Effect of Potassium Citrate Salts on the Transport Behavior of L-Alanine in Aqueous Solutions at $T = (293.15 \text{ to } 308.15)$ K

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The viscosities of binary aqueous solutions of L-alanine, potassium dihydrogen citrate (KH_2Cit), and tripotassium citrate (K_3Cit) have been measured at $T = (293.15, 298.15, 303.15, \text{and } 308.15)$ K. To obtain the effect of potassium citrate salts on the transport behavior of L-alanine in aqueous solutions, the viscosities of L-alanine in aqueous solutions of (0.18 (mass fraction 0.04), 0.50, and 1.00) $mol \cdot kg^{-1}$ KH_2Cit and in aqueous solutions of (0.14 (mass fraction 0.04), 0.50, and 1.00) $mol \cdot kg^{-1}$ K_3Cit at $T = (293.15, 298.15, 303.15, \text{and } 308.15)$ K have also been measured as a function of the concentration of amino acids. These data have been used to calculate viscosity *B* coefficients of KH_2Cit, K_3Cit, and alanine at different temperature.

Introduction

Electrolytes are known to influence the stability of biologically important molecules such as proteins.[1,2] Because proteins are complex molecules and their behavior in solutions is governed by a combination of many specific interactions, a direct study of electrolyte−protein interactions is difficult. Therefore, to obtain more insight into the hydration of proteins and noncovalent forces that stabilize their native structure, it is necessary to determine the effects of salts on the model compounds of proteins such as amino acids and peptides. Studies of the effect of concentration, temperature, and solutes such as electrolytes on the volumetric and transport properties of amino acids have proved to be very useful in elucidating the various interactions that occur in these solutions. Many research groups[3−17] have extensively studied transport behavior of amino acids in aqueous electrolyte solutions; however, regarding the transport behavior of aqueous electrolyte solutions, much less attention has been directed to organic salts, which have significant biological and industrial importance. Among the organic salts, citrates are of considerable significance in many biochemical and chemical processes, and these salts are produced in large quantities and used in the food, cosmetic, pharmaceutical, and chemical industries.[18−21] In continuation of our previous works on the volumetric and compressibility[22] and vapor−liquid equilibria[23,24] properties of alanine in aqueous potassium citrate salts solutions, the present work presents experimental data on the viscosity of alanine in water in aqueous solutions of (0.18, 0.50, and 1.00) molal potassium dihydrogen citrate (KH_2Cit) and in aqueous solutions of (0.14, 0.50, and 1.00) molal tripotassium citrate (K_3Cit) at $T = (293.15, 298.15, 303.15, \text{and } 308.15)$ K. Furthermore, the viscosities of binary aqueous solutions of KH_2Cit and K_3Cit have also been reported at different temperatures. The values of viscosity *B* coefficients were then calculated from the measured data. Although there are many reports on the transport properties of binary aqueous alanine solutions,[3] there are not any experimental data on the viscosity of binary aqueous solutions of KH_2Cit and K_3Cit in the literature. Furthermore, as far as we know, there is not any information on the effect of KH_2Cit and K_3Cit on the transport properties of aqueous solutions of alanine in the literature.

Experimental Section

Materials. Alanine (*S*-(+)-alanine) with purity of min 99 % was obtained from Merck. Potassium dihydrogen citrate ($C_6H_7KO_7$) and tripotassium citrate ($C_6H_5K_3O_7 \cdot H_2O$) with purity of min 99 % were obtained from Fluka. The amino acid and salts were used without further purification, and double-distilled, deionized water was used.

Apparatus and Procedures. All solutions were prepared by mass on a Sartorius CP124S balance precise to within ± 0.0001 g. Viscosities were measured with an Ostwald-type viscometer. It was assumed that the dynamic viscosity, η, was related to the time of flow according to

$$\eta = Ldt - \frac{Nd}{t} \tag{1}$$

where *t* is the flow time, *d* is the density of the solution,[22,25] and *L* and *N* are constants characteristic of the viscometer. The viscometer constants *L* and *N* were determined by a least-squares fit to eq 1 of the literature data for viscosity and density of water at the respective temperature. The temperature of the water bath was maintained at ± 0.01 K. The flow time of the investigated solutions was measured with precision better than 0.05 s. For each solution, the flow time was measured at least three times. The viscosity measurement was reproducible to within ± 0.05 %.

