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Effect of temperature and solvents on ultrasonic speed and thermo-acoustic parameters of epoxy resin of (2E, 6E)-bis (4-hydroxy benzylidene)-4-methylcyclohexanone solutions at four different temperatures

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ABSTRACT

The density (ρ), viscosity (η) and ultrasonic speed (U) of 1, 4-dioxane (DO), tetrahydrofuran (THF), chloroform (CF) and solutions (0.25-5 wt%) of epoxy resin of (2E, 6E)-bis(4-hydroxy benzylidene)-4-methylcyclohexanone have been investigated at 298, 303, 308 and 313 K to understand molecular interactions in solutions of different polarity. Various acoustical and thermodynamic activation parameters such as acoustical impedance (Z), adiabatic compressibility (κ_a), internal pressure (π), free volume (V_f), intermolecular free path length (L_f), van der Waals constant(b), viscous relaxation time (τ), classical absorption coefficient (α/f^2)cl, Rao`s molar sound function (R_m) and solvation number (S_n) were determined using ρ, η and U data and correlated with concentration (C) at four different temperatures (T). Good to excellent correlation between a given parameter and concentration is observed at all T. Linear or non-linear increase or decrease of studied acoustical and thermodynamic parameters with concentration of epoxy resin at different temperatures indicated existence of strong molecular interactions (solvent-solute and solute-solute) in the solutions. The non-linear increase of Sn with concentration of epoxy resin further supported the existence of strong molecular interactions and structure forming tendency of EMBHBC. The competing solvent-solute and solute-solute interactions are also supported by thermodynamic activation parameters (ΔG^*, ΔH^* and ΔS^*).

***Keywords*:** Epoxy resin, Density, Viscosity, Ultrasonic speed, Thermo-acoustic parameters, Solvation number

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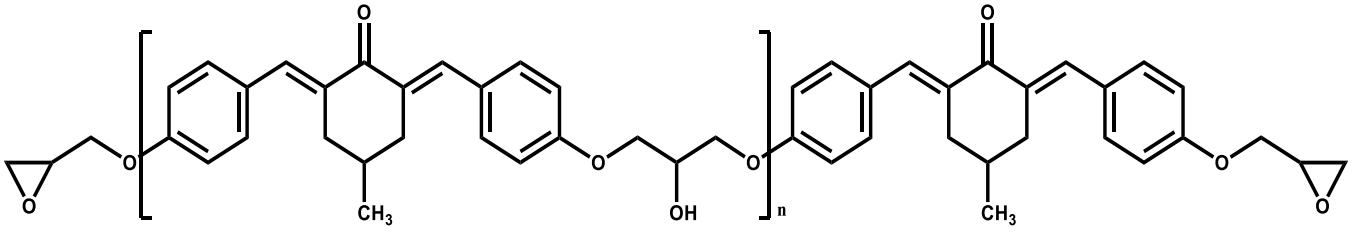
1. INTRODUCTION

Ultrasonic technique is most useful for investigating compatibility of polymer blends to achieve mechanical integrity, better adhesion and better processing, various organic liquids and their mixtures, aqueous and nonaqueous electrolytic and polymeric solutions[1-5]. Solvation number is a powerful parameter in determining the strength of the molecular interactions in the solutions. It provides information about structure making or structure breaking tendency of the solutes under study. Measurements of density, viscosity, and ultrasonic speed are very useful in understanding the nature of the molecular interactions in pure liquids, liquid mixtures[6-7], ionic interactions in aqueous electrolytic solutions and polymers, etc.[8-9] These parameters provide information about ionic, covalent, charge transfer, hydrogen bonding, hydrophilic interactions and hence molecular and structural properties of the liquid solutions, which are very important for polymer processing and their uses.

Epoxy resins are well known for their characteristic properties namely good to excellent thermal, mechanical and electrical properties, high strength and stiffness, good dielectric behavior, excellent resistance to chemicals, low shrinkage during cure, excellent hydrolytic stability, excellent adhesion, etc. make them suitable for increasing number of high performance engineering applications[10-13]. Epoxy resins are most widely used in land, marine and space transportations, adhesives, laminates, printed circuit boards, molds for casting and composite materials, in the aerospace and aircraft industries, etc.[14-20].

