Apparent molar volume and related parameters of some aqueous potassium amino acids as potential CO_2 absorbent

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Abstract - In this study; densities of aqueous potassium salt solutions of L-sarcosine, L-alanine, taurine and L-proline were measured at 298.15, 303.15, 308.15 and 313.15 K temperatures in 0.01-0.15 mol. L^{-1} concentrations range, on the basis of measured experimental density and viscosity values, the apparent molar volumes (V_ϕ) the partial molar volumes (V_ϕ^0), expansion coefficient (E^ω), Hepler's constant ($\partial^2 V_\phi^0 / \partial T^2$) were determined.
***Index Terms*: L-Alanine; CO_2; Density; Apparent molar volume.**

I. Introduction

Global warming is worldwide the most alarming environmental problem of this era. It is concerned for corresponding climate change and its potential impact on humankind. Excess CO_2 (carbon dioxide) emissions from a number of sources, including the combustion of fossil fuels for energy production and other industrial and human activities, is the primary contributor to global warming [1,2].

Thus, it is the major target for researchers to reduce emission of CO_2 by several pre and post techniques which have been introduced in the gas sweetening industries. Additionally, it may be necessary for operational, financial, or environmental considerations. There are several ways to remove CO_2 from flue gas, before they escape in the atmosphere. In these processes, alkanolamines scrubbers and their combinations are frequently utilised [3]. Alkanolamines degrades in oxygen-rich environments, producing very hazardous degradation compounds [4]. These demerits of amine-based solvents create limitations as an absorbent in CO_2 absorption operations.

Alkali metal amino acid salts (AAS) recently recognized as appealing substituent for alkanolamine and various research have proved their interaction with CO_2 [5,6]. AAS resembles amines in functional group and interacts with CO_2 in similar way. Despite being costlier than alkanolamines, AAS offer several special benefits such greater resistance to oxidation [7], minimal volatility, increased surface tension and rapid absorption [8].

For designing gas–liquid contactors, process modelling, and working of the equipments for a particular absorbent, its physico-chemical properties like density, viscosity data is needed [9-12]. These details are also required to predict kinetics study from experiments on CO_2 absorption rates [13,14].

For aqueous potassium salt solutions of L-sarcosine, L-alanine, taurine and L-proline as of yet, there are no reports of such properties and related parameters in the open literature by using this technique and at such concentration range. Thus, in these work, a new data is presented on density, apparent molar volumes (V_ϕ) the partial molar volumes (V_ϕ^0), expansion coefficient (E^ω) and Hepler's constant ($\partial^2 V_\phi^0 / \partial T^2$), of aqueous potassium salt solutions of above mentioned amino acids.

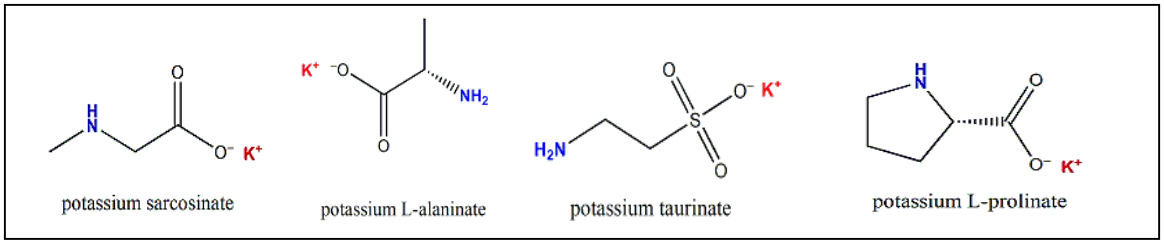
II. EXPERIMENTAL SECTION

Materials and AAS preparation

The amino acids, L-sarcosine (Sar, $C_3H_7NO_2$, CAS No. 107-97-1, 99% purity) was purchased from Loba Chemie Pvt. Ltd., while L-alanine (Ala CAS No. 56-41-7, 99% purity) and L-proline (Pro, $C_5H_9NO_2$, CAS No. 147-85-3, 99% purity) were purchased from S D Fine-Chem Ltd, India, respectively. Taurine (Tau, $C_2H_7NO_3S$, CAS No. 107-35-7, ≥99.00% purity) and potassium hydroxide (KOH, CAS No. 1310-58-3, GR, 98 % purity) from Merck.

