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RESEARCH ARTICLE

Volumetric Properties of Aqueous Sodium Salt of Amino Acids as CO_2 Capture Solvent

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Abstract

Objectives: To produce new and accurate data of density of aqueous solution of amino acid salts at different temperatures and to correlate it with molality. **Methods**: The densities of aqueous solutions of sodium salts of Amino acids such as L-cysteine, L-leucine, L-proline and L-valine have been measured using double-arm Pycnometer, placed in a transparent glass-walled water bath having thermal stability of (0.01 K) at concentrations range (0.01 to 0.15) mol L^{-1} and at 298.15, 303.15, 308.15, and 313.15 K. From density data ahead, apparent molar volumes (V_ϕ), the partial molar volumes ($V_\phi{}^0$), expansion coefficient (E^∞) and Hepler's constant $\left(\partial^2 V_\phi 0/\partial T^2\right)$were calculated and analysed on the basis of the intermolecular interaction and molecular structure. **Findings:** The densities are observed to increase with concentration and decrease with increasing temperature. The positive values of partial molar volume ($V_\phi{}^0$) indicate strong sodium amino acids -water interactions. **Novelty:** For studied aqueous sodium salt solution of Amino acids, such properties have not yet been reported in the open literature and at such a lower concentrations range (0.01 to 0.15) mol L^{-1}.

Keywords: Density; Sodium Salt Amino Acid; Apparent Molar Volume; Helper's Constant

1 Introduction

The main contributor for adverse effect on climate is excessive CO_2 emissions due to fossil fuel combustion, and other relative activities to meet the increasing energy demand[(1)]. Therefore, separation of carbon dioxide (CO_2) from a process gas stream before entering the atmosphere, is an important part in most industrial operations and is also important from the point of view of economical and/or environmental aspects. Among CO_2 capture technologies, chemical absorption method using a suitable solvent has been extensively applied for CO_2 removal.

In such operations, alkanolamine-based absorbents and their combinations with other compounds are being used extensively[(2)]. Alkanolamines due to few demerits[(3)] restrict their use for CO_2 removal processes. Alkanolamines, which are currently

utilised, could be replaced with aqueous alkaline salts of amino acids. Alkaline salt solutions of amino acids exhibit similar action toward CO_2 in flue gas because amino acid salts have the same amine functionality as alkanolamines[4]. Despite being expensive than alkanolamines, amino acids have several special benefits, such as resistance to oxidative deterioration[5], negligible volatility, and quick absorption rates[6].

Physicochemical property such as density of absorbents are necessary for detailed characterization of the solvent for CO_2 capture and they are required in the process modelling, simulation and construction of gas–liquid contactor for CO_2 absorption and regeneration[7–9]. These details are also required to extrapolate chemical reaction kinetics from experiments on CO_2 absorption rates[10].

Many physicochemical studies of amino acids salt solutions have been presented density data previously but all at higher concentrations and using different method. To the best of our knowledge for aqueous sodium salt solutions of cysteine, leucine, proline, and valine such data have not yet been reported in the open literature at such lower concentrations range (0.01 to 0.15) mol L^{-1}. Thus, in the present work, we presented new experimental data on density and apparent molar volumes (V_ϕ), the partial molar volumes ($V_\phi{}^0$), expansion coefficient (E^∞) and Hepler's constant $\left(\partial^2 V_\phi 0/\partial T^2\right)$of aqueous sodium salt solutions of amino acids. Another aim of this work was to represent the experimental values as a function of temperature and concentration using suitable correlations, which can be useful in calculations for the design of processes utilizing the studied solvents.

2 Methodology

2.1 Materials and amino acid salt preparation

The amino acids L-cysteine (CAS No. 52-90-4, 99.0% purity) and L-leucine (CAS No. 61-90-5, 99.0% purity) were purchased from LOBA CHEMIE PVT. LTD., while L-proline (CAS No. 147-85-3, 99.0% purity) and L-valine (CAS No. 72-18-4, 99.0% purity) were supplied by S D Fine-Chem Ltd, India. Sodium hydroxide (CAS No. 1310-73-2, GR, 98 % purity) was purchased from Merck. The aqueous amino acid salt solutions were prepared on weight by weight method by neutralizing amino acid dissolved in triply distilled water with an equimolar amount of NaOH[11]. Weighing was done on electronic balance accurate to 1 x 10^{-4} g.

