Measurement and Prediction of Densities of Ternary Aqueous Mixtures Involving Sodium Polyacrylate

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The densities of the binary aqueous solutions of sodium polyacrylate (NaPAA) at 20°C, 25°C, and 30°C up to 0.17 m and LiCl at 25°C and 30°C up to 3.13 m were measured using a vibrating tube digital densitimeter. The measured experimental data were then fitted to the polynomial $d = d_o + \Sigma A_i m^i$. The densities of the ternary aqueous systems NaPAA–NaCl, NaPAA–LiCl, and NaPAA–sucrose were also measured from 20°C to 30°C. The isopycnotic equation, $\Sigma m_i / m_{oi} = 1$ was used to predict the densities of the ternary aqueous systems mentioned. The results show that predicted and observed density values are in good agreement. The overall percentage error of density prediction for the system NaPAA–NaCl–H_2O is 0.067. For the system NaPAA–LiCl–H_2O, the overall percentage error is 0.074; and, for the system NaPAA–sucrose–H_2O, the overall percentage error is 0.065.

Keywords: Aqueous solutions, density, isopycnotic equation, molality, multicomponent solutions, *and* sodium polyacrylate (NaPAA).

INTRODUCTION

Many industrial processes involve systems of aqueous solutions containing more than one solute. Although the densities of a large number of aqueous ternary solutions have been measured (Teng and Mather 1996), the direct experimental determination of the densities of aqueous multicomponent solutions is tedious and troublesome. In addition, the number of possible combinations of individual solutes in aqueous solutions is tremendously large. It is, therefore, useful to have reliable and convenient predictive methods to estimate the densities of aqueous multicomponent solutions from the binary density data.

Various methods have been proposed to predict or represent the densities of multicomponent aqueous solutions. These methods have been tested mainly on electrolyte–electrolyte mixtures. Likewise, these methods have been compared based on their applicabilities (Teng and Mather 1996). The method, however, that can be used to predict the densities of multicomponent aqueous solutions involving electrolytes and nonelectrolytes, as well as systems involving polymers (Teng and Teng 2004), is the *isopycnotic equation,*

$$\Sigma m_i / m_{oi} = 1 \quad (1)$$

where m_i is the molality of solute i in the multicomponent solution and m_{oi} is the molality of solute i in its binary solution at the same density as the multicomponent solution. The method is based on solutions having the same density or the so-called *isopycnotic solutions* (Teng and Lenzi 1975a). It assumes a linear relation between the solute molalities of binary and multicomponent aqueous solutions at the same density.

Equation 1 states that when isopycnotic binary solutions are mixed, the resultant multicomponent solution is also *isopycnotic*, or has the same density. This relation assumes negligible short-range solute–solute interactions and hydration cross-effects or their mutual cancellation. The use of Equation 1 for density prediction requires the density values of the binary aqueous solutions of the solutes involved. Thus, having the experimental data on good density–concentration relation for each binary aqueous solution is essential.

The isopycnotic mixing rule has been used to test the density predictive accuracy of aqueous electrolyte–electrolyte, electrolyte–nonelectrolyte, and nonelectrolyte–nonelectrolyte systems at atmospheric pressure and using various temperatures (Teng and Lenzi 1975a, Teng et al. 1994, Teng 2003).

However, relatively little information on the measurement and prediction densities of aqueous multicomponent systems involving polyelectrolytes have been published. Thus, the present study measures the densities of, and attempts both to extend and test the applicability of the isopycnotic mixing rule to, multicomponent aqueous systems involving polyelectrolytes at various temperatures.

EXPERIMENTAL

The chemicals used in the present work include sodium polyacrylate (NaPAA) with 2,100 molecular weight and 99.7% purity, sodium chloride (NaCl) with 99.8% purity, and sucrose with 99.5% purity, which were all obtained from Fluka Chemicals; and lithium chloride (LiCl) with 99.0% purity, from Merck Laboratories. These solutes were used without further purification.

On the one hand, the aqueous binary solutions of the systems NaPAA were prepared with up to 0.17 m (molality). On the other hand, the aqueous ternary solutions of the systems NaPAA–NaCl, NaPAA–LiCl, and NaPAA–sucrose were prepared using various combinations of the solutes. These aqueous solutions were prepared by weight using double-distilled water. The densities of these solutions were then measured at 20°C, 25°C, and 30°C using a vibrating tube digital densitometer (Anton Paar DMA 58) which has a built-in constant temperature bath that controls temperatures to within ±0.01°C. The densitometer was calibrated using pure water and dry air (Kell 1975, Perry and Green 1984). Calibrations were done regularly to ensure the accuracy of results. Note that the densitometer has an accuracy of 1×10^{-5} g/cm^3 and a precision of $\pm 0.5 \times 10^{-5}$ g/cm^3.

