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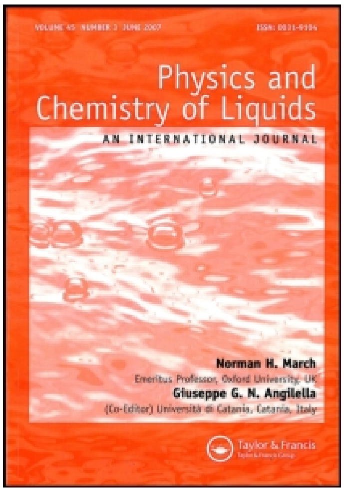

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Muhammad A. Saleh[a]; Shamim Akhtar[a]; M. Shamsuddin Ahmed[a]; Mohammad Hemayet Uddin[b]
[a] Department of Chemistry, University of Chittagong, Chittagong-4331, Bangladesh [b] Amino Science Research Laboratory, Ajinomoto Co. Inc., Kawasaki, Japan

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Density, excess molar volume, viscosity and thermodynamic activation of viscous flow of water + ethylenecarbonate

MUHAMMAD A. SALEH*†, SHAMIM AKHTAR†,
M. SHAMSUDDIN AHMED† and MOHAMMAD HEMAYET UDDIN‡

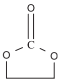
†Department of Chemistry, University of Chittagong, Chittagong-4331, Bangladesh
‡Amino Science Research Laboratory, Ajinomoto Co. Inc., Kawasaki, Japan

(*Received 4 March 2005*)

Densities and viscosities for the system, water (W) + ethylenecarbonate (EC), have been determined for the entire range of composition at temperatures ranging from 313.15 to 333.15 K. Density, excess molar volume, viscosity, excess viscosity and thermodynamic activation parameters for viscous flow have been calculated and plotted against mole fraction of EC. The measured properties and some of the derived properties have been fitted to appropriate polynomial equations. These have been explained in terms of factors, such as dipole–dipole interaction, partial accommodation of water molecules into the structural network of EC and H-bonding between EC and H_2O.

Keywords: Density; Excess molar volume; Viscosity; Thermodynamic activation parameters; Ethylenecarbonate

1. Introduction

Ethylenecarbonate (EC), , is a dipolar aprotic solvent with remarkably high dielectric constant [1–3] ($\varepsilon = 90.6$ and 89.6 at 36.5 and 40°C, respectively) and high dipole moment [1,2] ($\mu = 4.6\,\mathrm{D}$). The freezing point and boiling point of EC are 36.5 and 244°C, respectively at 740 mm pressure. It is partially miscible with water at room temperature but completely miscible at 40°C and above. El-Harakany *et al.* [3] reported the density, viscosity and dielectric constant data of the system EC + water up to ~0.65 mole fraction of EC at 298.15–318.15 K. Cunningham *et al.* [4] and D'Aprano and co-workers [5,6] measured the density, viscosity and dielectric constant of this system at 298.15 K in a similar concentration range. Cabon *et al.* [7] reported the density, viscosity and dielectric constant of the system for the entire range of composition at 313.15 K. Here we are reporting the density, viscosity and thermodynamic

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*Corresponding author. Fax: 880-31-726310. Email: masaleh786@yahoo.com

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activation parameters of viscous flow of the system EC + water for the entire range of concentration at temperatures between 313.15 and 333.15 K. In the recent past we have reported the volumetric, viscometric and thermodynamic properties of aqueous solutions of protic and aprotic solvents, such as alcohols [8–10], diols [11–13], acetone [14], amines and diamines [15–19], amides [20], dimethylsulfoxide, 1,4-dioxane and tetrahydrofuran [21,22], the results of which are in many respects similar to those of the present system.

2. Experimental

Ethylenecarbonate was procured from Aldrich, with quoted purity of 98%. The substance was used without any further purification. Redistilled water was used in the preparation of the solutions. An analytical balance of accuracy ±0.0001 g was used in density measurement. The solutions were prepared by weighing masses of the components by the same balance. The mole fraction was accurate up to the fourth decimal place. The density was measured by a 25 mL specific gravity bottle previously calibrated with redistilled water. In viscosity measurement an Ostwald U-tube viscometer with sufficiently long efflux time was used, so that no kinetic energy correction was necessary. The flow time was recorded by an electronic timer accurate up to ±0.01 s. For every measurement, a thermostatic water bath controlled to ±0.05 K was used. The average uncertainty in the measured density and viscosity was not more than $0.14\,\mathrm{kg\,m^{-3}}$ and $4 \times 10^{-7}\,\mathrm{kg\,m^{-1}\,s^{-1}}$, respectively.