All chemicals were used as obtained. The aqueous AAS solutions were made by dissolving equimolar amount of KOH and amino acid in triple distilled water[15]. Masses of materials were taken on Electronic balance accurate to ±0.1 mg.

Figure 1. Structures of potassium salt of L-sarcosine, L-alanine, taurine and L-proline.



Density measurements

Density measurements were undertaken by using 15 cc bi-capillary pycnometer [16] at atmospheric pressure. Pycnometer was immersed in transparent glass water vessel with thermostat to maintain the constant temperature. Triply distilled water and pure solvents were used to calibrated pycnometer as described in our previous work [17]. All of the measurements were made three times and their average was considered. At temperatures 298.15, 303.15, 308.15, and 313.15 K, the measurements were done for studied AAS concentrations ranging from 0.01 to 0.15 m.

III. RESULTS AND DISCUSSIONS

The density data for aqueous potassium salt of L-sarcosine, L-alanine taurine and L-proline solutions at concentration range (0.01 to 0.15) m and at temperatures (298.15, 303.15, 308.15 and 313.15) K are presented in Table 1.

From Table 1, it is observed that both, density increases with the molality whereas falls with rise in temperature.

Density parameters

Equation 1 was used to determine the apparent molar volumes [18] of K-amino acid solutions from experimental density values.

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

where ρ_0 and ρ represents density of solvent and the solution while M, m, are the molar mass of the solute and molality of the studied solutions, respectively. From Table 2, Figure 2, Figure 3, Figure 4 and Figure 5 it has been found that the apparent molar volume increases with both temperature and molality of the solution.

Using Equation 2, the calculated V_ϕ is correlated with molal concentration [19].

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

where m, V_s and V_ϕ^0 are the molality, solute-solute interaction parameter and partial molar volume, respectively.

The values of V_s and V_ϕ^0 were calculated using the least square method. Both V_ϕ^0 and V_s values are directly proportional to the temperature. This indicates that as temperature goes up, the electrostriction action of water decreases. The partial molar volume is a key indicator that shows the solute-solvent interactions. V_ϕ^0 values are positive which indicate strong potassium amino acids-water interactions.

The partial molar volumes of the K-salt amino acids is in the order:

V_ϕ^0 (K-alaninate) < (K V_ϕ^0 (K-sarcosinate) < V_ϕ^0 (K-taurine) < V_ϕ^0 (K-prolinate) at same temperature. Figure 6 shows the variation of V_ϕ^0 for studied AAS. Smaller V_ϕ^0 value in K-alaninate is due to the shorter contact distance between the solute and solvent, and the stronger hydrogen bond interaction between the -NH_2 (polar group) of K- alaninate and the -OH bond of the solvent water [20]. Volumetric characteristics are also significantly influenced by the hydrophobic hydration of the alkyl chain of potassium amino acid. It is observed that the hydrophobic hydration interaction would increase the volume and decrease the compressibility [21]. In K-prolinate, the alkyl chain is larger hence contributing for its higher V_ϕ^0 values.

The V_ϕ^0 values varies with temperature according to the Equation 3.

$$[V_\phi^0 = a_0 + a_1T + a_2T^2] \quad (3)$$

where a_0, a_1 and a_2 are constants. For the calculations of a_0, a_1 and a_2 values, Scilab application was used. Equation 3, on differentiation with respect to temperature gives the partial molar expansion (E^∞).

$$E^\infty = (\partial V_\phi^0 / \partial T) = (a_1 + a_2T) \quad (4)$$

E^∞ values are positive and increases with respect to temperature. For all of the investigated amino acid salt solutions, the positive values of E^∞ indicates significant solute-solvent interactions.

