Density, Viscosity, and Electrical Conductivity in the Potassium Sulfate + Water + 1-Propanol System at Different Temperatures

Yecid P. Jimenez, María Elisa Taboada, Elsa K. Flores, and Héctor R. Galleguillos*

Centro de Investigación Científico y Tecnológico para la Minería (CICITEM), Departamento de Ingeniería Química, Universidad de Antofagasta, Chile

Experimental data of density, absolute viscosity, and electric conductivity for the $K_2SO_4 + H_2O$ + 1-propanol system have been determined at (303.15, 308.15, 313.15, and 318.15) K. Different mass fractions of alcohol/water (free salt) were studied in the range from 0 to 0.55. For these mass fractions of 1-propanol/water, the range of variation of potassium sulfate was from (0.0168 to 0.698) mol·kg^{-1}. The Williams, Landel, and Ferry equation was used to fit the absolute viscosity and equivalent conductance (determined from electric conductivity) data, and mean absolute deviations of 0.017 mPa·s and 0.19 (cm^2·equiv Ω^{-1}) were obtained, respectively. The glass-transition temperature was estimated with the experimental data of viscosity and equivalent conductance. Because the values obtained are relatively similar, we conclude that both transport properties are governed by the same molecular movement. Knowledge of the evaluated properties is useful in the study of the drowning-out crystallization process.

1. Introduction

In a previous article, we reported solubility, refractive index, density, viscosity, and electric conductivity data of saturated solutions of potassium sulfate in water + 1-propanol at different temperatures.[1] The purpose of the previous work was to obtain useful properties in the study of the drowning-out crystallization process of potassium sulfate using 1-propanol as the second solvent. This process has a number of advantages over other methods of crystallization. These generally lie in the possibility of carrying out the operation at ambient temperature and obtaining crystals of high purity.[2] If this process is carried out at 298.15 K, then it is necessary to know certain physical properties at high temperatures to improve the separation process control because dissolution stages previous to the drowning-out crystallization process are required. In general, these stages are carried out at temperatures above 298.15 K. The objective of the present work is to provide accurate data of physical properties to obtain better control in the separation of potassium sulfate by the drowning-out crystallization process. Furthermore, the experimental information obtained in the present article is a complement for other research conducted by our group.[3]

Data on physical properties of unsaturated solutions in the potassium sulfate + water + 1-propanol system are scarce, except for some recent studies that reported experimental data for similar systems. Hervello and Sánchez[4] measured densities of ammonium, sodium, and potassium sulfates in ethanol + water solutions. This study was carried out in the temperature range of (283.15 to 298.15) K and with saline concentrations from zero to the solubility limit. Nikam et al.[5] measured the viscosity of ammonium, potassium, and aluminum sulfate in water + *N*,*N*-dimethylformamide solutions at (298.15 and 308.15) K and molalities between (0.0081 and 0.1000) mol·kg^{-1}.

* Corresponding author. E-mail: hgalleguillos@uantof.cl. Fax: 56-55-637801.

Data on the densities, absolute viscosities, and electrical conductivities for unsaturated solutions of potassium sulfate in aqueous 1-propanol mixtures are provided at (303.15, 308.15, 313.15, and 318.15) K. The experimental study includes different mass fractions of 1-propanol/water within the range of 0 to 0.55. For these mass fractions of propanol/water, the concentration of potassium sulfate studied corresponds to the concentration of saturation at 298.15 K, obtained in a previous article.[1] The absolute viscosity and equivalent conductance (obtained from electric conductivity) data, together with the data at 298.15 K, reported under saturation conditions were analyzed with the Williams, Landel, and Ferry[6] equation (WLF). This equation was originally developed for amorphous polymers and "glass"-forming systems and describes the dependence of the transport properties with respect to temperature. The WLF equation is empirical; however, it can be theoretically justified through free-volume theory.[6] Furthermore, it is a simple equation whose constants can give a reasonable physical interpretation of the mass transport in the solution. Lo Surdo and Wirth[7] successfully used this expression for concentrated aqueous solutions of tetraalkylammonium bromides, NH_4Br and LiBr, and obtained valuable information about the molecular movement and the structure of the solutions studied.

