Regular Article

PHYSICAL CHEMISTRY RESEARCH
Published by the
Iranian Chemical Society
www.physchemres.org
info@physchemres.org

Phys. Chem. Res., Vol. 7, No. 2, 347-363, June 2019
DOI: 10.22036/pcr.2019.166303.1583

Study of Excess Properties of Binary and Ternary Mixtures of Trichloroethene, Ethanoic Acid, and *N*,*N*-Dimethylformamide at Different Temperatures

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(Received 7 January 2019, Accepted 22 February 2019)

Density, viscosity, and refractive index measurements were performed for a ternary mixture of trichloroethene + ethanoic acid + *N*,*N*-dimethylformamide and their binary mixtures in the whole composition range. Density data were obtained within the temperature range 293.15-303.15 K and viscosity and refractive index data were measured at 298.15 K. Excess molar volumes, viscosity deviations, and refractive index deviations were calculated from the experimental data. The V_m^E values for the ternary mixture and also for the two binary mixtures of trichloroethene (1) + *N*,*N*-dimethylformamide (3), and ethanoic acid (2) + *N*,*N*-dimethylformamide (3) were negative and became more negative by increasing the temperature. For the trichloroethene (1) + ethanoic acid (2) mixture, the values were positive and became more positive with rising temperature. An inverse trend was observed for viscosity deviations of the mixtures. The refractive index deviations were positive for all the mixtures. The experimental data for the binary and ternary mixtures were correlated with Redlich-Kister, and Cibulka equations, respectively.

Keywords: Density, Viscosity, Refractive index, Ternary mixture

INTRODUCTION

Molecular interactions between the liquid mixture constituents lead to special behavior in real solutions. These solutions have attracted the attention of many researchers from thermodynamic point of view. The study of excess properties can offer helpful information about the particular interactions and macroscopic behavior of fluid mixtures. In fact, the nature of molecular interactions can be understood from the data. In addition, these data are important in industrial process designing and also to test theories of solution. Many studies have been done in this field on the binary and ternary mixtures [1-10].

Some studies have been reported for excess properties of binary and ternary mixtures containing trichloroethene or *N*,*N*-dimethylformamide (DMF) with polar and non-polar solvents [1,9,11-18]. In this paper, ternary mixture of (trichloroethene + ethanoic acid + *N*,*N*-dimethylformamide) and their binary mixtures have been selected in order to study the excess properties.

The selected chemicals are very important industrially. *N*,*N*-dimethylformamide and trichloroethene are common industrial solvents and ethanoic acid is an important chemical reagent, so, their mixture and the study of their interactions can be helpful in order to use the most adequate solvent in the industrial process. The densities ρ, for the mixtures have been measured over a wide range of composition at temperatures from 293.15-303.15 K. Viscosities, η, and refractive index, n_D, measurements were carried out for the mixtures at 298.15 K. The excess molar volumes and deviation properties (viscosity and refractive index deviations) were calculated from the experimental data. Excess molar volumes and deviations of viscosity for ethanoic acid + DMF binary mixture were compared with the obtained values at 303.15 K in the literature [18]. The agreements between the experimental data and their

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Table 1. Name, Purity Grade, Supplier, CAS Number, Density ρ, and Refractive Index n_D^{25}, of the Pure Components at 298.15 K.

Component	Purity (mass fraction)	Supplier	CAS number	$\rho \times 10^{-3}$ (kg m^{-3})		n_D^{25}	
				Expt.	Lit.	Expt.	Lit.
Trichloroethene	> 99.5	Merck	79-01-6	1.45550	1.45475[a]	1.4740	1.4750[d]
N,N-dimethylformamide	> 99.5	Merck	68-12-2	0.94395	0.94385[b]	1.4283	1.4283[e]
Ethanoic acid	> 99.8	Merck	64-19-7	1.04376	1.04376[c]	1.3720	1.3703[c]

Standard uncertainties u are u(ρ) = 0.05 kg m^{-3} and u(n_D) = 2×10^{-4}. [a]Ref. [14]. [b]Ref. [21]. [c]Ref. [22]. [d]Ref. [23]. [e]Ref. [24].

corresponding literature values were good. For correlation of the experimental data for the binary and ternary mixtures Redlich-Kister [19] and Cibulka [20] equations were employed, respectively.

EXPERIMENTAL

Materials

High-purity grade organic liquids, trichloroethene (> 99.5 mass%), ethanoic acid (> 99.8 mass%) and DMF (> 99.5 mass%), were supplied from Merck. The sources of the substances and their purity grades are given in Table 1. The chemicals were used without further purification. The densities and refractive indices of the pure substances were measured and compared with the corresponding literature values [14,21-24]. Good agreement was observed between the experimental and literature values as reported in Table 1.

Apparatus and Procedure

The binary and ternary mixtures were prepared in dark airtight stopper bottles gravimetrically by a Mettler AB 204-N balance with an uncertainty of 1×10^{-7} kg. The uncertainty in the mole fraction was estimated to be less than 1×10^{-4}. The density of the samples was measured with an Anton Paar digital vibrating u-tube densimeter (model DMA 4500) with an uncertainty of 0.05 kg m^{-3} whose cell temperature was controlled with an uncertainty of 0.01 K, with a solid-state thermostat. The density measurements were performed at T = (293.15, 298.15 and 303.15) K. The viscosity of pure components and mixtures was measured by Ubbelohde viscometer with an uncertainty of 5×10^{-3} mPa s at 298.15 K. Water and 1-butanol were used for calibration of the viscometer and an electronic digital stopwatch was used for flow time measurements with readability of 0.01 s. Refractive index measurements were performed at 298.15 K with an Abbé refractometer with an uncertainty of 0.0002.

