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Viscosity and Density of Ternary Solution of Calcium Chloride + Sodium Chloride + Water from T = (293.15 to 323.15) K

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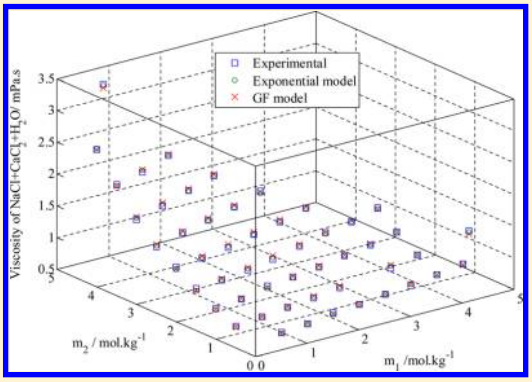
ABSTRACT: Viscosities and densities of ternary systems of $CaCl_2$−NaCl−water were measured in the range of T = (293.15 to 323.15) K at 5 K intervals and up to 4.5 mol·kg^{-1}. Two equations based on the Exponential and Goldsack and Franchetto models were applied to correlate the experimental viscosity data as a function of concentration and temperature. The optimized parameters showed that the presence of $CaCl_2$ had a prevailing effect on the viscosity of the ternary solutions than NaCl. The dependency of the viscosity optimized parameters on temperature was investigated, too. The average absolute deviation between calculated and experimental viscosities was below 1.4 %. The work compared the above-mentioned two models to the known extended Jones−Dole equation and found that both models do correlate the viscosity at higher concentrations better than the Jones−Dole equation. However, the exponential model shows the superior representation for the experimental viscosity values over the other two studied models. Density data were successfully predicted with an average absolute deviation of less than 0.45 %.



1. INTRODUCTION

Calcium and sodium chlorides naturally exist in most of natural brines such as oceans, seawater, and concentrated brines. Brines could be natural ones such as the Dead Sea and Great Salt Lake or could be man-made ones such as brine disposal from different inland desalination and mining processes. Desalination plants are increasingly being used in inland areas of many noncostal countries for water supply for domestic purposes. The reject brine (also known as concentrate) is disposed to evaporation ponds. This is a common practice in arid or semiarid areas. Evaporation ponds have long been used for salt production in many parts of the world. Among other transport properties, viscosity and density are required to design evaporation ponds.[1] Owing to stringent environmental regulations on brine disposal from desalination plants, many projects have been established to utilize brine water produced from these plants. The process involves multiple evaporation, cooling, and crystallization processes. While achieving zero liquid discharge to the environment through this practice, getting saleable chemical products is achieved. Among saleable products are sodium chloride and calcium chloride. The potential markets and application of $CaCl_2$ are as road base stabilization, sodic soil remediation, dust suppression, and drip feed application. Knowledge of thermodynamic and transport properties of aqueous solutions is important not only in engineering and designing new technological processes but also in developing theoretical models.[1] The density and viscosity of aqueous solutions are required in models that determine fluid flow, heat, and mass transfer. The values of such quantities may sometimes be obtained from tables but it is usually found that even the most extensive physicochemical tables do not contain all the data necessary for designing a technological process.[2] Consequently, reliable and accurate data that can be applied to wide ranges of temperatures and concentrations are required.

2. EXPERIMENTAL

Materials. Information about the chemicals used in this work is given in Table 1. Stock solutions were prepared by completely dissolving preweighed amounts of $CaCl_2·2H_2O$ and NaCl in double distilled water (MilliQ purification system). MilliQ water was supplied from a Millipore water system with a resistivity of 18.2 mΩ·cm. All chemicals were used without further purification. Stock solutions of both $CaCl_2$ and NaCl were prepared at room temperature and left for 48 h before they were used to check for any possible salt precipitation so that stable solutions are guaranteed. Ratios of $CaCl_2$ and NaCl solutions were prepared from the stock solutions by mass. A series of solutions of different concentrations were made by dilution. The ternary system of water and the salts were prepared gravimetrically using a precise analytical balance

Table 1. Chemicals Description

chemical name	sources	initial mass fraction purity	purification method
calcium chloride dihydrate	BDH	0.99	none
sodium chloride	Fisher Scientific	0.995	none

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(Kern model ABS220-4) within an accuracy of 0.0001 g. The sample was discarded when salt precipitation was observed due to mixing. This was considered as the maximum concentration in this study. The three components of the mixed blends obtained were denoted as i = 1 for NaCl, i = 2 for $CaCl_2$, and i = 3 for H_2O.

Kinematic viscosities were measured using a manufacturer calibrated Ubbelhode viscometer (Schott-Gerät). The viscometer has a capillary diameter of 0.00053 m (capillary type 0a) and was further calibrated with double deionized water. The kinematic viscosity of a given solution was determined using stop watch from the transit time of the liquid meniscus through the capillary of the viscometer. The time was measured with a precision of ± 0.01 s. To ensure reproducibility of the data, each measurement was repeated five times. A maximum deviation of 0.4 % was observed in the measurements. Viscosity was measured over a temperature T = (293.15 to 323.15) K in 5 K intervals. The studied molality range was between (0.5 and 4.5) mol·kg^{-1}. Densities of the solution were measured precisely using an Anton Paar DMA 4500 M density meter with an oscillating U-tube sensor. The basic principle of the density measurements through vibrating tube densimeter technique is that the period of the oscillation of the vibrating tube is related to the density of the fluid inside the tube. Since the vibrating tube densimeter measurement is not absolute; the response of the instrument must be calibrated against fluids of known density, prior to the actual experiments on the liquids. For this purpose, a fluid with very well-known density is used in our calibration stages. We used double deionized water and toluene for this purpose. The uncertainty in our temperature measurements is estimated to be 50 mK (k = 1).

The same solutions prepared for density measurements were also used to determine their kinematic viscosity. The accuracy of the density measurement was 0.00005 g·cm^{-3} and repeatability was 0.00001 g·cm^{-3}. The dynamic viscosity was calculated using eq 1.

$$\frac{\eta}{\rho} = kt \tag{1}$$

where k is the viscometer constant provided by the manufacturer and t is the flow time in seconds. For viscosity, the temperature was controlled with a thermostatted water bath. The precision of the temperature control was ± 0.01 K. The uncertainty in the dynamic viscosity measurements was 0.003 mPa·s

3. RESULTS AND DISCUSSION

3.1. Experimental Data. Densities and viscosities of the ternary aqueous solutions of sodium chloride and calcium chloride over a range of temperatures (293.15 to 323.15 K) are presented in Tables 2 to 8 at given molalities of NaCl (m_1) and $CaCl_2$ (m_2) in the range of (0 to 4.5) mol·kg^{-1}.

Both density and viscosity increase, as expected, with increase in molalities of solutes NaCl (m_1) and $CaCl_2$ (m_2). The quantitative effect of each of the solutes was analyzed separately. Referring to Table 2, for example, an increase in molality of NaCl (m_1) from 0.5 to 1 increases the density by 1.59 % and viscosity by 4.87 %. On the other hand, the same increase in molality of $CaCl_2$ increases the density by 3.80 % and viscosity by 9.55 %. So it is clear that $CaCl_2$ plays a dominant role in controlling the physical properties of the ternary solution and increasing both density and viscosity by a factor of 2. These values are consistent with those reported in

