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Volumetric Properties, Viscosities, Refractive Indices, and Surface Tensions for Aqueous Genosorb 1753 Solutions

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The densities and viscosities of aqueous solutions of Genosorb 1753 (Selexol) were measured in the range (298.15 to 343.15) K. Refractive indices in the range (293.15 to 333.15) K and surface tensions in the range (298.15 to 323.15) K were also measured. Genosorb 1753 is a widely used physical solvent, a mixture of polyethylene glycol dimethyl ethers. All the experimental data were correlated using polynomials as a function of the temperature and concentration.

Introduction

Allied Chemical Corporation patented the Selexol process in the late 1960s. The process was later purchased in 1982 by Norton and consequently sold to Union Carbide in 1990. Dow Chemical Co. finally acquired it in 2001. The Selexol process uses an equivalent of Genosorb 1753 as the absorption liquid. It is a mixture of polyethylene glycol dimethyl ethers $CH_3O(CH_2CH_2O)_nCH_3$ with n mainly between 4 and 10. It is suitable for use extensively and reliably as a physical absorption medium in acid gas removal, in waste air treating processes, and to clean synthesis gases.[1-3]

Schmidt[4] mentioned that Selexol has a high absorptive power for hydrogen sulfide (H_2S), mercaptans (R−SH), and other sulfur-containing compounds (CS_2, COS). Selexol is considered to be much more selective to sulfur dioxide than carbon dioxide, a major constituent of flue gas streams. Like all physical solvents, it requires very little energy for regeneration. Vaporization, foaming, and degradation losses of Selexol are small, and it is therefore considered as an environmentally friendly product.[3] The fact that it has some lubricity and is solid free result in a reduced level of maintenance in operations.[5] For all these reasons and many others, Selexol is used in over 60 gas treating plants. Selexol and Rectisol (methanol) are the most widely used solvents for integrated gasification combined cycle (IGCC) synthesis gases. To our knowledge, there is no published data for the densities, viscosities, refractive indices, or surface tensions for aqueous Genosorb 1753 (Selexol) solutions.

In this work, the densities, viscosities, refractive indices, and surface tensions of the binary systems of water (1) + Genosorb 1753 (2) are studied over the entire mass fraction range and at various temperatures to cover a wide range of temperatures required in industrial applications. All data were correlated with a polynomial equation as a function of the temperature and mass fraction.

Experimental Section

Genosorb 1753 was obtained from Clariant International Ltd. and was used without further purification. Low-resolution electrospray ionization (ESI) results done at the University of Alberta (Mass Spectrometry Laboratory) concluded that the

weight average molecular weight was 360.9 and that the number average molecular weight was 339.9. All solutions were prepared with deionized water. An analytical balance Ohaus (Model Ap 205 D, Florham Park, NJ) was used to prepare gravimetrically the binary mixtures of Genosorb 1753 and deionized water with a precision of ±0.1 mg. The overall possible uncertainty in the mass fractions is around ±0.0001. Densities were measured for deionized water, Genosorb 1753, and their binary mixtures using an Anton Paar DMA 4500 densimeter. The apparatus consists of a glass U tube with a PT100 platinum resistance thermometer inside a thermostatic jacket with an uncertainty of 0.01 K. The sample density is a function of the oscillation frequency. At each temperature, the relationship between the density and the oscillation frequency is

$$\rho = A + B\tau^2 \tag{1}$$

where ρ is the liquid density and τ is the period of oscillation. The calibration was done using air and water at ambient temperature. The densities of water were measured in the temperature range (279.15 to 353.15) K and were compared with the values measured by Bettin et al.[6] and with the values provided in the instruction manual of Anton Paar. The calibration was acceptable if the measurements were within $\pm 3 \times 10^{-5}$ g·cm^{-3} of the published values. The uncertainty of our density data was estimated to be 5×10^{-5} g·cm^{-3}.