RESULTS AND DISCUSSION

Experiments

The densities, ρ, viscosities, η, and refractive index, n_D, measurements were done for the binary and ternary mixtures of trichloroethene, ethanoic acid and *N*,*N*-dimethylformamide. The following equations were applied to calculate the excess molar volumes, V_m^E, viscosity deviations, $\Delta\eta$, and deviation of refractive index, Δn_D, from the experimental data. Uncertainty in determination of V_m^E was 3×10^{-9} m^3 mol^{-1}.

$$V_m^E / m^3 \cdot mol^{-1} = \sum_{i=1}^{n} x_i M_i (\rho^{-1} - \rho_i^{-1}), \quad (1)$$

$$\Delta Y = Y - \sum_{i}^{n} (Y_i x_i), \quad (2)$$

where ρ is the density of the mixture and x_i, M_i, ρ_i are mole

fraction, molecular mass, and the density of component *i,* respectively. *Y* in the second equation represents η or n_D. The results are given in Tables 2-5 and represented graphically in Figs. 1-5.

The values of V_m^E and $\Delta\eta$, for the binary mixture of ethanoic acid (2) + dimethylformamide (3) were compared with the literature values [18] at 303.15 K and represented in Figs. 1c and 3a. The agreement between them was good.

The values of the excess molar volumes, V_m^E, are positive for trichloroethene (1) + ethanoic acid (2) binary mixture (Fig. 1a) with a maximum around $x_1 \approx 0.5$ and become more positive with increasing temperature over the entire range of composition and at T = (293.15, 298.15 and 303.15) K.

Negative trend was observed for trichloroethene (1) + DMF (3) and ethanoic acid (2) + DMF (3) mixtures with a minimum around $x_1 \approx 0.6$ over the whole composition range and temperatures and became more negative by increasing the temperature (Figs. 1b , c).

Ternary mixture of trichloroethene (1) + ethanoic acid (2) + DMF (3) show negative values for V_m^E (Fig. 2) and become more negative with rising temperature.

As can be seen from Tables 3 and 5, the values of $\Delta\eta$ are positive for trichloroethene (1) + ethanoic acid (2) + DMF (3) ternary mixture and also for binary mixtures of trichloroethene and ethanoic acid with DMF. Negative values are observed for viscosity deviations mixture trichloroethene (1) + ethanoic acide (2) over the entire range of mole fractions at 298.15 K. Graphical representations of the binary and ternary mixtures are given in Fig. 3a and Fig. 4, respectively. The viscosity deviations are functions of interactions as well as size and shape of molecules [7].

Refractive index deviation, Δn_D, was positive for ternary mixture of trichloroethene (1) + ethanoic acid (2) + DMF (3) and the three binary mixtures (Tables 3 and 5). Graphical representations of Δn_D for the binary and ternary mixtures are given in Figs. 3b and Fig. 5, respectively.

The observed V_m^E values are resultant from the

Table 2. Densities, ρ, and Excess Molar Volumes, V_m^E, for Binary Mixtures at Temperature Range (293.15-303.15) K

x_1	$\rho \times 10^{-3}$ (kg m^{-3})	$V_m^E \times 10^6$ (m^3 mol^{-1})	$\rho \times 10^{-3}$ (kg m^{-3})	$V_m^E \times 10^6$ (m^3 mol^{-1})	$\rho \times 10^{-3}$ (kg m^{-3})	$V_m^E \times 10^6$ (m^3 mol^{-1})
	Trichloroethene (1) + ethanoic acid (2)					
	T = 293.15 K		T = 298.15 K		T = 303.15 K	
0.0764	1.09306	0.216	1.08701	0.224	1.08095	0.232
0.1603	1.13827	0.366	1.13183	0.379	1.12538	0.393
0.2216	1.16910	0.456	1.16240	0.474	1.15568	0.492
0.3188	1.21533	0.530	1.20827	0.552	1.20118	0.574
0.4206	1.26019	0.558	1.25281	0.581	1.24538	0.606
0.4739	1.28219	0.562	1.27467	0.585	1.26703	0.614
0.5533	1.31383	0.527	1.30608	0.552	1.29808	0.589
0.6585	1.35306	0.456	1.34513	0.475	1.33713	0.497
0.7403	1.38169	0.380	1.37359	0.398	1.36544	0.416
0.8112	1.40537	0.296	1.39716	0.310	1.38892	0.323

Table 2. Continued

Trichloroethene (1) + dimethylformamide (3)						
	T = 293.15 K		T = 298.15 K		T = 303.15 K	
0.0819	0.99799	-0.059	0.99293	-0.061	0.98785	-0.062
0.1515	1.03890	-0.110	1.03358	-0.113	1.02825	-0.116
0.2275	1.08239	-0.155	1.07680	-0.159	1.07120	-0.164
0.3170	1.13248	-0.212	1.12658	-0.218	1.12065	-0.224
0.4058	1.18070	-0.258	1.17447	-0.265	1.16822	-0.272
0.4986	1.22958	-0.295	1.22302	-0.303	1.21643	-0.311
0.5477	1.25481	-0.308	1.24807	-0.316	1.24129	-0.324
0.6297	1.29582	-0.312	1.28877	-0.319	1.28170	-0.327
0.7319	1.34509	-0.285	1.33766	-0.290	1.33020	-0.297
0.8104	1.38154	-0.240	1.37382	-0.244	1.36607	-0.249
0.8736	1.40989	-0.181	1.40195	-0.185	1.39396	-0.188
0.9542	1.44487	-0.083	1.43662	-0.084	1.42834	-0.086
Ethanoic acid (2) + dimethylformamide (3)						
	T = 293.15 K		T = 298.15 K		T = 303.15 K	
0.0552	0.95439	-0.118	0.94962	-0.122	0.94484	-0.125
0.1800	0.96802	-0.394	0.96324	-0.406	0.95845	-0.418
0.2210	0.97255	-0.471	0.96777	-0.486	0.96297	-0.500
0.3083	0.98289	-0.659	0.97803	-0.675	0.97322	-0.694
0.4114	0.99516	-0.833	0.99031	-0.856	0.98545	-0.879
0.4793	1.00370	-0.949	0.99880	-0.973	0.99390	-0.998
0.5727	1.01434	-0.997	1.00937	-1.022	1.00439	-1.047
0.6394	1.02168	-0.991	1.01664	-1.016	1.01160	-1.040
0.7211	1.02998	-0.917	1.02486	-0.940	1.01973	-0.963
0.8115	1.03817	-0.749	1.03290	-0.767	1.02763	-0.785
0.8865	1.04383	-0.526	1.03844	-0.539	1.03304	-0.551
0.9680	1.04834	-0.179	1.04277	-0.183	1.03718	-0.186

Standard uncertainties (u) are u(ρ) = 0.05 kg m^{-3} and u(T) = 0.01 K and the combined expanded uncertainty (U_c) are U_c (x) = 1 × 10^{-4} and U_c (V_m^E) = 3 × 10^{-9} m^3 mol^{-1} (0.95 level of confidence).