Table 2. Experimental Density ρ, Viscosity η, and the Calculated Viscosities at T = 293.15 K and Experimental Pressure of 0.1 MPa for NaCl (1) + $CaCl_2$ (2) + H_2O (3) System[a]

	experimental data		calculated viscosity/mPa·s		predicted density
m_1	ρ	η	Exponential model	GF model	ρ
mol·kg^{-1}	g·cm^{-3}	mPa·s			g·cm^{-3}
			m_2 = 0.5		
0.5	1.06063	1.2117	1.2055	1.2126	1.0611
1.0	1.07752	1.2707	1.2755	1.2705	1.0789
1.5	1.0957	1.3283	1.3498	1.3381	1.0960
2.0	1.11139	1.4081	1.4279	1.4101	1.1126
3.0	1.14377	1.5362	1.5968	1.5764	1.1442
3.5	1.15901	1.6715	1.6909	1.6724	1.1595
4.5	1.18757	1.9033	1.8911	1.8761	1.1880
			m_2 = 1.0		
0.5	1.1010	1.3921	1.3999	1.4180	1.1013
1.0	1.1180	1.4525	1.4814	1.4889	1.1178
1.5	1.1336	1.5709	1.5676	1.5678	1.1337
2.0	1.1498	1.6497	1.6575	1.6512	1.1492
2.5	1.1648	1.7711	1.7530	1.7439	1.1642
3.0	1.1795	1.8541	1.8547	1.8421	1.1788
3.5	1.1939	1.9579	1.9619	1.9480	1.1930
			m_2 = 1.5		
0.5	1.1378	1.6087	1.6355	1.6429	1.1376
1.0	1.1536	1.6846	1.7308	1.7254	1.1531
1.5	1.1687	1.7709	1.8317	1.8161	1.1685
2.0	1.1834	1.9181	1.9370	1.9128	1.1827
2.5	1.1978	2.0525	2.0492	2.0179	1.1970
3.0	1.2119	2.1959	2.1655	2.1269	1.2109
3.5	1.2250	2.3604	2.2937	2.2478	1.2246
			m_2 = 2.0		
0.5	1.1744	1.9005	1.9218	1.9038	1.1728
1.0	1.1877	1.9865	2.0335	1.9991	1.1874
1.5	1.2020	2.1588	2.1484	2.0994	1.2017
2.0	1.2155	2.2624	2.2762	2.2126	1.2157
2.5	1.2299	2.4415	2.4084	2.4185	1.2295
			m_2 = 2.5		
0.5	1.2086	2.2413	2.2717	2.2265	1.2064
1.0	1.2227	2.3909	2.4038	2.3841	1.2205
1.5	1.2364	2.5484	2.5436	2.5492	1.2343
2.0	1.2497	2.7985	2.6912	2.7212	1.2480
			m_2 = 3.0		
0.5	1.2409	2.6767	2.7535	2.6963	1.2390
1.0	1.2542	2.8433	3.0005	2.8803	1.2528
1.5	1.2672	3.0466	3.2785	3.0733	1.2665
			m_2 = 3.5		
0.5	1.2722	3.2011	3.3500	3.2737	1.2717
1.0	1.2849	3.4463	3.6821	3.4872	1.2854
			m_2 = 4.5		
0.5	1.3278	4.8306	4.6975	4.7475	1.3352
AAD % =			1.35	1.33	0.080
SD =			0.0396	0.0414	0.0016
delta =			0.0097		

[a]The standard uncertainties (u) are $u(T)$ = 0.01 K, $u(m)$ = 1.0·10^{-4} mol·kg^{-1}. The combined expanded uncertainty (U_c) are $U_c(\rho)$ = 5.0·10^{-5} g·cm^{-3} (0.95 level of confidence) and $U_c(\eta)$ = 0.003 mPa·s (0.95 level of confidence).

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Table 3. Experimental Density ρ, Viscosity η, and the Calculated Viscosities at T = 298.15 K and Experimental Pressure of 0.1 MPa for the NaCl (1) + $CaCl_2$ (2) + H_2O (3) System[a]

	experimental data					predicted density
m_1	ρ	η	calculated viscosity/mPa·s			ρ
mol·kg^{-1}	g·cm^{-3}	mPa·s	Exponential model	GF model	extended Jones−Dole	g·cm^{-3}
			m_2 = 0.5			
0.5	1.0589	1.0863	1.0769	1.0822	1.0745	1.0594
1.0	1.0757	1.1360	1.1394	1.1340	1.1229	1.0770
1.5	1.0938	1.1796	1.2057	1.1941	1.1773	1.0941
2.0	1.1090	1.2629	1.2755	1.2579	1.237	1.1107
3.0	1.1416	1.3713	1.4264	1.4048	1.3667	1.1424
3.5	1.1566	1.4954	1.5104	1.4894	1.4349	1.1579
4.5	1.1850	1.6740	1.6893	1.6685	1.5627	1.1869
			m_2 = 1.0			
0.5	1.0991	1.2486	1.2505	1.2661	1.2371	1.0993
1.0	1.1160	1.3630	1.3233	1.3282	1.2855	1.1157
1.5	1.1314	1.4084	1.4003	1.3974	1.3400	1.1317
2.0	1.1476	1.4789	1.4806	1.4704	1.3996	1.1473
2.5	1.1626	1.5646	1.5659	1.5514	1.4632	1.1625
3.0	1.1771	1.6577	1.6568	1.6373	1.5293	1.1774
3.5	1.1913	1.7684	1.7525	1.7298	1.5962	1.1920
			m_2 = 1.5			
0.5	1.1357	1.4460	1.4610	1.4655	1.4240	1.1353
1.0	1.1514	1.5168	1.5459	1.5369	1.4723	1.1509
1.5	1.1664	1.5852	1.6336	1.6154	1.5299	1.1665
2.0	1.1810	1.7186	1.7302	1.6992	1.5865	1.1810
2.5	1.1953	1.8334	1.8303	1.7903	1.6501	1.1957
3.0	1.2093	1.9187	1.9357	1.8848	1.7162	1.2101
3.5	1.2223	2.0951	2.0490	1.9896	1.7831	1.2244
			m_2 = 2.0			
0.5	1.1722	1.7050	1.7167	1.6949	1.6567	1.1703
1.0	1.1853	1.7852	1.8165	1.7765	1.7051	1.1852
1.5	1.1995	1.9015	1.9214	1.8625	1.7596	1.1999
2.0	1.2130	2.0113	2.0334	1.9598	1.8192	1.2144
2.5	1.2273	2.1733	2.1514	2.0613	1.8828	1.2288
			m_2 = 2.5			
0.5	1.2062	2.0089	2.0293	2.0059	1.9454	1.2037
1.0	1.2202	2.1320	2.1469	2.1429	1.9937	1.2183
1.5	1.2338	2.2766	2.2720	2.2863	2.0482	1.2327
2.0	1.2470	2.4645	2.4035	2.4356	2.1079	1.2472
			m_2 = 3.0			
0.5	1.2384	2.4119	2.4124	2.4148	2.3061	1.2360
1.0	1.2516	2.5483	2.5522	2.5741	2.3545	1.2505
1.5	1.2644	2.7183	2.7000	2.7411	2.4090	1.2650
			m_2 = 3.5			
0.5	1.2695	2.8663	2.8843	2.9129	2.7688	1.2682
1.0	1.2821	3.0776	3.0523	3.0969	2.8171	1.2829
			m_2 = 4.5			
0.5	1.3248	4.3075	4.1951	4.1687	4.0439	1.3298
AAD % =			1.18	1.40	6.120	0.083
SD =			0.0298	0.0428	0.1629	0.0014
delta =			0.0073			

[a]The standard uncertainties (u) are $u(T)$ = 0.01 K, $u(m)$ = 1.0·10^{-4} mol·kg^{-1}. The combined expanded uncertainty (U_c) are $U_c(\rho)$ = 5.0·10^{-5} g·cm^{-3} (0.95 level of confidence) and $U_c(\eta)$ = 0.003 mPa·s (0.95 level of confidence).

the literature trend,[3] which reports that, in general, viscosity of electrolyte type 2:1($CaCl_2$ in this case) increases more rapidly than that of 1:1 (NaCl) electrolyte.

To compare the effect of different divalent ions on the viscosity, the viscosity data of the ternary system $MgCl_2$ + NaCl + H_2O at 298.15 K from our previously published data were used.[4] Figure 1 shows that Mg^{2+} has a higher effect on the solution viscosity compared to Ca^{2+} ions. As both salts $CaCl_2$ and $MgCl_2$ are 2:1 type, higher viscosity for the case of Mg^{2+} is attributed to larger charge-to-size ratio as reported by other researcher.[5] The same comparison for the density of both systems was performed and is presented in Figure 2. The

