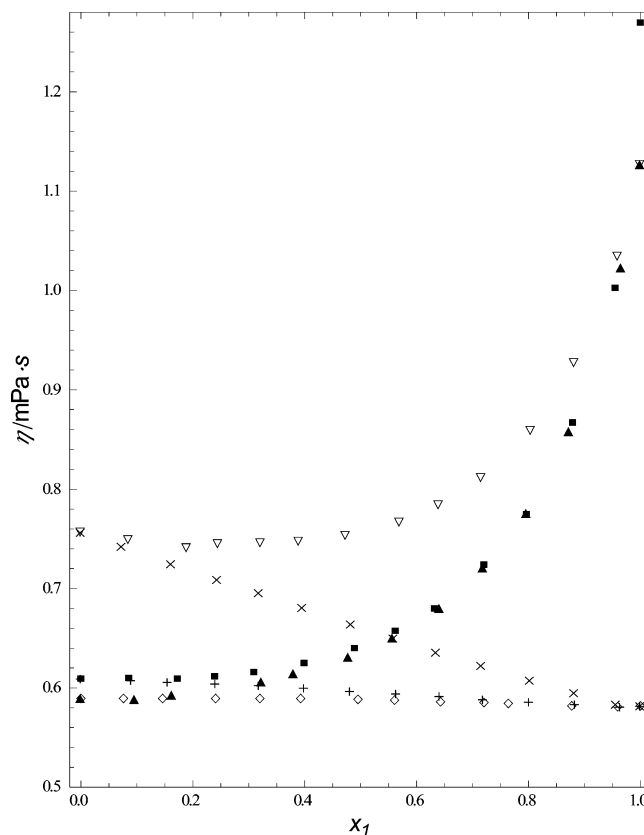
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Table 1. Purity Grades, Densities, ρ , Refractive Indices, n_D , and Viscosities, η , of the Pure Components at 298.15 K and Comparison with Literature Values

component	purity		$\rho \cdot 10^3 / \text{kg} \cdot \text{m}^{-3}$		$\eta / \text{mPa} \cdot \text{s}$		n_D	
	mass fraction		exptl	lit.	exptl	lit.	exptl	lit.
ethanoic acid	0.998		1.04358	1.04365 ³	1.127	1.115 ³	1.3698	1.3697 ¹⁰
trichloroethylene	0.995		1.45553	1.45537 ¹¹	0.582	0.532 ⁴	1.4750	1.47448 ¹¹
1,2-dimethylbenzene	≥ 0.99		0.87557	0.87573 ⁹	0.757	0.7540 ⁶	1.5024	1.5030 ⁸
1,3-dimethylbenzene	≥ 0.99		0.85988	0.85983 ⁹	0.589	0.5892 ⁶	1.4944	1.4945 ⁷
1,4-dimethylbenzene	≥ 0.99		0.85668	0.85662 ⁵	0.609	0.6078 ⁶	1.4929	1.4934 ⁸

**Figure 1.** Experimental excess molar volumes for the binary mixtures of ethanoic acid (1) or trichloroethylene (1) with dimethylbenzenes (2) at 298.15 K and comparison with the literature at 313.15 K and 0.8 MPa: \blacktriangle , ethanoic acid + 1,3-dimethylbenzene; ∇ , ethanoic acid + 1,2-dimethylbenzene; \blacksquare , ethanoic acid + 1,4-dimethylbenzene; \blacktriangledown , ethanoic acid + 1,2-dimethylbenzene, ref 13; \triangle , ethanoic acid + 1,4-dimethylbenzene, ref 13; \diamond , trichloroethylene + 1,3-dimethylbenzene; \times , trichloroethylene + 1,2-dimethylbenzene; $+$, trichloroethylene + 1,4-dimethylbenzene.

where k and c are the viscometer constants and t , ρ , η , and ν are the efflux time, density, dynamic, and kinematic viscosities, respectively. The viscometers were calibrated with spectroscopic grade 1-butanol and bidistilled fresh water at the working temperature. An electronic digital stop watch with readability of ± 0.01 s was used for the flow time measurements. At least three repetitions of each data set were obtained, and the results were averaged. The temperature of the samples was controlled with an external thermostat. The uncertainty in dynamic viscosities is of the order of $\pm 3 \cdot 10^{-3}$ mPa·s.

