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Thermodynamic equilibrium of the polyethylene glycol 2000 and sulphate salts solutions

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ABSTRACT

In this research, the (liquid + liquid) and (vapour + liquid) equilibria of polyethylene glycol 2000 with salts Na_2SO_4, $ZnSO_4$, $(NH_4)_2SO_4$, $Al_2(SO_4)_3$ and $MgSO_4$ were investigated. Constant water activity curves and water activity data for the (vapour + liquid) equilibrium have been measured using the isopiestic method at $T = 298.15$ K. Furthermore, binodal values of aqueous two-phase systems for (liquid + liquid) equilibrium were determined at $T = (298.15$ and $308.15)$ K. A relation between the salting-out effect of electrolytes on the polymer aqueous solution and the slopes of constant water activity curves are reported. It was found that the slopes of constant water activity curves of aqueous two-phase systems, in two-phase and one-phase regions, have positive and negative deviation, respectively, from the linear isopiestic relation. Finally, the effect of temperature and cation of sulphate salts on the (liquid + liquid) and (vapour + liquid) equilibria was investigated.

1. Introduction

Aqueous two-systems (ATPSs) are produced by mixing two materials with different structures, such as polyethylene glycol (PEG) and dextran [1–3] or a polymer and a salt including polypropylene glycol (PPG) with cosmotropic (*i.e.* water structure) salt such as tripotassium citrate [4]. ATPSs have been used for the extraction of biological materials such as enzymes and proteins [5].Ternary solutions of hydrophobic solutes in aqueous salt solutions have been used for the study of salting effects [6–9]. Salting effect is namely the variation in solubility of a nonelectrolyte (such as polymer) in an aqueous solution *via* the addition of an electrolyte (such as salt) [10]. Essentially, solubility of a polymer can be increased or decreased with an increase in concentrations of added salt, known as salting-out and salting-in, respectively [10].

The formation of aqueous two-phase systems in mixtures of PEG and electrolytes in water has been systematically studied by Ananthapadmanabhan *et al.* [11,12]. Zhao *et al.* [13] studied (liquid + liquid) equilibrium (LLE) for ATPSs of {polypropylene glycol400 + ($MgSO_4$, $(NH_4)_2SO_4$ KCl and KAc) + H_2O} at different temperatures. They found that ions with a higher valence are better salting-out operatives than ions with a lower valence. Elsewhere, Zafarani-Moattar and Nemati-Kande [14] investigated LLE for ATPSs of {polyethylene glycol dimethylether (PEG-DME2000) + tri-potassium phosphate + H_2O} at different temperatures. Da Silva and Loh [15] carried out investigations on enthalpies of ternary aqueous solutions of (PEG + dextran + water) by colorimetric measurements. They reported a direct relation between the phase separation and an enthalpy of solution. They also found that phase separation was accompanied by an enthalpy increase indicating that entropy increase was the driving force for aqueous two-phase systems formation. Recently, using different polymers and salts Sadeghi and Jahani [8] through the isopiestic method, obtained further evidence for the salting-out and salting-in of water-soluble polymers in aqueous salt solutions. Following their work, the present study was carried out to investigate the salting-out effect of PEG2000 in aqueous sulphate salts solutions with the isopiestic method, as well as the (liquid + liquid) and (vapour + liquid) equilibria of polyethylene glycol (PEG2000) with salts Na_2SO_4, $ZnSO_4$, $(NH_4)_2SO_4$, $Al_2(SO_4)_3$ and $MgSO_4$.

2. Experimental

2.1. Materials

Polyethylene glycol (PEG) molar mass 2000, $MgSO_4$, Na_2SO_4, $ZnSO_4$ were purchased from Merck, and $Al_2(SO_4)_3$ and $(NH_4)_2SO_4$ were obtained from Aldrich (GR, $\geqslant 0.98$ mass fraction purity). All preparations were made in double distilled water. Table 1 summarises relevant information on provenance and purity of materials studied.

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TABLE 1
Provenance and purity of the compounds investigated.

Compound	Supplier	Mass fraction purity (supplier)
Polyethylene glycol 2000 (PEG2000)	Merck	⩾0.995
$MgSO_4$	Merck	⩾0.980
Na_2SO_4	Merck	⩾0.990
$ZnSO_4$	Merck	⩾0.980
$Al_2(SO_4)_3$	Aldrich	⩾0.985
$(NH_4)_2SO_4$	Aldrich	⩾0.990

2.2. Liquid liquid equilibrium measurements

To measure liquid liquid equilibrium, the binodal curves were obtained through the titration method. Here, a polymer solution of known mass fraction was placed in the glass vessel (volume 50 cm^3) and a salt solution of known concentration added to the point when the mixture became turbid indicating the two-phase formation. Water was then added until the turbidity disappeared and the procedure was repeated on and on. After each addition, the vessel was weighed on an analytical balance with a precision of $\pm 1 \cdot 10^{-3}$ g, and the mass fraction of each component was determined from those masses. During the whole process, the vessel was provided with an external jacket in which water circulated at constant temperature. Using a thermostat, the temperature was maintained to within ±0.2 K.