RESULTS AND DISCUSSION

Densities of aqueous binary solutions of NaPAA and LiCl

The densities of aqueous binary solutions were measured as a function of concentration at different temperatures. The densities measured for the aqueous binary solutions of NaPAA at 20°C, 25°C, and 30°C are given in Table 1. It has been observed that the density of aqueous binary solutions of NaPAA increases with concentration and decreases with temperature.

In contrast, the densities of aqueous binary solutions of LiCl were measured at 25°C and 30°C. From the results shown in Table 2, one can observe trends similar to that for NaPAA. The densities of aqueous binary solutions at a given temperature can be represented by the following concentration polynomial (Teng and Lenzi 1975b):

Table 1. Experimental Density Data for NaPAA + H_2O at 20°C, 25°C, and 30°C

Molality, *m*	Density, *d* (g/cm³)		
(moles/kg)	20°C	25°C	30°C
0.01570	1.01714	1.01557	1.01290
0.02059	1.01867	1.01589	1.01493
0.02418	1.02194	1.02089	1.01866
0.02955	1.02692	1.02532	1.02366
0.03552	1.03205	1.03035	1.02869
0.04169	1.03796	1.03677	1.03498
0.04991	1.04545	1.04412	1.04210
0.05328	1.04880	1.04641	1.04505
0.06059	1.05556	1.05353	1.05153
0.06344	1.05751	1.05613	1.05430
0.07496	1.06719	1.06585	1.06457
0.08180	1.07425	1.06977	1.06960
0.08784	1.08027	1.07557	1.07527
0.09663	1.08633	1.08166	1.08121
0.10186	1.09133	1.08534	1.08456
0.11187	1.10014	1.09571	1.09488
0.13169	1.11161	1.10333	1.10214
0.15026	1.11940	1.11024	1.10934
0.16111	1.12329	1.11630	1.11517
0.16850	1.12472	1.12238	1.12066

$$d = d_0 + \Sigma A_i m^i \qquad (2)$$

where d_0 is the density of pure water at a given temperature and A_i is the polynomial coefficient. Equation 2 has been used to fit the density data of the aqueous binary systems of NaPAA, NaCl, LiCl, and sucrose at 20°C, 25°C, and 30°C. The polynomial coefficients are tabulated in Table 3. Meanwhile, the standard deviation is calculated from the following equation:

$$\sigma = \sqrt{\frac{\sum\left(d^{obs} - d^{cal}\right)^2}{(n-p)}} \qquad (3)$$

where d^{obs} = observed density
d^{cal} = calculated density from Equation 2 and the coefficients in Table 3
n = no. of data points
p = no. of parameters

Table 3 shows that fitting the density data of various binary aqueous solutions into the equation give reasonably low deviations, in the order of 10^{-4}. Equation 2, together with the coefficients listed in Table 3, can be used for the interpolation and is needed in Equation 1 for the density prediction of multicomponent aqueous solutions.

Table 2. Experimental Density Data for LiCl + H_2O at 25°C and 30°C

Molality, *m*	Density, *d* (g/cm³)	
(moles/kg)	25°C	30°C
0.18784	1.00091	0.99958
0.49253	1.00789	1.00641
0.60803	1.01049	1.00913
0.88740	1.01662	1.01514
0.99751	1.01919	1.01728
1.09522	1.02109	1.01954
1.11740	1.02141	1.02009
1.17264	1.02295	1.02151
1.41542	1.02777	1.02622
1.62195	1.03211	1.03048
1.89368	1.03723	1.03551
2.31328	1.04581	1.04434
2.52466	1.04991	1.04829
2.58805	1.05142	1.05001
3.12858	1.06015	1.05852

Densities of ternary aqueous systems

The densities of ternary solutions of NaPAA-NaCl-H_2O, NaPAA-LiCl-H_2O, and NaPAA-sucrose-H_2O were measured at 20°C, 25°C, and 30°C, respectively. For NaPAA-NaCl-H_2O, NaPAA-LiCl-H_2O, and NaPAA-sucrose-H_2O, the results appear in sequence in Tables 4, 5, and 6.