2.2 Reaction of CO2 with aqueous Na- salt of amino acid

The neutralised sodium salts of amino acids react with CO_2 in a similar manner to that of "regular" a primary or secondary amines, i.e., by forming carbamate and bicarbonate.

Preparation of amino acid salt

$$NaOH + {}^{-}OOC - CHR - NH_3{}^{+} \longrightarrow Na^{+}{}^{-}OOC - CHR - NH_2 + H_2O$$

Carbamate formation (like in primary and secondary amines)

$$CO_2 + {}^{-}OOC - CHR - NH_2 \longleftrightarrow \left({}^{-}OOC - CHR - NH - COO^{-}\right) + {}^{-}OOC - CHR - NH_3{}^{+}$$

Carbamate hydrolysis

$$\left({}^{-}OOC - CHR - NH - COO^{-}\right) + H_2O \longleftrightarrow {}^{-}OOC - CHR - NH_2 + HCO_3^{-}$$

The reaction between a particular amino acid salt and CO_2 is influenced by a number of variables, such as the amino acid's structure and on the chemical environment of amine group in a single molecule.

2.3 Density measurement

The densities were measured using a 15-cm^3 double-arm bi-capillary Pycnometer[12]. Pycnometer was dipped in a transparent glass-walled water bath with a thermal stability of ±0.01 K using a thermostat for maintaining the constant temperature. With the help of triple-distilled water and pure solvents, the pyrometer calibration was done. The densities of sodium amino acid salt(Na-AAS) solutions in water were calculated using the same methods. All of the measurements were obtained for concentrations range of 0.01 to 0.15 m and at the following temperatures: 298.15, 303.15, 308.15, and 313.15 K.

3 Results and Discussion

The measured density values for aqueous solutions of Na-AAS at concentrations ranging between 0.01 to 0.15 m and at temperatures 298.15, 303.15, 308.15, and 313.15 K are presented in Table 1. The densities are observed to increase with concentration (molality) and decreases with rise in temperature.

By using experimental density data, the apparent molar volumes[13,14] of Na-AAS solutions were calculated by the following Equation (1).

$$V_\phi = M/\rho^- \{(\rho^- \rho_0)/(m\rho\rho_0)\} \quad (1)$$

where M and m are the molar mass of the solute(Na-AAS) and molality of the Na-AAS solutions, whereas ρrepresents density of the solution and $\rho_0$represents density of solvent. The apparent molar volumes of all studied Na-salt of amino acid solutions are placed in Table 2 .

Following observations can be seen from Table 2, Figures 1, 2, 3 and 4, it is observed that:

i. For all studied Na-AAS solutions, the apparent molar volume increase with molality of the solutions.

ii. Apparent molar volume increase with increasing temperature for all studied Na-AAS aqueous solutions.

Equation (2) is used to correlate values of V_ϕ with molality[15].

$$\left[V_\phi = V_\phi^0 + V_s m^{0.5}\right] \quad (2)$$

where $V_\phi{}^0$, V_s and m are the partial molar volume, solute-solute interaction parameter and molality, respectively. For calculating $V_\phi{}^0$ and $V_s$values the least square method was employed.

Both $V_\phi{}^0$ and V_s values increases as temperature increases. This indicates that with increase in the temperature, the electrostriction effect of water reduces and water molecules in secondary solvation layer release into the bulk of the water. All the values of ($V_\phi{}^0$) are positive which indicates strong (Na-AAS)-water interactions. $V_\phi{}^0$ is an important parameter that shows the solute-solvent interactions.

The partial molar volumes at same temperature of studied sodium salt of amino acids is observed to increase in the order:

$V_\phi{}^0$(Na-leucinate) > $V_\phi{}^0$ (Na-valinate) > $V_\phi{}^0$ (Na-prolinate) > $V_\phi{}^0$ (Na-cysteinate)

Variation of $V_\phi{}^0$ with the temperature can be explained by Equation (3).

$$\left[V_\phi 0 = a_0 + a_1 T + a_2 T^2\right] \quad (3)$$

where a_0, a_1 and a_2 are constants and their values were calculated using Scilab application.

The partial molar expansion (E^∞) is obtained from expression 3 on differentiation with respect to temperature.

$$E^\infty = \left(\partial V_\phi 0/\partial T\right) = (a_1 + 2a_2 T) \quad (4)$$

E^∞ values are positive and increases with increase in temperature. The positive values of E^∞ indicate strong solute (amino acid salt)-solvent(water) interactions in all investigated amino acids salt solutions.

