Density, Refractive Index, Viscosity, and Electrical Conductivity in the Na_2CO_3 + Poly(ethylene glycol) + H_2O System from (293.15 to 308.15) K

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Data are presented on the density, refractive index, viscosity, and electrical conductivity of unsaturated solutions of sodium carbonate + poly(ethylene glycol) + water at four temperatures between (293.15 and 308.15) K. The range of concentration of the solutions was from 0 to 7 mass % Na_2CO_3 and from 0 to 40 mass % poly(ethylene glycol) (PEG) with an average molecular weight of 2000. The experimental data on density, refractive index, and viscosity were correlated using Othmer's rule. The data on electrical conductivity were transformed to molar conductance and were correlated by group according to the percentage of PEG in each system.

Introduction

Studies of aqueous biphasic systems have increased in recent years because these represent an efficient method applicable to the extractive separation of chemicals. Our interest in developing processes for the extraction of iodine led us to study some biphasic systems formed from poly(ethylene glycol) + salt + water.[1−4] In one of these studies, we presented experimental data on the liquid−liquid equilibrium at 298.15 K for the PEG 2000 + sodium carbonate + water system.[4] The present paper is a continuation of this study and presents experimental data on the density, refractive index, viscosity, and electrical conductivity of unsaturated solutions in the preceding system. Measurements of these properties were carried out at four different temperatures from (293.15 to 308.15) K. The concentration interval for the sodium carbonate was from 0 to 7% on a mass/mass basis, and that for PEG 2000 varied from 0 to 40 mass %. Few data have been reported in the literature on the physical properties of and transports for aqueous systems containing PEG and salt.

Snyder et al.[5] measured the density and viscosity for this type of solution at 298.15 K in biphasic equilibrium. The molar masses of PEG used in these measurements were 1000, 3350, and 8000, and the salts used included magnesium sulfate, sodium sulfate, ammonium sulfate, sodium carbonate, and potassium phosphate.

Mei et al.[6] measured the density and viscosity for two aqueous systems: PEG + K_3PO_4 and PEG + $(NH_4)_2SO_4$. Measurements of these two properties were carried out with unsaturated solutions as well as with solutions in liquid−liquid equilibrium. This study was carried out at 293.15 K and at molar masses of PEG of 1000, 2000, 4000, 6000, and 20000.

Zafarani-Moattar et al.[7] and Zafarani-Moattar and Mehrdad[8] presented experimental data for the densities of different aqueous mixtures of PEG + salt at temperatures of (298.15, 308.15, and 318.15) K. In the first study, they used PEG having molar masses of 1000 and 6000 and included the salts K_2HPO_4, KH_2PO_4, Na_2SO_4, Na_2CO_3, and $(NH_4)_2SO_4$. In the second study, the molar masses of PEG were 2000 and 4000, and the salts used were $NaHSO_4$, NaH_2PO_4, and Na_2HPO_4.

Graber et al.[2] experimentally measured the refractive index, density, and viscosity for the $NaNO_3$ + H_2O + PEG 4000 system. This study was carried out at six temperatures between (288.15 and 313.15) K.

We have not been able to find any data in the literature on experimental values for the refractive index, viscosity, and electrical conductivity for the system presently evaluated.

Experimental Section

Materials. Test solutions were prepared using sodium carbonate (Merck >99.9%), predried in an oven at 120 °C for 24 h. The PEG was of synthesis grade (Merck) and had a nominal molecular weight of 2000. This reagent was subjected to drying in an oven for 7 days at 50 °C. Gel permeation chromatography (GPC) evaluation of the PEG showed an average molecular weight of 2078, a number-average molecular weight of 1997, and a polydispersity of 1.0488. Both reagents were used without further purification. Ultrapure water (conductivity = 0.05 μS/cm), obtained by passing distilled water trough a Millipore ultrapure cartridge kit, was used in obtaining all measurements.

Apparatus and Procedures. The solutions were prepared by mass, using an analytical balance with a precision of ±0.07 mg (Mettler Toledo, model AX204). The densities of the solutions were measured in triplicate by means of a vibrating tube digital densimeter, model DE-50 (Mettler Toledo) having an uncertainty of $\pm 2 \times 10^{-5}$ g·cm^{-3}.