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Table 4. Density ρ, Viscosity η, and Calculated Viscosities at T = 303.15 K and Experimental Pressure of 0.1 MPa for the NaCl (1) + $CaCl_2$ (2) + H_2O (3) System[a]

	experimental data				predicted density
m_1	ρ	η	calculated viscosity/mPa·s		ρ
			Exponential model	GF model	
mol·kg^{-1}	g·cm^{-3}	mPa·s			g·cm^{-3}
			m_2 = 0.5		
0.5	1.0567	0.9797	0.9689	0.9764	1.0575
1.0	1.0738	1.0237	1.0252	1.0244	1.0763
1.5	1.0917	1.0754	1.0849	1.0796	1.0931
2.0	1.1066	1.1385	1.1477	1.1378	1.1093
3.0	1.1394	1.2363	1.2835	1.2707	1.1401
3.5	1.1541	1.3452	1.3590	1.3469	1.1551
4.5	1.1824	1.5203	1.5200	1.5076	1.1828
			m_2 = 1.0		
0.5	1.0972	1.1279	1.1252	1.1485	1.0986
1.0	1.1139	1.2335	1.1907	1.2062	1.1147
1.5	1.1292	1.2744	1.2600	1.2699	1.1303
2.0	1.1452	1.3542	1.3322	1.3367	1.1453
2.5	1.1601	1.4248	1.4090	1.4105	1.1600
3.0	1.1746	1.5140	1.4907	1.4883	1.1742
3.5	1.1887	1.5884	1.5769	1.5720	1.1880
			m_2 = 1.5		
0.5	1.1336	1.3096	1.3146	1.3362	1.1344
1.0	1.1492	1.3731	1.3911	1.4026	1.1495
1.5	1.1641	1.4307	1.4723	1.4752	1.1645
2.0	1.1786	1.5451	1.5569	1.5520	1.1783
2.5	1.1928	1.6563	1.6470	1.6353	1.1922
3.0	1.2067	1.7478	1.7405	1.7213	1.2058
3.5	1.2197	1.9143	1.8435	1.8165	1.2192
			m_2 = 2.0		
0.5	1.1699	1.5378	1.5447	1.5534	1.1691
1.0	1.1830	1.6027	1.6345	1.6294	1.1833
1.5	1.1970	1.7373	1.7268	1.7091	1.1972
2.0	1.2104	1.8087	1.8295	1.7987	1.2109
2.5	1.2246	1.9525	1.9357	1.8918	1.2243
			m_2 = 2.5		
0.5	1.2038	1.8195	1.8259	1.8176	1.2023
1.0	1.2176	1.9303	1.9320	1.9399	1.2160
1.5	1.2311	2.0458	2.0444	2.0677	1.2294
2.0	1.2443	2.2189	2.1631	2.2007	1.2428
			m_2 = 3.0		
0.5	1.2359	2.1580	2.1708	2.1885	1.2345
1.0	1.2489	2.2990	2.2970	2.3304	1.2479
1.5	1.2618	2.4463	2.4315	2.4791	1.2612
			m_2 = 3.5		
0.5	1.2668	2.5701	2.6030	2.6399	1.2668
1.0	1.2793	2.7576	2.7543	2.8036	1.2802
			m_2 = 4.5		
0.5	1.3218	3.8329	3.7756	3.7768	1.3298
AAD % =			1.09	1.44	0.120
SD =			0.0249	0.0339	0.0018
delta =			0.0061		

[a]The standard uncertainties (u) are $u(T)$ = 0.01 K, $u(m)$ = 1.0·10^{-4} mol·kg^{-1}. The combined expanded uncertainty (U_c) are $U_c(\rho)$ = 5.0·10^{-5} g·cm^{-3} (0.95 level of confidence) and $U_c(\eta)$ = 0.003 mPa·s (0.95 level of confidence).

Table 5. Density ρ, Viscosity η, and Calculated Viscosities at T = 308.15 K and Experimental Pressure of 0.1 MPa for the NaCl (1) + $CaCl_2$ (2) + H_2O (3) System[a]

	experimental data				predicted density
m_1	ρ	η	calculated viscosity/mPa·s		ρ
			Exponential model	GF model	
mol·kg^{-1}	g·cm^{-3}	mPa·s			g·cm^{-3}
			m_2 = 0.5		
0.5	1.0537	0.8866	0.8776	0.8880	1.0556
1.0	1.0717	0.9346	0.9286	0.9422	1.0729
1.5	1.0895	0.9727	0.9826	0.9987	1.0896
2.0	1.1043	1.0242	1.0395	1.0541	1.1057
3.0	1.1367	1.1232	1.1625	1.1690	1.1360
3.5	1.1516	1.2224	1.2310	1.2298	1.1506
4.5	1.1797	1.3920	1.3767	1.3490	1.1774
			m_2 = 1.0		
0.5	1.0951	1.0266	1.0191	1.0383	1.0952
1.0	1.1117	1.1207	1.0784	1.1024	1.1111
1.5	1.1269	1.1578	1.1412	1.1679	1.1265
2.0	1.1428	1.2111	1.2066	1.2324	1.1412
2.5	1.1576	1.2820	1.2762	1.2996	1.1554
3.0	1.1720	1.3526	1.3502	1.3669	1.1691
3.5	1.1861	1.4437	1.4282	1.4360	1.1822
			m_2 = 1.5		
0.5	1.1314	1.1885	1.1907	1.2104	1.1309
1.0	1.1469	1.2404	1.2599	1.2847	1.1456
1.5	1.1616	1.3021	1.3314	1.3607	1.1602
2.0	1.1761	1.4034	1.4101	1.4368	1.1734
2.5	1.1902	1.5107	1.4917	1.5151	1.1865
3.0	1.2040	1.5799	1.5776	1.5923	1.1991
3.5	1.2169	1.6964	1.6699	1.6743	1.2112
			m_2 = 2.0		
0.5	1.1676	1.3979	1.3991	1.4217	1.1655
1.0	1.1805	1.4576	1.4805	1.5087	1.1791
1.5	1.1945	1.5575	1.5660	1.5948	1.1922
2.0	1.2079	1.6460	1.6572	1.6870	1.2048
2.5	1.2219	1.7572	1.7534	1.7784	1.2169
			m_2 = 2.5		
0.5	1.2014	1.6643	1.6538	1.6770	1.1987
1.0	1.2151	1.7502	1.7497	1.7792	1.2113
1.5	1.2285	1.8541	1.8516	1.8833	1.2235
2.0	1.2415	2.0006	1.9588	1.9889	1.2352
			m_2 = 3.0		
0.5	1.2333	1.9446	1.9661	1.9865	1.2311
1.0	1.2462	2.0778	2.0800	2.1069	1.2429
1.5	1.2590	2.2088	2.2005	2.2302	1.2543
			m_2 = 3.5		
0.5	1.2641	2.3336	2.3507	2.3700	1.2640
1.0	1.2765	2.4939	2.4876	2.5125	1.2750
			m_2 = 4.5		
0.5	1.3188	3.4398	3.4189	3.3920	1.3289
AAD % =			0.90	1.63	0.2162
SD =			0.0196	0.0314	0.0034
delta =			0.0048		

[a]The standard uncertainties (u) are $u(T)$ = 0.01 K, $u(m)$ = 1.0·10^{-4} mol·kg^{-1}. The combined expanded uncertainty (U_c) are $U_c(\rho)$ = 5.0·10^{-5} g·cm^{-3} (0.95 level of confidence) and $U_c(\eta)$ = 0.003 mPa·s (0.95 level of confidence).

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Table 6. Density ρ, Viscosity η, and Calculated Viscosities at T = 313.15 K and Experimental Pressure of 0.1 MPa for the NaCl (1) + $CaCl_2$ (2) + H_2O (3) System[a]

