

THERMODYNAMIC STUDY OF SOME ALCOHOLS IN DILUTE AQUEOUS SOLUTION

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ABSTRACT. An apparent molar volume ϕ_v of 1-pentanol, 1-hexanol, 1-heptanol, and 1-octanol in dilute aqueous solution has been particular for density measurements at 298.15 K. A restrictive apparent molar volumes ϕ_v° at infinite dilution of these compounds were investigated based on Masson's equation. Based on the Jone-Dole equation, A and B viscosity constants for four alcohols have been identified. This liquid offers resilient solute-solvent interaction. The modified Jone-Dole equation has also been employed with the experimental consequences using four liquids as solutes in dilute aqueous solutions.

Keywords: Alcohols, Apparent molar volume, Modified Jone-Dole equation.

INTRODUCTION

Several facts about serious water-solute interaction in solution chemistry have been based on the familiarity of apparent molar volume. Indeed, in extremely dilute aqueous solution, the dual features of apparent molar volume and viscosity were required to build up an understanding of inter-molecular interactions [1,2]. In this paper, our converge is about dilute aqueous solutions, that provide wide-ranging characteristics for the structures of the solution. Henceforth volumetric and viscometric investigations about these organic liquids were implemented in extremely dilute aqueous media [3-5].

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Alcohols are feasibly taken into consideration as derivatives of water in which an alkyl group substitutes one hydrogen atom. The unshared electron in an oxygen outer shell conveys significant characteristics in the structure of the alcohols. Alcohols are water-like in their natural characteristics since their hydroxyl ratio in the C-H bonding has been raised. Numerous reported papers about volumetric properties had discussed numerous mixes of alcohols and water.

Alcohols are applied as solvents, co-solvents, alcohols-water mixtures, at all times, acting as attention-grabbing due to their anomalous performance like the maximum presence of a viscosity-composition and lower partial molar volume [6-8] than their volume in the "pure" alcohol state [9-12]. Alcohols stand for industrial biological amphiphilic materials in a liquid state in accordance with the hydrogen bonding of their O-H clusters. They are self-associated and polar liquids, and they are of specific interest as alcohols are powerful liquids with a three-dimensional system of hydrogen bonds and can be connected with any other group taking several degrees of polar attraction [13-15]. Water molecules might be bound to the biological solvent in the widespread techniques. Alcohols remarkably vary from other biological solvents and from each other based on the degree and extent of self-association [16-18]. An important consideration was paid in the past for altering hydrogen-bonded structures of alcohol pure water in a mixing activity. Previously, the water-alcohol hydrogen bond was, in general, sturdier than the alcohol-alcohol bond. Introducing water into pure alcohols can collapse the self-association in alcohols. The new hydrogen bonds are feasibly made among water molecules and alcohols [19-21]. While explaining the volumetric properties of powerfully interconnected systems like alcohol-water combinations.

It is essential to adopt these consequences. Accordingly, we investigated, in this paper, the partial molar volume for water in several alcohols with the intention of providing a superior interpretation of these factors that contribute significantly to a volumetric performance of powerfully related mixtures [22,23]. The current work inspected experimental data of viscosities (η), and densities (ρ) at 298.15 K, for (1-pentanol, 1-hexanol, 1-heptanol, and 1-octanol) in dilute aqueous solutions which were used to calculate apparent molar volume (ϕv) and Jone-Dole coefficients.

RESULTS AND DISCUSSION

For all alcohols, 1-pentanol, 1-hexanol, 1-heptanol, and 1-octanol, the values under dissimilar concentrations in aqueous solution were perceived. The data for viscosity for each solute under dissimilar concentrations were employed to determine the interaction parameter in aqueous solution. The interaction parameters were obtained based on Jon-Dole's Eq. [24, 25].

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

Here, A and B stand for the constants regarding ion-ion besides ion-solvent interaction correspondingly, while C stands for a molar concentration. The B magnitudes were acquired based on linear plots between $(\eta/\eta_0 - 1)/\sqrt{C}$ and \sqrt{C} . These plots were depicted in Fig. 1. A and B coefficients were considered from the intercepts and slope for each biological material as specified in Table 1.