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3. Results and discussion

The densities and viscosities of pure EC at different temperatures are listed in table 1 together with the literature values, wherever possible, for comparison, in which the agreement between the measured and literature values has been found to be satisfactory. EC is highly polar as indicated by the high dipole moment and dielectric constant, as mentioned earlier. The high values of boiling point (244°C),

Table 1. Densities, $\rho \times 10^{-3}$ ($\mathrm{kg\,m^{-3}}$), and viscosities, $\eta \times 10^{4}$ ($\mathrm{kg\,m^{-1}\,s^{-1}}$), of pure EC at different temperatures.

		Temperature (K)				
Compound	Properties	313.15	318.15	323.15	328.15	333.15
EC	ρ	1.3164 (1.3214)[a] (1.3220)[a] (1.3215)[b] (1.321991)[c]	1.3109	1.3052	1.300	1.2938
	η	18.653 (19.0)[a] (19.17)[a] (18.79)[c]	17.225	15.951 (16.9)[b]	14.860	13.874

[a] Ref. [23] and the references cited therein. [b] Ref. [25]. [c] Ref. [24].

Table 2. Densities, $\rho \times 10^{-3}$ (kg m^{-3}), excess molar volumes, $V_m^E \times 10^6$ (m^3 mol^{-1}), of the system, water (x_1) + EC (x_2), at different temperatures.

T (K)	313.15		318.15		323.15		328.15		333.15	
x_2	ρ	V_m^E	ρ	V_m^E	ρ	V_m^E	ρ	V_m^E	ρ	V_m^E
					Water (x_1) + EC (x_2)					
0.0000	0.9922	0.000	0.9902	0.000	0.9881	0.000	0.986	0.000	0.9831	0.000
0.0998	1.0921	−0.124	1.0885	−0.110	1.0848	−0.095	1.081	−0.083	1.0769	−0.069
0.1996	1.1527	−0.128	1.1483	−0.107	1.1438	−0.087	1.139	−0.067	1.1346	−0.053
0.2995	1.1938	−0.091	1.1890	−0.069	1.1839	−0.043	1.179	−0.027	1.1738	−0.002
0.3994	1.2247	−0.070	1.2197	−0.050	1.2144	−0.026	1.209	0.0001	1.2034	0.027
0.4996	1.2485	−0.048	1.2429	−0.015	1.2373	0.012	1.232	0.029	1.2263	0.053
0.6004	1.2677	−0.034	1.2620	−0.004	1.2563	0.021	1.251	0.035	1.2451	0.057
0.7006	1.2824	0.012	1.2766	0.042	1.2708	0.065	1.265	0.073	1.2591	0.094
0.8038	1.2948	0.064	1.2893	0.076	1.2835	0.094	1.278	0.109	1.2720	0.121
0.9001	1.3055	0.067	1.2998	0.083	1.2941	0.090	1.289	0.091	1.2828	0.098
1.000	1.3164	0.000	1.3109	0.000	1.3052	0.000	1.300	0.000	1.2938	0.000

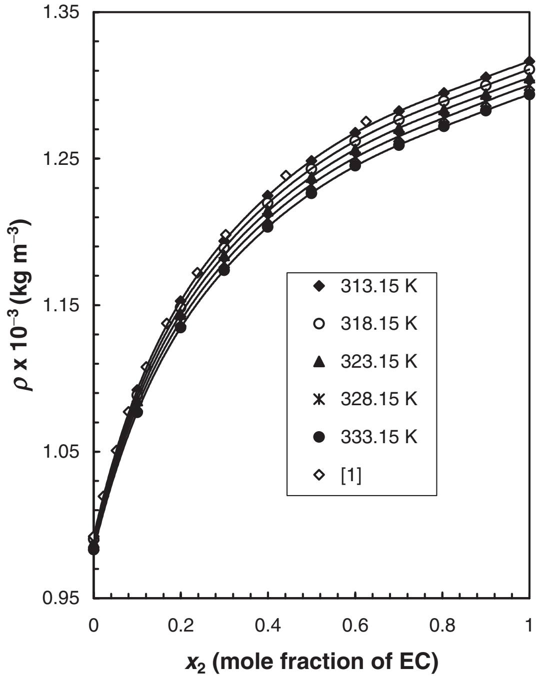

Figure 1. Variation of density, ρ, against mole fraction of EC for the system water (x_1) + EC (x_2).

density (1.3164 g cm^{-3} at 40°C) and viscosity (18.653×10^{-4} kg m^{-1}s^{-1} at 40°C) of EC indicate that the molecule is strongly associated through dipolar interaction. Liquid EC is thought to form clusters of an average of 8.3 monomers per cluster through dipole–dipole interaction [1].