2.3. (Vapour + liquid) equilibrium measurements

In this study through the isopiestic method, the water activities and constant water activity curves of different systems were obtained [8,16]. The isopiestic apparatus employed is essentially similar to that used by Ochs *et al.* [17]. The apparatus used here consisted of a nine-leg manifold attached to round-bottom flasks. One flask contained the standard pure NaCl solution, one contained pure PEG2000 solution, two others contained pure salts such as Na_2SO_4 and $ZnSO_4$ solutions, two other flasks contained (PEG2000 + Na_2SO_4) solutions, two flasks contained (PEG2000 + $ZnSO_4$) solutions, and the central flask was used as a double-distilled water reservoir. To ensure equilibrium, the apparatus was kept in constant temperature bath at least for 6 days

TABLE 2
Binodal data as molalities, m_s / (mol. kg^{-1}) and weight fractions, w_p for (PEG2000 (p) + salt (s) + H_2O(w)) systems at different temperature.

PEG2000(p) + $ZnSO_4$(s) + H_2O (w)		PEG2000(p) + Na_2SO_4(s) + H_2O (w)		PEG2000(p) + $(NH_4)_2SO_4$(s) + H_2O (w)		PEG2000(p) + $MgSO_4$(s) + H_2O (w)		PEG2000(p) + $Al_2(SO_4)_3$(s) + H_2O (w)	
w_p	m_s	m_s	w_p	m/z	m_s	w_p	m_s	w_p	m_s
					T = 298.15 K				
0.183	0.315	0.183	0.526	0.167	0.949	0.197	0.223	0.15	0.096
0.179	0.321	0.160	0.590	0.150	0.967	0.180	0.247	0.143	0.099
0.157	0.364	0.147	0.615	0.128	1.053	0.156	0.277	0.128	0.104
0.137	0.410	0.126	0.683	0.103	1.153	0.131	0.319	0.110	0.112
0.116	0.438	0.106	0.726	0.087	1.205	0.114	0.353	0.089	0.125
0.097	0.487	0.086	0.780	0.057	1.340	0.097	0.373	0.073	0.133
0.080	0.517	0.071	0.820	0.042	1.396	0.081	0.401	0.059	0.144
0.069	0.550	0.059	0.871	0.033	1.434	0.068	0.422	0.048	0.150
0.058	0.575	0.050	0.892	0.024	1.462	0.058	0.436	0.039	0.156
0.049	0.603	0.042	0.914	0.018	1.557	0.051	0.455	0.032	0.163
0.043	0.622	0.035	0.938	0.009	1.583	0.044	0.465	0.026	0.167
0.037	0.640	0.030	0.957	0.007	1.775	0.037	0.480	0.021	0.172
0.032	0.662	0.025	0.976	0.005	1.786	0.031	0.481	0.018	0.180
0.028	0.684	0.021	1.004			0.026	0.502	0.015	0.181
0.024	0.707	0.017	1.008			0.021	0.509	0.011	0.182
0.019	0.725					0.016	0.518	0.008	0.198
0.016	0.747					0.010	0.548	0.006	0.202
0.013	0.754							0.004	0.211
0.009	0.761							0.002	0.213
0.006	0.788								
					T = 308.15 K				
0.179	0.296	0.207	0.480	0.188	0.852	0.191	0.223	0.179	0.067
0.170	0.306	0.194	0.488	0.177	0.885	0.183	0.228	0.163	0.076
0.156	0.335	0.169	0.547	0.153	0.947	0.154	0.268	0.151	0.083
0.138	0.372	0.137	0.602	0.126	1.032	0.127	0.303	0.137	0.091
0.132	0.381	0.109	0.702	0.102	1.110	0.104	0.339	0.120	0.098
0.111	0.423	0.088	0.746	0.081	1.169	0.084	0.370	0.104	0.110
0.090	0.467	0.071	0.792	0.065	1.224	0.077	0.383	0.090	0.118
0.074	0.504	0.058	0.827	0.053	1.261	0.061	0.400	0.075	0.126
0.061	0.540	0.047	0.860	0.044	1.308	0.050	0.422	0.065	0.135
0.046	0.581	0.040	0.899	0.036	1.341	0.041	0.439	0.056	0.141
0.039	0.596	0.033	0.923	0.030	1.392	0.035	0.457	0.047	0.149
0.031	0.631	0.027	0.943	0.026	1.417	0.025	0.463	0.040	0.153
0.026	0.649	0.022	0.982	0.022	1.449	0.019	0.492	0.033	0.158
0.024	0.658	0.019	1.017	0.013	1.504	0.014	0.512	0.028	0.164
0.021	0.678	0.016	1.019	0.011	1.594	0.011	0.539	0.023	0.171
0.018	0.697	0.012	1.023	0.009	1.608	0.009	0.569	0.016	0.178
0.014	0.711	0.009	1.080	0.007	1.727	0.007	0.582	0.009	0.192
0.012	0.721	0.008	1.112	0.006	1.748	0.005	0.614		
0.009	0.746	0.006	1.176						
0.007	0.808								
0.005	0.869								

The uncertainty in m_s and T are 0.001 mol. kg^{-1} and ± 0.2 K, respectively.