The densities of the points m_1 = 0.02, m_2 = 0.08 and m_1 = 0.041, m_2 = 0.059 in Table 4 show that the contribution of NaPAA to density is higher than that of NaCl. Similarly, an inspection of points m_1 = 0.010, m_2 = 0.095 and m_1 = 0.051, m_2 = 0.051 in Table 5 reveal a higher contribution of NaPAA to density than that of LiCl. In Table 6, the densities of points m_1 = 0.051, m_2 = 0.050 and m_1 = 0.080, m_2 = 0.020 exhibit the same greater contribution to density for NaPAA than

Table 3. Coefficients for the Polynomial (See Equation 2) for the Density of Aqueous Binary Solutions at 20°C, 25°C, and 30°C

Aqueous systems	Temp. (°C)	A_1/A_5	A_2/A_6	A_3/A_7	A_4	σ
NaPAA	20	0.101966E+1[$]/ -0.827878E+4	-0.105106E+1/ 0.200591E+5	-0.433623E+2	0.106389E+4	0.53E-3
	25	0.104693E+1/ 0.162605E+4	-0.435071E+1/	0.698426E+2	-0.602898E+3/	0.46E-3
	30	0.103409E+1/ 0.193808E+4	-0.483807E+1	0.874646E+2	-0.736509E+3	0.38E-3
NaCl	20*	0.426640E-1	-0.232520E-2	0.123550E-3	-0.230100E-4	0.83E-3
	25*	0.409590E-1	-0.205450E-2	0.211190E-3	0.119150E-5	0.14E-4
	30*	0.412740E-1	-0.203840E-2	0.996950E-4	-	0.71E-3
LiCl	20#	0.248558E-1/ 0.213104E-6	-0.135134E-2	0.122473E-3	-0.778574E-5	0.33E-4
	25	0.196275E-1/ -0.416744E-3	0.781103E-2	-0.800667E-2	0.308280E-2	0.14E-3
	30	0.196709E-1/ -0.444304E-3	0.766513E-2	-0.813992E-2	-0.444304E-3	0.20E-3
Sucrose	20	0.135250/ -0.222770E-3	-0.337030E-1/ 0.565260E-4	0.734390E-2/- 0.378730E-5	-0.537160E-3	0.32E-3
	25	0.130710/ 0.212750E-4	-0.275400E-1	0.453190E-2	-0.468220E-3	-0.21E-4
	30@	0.131038	-0.297597E-1	0.403752E-2	-	0.81E-4

$ 0.101966E + 1 = 0.101966 x 10^{+1}

\# Lide 1993–94.

* Rohana et al. 1999

@ Rohana 1997

for sucrose. The densities of all the ternary mixtures, however, decrease with temperature.

Equation 1 was used to predict the densities of the ternary systems NaPAA–NaCl–H_2O, NaPAA–LiCl–H_2O, and NaPAA–sucrose–H_2O at 20°C, 25°C, and 30°C, respectively. The average predictive errors for the system NaPAA–NaCl–H_2O of 0.090%, 0.040%, and 0.069 % correspond to ±1.573 x 10^{-3}, ±3.90 x 10^{-4}, and ±7.262 x 10^{-4} in density at 20 °C, 25°C, and 30°C, respectively. Meanwhile, the density predictive errors for the system NaPAA–LiCl–H_2O are 0.096%, 0.090 %, and 0.037 % correspond to ±5.433 x 10^{-4}, 8.20 x 10^{-4}, and ±3.35 x 10^{-4} in density at 20 °C, 25°C, and 30 °C. In comparison, the density predictive errors for the system NaPAA–sucrose–H_2O of 0.086%, 0.059%, and 0.050% correspond to ±8.31 x 10^{-4}, ±6.17 x 10^{-4}, and ±5.42 x 10^{-4} in density at 20°C, 25°C, and 30°C, respectively. Hence, the overall density predictive error is 0.065% or ±7.22 x 10^{-4} in density.