Densities and excess molar volumes of the system, W + EC, at temperatures, 313.15, 318.15, 323.15, 328.15 and 333.15 K, have been shown in table 2. The densities have been plotted against the mole fraction of EC, x_2, in figure 1, which shows a rapid initial increase in density upon addition of EC. The increment continues until the pure state

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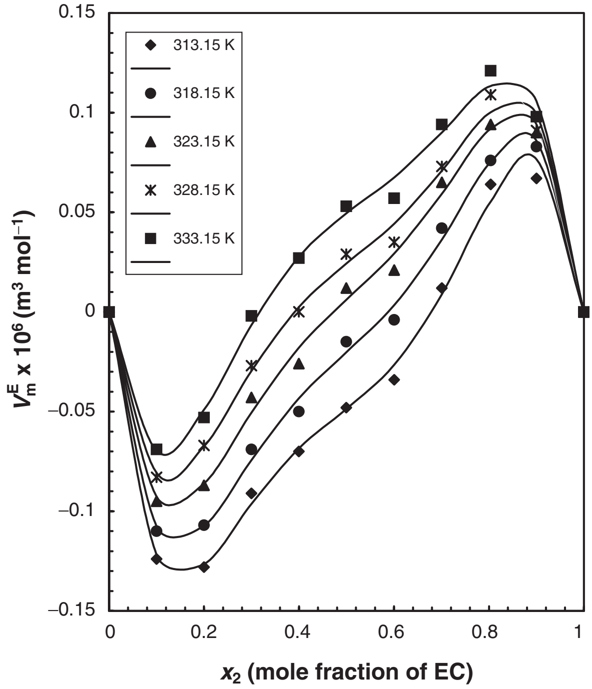

Figure 2. Variation of excess molar volume, V_m^E, against mole fraction of EC for the system water (x_1) + EC (x_2).

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of EC is reached, but at a slower rate. Density data for W + EC at 313.15 K between 0–0.65 mole fraction of EC of [3], as put in figure 1, are found to fit well with our density curve. Densities, ρ/kg m^{-3}, viscosities, η/kg m^{-1}s^{-1}, and free energies of activation for viscous flow, $\Delta G^{\neq}$/kJ mol^{-1}, have been fitted to the general polynomial equation of the form,

$$Y = \sum_{i=0}^{n} A_i x_2^i \tag{1}$$

where Y stands for each of the above properties. The coefficients, A_i, and the squares of the regression coefficients, r^2, are shown in table 6.

The excess molar volumes, V_m^E, have been calculated by the following equation,

$$V_m^E = [(x_1 M_1 + x_2 M_2)/\rho - \{(x_1 M_1)/\rho_1 + (x_2 M_2)/\rho_2\}] \tag{2}$$

where x_1, M_1 and ρ_1 are the mole fraction, molar mass and density, respectively, of pure water, x_2, M_2, ρ_2 are the corresponding quantities for EC and ρ is the density of the solution. Excess molar volumes have been plotted against mole fraction of EC, x_2, in figure 2. The excess properties have been fitted to a Redlich–Kister polynomial equation of the form,

$$Y^E = x_1 x_2 \sum_{i=0}^{n} A_i (1 - 2x_1)^i \tag{3}$$

where Y^E represents each of V_m^E, η^E and $\Delta G^{\neq E}$. The coefficients of the equation, A_i, and the standard deviations, σ, are listed in table 7.

An examination of V_m^E *versus* x_2 curves reveals that:

(a) V_m^E are negative in the water-rich region, but positive in the EC-rich region.
(b) The system showed extrema. Minima and maxima have been observed, respectively, at ~0.15 and ~0.85 mole fraction of EC.
(c) With the rise of temperature, both the minima and maxima shift slightly towards the left along the composition axis.
(d) The effect of temperature on V_m^E for the system is positive i.e. $\delta V_m^E/\delta T$ is positive.