To the best of our knowledge no work has been reported on ultrasonic studies of photosensitive epoxy resin of (2E, 6E)-bis(4-hydroxy benzylidene)-4-methylcyclohexanone solutions, which encouraged us to investigate present work. In this paper we have reported the effect of concentration, temperature and nature of solvents and epoxy resin on molecular interactions occurring in the epoxy resin solutions. The study is carried out over a narrow temperature range from 298 to 313 K and concentration range from 0.25 to 5 wt %. Various acoustical and thermodynamic activation parameters are evaluated to understand molecular interactions in resin solutions of different polarity. The molecular structure of epoxy resin is shown below.



Epoxy resin of (2E, 6E)-bis (4-hydroxy benzylidene)-4-methylcyclohexanone (EMBHBC)

2. EXPERIMENTAL

2. 1. Materials and Methods

1,4-Dioxane (DO), chloroform (CF) and tetrahydrofuran (THF) were supplied by Spectrochem Pvt. Ltd, Mumbai and were purified according to literature methods[21]. The epoxy resin of (2E, 6E)-bis(4-hydroxy benzylidene)-4-methylcyclohexanone (EMBHBC) used in the

present investigation was synthesized and purified according to our recent publication[22]. The epoxy equivalent weight and weight average molecular weight of EMBHBC were 898.3 and 1092, respectively. DO, THF and CF were distilled on a 91 cm long fractionation column after being refluxed overnight on sodium-potassium alloy. Care has been taken that traces of moisture do not affect their dielectric constants or solvating power and contribute only insignificantly to their conductance. In view of this, the investigation was carried out in a closed system but not on a high vacuum line. The middle fraction of the distillate was used. Distilled water of conductivity range 3×10^{-8} to 5×10^{-8} S. m^{-1} at 25 °C was distilled with the help of Millipore (Elix) distillation unit. 5 wt % stock solutions (100 ml) of EMBHBC in DO, THF and CF were prepared at room temperature. From these stock solutions, a series of dilute solutions were prepared in airtight 25 ml volumetric flasks and stored at room temperature.

The density (ρ), viscosity (η), and ultrasonic speed (U) measurements on pure THF, CF and 1,4-dioxane and their EMBHBC solutions (0.25-5.0 wt%) were carried out at four different temperatures: 298, 303, 308 and 303 K. The density and ultrasonic speed measurements were carried out on a density and sound velocity meter supplied by Anton Paar (DSA 5000 M), Gmbh, Graz, Austria. The repeatability in density, ultrasonic speed, and temperature measurements were $\pm 1 \times 10^{-3}$ kg m^{-3}, $\pm 1 \times 10^{-1}$ ms^{-1}, and $\pm 1 \times 10^{-3}$ K, respectively.

The adjustment and calibration of DSA 5000 M was done with air and Millipore–distilled water over a temperature range from 298 to 313 K. Viscosity measurements were carried out by using an Ubbelohde type viscometer. The repeatability in viscosity measurements was ±0.1 %. The viscosity measurements were repeated at least three times for each sample and average value was considered.

A constant temperature bath (Nova Instruments, Model NV8550E, Ahmedabad) with an accuracy of ±0.1 K was used for maintaining constant temperature during viscosity measurements. The flow times of pure solvents and solutions were measured with a digital RACER HS 10 W stopwatch with an accuracy of ±0.01 s. Mass measurements were carried out on an analytical balance (AB 204-S; Mettler Toledo, Switzerland) with an uncertainty of $\pm 1 \times 10^{-4}$ kg. Experimental and literature values of ρ, η and U are reported in Table 1[23-31].

2. 2. Theoretical Equations

Various acoustical and thermodynamic activation parameters were determined according to following theoretical equations:

Specific acoustical impedance (Z):

$$Z = U\rho \tag{1}$$

Adiabatic compressibility (κ_a):

Adiabatic compressibility (κ_a) can be evaluated according to Newton and Laplace:

$$\kappa_a = \frac{1}{U^2\rho} \tag{2}$$

Internal pressure (π)[32]:

$$\pi = b' RT \left(\frac{K'\eta}{U}\right)^{1/2} \frac{\rho^{2/3}}{M^{7/6}} \quad (3)$$

where b′ is the packing factor (2), K′ is a constant (4.28×10^9). R is the gas constant (8.3143 J K^{-1} mol^1).