Table 3. Viscosities, η, Refractive Index, n_D, Deviation of Viscosities $\Delta\eta$, and Deviation of Refractive Index, Δn_D, of Binary Mixtures at Temperature 298.15 K

x	η (mPa s)	n_D	$\Delta\eta$ (mPa s)	Δn_D
Trichloroethene (1) + ethanoic acid (2)				
0.0837	0.959	1.3771	-0.122	-0.0035
0.1620	0.870	1.3886	-0.169	0.0000
0.2477	0.782	1.4002	-0.210	0.0029
0.2960	0.748	1.4058	-0.217	0.0036
0.3989	0.695	1.4175	-0.214	0.0047
0.4781	0.676	1.4259	-0.190	0.0050
0.5604	0.649	1.4339	-0.172	0.0046
0.6930	0.615	1.4464	-0.134	0.0036
0.7298	0.610	1.4498	-0.118	0.0032
0.8232	0.598	1.4588	-0.080	0.0027
0.8783	0.595	1.4639	-0.053	0.0021
0.9720	0.580	1.4720	-0.016	0.0007
Trichloroethene (1) + N,N-dimethyl formamide (3)				
0.0793	0.813	1.4328	0.027	0.0009
0.1628	0.825	1.437	0.057	0.0012
0.2488	0.831	1.4418	0.082	0.0021
0.3216	0.827	1.4462	0.095	0.0031
0.4024	0.818	1.4506	0.103	0.0038
0.4807	0.801	1.4543	0.104	0.0039
0.5600	0.778	1.4581	0.099	0.0041
0.6485	0.746	1.462	0.087	0.0039
0.7183	0.719	1.4649	0.075	0.0036
0.8019	0.675	1.4684	0.049	0.0033
0.8844	0.634	1.4708	0.027	0.0019
0.9659	0.602	1.4736	0.014	0.0010

Table 3. Continued

Ethanoic acid (2) + N,N-dimethyl formamide (3)				
0.0756	0.872	1.426	0.044	0.0020
0.1534	0.968	1.4233	0.115	0.0036
0.2340	1.060	1.421	0.181	0.0059
0.3126	1.203	1.4179	0.298	0.0072
0.3940	1.361	1.4154	0.430	0.0093
0.4764	1.524	1.4118	0.566	0.0103
0.5550	1.688	1.4077	0.705	0.0106
0.6392	1.772	1.403	0.762	0.0107
0.7131	1.806	1.3981	0.772	0.0099
0.7980	1.713	1.391	0.652	0.0076
0.8750	1.551	1.384	0.465	0.0050
0.9767	1.225	1.3729	0.106	-0.0004

Standard uncertainties (u) are u(ρ) = 0.05 kg m^{-3}, u(T) = 0.01 K and u(n_D) = 2×10^{-4} and the combined expanded uncertainties (U_c) are U_c (x) = 1×10^{-4} and U_c (η) = 5×10^{-3} mPa s (0.95 level of confidence).

Table 4. Densities, ρ, and Excess Molar Volume, V_m^E, of {Trichloroethene (1) + Ethanoic Acid (2)+ Dimethylformamide (3)} Ternary Mixture at Different Temperatures (293.15-303.15)

x_1	x_2	$\rho \times 10^{-3}$ (kg m^{-3})	$V_m^E \times 10^6$ (m^3 mol^{-1})	$\rho \times 10^{-3}$ (kg m^{-3})	$V_m^E \times 10^6$ (m^3 mol^{-1})	$\rho \times 10^{-3}$ (kg m^{-3})	$V_m^E \times 10^6$ (m^3 mol^{-1})
		T = 293.15 K		T = 298.15 K		T = 303.15 K	
0.0976	0.0915	1.01786	-0.244	1.01273	-0.253	1.00759	-0.261
0.1000	0.1961	1.03228	-0.451	1.02711	-0.465	1.02193	-0.480
0.1050	0.2921	1.04797	-0.638	1.04275	-0.657	1.03751	-0.676
0.1030	0.3970	1.06048	-0.782	1.05518	-0.803	1.04988	-0.825
0.1035	0.4939	1.07347	-0.858	1.06808	-0.880	1.06268	-0.902
0.1018	0.5953	1.08402	-0.800	1.07852	-0.820	1.07300	-0.840
0.1020	0.7039	1.09500	-0.592	1.08931	-0.605	1.08362	-0.620
0.0998	0.7998	1.10117	-0.271	1.09529	-0.276	1.08940	-0.281

