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(RECOMMENDED CITATION)

INVESTIGATION ON THERMODYNAMIC PROPERTIES FOR BINARY SYSTEMS OF WATER + FORMIC, ACETIC, TRICHLOROACETIC, LACTIC, AND CITRIC ACID AT T = 292.15 K AND ATMOSPHERIC PRESSURE

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ABSTRACT. Thermodynamic properties (viscosities, refractive indices, and densities) for aqueous solutions of formic acid, acetic acid, trichloroacetic acid, lactic acid, and citric acid have been measured at T = 292.15 K and atmospheric pressure. The measurements were carried out over the whole range of composition. Investigations on these thermodynamic data help us to better understanding of interaction between solvent and solute molecules in these aqueous solutions. Also from these data, for aqueous solution of formic acid and acetic acid the excess molar volumes, viscosity deviations, and change of refractive indices on mixing were calculated and fitted to the Redlich-Kister polynomial equation to estimate the adjustable parameters and the standard errors. Also for aqueous solutions of this study the experimental values of refractive index and viscosity were correlated using the experimental equation and Jones-Dole equation, respectively.

Key words: *Viscosity, Refractive index, Jones-Dole equation, Density, Excess molar volume*.

INTRODUCTION

The study on thermodynamic properties of liquid mixtures and solutions finds direct applications in food, drug, cosmetic and detergent industries [1]. Also, investigations on the thermodynamic properties of binary liquid mixtures have been done to gain information about intermolecular interaction and change in packing efficiencies with compositions [2-4].

There are two prevailing methods for the production of organic acids: fermentation and chemical synthesis. From the viewpoint of sustainable development and human health, the former is preferred to produce the organic acids which are metabolic intermediates or products.

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Formic acid is an important intermediate in chemical synthesis and occurs naturally, most notably in the venom of bee and ant stings. Owing to its tendency to hydrogen-bond, gaseous formic acid does not obey the ideal gas law [5].

Acetic acid can be extracted from vegetable wastes and found in many manufacturing processes as both a product and precursor for such products as acetate plastic, acetic anhydride, ester solvent, vinegar, and aspirin [6-8].

Trichloroacetic acid is an analogue of acetic acid in which the three hydrogen atoms of the methyl group have all been replaced by chlorine atoms. It is widely used in biochemistry for the precipitation of macromolecules such as proteins, DNA and RNA.

Citric acid is the most widely used organic acid in the field of foods and pharmaceuticals. It is used as an acidulating agent in beverages, confectioneries, in pharmaceutical syrups, elixirs, in effervescent powders and tablets, to adjust the pH of food [9]. It is generally produced by surface or submerged fungal fermentation mainly with Aspergillus niger. However, the highest citric acid production has been obtained with the submerged fermentation method [10].

Lactic acid is an important organic acid that is used in various clinical, food and non-food applications [11]. Both fermentation and chemical synthesis are used for producing lactic acid. Lactic acid is of particular interest as a starting material for producing biodegradable poly (lactic acid) plastics [12,13]. A substantial commercial interest exists in producing these plastics from renewable resources such as starch-derived glucose via fermentation, because of increasing emphasis on sustainable production processes [14].

As seen in above phrases, organic acids (and their binary aqueous solutions) have been widely used in foods, fruit and beverages, pharmaceuticals, dental, cosmetics, detergents, plastics, resins, and other biochemical or chemical products [15-20], and thus have a close relationship with human's daily life. Therefore, study on the thermodynamic properties of aqueous solutions of organic acids can be used in the various fields of industry and research.

Also, strong hydrogen bonds can be formed between solute (formic, acetic, trichloroacetic, lactic, and citric acid) and solvent (water) molecules due to their –OH groups. Hydrogen bonding has key role for dissolving the acids in water. Hydrogen bonded systems are very interesting because hydrogen bonds play a vital role in chemical, physical, and biological processes and all of the substrates in this study have strong hydrogen bonds [21].

In this work, we have measured densities (ρ), refractive indices (n_D), and dynamic viscosities (η) for aqueous solution of trichloroacetic acid, lactic acid, and citric acid, also densities (ρ), refractive indices (n_D), dynamic viscosities (η), viscosity deviations ($\Delta\eta$), excess molar volumes (V^E), and change of refractive indices on mixing (Δn_D) for aqueous solution of formic acid and acetic acid at 292.15 K and over entire mole fractions.

RESULTS AND DISCUSSION

The experimental data on densities (ρ), refractive indices (n_D), dynamic viscosities (η), excess molar volumes (V^E), viscosity deviations ($\Delta\eta$), and change of refractive indices on mixing (Δn_D) for aqueous solutions of formic acid and acetic acid at 292.15 K are listed in Table 1. Also, the densities (ρ), refractive indices (n_D), and dynamic viscosities (η) for aqueous solutions of trichloroacetic acid, lactic acid, and citric acid at 292.15 K are listed in Table 2.