Viscosities were measured with five different U-tube Glass Cannon−Ubbelohde viscometers to cover, with precision,[7] the range of temperatures from (298.15 to 343.15) K. The viscometers were placed in a well-stirred constant temperature bath (model CT 500, Cannon Instrument Company, State College, PA). The uncertainty of the water bath temperature was ±0.01 °C as measured by the Ertco-Hart RTD high-precision digital thermometer (Model 850 C, West Patterson, NJ). The efflux time was measured manually using a digital stopwatch having an accuracy of 0.01 s. Each datum was an average of at least four runs with a maximum deviation in the kinematic viscosity of ±0.1 % at each temperature for all mass fractions. The uncertainty of the viscosity measurements was estimated to be 1 % when compared with the literature values. The equation for kinematic viscosity, according to Poiseuille's law, is

$$\nu = k_1 t - k_2/t \tag{2}$$

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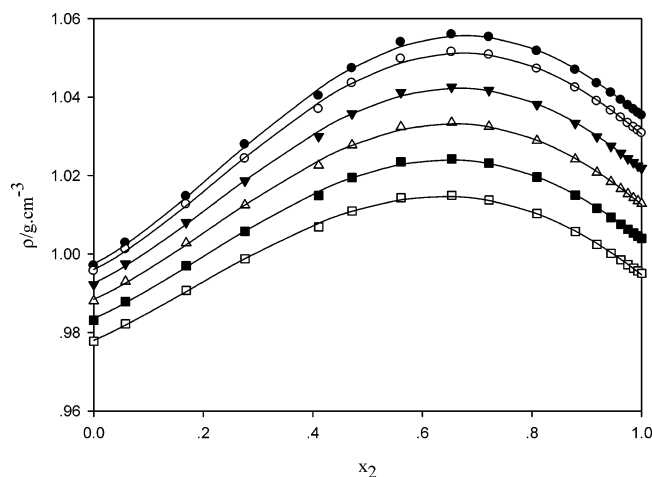
Figure 1. Densities of the water (1) + Genosorb 1753 (2) system at various temperatures: ●, 298.15 K; ○, 303.15 K; ▼, 313.15 K; △, 323.15 K; ■, 333.15 K; □, 343.15 K; —, eq 3.

Table 1. Densities of the Water (1) + Genosorb 1753 (2) Mixture from (298.15 to 343.15) K

			T/K			
x_2	298.15	303.15	313.15	323.15	333.15	343.15
			ρ/g·cm^{-3}			
0.0000	0.99705	0.99569	0.99226	0.98805	0.98317	0.97778
0.0581	1.00285	1.00127	0.99749	0.99301	0.98789	0.98220
0.1688	1.01474	1.01268	1.00806	1.00283	0.99703	0.99071
0.2761	1.02796	1.02433	1.01866	1.01245	1.00583	0.99876
0.4105	1.04033	1.03696	1.02997	1.02260	1.01491	1.00690
0.4715	1.04736	1.04358	1.03582	1.02779	1.01950	1.01095
0.5608	1.05403	1.04979	1.04121	1.03243	1.02349	1.01436
0.6534	1.05597	1.05153	1.04259	1.03350	1.02428	1.01493
0.7214	1.05532	1.05080	1.04172	1.03251	1.02319	1.01377
0.8091	1.05177	1.04723	1.03813	1.02893	1.01966	1.01030
0.8790	1.04696	1.04243	1.03335	1.02419	1.01499	1.00573
0.9186	1.04354	1.03899	1.02992	1.02082	1.01167	1.00247
0.9441	1.04113	1.03659	1.02752	1.01843	1.00933	1.00019
0.9621	1.03931	1.03477	1.02571	1.01664	1.00759	0.99850
0.9751	1.03795	1.03341	1.02438	1.01534	1.00631	0.99729
0.9853	1.03688	1.03236	1.02335	1.01433	1.00535	0.99637
0.9935	1.03600	1.03149	1.02249	1.01353	1.00457	0.99565
1.0000	1.03534	1.03083	1.02185	1.01289	1.00398	0.99508

where t is the efflux time and k_1 and k_2 are the viscometer constants. The second term in the equation represents the correction due to the kinetic energy and was found to be negligible.[8] The absolute viscosity (η) results from multiplying the time by the calibration constant of the viscometer and by the density of the sample.

Refractive indices of aqueous Genosorb 1753 solutions were measured with an Atago RX-5000-α refractometer. Refractive indices of deionized water were measured and compared with the available literature data. The uncertainty in refractive index measurements was about 0.0001.