The refractive index of each solution was measured in triplicate using a Mettler Toledo model RE-40 refractometer having an uncertainty of $\pm 1 \times 10^{-4}$. Further details are given in our earlier work.[2]

The kinematics viscosities of the solutions were measured with an automatic Schott-Gerate AVS 310 laser viscosimeter, which measured the transit time of the liquid meniscus through a capillary, with a precision of ±0.1 s. A calibrated Micro-Oswald viscosimeter was immersed in a transparent Schott-Gerate CT 52 thermostatic bath, with a temperature precision of ±0.05 K. The dynamic viscosity

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Table 1. Values for the Density ρ, Refractive Index n_D, Viscosity η, and Electrical Conductivities k in Aqueous Solutions of Na_2CO_3 and PEG-2000 for Different Mass Fractions of Sodium Carbonate (w_1) and PEG (w_2) between (293.15 and 308.15) K

$100w_1$	$100w_2$	ρ/g·cm^{-3}	n_D	η/mPa·s	mS·cm^{-1}	$100w_1$	$100w_2$	ρ/g·cm^{-3}	n_D	η/mPa·s	k/mS·cm^{-1}
					T = 293.15 K						
0.999	0.0	1.00866	1.3352	1.072	14.40	6.001	9.997	1.07833	1.3603	3.468	36.50
2.000	0.0	1.01919	1.3375	1.121	25.59	1.001	19.999	1.04386	1.3634	5.466	7.07
3.000	0.0	1.02943	1.3395	1.213	35.20	2.000	20.000	1.05401	1.3659	5.718	12.09
4.000	0.0	1.03991	1.3418	1.242	43.90	3.000	20.000	1.06521	1.3682	6.376	16.21
5.000	0.0	1.05028	1.3439	1.306	51.80	1.001	30.000	1.06195	1.3785	11.487	3.92
6.000	0.0	1.06085	1.3461	1.407	59.10	2.002	29.999	1.07295	1.3814	13.545	6.28
7.000	0.0	1.07135	1.3482	1.488	65.30	1.001	40.000	1.08124	1.3949	27.254	2.02
1.000	10.000	1.02665	1.3490	2.501	9.44	0.0	10.000	1.01565	1.3466	2.355	
2.000	10.001	1.03703	1.3515	2.598	16.60	0.0	19.999	1.03342	1.3608	5.200	
3.001	10.000	1.04756	1.3537	2.790	22.40	0.0	29.999	1.05126	1.3759	10.784	
4.003	10.000	1.05755	1.3561	2.936	27.80	0.0	40.003	1.07076	1.3916	24.826	
5.007	9.999	1.06788	1.3582	3.154	32.50						
					T = 298.15 K						
0.999	0.0	1.00738	1.3347	0.952	14.55	6.001	9.997	1.07631	1.3596	3.037	42.00
2.000	0.0	1.01803	1.3369	0.996	25.92	1.001	19.999	1.04177	1.3626	4.691	7.30
3.000	0.0	1.02794	1.3390	1.082	35.60	2.000	20.000	1.05185	1.3649	4.906	12.56
4.000	0.0	1.03848	1.3412	1.103	44.50	3.000	20.000	1.06309	1.3675	5.460	16.82
5.000	0.0	1.04862	1.3433	1.159	52.40	1.001	30.000	1.05949	1.3776	9.692	4.58
6.000	0.0	1.05929	1.3454	1.247	59.70	2.002	29.999	1.07031	1.3803	11.355	7.38
7.000	0.0	1.06952	1.3475	1.317	66.20	1.001	40.000	1.07813	1.3936	22.355	2.50
1.000	10.000	1.02413	1.3483	2.181	10.76	0.0	10.000	1.01362	1.3460	2.051	
2.000	10.001	1.03456	1.3508	2.266	19.00	0.0	19.999	1.03117	1.3601	4.451	
3.001	10.000	1.04526	1.3529	2.431	25.50	0.0	29.999	1.04889	1.3749	9.101	
4.003	10.000	1.05539	1.3553	2.559	31.70	0.0	40.003	1.06771	1.3906	20.472	
5.007	9.999	1.06594	1.3575	2.750	37.30						
					T = 303.15 K						
0.999	0.0	1.00589	1.3340	0.853	14.75	6.001	9.997	1.07407	1.3587	2.710	47.70
2.000	0.0	1.01629	1.3362	0.893	26.26	1.001	19.999	1.03986	1.3616	4.064	7.55
3.000	0.0	1.02628	1.3384	0.967	36.10	2.000	20.000	1.04957	1.3642	4.256	12.96
4.000	0.0	1.03665	1.3406	0.987	45.10	3.000	20.000	1.06022	1.3665	4.727	17.44
5.000	0.0	1.04679	1.3426	1.033	53.10	1.001	30.000	1.05678	1.3768	8.302	5.30
6.000	0.0	1.05718	1.3447	1.113	60.70	2.002	29.999	1.06756	1.3790	9.670	8.54
7.000	0.0	1.06757	1.3468	1.174	67.10	1.001	40.000	1.07495	1.3922	18.600	2.95
1.000	10.000	1.02229	1.3476	1.905	12.10	0.0	10.000	1.01189	1.3455	1.816	
2.000	10.001	1.03263	1.3499	1.996	21.40	0.0	19.999	1.02887	1.3593	3.859	
3.001	10.000	1.04303	1.3522	2.138	29.10	0.0	29.999	1.04627	1.3742	7.772	
4.003	10.000	1.05346	1.3544	2.253	36.10	0.0	40.003	1.06460	1.3895	17.089	
5.007	9.999	1.06376	1.3568	2.418	42.20						
					T = 308.15 K						
0.999	0.0	1.00421	1.3334	0.770	14.95	6.001	9.997	1.07173	1.3578	2.416	53.60
2.000	0.0	1.01453	1.3356	0.803	26.57	1.001	19.999	1.03702	1.3608	3.558	7.78
3.000	0.0	1.02446	1.3377	0.867	36.50	2.000	20.000	1.04735	1.3634	3.778	13.33
4.000	0.0	1.03477	1.3399	0.890	45.60	3.000	20.000	1.05774	1.3657	4.132	17.97
5.000	0.0	1.04483	1.3419	0.936	53.70	1.001	30.000	1.05398	1.3758	7.123	6.03
6.000	0.0	1.05523	1.3441	1.001	61.50	2.002	29.999	1.06474	1.3781	8.318	9.75
7.000	0.0	1.06549	1.3461	1.052	68.00	1.001	40.000	1.07162	1.3907	15.698	3.41
1.000	10.000	1.02030	1.3466	1.692	13.56	0.0	10.000	1.00998	1.3447	1.612	
2.000	10.001	1.03052	1.3491	1.771	23.90	0.0	19.999	1.02647	1.3583	3.378	
3.001	10.000	1.04090	1.3515	1.895	32.90	0.0	29.999	1.04356	1.3734	6.706	
4.003	10.000	1.05107	1.3536	1.999	40.40	0.0	40.003	1.06138	1.3883	14.458	
5.007	9.999	1.06146	1.3559	2.145	47.40						

