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Effect of Concentration on the Viscosity of Some Carboxylic Acids in Diluted Aqueous Solutions

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Abstract

In the current study, the effect of concentration on the viscosity of formic acid, acetic acid, and propanoic acid in an aqueous solution is investigated. The apparent molar volume (ϕ_v) was specified from density measurements at 298.15 K. A restrictive apparent molar volume ϕ_v° under unlimited dilutions of these carboxylic acids has been determined based on Masson's equation. The B and A coefficients for viscosity have been determined using viscosity data for the Jones-Dole equation for all studies, and a positive value of the B-coefficient indicates strong solute-solvent interaction. The modified Jones-Dole equation was projected using a ratio of mole fractions of solute and solvent.

Keywords: Apparent molar volume, Carboxylic acids, Jones-Dole equation, Viscosity and B-coefficient.

تأثير التركيز على لزوجة بعض الاحماض الكربوكسيلية في المحاليل المائية المخففة

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الخلاصة

في الدراسة الحالية، تم دراسة تأثير التركيز على لزوجة كل من الحوامض (الفورميك، الخليك، و البرويانويك) في المحلول المائي، استخدمت النتائج لحساب الحجم المولاري الظاهري (ϕ_v) من قياس الكثافة عند 298.15 كلفن. قيس الحجم المولاري الظاهري المحدد ϕ_v° للمحاليل المخففة للحوامض الكربوكسيلية بناء على معادلة ماسون، استخدمت قياسات اللزوجة لحساب معاملي جونز-دول B و A لجميع الدراسات، وتشير القيمة الموجبة لمعامل B إلى تداخل مذاب-مذيب قوي. تم عرض معادلة جونز دول المعدلة باستخدام نسب الكسور المولية للمذاب و المذيب.

1. Introduction

Important physicochemical properties of organic compound solutions are the hydrophobic and hydrophilic interactions between these solutes and water, as well as their effects on the structure of water. For theoretical and practical applications, in particular, the viscometric characteristics of aqueous carboxylic acid solutions are significant. Their study offers imperative information about the nature and influence of interactions between nonpolar and

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polar water groups on water structure [1-2], and the physical-chemical properties are useful to know the properties of liquid solutions [3-7]. Carboxylic acids have a distinctive solubility characteristic in both aqueous and non-aqueous solutions. These molecules display hydrophobic interactions [8-10] that have already been published. Carboxylic acids are used as inhibitors for corrosion and as surfactants and metal finishing compounds in the manufacture of polyesters, polyols, and polyamides in the synthesis of pharmaceutical products [11-16]. A perspective on the dynamic architectures of water molecules in varied environments is also required in such aqueous systems. Water itself is closely connected with solute molecules and has a high propensity to mix. The carboxylic acid group (the name derived from the relation between carbonyl and hydroxyl) is the organic compound. They are capable of forming water-like hydrogen bonds. The interactions between water and carboxylic acids are quite complicated; both acids and water are self-associated fluids by the H-bonding mechanism. Hydrophilic COOH and hydrophobic stand for the groups of carboxylic acids; they are entirely different in their modes of contact with water. The hydrophilic COOH acid group is formed by hydrophilic interactions to form an H-bond of water and disrupt the usual water structure, whereas the alkyl group promotes hydrophobic molecular structures around this group. In the field of solution chemistry, a deeper understanding of the relationship between water and acids is critical because it can provide valuable knowledge about hydrophilic and hydrophobic interactions [17-23]. The viscosity, B-coefficient, and Jone-Dole equation of formic, acetic, and propanoic acids in water are described in the current study as functions of composition at 298.15 K.

2. Experimental

The carboxylic acids (99% purity) were supplied by Fluka Company and employed in this study. The viscosity was measured using a calibrated Ubbelohde suspended viscometer to change the bath temperature to ± 0.01 K at 298.15 K to provide the finished values with a viscosity level. The empiricists completed the experiment at least three times, and the results were accurate. The reported viscosity values were also observed in this variation.