Table 1. A and B coefficient for aqueous 1-pentanol, 1-hexanol, 1-heptanol, and 1-octanol under 298.15 K based on Jones-Dole equation

1-Pentanol			1-Hexanol			1-Heptanol			1-Octanol		
S. no.	\sqrt{C}	$(\eta/\eta_0-1)/\sqrt{C}$	S. no.	\sqrt{C}	$(\eta/\eta_0-1)/\sqrt{C}$	S. no.	\sqrt{C}	$(\eta/\eta_0-1)/\sqrt{C}$	S. no.	\sqrt{C}	$(\eta/\eta_0-1)/\sqrt{C}$
1	0.19644	0.21507	1	0.20164	0.22776	1	0.21608	0.30998	1	0.24222	0.33496
2	0.22614	0.25108	2	0.22863	0.27785	2	0.24479	0.37821	2	0.28078	0.42552
3	0.26876	0.27805	3	0.27081	0.32189	3	0.28084	0.45296	3	0.31084	0.49166
4	0.30237	0.30863	4	0.31283	0.38898	4	0.31549	0.52559	4	0.34479	0.54626
5	0.34319	0.35785	5	0.33314	0.45326	5	0.33835	0.55329	5	0.36828	0.60984
6	0.36364	0.37625	6	0.36388	0.51145	6	0.37116	0.59611	6	0.39595	0.66435
7	0.39148	0.42231	7	0.39829	0.57651	7	0.39865	0.63933	7	0.42243	0.77332
8	0.42033	0.44948	8	0.42291	0.60763	8	0.42064	0.70802	8	0.44467	0.79493
9	0.43866	0.47522	9	0.44472	0.62554	9	0.43845	0.74498	9	0.46312	0.84831
10	0.45339	0.49896	10	0.46679	0.64587	10	0.47615	0.78227	10	0.48546	0.90922

In view of that, A= -0.008 (dm^{3/2}.mol^{-1/2}), A= -0.1115 (dm^{3/2}.mol^{-1/2}),
 A= -0.0651 (dm^{3/2}.mol^{-1/2}), A=-0.2443 (dm^{3/2}.mol^{-1/2}).
 B= 1.0908 (L.mol⁻¹), B= 1.6762 (L.mol⁻¹), B= 1.8116 (L.mol⁻¹),
 B= 2.3524 (L.mol⁻¹).
 Linearity=0.9899, 0.9886, 0.9919, 0.9938.
 C=molar concentration (mol/L)

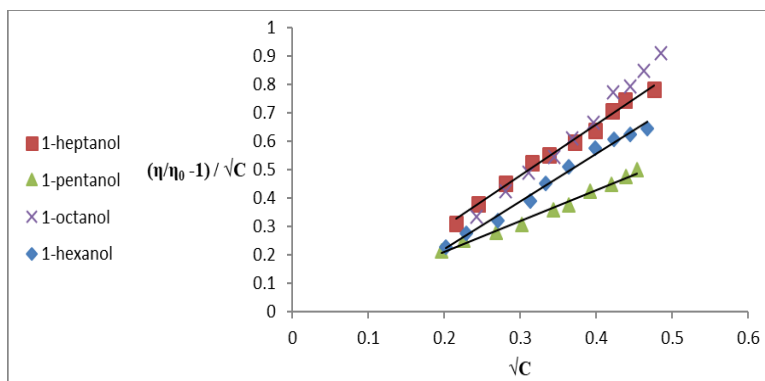


Figure 1. Jones-Dole plot \sqrt{C} versus $(\eta/\eta_0 - 1)/\sqrt{C}$ for alcohols at 298.

Table 2. Change of η/η_0 with concentration of 1-pentanol, 1-hexanol, 1-heptanol and 1-octanol under 298.15 K

1-Pentanol			1-Hexanol			1-Heptanol			1-Octanol		
S. no.	Concentration (mol/L)	η/η_0	S. no.	Concentration (mol/L)	η/η_0	S. no.	Concentration (mol/L)	η/η_0	S. no.	Concentration (mol/L)	η/η_0
1	0.03859	1.04225	1	0.04066	1.04996	1	0.04669	1.06698	1	0.05867	1.08113
2	0.05114	1.05678	2	0.05227	1.08432	2	0.05992	1.09258	2	0.07884	1.11948
3	0.07223	1.07473	3	0.07334	1.12851	3	0.07887	1.12721	3	0.09664	1.15282
4	0.09143	1.09332	4	0.09786	1.15334	4	0.09954	1.16582	4	0.11888	1.18834
5	0.11778	1.12282	5	0.11098	1.17565	5	0.11448	1.18719	5	0.13653	1.22459
6	0.13224	1.13682	6	0.13241	1.18611	6	0.13776	1.22121	6	0.15678	1.26305
7	0.15326	1.16558	7	0.15864	1.22558	7	0.15892	1.25487	7	0.17845	1.32667
8	0.17668	1.18893	8	0.17885	1.24772	8	0.17694	1.29782	8	0.19773	1.35348
9	0.19242	1.20846	9	0.19778	1.26537	9	0.19224	1.32664	9	0.21448	1.39287
10	0.20557	1.22623	10	0.21789	1.30112	10	0.22672	1.37248	10	0.23567	1.44139

Accordingly, η is the viscosity of solution and η_0 is the viscosity of water.