Free volume (V_f)[32]:

$$V_f = \left[\frac{MU}{K'\eta}\right]^{3/2} \quad (4)$$

Inter molecular free path length(L_f)[33]:

$$L_f = K_J(\kappa a)^{1/2} \quad (5)$$

where K_J is the Jacobson′s temperature dependent constant [K_J = (93.875+0.375T)× 10^{-8}] van der Waals constant (b)[34]:

$$b = \frac{M}{\rho}\left[1 - \left[\frac{RT}{MU^2}\right]\left[\sqrt{1 + \frac{MU^2}{3RT}} - 1\right]\right] \quad (6)$$

where M is the apparent molecular mass of the solution, R is the gas constant and T is the absolute temperature.

Viscous relaxation time (τ)[34]:

The resistance offered by viscous force in the flow of sound wave appears as a classical absorption and associated with it is the viscous relaxation time:

$$\tau = \frac{4\eta}{3\rho U^2} \quad (7)$$

Classical absorption coefficient $(\alpha/f^2)_{cl}$[35]:

$$\left(\frac{\alpha}{f^2}\right)_{cl} = \frac{8\pi^2\eta}{3U^3\rho} \quad (8)$$

Rao′s molar sound function (Rm) [36]:

$$Rm = \frac{M}{\rho}U^{1/3} \quad (9)$$

Solvation number (Sn): The number of grams of solvent molecules connected in the apparent solvation of 1 g of solute assuming that the solvent molecules participating in the solvation are effectively incompressible due to strong localized electronic fields is expressed as

$$n = \left[1 - \frac{\kappa_a(100 - X)}{\kappa_{a_1} X}\right] \tag{10}$$

where X is the number of grams of solute in 100 g of the solution. The solvation number (Sn) can be expressed as

$$Sn = \frac{M_2}{M_1\left(1 - \frac{\kappa_a}{\kappa_{a_1}}\right)\left(\frac{100 - X}{X}\right)} \tag{11}$$

where M_1 and M_2 are the molecular masses of solvent and solute, respectively.

The Gibbs free energy of activation (ΔG*), enthalpy of activation (ΔH*) and entropy of activation (ΔS*) can be determined by using viscous relaxation time data at different concentrations and temperatures.

$$\frac{1}{\tau} = \frac{kT}{h} e^{\frac{-\Delta G^*}{RT}} \tag{12}$$

$$ln\frac{1}{\tau T} = ln\frac{k}{h} + \frac{\Delta S^*}{R} - \frac{\Delta H^*}{RT} \tag{13}$$

where k is the Boltzmann constant and h is the Planck`s constant.

3. RESULTS AND DISCUSSION

The density, viscosity and ultrasonic speed of pure solvents and EMBHBC solutions were determined at 298, 303, 308 and 313 K and are reported in Table 2 from which it is clear that ρ, η and U increased linearly with concentration (C) and decreased linearly with temperature (T) except CF system in which density is decreased with C. The density of CF is greater than that of EMBHBC solutions and therefore the density of the solutions decreased with C, while densities of DO and THF are smaller than that of EMBHBC so ρ increased with C in these systems confirming the law of additivity. The concentration and temperature dependence of ρ, η and U data were tested by least squares analysis. The degree of linearity was judged on the basis of regression coefficient (R^2). A very good to excellent correlation between these parameters and concentration is observed in the studied solvent systems at four different temperatures except viscocity (Table 2). From Table 2, it is clear that the change in ρ and U with C and T are not as appreciable as η because molecular motion is much more affected by polymer–solvent and polymer–polymer interactions in solutions. The increase of ρ, η and U with C supported increase in cohesive forces due to powerful molecular interactions, while decrease of these parameters with T indicated decrease in cohesive forces. The increasing temperature has two opposite effects namely increase of molecular interactions (structure formation) and destruction of structure formed previously as a result of thermal fluctuation[37].

With a view to understand the effect of concentration, temperature, nature of solvents and the structure of resin on solvophilicity or solvophobicity, various acoustical and thermodynamic activation parameters were derived according to equations (1-13) by using ρ, η and U data at

different temperatures and were correlated with C and T. The least –squares equations along with regression coefficients (R^2) are reported in Tables 3-5, respectively for DO-EMBHBC, THF-EMBHBC and CF-EMBHBC solutions. From these tables it is observed that there is a good to excellent correlation between given a parameter with C at a given T, which furnished wealth of information regarding strength of molecular interactions occurring in the solutions. The linear decrease of adiabatic compressibility (κa) and free path length (L_f) with C and linear increase with T; and linear increase of free volume (V_f) with C and T in DO and THF systems supported existence of strong molecular interactions.