It is clear that the density, viscosity, and refractive index at experimental temperature increase as the mole fraction of solutions increases. One of the reasons for this effect can be increasing of the interaction between solute and solvent molecules in solution due to increasing of the number of solute molecules.

Table 1. Densities (ρ), viscosities (η), refractive indices (n_D), excess molar volumes (V^E), viscosity deviations ($\Delta\eta$), and change of refractive indices on mixing (Δn_D) for different aqueous solutions at T = 292.15 K as a function of mole fractions (x_2)

Water (1) + Formic acid (2)

c_2(mol.L^{-1})	x_1	x_2	ρ(g.cm^{-3})	η(mPa.s)	n_D	V^E(cm^3.mol^{-1})	$\Delta\eta$(mPa.s)	Δn_D
0.2749	0.9950	0.0050	1.0009	1.0163	1.3335	-0.0107	0.0098	0.0003
0.8192	0.9850	0.0150	1.0071	1.0310	1.3350	-0.0409	0.0167	0.0014
1.8774	0.9650	0.0350	1.0186	1.0593	1.3375	-0.0911	0.0294	0.0032
3.3915	0.9350	0.0650	1.0346	1.0991	1.3410	-0.1574	0.0457	0.0055
5.2798	0.8950	0.1050	1.0537	1.1479	1.3450	-0.2286	0.0633	0.0080
7.0323	0.8550	0.1450	1.0706	1.1926	1.3490	-0.2829	0.0767	0.0104
8.6586	0.8150	0.1850	1.0856	1.2339	1.3515	-0.3226	0.0867	0.0114
10.1671	0.7750	0.2250	1.0987	1.2729	1.3540	-0.3447	0.0945	0.0124
11.5687	0.7350	0.2650	1.1104	1.3103	1.3565	-0.3558	0.1006	0.0133
12.8680	0.6950	0.3050	1.1209	1.3468	1.3585	-0.3577	0.1059	0.0138
13.4935	0.6750	0.3250	1.1258	1.3650	1.3595	-0.3568	0.1084	0.0140
14.3834	0.6450	0.3550	1.1327	1.3926	1.3605	-0.3519	0.1126	0.0139
15.2316	0.6150	0.3850	1.1393	1.4209	1.3615	-0.3475	0.1175	0.0137
15.7759	0.5950	0.4050	1.1436	1.4402	1.3620	-0.3461	0.1211	0.0134
16.5639	0.5650	0.4350	1.1499	1.4702	1.3630	-0.3304	0.1277	0.0133

Water (1) + Acetic acid (2)

0	1.0000	0.0000	0.9980	1.0026	1.3330	0	0	0
0.5445	0.9900	0.0100	1.0029	1.0682	1.3355	-0.0617	0.0634	0.0021
1.5988	0.9695	0.0305	1.0113	1.1988	1.3390	-0.1673	0.1895	0.0048
3.1194	0.9370	0.0630	1.0228	1.3919	1.3460	-0.3224	0.3754	0.0106
4.2971	0.9090	0.0910	1.0311	1.5459	1.3505	-0.4432	0.5233	0.0140
5.4419	0.8790	0.1210	1.0387	1.6990	1.3545	-0.5621	0.6697	0.0168
6.5102	0.8480	0.1520	1.0450	1.8451	1.3585	-0.6666	0.8090	0.0196
7.5372	0.8150	0.1850	1.0506	1.9880	1.3620	-0.7666	0.9446	0.0219

8.6484	0.7750	0.2250	1.0558	2.1444	1.3650	-0.8659	1.0922	0.0233
9.5641	0.7380	0.2620	1.0595	2.2730	1.3675	-0.9417	1.2127	0.0244
10.4715	0.6970	0.3030	1.0626	2.3975	1.3700	-1.0098	1.3281	0.0253
11.1098	0.6650	0.3350	1.0643	2.4814	1.3715	-1.0489	1.4050	0.0256
11.5810	0.6395	0.3605	1.0654	2.5397	1.3730	-1.0754	1.4577	0.0261
12.2835	0.5980	0.4020	1.0667	2.6175	1.3740	-1.1076	1.5263	0.0255
13.0381	0.5480	0.4520	1.0676	2.6824	1.3755	-1.1301	1.5802	0.0251
--	0.4640[a]	0.5360	1.0679	2.7154	1.3765	-1.1321	1.5947	0.0229
--	0.3295[a]	0.6705	1.0657	2.5221	1.3770	-1.0306	1.3718	0.0182
--	0.2420[a]	0.7580	1.0627	2.2601	1.3765	-0.8832	1.0905	0.0143
--	0.1450[a]	0.8550	1.0581	1.8811	1.3745	-0.6350	0.6901	0.0086
--	0.0000[a]	1.0000	1.0476	1.2229	1.3715	0	0	0

[a]: In these mole fractions, acetic acid is solvent and water is solute.