Evaluation of B coefficients for each alcohol was positive in aqueous solutions thereby signifying the existence of a strong ion-solvent interactions in the solution. These organic materials are like structure-makers in water. The A value gotten from all alcohols was negative and estimated for non-electrolytes as solute that stands for the ion-ion interaction measurement [26-

28]. A depiction of (η/η_0) versus concentration must be linear taking slope magnitude equivalent to B coefficient for non-electrolytes and the equation 2 applicability. The data from the experiments was employed for examining how the experimental consequences of viscosity agree with Eq.2 for non-electrolyte molecules. The magnitudes were shown in Table 2 and in Fig. 2.

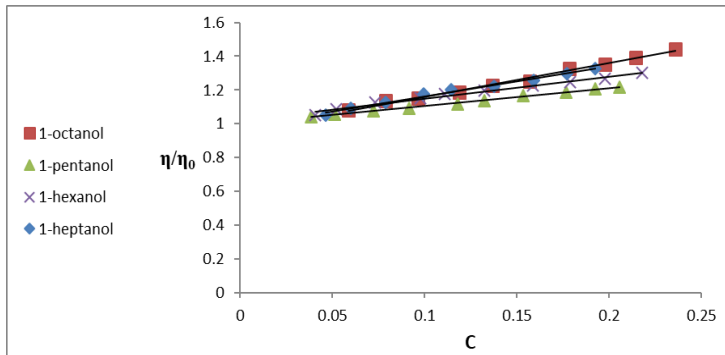


Figure 2. Plot (C) versus (η/η_0) for alcohols at 298.15 K

$$\eta/\eta_0 = BC+1 \dots\dots\dots (2)$$

Table 3. Ax and Bx amounts for aqueous 1-pentanol, 1-hexanol, 1-heptanol and 1-octanol under 298.15 K based on modified Jone-Dole equation

1-Pentanol			1-Hexanol			1-Heptanol			1-Octanol		
S. no.	$(\sqrt{X_s/X_w})$	$(\eta/\eta_0 - 1)/\sqrt{X_s/X_w}$	S. no.	$(\sqrt{X_s/X_w})$	$(\eta/\eta_0 - 1)/\sqrt{X_s/X_w}$	S. no.	$(\sqrt{X_s/X_w})$	$(\eta/\eta_0 - 1)/\sqrt{X_s/X_w}$	S. no.	$(\sqrt{X_s/X_w})$	$(\eta/\eta_0 - 1)/\sqrt{X_s/X_w}$
1	0.04788	0.88238	1	0.05248	0.95198	1	0.05884	1.13834	1	0.06158	1.31747
2	0.06102	0.93038	2	0.08616	0.97865	2	0.07969	1.16175	2	0.08929	1.33812
3	0.07631	0.97927	3	0.12149	1.05778	3	0.10658	1.19376	3	0.11169	1.36825
4	0.09097	1.02579	4	0.13982	1.09669	4	0.13437	1.23406	4	0.13359	1.40979
5	0.11607	1.05811	5	0.15772	1.11367	5	0.14899	1.25635	5	0.15576	1.44187
6	0.12399	1.10348	6	0.16362	1.13742	6	0.17061	1.29668	6	0.18021	1.45976
7	0.14508	1.14132	7	0.19159	1.17737	7	0.19344	1.31756	7	0.21636	1.50985
8	0.15993	1.18133	8	0.20479	1.20963	8	0.22082	1.34867	8	0.22856	1.54652
9	0.16951	1.22978	9	0.21421	1.23887	9	0.23343	1.39933	9	0.24763	1.58657
10	0.18081	1.25119	10	0.23773	1.26665	10	0.26264	1.41822	10	0.27509	1.60448

As clarified in Table 3, the magnitudes for concentration were used for calculating x_s and x_w in addition to the obtained date. The linear plot $(\sqrt{X_s/X_w})$ vs. $(\eta/\eta_0-1)/\sqrt{X_s/X_w}$ ratifies a veracity modified Jone-Dole Eq. as specified below.