The Hepler's constant $\left(\partial^2 V_\phi 0/\partial T^2\right)$ [16] is helpful to understand the structure making/breaking behavior of the solute which is calculated by the following expression (5).

$$\left[\left(\partial^2 V_\phi 0/\partial T^2\right) = 2a_2\right] \quad (5)$$

The Hepler's constant $\left(\partial^2 V_\phi 0/\partial T^2\right)$ values for all studied sodium salt of amino acids shows the following trend:

$\left(\partial^2 V_\phi^\circ/\partial T^2\right)$ (Na-leucinate) < $\left(\partial^2 V_\phi^\circ \partial T^2\right)$ (Na-valinate) < $\left(\partial^2 V_\phi^\circ/\partial T^2\right)$ (Na-prolinate) < $\left(\partial^2 V_\phi^\circ/\partial T^2\right)$ (Na-cysteinate)

Table 3 collectively shows the values of partial molar volumes($V_\phi{}^0$), expansion coefficient (E^∞) and Hepler's constants. The variation of $V_\phi{}^0$ vs temperature (T) of all investigated Na-amino acid is linear. The positive values of Hepler's constants suggest structure making behavior of solute in solution. All investigated amino acids salts shows the structure making effect in their solutions.

Table 1. Densities (ρ/ kg.m^{-3}) of sodium cysteinate, sodium leucinate, sodium prolinate and sodium valinate at different temperatures

m(kg.mol^{-1})	ρ (kg.m^{-3})				m(kg.mol^{-1})	ρ (kg.m^{-3})			
	298.15 K	303.15 K	308.15 K	313.15 K		298.15 K	303.15 K	308.15 K	313.15 K
Sodium cysteinate					**Sodium leucinate**				
0	997.044	995.646	994.032	992.211	0	997.044	995.646	994.032	992.211
0.00975	997.721	996.322	994.706	992.882	0.01002	997.497	996.097	994.48	992.656
0.03061	999.163	997.762	996.141	994.311	0.03050	998.417	997.013	995.39	993.559
0.05147	1000.598	999.195	997.569	995.733	0.05098	999.330	997.922	996.293	994.456
0.07099	1001.935	1000.530	998.900	997.058	0.06973	1000.161	998.749	997.114	995.271
0.09091	1003.294	1001.887	1000.250	998.404	0.08976	1001.043	999.627	997.986	996.137
0.11083	1004.648	1003.239	1001.600	999.745	0.10979	1001.920	1000.500	998.853	996.998
0.13075	1005.997	1004.586	1002.940	1001.081	0.13074	1002.832	1001.408	999.755	997.893
0.15066	1007.341	1005.927	1004.280	1002.410	0.15169	1003.739	1002.311	1000.65	998.783
Sodium prolinate					**Sodium valinate**				
0.01179	997.683	996.284	994.668	992.844	0.00990	997.515	996.115	994.499	992.675
0.03411	998.886	997.485	995.865	994.035	0.02581	998.268	996.865	995.245	993.417
0.05323	999.911	998.508	996.884	995.050	0.04506	999.174	997.767	996.143	994.309
0.06950	1000.779	999.375	997.748	995.909	0.07777	1000.702	999.288	997.658	995.814
0.09007	1001.872	1000.466	998.835	996.991	0.09722	1001.604	1000.187	998.552	996.702
0.11114	1002.986	1001.578	999.944	998.094	0.11135	1002.257	1000.837	999.199	997.345
0.12918	1003.936	1002.527	1000.890	999.034	0.13112	1003.167	1001.743	1000.100	998.240
0.15700	1005.394	1003.981	1002.340	1000.477	0.15192	1004.119	1002.690	1001.040	999.177