V_f increased linearly with T, while it decreased nonlinearly with C in CF system also supported presence of strong molecular interactions. Other acoustical parameters such as specific acoustic impendence (Z), van der Waals constant (b), classical absorption coefficient (α/f^2)cl and viscous relaxation time (τ) also supported existence of strong molecular interactions. π, V_f and τ are three basic thermodynamic parameters for liquid systems. Internal pressure of a solution is a single factor, which appears to vary with intermolecular interactions namely solvation, ion–solvent interactions, solute–solvent interaction and quantum mechanical forces of dispersion and dielectric forces, which play an important role in transport properties of solutions.

Decrease of π and increase of V_f and vice versa are measure of cohesion forces. In solution both solvent-polymer and polymer-polymer interactions occur and overall value is decided by the predominant interactions and as a result nonlinear behavior is observed in many cases. This molecular interactions depend upon the nature of solvent and solute, pressure, temperature, structure and presence of substituents, etc. Strong polymer-polymer interactions are supported by nonlinear increase of Sn with C and nonlinear decrease with T. Nonlinear variations of Sn with C and T further supported the presence of strong dipole-dipole interactions and competing solute-solute and solvent–solute interactions with increasing solution concentrations. Rao`s molar sound function and van der Waals constant increased with C and T suggested that there is no complex or aggregate formation taken place in all the systems.

In DO-EMBHBC, Z, Rm and b increased linearly with C, while π, τ and $(\alpha/f^2)_{cl}$ increased nonlinearly with C. κ_a and L_f decreased linearly with C and V_f decreased nonlinearly with C. Z, π, τ and $(\alpha/f^2)_{cl}$ decreased with T. Practically little temperature effect was observed on R_m. In THF-EMBHBC, Z, Rm, and b increased linearly with C, while V_f, τ and (α/f^2)cl decreased nonlinearly with C. κ_a, L_f and π decreased nonlinearly with C. Z, Rm, π, τ and (α/f^2)cl decreased with T, while κ_a, L_f, b and V_f increased with T. Practically little temperature effect was observed on Rm. In CF-EMBHBC, Z, Rm, and b increased linearly with C, while π, V_f, τ and $(\alpha/f^2)_{cl}$ increased nonlinearly with C. Z, π, τ and $(\alpha/f^2)_{cl}$ decreased with T, while κ_a, L_f, b and V_f increased with T. Practically no effect temperature was observed on Rm. The linear/nonlinear increase/decrease of the acoustical parameters with C and T suggested presence of strong molecular parameters in EMBHBC solutions.

The plots of solvation number against concentration for DO-EMBHBC, THF-EMBHBC and CF-EMBHBC solutions at four different temperatures are shown in Figs. 1-3 from which it is observed that Sn increased nonlinearly with C at all temperatures confirming powerful molecular interactions (solvent-solute and solute-solute) in the solutions. In DO-EMBHBC and THF-EMBHBC systems Sn increased nonlinearly with C and increased up to 303 K and then decreased with T. In CF-EMBHBC Sn increased nonlinearly with C and T. The nonlinear variation of Sn with C at a given T confirmed competing solvent-solute and solute-solute interactions.

Ether, carbonyl, hydroxyl and methyl groups of EMBHBC are polar groups either having δ_+ or δ_- partial charges. The lone pairs of electrons of DO and THF, and Cl-atoms of CF have δ_- partial charges and H-atom possesses δ_+ charge. The dipole-dipole interactions of opposite types favor structure formation, while of the same types favor structure disruption i.e. structure formed previously. Predominant dipole-dipole interactions decide either structure formation or disruption. In the present case it is observed that the nature of solvents, EMBHBC, concentration and temperature played important role on molecular interactions. From the solvation study it is observed that EMBHBC possesses structure forming tendency in the studied systems and hence affecting processing from solutions.