The surface tensions for binary mixtures of Genosorb 1753 with water were measured by a roughened platinum plate-detachment method using the K100 Tensiometer (Kruss, USA) under atmospheric pressure. Before each measurement, the plate was thoroughly cleaned and flame-dried, which allowed the removal of any surface active contaminants and the formation of a new and clean surface. Each value reported was an average of at least four measurements, where the reproducibility of replicate measurements on the same sample was within 0.5 %. The plate perimeter was introduced in the control program that automatically displayed the surface tension values. The temperature was controlled within 0.01 K. The uncertainty of the surface tension measurements was estimated to be 0.05 mN·m^{-1}.

Table 2. Coefficients a_i, b_i, and c_i and the AADs Obtained for Aqueous Genosorb 1753 Solutions from the Correlation Equations

	a_i	b_i	c_i
		Density, Eq 3	
$i = 0$	7.588E−01	1.873E−03	−3.598E−06
$i = 1$	8.962E−01	−4.981E−03	7.432E−06
$i = 2$	5.297E−01	7.412E−04	−5.781E−06
$i = 3$	−1.673E+00	3.927E−03	9.287E−07
$i = 4$	8.018E−01	−2.527E−03	1.129E−06
AAD (%)		0.03	
		Viscosity, Eq 5	
$i = 0$	−2.681E+00	8.103E+02	−8.718E+03
$i = 1$	5.518E+01	−3.559E+04	5.886E+06
$i = 2$	8.755E+00	−8.704E+03	1.824E+06
$i = 3$	−5.344E+02	3.542E+05	−5.810E+07
$i = 4$	8.809E+02	−5.781E+05	9.385E+07
$i = 5$	−4.080E+02	2.669E+05	−4.322E+07
AAD (%)		1.01	
		Refractive Index, Eq 6	
$i = 0$	1.369E+00	−1.312E−04	
$i = 1$	2.830E−01	−4.371E−04	
$i = 2$	−9.288E−02	1.718E−04	
AAD (%)		0.07	
		Surface Tension, Eq 7	
$i = 0$	1.201E+02	−1.618E−01	
$i = 1$	1.443E+02	−1.523E+00	
$i = 2$	−2.287E+03	1.170E+01	
$i = 3$	6.716E+03	−2.982E+01	
$i = 4$	−7.351E+03	3.078E+01	
$i = 5$	2.723E+03	−1.109E+01	
AAD (%)		0.85	

Table 3. Viscosities of Water (1) + Genosorb 1753 (2) Mixtures from (298.15 to 343.15) K

			T/K			
x_2	298.15	303.15	313.15	323.15	333.15	343.15
			η/mPa·s			
0.0000	0.897	0.804	0.659	0.550	0.470	0.407
0.0581	1.08	0.998	0.806	0.667	0.564	0.483
0.1688	2.04	1.49	1.17	0.9820	0.828	0.693
0.2761	3.18	2.75	1.76	1.39	1.13	0.964
0.4715	6.17	5.13	3.67	2.75	2.06	1.65
0.5608	8.61	7.06	4.93	3.61	2.75	2.17
0.6534	10.2	8.29	5.74	4.18	3.17	2.49
0.8091	10.6	8.77	6.24	4.64	3.58	2.85
0.8790	9.57	8.04	5.87	4.46	3.51	2.83
0.9186	8.78	7.45	5.54	4.27	3.39	2.77
0.9441	8.26	7.05	5.32	4.14	3.32	2.72
0.9621	7.88	6.78	5.16	4.05	3.26	2.75
0.9751	7.66	6.59	5.04	3.98	3.22	2.67
0.9853	7.49	6.47	4.97	3.94	3.20	2.66
0.9935	7.37	6.38	4.92	3.90	3.18	2.66
1.0000	7.28	6.35	4.89	3.89	3.18	2.65