Table 2. Apparent molar volume (V_ϕ /m^3•mol^{-1}) of sodium cysteinate, sodium leucinate, sodium prolinate and sodium valinate in water at different temperatures

m (kg.mol^{-1})	10^6• V_ϕ (m^3•mol^{-1})				m (kg.mol^{-1})	10^6• V_ϕ (m^3•mol^{-1})			
	298.15 K	303.15 K	308.15 K	313.15 K		298.15 K	303.15 K	308.15 K	313.15 K
Sodium cysteinate					**Sodium leucinate**				
0.00975	73.6670	73.7756	73.9893	74.3090	0.01002	108.0824	108.3717	108.7769	109.1976
0.03061	73.7716	73.8761	74.1141	74.4206	0.03050	108.1769	108.4638	108.8655	109.3159
0.05147	73.8420	73.9460	74.1890	74.4933	0.05098	108.2540	108.5409	108.9424	109.3793
0.07099	73.8965	74.0023	74.2378	74.5469	0.06973	108.3046	108.5965	109.0057	109.4450
0.09091	73.9441	74.0506	74.2920	74.6028	0.08976	108.3583	108.6505	109.0599	109.4963
0.11083	73.9840	74.0909	74.3363	74.6482	0.10979	108.4036	108.6961	109.1059	109.5407
0.13075	74.0197	74.1271	74.3753	74.6882	0.13074	108.4461	108.7375	109.1455	109.5849
0.15066	74.0487	74.1631	74.4135	74.7338	0.15169	108.4830	108.7737	109.1807	109.6236
Sodium prolinate					**Sodium valinate**				
0.01179	82.9459	83.0712	83.2890	83.6000	0.00990	91.6396	91.9049	92.1809	92.5702
0.03411	83.0435	83.1724	83.3971	83.7184	0.02581	91.7235	91.9808	92.2881	92.6457
0.05323	83.0999	83.2352	83.4724	83.7742	0.04506	91.7941	92.0579	92.3550	92.7308
0.06950	83.1477	83.2756	83.5123	83.8294	0.07777	91.8886	92.1592	92.4406	92.8247
0.09007	83.1954	83.3260	83.5648	83.8788	0.09722	91.9383	92.1987	92.4910	92.8782
0.11114	83.2417	83.3737	83.6040	83.9240	0.11135	91.9660	92.2289	92.5210	92.9066
0.12918	83.2745	83.4024	83.6388	83.9615	0.13112	92.0012	92.2652	92.5634	92.9506
0.15700	83.3210	83.4592	83.6951	84.0098	0.15192	92.0410	92.3111	92.6058	92.9922

Table 3. Partial molar volume ($V_\phi{}^0$), solute-solute interaction parameter (V_s), expansion coefficient (E^∞), Hepler's constant $\left(\partial^2 V_\Phi^\circ \partial T^2\right)$.

Parameter	298.15 K	303.15 K	308.15 K	313.15 K	298.15 K	303.15 K	308.15 K	313.15 K
Sodium cysteinate					**Sodium leucinate**			
$10^6\ V_\phi{}^0$	73.5390	73.6428	73.8542	74.1634	107.9376	108.2239	108.6249	109.0535
$10^6\ V_s$	1.3299	1.3443	1.4473	1.4556	1.4014	1.4161	1.4364	1.4699
$10^6\ E^\infty$	0.01080	0.0314	0.0521	0.07270	0.05362	0.06785	0.08209	0.09632
$10^6 10^6 \left(\partial^2 V_\Phi^\circ / \partial T^2\right)^2 p$	0.00413				0.00285			
Sodium prolinate					**Sodium valinate**			
$10^6\ V_\phi{}^0$	82.8010	82.9249	83.1415	83.4502	91.5012	91.7614	92.0480	92.4177
$10^6\ V_s$	1.3150	1.3399	1.3971	1.4215	1.3883	1.4035	1.4251	1.4695
$10^6\ E^\infty$	0.01562	0.03406	0.05251	0.07096	0.0466	0.0617	0.0768	0.0919
$10^6 \left(\partial^2 V_\Phi^\circ / \partial T^2\right) p$	0.00369				0.00302			

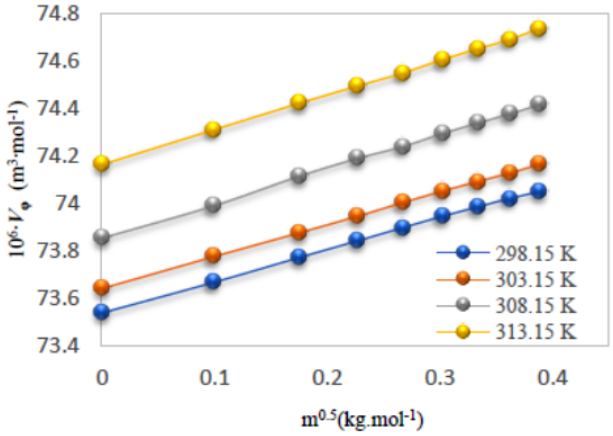

Fig 1. Plot of V_ϕ vs $m^{0.5}$ of sodium cysteinate in water at different temperatures (T)