**Figure 2.** Experimental viscosities for the binary mixtures of ethanoic acid (1) or trichloroethylene (1) with dimethylbenzenes (2) at 298.15 K: \blacktriangle , ethanoic acid + 1,3-dimethylbenzene; ∇ , ethanoic acid + 1,2-dimethylbenzene; \blacksquare , ethanoic acid + 1,4-dimethylbenzene; \diamond , trichloroethylene + 1,3-dimethylbenzene; \times , trichloroethylene + 1,2-dimethylbenzene; $+$, trichloroethylene + 1,4-dimethylbenzene.

RESULTS AND DISCUSSION

Excess molar volumes for binary mixtures were calculated from the density data by the following equation:

$$V_m^E = \sum_{i=1}^2 x_i M_i (\rho^{-1} - \rho_i^{-1}) \quad (2)$$

where M_i is the molar mass of component i and ρ and ρ_i are the densities of a mixture and pure component, respectively.

According to the error propagation law the average uncertainty in V_m^E are estimated to $\pm 3 \cdot 10^{-9}$ m³·mol⁻¹. The excess molar volume, viscosity, and refractive index for the binary mixtures are reported in Tables 2 to 5 and graphically presented in Figures 1 to 3.

Table 2. Densities, ρ , and Excess Molar Volumes, V_m^E , for the Binary Mixtures of Ethanoic Acid (1) + Dimethylbenzenes (2) at Different Temperatures

x_1	$\rho \cdot 10^3$	$V_m^E \cdot 10^6$	$\rho \cdot 10^3$	$V_m^E \cdot 10^6$	$\rho \cdot 10^3$	$V_m^E \cdot 10^6$
	kg·m ⁻³	m ³ ·mol ⁻¹	kg·m ⁻³	m ³ ·mol ⁻¹	kg·m ⁻³	m ³ ·mol ⁻¹
Ethanoic Acid (1) + 1,3-Dimethylbenzene (2)						
	T = 293.15 K		T = 298.15 K		T = 303.15 K	
0.0000	0.86417		0.85988		0.85558	
0.0777	0.86999	0.159	0.86562	0.164	0.86124	0.171
0.1623	0.87698	0.322	0.87254	0.330	0.87269	0.438
0.2143	0.88173	0.409	0.87722	0.422	0.87939	0.549
0.2833	0.88860	0.512	0.88400	0.529	0.88659	0.638
0.3500	0.89597	0.595	0.89129	0.614	0.89118	0.687
0.3896	0.90067	0.640	0.89594	0.661	0.90300	0.765
0.4801	0.91273	0.714	0.90788	0.736	0.91543	0.802
0.5621	0.92538	0.750	0.92041	0.773	0.92559	0.796
0.6204	0.93570	0.746	0.93066	0.767	0.94586	0.767