3. Results and discussion

For the estimation of B magnitude from the η/η_0 (η = viscosity of solutions, η_0 = viscosity of solvent) plot vs. C, experimental data for three carboxylic acids should be used, with linear values corresponding to the B-coefficient. The applicability of Equation 1 was taken into account in the case of non-electrolytes. The diagram obtained from η/η_0 to C magnitudes (Figure 1) shows that the intercept value is almost one. Table 1 and Figure 1 depict the details for carboxylic acids. From the plots, it has become understandable that our study's experimental findings validate the lessened equation 2 applicability of Jone-Dole [24,25].

Table 1: η/η_0 alteration based on the concentration of formic acid, acetic acid, and propanoic acid at 298.15 K

Formic acid			Acetic acid			Propanoic acid		
s. no.	Concentration (mol.dm ⁻³)	η/η_0	s. no.	Concentration (mol.dm ⁻³)	η/η_0	s. no.	Concentration (mol.dm ⁻³)	η/η_0
1	0.03951	1.00805	1	0.02665	1.01733	1	0.04113	1.04714
2	0.05836	1.01555	2	0.04604	1.03232	2	0.06225	1.06393
3	0.07081	1.02632	3	0.05963	1.04222	3	0.08188	1.08598
4	0.08516	1.03522	4	0.07911	1.05172	4	0.10112	1.10311
5	0.09841	1.04517	5	0.09789	1.06283	5	0.12115	1.14409
6	0.11602	1.06639	6	0.11787	1.08472	6	0.14049	1.15476
7	0.13034	1.07449	7	0.13744	1.09099	7	0.16224	1.17523
8	0.15022	1.08661	8	0.15076	1.10453	8	0.18183	1.19824
9	0.17022	1.11095	9	0.17073	1.11443	9	0.20172	1.22399
10	0.19033	1.12329	10	0.18532	1.12133	10	0.22066	1.24423
11	0.21031	1.13721	11	0.21118	1.14963	11	0.23398	1.26708

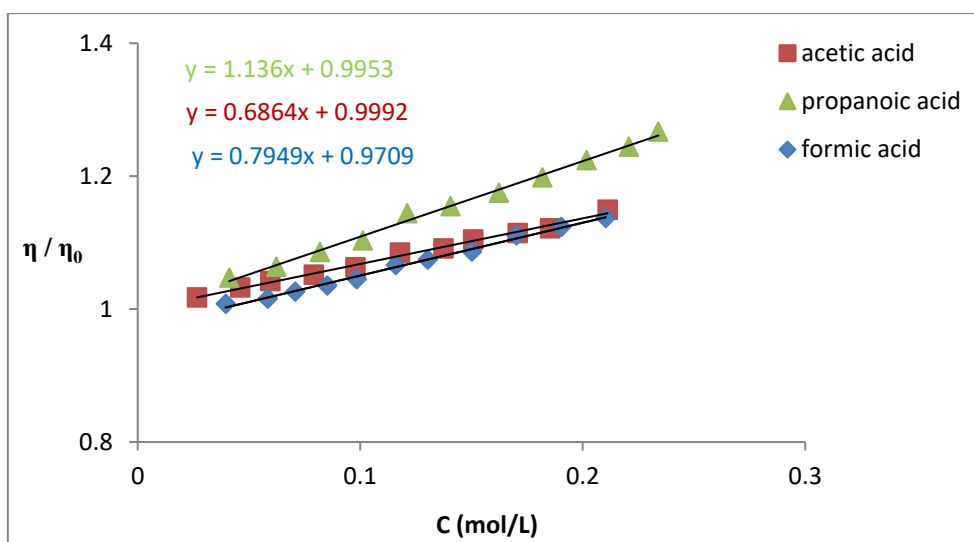


Figure 1 : Plot (η/η_0) vs. (C) for carboxylic acids at 298.15 K

$$\eta/\eta_0 = BC+1 \quad \dots\dots\dots (1)$$

For determining intermolecular interaction in aqueous solution, the magnitudes of η/η_0 obtained at various concentrations were used. With the aid of a Jone-Dole equation [26-28], the parameter of interactions was achieved.