Results and Discussion

Table 1 presents the experimental density values for (Genosorb 1753 + water) in the temperature range (283.15 to 343.15) K throughout the whole concentration range. The density increases with decreasing temperature. In Figure 1, the maximum values of the density occur at around 65 mass %. The measured density values were regressed by the following equation:

$$\rho/\text{g·m}^{-3} = \sum_{i=0}^{4} [a_i + b_i T + c_i T^2 (x_2)^i] \tag{3}$$

where ρ is the density of the solution, T is the absolute temperature in K, a_i, b_i, and c_i are the regression coefficients, and x_2 is the Genosorb 1753 mass fraction. The regression coefficients are listed in Table 2 with the absolute average deviations (AADs) from the fit. The average absolute deviation was 0.03 %.
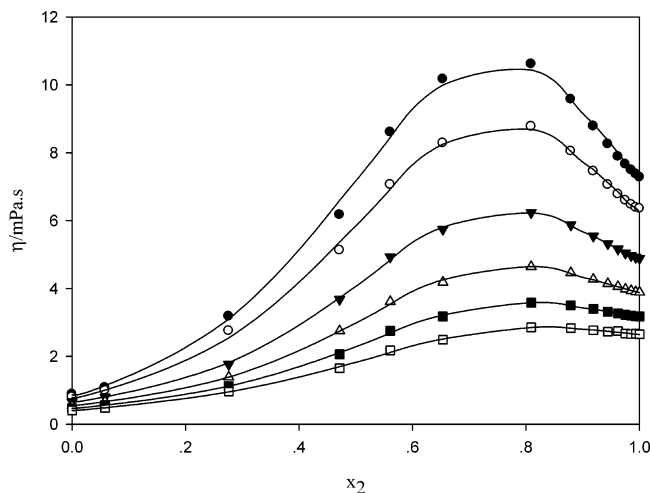
Figure 2. Viscosities of the water (1) + Genosorb 1753 (2) system at various temperatures: ●, 298.15 K; ○, 303.15 K; ▼, 313.15 K; △, 323.15 K; ■, 333.15 K; □, 343.15 K; —, eq 5.
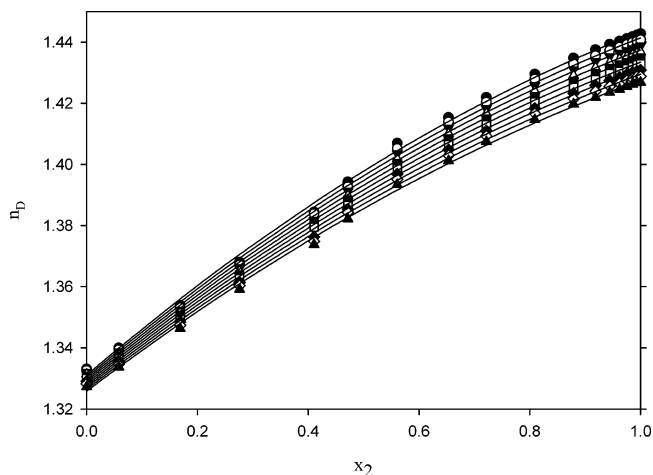

Figure 3. Refractive indices of the water (1) + Genosorb 1753 (2) system at various temperatures: ●, 293.15 K; ○, 398.15 K; ▼, 303.15 K; ▽, 308.15 K; ■, 313.15 K; □, 318.15 K; ◆, 323.15 K; ◇, 328.15 K; ▲, 333.15 K; —, eq 6.
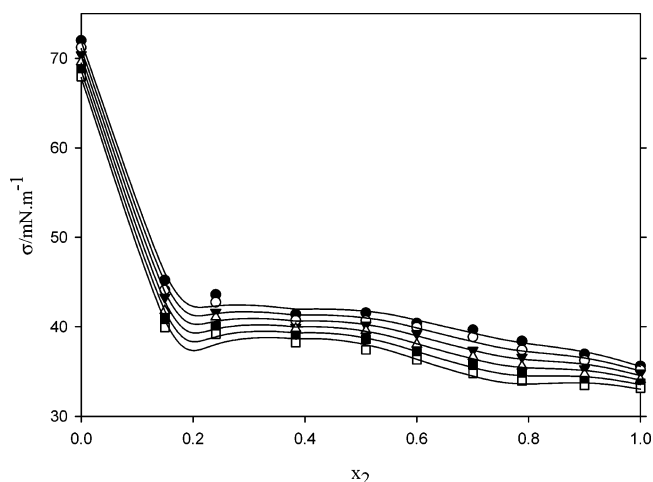
The absolute average deviation (AAD) was calculated as

$$AAD = \frac{\sum \frac{|y_i^{exptl} - y_i^{calcd}|}{y_i^{exptl}}}{n} \qquad (4)$$

where y_i is the density, n is the number of densities, and y_i^{exptl} and y_i^{calcd} represent experimental and calculated values.