0.7214	0.95629	0.720	0.95108	0.739	0.96994	0.612
0.8155	0.98067	0.575	0.97531	0.589	0.98844	0.469
0.8758	0.99934	0.442	0.99389	0.451	1.02308	0.149
0.9672	1.03428	0.141	1.02866	0.142	0.86124	0.171
1.0000	1.04932		1.04358		1.03801	
Ethanoic Acid (1) + 1,2-Dimethylbenzene (2)						
	T = 293.15 K		T = 298.15 K		T = 303.15 K	
0.0000	0.87977		0.87557		0.87136	
0.0479	0.88296	0.102	0.87872	0.104	0.87446	0.108
0.1264	0.88876	0.241	0.88442	0.249	0.88007	0.259
0.2399	0.89821	0.427	0.89374	0.441	0.88926	0.457
0.2632	0.90031	0.465	0.89582	0.479	0.89131	0.497
0.3036	0.90417	0.521	0.89962	0.538	0.89506	0.558
0.4089	0.91571	0.615	0.91104	0.633	0.90634	0.657
0.4323	0.91849	0.636	0.91377	0.656	0.90903	0.682
0.4790	0.92447	0.662	0.91970	0.681	0.91491	0.707
0.5609	0.93590	0.713	0.93090	0.743	0.92608	0.761
0.6332	0.94771	0.712	0.94268	0.734	0.93766	0.760
0.7184	0.96407	0.664	0.95892	0.682	0.95375	0.708
0.7912	0.98062	0.581	0.97533	0.596	0.97003	0.620
0.8814	1.00553	0.406	1.00008	0.415	0.99474	0.425
0.9652	1.03487	0.141	1.02928	0.141	1.02369	0.149
1.0000	1.04932		1.04358		1.03801	
Ethanoic Acid (1) + 1,4-Dimethylbenzene (2)						
	T = 293.15 K		T = 298.15 K		T = 303.15 K	
0.0000	0.86102		0.85668		0.85233	
0.0415	0.86409	0.089	0.85971	0.092	0.85531	0.096
0.1166	0.87008	0.241	0.86562	0.249	0.86115	0.259
0.1570	0.87355	0.317	0.86905	0.327	0.86453	0.341
0.1651	0.87428	0.330	0.86976	0.343	0.86524	0.356
0.2466	0.88200	0.467	0.87740	0.482	0.87279	0.500
0.2659	0.88401	0.491	0.87938	0.508	0.87476	0.526
0.3246	0.89049	0.557	0.88578	0.578	0.88108	0.599
0.4234	0.90244	0.681	0.89764	0.701	0.89281	0.728
0.4717	0.90904	0.725	0.90417	0.747	0.89929	0.774
0.5505	0.92133	0.749	0.91635	0.771	0.91138	0.798
0.6435	0.93819	0.747	0.93307	0.769	0.92795	0.797
0.7299	0.95701	0.689	0.95178	0.707	0.94653	0.734
0.8099	0.97797	0.578	0.97261	0.592	0.96724	0.614
0.8851	1.00176	0.414	0.99629	0.422	0.99081	0.439
0.9601	1.03099	0.166	1.02540	0.166	1.01976	0.179
1.0000	1.04932		1.04358		1.03801	