Table 4. Continued

0.2008	0.0980	1.07958	-0.289	1.07406	-0.298	1.06854	-0.309
0.1989	0.2062	1.09335	-0.487	1.08780	-0.503	1.08224	-0.520
0.2011	0.2991	1.10794	-0.638	1.10231	-0.657	1.09667	-0.676
0.1998	0.3952	1.12024	-0.704	1.11453	-0.724	1.10879	-0.743
0.1998	0.4987	1.13402	-0.707	1.12816	-0.724	1.12228	-0.741
0.2001	0.6003	1.14501	-0.502	1.13897	-0.514	1.13291	-0.525
0.1983	0.7024	1.15250	-0.140	1.14622	-0.140	1.13991	-0.139
0.3048	0.1001	1.13955	-0.347	1.13365	-0.358	1.12773	-0.370
0.2982	0.2035	1.15038	-0.458	1.14445	-0.474	1.13849	-0.490
0.3023	0.3050	1.16915	-0.651	1.16308	-0.668	1.15699	-0.685
0.2975	0.4049	1.17974	-0.619	1.17355	-0.634	1.16733	-0.649
0.2990	0.5045	1.19197	-0.419	1.18560	-0.428	1.17919	-0.437
0.2978	0.6023	1.19847	0.028	1.19185	0.030	1.18509	0.040
0.4069	0.0928	1.19426	-0.322	1.18799	-0.333	1.18169	-0.345
0.4046	0.1969	1.21052	-0.537	1.20416	-0.552	1.19776	-0.567
0.4033	0.3017	1.22433	-0.500	1.21783	-0.513	1.21130	-0.526
0.4040	0.3982	1.23647	-0.325	1.22974	-0.331	1.22293	-0.332
0.4046	0.4858	1.24629	-0.069	1.23937	-0.067	1.23243	-0.065
0.4959	0.1034	1.24448	-0.418	1.23786	-0.430	1.2312	-0.442
0.4962	0.2023	1.25911	-0.413	1.25240	-0.427	1.24563	-0.440
0.5036	0.2977	1.27520	-0.248	1.26822	-0.253	1.26118	-0.257
0.4961	0.3993	1.28420	-0.052	1.27702	-0.050	1.26977	-0.046
0.5966	0.1059	1.29622	-0.371	1.28919	-0.381	1.28205	-0.386
0.5997	0.2039	1.31233	-0.315	1.30538	-0.338	1.29813	-0.345
0.5959	0.3003	1.32174	-0.045	1.31426	-0.040	1.30639	-0.013
0.6984	0.1017	1.34523	-0.290	1.33783	-0.299	1.33036	-0.306
0.6894	0.2028	1.35426	-0.090	1.34662	-0.088	1.33892	-0.086
0.7899	0.1088	1.38786	-0.104	1.38002	-0.105	1.37213	-0.105

Standard uncertainties (u) are u(ρ) = 0.05 kg m^{-3} and u(T) = 0.01 K and the combined expanded uncertainties (U_c) are U_c (x) = 1 × 10^{-4} and U_c (V_m^E) = 3 × 10^{-9} m^3 mol^{-1} (0.95 level of confidence).

Table 5. Viscosities, η, Deviation of Viscosities, $\Delta\eta$, Refractive Index, n_D, and Deviation of Refractive Index, Δn_D, of Ternary Mixture at 298.15 K

x_1	x_2	η (mPa s)	$\Delta\eta$ (mPa s)	n_D	Δn_D
Trichloroethene (1) + ethanoic acid (2) + *N*,*N*-dimethylformamide (3)					
0.0976	0.0915	0.905	0.093	1.4308	0.0032
0.1000	0.1961	1.036	0.191	1.4264	0.0045
0.1050	0.2921	1.168	0.293	1.4247	0.0080
0.1030	0.397	1.330	0.420	1.4211	0.0104
0.1035	0.4939	1.463	0.523	1.4164	0.0112
0.1018	0.5953	1.531	0.557	1.4092	0.0097
0.1020	0.7039	1.428	0.42	1.4020	0.0087
0.0998	0.7998	1.253	0.213	1.3935	0.0056
0.2008	0.0980	0.915	0.124	1.4365	0.0045
0.1989	0.2062	1.031	0.205	1.4330	0.0072
0.2011	0.2991	1.151	0.295	1.4292	0.0085
0.1998	0.3952	1.288	0.401	1.4264	0.0112
0.1998	0.4987	1.325	0.404	1.4206	0.0112
0.2001	0.6003	1.246	0.293	1.4133	0.0096
0.1983	0.7024	1.080	0.094	1.4056	0.0077
0.3048	0.1001	0.908	0.140	1.4409	0.0042
0.2982	0.2035	1.006	0.203	1.4384	0.0079
0.3023	0.3050	1.108	0.273	1.4347	0.0097
0.2975	0.4049	1.149	0.281	1.4302	0.0110
0.2990	0.5045	1.108	0.208	1.4243	0.0107
0.2978	0.6023	0.975	0.043	1.4153	0.0072
0.4069	0.0928	0.890	0.146	1.4477	0.0059
0.4046	0.1969	0.952	0.174	1.4444	0.0086
0.4033	0.3017	1.008	0.196	1.4399	0.0101
0.4040	0.3982	1.002	0.160	1.4348	0.0104

Table 5. Continued

0.4046	0.4858	0.893	0.023	1.4289	0.0094
0.4959	0.1034	0.856	0.129	1.4521	0.0069
0.4962	0.2023	0.900	0.141	1.4441	0.0044
0.5036	0.2977	0.899	0.112	1.4438	0.0091
0.4961	0.3993	0.825	0.003	1.4372	0.0086
0.5966	0.1059	0.807	0.102	1.4564	0.0067
0.5997	0.2039	0.832	0.096	1.4507	0.0064
0.5959	0.3003	0.767	-0.001	1.4465	0.0078
0.6984	0.1017	0.748	0.067	1.4602	0.0056
0.6894	0.2028	0.728	0.012	1.4552	0.0067
0.7899	0.1088	0.687	0.024	1.4629	0.0045

Standard uncertainties (u) are u(ρ) = 0.05 kg m^{-3}, u(T) = 0.01 K and u(n_D) = 2×10^{-4} and the combined expanded uncertainties (U_c) are U_c (x) = 1×10^{-4} and U_c (η) = 6×10^{-3} mPa s (0.95 level of confidence).

competition between the two positive and negative contributions to V_m^E. Trichloroethene is an unassociated and polar liquid having a dipole moment of μ= 0.8 D [13], and ethanoic acid is self-associated through hydrogen bonding because of the presence of electron donor and electron acceptor sites [25]. DMF is also highly polar solvent having a dipole moment of μ = 3.24 [21]. During the mixing of trichloroethene, DMF and ethanoic acid with each other, the dissociation of self-associated ethanoic acid occurs and provides a positive contribution to V_m^E. In addition, disruption of the dipolar order in the components has a positive effect. The polar interactions between unlike molecules, donor-acceptor interactions, or the formation a new H-bonded molecular complex in the binary mixtures have a negative contribution to V_m^E. The mixing of trichloroethene with ethanoic acid leads to positive V_m^E values. In this process, dissociation of self-associated ethanoic acid by trichloroethene molecules is a dominant contribution. The mixing of trichloroethene and ethanoic acid with DMF leads to contraction in volume and provides a negative contribution to V_m^E. The study results show that polar interactions between unlike molecules are dominant contributions for the systems except for trichloroethene (1) + ethanoic acid (2) binary mixture where is in an agreement with the $\Delta\eta$ values. The negative $\Delta\eta$ values are attributed to the predominance of the dispersion forces [7].