Table 2. Densities (ρ), viscosities (η) and refractive indices (n_D) for different aqueous solutions at T = 292.15 K as a function of mole fractions (x_2)

Water (1) + Trichloroacetic acid (2)

c_2 (mol.L^{-1})	x_1	x_2	ρ(g.cm^{-3})	η(mPa.s)	n_D
0.2723	0.9950	0.0050	1.0203	1.1041	1.3390
0.5346	0.9900	0.0100	1.0399	1.2196	1.3440
0.7869	0.9850	0.0150	1.0589	1.3348	1.3485
1.0303	0.9800	0.0200	1.0773	1.4495	1.3530
1.2651	0.9750	0.0250	1.0949	1.5640	1.3575
1.4905	0.9700	0.0300	1.1110	1.6781	1.3615
1.7100	0.9650	0.0350	1.1283	1.7919	1.3655
1.9210	0.9600	0.0400	1.1438	1.9055	1.3695
2.1245	0.9550	0.0450	1.1589	2.0187	1.3730
2.3210	0.9500	0.0500	1.1732	2.1315	1.3765
2.5104	0.9450	0.0550	1.1868	2.2440	1.3797
2.6936	0.9400	0.0600	1.1999	2.3562	1.3830
2.8699	0.9350	0.0650	1.2122	2.4682	1.3855
3.0403	0.9300	0.0700	1.2239	2.5797	1.3880
3.2038	0.9250	0.0750	1.2348	2.6910	1.3905
3.3615	0.9200	0.0800	1.2452	2.8019	1.3930
3.5134	0.9150	0.0850	1.2549	2.9125	1.3950
3.6588	0.9100	0.0900	1.2638	3.0228	1.3970
3.7989	0.9050	0.0950	1.2722	3.1328	1.3985
3.9331	0.9000	0.1000	1.2799	3.2424	1.4000

Water (1) + Lactic acid (2)

0.2725	0.9950	0.0050	1.0026	1.0067	1.3360
0.5379	0.9900	0.0100	1.0080	1.1018	1.3380
0.8464	0.9840	0.0160	1.0141	1.2132	1.3405
1.2197	0.9760	0.0240	1.0221	1.3579	1.3440
1.4344	0.9720	0.0280	1.0259	1.4289	1.3455
1.6684	0.9670	0.0330	1.0307	1.5166	1.3475

1.8961	0.9620	0.0380	1.0352	1.6036	1.3495
2.1613	0.9560	0.0440	1.0404	1.707	1.3520
2.4191	0.9500	0.0500	1.0455	1.8102	1.3540
3.5946	0.9200	0.0800	1.0682	2.3347	1.3640
4.2877	0.9000	0.1000	1.0812	2.7100	1.3695
5.0687	0.8750	0.1250	1.0955	3.2326	1.3760
6.1511	0.8350	0.1650	1.1146	4.2484	1.3845
7.1721	0.7900	0.2100	1.1319	5.7484	1.3925
7.7618	0.7600	0.2400	1.1417	7.0047	1.3975
8.2901	0.7300	0.2700	1.1504	8.4923	1.4010
8.7664	0.7000	0.3000	1.1580	10.2274	1.4050
9.2033	0.6700	0.3300	1.1655	12.2207	1.4080
9.5977	0.6400	0.3600	1.1718	14.4772	1.4110
9.9566	0.6100	0.3900	1.1773	16.9966	1.4135
10.2805	0.5800	0.4200	1.1817	19.7729	1.4160
10.4762	0.5600	0.4400	1.1838	21.7612	1.4170

Water (1) + Citric acid (2)