2. Experimental Section

The reagents used in this research were supplied by Merck and were used directly without further purification (potassium sulfate ≥ 99 %, grade absolute 1-propanol ≥ 99.5 %). Prior to use, potassium sulfate was dried in an oven at 393 K for 24 h. Distilled deionized water was used in all procedures. We prepared the solutions by mass by using an analytical balance with a precision of 0.07 mg (Mettler Toledo, model AX204). For every temperature, seven unsaturated solutions were prepared with different mass fractions alcohol/water (free salt) and different concentrations of K_2SO_4. The variation range of mass fraction of 1-propanol was 0 to 0.55, whereas the variation range of the molality of potassium sulfate was from (0.0168 to 0.698)

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mol·kg^{-1}. The concentration of K_2SO_4 in every solution corresponded to the molality obtained under saturation conditions at 298.15 K.[1]

The physical properties were measured in triplicate of each solution to the specific temperature. The densities of the solutions were measured with a Mettler Toledo DE-50 vibrating tube densimeter, always obtaining an uncertainty of less than $\pm 5 \cdot 10^{-2}$ kg·m^{-3}. The densimeter was calibrated at atmospheric pressure using air and distilled deionized water as a reference substance prior to the initiation of each run of measurements at a given temperature. The densimeter had self-contained Peltier systems for temperature control with an uncertainty of ± 0.01 K. The time to reach the temperature stability was 600 s.

The kinematic viscosities were measured with calibrated Micro-Ostwalt viscometers. A Schott-Gerate automatic measuring unit (model AVS 310) equipped with a thermostat (Schott-Gerate, model CT 52) in which the temperature was regulated to within ± 0.05 K was used for measurements. We obtained the absolute viscosity by multiplying the kinematic viscosity by the corresponding density. The uncertainty in viscosity measurements is $\pm 5 \cdot 10^{-3}$ mPa·s.

Measurements of electrical conductivity were carried out using an Orion model 170 conductimeter with a precision of ≤ 0.5 % of the value measured and calibrated using a standard KCl solution. The uncertainty was estimated to be less than ± 0.7 %.

3. Results and Discussion

Table 1 presents the densities (ρ), viscosities (η), and electrical conductivities (κ) of the unsaturated solutions for the K_2SO_4 + H_2O + 1-propanol system. To observe the tendency of these properties from saturated solutions, the experimental data at 298.15 K has been included.[1] The values of equivalent conductance (Λ) in Table 1 were calculated through the following equation

$$\Lambda = \frac{1000\kappa}{N} \tag{1}$$

where N is equivalent concentration (normality).

It was not possible to compare our data with literature values because of the lack of experimental data for the present system. However, these properties for the aqueous solution of potassium sulfate can be obtained using the Novotny and Söhnel equation for the density[8] and the Laliberté equation for the absolute viscosity.[9] A good agreement between the calculated values with equations and the experimental data is observed because the mean absolute deviations were ± 0.3 kg·m^{-3} and ± 0.0191 mPa·s.

The absolute viscosity and equivalent conductance data were analyzed with the WLF[6] equation following the same procedure developed by Lo Surdo and Wirth.[7] For a reference temperature (T_0), the WLF equation can be expressed as

$$\begin{aligned} \log a_{T_0}(T) &= \frac{-C_1^0(T - T_0)}{C_2^0 + T - T_0} \\ \log b_{T_0}(T) &= \end{aligned} \tag{2}$$

where

$$a_{T_0}(T) = \frac{\eta T_0 \rho_0}{\eta_0 T \rho} \tag{3}$$

$$b_{T_0}(T) = \frac{\Lambda T_0 \rho_0}{\Lambda_0 T \rho} \tag{4}$$

where η, Λ, and ρ are absolute viscosity, equivalent conductance, and density of the solution at the temperature, T, respectively; η_0, Λ_0, and ρ_0 are the corresponding quantities at T_0; and C_1^0 and C_2^0 are properties of the particular system at T_0. In the present work, the reference temperature was arbitrarily chosen to be T_0 = 298.15 K. For every solution with a determined concentration of K_2SO_4 (or a determined mass fraction of 1-propanol), the coefficients C_1^0 and C_2^0 were obtained through a fit of the experimental data to eq 2. The values of these coefficients and mean absolute deviations are presented in Table 2. According to the deviations obtained, there is a very good agreement between the calculated and experimental values.