Correlations

Redlich-Kister polynomial [19] was applied to correlate the experimental data of excess molar volumes, viscosity deviations, and refractive index deviation for the binary mixtures:

$$Y = x_1(1-x_1)\sum_{i=0}^{k} A_i(1-2x_1)^i, \quad (3)$$

where Y = (V^E, $\Delta\eta$ or Δn_D), x_1 is the mole fraction of component 1, and k is the degree of the polynomial expansion.

Temperature dependence of the fitting parameters for the excess molar volumes is expressed by the following equation.

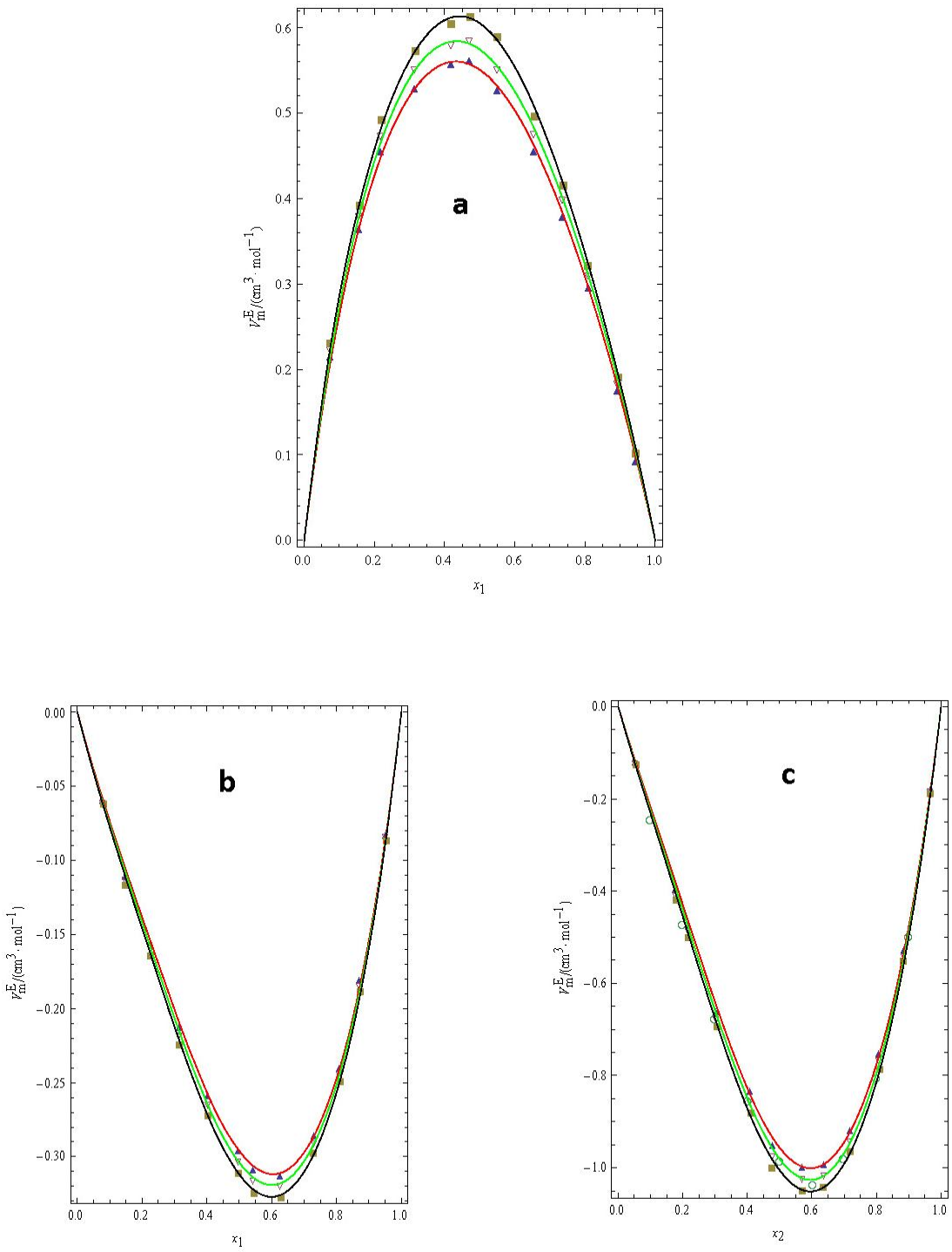

Fig. 1. Excess molar volumes, V_m^E, of binary mixtures at different temperatures: ▲, 293.15 K; ⅄, 298.15 K; ®, 303.15 K; ○, ref. 18 at 303.15 K, for: (a) trichloroethylene (1) + ethanoic acid (2); (b) trichloroethene (1) + dimethylformamide (3); (c) ethanoic acid (2) + dimethylformamide (3). The solid lines represent the values calculated from temperature dependent Redlich-Kister equation.

