International Journal of Current Advanced Research
ISSN: O: 2319-6475, ISSN: P: 2319-6505, Impact Factor: SJIF: 5.995
Available Online at www.journalijcar.org
Volume 6; Issue 12; December 2017; Page No. 8359-8361
DOI: http://dx.doi.org/10.24327/ijcar.2017.8361.1345

Research Article

EXCESS AND APPARENT MOLAR VOLUMES OF ANIONIC AND CATIONIC SALTS IN AQUEOUS AND METHANOLIC SOLUTIONS AT 303.15 K

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ARTICLE INFO

Article History:
Received 15th September, 2017
Received in revised form 25th October, 2017
Accepted 23rd November, 2017
Published online 28th December, 2017

Key words:

Surfactants, Solvents, Excess and Apparent Molar Volume, solute-solvent and solute-solute interactions.

ABSTRACT

The excess and apparent molar volumes of aqueous and methanolic solutions of tetra butyl ammonium hydrogen sulphate (TBAHS) and tetra butyl ammonium chloride(TBAC) including those of the pure liquids (water and methanol) have been derived at 303.15 K over a broad range of composition using experimentally measured parameters. The derived parameters are plotted against molarities of the solutions and an attempt has been made to study the solute –solute and solute – solvent interactions involved in the system. The excess and apparent molar volume values are found to be negative for all the mixtures at the study temperature thus showing increased stability.

INTRODUCTION

Thermodynamic properties and excess molar volumes at various concentrations are required for the development of reliable predictive models for systems containing ionic liquids. An anionic fluid is definite as a salted with a melting temperature lower the boiling point of water. Generally of the salts recognized in the literature as ionic fluid at room temperature, and regularly at significantly minor temperature[1]. For all the systems studied, the excess molar volumes were negative over the entire composition range at desired temperatures. The excess properties were found to be either negative or positive depending on the nature of molecular interactions and structural effects of the liquid mixtures[2]. In recent years, there has been renewed interest in theoretical and experimental investigations of the excess thermodynamic properties of binary mixtures.

The study of properties of liquid mixtures and solutions finds direct applications in chemical and biochemical industry[3]. A survey of literature indicates that Radhamma et al. reported the excess molar volumes of binary mixtures of Dimethyl sulfoxide with Chloroethanes at 303.15K[4], Oana Cioclirlan and Olga Iulian[5] Harish Kumar and Deepika[6] Vijayakumar Naidu et al.[7], Fabio Comelli et al.[8] and others[9-13] reported the various excess properties of the liquid mixtures containing Dichloromethane, 1,2-Dichloroethane, Dimethyl sulfoxide as one component.

The present work describes the computational of excess molar volumes (V_m^E) and apparent molar volume (V_ϕ) of TBAHS & TBAC in methanol and waters, over the entire mole fraction range up to infinity at temperature 303.15 K, using density data which were determined experimentally.

MATERIALS AND METHODS

Materials

The surfactants used were the following: tetra butyl ammonium hydrogen sulphate (TBAHS) and tetra butyl ammonium chloride (TBAC). The densities of the pure fluid and the mixtures were determined at 303.15K and at atmospheric pressure. The ionic liquid, methanol and water were used further purification.

A stockpile solution for each salt was ready by mass and the effective solutions were obtained by mass of chemical used, it was complete by compare the dilution. The fluid were store in dark bottles over 0.4 nm molecular sieve to reduced water content and were partially degassed with a vacuum pump. The cleanness of each compound was chequered by gas chromatography and indicate that the mole fraction cleanness was superior than 0.99. The cleanness of the clean solvents was also resolute by comparison of the experimental density values with literature density values.

Apparatus and methods

The density of the pure module and their mixture were considered with the bi-capillary pyknometer. The pyknometer was calibrated with double distilled water at atmospheric

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pressure. The fluid mixtures were arranged by mass in every air fixed bottle using an electronically balance model SHIMADZUAX – 200 correct to inside 0.1 mg. The standard doubt in the composition of the mixture was approximate to be less than ±0.0001. The density values with doubt of $\pm1\times10^{-4}$ $g.cm^{-3}$ and reproducible to $\pm6\times10^{-4}$ $g.cm^{-3}$.

Table 1 Densities (ρ, $g.cm^{-3}$) of pure liquid and comparison with literature at 303.15K

Liquid	Density(ρ)	
	Experimental	Literature
Water	0.9960	0.9960
Methanol	0.7814	0.782

RESULT AND DISCUSSION

Excess molar volume

The investigational results and the available literature[14] values of density of the clean fluid at the 303.15K temperature and atmospheric pressure are reported in table 1. The excess molar volumes of the studied systems were calculated from the experimental density values, applying the Equation 1.

$$V_m^E = x_1M_1\,(1/\rho+1/\rho_1) + x_2M_2\,(1/\rho+1/\rho_2) \qquad ....1$$

Where ρ_1 and ρ_2 are the densities of the pure components, x_1 and x_2 is mole fractions, M_1 andM_2 are molar masses, and ρ is the density of the mixture. The excess molar volumes of studied system at 303.15K temperature are negative indicating specific solute-solute and solute-solvent interaction.