Thermodynamic activation parameters ΔG^*, ΔH^* and ΔS^* were determined by using viscous relaxation time data according to Eq. (12) & (13) and are reported in Table 6. In DO-EMBHBC ΔG^* increased linearly with C and decreased with increasing T. ΔH^* is positive and increased with C. ΔS^* is negative and decreased with C. In THF-EMBHBC ΔG^* increased linearly with C and decreased up to 303 K and 1% concentration and then increased with T. Above 1% concentration ΔG^* decreased with T and then increased with T. ΔH^* is positive and increased with C. ΔS^* is negative and decreased with C. In CF-EMBHBC, ΔG^* is increased linearly with C and decreased up to 308 K and then increased with T. ΔH^* is positive and decreased with C. ΔS^* is negative and decreased up to 0.5% concentration and then it is positive and increased with C.

In any solution at equilibrium two opposite processes namely condensation and evaporation take place simultaneously. Depending upon nature of solvents and solutes as well as their molecular structure, solvent-solvent, solvent-solute and solute-solute interactions take place in the solutions. In case of structure forming tendency of the solute strong solvent-solute interactions result into predominant condensation process over evaporation process and vice versa. With increasing solute concentration solute-solute interactions also compete and affect the thermodynamic and transport properties. Small negative or positive values of ΔS^* confirmed that condensation process is predominant over evaporation process and hence EMBHBC possesses structure forming tendency in the studied solvent systems. Thus, thermodynamic activation parameters along with acoustical parameters and solvation number proved strong molecular interactions in the solutions.

4. CONCLUSIONS

From experimental findings, it is concluded that linear/nonlinear increase/decrease of various acoustical parameters, solvation number and thermodynamic activation parameters with C and T supported powerful solvent-solute and solute-solute interactions completing in EMBHBC solutions. Studied parameters showed very good to excellent correlation with C at different temperatures except few cases in which fairly good correlation with C is observed.

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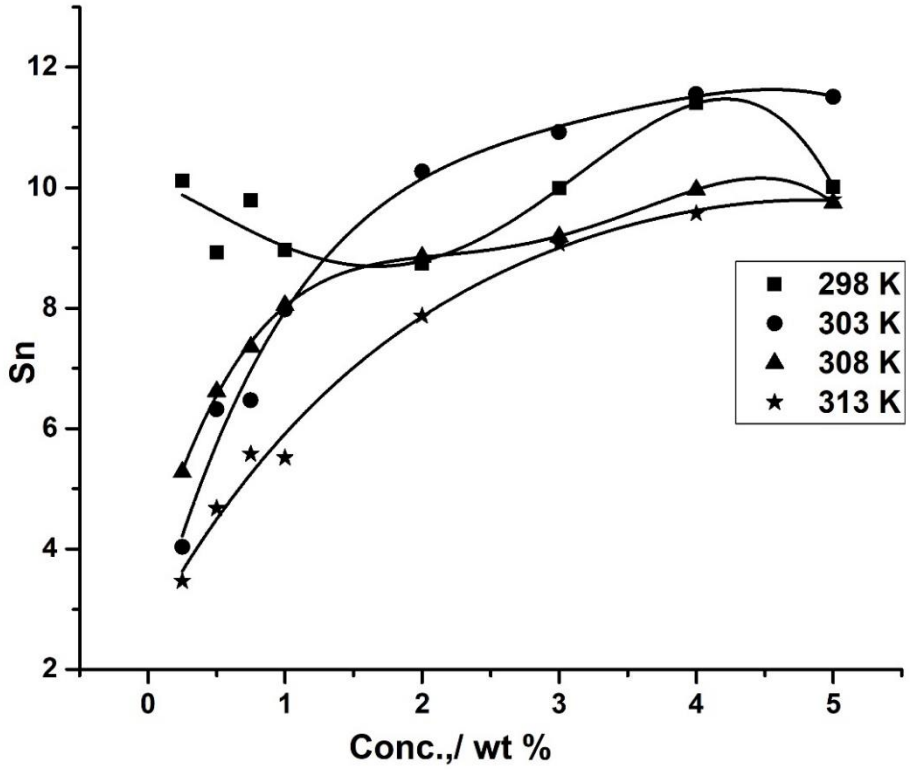

Fig. 1. Plots of solvation number (S_n) against concentration (C) for DO- EMBHBC solutions at 298K, 303 K, 308 K and 313 K.