$$(\eta/\eta_0 - 1)/\sqrt{C} = A+B\sqrt{C} \quad \dots\dots\dots (2)$$

Here, (η/η_0) stands for the relative viscosity, A and B characterize constants regarding the ion-ion and ion-solvent interaction separately, and C stands for a molar concentration. The magnitudes of A and B have been acquired based on an intercept and the slopes of the linear plots of $(\eta/\eta_0-1)/\sqrt{C}$ versus \sqrt{C} . The magnitudes are specified in Table 2 and Figure 2.

Table 2: A and B amounts regarding aqueous formic acid, acetic acid, and propanoic acid at 298.15 K for the Jone-Dole equation

Formic acid			Acetic acid			Propanoic acid		
s. no.	\sqrt{C}	$(\eta/\eta_0-1)/\sqrt{C}$	s. no.	\sqrt{C}	$(\eta/\eta_0-1)/\sqrt{C}$	s. no.	\sqrt{C}	$(\eta/\eta_0-1)/\sqrt{C}$
1	0.19877	0.04051	1	0.16325	0.10616	1	0.20281	0.23245
2	0.24158	0.06437	2	0.21457	0.15063	2	0.24950	0.25627
3	0.26611	0.09891	3	0.24419	0.17291	3	0.28615	0.30047
4	0.29182	0.12069	4	0.28126	0.18389	4	0.31796	0.32429
5	0.31370	0.14399	5	0.31288	0.20082	5	0.34807	0.36849
6	0.34062	0.19491	6	0.34335	0.24611	6	0.37482	0.41291
7	0.36103	0.20633	7	0.37073	0.24675	7	0.40279	0.43503
8	0.38758	0.22346	8	0.38828	0.26923	8	0.42642	0.46492
9	0.41258	0.26892	9	0.41319	0.27694	9	0.44913	0.49873
10	0.43627	0.28261	10	0.43049	0.28184	10	0.46974	0.51994
11	0.45861	0.29917	11	0.45954	0.32561	11	0.48371	0.55215

Accordingly, $A = -0.1825$ ($\text{dm}^{3/2} \text{ mole}^{-1/2}$), $A = -0.003$ ($\text{dm}^{3/2} \text{ mole}^{-1/2}$), $A = -0.0283$ ($\text{dm}^{3/2} \text{ mole}^{-1/2}$), $B = 1.0656$ ($\text{dm}^3 \cdot \text{mol}^{-1}$), $B = 0.6884$ ($\text{dm}^3 \cdot \text{mol}^{-1}$), and $B = 1.166$ ($\text{dm}^3 \cdot \text{mol}^{-1}$). Linearity = 0.9815; Linearity = 0.9896; Linearity = 0.988.