The sign of V_m^E depends upon the relative strengths between the contractive factors and the expansive factors. The factors responsible for volume contraction are:

(a) Specific interaction between the component molecules.
(b) Interstitial accommodation of molecules of one component into the vacant spaces of molecules of the other component. This occurs preferentially when the size difference between the component molecules is large, or when large gaps are available in the structural network of molecules.
(c) Weak physical forces, such as dipole–dipole or dipole-induced dipole interactions or van der Waals forces.

The factors that cause expansion in volume are the following:

(a) dispersion force,
(b) steric hindrance of component molecules,
(c) unfavourable geometric fitting,
(d) electrostatic repulsion, etc.

The negative part of V_m^E curves of the system asserts that the combined effect of the factors responsible for volume contraction outweigh the combined effect of the factors causing volume expansion. Ethylenecarbonate, with lone pairs of electrons on several sites, is highly prone to form H-bonding with water. Again, since the component molecules are highly polar, we expect the dipole–dipole type of interaction to take place between them. The ratio of the molar volumes of EC to water, calculated on the basis of molar masses and densities at 313.15 K is 3.68. This value is indeed very large, indicating quite a large size difference between W and EC. This implies that the probability is high for the smaller water molecules, either in segregated or monomeric forms, to occupy the vacant spaces offered by the network of large EC molecules.

The positive part of V_m^E in the EC-rich region of the system implies that the combined effect of the factors responsible for volume expansion outweighs the combined effect of the factors causing volume contraction.

Table 3 represents the viscosities, η, and excess viscosities, η^E, at different temperatures. Figure 3 shows the variation of viscosity against mole fraction of EC. Three regions of viscosity curves, though not well-defined, have been identified: a water-rich region in which viscosity rises fairly rapidly, followed by a region wherein there is a slow rise of viscosity and then an EC-rich region wherein there is relatively faster rise of viscosity. The water-rich region of rapid rise of viscosity corresponds roughly to the region of negative V_m^E (figure 2), and is attributed to strong H-bonding between EC and W. In the EC-rich region, it is believed that EC molecules are self-associated in large proportion and the species so formed are assumed to form rather weak

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Table 3. Experimental viscosities, η, and excess viscosities, $\eta^E(10^4\,\mathrm{kg\,m^{-1}\,s^{-1}})$, of the system, water (x_1) + EC (x_2), at different temperatures.

T/K	313.15		318.15		323.15		328.15		333.15	
x_2	η	η^E	η	η^E	η	η^E	η	η^E	η	η^E
					Water (x_1) + EC (x_2)					
0.0000	6.554	0.000	5.987	0.000	5.5003	0.000	5.071	0.000	4.700	0.000
0.0998	8.747	1.472	7.974	1.321	7.297	1.180	6.718	1.073	6.209	0.972
0.1996	10.520	2.444	9.561	2.168	8.747	1.944	8.042	1.758	7.436	1.602
0.2995	11.822	2.857	10.741	2.525	9.835	2.268	9.050	2.053	8.364	1.864
0.3994	12.756	2.804	11.630	2.499	10.682	2.267	9.841	2.050	9.112	1.870
0.4996	13.467	2.415	12.331	2.180	11.340	1.977	10.487	1.810	9.740	1.668
0.6004	14.205	1.923	13.033	1.742	12.013	1.590	11.142	1.472	10.359	1.356
0.7006	14.938	1.299	13.747	1.194	12.701	1.104	11.800	1.030	10.998	0.964
0.8038	15.756	0.603	14.567	0.567	13.488	0.544	12.561	0.526	11.725	0.505
0.9001	16.909	0.107	15.618	0.119	14.488	0.146	13.500	0.153	12.649	0.196
1.000	18.653	0.000	17.225	0.000	15.951	0.000	14.860	0.000	13.874	0.000