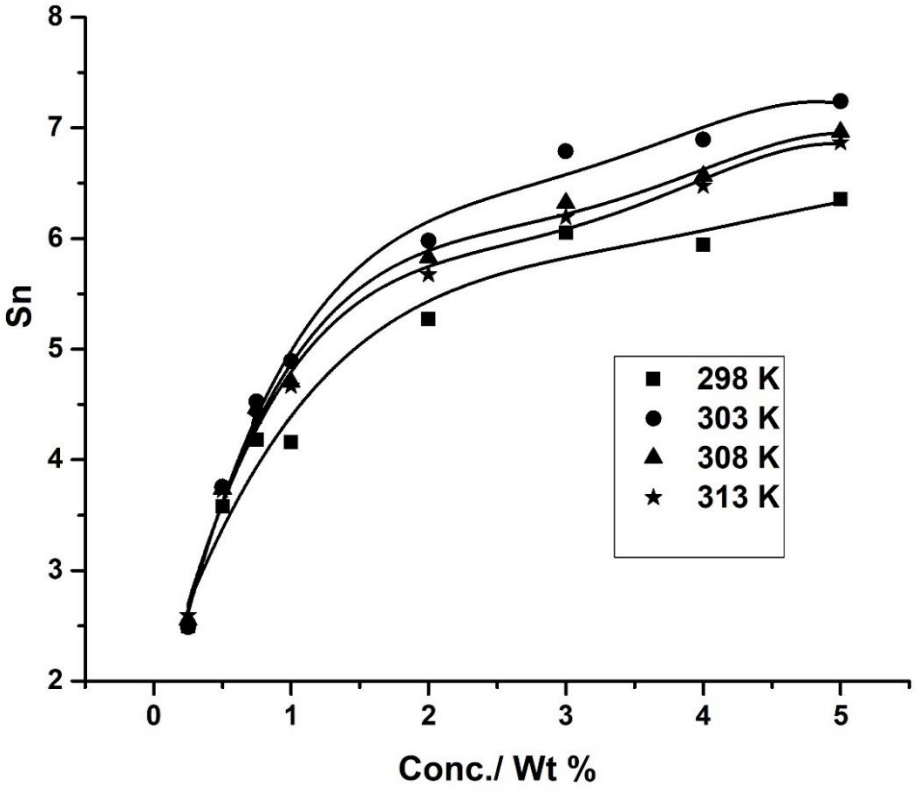

Fig. 2. Plots of solvation number (S_n) against concentration (C) for THF- EMBHBC solutions at 298 K, 303 K, 308 K and 313 K.