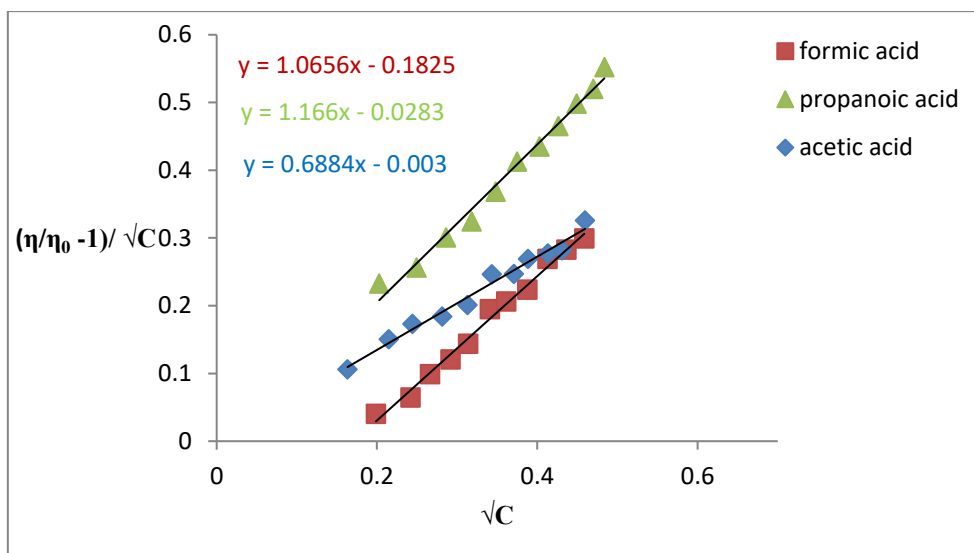


Figure 2: Jones-Dole plot $(\eta/\eta_0 - 1)/\sqrt{C}$ versus \sqrt{C} for carboxylic acids at 298.15 K

The B-coefficient for three carboxylic acids, measured based on the Jones-Dole equation, was positive. Namely, they represent 'structure makers' in a highly diluted aqueous solution. The magnitude of the A Coefficient has been small, implying that the probability of solute-solute interaction has been small compared with the intermolecular attraction between solute and solvent. It proposes the formation of an internal hydrogen bond due to the presence of the hydroxyl group and the subsequent contraction that occurs as a result of the strong polar-polar interaction among carboxylic clusters hydrated with water [29]. In this paper, by using a ratio of mole fractions of solute and solvent (n_s/n_w) instead of the concentration of solute, the Jones-Dole equation has been modified in place of the concentration of solutes that are also accountable for solute-solute and solute-solvent interactions. A suggested relation has been correlated with the original equation, and the equation with the modifications is more accurate as a result of the greater measurements of slopes. For three carboxylic acids, the salts utilizing concentration values, n_s and n_w , have been considered, and the obtained data are explained in Table 3. Based on the linear plots of $(\eta/\eta_0 - 1)/\sqrt{n_s/n_w}$, vs. $\sqrt{n_s/n_w}$ Ax and Bx are the coefficients of the modified Jones-Dole equation magnitudes for carboxylic acids, which have been calculated from the intercept and slope, respectively (Figure 3), for testing the validity of the reformed equation. Accordingly, the modified Jones-Dole equation is specified by Equation 3.

$$\frac{(\eta/\eta_0 - 1)}{\sqrt{n_s/n_w}} = Ax + Bx \sqrt{\frac{n_s}{n_w}} \dots\dots\dots (3)$$

Here, n_s stand for a mole fraction of solute, and n_w stands for a mole fraction of solvent water. The adopted concentration range in this paper has been optimal for the soundness of Staudinger, the Jones-Dole equation, and the modified Jones-Dole equation that behaves as a structure maker [30-32].

Table 3: Ax and Bx coefficients regarding aqueous formic acid, acetic acid, and propanoic acid at 298.15 K for the modified Jone-Dole equation

Formic acid			Acetic acid			Propanoic acid		
s. no.	$\sqrt{n_s/n_w}$	$(\eta/\eta_0-1)/\sqrt{n_s/n_w}$	s. no.	$\sqrt{n_s/n_w}$	$(\eta/\eta_0-1)/\sqrt{n_s/n_w}$	s. no.	$\sqrt{n_s/n_w}$	$(\eta/\eta_0-1)/\sqrt{n_s/n_w}$
1	0.02145	0.37529	1	0.02825	0.61124	1	0.04076	1.15648
2	0.03126	0.49744	2	0.04351	0.74282	2	0.05223	1.22406
3	0.03956	0.66532	3	0.05162	0.81791	3	0.06753	1.27322
4	0.04844	0.72709	4	0.06152	0.84072	4	0.07837	1.31573
5	0.05879	0.76833	5	0.07264	0.86495	5	0.09413	1.53076
6	0.06799	0.97647	6	0.08509	0.99556	6	0.09767	1.58419
7	0.07399	1.00676	7	0.08987	1.01248	7	0.10778	1.62581
8	0.07949	1.08957	8	0.09854	1.06079	8	0.11759	1.68586
9	0.09543	1.16956	9	0.10672	1.07229	9	0.12439	1.80085
10	0.09932	1.24134	10	0.11211	1.08223	10	0.13214	1.84827
11	0.10589	1.29557	11	0.12731	1.17532	11	0.13879	1.92435