was obtained by multiplying the kinematic viscosity by the corresponding density. The results given in Table 1 are the average of three determinations for each solution and showed an uncertainty of $\pm$0.001 mPa·s.

Measurements of the electrical conductivity were carried out using an Orion model 170 conductimeter, calibrated using a standard KCl solution. The uncertainty was $\pm$0.038 mS·cm^{-1}.

Results and Discussion

Table 1 lists the experimental values obtained for the density (ρ), refractive index (n_D), viscosity (η), and electrical conductivity (k) for the system studied as a function of the temperature and concentration, where w_1 and w_2 are the mass fractions of Na_2CO_3 and PEG 2000, respectively. Beginning with a PEG concentration of 20% in the system, the range of variation of the sodium carbonate was limited because its solubility decreases markedly with increasing PEG concentration.

Table 1 shows that for any given mixture the refractive index, density, and viscosity always decrease with increasing temperature. In contrast, the electrical conductivity demonstrates the inverse behavior. The dependency of the first three properties on concentration at a given temperature can be noted at a constant concentration of Na_2CO_3 or PEG 2000. In both cases, the refractive index, as well as the density and the viscosity, increase with increasing Na_2CO_3 or PEG concentration.

In the case of viscosity, Figure 1 (with w_1 = 0.01 constant) and Figure 2 (with w_2 = 0.10 constant) more clearly show the above cited tendencies. It is also observed from these Figures that the concentration of PEG has a greater effect than the concentration of sodium carbonate on the magnitude reached by the viscosity of the mixture.

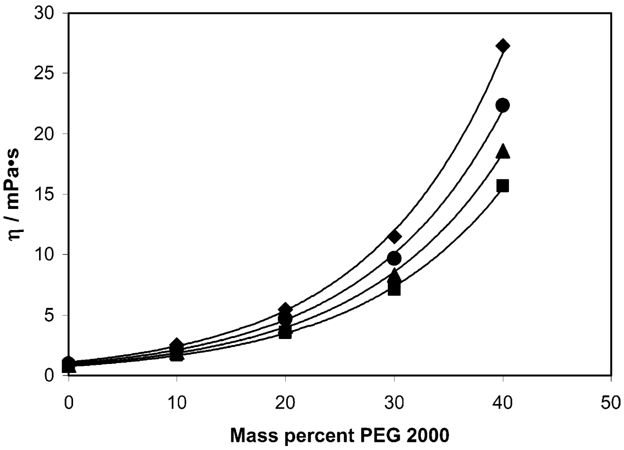

Figure 1. Viscosity of PEG 2000 + H_2O + Na_2CO_3 (1 mass %) system at different temperatures: ♦, 293.15 K; ●, 298.15 K; ▲, 303.15 K; and ■, 308.15 K.