Notes: $A_x= 0.7664$, $A_x= 0.8417$, $A_x= 1.0479$, $A_x= 1.2174$, $B_x= 2.6623$, $B_x= 1.7915$, $B_x=1.4203$, $B_x= 1.4169$. Linearity= 0.9911, Linearity= 0.9905, Linearity= 0.911, Linearity=0.9891

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

Where A_x and B_x stand for the coefficients. They represent the interactions measured among solute-solute and solute-solvent. A corresponding plot has been illustrated in Fig. 3. The positive magnitudes of A_x and B_x gotten in the paper indicate the existence of ion-solvent interaction and solute-solute interaction [29,30]. The concentration extent applied in the project was optimal for a veracity of Staudinger, Jone-Dole equation in addition to the modified Jone- Dole equation that behaves like a “structure maker” [31].

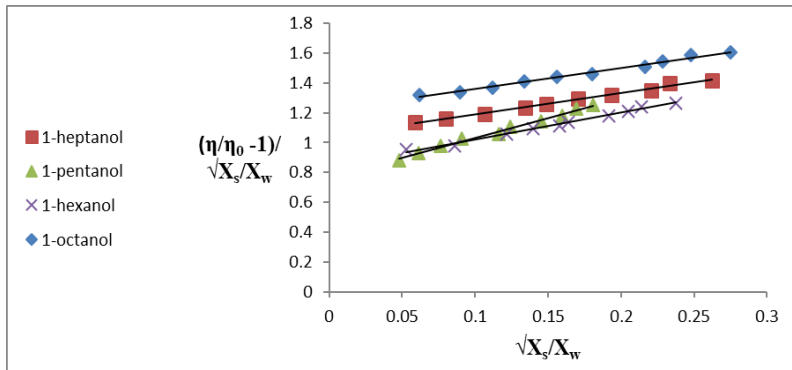


Figure 3. Modified Jone-Dole plot $\sqrt{X_s/X_w}$ versus $(\eta/\eta_0-1)/\sqrt{X_s/X_w}$ for alcohols at 298.15 K.

The apparent molar volumes (ϕ_v) of alcohols was determined based on the measured densities in dilute aqueous solution by [32-34].

$$\phi_v = \frac{M_s}{\rho_0} + \frac{1000(\rho_0-\rho)}{c} \dots\dots (4)$$

Where M_s represents the molecular weight of alcohol, C is an alcohol concentration in mol/L and ρ_0 stands for a density of a pure solvent. The computed amounts of apparent molar volume for 1-pentanol, 1-hexanol, 1-heptanol, and

1-octanol are given in Table 5 and plotted in Fig.4. The magnitudes for apparent molar volumes (standard partial molar volume) ($V\phi^\circ$) have been determined through least-squares fit to Masson's equation at infinite dilutions [35-37].

Table 4. A change of densities with concentration of 1-pentanol, 1-hexanol, 1-heptanol and 1- octanol under 298.15 K

1-Pentanol			1-Hexanol			1-Heptanol			1-Octanol		
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)	S. no.	Concentration (mol/L)	Density (gm/cm ³)
1	0.0000	0.997046	1	0.0000	0.997046	1	0.0000	0.997046	1	0.0000	0.997046
2	0.03859	0.99908	2	0.04060	0.99966	2	0.04669	1.00043	2	0.05867	1.00206
3	0.05114	0.99969	3	0.05227	1.00031	3	0.05992	1.00263	3	0.07884	1.00356
4	0.07223	1.00067	4	0.07334	1.00154	4	0.07887	1.0040	4	0.09664	1.00487
5	0.09143	1.00153	5	0.09786	1.00292	5	0.09954	1.00489	5	0.11888	1.00652
6	0.11778	1.00272	6	0.11098	1.00366	6	0.11448	1.00632	6	0.13653	1.00786
7	0.13224	1.00331	7	0.13241	1.00474	7	0.13778	1.00641	7	0.15678	1.00919
8	0.15326	1.00421	8	0.15864	1.00605	8	0.15892	1.00764	8	0.17845	1.01069
9	0.17668	1.00506	9	0.17885	1.00708	9	0.17694	1.00862	9	0.19773	1.01203
10	0.19242	1.00562	10	0.19778	1.00801	10	0.19224	1.00946	10	0.21448	1.0294
11	0.20556	1.00601	11	0.21789	1.00891	11	0.22672	1.01142	11	0.23567	1.01425