0.0505	0.9990	0.0010	1.0026	1.0321	1.3340
0.1498	0.9970	0.0030	1.0119	1.0840	1.3370
0.2472	0.9950	0.0050	1.0210	1.1399	1.3400
0.3428	0.9930	0.0070	1.0299	1.2000	1.3430
0.4363	0.9910	0.0090	1.0385	1.2643	1.3455
0.5286	0.9890	0.0110	1.0469	1.3330	1.3480
0.6189	0.9870	0.0130	1.0550	1.4061	1.3505
0.7071	0.9850	0.0150	1.0630	1.4837	1.3525
0.7941	0.9830	0.0170	1.0708	1.5660	1.3550
0.8789	0.9810	0.0190	1.0783	1.6530	1.3575
0.9624	0.9790	0.0210	1.0858	1.7448	1.3600
1.0443	0.9770	0.0230	1.0930	1.8416	1.3620
1.1246	0.9750	0.0250	1.1001	1.9434	1.3640
1.2035	0.9730	0.0270	1.1070	2.0504	1.3660
1.2810	0.9710	0.0290	1.1139	2.1625	1.3685
1.3573	0.9690	0.0310	1.1206	2.2801	1.3705
1.4319	0.9670	0.0330	1.1271	2.4030	1.3725
1.5055	0.9650	0.0350	1.1336	2.5315	1.3745

The values of V^E for aqueous solution of formic acid and acetic acid were calculated from the density data using the following equation [22]:

$$V^E = (x_1M_1 + x_2M_2)/\rho - (x_1M_1/\rho_1 + x_2M_2/\rho_2) \qquad (1)$$

In this equation x_1, x_2 are mole fractions. M_1, M_2 are the molar masses. ρ_1, ρ_2 are the densities of pure components 1, 2 respectively.

The change of refractive index on mixing (Δn_D) for aqueous solution of formic acid and acetic acid was calculated from following equation [23]:

$$\Delta n_D = n_D - (x_1n_{D1} + x_2n_{D2}) \qquad (2)$$

In this equation n_D, n_{D1}, n_{D2} are the refractive index of mixture, pure components 1, 2 respectively.

The viscosity deviation ($\Delta\eta$) for aqueous solution of formic acid and acetic acid was calculated from following equation [24]:

$$\Delta\eta = \eta - (x_1\eta_1 + x_2\eta_2) \tag{3}$$

where η, η_1, η_2 are the viscosity of mixture, pure components 1, 2 respectively.

The values of excess properties for aqueous solutions were fitted to the Redlich-Kister polynomial equation [25]:

$$Y = x_1(1 - x_1)\sum_{i=0}^{n} A_i(2x_1 - 1)^i \tag{4}$$

where Y = V^E or Δn_D or $\Delta\eta$, A_i are adjustable parameters, and x_1 is the mole fraction of component 1.

For aqueous solutions of this study the values of these parameters, A_i, along with the standard errors, σ, are listed in Table 3.

Table 3. Coefficients of the Redlich-Kister equation and standard deviations for excess molar volumes, viscosity deviations, and change of refractive indices on mixing for different aqueous solutions at T = 292.15 K

Water (1) + Acetic acid (2)

property	A_0	A_1	A_2	A_3	σ
V^E (cm^3.mol^{-1})	-4.5818	0.3676	-0.8267	-0.8898	0.0140
$\Delta\eta$ (mPa.s)	6.5422	-0.1647	-2.4861	2.6762	0.0258
Δn_D	0.0954	0.0426	0.0302	0.0292	0.0002

Water (1) + Formic acid (2)

V^E (cm^3.mol^{-1})	-1.6706	4.3653	-15.2023	10.7156	0.0102
$\Delta\eta$ (mPa.s)	0.5442	0.0219	-0.9119	1.4238	0.0045
Δn_D	0.0513	0.0392	-0.0280	0.0491	0.0003

In each case, the optimum number of coefficients A_i was determined from an examination of the variation of the standard deviation [26]:

$$\sigma(Y) = [\Sigma(Y_{cal} - Y_{exp})^2/(n - m)]^{(1/2)} \tag{5}$$

where n is the total number of experimental values and m is the number of parameters.

Most studies on viscosity are confined to the description of dilute solutions of solutes via determination of the A- and B-coefficients in the Jones-Dole equation [27]:

$$\frac{\eta}{\eta_\circ} = 1 + Ac^{1/2} + Bc \qquad (6)$$

In this equation c, η, and $\eta_\circ$ are the molar concentration of solution, viscosities of solution, and solvent responsively. Values of the fitted parameters A and B are listed in Table 4.

Table 4. Values of constants A, B, coefficient of determination R^2 (according of Eq 6), and standard deviations σ for different aqueous solutions at T = 292.15 K

systems	A(L$^{1/2}$·mol$^{-1/2}$)	B(L·mol^{-1})	R^2	σ
Formic acid + water	-0.0274	0.0331	0.9976	0.0054
Acetic acid + water	-0.0561	0.1473	0.9990	0.0040
Trichloroacetic acid + water	-0.4762	0.7606	0.9986	0.0364
Lactic acid + water	-3.2774	0.1202	0.9970	0.3486
Citric acid + water	-1.5152	1.8882	0.9970	0.0450

The values of refractive index for aqueous solutions can be fitted by following experimental equation [28]:

$$n_D = A_n m + n^*_{D(c)} \qquad (7)$$

where m is the molar concentration of the aqueous solution, $n^*_{D(c)}$ is the refractive index of solvent (water) and A_n is an experimental parameter that depends on physical and chemical properties of solute molecules such as molecular weight, polarity, electrical charge, and shape.