To get the information regarding structure making/breaking behavior of the solute the Hepler's constant [22] can be helpful which is calculated by the following expression 5.

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

Table 3 show the values of V_ϕ^0, V_s, E^∞ and Hepler's constant. All the values of Hepler's constants are positive which is an indication of structure making behavior of solute in solution.

Table 1. Densities (□) of potassium salt of sarcosine, alanine, taurine and proline at different temperatures.

m (mol. kg^{-1})	ρ (kg.m^{-3})				m (mol. kg^{-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
	potassium sarcosinate					**potassium alaninate**			
0.00000	997.044	995.646	994.032	992.211	0.00000	997.044	995.646	994.032	992.211
0.01168	998.701	997.298	995.676	993.844	0.01000	997.625	996.225	994.609	992.785
0.03137	999.732	998.326	996.699	994.86	0.03163	998.876	997.472	995.851	994.020
0.05103	1000.768	999.358	997.726	995.881	0.05155	1000.022	998.614	996.989	995.152
0.07087	1001.756	1000.343	998.706	996.854	0.07331	1001.269	999.856	998.227	996.383
0.08987	1003.046	1001.629	999.985	998.124	0.08932	1002.183	1000.767	999.134	997.285
0.11479	1003.585	1002.166	1000.520	998.655	0.10603	1003.133	1001.714	1000.077	998.223
0.12524	1004.888	1003.465	1001.812	999.938	0.13095	1004.545	1003.120	1001.478	999.616
0.15060	997.663	996.263	994.646	992.821	0.15514	1005.910	1004.480	1002.832	1000.961
	potassium taurinate					**potassium prolinate**			
0.01168	997.948	996.547	994.929	993.103	0.00962	997.610	996.210	994.594	992.77
0.03137	999.465	998.059	996.434	994.600	0.03077	998.847	997.443	995.822	993.992

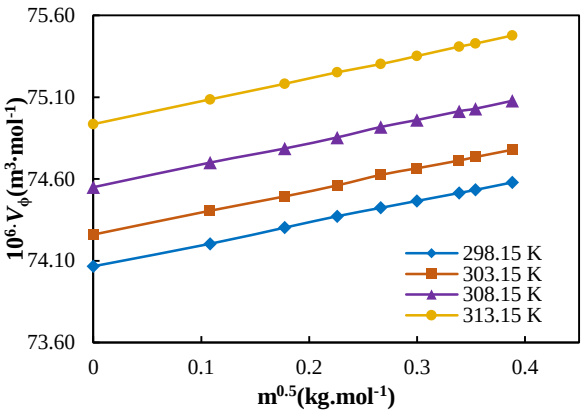
0.05610	1001.360	999.947	998.314	996.469	0.04830	999.866	998.459	996.834	994.998
0.06980	1002.405	1000.989	999.351	997.500	0.07008	1001.125	999.714	998.085	996.242
0.09267	1004.143	1002.720	1001.074	999.213	0.08586	1002.032	1000.619	998.986	997.138
0.11479	1005.815	1004.387	1002.733	1000.862	0.10103	1002.901	1001.485	999.849	997.996
0.13524	1007.354	1005.921	1004.259	1002.379	0.13157	1004.64	1003.219	1001.577	999.714
0.15060	1008.506	1007.069	1005.401	1003.514	0.14960	1005.661	1004.237	1002.591	1000.723

Table 2. Apparent molar volume (V_ϕ) of potassium salt of sarcosine, alanine, taurine and proline in water at different temperatures.