Table 3. Densities, ρ , and Excess Molar Volumes, V_m^E , for the Binary Mixtures of Trichloroethylene (1) + Dimethylbenzenes (2) at Different Temperatures

x_1	$\rho \cdot 10^3$	$V_m^E \cdot 10^6$	$\rho \cdot 10^3$	$V_m^E \cdot 10^6$	$\rho \cdot 10^3$	$V_m^E \cdot 10^6$
	kg·m ⁻³	m ³ ·mol ⁻¹	kg·m ⁻³	m ³ ·mol ⁻¹	kg·m ⁻³	m ³ ·mol ⁻¹
Trichloroethylene (1) + 1,3-Dimethylbenzene (2)						
	T = 293.15 K		T = 298.15 K		T = 303.15 K	
0.0000	0.86417		0.85988		0.85558	
0.0494	0.88620	-0.010	0.88177	-0.011	0.87734	-0.012
0.0796	0.89993	-0.018	0.89543	-0.019	0.89091	-0.019
0.1531	0.93434	-0.025	0.92962	-0.025	0.92488	-0.026
0.2300	0.97187	-0.032	0.96692	-0.034	0.96195	-0.034
0.3097	1.01252	-0.037	1.00732	-0.038	1.00209	-0.039
0.4065	1.06466	-0.048	1.05910	-0.048	1.05353	-0.050
0.4841	1.10860	-0.050	1.10278	-0.053	1.09693	-0.056
0.5561	1.15133	-0.048	1.14520	-0.050	1.13905	-0.052
0.6453	1.20686	-0.039	1.20035	-0.041	1.19384	-0.045
0.7090	1.24860	-0.035	1.24179	-0.036	1.23495	-0.037
0.7989	1.31061	-0.025	1.30335	-0.026	1.29606	-0.027
0.8937	1.38016	-0.016	1.37241	-0.018	1.36461	-0.019
0.9740	1.44288	-0.004	1.43466	-0.006	1.42638	-0.006
1.0000	1.46394		1.45553		1.44708	
Trichloroethylene (1) + 1,2-Dimethylbenzene (2)						
	T = 293.15 K		T = 298.15 K		T = 303.15 K	
0.0000	0.87977		0.87557		0.87136	
0.0880	0.91903	-0.017	0.91458	-0.017	0.91012	-0.017
0.1511	0.94833	-0.033	0.94370	-0.034	0.93906	-0.035
0.2426	0.99267	-0.057	0.98775	-0.057	0.98282	-0.059
0.3249	1.03435	-0.064	1.02915	-0.065	1.02395	-0.067
0.3895	1.0684	-0.067	1.06298	-0.069	1.05754	-0.070
0.4775	1.11688	-0.072	1.11115	-0.076	1.10538	-0.078
0.5495	1.15843	-0.069	1.15241	-0.073	1.14634	-0.075
0.6384	1.21222	-0.067	1.20579	-0.070	1.19932	-0.071
0.7132	1.25966	-0.058	1.25289	-0.061	1.24608	-0.064
0.7900	1.31086	-0.053	1.30368	-0.054	1.29647	-0.056
0.8776	1.37225	-0.040	1.36460	-0.042	1.35692	-0.044
0.9583	1.43195	-0.017	1.42379	-0.017	1.41562	-0.018
1.0000	1.46394		1.45553		1.44708	
Trichloroethylene (1) + 1,4-Dimethylbenzene (2)						
	T = 293.15 K		T = 298.15 K		T = 303.15 K	
0.0000	0.86102		0.85668		0.85233	
0.0843	0.89917	-0.042	0.89460	-0.042	0.89002	-0.043
0.1806	0.94497	-0.077	0.94012	-0.078	0.93527	-0.081
0.2528	0.98096	-0.096	0.97588	-0.097	0.97080	-0.099
0.3239	1.01791	-0.113	1.01259	-0.113	1.00728	-0.116
0.4030	1.06083	-0.121	1.05525	-0.123	1.04965	-0.125
0.4900	1.11044	-0.125	1.10453	-0.127	1.09861	-0.129
0.5689	1.15779	-0.126	1.15157	-0.128	1.14535	-0.133
0.6381	1.20131	-0.121	1.19480	-0.123	1.18825	-0.124
0.7202	1.25550	-0.107	1.24862	-0.109	1.24169	-0.110
0.7975	1.30915	-0.084	1.30188	-0.085	1.29456	-0.085
0.8925	1.37916	-0.056	1.37140	-0.058	1.36359	-0.059
0.9582	1.43028	-0.027	1.42214	-0.029	1.41395	-0.029
1.0000	1.46394		1.45553		1.44708	

The excess molar volumes for ethanoic acid (1) + 1,2-dimethylbenzene (2), 1,3-dimethylbenzene (2), or 1,4-dimethylbenzene (2) are positive over the entire mole fraction range and almost symmetrical with a maximum around $x_1 \approx 0.6$

and increase with increasing temperatures from (293.15 to 303.15) K. The V_m^E values were compared with the data reported in the literature¹³ at different temperatures and pressures. They are graphically represented in Figure 1. The

Table 4. Viscosities, η , for the Binary Mixtures of Ethanoic Acid (1) or Trichloroethylene (1) with Dimethylbenzenes (2) at 298.15 K