For mixtures of this study, the values of A_n, n^*_D and relative deviations between the experimental values of n^*_D (in literatures) [25], and calculated values of n^*_D from Eq. (6) at different temperatures are listed in Table 5.

Table 5. Values of constants A_n and n^*_D (according of Eq 7) and relative deviations RD (n^*_D) for different aqueous solutions at T = 292.15 K

systems	M_{solute}(g.mol^{-1})	A_n(L·mol^{-1})	n^*_D	R^2	RD (for n^*_D)
Formic acid + water	46.03	0.0018	1.3346	0.9896	0.0012
Acetic acid + water	60.05	0.0033	1.3351	0.9889	0.0016
Trichloroacetic acid + water	163.38	0.0169	1.3360	0.9966	0.0023
Lactic acid + water	90.08	0.0080	1.3344	0.9995	0.0011
Citric acid + water	192.12	0.0275	1.3332	0.9996	0.0002

The relative deviations (RD) for n^*_D were calculated according to following equation:

$$RD = \left| \frac{n_D^* - n_{D(c)}^*}{n_D^*} \right| \tag{8}$$

where $n^*_{D(c)}$ is the calculated value of refractive index of water from Eq. (7) and n^*_D is the experimental value of refractive index of water (in literature) at same temperature.

The values of thermodynamic properties for solutions of this study can be dependent on two factors. The first factor is the molar concentration of solute in mixture. As seen in Tables 1 and 2 (also in figures1 and 2), the thermodynamic properties for solution of this study increase as the molar concentration (or mole fraction) of solutes increases. The second factor is the strength of bonds between solvent and solute molecules due to the values of polarity (dipole-dipole interaction and the H-bonds) and electrical charge of solute molecules. In aqueous solutions of organic acids, the type and form of group (or groups) that attached to carbon (in COOH) can be effective on the strength of bonds between solvent and solute molecules. In some cases one factor outbalances another and in some cases both factors are effective. The second factor is important in excess thermodynamic properties (especially in most important of these properties: excess molar volumes) [29].

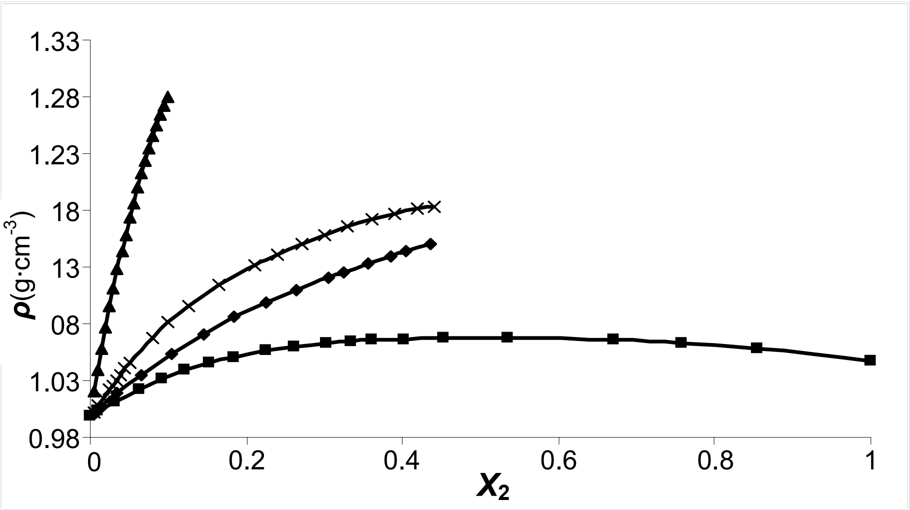

Figure 1. Densities (ρ) plotted against mole fraction of solute (x_2) at T = 292.15 K for different aqueous solutions of: ♦, formic acid; ■, acetic acid; ▲, trichloroacetic acid; ×, lactic acid.