Results and Discussion

Experimental data of viscosity (η) for various solutions determined at $T = (293.15, 298.15, 303.15, \text{and } 308.15)$ K are given in Tables 1, 2, and 3. The relative viscosities, η_r ($\eta_r = \eta/\eta_0$, where η and η_0 are the viscosities of solution and solvent, respectively), have been used to calculate the viscosity *B* coefficients of alanine using the limiting Jones−Dole equation[26]

$$\eta_r = 1 + Bc \tag{2}$$

where *c* is molarity. The following Jones−Dole equation[26] was used for the correlation of the relative viscosities of binary aqueous KH_2Cit and K_3Cit solutions

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$$\eta_r = 1 + Ac^{0.5} + Bc \qquad (3)$$

The values of the B coefficients have been summarized in Table 4. In general, viscosity B coefficients reflect solute−solvent interactions.[3] The positive B coefficients suggest kosmotropes (structure-making) because strongly hydrated solutes exhibit a larger change in viscosity with concentration, whereas negative B coefficients indicate chaotropes (structure-breaking) for weakly hydrated solutes. However, the B coefficients may not be indicative, especially for large hydrophobic solutes. One improvement is to divide the B coefficient by infinite dilution partial molar volume of the solute because large molecules usually exhibit greater B coefficients.[27] For this reason, the values of B/V_ϕ^0 are also listed in Table 4.

Table 1. Experimental Viscosity, η/mPa·s, of KH_2Cit and K_3Cit in Water at Different Temperature, T, and Salt Molarity, c_{ca}

$T = 293.15$ K		$T = 298.15$ K		$T = 303.15$ K		$T = 308.15$ K	
c_{ca}	η	c_{ca}	η	c_{ca}	η	c_{ca}	η
$mol \cdot L^{-1}$	$mPa \cdot s$	$mol \cdot L^{-1}$	$mPa \cdot s$	$mol \cdot L^{-1}$	$mPa \cdot s$	$mol \cdot L^{-1}$	$mPa \cdot s$
KH_2Cit (ca) + H_2O (w)							
0.0000	1.002	0.0000	0.890	0.0000	0.797	0.0000	0.719
0.0215	1.013	0.0215	0.897	0.0214	0.806	0.0214	0.727
0.0659	1.040	0.0658	0.923	0.0657	0.831	0.0656	0.751
0.1082	1.064	0.1080	0.942	0.1079	0.851	0.1077	0.763
0.1540	1.087	0.1538	0.963	0.1535	0.869	0.1533	0.778
0.1998	1.113	0.1996	0.986	0.1992	0.886	0.1989	0.795
0.2460	1.142	0.2457	1.014	0.2453	0.907	0.2448	0.813
0.2872	1.169	0.2868	1.040	0.2863	0.928	0.2858	0.831
0.3390	1.201	0.3385	1.067	0.3379	0.957	0.3373	0.854
K_3Cit (ca) + H_2O (w)							
0.0000	1.002	0.0000	0.890	0.0000	0.797	0.0000	0.719
0.0073	1.015	0.0072	0.900	0.0072	0.809	0.0072	0.729
0.0145	1.014	0.0145	0.899	0.0145	0.804	0.0144	0.728
0.0441	1.043	0.0441	0.922	0.0440	0.838	0.0439	0.752
0.0726	1.064	0.0725	0.945	0.0724	0.855	0.0723	0.767
0.1035	1.084	0.1034	0.966	0.1032	0.871	0.1031	0.784
0.1335	1.106	0.1333	0.991	0.1331	0.891	0.1329	0.800
0.1655	1.133	0.1653	1.013	0.1650	0.912	0.1647	0.817
0.1949	1.158	0.1947	1.032	0.1944	0.932	0.1940	0.831
0.2281	1.192	0.2278	1.060	0.2274	0.959	0.2270	0.850

Table 2. Experimental Viscosity, η/mPa·s, of Alanine (A) in Aqueous KH_2Cit Solutions at Different Temperature, T, and Alanine Molarity, c_A