η		η	
x_1	mPa·s	x_1	mPa·s
Ethanoic Acid (1) + 1,3-Dimethylbenzene (2)		Ethanoic Acid (1) + 1,2-Dimethylbenzene	
0.0962	0.5885	0.0852	0.7491
0.1625	0.5929	0.1881	0.7412
0.3223	0.6061	0.2447	0.7448
0.3797	0.6144	0.3206	0.7457
0.4773	0.6308	0.3894	0.7476
0.5570	0.6504	0.4729	0.7532
0.6405	0.6798	0.5694	0.7667
0.7182	0.7206	0.6388	0.7838
0.7955	0.7754	0.7151	0.8113
0.8721	0.8578	0.8031	0.8592
0.9649	1.0231	0.8817	0.9274
		0.9589	1.0346
Ethanoic Acid (1) + 1,4-Dimethylbenzene (2)		Trichloroethylene (1) + 1,3-Dimethylbenzene (2)	
0.0863	0.6099	0.0768	0.5895
0.1730	0.6095	0.1465	0.5893
0.2386	0.6117	0.2415	0.5895
0.3096	0.6159	0.3204	0.5897
0.3987	0.6250	0.3935	0.5893
0.4897	0.6398	0.4960	0.5883
0.5621	0.6575	0.5613	0.5875
0.6323	0.6800	0.6423	0.5863
0.7212	0.7243	0.7204	0.5851
0.7965	0.7753	0.7639	0.5844
0.8784	0.8675	0.8774	0.5823
0.9550	1.0026	0.9596	0.5808
Trichloroethylene (1) + 1,2-Dimethylbenzene (2)		Trichloroethylene (1) + 1,4-Dimethylbenzene (2)	
0.0721	0.7421	0.0897	0.6075
0.1615	0.7250	0.1540	0.6060
0.2437	0.7095	0.2402	0.6043
0.3181	0.6959	0.3180	0.6026
0.3957	0.6808	0.3990	0.5999
0.4824	0.6644	0.4801	0.5968
0.5580	0.6498	0.5624	0.5940
0.6346	0.6363	0.6400	0.5915
0.7158	0.6224	0.7180	0.5888
0.8020	0.6081	0.8000	0.5861
0.8818	0.5950	0.8834	0.5834
0.9559	0.5836	0.9632	0.5808

Table 5. Refractive Index, n_D , for the Binary Mixtures of Ethanoic Acid (1) or Trichloroethylene (1) with Dimethylbenzenes (2) at 298.15 K

x_1	n_D	x_1	n_D
Ethanoic Acid (1) + 1,3-Dimethylbenzene (2)		Ethanoic Acid (1) + 1,2-Dimethylbenzene (2)	
0.0962	1.4877	0.0852	1.4965
0.1625	1.4829	0.1881	1.4875
0.3223	1.4682	0.2447	1.4816
0.3797	1.4616	0.3206	1.4747
0.4773	1.4523	0.3894	1.4672
0.5570	1.4424	0.4729	1.4579
0.6405	1.4319	0.5569	1.4472
0.7182	1.4210	0.6360	1.4363

Table 5. continued

x_1	n_D	x_1	n_D
Ethanoic Acid (1) + 1,3-Dimethylbenzene (2)		Ethanoic Acid (1) + 1,2-Dimethylbenzene (2)	
0.7955	1.4066	0.7151	1.4240
0.8721	1.3931	0.8031	1.4099
0.9649	1.3773	0.8817	1.3951
		0.9589	1.3790
Ethanoic Acid (1) + 1,4-Dimethylbenzene (2)		Trichloroethylene (1) + 1,3-Dimethylbenzene (2)	
0.0863	1.4874	0.0850	1.4932
0.1730	1.4805	0.1622	1.4922
0.2386	1.4748	0.2415	1.4908
0.3096	1.4682	0.3204	1.4894
0.3987	1.4598	0.3935	1.4880
0.4897	1.4498	0.4960	1.4859
0.5621	1.4414	0.5613	1.4845
0.6323	1.4325	0.6429	1.4825
0.7212	1.4202	0.7226	1.4807
0.7965	1.4084	0.8061	1.4789
0.8784	1.3939	0.8832	1.4773
0.9550	1.3791	0.9596	1.4756
Trichloroethylene (1) + 1,2-Dimethylbenzene (2)		Trichloroethylene (1) + 1,4-Dimethylbenzene (2)	
0.0721	1.5010	0.0897	1.4921
0.1615	1.4990	0.1540	1.4911
0.2437	1.4973	0.2402	1.4897
0.3075	1.4958	0.3180	1.4885
0.3957	1.4936	0.3990	1.4873
0.4824	1.4917	0.4801	1.4860
0.5643	1.4896	0.5624	1.4844
0.6346	1.4875	0.6400	1.4829
0.7158	1.4847	0.7210	1.4811
0.8060	1.4813	0.7988	1.4794
0.8818	1.4788	0.8834	1.4775
0.9637	1.4762	0.9610	1.4753

viscosity and refractive index of these systems are graphically represented in Figures 2 and 3. The literature data of viscosity of ethanoic acid + 1,4-dimethylbenzene at other temperatures and pressures¹⁴ follow the same trends with our experimental data. The dissociation of self-associated ethanoic acid causes positive excess molar volume.