Notes: Ax, Bx for formic acid = 0.1913, 10.539; Ax, Bx for acetic acid = 0.5007, 5.4364, Ax, Bx for propanoic acid = 0.7673, 8.1473; Linearity (0.9814, 0.9743, and 0.9763) for formic acid, acetic acid, and propanoic acid, respectively.

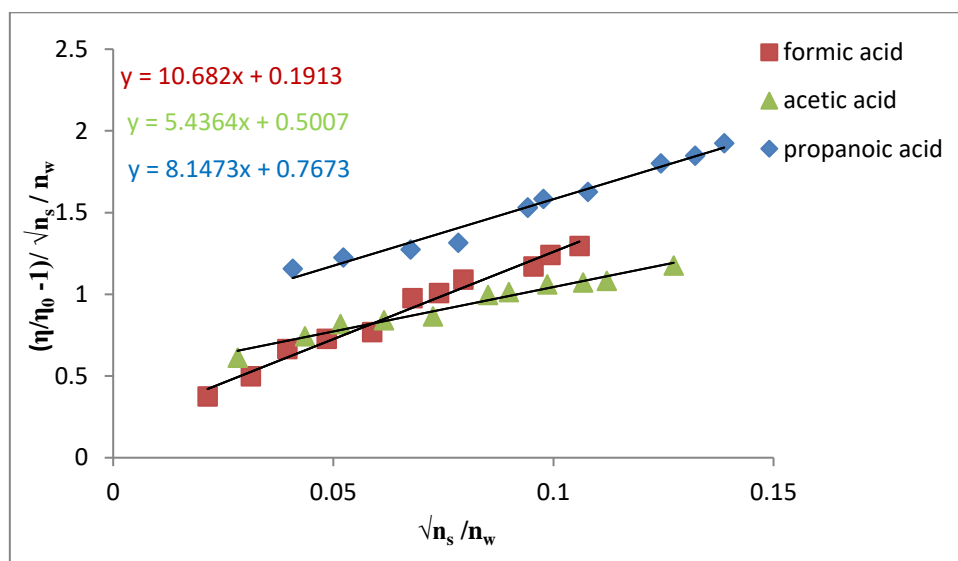


Figure 3: Modified Jone-Dole plot $(\eta/\eta_0-1)/\sqrt{n_s/n_w}$ versus $\sqrt{n_s/n_w}$ for carboxylic acids at 298.15 K

4. Volumetric studies

It can be safely concluded that the densities of the solution of the carboxylic acid have been employed for calculating the apparent molar volume (ϕ_v) of the solute based on equation 4 [33,34]

$$\phi_v = \frac{M}{d_0} + \frac{10^3(d_0-d)}{d_0 C} \dots\dots\dots (4)$$

Here, M stands for a molar solute mass, d and d_0 stand for densities ($gm.cm^{-3}$) of solution and pure solvent, respectively, and C stands for solute molarity (mol/L). Regarding three carboxylic acids, (ϕ_v) magnitudes have been determined at diverse concentrations; the values

obtained are given in Tables and plotted in Figure 4. The magnitudes of intercept and slope were estimated using Masson's relation given by Equation 5 [35-38].

$$\phi_v = \phi_v^\circ + S_v\sqrt{C} \quad \dots\dots\dots (5)$$

ϕ_v° = Limiting apparent molar volume.