	experimental data				predicted density
m_1	ρ	η	calculated viscosity/mPa·s		ρ
			Exponential model	GF model	
mol·kg^{-1}	g·cm^{-3}	mPa·s			g·cm^{-3}
			m_2 = 0.5		
0.5	1.0502	0.8064	0.7997	0.8044	1.0535
1.0	1.0696	0.8524	0.8461	0.8458	1.0707
1.5	1.0871	0.8934	0.8954	0.8924	1.0873
2.0	1.1019	0.9460	0.9472	0.9411	1.1032
3.0	1.1342	1.0260	1.0593	1.0510	1.1330
3.5	1.1491	1.1168	1.1217	1.1134	1.1472
4.5	1.1770	1.2540	1.2545	1.2443	1.1726
			m_2 = 1.0		
0.5	1.0929	0.9380	0.9286	0.9482	1.0929
1.0	1.1094	1.0245	0.9827	0.9974	1.1086
1.5	1.1246	1.0584	1.0399	1.0510	1.1237
2.0	1.1404	1.1059	1.0995	1.1066	1.1380
2.5	1.1552	1.1626	1.1629	1.1677	1.1517
3.0	1.1694	1.2374	1.2303	1.2318	1.1646
3.5	1.1834	1.2848	1.3014	1.3003	1.1768
			m_2 = 1.5		
0.5	1.1291	1.0846	1.0850	1.1051	1.1282
1.0	1.1445	1.1302	1.1480	1.1614	1.1424
1.5	1.1592	1.1872	1.2131	1.2222	1.1563
2.0	1.1735	1.2841	1.2849	1.2861	1.1687
2.5	1.1876	1.3817	1.3592	1.3549	1.1808
3.0	1.2013	1.4363	1.4375	1.4256	1.1920
3.5	1.2142	1.5436	1.5216	1.5034	1.2025
			m_2 = 2.0		
0.5	1.1652	1.2788	1.2749	1.2868	1.1619
1.0	1.1781	1.3482	1.3490	1.3510	1.1746
1.5	1.1919	1.4151	1.4269	1.4175	1.1865
2.0	1.2052	1.4980	1.5100	1.4918	1.1976
2.5	1.2191	1.6034	1.5977	1.6110	1.2079
			m_2 = 2.5		
0.5	1.1989	1.5114	1.5070	1.5004	1.1939
1.0	1.2125	1.5939	1.5943	1.5979	1.2049
1.5	1.2258	1.6829	1.6872	1.6995	1.2151
2.0	1.2387	1.8232	1.7849	1.8050	1.2244
			m_2 = 3.0		
0.5	1.2307	1.7825	1.7915	1.7973	1.2245
1.0	1.2435	1.9264	1.8953	1.9097	1.2337
1.5	1.2562	2.0003	2.0051	2.0272	1.2420
			m_2 = 3.5		
0.5	1.2613	2.1131	2.1420	2.1559	1.2547
1.0	1.2737	2.2613	2.2667	2.2847	1.2619
			m_2 = 4.5		
0.5	1.3158	3.0903	3.1153	3.0493	1.3119
AAD % =			0.86	1.10	0.4463
SD =			0.0174	0.0196	0.0069
delta =			0.0044		

[a]The standard uncertainties (u) are $u(T)$ = 0.01 K, $u(m)$ = 1.0·10^{-4} mol·kg^{-1}. The combined expanded uncertainty (U_c) are $U_c(\rho)$ = 5.0·10^{-5} g·cm^{-3} (0.95 level of confidence) and $U_c(\eta)$ = 0.003 mPa·s (0.95 level of confidence).

Table 7. Density ρ, Viscosity η, and Calculated Viscosities at T = 318.15 K and Experimental Pressure of 0.1 MPa for the NaCl (1) + $CaCl_2$ (2) + H_2O (3) System[a]

	experimental data				predicted density
m_1	ρ	η	calculated viscosity/mPa·s		ρ
			Exponential model	GF model	
mol·kg^{-1}	g·cm^{-3}	mPa·s			g·cm^{-3}
			m_2 = 0.5		
0.5	1.0463	0.7413	0.7327	0.7177	1.0513
1.0	1.0672	0.7808	0.7752	0.7592	1.0685
1.5	1.0844	0.8212	0.8203	0.8050	1.0851
2.0	1.1000	0.8674	0.8679	0.8522	1.1011
3.0	1.1316	0.9425	0.9705	0.9567	1.1310
3.5	1.1464	1.0220	1.0277	1.0154	1.1451
4.5	1.1742	1.1468	1.1494	1.1373	1.1702
			m_2 = 1.0		
0.5	1.0904	0.8619	0.8508	0.8385	1.0909
1.0	1.1070	0.9416	0.9003	0.8898	1.1066
1.5	1.1222	0.9729	0.9528	0.9444	1.1216
2.0	1.1378	1.0157	1.0074	1.0002	1.1359
2.5	1.1525	1.0738	1.0654	1.0605	1.1494
3.0	1.1667	1.1324	1.1272	1.1231	1.1621
3.5	1.1807	1.1850	1.1924	1.1894	1.1740
			m_2 = 1.5		
0.5	1.1267	0.9980	0.9940	0.9794	1.1261
1.0	1.1420	1.0393	1.0518	1.0395	1.1402
1.5	1.1568	1.0903	1.1115	1.1028	1.1539
2.0	1.1709	1.1756	1.1772	1.1686	1.1660
2.5	1.1849	1.2758	1.2453	1.2382	1.1776
3.0	1.1986	1.3321	1.3171	1.3089	1.1883
3.5	1.2114	1.4074	1.3941	1.3861	1.1980
			m_2 = 2.0		
0.5	1.1627	1.1836	1.1680	1.1511	1.1596
1.0	1.1756	1.2248	1.2360	1.2208	1.1719
1.5	1.1893	1.3068	1.3073	1.2918	1.1833
2.0	1.2025	1.3747	1.3835	1.3697	1.1937
2.5	1.2164	1.4667	1.4638	1.4759	1.2031
			m_2 = 2.5		
0.5	1.1963	1.3907	1.3807	1.3814	1.1910
1.0	1.2098	1.4586	1.4607	1.4684	1.2012
1.5	1.2231	1.5453	1.5458	1.5589	1.2104
2.0	1.2359	1.6651	1.6353	1.6527	1.2184
			m_2 = 3.0		
0.5	1.2279	1.6223	1.6413	1.6506	1.2207
1.0	1.2407	1.7729	1.7365	1.7505	1.2285
1.5	1.2533	1.8309	1.8370	1.8547	1.2350
			m_2 = 3.5		
0.5	1.2586	1.9467	1.9625	1.9743	1.2496
1.0	1.2708	2.0637	2.0767	2.0883	1.2544
			m_2 = 4.5		
0.5	1.3127	2.8217	2.8543	2.7760	1.3023
AAD % =			0.98	1.50	0.5158
SD =			0.0177	0.0221	0.0082
delta =			0.0043		

[a]The standard uncertainties (u) are $u(T)$ = 0.01 K, $u(m)$ = 1.0·10^{-4} mol·kg^{-1}. The combined expanded uncertainty (U_c) are $U_c(\rho)$ = 5.0·10^{-5} g·cm^{-3} (0.95 level of confidence) and $U_c(\eta)$ = 0.003 mPa·s (0.95 level of confidence).

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Table 8. Density ρ, Viscosity η, and Calculated Viscosities at T = 323.15 K and Experimental Pressure of 0.1 MPa for NaCl (1) + $CaCl_2$ (2) + H_2O (3) System[a]

	experimental data				predicted density
m_1	ρ	η	calculated viscosity/mPa·s		ρ
mol·kg^{-1}	g·cm^{-3}	mPa·s	Exponential model	GF model	g·cm^{-3}
			m_2 = 0.5		
0.5	1.0424	0.6816	0.6746	0.6811	1.0493
1.0	1.0646	0.7226	0.7138	0.7163	1.0663
1.5	1.0815	0.7580	0.7554	0.7557	1.0828
2.0	1.0981	0.8061	0.7991	0.7965	1.0989
3.0	1.1288	0.8688	0.8936	0.8881	1.1297
3.5	1.1437	0.9449	0.9463	0.9400	1.1447
4.5	1.1714	1.0535	1.0583	1.0480	1.1723
			m_2 = 1.0		
0.5	1.0874	0.7947	0.7834	0.8063	1.0881
1.0	1.1045	0.8678	0.8290	0.8472	1.1042
1.5	1.1197	0.8966	0.8773	0.8916	1.1197
2.0	1.1352	0.9460	0.9276	0.9375	1.1348
2.5	1.1499	0.9855	0.9810	0.9878	1.1494
3.0	1.1640	1.0404	1.0380	1.0404	1.1634
3.5	1.1779	1.0893	1.0979	1.0966	1.1770
			m_2 = 1.5		
0.5	1.1243	0.9207	0.9153	0.9417	1.1238
1.0	1.1394	0.9614	0.9685	0.9876	1.1388
1.5	1.1542	1.0087	1.0234	1.0373	1.1537
2.0	1.1682	1.0864	1.0840	1.0893	1.1674
2.5	1.1821	1.1833	1.1467	1.1453	1.1809
3.0	1.1957	1.2199	1.2127	1.2027	1.1939
3.5	1.2085	1.2900	1.2837	1.2659	1.2064
			m_2 = 2.0		
m_2=2.0					
0.5	1.1601	1.0884	1.0755	1.0973	1.1585
1.0	1.1730	1.1325	1.1381	1.1488	1.1725
1.5	1.1866	1.1974	1.2038	1.2023	1.1860
2.0	1.1998	1.2638	1.2739	1.2622	1.1989
2.5	1.2136	1.3462	1.3479	1.3604	1.2113
			m_2 = 2.5		
m_2=2.5					
0.5	1.1937	1.2754	1.2713	1.2726	1.1917
1.0	1.2071	1.3517	1.3450	1.3525	1.2046
1.5	1.2203	1.4175	1.4234	1.4355	1.2169
2.0	1.2331	1.5198	1.5058	1.5215	1.2287
			m_2 = 3.0		
0.5	1.2253	1.4976	1.5113	1.5181	1.2234
1.0	1.2379	1.6147	1.5989	1.6096	1.2351
1.5	1.2505	1.6839	1.6915	1.7051	1.2462
			m_2 = 3.5		
0.5	1.2558	1.7812	1.8070	1.8123	1.2541
1.0	1.2679	1.8900	1.9123	1.9167	1.2645
			m_2 = 4.5		
0.5	1.3097	2.5754	2.6282	2.5383	1.3090
AAD % =			1.03	1.10	0.1354
SD =			0.0181	0.0175	0.0021
delta =			0.0044		

[a]The standard uncertainties (u) are $u(T)$ = 0.01 K, $u(m)$ = 1.0·10^{-4} mol·kg^{-1}. The combined expanded uncertainty (U_c) are $U_c(\rho)$ = 5.0·10^{-5} g·cm^{-3} (0.95 level of confidence) and $U_c(\eta)$ = 0.003 mPa·s (0.95 level of confidence).