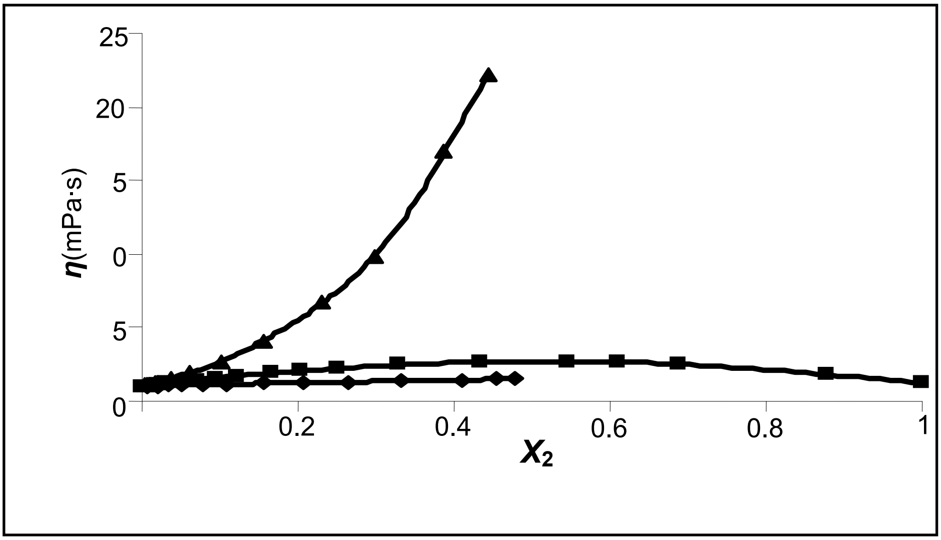

Figure 2. Viscosities (η) plotted against mole fraction of solute (x_2) at T = 292.15 K for different aqueous solutions of: ♦, formic acid; ■, acetic acid; ▲, lactic acid.

For mixtures of this study the maximum value of refractive index and viscosity is observed for (lactic acid + water). In this case both factors are effective due to high molar concentration of solution (10.5213 $mol{\cdot}L^{-1}$) and electron acceptor effect of oxygen in (OH).

Also the maximum value of density is observed for (trichloroacetic acid + water). In this case the second factor exceeds first factor due to more electron acceptor effect of Cl than oxygen atom in (OH).

It can be summarized that V^E values may be affected by three factors. The first factor is the interaction among molecules, such as the formation of hydrogen bonds or of charge transfer complexes. The positive excess molar volumes for the solution can be a result of the breaking of the H-bonds (weaker hydrogen bonds) and complexes between solvent and solute. Forming hydrogen bonds (stronger H-bonds) and complexes bring negative values of excess molar volumes. The second factor is the physical intermolecular forces, including electrostatic forces between charged particles and between permanent dipoles, induction forces between a permanent dipole and an induced dipole, and forces of attraction (dispersion forces) and repulsion between nonpolar molecules. Physical intermolecular forces are usually weak, and the sign of V^E values may be positive or negative, but the absolute values are small. The third factor is the structural characteristics of the component, arising from geometrical fitting of one component into the other's structure, due to the differences in shape and size of component and free volume. Similar to the excess molar volumes, viscosity deviations are related to the molecular interaction between the components of mixtures as well as to the size and shape of molecules. Positive values of $\Delta\eta$ are indicative of strong interactions whereas negative values indicate weaker interactions [30,31].

As seen in figures 3 and 4, for aqueous solution of formic acid and acetic acid over the entire ranges of mole fractions the values of V^E are negative and also, the values of $\Delta\eta$ and Δn_D are positive at 292.15 K. In these solutions the forces between solute and solvent molecules (formic acid-water and acetic acid-water) are dipole-ionic while there are hydrogen bonds between molecules in pure compounds of these solutions. Ionic-dipole bond (the bond between CH_3COO^- and H_2O also, $HCOO^-$ and H_2O) is stronger than hydrogen bond. Also, the molecules in these solutions are closer together (as compared with acetic acid and formic acid) due to the smaller size of solvent molecules (water) than solute molecules (formic acid and acetic acid). Therefore, interaction between molecules in these solutions is stronger than between pure components. In this case, the first factor and third factor (the structural characteristics of the component, arising from geometrical fitting of one component into the other's structure) are very effective [32].