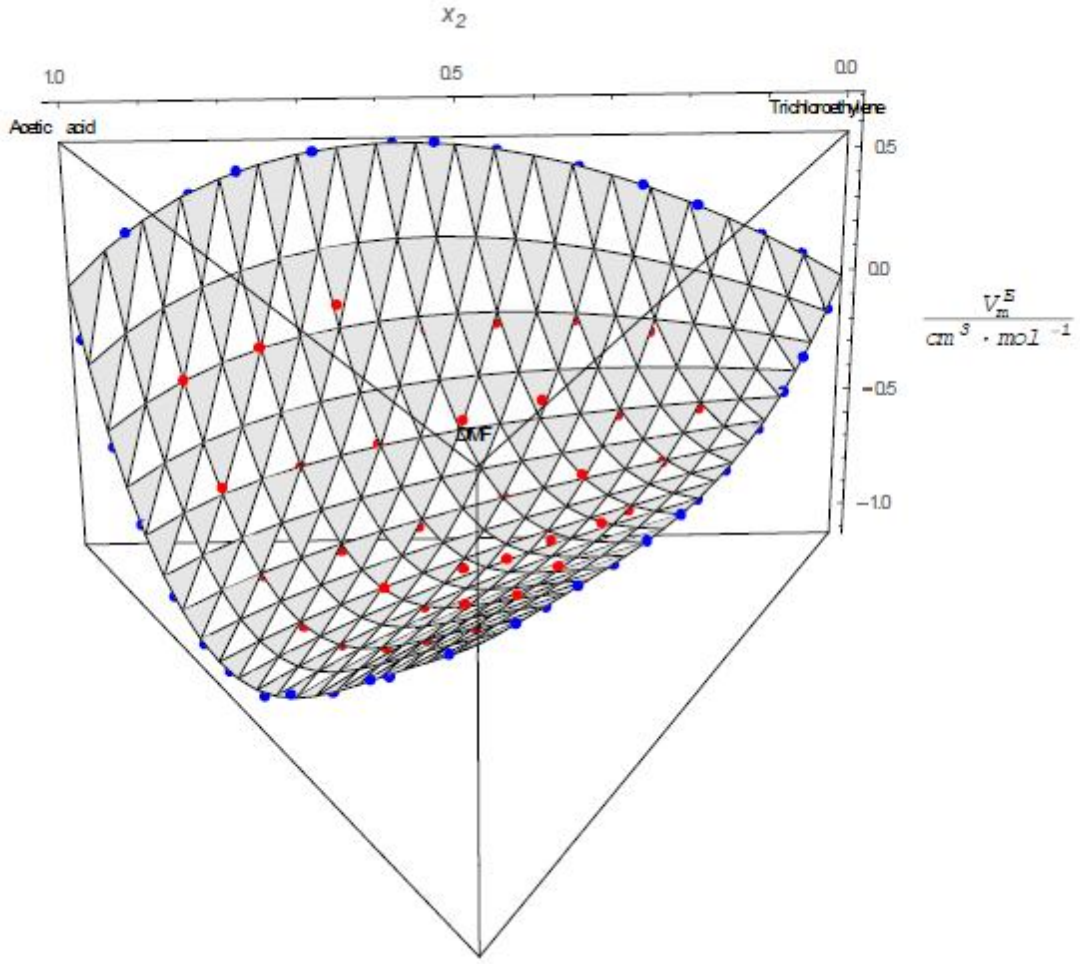

Fig. 2. Excess molar volumes, V_m^E, of ternary mixture of {trichloroethene (1) + ethanoic acid (2) + *N*,*N*-dimethylformamide (3)} at 293.15 K. • represents the experimental points. Curves represent the values calculated from Cibulka equation. The unit in the triangle plot is mole fraction.

$$A_i = \sum_{j=0}^{2} B_{ij} T^j , \tag{4}$$

The adjustable temperature and independent parameters, B_{ij}, are derived by the least squares method and are reported in Tables 6 and 7 along with the standard deviations defined as:

$$\sigma = \left(\sum_{i=1}^{n} (Y_{exp} - Y_{cal})^2 / (n-p) \right)^{1/2} , \tag{5}$$

where n is the number of experimental points, and p is the number of adjustable parameters in Eq. (3).

Cibulka equation [20] was applied to correlate the experimental data (V^E, $\Delta\eta$ and Δn_D) of the ternary mixture.

$$Y^E = Y_{12}^E + Y_{13}^E + Y_{23}^E + x_1 x_2 x_3 \left(B_1 + B_2 x_1 + B_3 x_2 \right) \tag{6}$$

For excess molar volume, every B_p ternary parameter is a function of temperature as expressed in Eq. (4). Tables 6 and 7 report the adjustable parameters along with the standard deviation, σ.