$T = 293.15$ K		$T = 298.15$ K		$T = 303.15$ K		$T = 308.15$ K	
c_A	η	c_A	η	c_A	η	c_A	η
$mol \cdot L^{-1}$	$mPa \cdot s$	$mol \cdot L^{-1}$	$mPa \cdot s$	$mol \cdot L^{-1}$	$mPa \cdot s$	$mol \cdot L^{-1}$	$mPa \cdot s$
$m_{ca} = 0.00\ mol \cdot kg^{-1}$							
0.0000	1.002	0.0000	0.890	0.0000	0.797	0.0000	0.719
0.1684	1.026	0.1682	0.910	0.1679	0.814	0.1677	0.732
0.2801	1.068	0.2798	0.939	0.2794	0.838	0.2789	0.754
0.3958	1.100	0.3953	0.970	0.3947	0.865	0.3941	0.775
0.5133	1.128	0.5126	0.995	0.5118	0.888	0.5110	0.802
0.6276	1.155	0.6268	1.024	0.6258	0.914	0.6248	0.823
0.7429	1.207	0.7420	1.063	0.7408	0.953	0.7396	0.850
0.8563	1.242	0.8551	1.100	0.8538	0.977	0.8523	0.877
$m_{ca} = 0.18\ mol \cdot kg^{-1}$ (mass fraction 0.04)							
0.0000	1.074	0.0000	0.954	0.0000	0.853	0.0000	0.766
0.0571	1.091	0.0570	0.969	0.0569	0.865	0.0568	0.777
0.1700	1.124	0.1697	0.997	0.1695	0.891	0.1692	0.800
0.2870	1.161	0.2866	1.027	0.2862	0.922	0.2857	0.826
0.4050	1.199	0.4044	1.062	0.4037	0.951	0.4030	0.852
0.5235	1.239	0.5228	1.101	0.5219	0.980	0.5210	0.880
0.6364	1.283	0.6355	1.136	0.6344	1.013	0.6333	0.905
0.7561	1.335	0.7550	1.177	0.7538	1.043	0.7524	0.937
0.8756	1.385	0.8743	1.224	0.8729	1.087	0.8712	0.980
$m_{ca} = 0.50\ mol \cdot kg^{-1}$							
0.0000	1.237	0.0000	1.089	0.0000	0.970	0.0000	0.876
0.0588	1.256	0.0587	1.109	0.0586	0.986	0.0585	0.889
0.1751	1.301	0.1748	1.149	0.1745	1.022	0.1742	0.919
0.2957	1.349	0.2952	1.193	0.2947	1.058	0.2941	0.953
0.4156	1.393	0.4149	1.234	0.4141	1.092	0.4133	0.984
0.5361	1.437	0.5352	1.278	0.5342	1.126	0.5332	1.015
0.6576	1.485	0.6565	1.324	0.6553	1.164	0.6540	1.050
0.7752	1.540	0.7739	1.376	0.7724	1.202	0.7709	1.086
0.9043	1.597	0.9028	1.435	0.9012	1.249	0.8994	1.127
$m_{ca} = 1.00\ mol \cdot kg^{-1}$							
0.0000	1.419	0.0000	1.253	0.0000	1.117	0.0000	1.002
0.0579	1.442	0.0578	1.269	0.0577	1.137	0.0576	1.019
0.1829	1.495	0.1826	1.316	0.1822	1.177	0.1818	1.056
0.3057	1.553	0.3052	1.362	0.3046	1.215	0.3040	1.091
0.4294	1.611	0.4286	1.417	0.4278	1.256	0.4269	1.130
0.5540	1.674	0.5529	1.476	0.5519	1.302	0.5507	1.173
0.6741	1.744	0.6728	1.544	0.6715	1.357	0.6701	1.213
0.8023	1.821	0.8009	1.610	0.7993	1.413	0.7976	1.259
0.8973	1.876	0.8956	1.658	0.8938	1.460	0.8920	1.302

Table 3. Experimental Viscosity, η/mPa·s, of Alanine (A) in Aqueous K_3Cit Solutions at Different Temperature, T, and Alanine Molarity, c_A