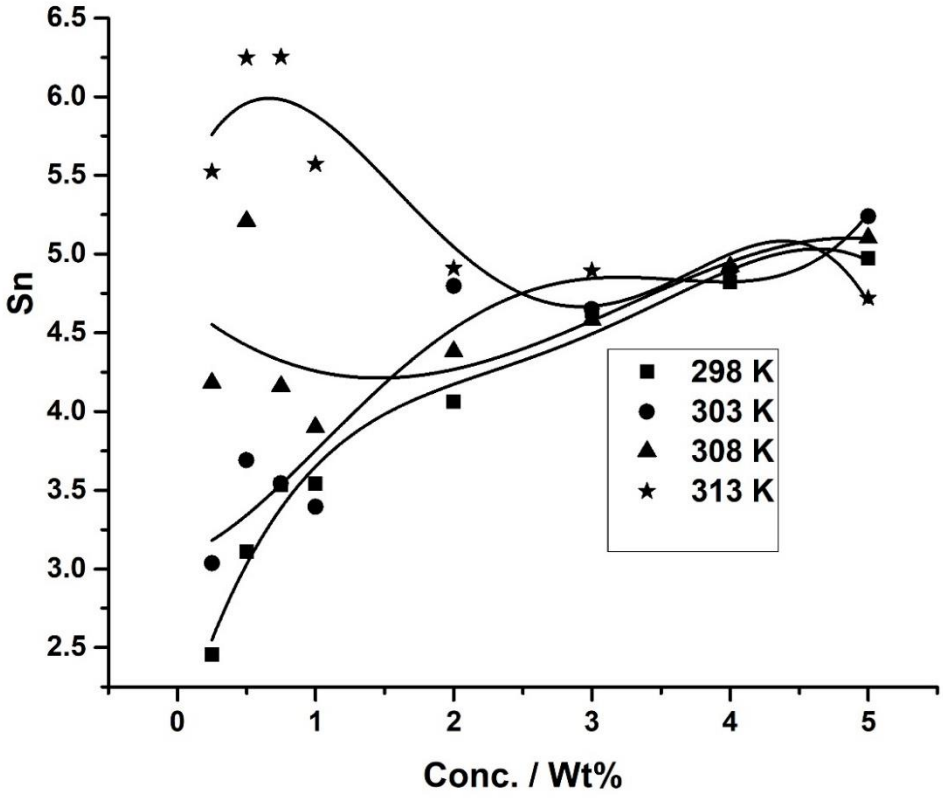

Fig. 3. Plots of solvation number (S_n) against concentration (C) for CF-EMBHBC solutions at 298 K, 303 K, 308 K and 313 K.

Table 1. Comparison of measured density (ρ), viscosity (η) and ultrasonic speed (U) data for DO, THF and CF with literature values at 298, 303, 308 and 313 K.

Temp. (K)	Density ($kg.m^{-3}$)		Viscosity (m.Pa.s)		Ultrasonic speed ($m.s^{-1}$)	
	Expt.	Lit.	Expt.	Lit.	Expt.	Lit.
DO						
298	1026.7	1026.8[23]	1.1702	1.1868[25]	1345.4	1344.3[23]
303	1021.1	1021.2[23]	1.0300	1.094[29]	1323.6	1322.3[23]
308	1015.6	1015.5[23]	0.9215	1.0026[25]	1301.3	1300.5[23]
313	1009.9	1011.8[23]	0.8307	0.8994[25]	1280.9	1279.7[24]
THF						
298	885.1	887.6[26]	0.5073	0.4580[27]	1275.6	1276.6[27]
303	880.7	882.1[26]	0.4387	0.4452[28]	1254.0	1254.25[24]
308	875.2	876.6[26]	0.3936	0.4125[27]	1230.4	1230.27[24]
313	869.7	871.1[26]	0.3499	0.3762[27]	1206.9	1206.46[24]
CF						
298	1477.8	1478.8[30]	0.613	-	983.8	983.86[30]
303	1468.0	1468.02[30]	0.548	0.560[31]	967.5	966.84[30]
308	1460.3	1458.23[30]	0.523	0.531[31]	949.8	949.89[30]
313	1447.4	1448.46[30]	0.481	0.511[31]	933.2	933.02[30]

Table 2. The density (ρ), viscosity (η) and ultrasonic speed (U) data for DO-EMBHBC, THF-EMBHBC and CF-EMBHBC solutions at 298, 303, 308 and 313 K.