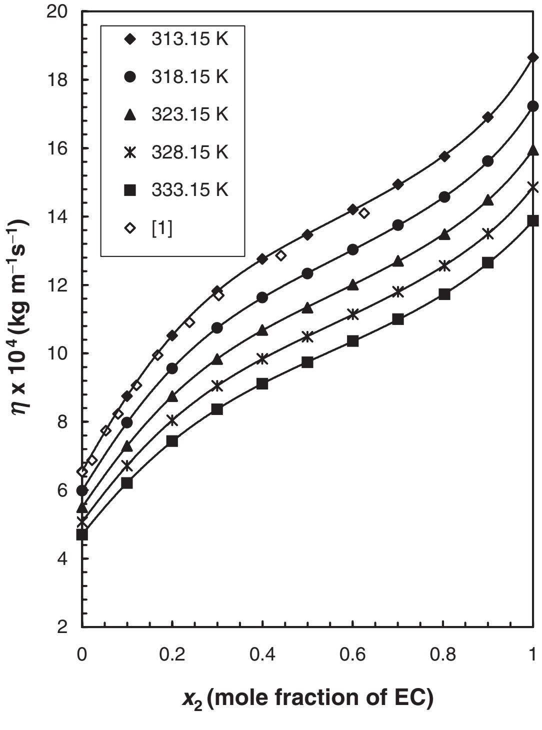

Figure 3. Variation of viscosity, η, against mole fraction of EC for the system water (x_1) + EC (x_2).

H-bonding with water. This probably accounts for a slower rise of viscosity. As the concentration of EC approaches its pure state, so does the viscosity approach the value of pure EC. This explains the faster rise of viscosity in this region.

Excess viscosities, η^E, have been calculated by using the following equation,

$$\eta^E = \eta - \exp(x_1 \ln \eta_1 + x_2 \ln \eta_2) \tag{4}$$

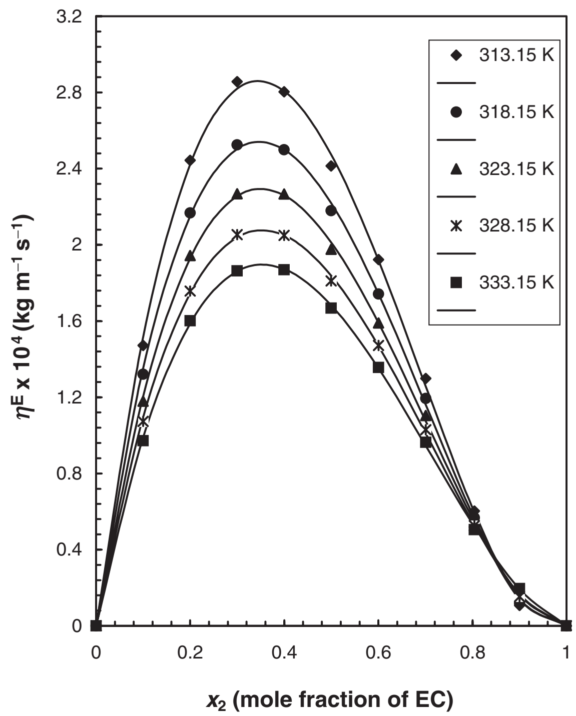

Figure 4. Variation of excess viscosity, η^E, against mole fraction of EC for the system water (x_1) + EC (x_2).

Table 4. Free energies of activation, $\Delta G^{\neq}$ (kJ mol^{-1}), and excess free energies of activation, $\Delta G^{\neq E}$ (kJ mol^{-1}), for viscous flow of the system, water (x_1) + EC (x_2) at different temperatures.

T (K)	313.15		318.15		323.15		328.15		333.15	
x_2	$\Delta G^{\neq}$	$\Delta G^{\neq E}$	$\Delta G^{\neq}$	$\Delta G^{\neq E}$	$\Delta G^{\neq}$	$\Delta G^{\neq E}$	$\Delta G^{\neq}$	$\Delta G^{\neq E}$	$\Delta G^{\neq}$	$\Delta G^{\neq E}$
Water (x_1) + EC (x_2)										
0.0000	8.834	0.000	8.752	0.000	8.669	0.000	8.586	0.000	8.503	0.000
0.0998	10.190	0.745	10.125	0.750	10.060	0.755	9.995	0.760	9.927	0.765
0.1996	11.169	1.113	11.118	1.120	11.067	1.126	11.016	1.132	10.965	1.138
0.2995	11.896	1.229	11.858	1.235	11.821	1.242	11.783	1.249	11.745	1.255
0.3994	12.459	1.180	12.437	1.190	12.415	1.200	12.394	1.210	12.372	1.219
0.4996	12.921	1.029	12.915	1.042	12.909	1.055	12.903	1.067	12.898	1.080
0.6004	13.345	0.839	13.352	0.850	13.359	0.862	13.367	0.875	13.374	0.886
0.7006	13.735	0.613	13.754	0.626	13.774	0.638	13.794	0.650	13.814	0.663
0.8038	14.121	0.368	14.153	0.379	14.184	0.390	14.216	0.401	14.247	0.412
0.9001	14.503	0.160	14.545	0.170	14.588	0.179	14.630	0.189	14.672	0.198
1.000	14.954	0.000	15.000	0.000	15.045	0.000	15.091	0.000	15.137	0.000