$T = 293.15$ K		$T = 298.15$ K		$T = 303.15$ K		$T = 308.15$ K	
c_A	η	c_A	η	c_A	η	c_A	η
$mol \cdot L^{-1}$	$mPa \cdot s$	$mol \cdot L^{-1}$	$mPa \cdot s$	$mol \cdot L^{-1}$	$mPa \cdot s$	$mol \cdot L^{-1}$	$mPa \cdot s$
$m_{ca} = 0.14\ mol \cdot kg^{-1}$ (mass fraction 0.04)							
0.0000	1.072	0.0000	0.946	0.0000	0.844	0.0000	0.758
0.0577	1.085	0.0576	0.960	0.0575	0.859	0.0574	0.772
0.1722	1.120	0.1719	0.989	0.1717	0.890	0.1714	0.799
0.2875	1.156	0.2871	1.024	0.2867	0.923	0.2862	0.825
0.4045	1.192	0.4040	1.063	0.4033	0.955	0.4026	0.850
0.5150	1.234	0.5143	1.097	0.5134	0.987	0.5125	0.878
0.6327	1.277	0.6318	1.135	0.6308	1.019	0.6297	0.906
0.7522	1.322	0.7512	1.171	0.7500	1.055	0.7486	0.931
0.8659	1.370	0.8647	1.211	0.8633	1.084	0.8617	0.965
$m_{ca} = 0.50\ mol \cdot kg^{-1}$							
0.0000	1.265	0.0000	1.123	0.0000	1.003	0.0000	0.908
0.0610	1.287	0.0609	1.145	0.0608	1.022	0.0607	0.925
0.1819	1.330	0.1816	1.182	0.1813	1.062	0.1809	0.959
0.3017	1.380	0.3012	1.232	0.3007	1.100	0.3001	0.986
0.4272	1.432	0.4265	1.276	0.4258	1.142	0.4250	1.023
0.5494	1.482	0.5486	1.320	0.5476	1.178	0.5466	1.055
0.6755	1.531	0.6744	1.360	0.6732	1.214	0.6720	1.087
0.7929	1.591	0.7916	1.404	0.7903	1.250	0.7888	1.125
0.9149	1.645	0.9134	1.453	0.9118	1.297	0.9101	1.164
$m_{ca} = 1.00\ mol \cdot kg^{-1}$							
0.0000	1.478	0.0000	1.320	0.0000	1.187	0.0000	1.070
0.0641	1.507	0.0640	1.342	0.0639	1.209	0.0637	1.085
0.1898	1.558	0.1895	1.389	0.1892	1.245	0.1888	1.120
0.2977	1.605	0.2972	1.431	0.2967	1.281	0.2961	1.151
0.4485	1.683	0.4478	1.496	0.4470	1.335	0.4461	1.202
0.5747	1.747	0.5737	1.551	0.5727	1.382	0.5716	1.242
0.7056	1.816	0.7043	1.609	0.7031	1.435	0.7017	1.288
0.8338	1.884	0.8324	1.675	0.8309	1.486	0.8293	1.334
0.9662	1.973	0.9645	1.750	0.9628	1.553	0.9609	1.397

The viscosities of binary aqueous KH_2Cit and K_3Cit solutions are graphically represented in Figure 1 at different temperature. Figure 1 shows that at a certain concentration and temperature, the values of η for K_3Cit solutions are larger than those for KH_2Cit solutions. As can be seen from Table 4, both B and B/V_ϕ^0 for aqueous KH_2Cit and K_3Cit solutions have positive values, and the values of both B and B/V_ϕ^0 for aqueous K_3Cit solutions are larger than those for KH_2Cit solutions, suggesting a higher kosmotropicity of K_3Cit than KH_2Cit. This is because the triply charged Cit^{3-} ions are more hydrated than the singly charged H_2Cit^{1-} ions; therefore, the values of B and B/V_ϕ^0 for K_3Cit are larger than those for KH_2Cit. In fact, because of the additivity principle,[27] we have

$$B(K_3Cit) = 3B(K^+) + B(Cit^{3-}), \quad B(KH_2Cit) = B(K^+) + B(H_2Cit^-) \qquad (4)$$

From the values of the viscosity B coefficient for K^+ at different temperature,[27] the values of the viscosity B coefficient for anions Cit^{3-} and H_2Cit^{1-} have been determined, which are given in Table 5. The viscosities of binary aqueous KH_2Cit,