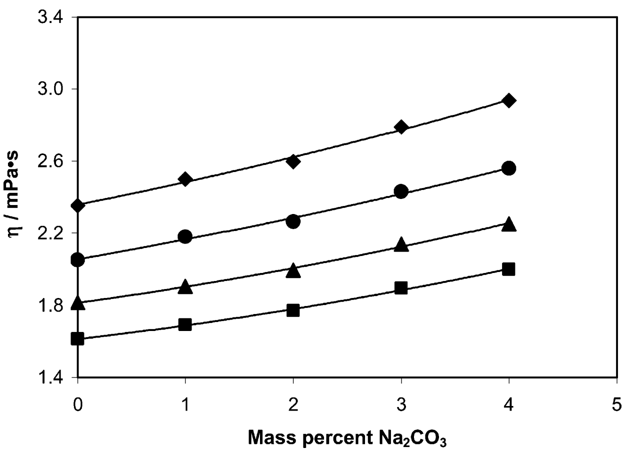

Figure 2. Viscosity of PEG 2000 (10 mass %) + H_2O + Na_2CO_3 system at different temperatures: ♦, 293.15 K; ●, 298.15 K; ▲, 303.15 K; and ■, 308.15 K.

The electrical conductivity for a constant PEG concentration always increases with increasing Na_2CO_3 concentration. However, the conductivity decreases with increasing PEG concentration when the concentration of Na_2CO_3 remains constant The latter may occur because of the large size of the PEG molecules, which interlace with each other to form a network that traps ions, thus decreasing ionic movement within the system.

Some experimental data on density, viscosity, and electrical conductivity have been reported in the scientific literature for binary systems containing Na_2CO_3 + H_2O (Zafarani-Moattar et al.[7]) and PEG 2000 + H_2O (Kirincic and Klofutar[9]). Because the concentrations reported in these studies do not coincide with the concentrations of the present study, it is difficult to make comparative analyses. Fortunately, some studies present equations obtained by making by fits of their experimental data. We have compared our experimental data with the data of others by the use of equations of the type cited above and have obtained good general agreement.

Zafarani-Moattar et al.[7] presented an equation for the apparent molal volume of the Na_2CO_3 + H_2O system at 298.15 K and 308.15 K. We determined the density values by employing this equation and our own concentrations. The absolute mean deviations between the calculated and experimental values were (10×10^{-5} and 40×10^{-5}) g·cm^{-3} at 298.15 K and 308.15 K, respectively. Kirincic and Klofutar[9] presented an equation for the apparent specific volume for the PEG 2000 + H_2O system at 298.15 K. We determined the density values using this equation and our concentrations and found an absolute mean deviation between calculated and experimental values of 20×10^{-5} g·cm^{-3}.

Table 2. Values for the Parameters in Equations 2 and 3 for the Refractive Index, Density, and Viscosity

	parameters for refractive index	parameters for density	parameters for viscosity
A_1	−0.8047	0.8320	7.6981
A_2	−0.5991	0.1324	8.0249
B_1	3.3628	7.1083	0.2846
B_2	2.4469	3.2955	1.5879
medium error %	0.02	0.2	4.4
maximum error %	0.09	0.6	16

Albright et al.[10] used the equation of Martin to fit the viscosity data of the PEG 2000 + H_2O system at 298.15 K. We determined dynamic viscosity values using this equation and our concentrations, finding that for PEG concentrations of (10, 20, and 30) mass % the absolute mean deviation between the calculated and experimental values was 0.07 mPa·s. When including the 40 mass % PEG concentration (that producing the most difference), the mean deviation increased to 0.5 mPa·s. Kirincic and Klofutar[11] presented a polynomial-type equation for the specific viscosity of aqueous PEG 2000 solutions at 298.15 K. Unfortunately, this equation is valid only for PEG concentration of less than 15 mass %. A value of 2.073 mPa·s was obtained for a PEG concentration of 10 mass %, which is in good agreement with our experimental value of 2.051 mPa·s.

Some data for the viscosity of the Na_2CO_3 + H_2O system at (291.15 and 298.15) K appear in ICT.[12] We fit these data to an empirical equation using six constants that were independent of the temperature. The absolute mean deviations between the calculated values and our experimental data were (0.03 and 0.02) mPa·s at (293.15 and 298.15 K), respectively.