Figure 4 represents the variation of excess viscosities, η^E, as a function of mole fraction of EC, with maxima occurring at ~0.35 mole fraction of EC. The position of maxima does not apparently change with temperature.

Enthalpies of activation, $\Delta H^{\neq}$, and entropies of activation, $\Delta S^{\neq}$, for viscous flow have been determined by using the following equation,

$$\ln(\eta V_m/hN) = \Delta H^{\neq}/RT - \Delta S^{\neq}/R \qquad (5)$$

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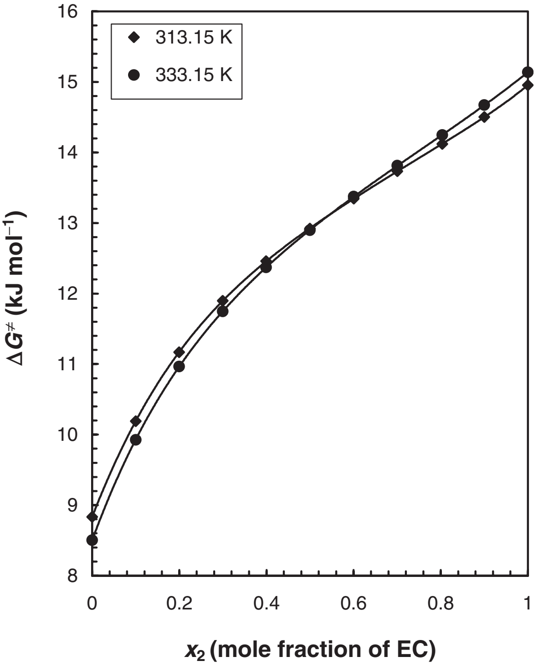

Figure 5. Variation of free energy of activation for viscous flow, $\Delta G^{\neq}$, against mole fraction of EC for the system water (x_1) + EC (x_2).

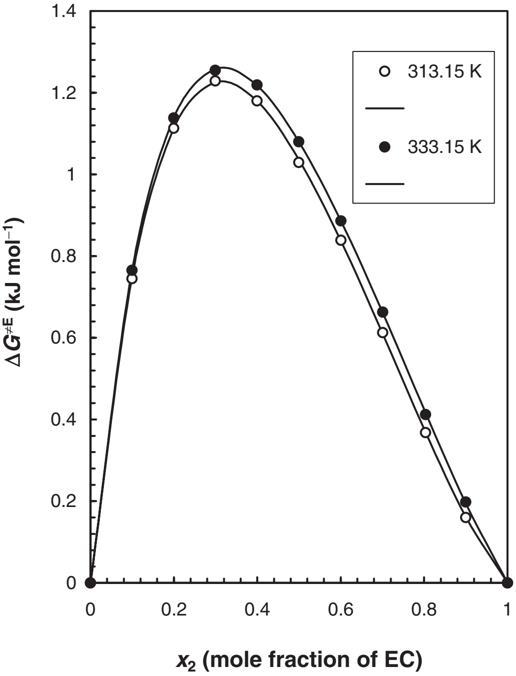

Figure 6. Variation of excess free energy of activation for viscous flow, $\Delta G^{\neq E}$, against mole fraction EC for the system water (x_1) + EC (x_2).