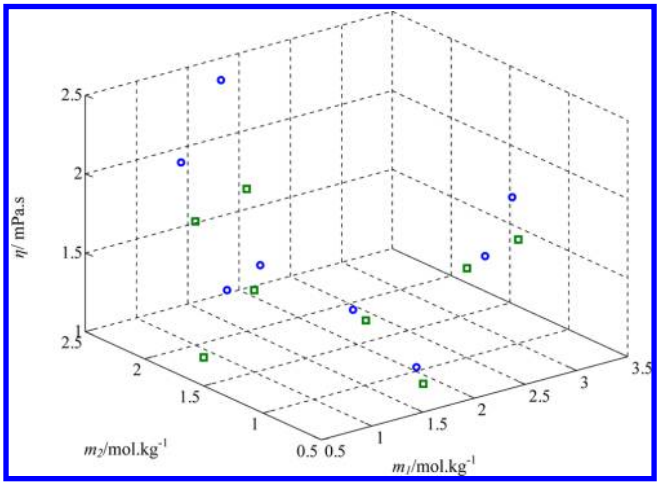

Figure 1. Comparison of viscosity data at T = 298.15 K between NaCl +$CaCl_2$+H_2O and NaCl+$MgCl_2$+H_2O: green squares, viscosity of NaCl+$CaCl_2$+H_2O; blue circles, viscosity of NaCl+$MgCl_2$+H_2O.

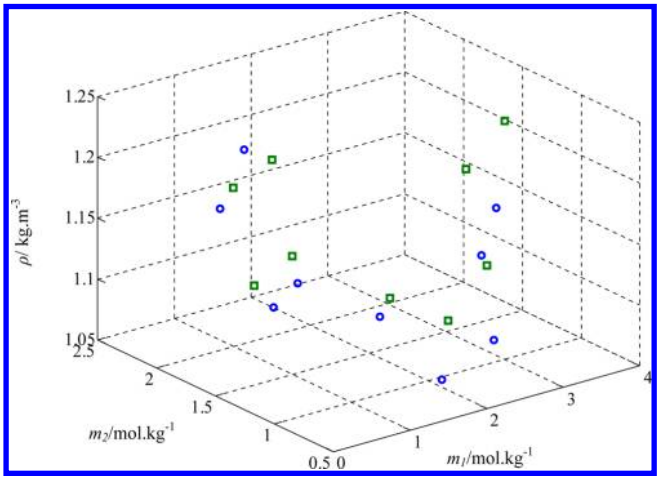

Figure 2. Comparison of density data at T = 308.15 K between NaCl +$CaCl_2$+H_2O and NaCl+$MgCl_2$+H_2O: green squares, Density of NaCl +$CaCl_2$+H_2O; blue circles, density of NaCl+$MgCl_2$+H_2O

density of the ternary system $CaCl_2$+NaCl+H_2O is higher than that of the ternary system $MgCl_2$+NaCl+H_2O when compared at the same molalities. This is because the molar mass of calcium is higher than the molar mass of the magnesium ions.

3.2. Modeling. Both viscosity and density of the ternary solutions were correlated and predicted using different models. The viscosity data were correlated by three available models in the literature; the exponential model, the mixing model developed by Goldsack and Franchetto,[6] referred to as the

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GF model in this paper, and the extended Jones−Dole model.[7] Density was predicted using the Kumar model.[8]

3.2.1. Exponential Model. The semiempirical exponential model is reported to be a successful model in predicting viscosity of binary solutions at high concentrations of salts.[9−12]

$$\eta = a \exp(bm + fm^2) \quad (2)$$

where a (mPa·s), b (kg.mol^{-1}), and f (kg^2.mol^{-2}) are adjustable parameters and m is the salt molality. In recent work, this model was extended for ternary solutions by assuming a linear combination of concentration of electrolytes.[13] This model is tested against the measured data in this work. The extended form of eq 2 is as follows

$$\eta = a \exp(b_1 m_1 + f_1 {m_1}^2 + b_2 m_2 + f_1 {m_2}^2) \quad (3)$$

where m_1 is molality of NaCl and m_2 is molality of $CaCl_2$. In this work, eq 3 was fitted to the data shown in Tables 2 to 8 at temperature T = (293.15 to 323.15) K.

NLINFIT functionl in MATLAB was used to fit eq 3 to the data generated in this work. NLINFIT function in MATLAB estimates the coefficients of a nonlinear regression function; using the least-squares method. It takes the independent variable (m_1 and m_2), the dependent variable (viscosity), and initial guess of coefficient as input and it returns the calculated values of the viscosity along with the estimated coefficients. Confidence intervals of the calculated values were determined using the NLPREDCI and NLPARCI functions. Another tool in MATLAB was used to verify the results. The optimization tool FMINSEARCH was used. The difference in the values of calculated viscosity by the two MATLAB tools was less than 0.035 %. Therefore, all the presented parameters are based on the NLINFIT tool.

Equation 3 was used to fit the data for each temperature. The coefficients b and f in eq 3 were found to be independent of temperature, while the coefficient a was found to be a strong function of temperature. Therefore, values of b and f were optimized and proven to be temperature independent. The optimized values of b and f are listed in Table 9. Values of

Table 9. Values of Coefficient b and f (eq 3) at the Studied Temperatures for NaCl+$CaCl_2$+H_2O System and NaCl +$MgCl_2$+H_2O[4]

ternary system	b_1 / kg·mol^{-1}	f_1 / kg^2·mol^{-2}	b_2 / kg·mol^{-1}	f_2 / kg^2·mol^{-2}
NaCl+$CaCl_2$+H_2O	0.113	−0.001	0.282	0.0116
NaCl+$MgCl_2$+H_2O	0.086	0.005	0.370	0.008

coefficient a are presented in Table 10 at different temperatures. The 95 % confidence interval for the calculated values of a are shown in Table 10, too. Half width of Confidence intervals are not more than 0.48 % of the calculated values which suggest that calculated values of a are reliable and dependable. Parameter a in eq 3 is related to temperature as shown in eq 4.

$$a = a_0 \exp\left(\frac{a_1}{T - a_2}\right) \quad (4)$$

where a_0 (mPa·s), a_1 (K), and a_2 (K) are adjustable parameters. Calculated values for a_0, a_1, and a_2 for the ternary $CaCl_2$+NaCl +H_2O are 0.0334, 490.810, and 148.18, respectively. The correlation is considered successful as the absolute maximum

Table 10. Values of Coefficient a (eq 3) at the Studied Temperatures for NaCl+$CaCl_2$+H_2O and NaCl +$MgCl_2$+H_2O[4]

T/K	a/mPa·s	95% CI[a] for a
	NaCl+$CaCl_2$+H_2O	
293.15	0.9876	0.9828 to 0.9924
298.15	0.8817	0.8781 to 0.8853
303.15	0.7953	0.7923 to 0.7983
308.15	0.7189	0.7165 to 0.7213
313.15	0.6541	0.652 to 0.6562
318.15	0.5998	0.5977 to 0.602
323.15	0.5535	0.5491 to 0.5535
	NaCl+$MgCl_2$+H_2O[4]	
298.15	0.8843	0.8818 - 0.8868
303.15	0.7923	0.7896- 0.7950
308.15	0.7129	0.7100 - 0.7158
313.15	0.6381	0.6324 - 0.6438
318.15	0.5900	0.5865 - 0.5935