One the one hand, a closer inspection of Tables 4 to 6 reveal the same absence of

Table 4. Density Prediction for Ternary Aqueous System NaPAA–NaCl at 20°C, 25°C, and 30°C

Aq. System	m_1	m_2	20°C			25°C			30°C		
			d^{exp}	d^{cal}	%error	d^{exp}	d^{cal}	%error	d^{exp}	d^{cal}	%error
NaPAA–NaCl	0.01	0.089	1.01265	1.01214	0.051	1.01054	1.01028	0.022	1.00877	1.00929	0.051
	0.02	0.08	1.02115	1.02148	0.032	1.01952	1.01964	0.014	1.01788	1.01836	0.047
	0.031	0.072	1.03028	1.03066	0.037	1.02893	1.02902	0.011	1.02689	1.02737	0.047
	0.041	0.059	1.03901	1.03934	0.032	1.03686	1.03781	0.097	1.03583	1.03600	0.017
	0.051	0.052	1.04745	1.04802	0.054	1.04573	1.04637	0.064	1.04398	1.04467	0.066
	0.061	0.04	1.0502	1.05666	0.129	1.05463	1.05463	0.003	1.05393	1.05321	0.068
	0.081	0.022	1.07127	1.07464	0.314	1.07028	1.07123	0.096	1.06301	1.06124	0.166
	0.091	0.012	1.08176	1.08240	0.059	1.07812	1.07823	0.012	1.07581	1.07483	0.091
	Average % error				0.09			0.04			0.07

Table 5. Density Prediction for the Ternary Aqueous System NaPAA–LiCl at 20°C, 25°C, and 30°C

Aq. System	m_1	m_2	20°C			25°C			30°C		
			d^{exp}	d^{cal}	%error	d^{exp}	d^{cal}	%error	d^{exp}	d^{cal}	%error
NaPAA–LiCl	0.01	0.095	1.01023	1.01073	0.049	1.00882	1.00967	0.086	1.00809	1.00780	0.029
	0.02	0.09	1.01918	1.02033	0.113	1.01753	1.01905	0.152	1.01691	1.01716	0.025
	0.03	0.084	1.02907	1.02930	0.022	1.02682	1.02774	0.091	1.02528	1.02595	0.066
	0.04	0.062	1.03710	1.03780	0.067	1.03572	1.03610	0.039	1.03390	1.03441	0.049
	0.051	0.051	1.04668	1.04728	0.057	1.04549	1.04553	0.051	1.04374	1.04390	0.041
	0.062	0.042	1.05686	1.05678	0.007	1.05367	1.05488	0.122	1.05345	1.05332	0.013
	Average % error				0.096			0.09			0.037

Table 6. Density prediction for the ternary aqueous system NaPAA–sucrose at 20°C, 25°C, and 30°C

System	M_1	m_2	20°C			25°C			30°C		
			d^{exp}	d^{cal}	%error	d^{exp}	d^{cal}	%error	d^{exp}	d^{cal}	%error
NaPAA–Suc	0.011	0.092	1.02403	1.02074	0.321	1.01910	1.01919	0.009	1.01719	1.01763	0.043
	0.02	0.081	1.02779	1.02836	0.055	1.02620	1.02678	0.076	1.02474	1.02509	0.034
	0.031	0.072	1.03588	1.03659	0.068	1.03395	1.03501	0.107	1.03390	1.03324	0.029
	0.041	0.061	1.04450	1.04445	0.005	1.04225	1.04283	0.06	1.04159	1.04108	0.049
	0.051	0.05	1.05278	1.05231	0.045	1.04988	1.05055	0.071	1.04884	1.04890	0.006
	0.062	0.041	1.06168	1.06061	0.101	1.05712	1.05849	0.132	1.05671	1.05705	0.034
	0.071	0.031	1.06759	1.06766	0.004	1.06441	1.06490	0.047	1.06440	1.06370	0.087
	0.08	0.02	1.07418	1.07460	0.039	1.07122	1.07117	0.016	1.06898	1.07026	0.12
	Average % error				0.086			0.059			0.05

systematic errors in density prediction as shown in other cases (Teng and Lenzi 1975a, Teng et al. 1994). On the other hand, the aforementioned results confirm the applicability of the isopycnotic mixing rule in the prediction of densities of multicomponent aqueous solutions that involve polyelectrolytes as well as nonelectrolytes at different temperatures.

CONCLUSIONS

Measuring the densities of the aqueous binary solutions of NaPAA from a temperature of 20°C to 30°C up to 0.17 m, reveal that density increases with concentration and decreases with temperature. The measured experimental data were then fit to the polynomial $d = do + SA_i m^i$.

In contrast, the densities of the ternary aqueous systems NaPAA–NaCl, NaPAA–LiCl, and NaPAA–sucrose which were measured at 20°C, 25°C, and 30°C, respectively, confirm a higher NaPAA contribution to density than for the other solutes studied. Using the isopycnotic mixing rule in predicting the densities of the mentioned multicomponent systems which involve polyelectrolytes resulted in an overall percentage error that is well below 0.1%.

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