The experimental viscosity results are presented in Table 3 with mass fractions for the binary solutions of aqueous Genosorb 1753 solutions at (298.15, 303.15, 313.15, 323.15, 333.15, and 343.15) K. The viscosity decreased with the increase in temperature. Figure 2 shows the viscosity curves with an S shape, and a similar and more accentuated curve exists when the viscosity is plotted against the mole fractions. There was a sharp increase in the viscosity of the mixture after the addition of Genosorb 1753 with a maximum value occurring at around 80 mass % (0.2 mol fraction of Genosorb 1753). The S shape of viscosity curves and the presence of a maximum of the viscosity deviation ($\Delta\eta$/mPa·s = $\eta - \eta_1 x_1 - \eta_2 x_2$) curves indicate a possible formation of stable complexes according to Fort and Moore,[9] in the ratio 1 mol of Genesorb 1753 to 4 mol of water.

Figure 4. Surface tensions of the water (1) + Genosorb 1753 (2) system at various temperatures: ●, 298.15 K; ○, 303.15 K; ▼, 308.15 K; △, 313.15 K; ■, 318.15 K; □, 323.15 K; —, eq 7.

The viscosities were correlated by the following equation

$$\log(\eta/\text{mPa·s}) = \sum_{i=0}^{5}[(a_i + b_i/T + c_i/T^2)(x_2)^i] \qquad (5)$$

Table 4. Refractive Index, n_D, for Water (1) + Genosorb 1753 (2) Mixtures from (293.15 to 333.15) K

	T/K								
x_2	293.15	298.15	303.15	308.15	313.15	318.15	323.15	328.15	333.15
					n_D				
0.0000	1.3331	1.3326	1.3320	1.3314	1.3307	1.3299	1.3291	1.3282	1.3273
0.0581	1.3400	1.3394	1.3387	1.3380	1.3372	1.3364	1.3355	1.3347	1.3337
0.1688	1.3539	1.3531	1.3523	1.3514	1.3505	1.3495	1.3486	1.3474	1.3464
0.2761	1.3680	1.3671	1.3662	1.3651	1.3638	1.3626	1.3614	1.3604	1.3592
0.4105	1.3844	1.3839	1.3817	1.3807	1.3805	1.3795	1.3763	1.3748	1.3738
0.4715	1.3943	1.3926	1.3912	1.3897	1.3883	1.3866	1.3853	1.3843	1.3822
0.5608	1.4069	1.4052	1.4035	1.4018	1.4002	1.3985	1.3969	1.3951	1.3934
0.6534	1.4153	1.4139	1.4119	1.4101	1.4083	1.4065	1.4048	1.4029	1.4012
0.7214	1.4219	1.4203	1.4183	1.4167	1.4148	1.4130	1.4110	1.4093	1.4075
0.8091	1.4295	1.4279	1.4259	1.4240	1.4222	1.4204	1.4183	1.4167	1.4147
0.8790	1.4348	1.4328	1.4309	1.4291	1.4271	1.4252	1.4232	1.4214	1.4197
0.9186	1.4375	1.4355	1.4336	1.4317	1.4297	1.4278	1.4258	1.4238	1.4219
0.9441	1.4393	1.4372	1.4353	1.4333	1.4314	1.4297	1.4275	1.4255	1.4236
0.9621	1.4403	1.4384	1.4364	1.4345	1.4325	1.4305	1.4285	1.4265	1.4246
0.9751	1.4412	1.4392	1.4372	1.4352	1.4332	1.4313	1.4294	1.4274	1.4255
0.9853	1.4418	1.4398	1.4378	1.4359	1.4339	1.4319	1.4300	1.4281	1.4262
0.9935	1.4423	1.4403	1.4384	1.4364	1.4344	1.4325	1.4305	1.4287	1.4267
1.0000	1.4427	1.4407	1.4388	1.4368	1.4348	1.4328	1.4308	1.4288	1.4269