[a]Confidence interval.

deviation was less than 0.18 %. So the final temperature-dependent viscosity model for ternary solution takes the following form

$$\eta = a_0 \exp\left(\frac{a_1}{T - a_2}\right) \exp(b_1 m_1 + f_1 {m_1}^2 + b_2 m_2 + f_2 {m_2}^2) \quad (5)$$

Viscosity values calculated by eq 5 are listed in Tables 2 to 8, column 4. Furthermore, experimental and calculated data were compared. The standard deviation (SD) and average absolute deviation (AAD) were calculated using eqs 6 and 7, respectively.

$$\mathrm{SD} = \left[\frac{\sum_{i=1}^{n} (\eta_{\mathrm{exp},i} - \eta_{\mathrm{cal},i})^2}{n - p}\right]^{1/2} \quad (6)$$

$$\mathrm{AAD}\ (\%) = \left[\sum \frac{|\eta_{\mathrm{exp},i} - \eta_{\mathrm{cal},i}|}{\eta_{\mathrm{exp},i}}\right]\frac{100}{n} \quad (7)$$

where n is the number of data points and p is the number of adjusted parameters. Values of AAD and SD are reported at the bottom of Tables (2 to 8. The maximum standard deviation was found to be 0.0396 mPa·s at 293.15 K but at other temperature it was less than 0.03 mPa·s. The average absolute deviations (AAD) were around 1 % with maximum value of 1.355 % for the data set of 293.15 K. Reliability of calculation was further confirmed by looking at a half width of 95 % confidence interval (delta) of calculated values of viscosity. Values of delta are reported in Tables 2 to 8. Values of delta range from 0.0043 to 0.0097 indicating that the calculated viscosity by the model is reliable.

Examining all the statistical analysis data above reveals that eq 5 fits very well the experimental data as can be observed in Figures 3, 4, and 5. Figure 3 experimental and calculated viscosity values are plotted against NaCl molality (m_1) at different $CaCl_2$ molality (m_2) at fixed temperature of 308.15 K. To better understand the effect of concentration on viscosity, a 3-D plot is generated by plotting calculated and experimental viscosity (z axis) against m_1 (x-axis) and m_2 (y-axis) as depicted in Figure 4. Figures 3 and 4 suggest that calculated viscosity by

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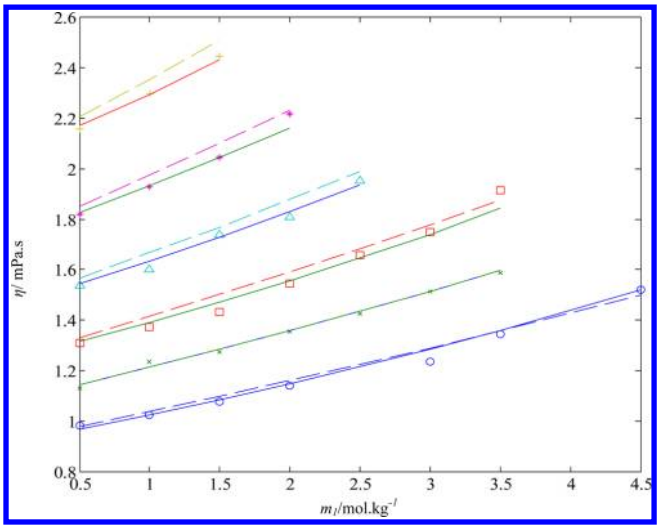

Figure 3. Experimental data and correlated values of viscosity of ternary aqueous solution of sodium chloride (m_1) and $CaCl_2$ (m_2) at 308.15 K: ○,m_2= 0.5; ×, m_2 = 1.0; □, m_2 = 1.5; △, m_2 = 2.0; ∗, m_2 = 2.5; +, m_2 = 3.0. Solid lines are exponential model and dotted line are GF model.

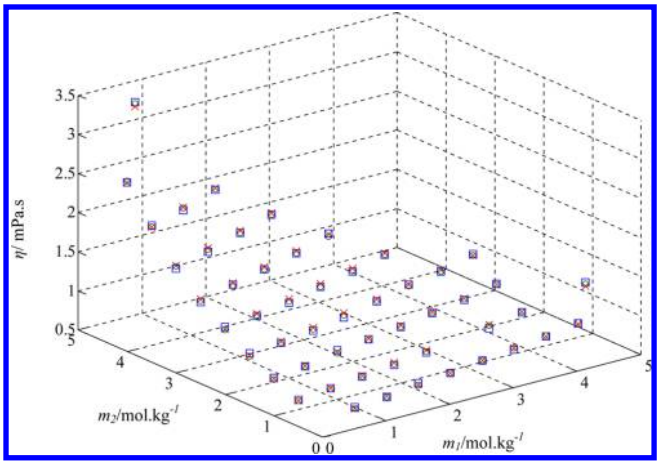

Figure 4. Experimental data and correlated values of viscosity of ternary aqueous solution of sodium chloride (m_1) and $CaCl_2$ (m_2) at 308.15 K. ○, experimental; □, exponential model; ×, GF model.

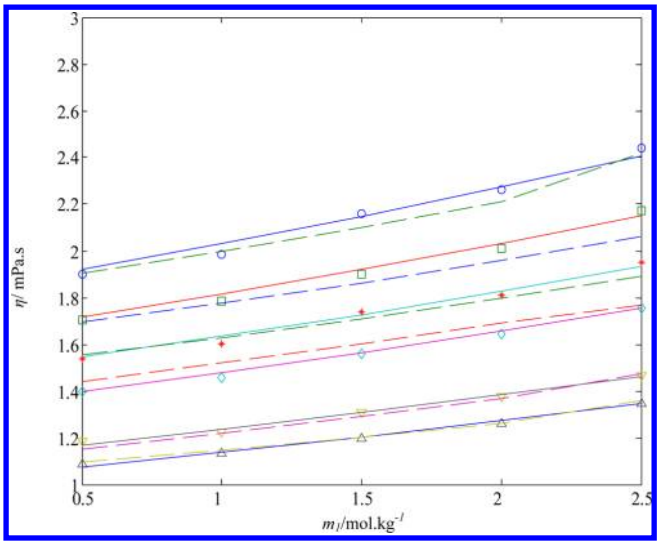

Figure 5. Experimental data and correlated values of viscosity of ternary aqueous solution of sodium chloride (m_1) and $CaCl_2$ (m_2) at various temperature and fixed molality m_2 = 2.0: ○, (T = 293.15 K); □, (T = 298.15 K); ∗, (T = 303.15 K); ◇, (T = 313.15 K); ▽, (T = 323.15 K), △, (T = 328.15 K). Solid lines are exponential model and dotted line are GF model.

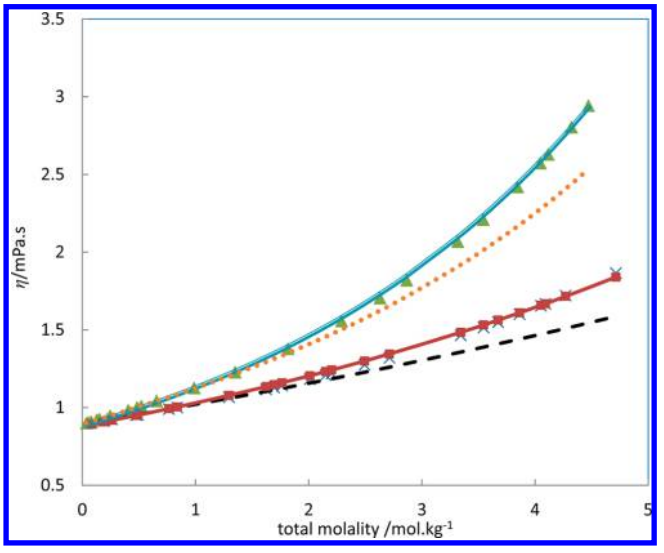

Figure 6. Experimental data[7] and correlated values (eq 5) of viscosity of ternary aqueous solution of sodium chloride (m_1) and $CaCl_2$ (m_2) at T = 298.15 K: ■, experimental data at m_2/m_1 = $^1/_3$; ▲, experimental data at m_2/m_1 = $^3/_1$. Solid lines are calculated viscosity by exponential model. Dotted lines are calculated viscosity by extended Jones−Dole model.

exponential equation matches the experimental data very closely at all molalities covered in this study. Figure 5 presents the experimental and calculated viscosities against molality (m_1) at various temperatures. It suggests that the exponential model predicts viscosity well at all temperatures studied.