S_v = Volumetric pairwise interaction coefficient.

For three carboxylic acids, ϕ_v° magnitudes are positive, suggesting a strong positive interaction of solute and solvent molecules. There is good solute-solute interaction present in aqueous solutions [39-42].

Table 4: The mutation of densities with a concentration of formic acid, acetic acid, and propanoic acid at temperature of 298.15 K

Formic acid			Acetic acid			Propanoic acid		
s. no.	Concentration (mol/L)	Density (gm/cm ³)	s. no.	Concentration (mol/L)	Density (gm/cm ³)	s. no.	Concentration (mol/L)	Density (gm/cm ³)
1	0.0000	0.99705	1	0.0000	0.99705	1	0.0000	0.99705
2	0.03951	0.99768	2	0.02665	0.99771	2	0.04113	0.99835
3	0.05836	0.99789	3	0.04604	0.99812	3	0.06225	0.99892
4	0.07081	0.99798	4	0.05963	0.99839	4	0.08188	0.99941
5	0.08516	0.99815	5	0.07911	0.99874	5	0.10112	0.99979
6	0.09841	0.99822	6	0.09789	0.99908	6	0.12115	1.00023
7	0.11602	0.99832	7	0.11787	0.99938	7	0.14049	1.00059
8	0.13034	0.99839	8	0.13744	0.99955	8	0.16224	1.00098
9	0.15022	0.99845	9	0.15076	0.99972	9	0.18183	1.00128
10	0.17022	0.99852	10	0.17073	0.99991	10	0.20172	1.00159
11	0.19033	0.99858	11	0.18532	1.00002	11	0.22066	1.00162
12	0.21031	0.99862	12	0.21118	1.00018	12	0.23398	1.00169

Table 5: Accounts ϕ_v of the Masson equation for aqueous formic acid, acetic acid, and to propanoic acid at 298.15 K

Formic acid			Acetic acid			Propanoic acid		
s. no.	\sqrt{C}	ϕ_v (cm ³ .mol ⁻¹)	s. no.	\sqrt{C}	ϕ_v (cm ³ .mol ⁻¹)	s. no.	\sqrt{C}	ϕ_v (cm ³ .mol ⁻¹)
1	0.19877	30.10729	1	0.16325	35.29401	1	0.20281	42.44938
2	0.24158	31.66076	2	0.21457	36.81174	2	0.24950	43.99846
3	0.26611	32.92388	3	0.24419	37.57407	3	0.28615	45.19871
4	0.29182	33.13619	4	0.28126	38.67482	4	0.31796	46.91314
5	0.31370	34.16659	5	0.31288	39.28921	5	0.34807	47.74289
6	0.34062	35.11018	6	0.34335	40.99954	6	0.37482	48.77911
7	0.36103	35.77636	7	0.37073	41.82722	7	0.40279	49.73614
8	0.38758	36.73968	8	0.38828	42.30116	8	0.42642	50.68277
9	0.41258	37.42394	9	0.41319	43.25472	9	0.44913	51.42523
10	0.43627	38.02151	10	0.43049	43.97736	10	0.46974	53.22191
11	0.45861	38.54789	11	0.45954	45.17846	11	0.48371	54.09914

Notes: $\phi_v^\circ = 23.846$, $\phi_v^\circ = 29.502$, $\phi_v^\circ = 33.983$, $S_v = 32.71$, $S_v = 33.315$, $S_v = 39.972$. C= molar concentration (mol/L)