Table 5. Surface Tensions of Water (1) + Genosorb 1753 (2) Mixtures from (298.15 to 323.15) K

			T/K			
x_2	298.15	303.15	308.15	313.15	318.15	323.15
			σ/mN·m^{-1}			
1.0000	35.60	35.19	34.84	34.10	33.68	33.14
0.9001	36.94	36.23	35.30	34.71	33.92	33.43
0.7882	38.39	37.41	36.60	35.59	34.85	33.93
0.7006	39.66	38.86	37.36	36.66	35.77	34.78
0.6002	40.41	39.95	39.23	38.04	37.10	36.30
0.5091	41.56	40.68	40.20	39.57	38.62	37.41
0.3837	41.39	40.71	39.94	39.79	38.82	38.23
0.2407	43.59	42.74	41.63	41.08	40.05	39.18
0.1497	45.21	44.11	43.30	41.79	40.98	39.91
0.0000	71.99	71.20	70.41	69.60	68.78	67.94

where η is the viscosity of the solution, T is the absolute temperature in K, a_i, b_i, and c_i are the regression coefficients, and x_2 is the Genosorb 1753 mass fraction. Table 2 lists the values of the parameters together with the ADDs of viscosities (η). The absolute average deviation between the experimental and calculated values was 1.01 %.

Experimentally measured refractive indices of the aqueous Genosorb 1753 solutions at (293.15, 298.15, 303.15, 308.15, 313.15, 318.15, 323.15, 328.15, and 333.15) K are listed in Table 4. Measured refractive indices values indicated a sharp increase in its values after the addition of Genosorb 1753 at all temperatures (Figure 3). The refractive indices were correlated by the equation

$$n_D = \sum_{i=0}^{2} [(a_i + b_i T)(x_2)^i] \qquad (6)$$

where n_D is the refractive index of the solution, T is the absolute temperature in K, a_i and b_i are the regression coefficients, and x_2 is the Genosorb 1753 mass fraction. The coefficients and the ADDs are presented in Table 2 in terms of temperatures and mass fractions. The average absolute deviation (ADD) was 0.07 %.

The experimental surface tension data of aqueous Genosorb 1753 solutions are presented in Table 5 for temperatures from (298.15 to 323.15) K. Figure 4 shows that the surface tension values decreased as the temperature and the mass fraction increased. A polynomial correlation was used to fit all the data of the surface tensions of aqueous Genosorb 1753 as a function of mass fraction (x_2) and temperature (T):

$$\sigma/\text{mN·m}^{-1} = \sum_{i=0}^{2} [(a_i + b_i T)(x_2)^i] \qquad (7)$$

where σ is the surface tension of the binary mixture, T is the absolute temperature, and a_i and b_i are the regression coef-

ficients, presented in Table 2. The average absolute deviation (ADD) between the experimental and correlated values was found to be 0.85 %.

Conclusions

Genosorb 1753 (Selexol) is one of the most important physical solvents used in the gas sweetening industry. The densities and viscosities of the binary mixture of water (1) + Genosorb 1753 (2) were studied from $T = (298.15$ to $343.15)$ K over the entire mass fraction range. The refractive indices of water (1) + Genosorb 1753 (2) were reported at temperatures between $T = (293.15$ and $333.15)$ K. The surface tensions were measured from $T = (298.15$ to $323.15)$ K. Both the density and the viscosity increased with a decrease in temperature. The maximum value of the density occurred at around 65 mass %. The S-shaped viscosity curves and a maximum in the viscosity deviation around 0.2 mol fraction suggest, according to Fort and Moore,[9] the possible formation of stable complexes in the ratio of 1:4. There was a sharp increase in the refractive index after the addition of Genosorb 1753 in water at all temperatures. The refractive index increased with the decrease in temperature and with an increase in mass %. The surface tension values decreased with increased temperature and mass fraction.

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