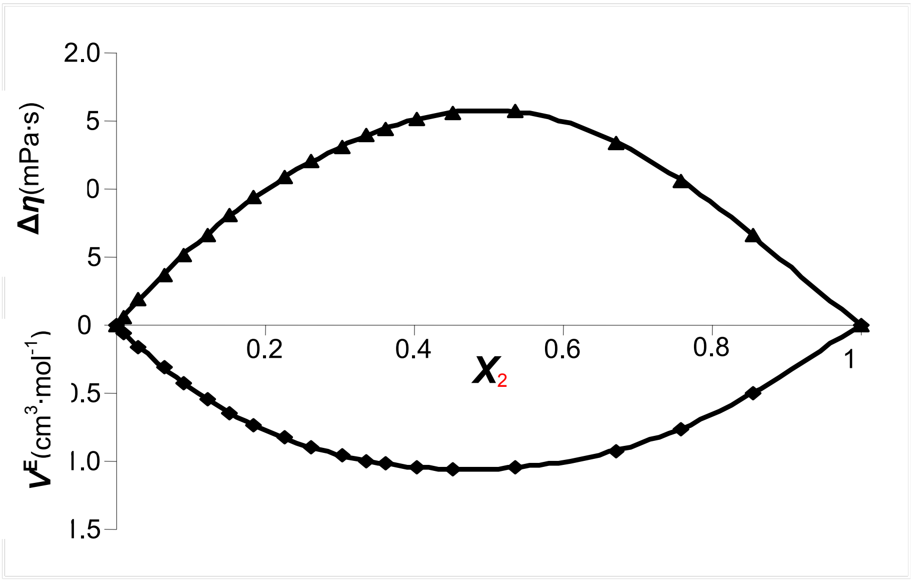

Figure 3. Viscosity deviations (▲) and excess molar volumes (♦) plotted against mole fraction of acetic acid (x_2) for aqueous solutions of acetic acid at T = 292.15 K.

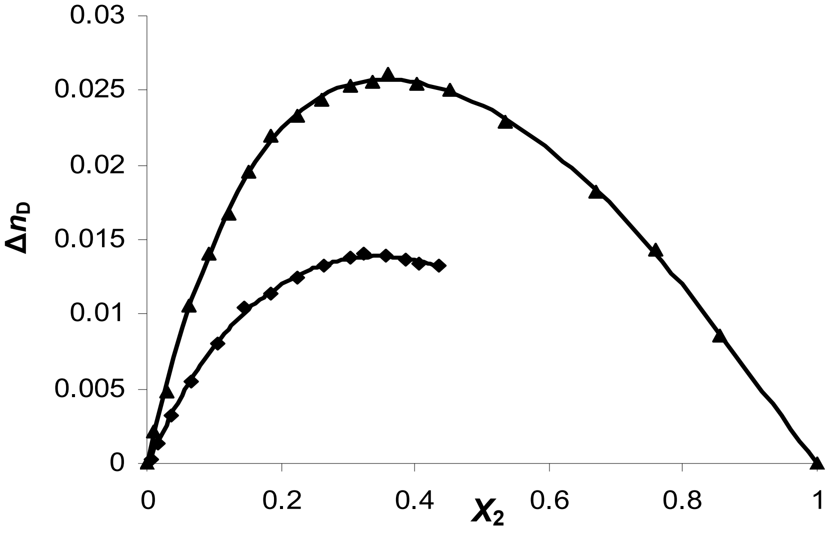

Figure 4. Change of refractive indices on mixing (Δn_D) plotted against mole fraction of solute (x_2) at T = 292.15 K for different aqueous solutions of: ♦, formic acid; ▲, acetic acid.

From Table 1, it can be seen that the values of V^E (absolute values), $\Delta\eta$, and Δn_D for aqueous solution of acetic acid are larger than those for aqueous solution of formic acid. In –COOH oxygen has partial negative electrical charge (-δ) and carbon has partial positive electrical charge (+δ) due to the more electronegative effect of oxygen than carbon. In –COOH the absolute value of (-δ) for oxygen increases as the electrodonor effect of (–R) group (that attached to carbon) increases. In acetic acid, $-CH_3$ is attached to carbon (C=O) while in formic acid hydrogen is attached to carbon.


(a)
(b)

Scheme 1. Structure of acetic acid (a) and formic acid (b)

The electrondonor effect of methyl group ($-CH_3$) is stronger than that of hydrogen (H) and thus the absolute value of (-δ) for oxygen in acetic acid molecule is larger than that of formic acid molecule. It can be due to the better interaction between solvent-solute molecules in aqueous solution of acetic acid then in aqueous solution of formic acid.

It is clear that according to Table 1 for aqueous solution of acetic acid the minimum and maximum value of V^E and $\Delta\eta$ appears at $x_{\text{acetic acid}} \approx 0.4520$ and 0.5360, respectively. Also, the maximum value of Δn_D appears at $x_{\text{acetic acid}} \approx 0.3605$.

As can be seen from the Table 5, the values of A_n depend on molecular weight of solute. In solutions of this study, the values of A_n increase as the molecular weight of solute increases.

Also a linear relation between refractive index and molar concentration is observed in figure 5. In addition, all these linear diagrams (n_D vs c) have the high R^2 ($R^2 \approx 0.999$).