Table 4. Viscosity *B* Coefficients of KH_2Cit and K_3Cit in Water and of Alanine in Aqueous KH_2Cit and K_3Cit Solutions at Different Temperature, *T*

$T =$	293.15 K	298.15 K	303.15 K	308.15 K	293.15 K	298.15 K	303.15 K	308.15 K
	$KH_2Cit + H_2O$				$K_3Cit + H_2O$			
$B/\mathrm{L \cdot mol^{-1}}$	0.612 ± 0.018	0.654 ± 0.024	0.562 ± 0.033	0.524 ± 0.033	0.771 ± 0.049	0.819 ± 0.029	0.762 ± 0.061	0.644 ± 0.030
B/V_ϕ^0	5.562[a]	5.978	5.000	4.627	8.217	8.600	7.909	6.628
	Alanine + KH_2Cit ($0.00\ \mathrm{mol \cdot kg^{-1}}$) + H_2O				Alanine + K_3Cit ($0.00\ \mathrm{mol \cdot kg^{-1}}$) + H_2O			
$B/\mathrm{L \cdot mol^{-1}}$	0.262 ± 0.008	0.252 ± 0.009	0.246 ± 0.010	0.237 ± 0.010	0.262 ± 0.008	0.252 ± 0.009	0.246 ± 0.010	0.237 ± 0.010
B/V_ϕ^0	4.358	4.189	4.054	3.890	4.358	4.189	4.054	3.890
	Alanine + KH_2Cit ($0.18\ \mathrm{mol \cdot kg^{-1}}$) + H_2O				Alanine + K_3Cit ($0.14\ \mathrm{mol \cdot kg^{-1}}$) + H_2O			
$B/\mathrm{L \cdot mol^{-1}}$	0.314 ± 0.006	0.307 ± 0.006	0.299 ± 0.004	0.299 ± 0.006	0.306 ± 0.005	0.316 ± 0.003	0.330 ± 0.001	0.310 ± 0.002
B/V_ϕ^0	5.181	5.043	4.893	4.880	5.003	5.144	5.349	5.006
	Alanine + KH_2Cit ($0.50\ \mathrm{mol \cdot kg^{-1}}$) + H_2O				Alanine + K_3Cit ($0.50\ \mathrm{mol \cdot kg^{-1}}$) + H_2O			
$B/\mathrm{L \cdot mol^{-1}}$	0.313 ± 0.003	0.338 ± 0.004	0.310 ± 0.002	0.309 ± 0.003	0.319 ± 0.003	0.318 ± 0.002	0.317 ± 0.002	0.302 ± 0.002
B/V_ϕ^0	5.094	5.483	5.016	4.986	5.122	5.073	5.041	4.788
	Alanine + KH_2Cit ($1.00\ \mathrm{mol \cdot kg^{-1}}$) + H_2O				Alanine + K_3Cit ($1.00\ \mathrm{mol \cdot kg^{-1}}$) + H_2O			
$B/\mathrm{L \cdot mol^{-1}}$	0.344 ± 0.006	0.344 ± 0.008	0.324 ± 0.006	0.320 ± 0.004	0.329 ± 0.005	0.320 ± 0.006	0.302 ± 0.005	0.297 ± 0.006
B/V_ϕ^0	5.546	5.531	5.197	5.122	5.179	5.025	4.728	4.655

[a] Values of V_ϕ^0 have been taken from refs 22 and 25.