Equation 5 was validated against experimental data for NaCl +$CaCl_2$+H_2O reported in the literature[7] as shown in Figure 6. It can be observed that eq 5 referred to as zn exponential equation fits very well the experimental data for both molality ratios (3 and $^1/_3$) and even at higher concentrations.

Our previously published data[4] for the ternary system of NaCl+$MgCl_2$+H_2O was also correlated by the exponential model (eq 5). This was done in order to investigate the effect of divalent ion Mg^{2+} compared to Ca^{2+}on viscosity. The optimized values of coefficients for this system are reported in Table 9. The value of coefficient b_2 is larger than that of $CaCl_2$. This suggests that, in ternary mixtures with water and sodium chloride, the contribution of $MgCl_2$ to viscosity is higher than that of $CaCl_2$. Values of coefficient a are presented in Table 10 at different temperatures. Coefficient a temperature dependence has the form of eq 4. Calculated values a_0, a_1, and a_2 for the ternary $MgCl_2$+NaCl+H_2O are 0.0399, 405.007, and 167.55, respectively. The maximum standard deviation was found to be 0.0359 mPa·s at 313.15 K but at all other temperatures it was less than 0.025 mPa·s. The average absolute deviations (AAD) were around 1 % at all temperatures except at 313.15 K it was 2.97 %. A representative plot of experimental and calculated data is presented in Figure 7 at 318.15 K. Statistical data for the fit and Figure 7 suggest that the exponential model fits the viscosity data of ternary mixture of

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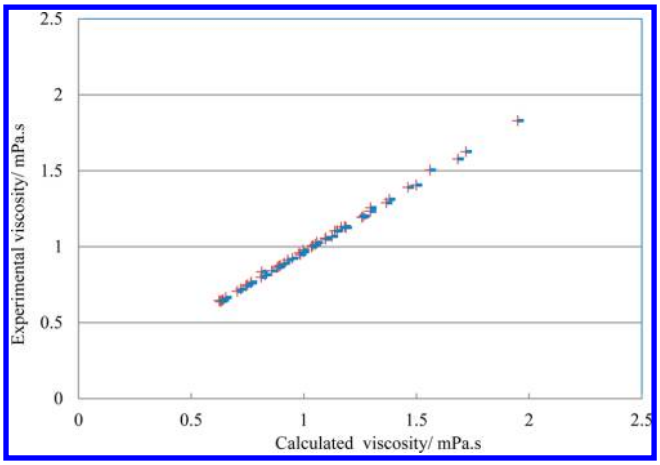

Figure 7. Experimental[4] data and correlated values for NaCl +$MgCl_2$+H_2O at 318.15 K: +, exponential model, −, GF model.

NaCl+$MgCl_2$+H_2O, too. Similar conclusions can be withdrawn at other temperatures.

3.2.2. Goldsack and Frachetto Model (GF Model). Goldsack and Frachetto[6] extended the theory of absolute rate of viscosity of liquids to concentrated single electrolyte solution and derived an equation of viscosity for a binary mixture.

$$\eta = \frac{\eta_w e^{XE}}{1 + XV} \tag{8}$$

where η is the viscosity of electrolyte solution, η_w is the viscosity of solvent, E and V are dimensionless free energy and volume parameters, and X is the appropriate mole fraction of solute. Detailed derivation of eq 8 can be found elsewhere.[6]

For a 1:1 electrolyte like NaCl, KCl, and $MgSO_4$ (total of two ions) X may be taken as the mole fraction of cations

$$X = \frac{m}{55.51 + 2m} \tag{9}$$

For 1:2 electrolytes like $CaCl_2$, $MgCl_2$, and $Ca(NO_3)_2$ (total of three ions),

$$X = \frac{m}{55.51 + 3m} \tag{10}$$

Goldsack and Frachetto extended their work and investigated the temperature dependence of the viscosity of solution of different electrolytes by calculating E and V parameters at different temperatures.[14] They adapted a single electrolyte model (eq 8) to predict the viscosity of electrolyte mixtures,[15] and later it was used by other researchers.[16,17] In that case eq 8 takes the form

$$\eta = \frac{\eta_w e^{(X_1E_1 + X_2E_2)}}{(1 + X_1V_1 + X_2V_2)} \tag{11}$$

For a mixed solution made up of electrolyte 1 and 2, X_1 and X_2 will be as follows.

$$X_1 = \frac{m_1}{55.51 + \nu_1 m_1 + \nu_2 m_2} \tag{12}$$

$$X_2 = \frac{m_2}{55.51 + \nu_1 m_1 + \nu_2 m_2} \tag{13}$$

Equations 8 to 13 were used in this work to predict the viscosity of mixtures of NaCl and $CaCl_2$. For this system of electrolytes the values ν_1 and ν_2 in eqs 12 and 13 are 2 and 3, respectively.

Using the binary data for NaCl and $CaCl_2$ solutions[18,19] and fitting them in eqs 8 to 10, E and V values were calculated by MATLAB nonlinear fit tool NLINFIT. Calculated values of E and V at different temperatures are reported in Table 11. The calculated values were inserted into eqs 11 to 13 to calculate the viscosity of ternary mixtures. E_2 and V_2 values are calculated for two molality ranges to get better parameter estimation as followed by other investigators.[16] Calculated values of viscosity of ternary solutions by this equation (referred to as the GF model) are also reported in Tables 2 to 8, column 5. Calculated values and experimental data were compared in order to assess the quality of correlation. The AAD was found to vary between 1.099 to 1.634, which is quite reasonable for a mixing model. Calculated viscosities and experimental viscosities are plotted against molality of NaCl (m_1) and molality of $CaCl_2$ (m_2) in Figures 3 to 5. The figures suggest that viscosity calculated by the GF model is in good agreement with the experimental ones. However, a comparison between the two models shows that the exponential model viscosity correlations are slightly better (AAD less than 1.3 %) than the GF model (AAD less than 1.6 %).

Table 11. Values of E and V at Different Temperatures for NaCl+$CaCl_2$+H_2O and NaCl+$MgCl_2$+H_2O

			molality 0 to 2		molality 2 to 5	
T/K	E_1	V_1	E_2	V_2	E_2	V_2
			NaCl+$CaCl_2$+H_2O			
293.15	15.56	12.08	28.44	12.00	43.44	42.98
298.15	15.34	11.57	27.04	9.93	41.85	37.77
303.15	15.09	11.02	27.95	10.25	41.72	36.66
308.15	14.85	10.5	32.41	15.68	40.82	34.23
313.15	14.61	9.99	28.06	9.97	40.34	32.75
318.15	14.22	9.33	35.00	22.00	39.57	30.46
323.15	14.19	9.16	26.23	6.86	39.05	29.10
			NaCl+$MgCl_2$+H_2O			
298.15	15.34	11.57	40.78	21.94		
303.15	15.08	11.02	39.23	19.17		
308.15	14.85	10.5	40.19	21.62		
313.15	14.61	9.99	36.32	17.07		
318.15	14.22	9.34	35.58	16.76		

To confirm the validity of GF model, it was also investigated against viscosity data for the ternary solution of NaCl +$MgCl_2$+H_2O from our previous work.[4] E and V values for $MgCl_2$ were calculated from viscosity data of binary $MgCl_2$ solutions available in the literature.[12,20] Calculated values of E and V are reported in Table 10. The average standard deviation was found to be around 0.05 mPa·s and the average absolute deviations (AAD) were around 2.5% at all temperatures. Experimental data and calculated data using GF model are plotted in Figure 7 (as an example). Both Figure 7 and statistical data of the fit suggest that the GF model fits better to the ternary solution of NaCl+$CaCl_2$+H_2O than that of NaCl +$MgCl_2$+H_2O.

3.2.3. Extended Jones–Dole Model. In our previous work[4] the extended Jones–Dole equation with three adjustable parameters was successfully used to correlate the viscosity of the ternary system NaCl+$MgCl_2$+H_2O for fixed molar ratios of two electrolytes. But it failed to predict the ternary system of

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$NaCl+CaCl_2+H_2O$ for the range of molalities (0 $mol\cdot kg^{-1}$ to 4.5 $mol\cdot kg^{-1}$) studied in this case.