Apparent molar volume

The apparent molar volume V_ϕ of the TBAC and TBAHS in aqueous solvents was considered by using the relation:

$$V_\phi = \frac{M}{\rho} - \frac{10^3\,(\rho-\rho_o)}{m\rho\rho_o} \qquad ....2$$

Where m is the molality of the solute (TBAC and TBAHS), ρ and ρ_o are the densities of the solution and the solvents, respectively; M is the molar mass of the solute (TBAC and TBAHS).

Table 2 Conc. In mole fractions, density and excess molar volumes for TBAHS and TBAC in aqueous and methanol at 303K

x_1	ρ	V_m^E	x_1	ρ	V_m^E
		TBAHS			
0.0004	0.7824	-0.00067	0.0001	0.9966	-0.0036
0.00081	0.7844	-0.0016	0.0003	0.9971	-0.0079
0.0012	0.7862	-0.0022	0.0005	0.9976	-0.0010
0.0016	0.7873	-0.0026	0.0007	0.9982	-0.014
0.0020	0.7889	-0.0034	0.0009	0.9989	-0.018
0.0024	0.7904	-0.0038	0.0010	0.9994	-0.022
0.0026	0.7916	-0.0042	0.0012	1.0000	-0.026
0.0032	0.7928	-0.0045	0.0014	1.0006	-0.029
0.0036	0.7940	-0.0050	0.0016	1.0012	-0.032
0.0040	0.7950	-0.0052	0.0018	1.0018	-0.036
		TBAC			
0.0004	0.7824	-0.00067	0.0001	0.9966	-0.0036
0.00081	0.7844	-0.0016	0.0003	0.9971	-0.0079
0.0012	0.7862	-0.0022	0.0005	0.9976	-0.0010
0.0016	0.7873	-0.0026	0.0007	0.9982	-0.014
0.0020	0.7889	-0.0034	0.0009	0.9989	-0.018
0.0024	0.7904	-0.0038	0.0010	0.9994	-0.022
0.0026	0.7916	-0.0042	0.0012	1.0000	-0.026
0.0032	0.7928	-0.0045	0.0014	1.0006	-0.029
0.0036	0.7940	-0.0050	0.0016	1.0012	-0.032
0.0040	0.7950	-0.0052	0.0018	1.0018	-0.036

Table 3 Density and apparent molar volumes for TBAHS in aqueous and methanol at 303K

m	ρ	Vϕ	M	ρ	Vϕ
		TBAHS			
0.0127	0.7830	-165.001	0.0100	0.9966	-42.545
0.0255	0.7841	-132.208	0.0200	0.9971	-37.503
0.0385	0.7850	-113.025	0.0301	0.9976	-35.468
0.0511	0.7873	-147.19	0.0401	0.9982	-37.244
0.0639	0.7889	-150.217	0.0502	0.9989	-40.331
0.0767	0.7903	-147.619	0.0602	0.9994	-39.617
0.0895	0.7916	-143.966	0.0702	1.0000	-39.971
0.102	0.7928	-140.247	0.0808	1.0006	-40.231
0.115	0.7940	-136.358	0.0903	1.0012	-40.448
0.127	0.7950	-132.279	0.100	1.0018	-40.618
		TBAC			
0.0127	0.7824	-0.00067	0.0100	0.9966	-42.545
0.0255	0.7844	-0.0016	0.0200	0.9971	-37.503
0.0385	0.7862	-0.0022	0.0301	0.9976	-35.468
0.0511	0.7873	-0.0026	0.0401	0.9982	-37.244
0.0639	0.7889	-0.0034	0.0502	0.9989	-40.331
0.0767	0.7904	-0.0038	0.0602	0.9994	-39.617
0.0895	0.7916	-0.0042	0.0702	1.0000	-39.971
0.102	0.7928	-0.0045	0.0808	1.0006	-40.231
0.115	0.7940	-0.0050	0.0903	1.0012	-40.448
0.127	0.7950	-0.0052	0.100	1.0018	-40.618

The plot of excess molar volume for aqueous and methanolic system studied vs. the mole fraction of the whole composition range is shown in figure 1&2. The excess molar volume for all system studied are negative, contributed by the chemical or specific intermolecular interaction that result in the excess volume. In aqueous solution the TBAHS and TBAC show almost equal results. As the mole fraction increases, excess molar volumes get decrease. The curves obtained are mostly negative and arise from interstitial accommodations of mixing components because of the difference in molar volume[16].