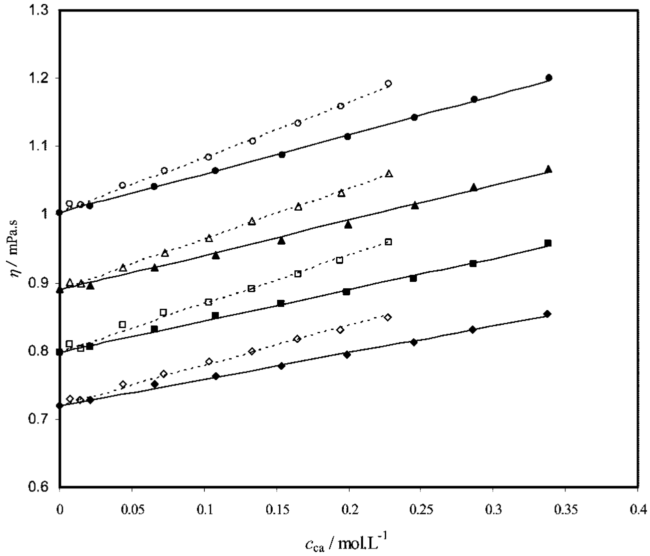

Figure 1. Plot of viscosity, η, of aqueous solutions of KH_2Cit and K_3Cit against molarity of electrolyte, c_{ca}, at different temperature: ●, $T = 293.15$ K (KH_2Cit); ▲, $T = 298.15$ K (KH_2Cit); ■, $T = 303.15$ K (KH_2Cit); ◆, $T = 308.15$ K (KH_2Cit); ○, $T = 293.15$ K (K_3Cit); △, $T = 298.15$ K (K_3Cit); □, $T = 303.15$ K (K_3Cit); ◇, $T = 308.15$ K (K_3Cit). Solid line, calculated for KH_2Cit; dotted line, calculated for K_3Cit.

Table 5. Viscosity *B* Coefficients of H_2Cit^- and Cit^{3-} in Water at Different Temperature, *T*

	H_2Cit^-				Cit^{3-}			
T	293.15 K	298.15 K	303.15 K	308.15 K	293.15 K	298.15 K	303.15 K	308.15 K
$B/\mathrm{L \cdot mol^{-1}}$	0.626	0.663	0.563	0.520	0.813	0.846	0.765	0.632

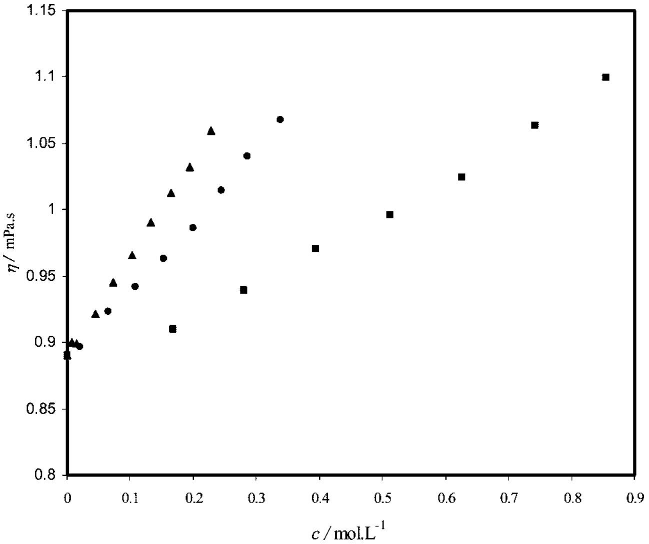

Figure 2. Plot of viscosity, η, of aqueous solutions of alanine, KH_2Cit, and K_3Cit against molarity of solute, c, at $T = 298.15$ K: ■, alanine; ●, KH_2Cit; ▲, K_3Cit.

K_3Cit, and alanine solutions are graphically represented in Figure 2 at 298.15 K. At a certain concentration and temperature, the values of η for alanine solutions are smaller than those for salt solutions. From Table 4, we can see that the values of both *B* and B/V_ϕ^0 for aqueous salt solutions are larger than those for alanine solutions, suggesting a higher kosmotropicity of K_3Cit or KH_2Cit than alanine. The selected (average) values of *B* and B/V_ϕ^0 for alanine in pure water at 298.15 K are (0.252 and 4.170) $\mathrm{dm^3 \cdot mol^{-1}}$,[3] respectively, which are in good agreement with our results reported in Table 4.