In rigor, the WLF equation uses T_g (experimental glass-transition temperature) as reference temperature instead of T_0, and thus the coefficient values change to C_1^g and C_2^g. The relationships between the coefficients C_1^0, C_2^0, and T_0 of eq 2, and C_1^g, C_2^g, and T_g of the WLF equation are given by the equations

Table 1. Density, ρ, Viscosity, η, Electrical Conductivity, κ, and Equivalent Conductance, Λ, of the K_2SO_4 + H_2O + 1-Propanol System for Various Fraction, w, in (1 − w)Water + w(1-Propanol)

m		ρ	η	κ	Λ
mol·kg^{-1}	w	kg·m^{-3}	mPa·s	S·m^{-1}	cm^2·equiv Ω^{-1}
		298.15 K[a]			
0.6981	0.0000	1085.9	1.0388	10.45	77.27
0.1817	0.1689	995.5	1.7233	1.69	48.20
0.0967	0.2858	961.2	2.1917	0.65	35.54
0.0594	0.3739	938.1	2.4580	0.31	28.11
0.0380	0.4443	921.1	2.5826	0.16	22.98
0.0250	0.4999	908.0	2.6536	0.09	19.89
0.0168	0.5456	897.9	2.6666	0.05	16.65
		303.15 K			
0.6981	0.0000	1084.4	0.9548	11.54	85.49
0.1816	0.1616	992.8	1.4898	1.93	55.22
0.0967	0.2810	958.1	1.8981	0.75	41.15
0.0594	0.3715	933.9	2.0849	0.32	32.80
0.0380	0.4415	917.5	2.2587	0.18	25.96
0.0250	0.4978	903.8	2.2805	0.10	22.21
0.0168	0.5439	893.0	2.3190	0.06	19.42
		308.15 K			
0.6982	0.0000	1082.5	0.8705	12.51	92.83
0.1817	0.1616	990.3	1.2989	2.18	62.50
0.0967	0.2810	954.7	1.6290	0.85	46.81
0.0594	0.3715	930.8	1.8321	0.37	36.57
0.0381	0.4415	913.4	1.9022	0.20	28.96
0.0250	0.4978	900.1	1.9707	0.11	24.52
0.0168	0.5438	889.5	1.9728	0.06	21.18
		313.15 K			
0.6980	0.0000	1080.2	0.7905	13.48	100.26
0.1816	0.1616	987.4	1.1377	2.42	69.61
0.0967	0.2809	951.6	1.4328	0.94	51.94
0.0592	0.3712	927.4	1.5806	0.44	40.47
0.0380	0.4415	909.9	1.6615	0.23	33.44
0.0250	0.4978	896.5	1.7089	0.13	27.99
0.0168	0.5439	885.8	1.7167	0.07	23.63
		318.15 K			
0.6980	0.0000	1078.3	0.7249	14.41	107.37
0.1816	0.1616	985.0	0.9672	2.65	76.41
0.0967	0.2809	948.8	1.2481	1.03	57.08
0.0592	0.3712	924.7	1.3945	0.49	45.20
0.0380	0.4415	907.1	1.4549	0.25	36.46
0.0250	0.4978	893.7	1.4904	0.14	30.32
0.0168	0.5439	882.9	1.5107	0.08	27.10

[a] At 298.15 K saturated solutions. Mean values.[1]

$$T_g = \frac{f(T_g) + \alpha_{f_0} T_0 - f(T_0)}{\alpha_{f_0}} \quad (5)$$

$$C_1^g = \frac{C_1^0 C_2^0}{(C_2^0 + T_g - T_0)} \quad (6)$$

$$C_2^g = C_2^0 + T_g - T_0 \quad (7)$$

where

$$\alpha_{f_0} = \frac{1}{2.303 C_1^0 C_2^0} \quad (8)$$

$$f(T_0) = \frac{1}{2.303 C_1^0} \quad (9)$$

$$f(T_g) = \frac{1}{2.303 C_1^g} \quad (10)$$

α_{f_0} is the thermal expansion of the free volume, and $f(T_0)$ and $f(T_g)$ are the fractional free volumes at temperatures T_0 and T_g, respectively. The T_g value for every solution with a determined concentration of potassium sulfate can be obtained by assuming the following:[7] (1) when the solutions are cooled, these pass through a glass-transition, and (2) at T_g, all substances have the same fractional free volume $f(T_g) = 0.025$ (this means that $C_1^g = 17.44$). In Table 3 are listed calculated values of T_g and C_2^g (eqs 5, 6, 7, 8, 9, and 10) with the absolute viscosity and equivalent conductance data. In this table, it is shown that the T_g values to a determined concentration of potassium sulfate are relatively similar.