Another methodology is followed here to predict the viscosity of the ternary solutions using the extended Jones–Dole model.[7] In this method the viscosity was predicted as shown in eq 14 from the binary data rather than correlating the ternary viscosity data.

$$\frac{\eta}{\eta_0} = 1 + A_1c_1^{1/2} + B_1c_1 + D_1c_1^{2} + E_1c_1^{3.5} + F_1c_1^{7} + A_2c_2^{1/2} + B_2c_2 + D_2c_2^{2} + E_2c_2^{3.5} + F_2c_2^{7} \quad (14)$$

where c is the concentration in $mol\cdot L^{-1}$, subscript 1 and 2 are for NaCl and $CaCl_2$ respectively; A and B values were calculated theoretically and the other coefficients of the model are calculated by fitting the binary data of NaCl and $CaCl_2$ data to the corresponding equation for binary as

$$\frac{\eta}{\eta_0} = 1 + Ac^{1/2} + Bc + Dc^{2} + Ec^{3.5} + Fc^{7} \quad (15)$$

Then the viscosity of the ternary solution was calculated by eq 14 assuming a simple additive rule. Figure 6 demonstrates that calculated viscosities by using a simple additive rule can be used at lower concentrations, but at higher concentrations calculated values become smaller and the difference increases as concentration increases. It is worth mentioning that extended Jones–Dole equation fits very well to the binary systems of both NaCl and $CaCl_2$ in water. The failure of the extended Jones–Dole equation using a simple additive rule can be attributed to the strong interaction of ions Na^+ and Ca^{2+} at higher concentration.

The extended Jones–Dole method of calculating the viscosity of a ternary solution was applied to our viscosity data. Theoretical values of A and B for the binary system of NaCl and $CaCl_2$ were taken from their work.[7] Coefficients values D to F were determined by correlating our binary data for a solution of NaCl and $CaCl_2$ to eq 15. The coefficients of the extended Jones–Dole equation are reported in Table 12,

Table 12. Coefficients of Extended Jones–Dole Equation for Binary Solutions of NaCl and $CaCl_2$

	A	B	D	10^4E	10^5F
NaCl	0.0061[c]	0.0799[c]	0.01762[a]	6.19[a]	
			0.1142[b]	−6.84[b]	
$CaCl_2$	0.0157[c]	0.0271[c]	0.4295[a]	65.5[a]	0.27[a]
			0.4712[b]	94[b]	3.02[b]

[a]Values from our binary data. [b]Literature value.[7] [c]Theoretically calculated values from literature.[7]

and these values are applied in eq 14 to calculate the viscosity of a ternary mixture. Calculated viscosities are listed in Table 3 and a representative plot for experimental and calculated values of viscosity is presented in Figure 8. Table 3 and Figure 8 confirm the results reported in a previous work[7] that calculated values of viscosity at high concentrations are not recommended and the deviation becomes more than 10 %.

3.2.4. Density Modeling. A simple equation for the prediction of ternary solution density was proposed by Kumar as follows:[8]

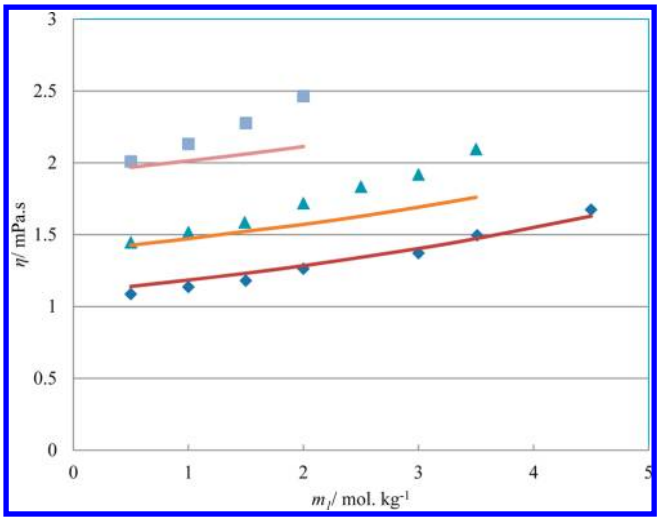

Figure 8. Experimental data (this work) and correlated values of viscosity by extended Jones–Dole equation of ternary aqueous solution of sodium chloride (m_1) and $CaCl_2$ (m_2) at 298.15 K: ◆, experimental data at m_2 = 0.5; ▲, m_2 = 1.5; ■, m_2 = 2.5. Solid lines are calculated viscosity by extended Jones–Dole.

$$\rho = \frac{(1000 + \sum_j m_jM_j)}{\left\{\left(\frac{1000}{d_o}\right)\left[\sum_j y_j\left(\left(\frac{d_o}{d_j^o}\right) - 1\right) + 1\right] + \sum_j\left(\frac{m_jM_j}{d_j^o}\right)\right\}} \quad (16)$$

where y_j is ionic strength fraction of the jth salt and can be written as

$$y_j = \frac{m_j}{m_j^o} \quad (17)$$

m_j is the molality of an electrolyte in mixture, m_j^o is the molality of jth aqueous electrolyte at the ionic strength of mixture, d_j^o is the density of aqueous jth electrolyte at the ionic strength of mixture and d_o is density of water.

Equation 16 was tested for the prediction of the density of a ternary solution and compared with our measured density data. A detailed calculation method for eq 16 can be found in other literature.[21−23] Predicted values of density at all studied temperature are reported in Tables 2 to 8 along with the absolute average deviation (AAD %) and standard deviation (SD). The AAD % ranges from 0.0678 to 0.4463 and the SD ranges from 0.0014 to 0.0082. A plot of the experimental density and predicted densities by eq 16 is presented in Figure 9. These statistical data and Figure 9 suggest that eq 16 proposed by Kumar predicts the density of the ternary salt solutions accurately for all concentrations and temperatures investigated in this study.

4. CONCLUSIONS

Detailed experimental measurements of density and viscosity of mixed blends of the NaCl–$CaCl_2$–water ternary system were conducted. Experimental measurements were reported for a wide range of molalities. Findings indicate that exponential and GF models can be used to correlate viscosities of mixed NaCl $+CaCl_2+H_2O$ ternary solutions. Furthermore, examination of the extended Jones–Dole equation proved to be less accurate at higher concentrations. For the exponential models only the parameter a showed temperature dependence and was

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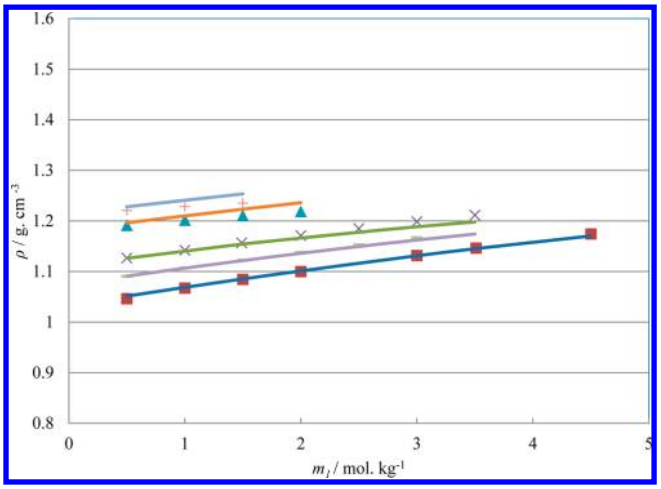

Figure 9. Experimental data and predicted values of the density of a ternary aqueous solution of sodium chloride (m_1) and $CaCl_2$ (m_2) at 318.15 K: ■, m_2 = 0.5; −, m_2 = 1.0; ×, m_2 = 1.5; ▲, m_2 = 2.5; +, m_2 = 3.0. Solid lines are predicted density by eq 16.

correlated with an exponential equation with three adjustable parameters enough to get good predictions for the viscosity of the studied ternary system. For GF model the values of parameters E and V (nondimensional free energy and volume parameters) at different temperature are presented. Comparison among the three models shows that the exponential model viscosity correlations are the best. The suggested equation by Kumar has predicted the density of the ternary NaCl +$CaCl_2$+H_2O solution very well.

Using our previous published data[4] about the NaCl +$MgCl_2$+H_2O system shows that the viscosity can still be well correlated by both GF and exponential models. Comparing the effect of $CaCl_2$ and $MgCl_2$ on viscosity and density of the ternary solutions with NaCl and H_2O shows that $MgCl_2$ has a more pronounced effect on the viscosity while $CaCl_2$ has a more pronounced effect on density.

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Notes

The authors declare no competing financial interest.

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