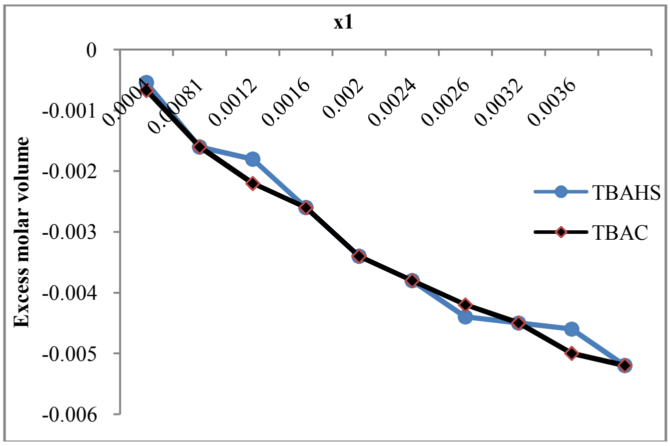

Figure 1 the excess molar volume against the mole fraction for TBAC and TBAHS in methenol at 303.15K.

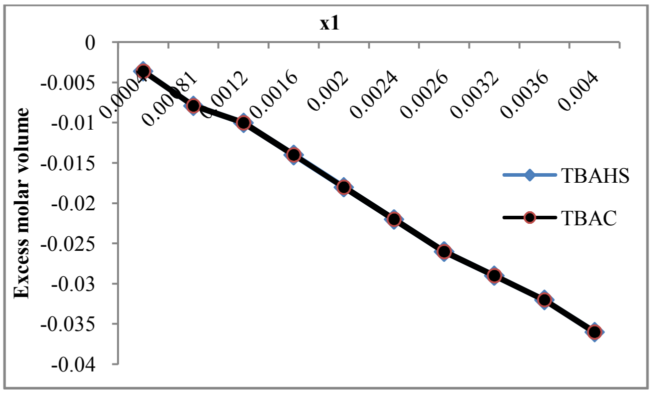

Figure 2 the excess molar volume against the mole fraction for TBAC and TBAHS in water at 303.15K.

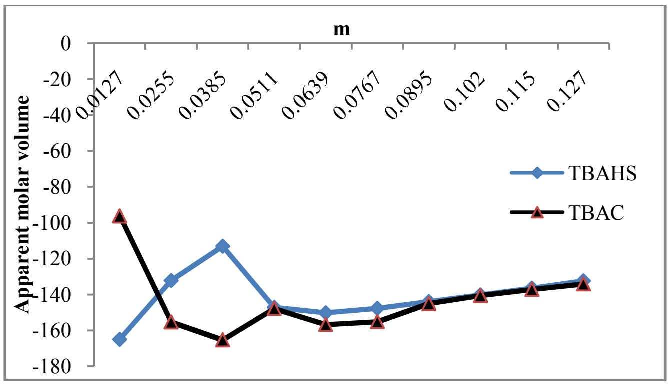

Figure 3 the apparent molar volume against the molarities for TBAC and TBAHS in methanol at 303.15K.

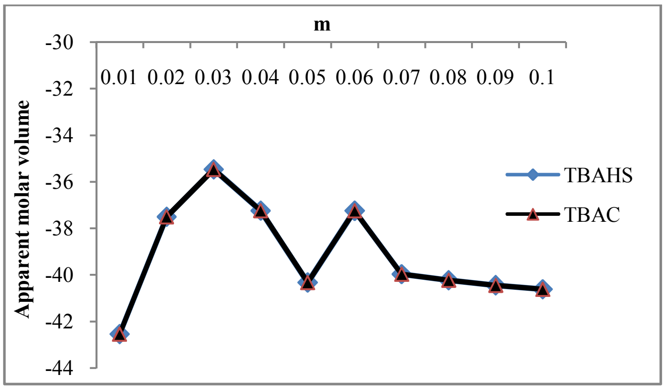

Figure 4 the apparent molar volume against the molarities for TBAC and TBAHS in water at 303.15K.

Figure 3 show variation of apparent molar volumes for the system TBAHS and TBAC in methanol. From mole fractions 0.0127 to 0.0511 the two salts show opposite behaviour, but after 0.0511 mole fraction concentrations, the two salts show almost same trend. The opposite behaviour can be explained in term of hydrogen bonding and chain length of anion in methanol solution. Figure 4 show the variation of apparent molar volume of TBAHS and TBAC in water against mole fraction, both of the curves show similar trends with some broad peaks which can be attributed to micellar structures.

CONCLUSION

The excess molar volume values decreases with increases chain length, from the experimental data the excess and apparent molar volume are calculated. The result obtained from the excess molar volume and apparent molar volume is found to be negative for all mixture at temperature study. The show that in water solute-solvent interaction is lower than that in methanol and is affected by change the anion while solute-solute interaction is not affected by changing the solvent.

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