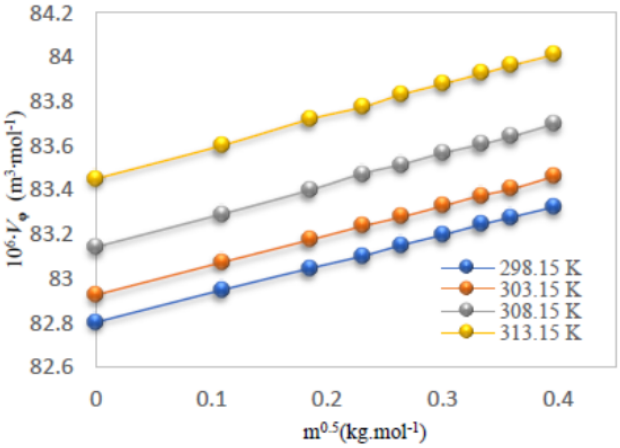

Fig 2. Plot of V_ϕ vs $m^{0.5}$ of sodium leucinate in water at different temperatures (T)

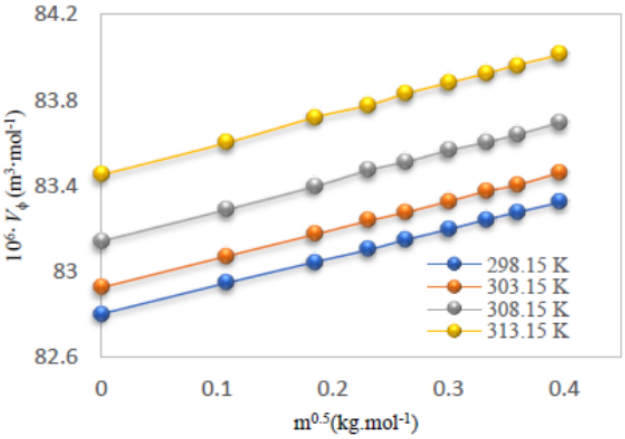

Fig 3. Plot of V_{ϕ} vs $m^{0.5}$ of sodium prolinate in water at different temperatures (T)

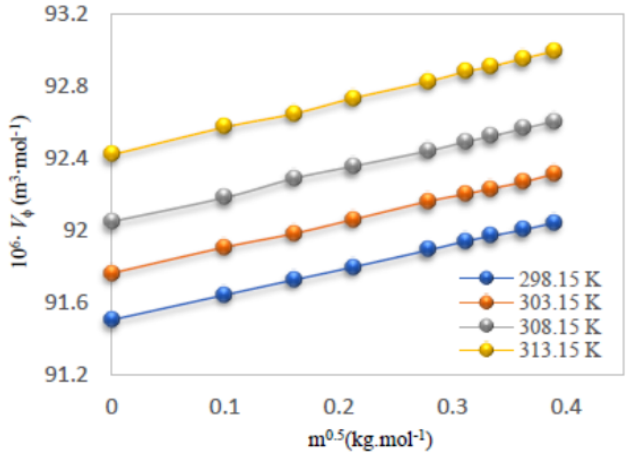

Fig 4. Plot of V_{ϕ} vs $m^{0.5}$ of sodium valinate in water at different temperatures (T)

4 Conclusion

The apparent molar volume increases both with the temperature and molality of the solutions for all studied Na-salt of amino acids + water systems. This could be due to increase in size of alkyl group in side chain of amino acids. This suggests that at higher temperature the electrostriction effect of water reduces and water molecules in secondary solvation layer release into the bulk of the water. All the values of partial molar volume (V_{ϕ}^{0}) are positive which indicates strong (Na-AAS) + water interactions. The positive values of V_{ϕ}^{0} and E^{∞} indicate strong sodium amino acids -water interactions. Higher value of V_{ϕ}^{0} and E^{∞} for Na-leucinate suggest greater solute-solvent interaction and for Na-cysteinate the lower V_{ϕ}^{0} and E^{∞} values suggest weaker solute-solvent interaction among all four studied AAS. Hepler's constants also have positive values, which indicates that sodium amino acids in aqueous solution have a structure making tendency.

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