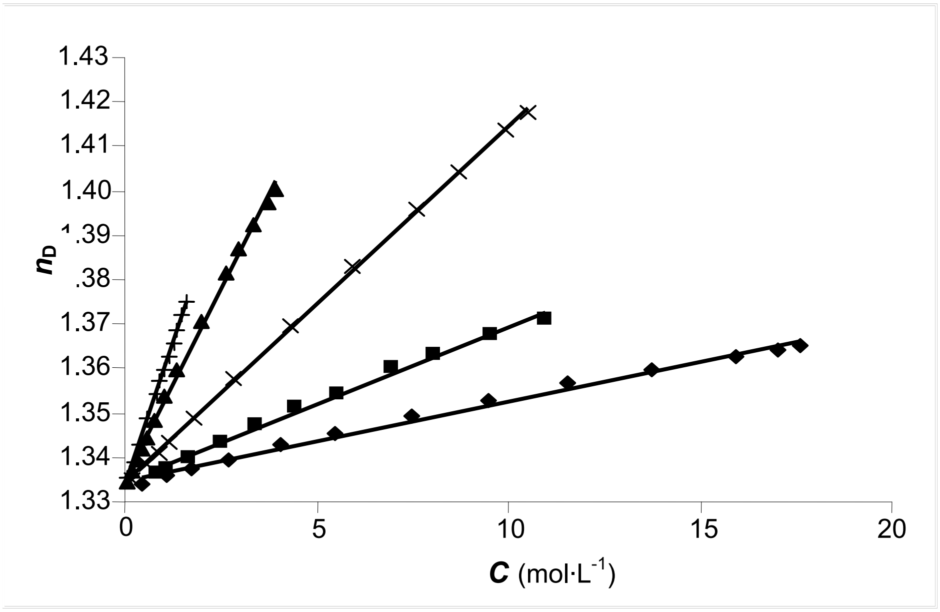

Figure 5. Refractive indices (n_D) plotted against molar concentration of solute (c) at T = 292.15 K for different aqueous solutions of: ♦, formic acid; ■, acetic acid; ▲, trichloroacetic acid; ×, lactic acid; +, citric acid.

CONCLUSIONS

Experimental viscosities, densities, and refractive indices at 292.15 K data were obtained for (acetic acid + water), (citric acid + water), and (lactic acid + water) over a wide range of composition. From the experimental viscosities, densities and refractive indices, values of viscosity deviations, excess molar volumes and change of refractive indices on mixing for solutions of this study were calculated.

It was found that for binary mixture of (acetic acid + water) all these calculated quantities for change of refractive indices on mixing and viscosity deviations are positive while these calculated quantities for excess molar volumes are negative. The Redlich-Kister polynomial equation was applied successfully for the correlation of V^E, $\Delta\eta$, and Δn_D.

EXPERIMENTAL

Materials

Formic acid, acetic acid, trichloroacetic acid, lactic acid, and citric acid were supplied from Fluka Company. The purity of trichloroacetic acid, lactic acid, and citric acid was 98% and purity of formic acid and acetic acid was 99%. These substances are used without further purification. All dilute solutions were prepared with double-distilled water. Binary mixtures were prepared by known masses of each liquid in air-tight stoppered glass bottles.

Apparatus and procedure

The mass measurements were made on a single pan Mettler balance to an accuracy of ±0.0001 g. No buoyancy corrections were applied. The possible error in mole fraction is calculated to be less than $\pm1\times10^{-4}$.

Density (ρ) measurements of pure components and binary mixtures over the possible composition range were carried out using a digital vibrating glass tube densimeter (DA-500E, China.). Densities were determined with the uncertainty of ± 0.0001 $g\cdot cm^{-3}$. It was calibrated with double distilled water and air.

The kinematic viscosity was measured with Ubbelohde viscometers with a Schott-Geräte automatic measuring unit model AVS400 provided with a transparent thermostat, which allows temperature stabilization with a tolerance of 0.01 K. Four Ubbelhode tubs with different capillary size (0.36, 0.46, 0.53 and 0.63 mm) were used in the experiments according to the different viscosity values of the mixtures. The calibration was carried out with double distilled water and glycerol (60% w/v). The uncertainty of the viscosity measurement was 0.0001 mPa.s. All of the experiments are repeated three times and then reported the average values. Refractive indices for the sodium D-line (n_D) were measured with an Abbe reftactometer (CARL ZEISS, Model A, Germany). A minimum of three independent readings were taken for each composition. The densities, viscosities and refractive indices of pure formic acid, acetic acid, and water were measured by these apparatus at T = 292.15 K. The uncertainties of the refractive index and viscosity are $\pm1\times10^{-4}$. Also the uncertainty of the temperature is ± 0.01 K.

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