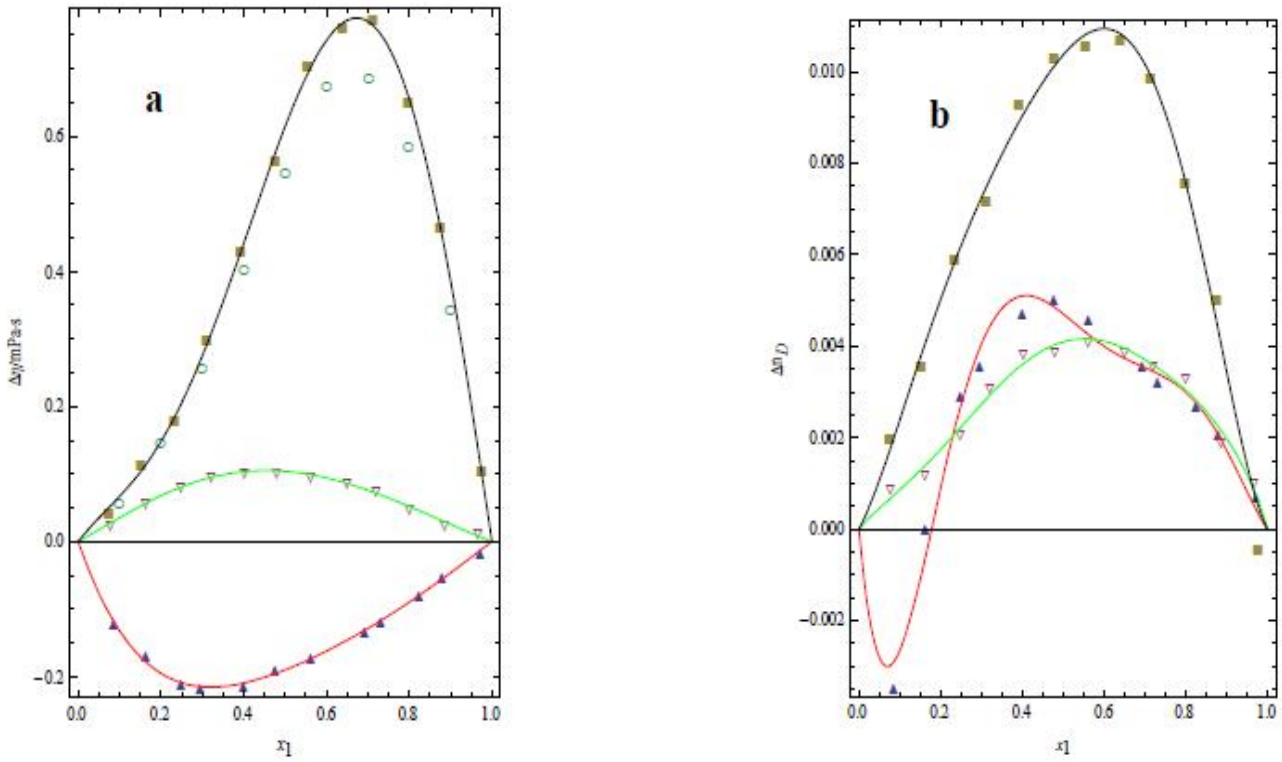

Fig. 3. (a) Viscosity deviations, $\Delta\eta$, and (b) deviation of refractive index, $\Delta\eta_D$, of binary mixtures at 298.15 K; for: ▲, trichloroethene (1) + ethanoic acid (2); ⅃, trichloroethene (1) + dimethylformamide (3); ○, ref. 18 at 303.15 K, ®,ethanoic acid (2) + dimethylformamide (3).

CONCLUSIONS

Excess molar volumes of trichloroethene (1) + ethanoic acid (2) + DMF (3) ternary mixture and their binary mixtures were determined from density measurements over the entire range of composition at different temperatures. Viscosity and refractive index deviations were obtained from the viscosity and refractive index measurements at 298.15 K. All the experimental data were fitted to the Redlich–Kister and Cibulka equations for binary and ternary mixtures, respectively. The values of the ternary and binary mixtures of trichloroethene and ethanoic acid with DMF were negative and became more negative with increasing temperature. Positive values were observed for trichloroethene (1) + ethanoic acid (2) mixture and became more positive with increasing temperature. The results interpreted in terms of competition between two positive and negative effects. Positive effect is due to dissociation of self-associated component and also disruption of the dipolar order in the components. Negative effect is due to polar interactions between unlike molecules, donor-acceptor interactions, or the formation of a new H-bonded molecular complex in the mixtures. Viscosity deviation values were positive for the ternary mixture and their binary mixtures except for trichloroethene (1) + ethanoic acide (2) mixture over the entire range of mole fractions. Positive trend was observed for deviation in refractive index of the mixtures. The trends are in agreement with the values.

ACKNOWLEDGMENTS

The authors would like to thank Bu-Ali Sina University for providing the necessary facilities to carry out the research.

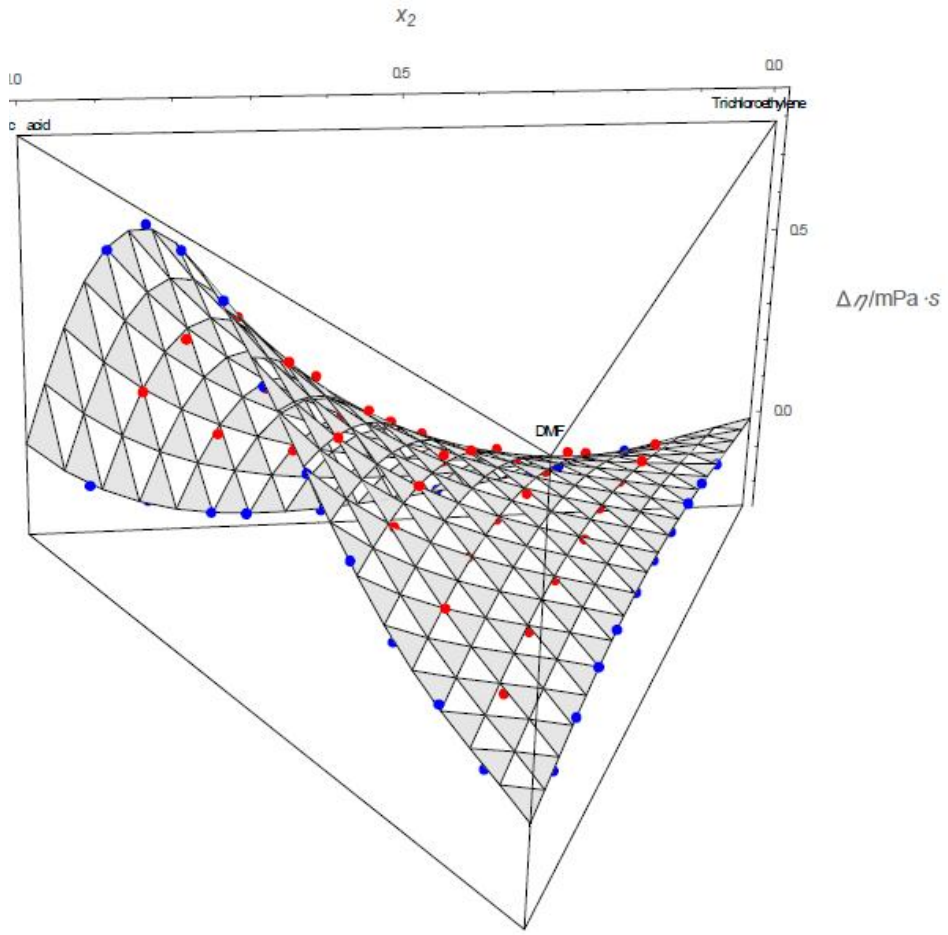

Fig. 4. Viscosity deviations, $\Delta\eta$, of ternary mixture of {trichloroethene (1) + ethanoic acid (2) + *N*,*N*-dimethyl-formamide (3)} at 298.15 K. • represents the experimental points. Curves represent the values calculated from Cibulka equation. The unit in the triangle plot is mole fraction.