m (mol. kg $^{-1}$)	**$10^6 \cdot V_\phi$ ($m^3 \cdot mol^{-1}$)**				**m (mol. kg $^{-1}$)**	**$10^6 \cdot V_\phi$ ($m^3 \cdot mol^{-1}$)**			
	298.15 K	303.15 K	308.15 K	313.15 K		298.15 K	303.15 K	308.15 K	313.15 K
	potassium sarcosinate					**potassium alaninate**			
0.01168	74.203	74.405	74.699	75.086	0.01000	69.076	69.292	69.512	69.837
0.03137	74.302	74.493	74.785	75.181	0.03163	69.170	69.377	69.619	69.961
0.05103	74.372	74.560	74.853	75.252	0.05155	69.242	69.453	69.688	70.024
0.07087	74.423	74.625	74.917	75.302	0.07331	69.293	69.515	69.741	70.082
0.08987	74.466	74.665	74.960	75.351	0.08932	69.327	69.547	69.781	70.121
0.11479	74.515	74.712	75.013	75.409	0.10603	69.369	69.585	69.824	70.162
0.12524	74.534	74.734	75.029	75.428	0.13095	69.417	69.642	69.878	70.219
0.15060	74.579	74.778	75.077	75.477	0.15514	69.456	69.681	69.922	70.273
	potassium taurinate					**potassium prolinate**			
0.01168	85.787	86.057	86.417	86.867	0.00962	94.437	94.696	94.964	95.346
0.03137	85.879	86.148	86.516	86.954	0.03077	94.561	94.807	95.096	95.459
0.05610	85.958	86.240	86.597	87.049	0.04830	94.634	94.873	95.162	95.544
0.06980	85.998	86.270	86.633	87.087	0.07008	94.709	94.947	95.223	95.609
0.09267	86.049	86.333	86.698	87.154	0.08586	94.762	94.989	95.273	95.661
0.11479	86.101	86.378	86.746	87.207	0.10103	94.802	95.033	95.313	95.703
0.13524	86.143	86.417	86.793	87.255	0.13157	94.876	95.105	95.381	95.774
0.15060	86.170	86.445	86.824	87.288	0.14960	94.913	95.141	95.418	95.807

Table 3. Partial molar volume (V_ϕ^0), solute-solute interaction parameter (V_s), expansion coefficient (E^∞), Hepler's constant ($\partial^2 V_\phi^0 / \partial T^2$).

T	298.15 K	303.15 K	308.15 K	313.15 K	298.15 K	303.15 K	308.15 K	313.15 K
Parameters		**potassium sarcosinate**				**potassium alaninate**		
10^6 V^0_ϕ	74.065	74.259	74.549	74.935	68.943	69.148	69.370	69.694
10^6 V_s	1.331	1.343	1.364	1.394	1.303	1.348	1.393	1.451
10^6 E^∞	0.02918	0.04839	0.06761	0.08682	0.03179	0.04360	0.05542	0.06724
10^6 $(\partial^2 V^0_\phi / \partial T^2)_p$		0.003843				0.002363		
		potassium taurinate				**potassium prolinate**		
10^6 V^0_ϕ	85.636	85.905	86.257	86.691	94.271	94.537	94.816	95.184
10^6 V_s	1.372	1.395	1.4502	1.523	1.665	1.555	1.559	1.622
10^6 E^∞	0.04554	0.06211	0.07868	0.09525	0.04509	0.05527	0.06545	0.07563
10^6 $(\partial^2 V^0_\phi / \partial T^2)_p$		0.003314				0.002036		



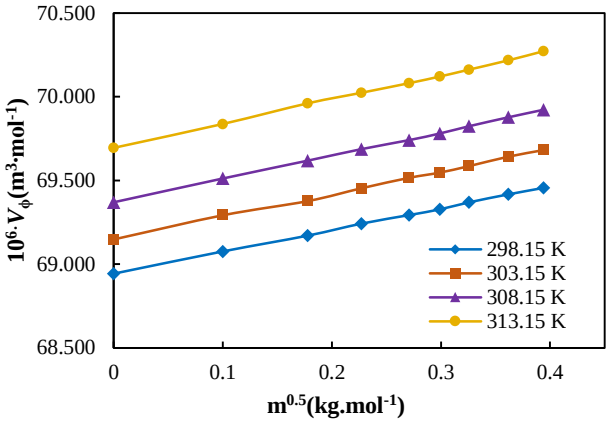


Figure 3. Plot of V_ϕ vs $m^{0.5}$ of potassium alaninate in water different temperatures (T)