Table 5. Enthalpies, $\Delta H^{\neq}$ (kJ mol^{-1}), excess enthalpies, $\Delta H^{\neq E}$ (kJ mol^{-1}), entropies, $\Delta S^{\neq}$ (J mol^{-1} K^{-1}) and excess entropies, $\Delta S^{\neq E}$ (J mol^{-1} K^{-1}) of activation for viscous flow of the system, water (x_1) + EC (x_2).

x_2	$\Delta H^{\neq}$	$\Delta H^{\neq E}$	$\Delta S^{\neq}$	$\Delta S^{\neq E}$	x_2	$\Delta H^{\neq}$	$\Delta H^{\neq E}$	$\Delta S^{\neq}$	$\Delta S^{\neq E}$
				Water (x_1) + EC (x_2)					
0.0000	14.023	0.000	16.57	0.0	0.6004	12.902	0.043	−1.42	−2.53
0.0998	14.268	0.439	13.02	−0.98	0.7006	12.496	−0.168	−3.95	−2.49
0.1996	14.360	0.725	10.19	−1.24	0.8038	12.144	−0.321	−6.31	−2.20
0.2995	14.252	0.810	7.52	−1.34	0.9001	11.848	−0.430	−8.48	−1.88
0.3994	13.815	0.567	4.33	−1.96	1.0000	12.084	0.000	−9.16	0.000
0.4996	13.283	0.229	1.16	−2.55					

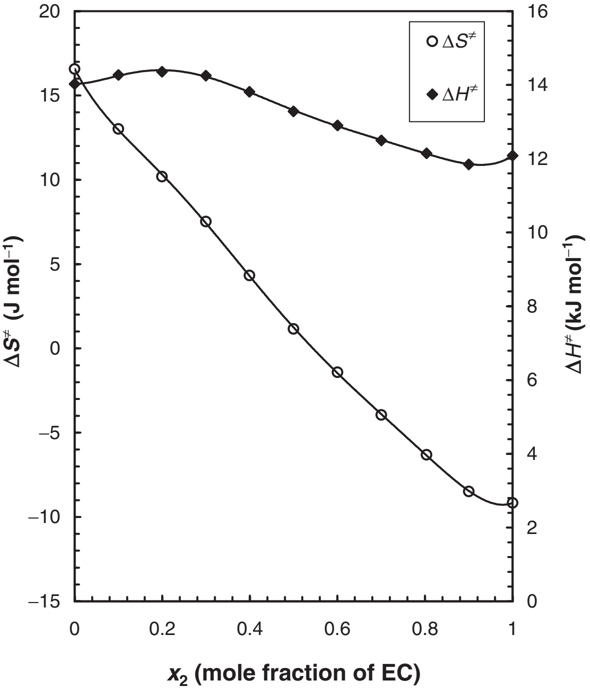

Figure 7. Variation of enthalpy, $\Delta H^{\neq}$, and entropy, $\Delta S^{\neq}$, of activation for viscous flow against mole fraction of EC for the system water (x_1) + EC (x_2).

From the slopes and intercepts of the above equation, obtained by the least squares method, $\Delta H^{\neq}$ and $\Delta S^{\neq}$ have been calculated.

The $\Delta G^{\neq}$ values have been obtained by using the equation,

$$\Delta G^{\neq} = \Delta H^{\neq} - T\Delta S^{\neq} \tag{6}$$

Excess thermodynamic properties have been calculated by the following equation,

$$Y^{E} = Y - (x_1 Y_1 + x_2 Y_2) \tag{7}$$

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Table 6. Coefficients, A_i, of equation (1) expressing density, $\rho \times 10^{-3}$ (kg m^{-3}), coefficient of viscosity, $\eta \times 10^4$ (kg m^{-1} s^{-1}), free energy of activation, $\Delta G^{\neq}$ (kJ mol^{-1}) and the squares of the regression coefficients, r^2, for the system, water (x_1) + EC (x_2) at different temperatures.