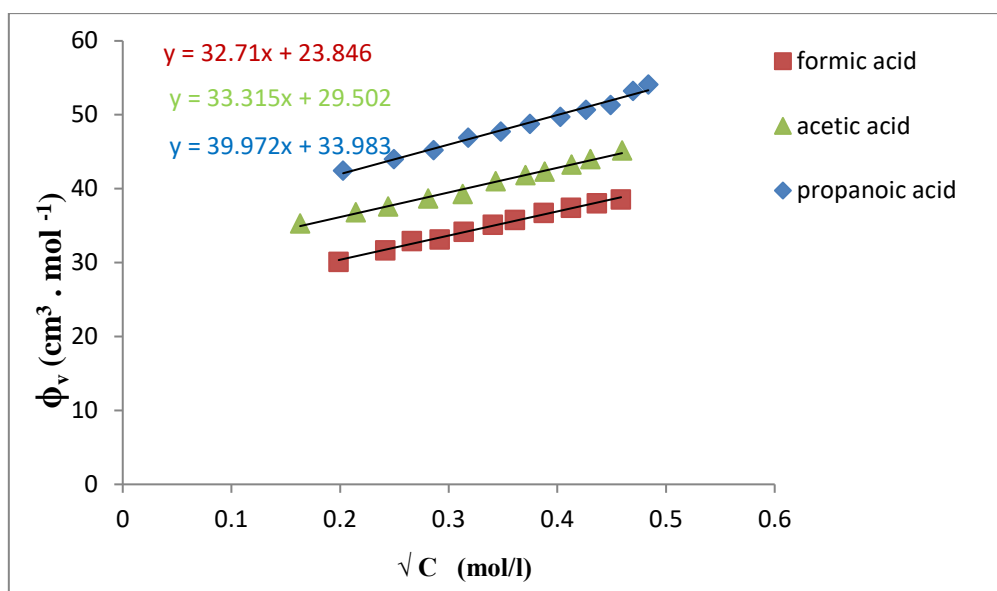


Figure 4: Masson plot molal volumes (ϕ_v) versus (\sqrt{C}) for carboxylic acids at 298.15 K.

By comparison, the results such as ϕ_v , S_v , and A and B coefficients in the present work with the other articles obtained and illustrated in Table 6. Solutions' viscosities rise with increasing solution concentrations. Propanoic acid was ultimately discovered to be the best acid due to the incredibly complicated interactions that exist between water and carboxylic acids. Through H-bonding, acids and water are both self-associated liquids. Except for formic acid, carboxylic acids have both a hydrophilic COOH group and a hydrophobic group [43].

Table 6: comparison the results such as ϕ_v , S_v , and A, B coefficients in the present work with the other article

Acid	Parameters	The present work	Reference 44	Reference 45	Reference 46	Reference 47
Acetic acid	ϕ_v° ($\text{cm}^3 \cdot \text{mol}^{-1}$)	29.502	51.884	-	51.737	-
	S_v	33.315	0.616	-	1.305	-
	A	-0.003	-	-	-	0.0030
	B	0.6884	-	-	-	0.295
Formic acid	ϕ_v° ($\text{cm}^3 \cdot \text{mol}^{-1}$)	23.846	-	35.035	36.134	-
	S_v	32.71	-	0.535	0.637	-
	A	-0.1825	-	-	-	0.0025
	B	1.0656	-	-	-	0.137
Propanoic acid	ϕ_v° ($\text{cm}^3 \cdot \text{mol}^{-1}$)	33.983	-	-	67.225	-
	S_v	39.972	-	-	1.686	-
	A	-0.0283	-	-	-	0.0032
	B	1.166	-	-	-	0.394

5. Conclusion

An analysis of the results suggests that the B-coefficient has been positive and reasonably high for carboxylic acids in the examined concentration range. This demonstrates the presence of strong ion-solvent interactions in dilute aqueous solutions. Additionally, the negative A-value for three carboxylic acids means that ion-ion or solute-solvent interactions have been very poor. For the dilute carboxylic acid due to hydrogen bond formation, the association

between viscosity data and solute concentration of polymolecular compounds suggested by Staudinger's was observed. The viscosity data matches the predictions for the Jone-Dole and reformed Jone-Dole equations.

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