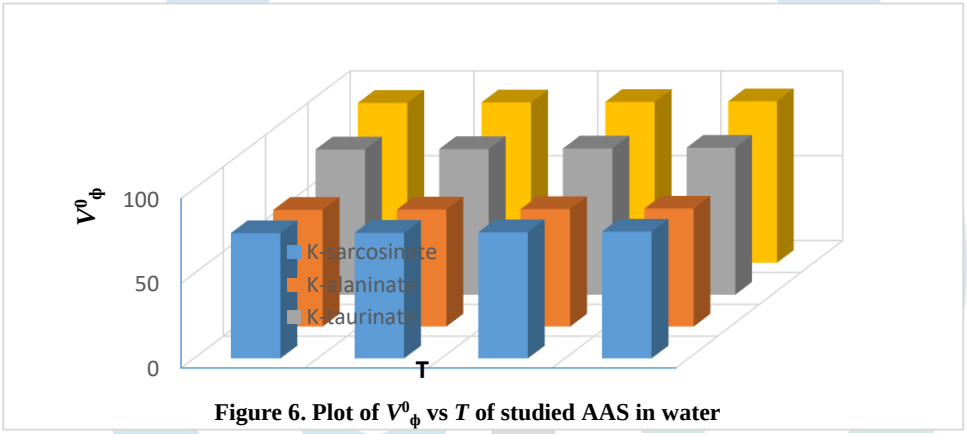
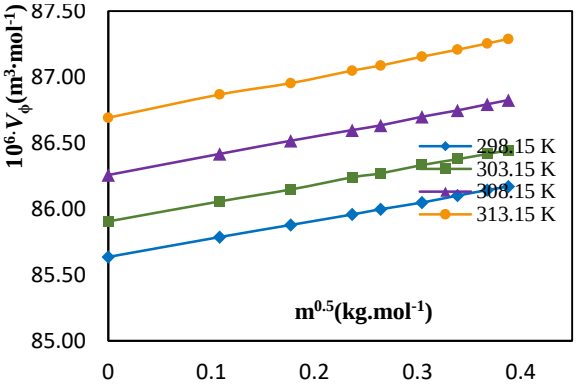


Figure 6. Plot of V^0_ϕ vs T of studied AAS in water

Figure 4 . Plot of V_ϕ vs $m^{0.5}$ of potassium taurinate in water at different temperatures (T)



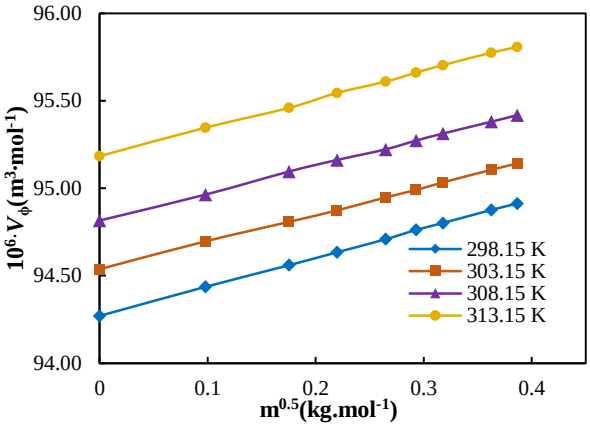


Figure 5 . Plot of V_ϕ vs $m^{0.5}$ of potassium prolinate in water at different temperatures (T)

CONCLUSION

The positive values of V_ϕ^0 indicate strong potassium amino acids-water interactions and found highest in K-prolinate and lowest in K-alaninate among all studied AAS. Positive values of E^∞ suggest the strong solute-solvent interactions. Hepler's constants have positive values which suggest structure making behavior potassium amino acids in solution. B value for all studied potassium salt of amino acids decreases as the temperature rises. As a result, it can be said that all studied potassium salt of amino acids are water structure makers.

DECLARATION OF CONFLICT OF INTEREST

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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