Table 5. Amounts ϕ_v of the Masson equation for aqueous 1-pentanol, 1-hexanol, 1-heptanol and 1-octanol under 298.15 K

1-Pentanol			1-Hexanol			1-Heptanol			1-Octanol		
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)	S. no.	\sqrt{C}	ϕ_v (cm ³ mol ⁻¹)
1	0.19644	35.31842	1	0.20164	37.69516	1	0.21608	43.73795	1	0.24222	46.50937
2	0.22614	36.30691	2	0.22863	39.51978	2	0.24479	44.77769	2	0.28078	47.19421
3	0.26876	37.52471	3	0.27081	40.64163	3	0.28084	45.74988	3	0.31084	48.77553
4	0.30237	38.90222	4	0.31283	41.86316	4	0.31549	46.52436	4	0.34479	49.97424
5	0.34319	39.72469	5	0.33314	42.23455	5	0.33835	47.92414	5	0.36828	50.39317
6	0.36364	40.50717	6	0.36388	43.67544	6	0.37116	48.39512	6	0.39595	52.06325
7	0.39148	41.09442	7	0.39829	44.96438	7	0.39865	49.64078	7	0.42243	52.97686
8	0.42033	42.44203	8	0.42291	45.57028	8	0.42064	50.83599	8	0.44467	53.58082
9	0.43866	43.21622	9	0.44472	46.19244	9	0.43845	51.62481	9	0.46312	55.14723
10	0.45339	44.14778	10	0.46679	47.13124	10	0.47615	52.69066	10	0.48546	56.21232

Notes: $\phi_v^\circ = 28.801$, $\phi_v^\circ = 31.326$, $\phi_v^\circ = 36.017$, $\phi_v^\circ = 36.224$, $S_v = 32.655$, $S_v = 33.75$, $S_v = 34.775$, $S_v = 40.066$. C= molar concentration (mol/L)

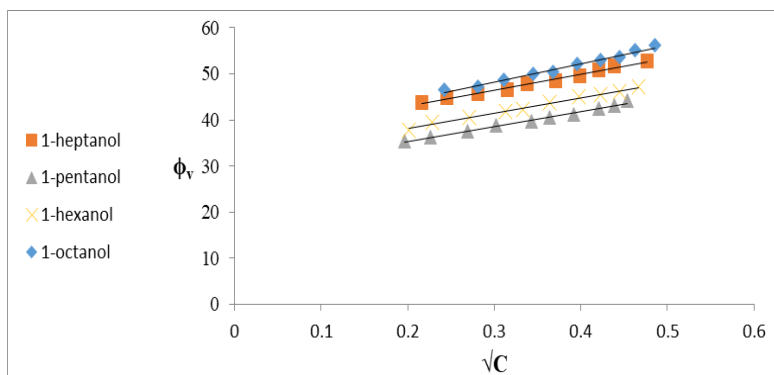


Figure 4. Masson plot apparent molal volumes (ϕ_v) versus (\sqrt{C}) for alcohols at 298.15 K

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

Where S_v is the experimental slope indicating solute-solute interaction and the (ϕ_v°) values are separated solute-solute interaction at infinite dilution and only inverted the presence of solute-solute interaction among solute as well as solvent molecules. The ϕ_v magnitude is positive specifying the positive interaction among solute and solvent molecules [38, 39]. The S_v is positive signifying which ions possess the worthy complex ion-forming and resilient ion-ion interacting level in aqueous solution [40, 41].

CONCLUSIONS

In this analysis, density and viscosity parameters were used to investigate the existence of interactions in alcohol-water. The good value of the B-coefficient suggests that ion-solvent interaction is present in any system and it was concluded that there is a relationship between alcohols and water molecules because of hydrogen bonding. Accordingly, it stands for the structure maker in the aqueous solution. It can be said that the proposed modified Jon-Dole equation in this study can be a model for gaining more information in the field of molecular interaction studies.

EXPERIMENTAL

Alcohols (1-pentanol, 1-hexanol, 1-heptanol, and 1-octanol) were provided by Aldrich company with 98% purity. The viscosity measurements as a suspended level Ubbelohde viscometer in a bath adjusted to ± 0.01 K at

298.15 k to determine the viscosities. Headed for giving the ending magnitudes, the experiments were repeated, at least three times, before the results were fixed.

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