Properties	Temperature (K)	A_0	A_1	A_2	A_3	A_4	A_5	A_6	r^2
ρ	313.15	0.9922	1.2961	−3.6155	7.3815	−9.2035	6.0882	−1.6225	> 0.9999
	318.15	0.9902	1.2692	−3.48	6.9754	−8.5689	5.6063	−1.4813	> 0.9999
	323.15	0.9881	1.2485	−3.4223	6.8856	−8.5043	5.5982	−1.4887	> 0.9999
	328.15	0.986	1.2291	−3.4098	7.064	−9.0414	6.1739	−1.7019	> 0.9999
	333.15	0.9831	1.2121	−3.3225	6.7402	−8.4229	5.6189	−1.5153	> 0.9999
η	313.15	6.5529	23.261	−4.4632	−101.11	231.52	−208.57	71.461	> 0.9999
	318.15	5.9868	21.364	−9.1152	−69.529	172.11	−159.27	55.684	> 0.9999
	323.15	5.5001	19.31	−8.6314	137.93	137.93	−125.02	43.049	> 0.9999
	328.15	5.0706	17.878	−10.574	107.94	107.94	−100.95	35.587	> 0.9999
	333.15	4.6984	16.718	−14.24	50.345	50.345	−45.964	15.972	> 0.9999
$\Delta G^{\neq}$	313.15	8.8341	15.894	−25.496	23.5	−2.6061	−11.159	5.9874	> 0.9999
	318.15	8.752	16.135	−26.497	27.554	−10.175	−4.5746	3.8057	> 0.9999
	323.15	8.669	16.393	−27.607	31.993	−18.496	2.7359	1.357	> 0.9999
	328.15	8.5859	16.65	−28.703	36.312	−26.39	9.4734	−0.838	> 0.9999
	333.15	8.5027	16.841	−29.181	38.487	−30.785	13.487	−2.2149	> 0.9999

Table 7. Coefficients, A_i, of Redlich–Kister equation, equation (3), expressing excess molar volumes, $V_m^E \times 10^6$ (m^3 mol^{-1}), excess viscosity, $\eta^E \times 10^4$ (kg m^{-1} s^{-1}), excess free energy of activation, $\Delta G^{\neq E}$ (kJ mol^{-1}) and standard deviation, σ, for the system, water (x_1) + EC (x_2) at different temperatures.

Properties	Temperature (K)	A_0	A_1	A_2	A_3	σ
V_m^E	313.15	−0.1381	0.4261	−1.2671	−0.1009	0.01684
	318.15	−0.0808	0.4277	−0.0634	1.4320	0.00636
	323.15	0.0247	0.4358	−0.0264	1.3473	0.00758
	328.15	0.0969	0.3774	0.0078	1.3638	0.00741
	333.15	0.1981	0.3579	0.0037	1.3437	0.00766
η^E	313.15	9.8895	−9.1943	−1.0622	−0.5774	0.04506
	318.15	8.8745	−7.8182	−0.8880	−0.9459	0.03160
	323.15	8.0505	−6.9335	−0.7070	−0.5012	0.02655
	328.15	7.3527	−6.0010	−0.5390	−0.7197	0.02156
	333.15	6.7292	−5.4057	−0.2527	0.2003	0.01681
$\Delta G^{\neq E}$	313.15	4.1427	−3.5182	1.4334	−0.8717	0.00445
	318.15	4.1861	−3.4905	1.4768	−0.8673	0.00331
	323.15	4.2312	−3.4641	1.5087	−0.8652	0.00250
	328.15	4.2755	−3.4365	1.5468	−0.8588	0.00264
	333.15	4.3183	−3.4012	1.5842	−0.8726	0.00301

The significances of Y and Y^E have been described earlier. Y_1 and Y_2 are the respective properties of the pure components, 1 and 2.

Table 4 lists the free energies of activation for viscous flow, $\Delta G^{\neq}$, and their excess values, $\Delta G^{\neq E}$. Figure 5 shows the variation of free energy at 313.15 and 333.15 K. The free energies increase systematically with the mole fraction of EC. Figure 6 shows the variation of $\Delta G^{\neq E}$ as a function of mole fraction of EC, with clear maxima at ~0.3 mole fraction of EC. The excess viscosity and excess free energy, both being positive but small in magnitude for the whole range of composition, indicate that the species formed in the solution system experience somewhat greater resistive force in the flow process than usual.

The enthalpies and entropies of activation for viscous flow, $\Delta H^{\neq}$ and $\Delta S^{\neq}$, and their excess values, $\Delta H^{\neq E}$ and $\Delta S^{\neq E}$, have been listed in table 5. Figure 7 shows the

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variation of $\Delta H^{\neq}$ and $\Delta S^{\neq}$ of the system as a function of mole fraction of EC. $\Delta S^{\neq}$ has been found to decrease almost linearly with the addition of EC to water, but $\Delta H^{\neq}$ shows an ill-defined maximum in the water-rich region. It is to be noted from table 5 that excess entropies, $\Delta S^{\neq \mathrm{E}}$, are negative for the whole range of composition, indicating that the species formed in the activated state of the flow process are more ordered than what can be expected ideally.

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