Table 6. Coefficients, A_{ij}, of Equations (3)-(6) for the Binary and Ternary Systems along with the Standard Deviations, σ, for the Fits of the Excess Molar Volumes over the Temperature Range (293.15-303.15) K

j \ *i*	0	1	2	3	4	σ ($cm^3\ mol^{-1}$)
Trichloroethene (1) + ethanoic acid (2)						
0	44.9826	-54.4117	-264.562	141.061	287.507	0.005
1	-0.308141	0.36937	1.79278	-0.951377	-1.94926	
2	0.00055333	-0.000620247	-0.00303477	0.00160564	0.00330602	

Table 6. Continued

Trichloroethene (1) + *N*,*N*-dimethylformamide (3)						
0	0.634051	10.6296	-64.9591	-7.12897	114.802	0.002
1	-0.00607976	-0.068371	0.432546	0.0473412	-0.7688	
2	-4.2790×10^{-7}	0.00011625	-0.00071924	-0.00007885	0.00128383	
Ethanoic acid (2) + *N*,*N*-dimethylformamide (3)						
0	0.284969-	-23.8811	-27.4264	49.2184	103.35	0.008
1	-0.00475742	0.166118	0.188265	-0.329516	-0.700521	
2	-0.00002498	-0.00026775	-0.0003178	0.00055128	0.00117789	
Trichloroethene (1) + ethanoic acid (2) + *N*,*N*-dimethylformamide (3)						
0	-399.624	985.852	274.61			0.025
1	2.71679	-6.61496	-1.88738			
2	-0.0046062	0.0109564	0.0031000			

Table 7. The Parameters of Equations (3)-(6) and Standard Deviation for the Fits of Viscosity and Refractive Index Deviations for the Binary and Ternary Mixtures at 298.15 K

	B_0	B_1	B_2	B_3	B_4	σ
			Trichloroethene (1) + ethanoic acid (2)			
$\Delta\eta$ (mPa s)	-0.759215	-0.48707	-0.364971	-0.17149	0.00749056	0.005
Δn_D	0.0188291	0.00208147	0.0370082	-0.0476369	-0.121094	0.0004
			Trichloroethene (1) + N,N-dimethylformamide (3)			
$\Delta\eta$ (mPa s)	0.416489	0.0998258	-0.10786	-0.0477554	-0.0215501	0.003

Table 7. Continued

Δn_D	0.0163839	-0.00514975	-0.00838721	-0.00424162	0.0118415	0.0002
	Ethanoic acid (2) +N,N-dimethylformamide (3)					
$\Delta\eta$ (mPa s)	2.45739	-3.19066	0.228317	1.52772	-0.217652	0.001
Δn_D	0.0414976	-0.0206774	0.00454884	0.0208042	-0.0292831	0.0004
	Trichloroethene (1) + ethanoic acid (2) + N,N-dimethylformamide (3)					
$\Delta\eta$ (mPa s)	2.94022	-2.24213	-5.57063			0.01
Δn_D	-0.0605095	0.141197	0.171977			0.0007

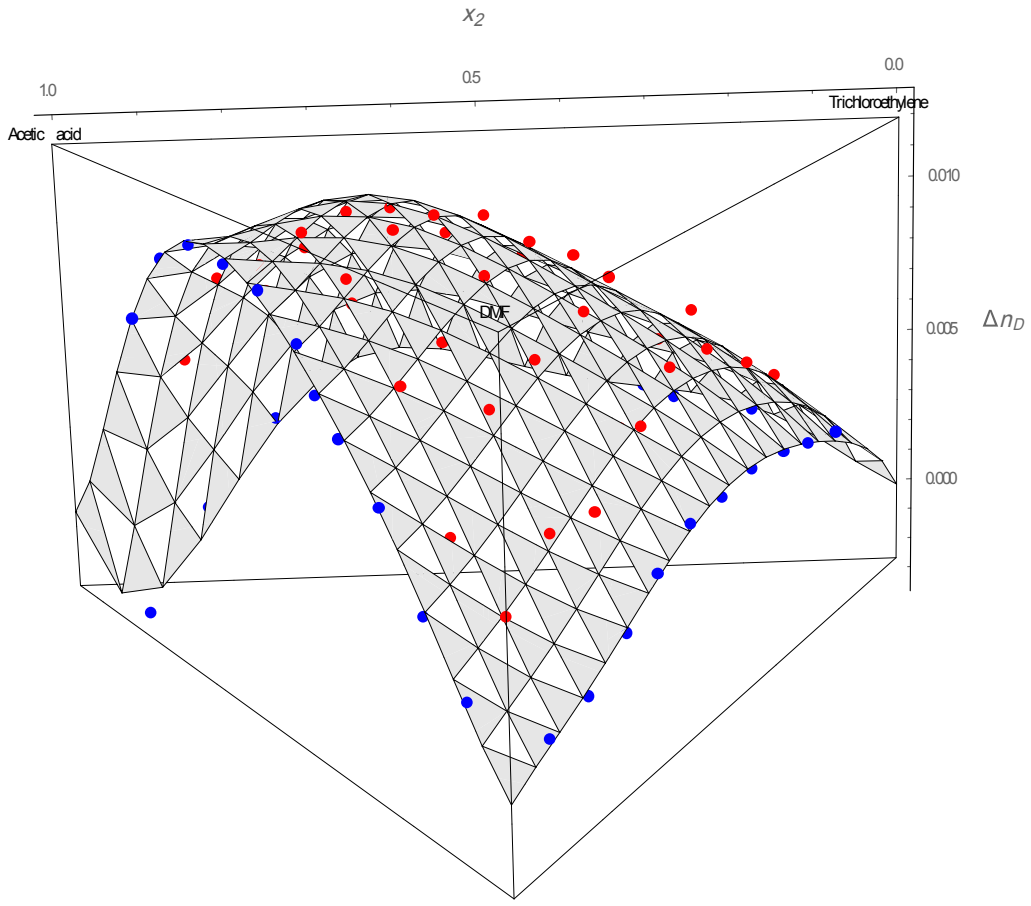

Fig. 5. Refractive index deviations, Δn_D, of ternary mixture of {trichloroethene (1) + ethanoic acid (2) + *N*,*N*-dimethyl-formamide (3)} at 298.15 K. • represents the experimental points. Curves represent the values calculated from Cibulka equation. The unit in the triangle plot is mole fraction.

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