When the T_g mean values obtained are compared with viscosity (222.35 K) and equivalent conductance data (222.02 K), it is observed that these are very similar. These results suggest that the same molecular motion is responsible for the behavior of the viscosity and conductance in the solutions studied in this work, and that this motion stops at T_g.

Table 2. Constants of Equation *2* and Mean Absolute Deviations

m		C_2^0	MAD[a]		C_2^0	MAD[a]
mol·kg^{-1}	C_1^0	K^{-1}	mPa·s	C_1^0	K^{-1}	cm^2·equiv Ω^{-1}
	Absolute Viscosity			Equivalent Conductance		
0.6981	0.9363	85.0572	0.0093	0.8361	79.6712	0.0971
0.1816	1.3552	85.0023	0.0188	1.1051	78.7085	0.0552
0.0967	1.0425	62.7040	0.0189	0.9256	61.1511	0.0480
0.0594	1.3113	80.0183	0.0109	1.1311	79.9257	0.2111
0.0380	1.3118	80.3884	0.0222	1.1151	81.2396	0.3331
0.0250	1.5207	92.9705	0.0192	1.1372	90.8630	0.2429
0.0168	1.3753	86.3399	0.0206	1.3162	97.0120	0.3343

[a] MAD = $(1/n) \sum |X_{exptl} - X_{calcd}|$.

Table 3. Values of T_g, C_2^g, and Activation Energy

m	T_g	C_2^g	ΔH_η	T_g	C_2^g	ΔH_Λ
mol·kg^{-1}	K	K^{-1}	kJ·mol^{-1}	K	K^{-1}	kJ·mol^{-1}
	Absolute Viscosity			Equivalent Conductance		
0.6981	217.6593	4.5665	14.384	222.2982	3.8195	12.998
0.1816	219.7531	6.6054	22.546	224.4290	4.9875	18.369
0.0967	239.1942	3.7482	22.218	240.2444	3.2455	18.892
0.0594	224.1482	6.0166	22.086	223.4081	5.1837	18.585
0.0380	223.8081	6.0465	23.013	222.1048	5.1944	18.513
0.0250	213.2860	8.1065	22.733	213.2120	5.9250	16.893
0.0168	218.6189	6.8088	22.731	208.4597	7.3217	18.619

In Table 3, the apparent activation energy values for the conductance, ΔH_Λ, and absolute viscosity, ΔH_η, calculated from the WLF equation (eq 11) have been also included

$$\begin{matrix}\Delta H_\eta = \\ \Delta H_\Lambda =\end{matrix} R \frac{\mathrm{d} \ln \Psi}{\mathrm{d}(1/T)} = \frac{2.303 R T^2 C_1^g C_2^g}{(C_2^g + T - T_g)^2} \quad (11)$$

where $\Psi = a_{T_g}(T)$ or $b_{T_g}(T)$. From Table 3, the ΔH_η values are always higher than ΔH_Λ for a determined concentration of K_2SO_4. Lo Surdo and Wirth[7] obtained a similar result with tetraalkylammonium bromide aqueous solutions, NH_4Br, and LiBr, and said that the opposing potential energy barrier is greater for the sheering stress encountered in viscous flow than it is for the electrical potential gradients encountered in electrical conduction.

Conclusions

Density, absolute viscosity, and electrical conductivity data for the K_2SO_4 + H_2O + 1-propanol system were measured at (303.15, 308.15, 313.15, and 318.15) K. The experimental data of transport properties, η and Λ, were fitted with the WFL equation (reference temperature = 298.15 K), and mean absolute deviations of 0.017 mPa·s and 0.19 (cm^2·equiv Ω^{-1}) were obtained, respectively. An analysis of the WLF equation concluded that the same molecular motion is responsible for the behavior of the viscosity and conductance in the solutions studied in this work.

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