Capewell et al.[13] presented an equation for the electrical conductivity for the Na_2CO_3 + H_2O system at 298.15 K. With this equation and our concentrations, we found that the values of electrical conductivity compared with our experimental data showed an absolute mean deviation of 0.4 mS·cm^{-1}.

Our experimental values for the refractive index, density, and viscosity were correlated using Othmer's[14] rule. The general expression for the three properties mentioned is

$$\ln Y_R = \ln \frac{Y}{Y_W} = A + B \ln Y_W \tag{1}$$

where Y_R is the relative property and represents the ratio between the value of the physical property Y of the mixture (refractive index, density, or viscosity) and that of water (Y_W), both at the same temperature. The density and viscosity of water are expressed in g·cm^{-3} and mPa·s, respectively.

A and B are constants, both depending on the mass fraction of sodium carbonate (w_1) and PEG (w_2) and independent of temperature:

$$A = A_1 w_1 + A_2 w_2 \tag{2}$$

$$B = B_1 w_1 + B_2 w_2 \tag{3}$$

Values for the constants A_1, A_2, B_1, and B_2 for the three properties are shown in Table 2.

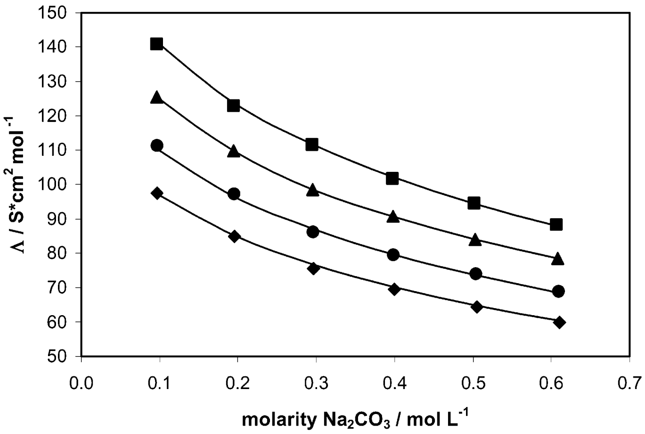

Figure 3. Experimental and calculated molar conductance of the PEG 2000 (10 mass %) + H_2O + Na_2CO_3 system at different temperatures: ♦, 293.15 K; ●, 298.15 K; ▲, 303.15 K and ■, 308.15 K; −, calculated values (eq 4).

Table 3. Values for the Parameters in Equation 4 for Molar Conductance

mass % of PEG	A_1	A_2	A_3	medium error %	maximum error %
0	3.6407	0.09685	−0.9238	0.41	0.79
10	−9.9051	0.86426	−1.0141	0.59	1.60
20	0.5700	0.23832	−1.2083	0.21	0.50
30	−13.0256	1.00662	−1.6968	0.63	1.20

For refractive index and density, we note that the absolute values of constants A_1 and B_1 are greater than those of A_2 and B_2. This indicates that the values of these two properties depend more on the presence of sodium carbonate than the presence of PEG in the system. However, we note for the viscosity that there is an inverse behavior where constants A_2 and B_2 are now greater than A_1 and B_1. This indicates that the presence of PEG has a greater influence on the value of the viscosity than the presence of sodium carbonate in the system, as observed in Figures 1 and 2.

Equation 1 presents a mean deviation of 0.02% (0.09% maximum) for experimental values of the refractive index. For the density, the mean deviation was 0.2% (0.6% maximum), and for the viscosity, the mean deviation was 4.4% (16% maximum). The values of the refractive index used in making the fit of the experimental data were those reported by Horvath,[15] and for the density and viscosity, we used the data reported by Isono.[16]

We were unable to find an equation having an acceptable deviation to use in presenting all of the data on conductivity as a function of the concentrations and temperature. For this, the experimental data were fit in groups according to the concentration of PEG in the system. The values for electrical conductivity were transformed to molar conductance (Λ) because these fits showed smaller deviations. For PEG, concentrations of 0, 10, 20, and 30 mass %, the equation is

$$\Lambda/(\mathrm{cm^2{\cdot}S{\cdot}mol^{-1}}) = \exp[A_1 + A_2T^{0.5} + A_3c^{0.5}] \qquad (4)$$

In the preceding equation, T is the temperature (K) and c is the concentration (M) of the sodium carbonate in the system. The values of the constants are listed in Table 3, together with the percent deviations. Figure 3 compares the values of molar conductance obtained by eq 4 (solid lines) with the experimental values obtained for the Na_2CO_3 + H_2O + PEG (10 mass %) system. The calculated values are in good agreement with the experimentally obtained values.

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