The excess molar volumes of trichloroethylene (1) + 1,2-dimethylbenzene (2), 1,3-dimethylbenzene(2), or 1,4-dimethylbenzene (2) are negative and decrease with increasing temperatures from (293.15 to 303.15) K and almost symmetrical with a minimum around $x_1 \approx 0.5$. The viscosity and refractive index of trichloroethylene (1) + dimethylbenzenes (2) are graphically represented in Figures 2 and 3.

According to our results and literature data,^{2,8,9,15} it is observed that the effect of the location of $-\text{CH}_3$ groups on the benzene rings in dimethylbenzenes on the trend of the measured properties depend on the other constituent of the mixtures.

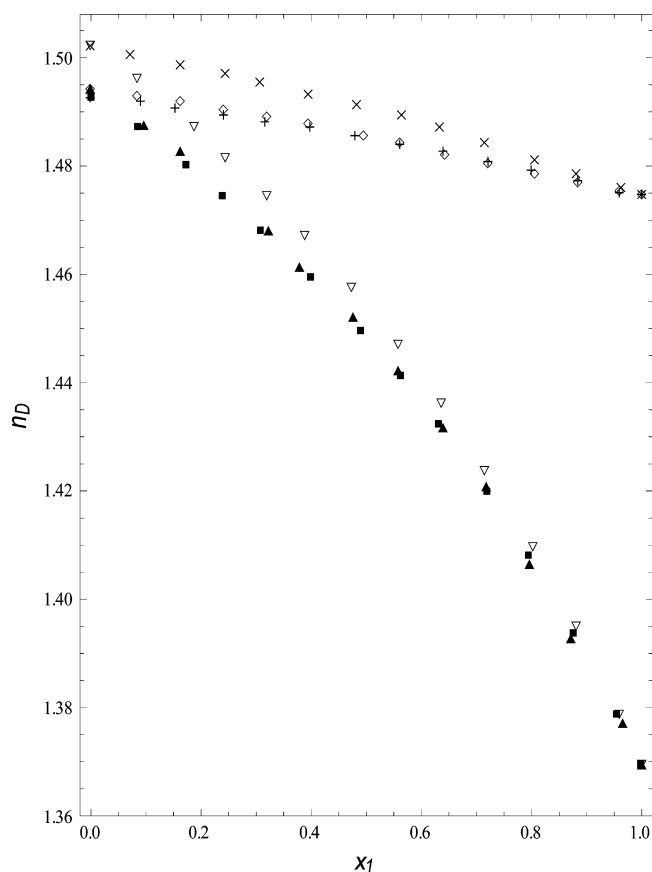


Figure 3. Experimental refractive indices for the binary mixtures of ethanoic acid (1) or trichloroethylene (1) with dimethylbenzenes (2) at 298.15 K: ▲, ethanoic acid + 1,3-dimethylbenzene; ▽, ethanoic acid + 1,2-dimethylbenzene; ■, ethanoic acid + 1,4-dimethylbenzene; ◇, trichloroethylene + 1,3-dimethylbenzene; ×, trichloroethylene + 1,2-dimethylbenzene; +, trichloroethylene + 1,4-dimethylbenzene.

CONCLUSION

This article reports the experimental densities, excess molar volumes, viscosity, and refractive index of binary mixtures of ethanoic acid and trichloroethylene with 1,2-dimethylbenzene, 1,3-dimethylbenzene, and 1,4-dimethylbenzene as a function of temperature and concentration. The dissociation of self-associated ethanoic acid causes positive excess molar volume. In the final analysis, it is observed that the effect of location of $-CH_3$ groups on the benzene rings in dimethylbenzenes on the trend of the measured properties depends on the other constituent of the mixtures.

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