Figure 3 shows the effect of KH_2Cit or K_3Cit concentration on the viscosity of alanine solutions at 298.15 K. The viscosities of alanine solutions increase with increasing salt concentration. As can be seen from Table 4, the values of both *B* and B/V_ϕ^0 for alanine in aqueous potassium citrate solutions are larger than those for alanine in pure water. From Figure 3, it can be seen that for a fixed alanine and electrolyte concentration, the charge of the anion of the electrolyte affects the value of the viscosity of alanine solutions. For the same molalities of two electrolytes, the value of η is larger in the presence of the electrolyte with higher anion charge than in the presence of the electrolyte with lower charge on the anion. In fact, the decreasing influence of the anions Cit^{3-} and H_2Cit^- on the viscosity of alanine is in the same order as the *B* coefficients of these anions in water. The viscosity *B* coefficients of both K_3Cit and KH_2Cit are larger than those of alanine; therefore, the water structure-making ability of alanine increases in the presence of these electrolytes and hence the viscosity of alanine increases. Also, because of the larger charge on Cit^{3-}, the interactions between Cit^{3-} and ammonium ions are stronger than the interactions between H_2Cit^{1-} and ammonium ions. The amino and carboxyl groups of alanine dissociate in aqueous solutions and become, respectively, negatively and positively charged or zwitterion ($^+NH_3-(CH_3CH)-COO^-$). The neutral dipolar species or zwitterions are the predominant species in the isoelectric solution of amino acids. In acidic solutions, cationic amino acid species

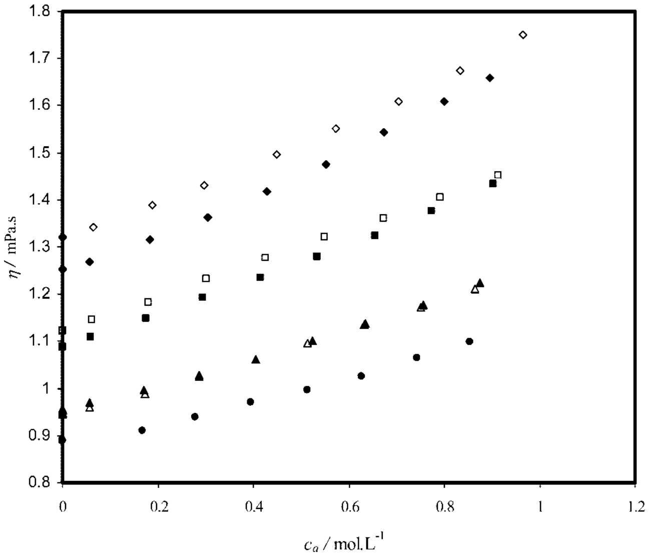

Figure 3. Plot of viscosity, η, of the solutions of alanine in aqueous KH_2Cit and K_3Cit solutions against molarity of alanine, c_A, in different electrolyte solutions at T = 298.15 K: ●, alanine in water; ▲, alanine in aqueous solution of 0.18m KH_2Cit; ■, alanine in aqueous solution of 0.50m KH_2Cit; ◆, alanine in aqueous solution of 1.00m KH_2Cit; △, alanine in aqueous solution of 0.14m K_3Cit; □, alanine in aqueous solution of 0.50m K_3Cit; ◇, alanine in aqueous solution of 1.00m K_3Cit.

($^+NH_3-(CH_3CH)-COOH$) become predominant, whereas anionic amino acid species ($NH_2-(CH_3CH)-COO^-$) become predominant in the basic solutions. KH_2Cit is an acidic salt; therefore, as mentioned above, in the aqueous solutions of KH_2Cit, the cationic form of alanine ($^+NH_3-(CH_3CH)-COOH$) becomes predominant, whereas the neutral dipolar form of alanine ($^+NH_3-(CH_3CH)-COO^-$) is predominant in the aqueous solutions of K_3Cit. Therefore, in the case of K_3Cit solutions, the interactions between K^+ and COO^- also exist, and we expect that K_3Cit has more effect on the viscosity of alanine than KH_2Cit.

Conclusions

Experimental data at T = (293.15, 298.15, 303.15, and 308.15) K for viscosity of binary aqueous KH_2Cit and K_3Cit solutions and viscosity of alanine in water, in water + KH_2Cit, and in water + K_3Cit have been reported. The viscosities and viscosity B coefficients for investigated binary solutions follow the order $K_3Cit > KH_2Cit >$ alanine. Furthermore, it was found that at constant electrolyte molality and temperature, the viscosity of alanine is influenced in the order $K_3Cit > KH_2Cit$.

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