Con. (%)	Density ρ, kg m^{-3}				Viscosity η, mPa s				Ultrasonic speed U, m s^{-1}			
	298 K	303 K	308 K	313 K	298K	303K	308K	313K	298 K	303 K	308 K	313 K
DO-EMBHBC												
0.00	1026.8	1021.1	1015.6	1010.0	1.209	1.078	0.995	0.932	1345.4	1323.6	1301.3	1280.9
0.25	1027.7	1022.5	1016.8	1010.8	1.241	1.134	1.027	0.937	1345.6	1324.7	1302.0	1282.0
0.50	1028.5	1022.9	1017.2	1011.6	1.270	1.170	1.056	0.948	1346.1	1325.0	1302.6	1282.5
0.75	1029.1	1023.5	1017.8	1012.2	1.308	1.201	1.074	0.967	1346.4	1325.8	1303.1	1283.0
1.00	1030.1	1023.7	1018.0	1013.0	1.355	1.230	1.086	0.991	1346.9	1326.0	1303.7	1284.0
2.00	1032.5	1025.4	1019.8	1014.6	1.397	1.259	1.117	1.001	1349.2	1327.2	1305.9	1285.3
3.00	1033.7	1027.5	1021.9	1016.2	1.439	1.281	1.140	1.027	1350.9	1328.5	1307.9	1286.9
4.00	1034.1	1029.1	1023.5	1018.0	1.473	1.309	1.173	1.048	1352.5	1330.0	1309.4	1288.8
5.00	1038.7	1031.6	1025.7	1020.1	1.493	1.327	1.211	1.055	1354.6	1331.4	1311.9	1290.6
THF-EMBHBC												
0.00	885.1	880.7	875.2	869.7	0.507	0.454	0.433	0.408	1275.6	1254.0	1230.4	1206.9
0.25	886.3	883.9	878.0	872.2	0.525	0.465	0.441	0.426	1279.1	1256.0	1232.6	1209.2
0.50	887.5	884.5	879.1	873.0	0.558	0.486	0.459	0.435	1280.0	1257.0	1233.4	1210.2
0.75	888.5	885.1	880.1	874.0	0.571	0.503	0.477	0.444	1281.0	1258.1	1234.2	1211.1
1.00	890.9	886.4	881.0	875.0	0.570	0.518	0.480	0.448	1282.0	1258.8	1235.4	1212.2
2.00	895.1	889.6	884.2	878.6	0.587	0.534	0.488	0.450	1285.3	1262.4	1239.0	1215.8
3.00	899.1	893.7	887.9	882.1	0.616	0.552	0.506	0.473	1287.9	1264.4	1242.4	1219.4
4.00	905.6	897.2	891.7	885.8	0.629	0.587	0.530	0.512	1291.6	1268.4	1246.0	1222.9
5.00	908.8	901.1	894.9	888.6	0.655	0.597	0.544	0.529	1295.0	1271.0	1249.1	1226.3
CF-EMBHBC												
0.00	1477.8	1468.0	1460.3	1447.4	0.613	0.548	0.523	0.481	983.8	967.5	949.8	933.2
0.25	1477.0	1467.1	1459.2	1447.0	0.636	0.574	0.531	0.492	984.8	968.8	950.8	933.9
0.50	1476.5	1466.5	1458.3	1446.4	0.638	0.576	0.533	0.486	985.7	969.6	951.5	934.5
0.75	1476.0	1466.1	1457.7	1445.8	0.648	0.572	0.541	0.509	986.4	970.7	952.8	935.1
1.00	1475.4	1465.6	1456.8	1444.9	0.654	0.582	0.544	0.514	987.5	971.9	953.9	936.1
2.00	1474.0	1463.9	1454.9	1443.8	0.680	0.605	0.571	0.536	990.5	973.9	957.0	939.2
3.00	1472.1	1462.5	1453.3	1442.3	0.698	0.638	0.603	0.565	992.9	977.3	960.0	942.3
4.00	1470.3	1461.2	1451.0	1441.1	0.744	0.672	0.639	0.592	995.9	979.9	962.9	945.3
5.00	1467.9	1459.3	1448.9	1439.2	0.771	0.698	0.663	0.630	998.9	982.5	965.8	949.0

Table 3. The least-squares equations and regression coefficients for DO-EMBHBC solutions at 298, 303, 308 and 313 K.

Parameter	Least squares equations (regression coefficients, R^2)			
	298 K	303 K	308 K	313 K
ρ (kg m^{-3})	2.0826C + 1027.4 (0.955)	1.9361C + 1021.7 (0.9914)	1.8933C + 1016.1 (0.9941)	1.9118C + 1010.5 (0.9905)
η × 10^{-3} (Pa s)	0.055C + 1.253 (0.9071)	0.0423C + 1.1435 (0.8321)	0.0378C + 1.0283 (0.9414)	0.0253C + 0.9431 (0.9314)
U (m s^{-1})	1.8648C + 1345.2 (0.9972)	1.4318C + 1324.3 (0.9865)	2.0647C + 1301.5 (0.9975)	1.8329C + 1281.5 (0.9892)
Z × 10^{-6} (kg m^{-2} s^{-1})	0.0047C + 1.3821 (0.9813)	0.004C + 1.353 (0.9911)	0.0046C + 1.3225 (0.9969)	0.0043C + 1.295 (0.9904)
κ_a × 10^{10} (Pa^{-1})	-0.0254C + 5.3784 (0.9889)	-0.0224C + 5.5809 (0.9899)	-0.0288C + 5.8094 (0.9972)	-0.0282C + 6.0252 (0.9894)
L_f × 10^{11} (m)	-0.0113C + 4.7688 (0.9889)	-0.0099C + 4.902 (0.99)	-0.0126C + 5.0465 (0.9972)	-0.0122C + 5.1855 (0.9896)
R_m × 10^4 ($m^{10/3}$ $s^{-1/3}$ mol^{-1})	0.3393C + 9.4678 (0.9998)	0.3419C + 9.4712 (0.9999)	0.3461C + 9.4681 (1)	0.3473C + 9.4713 (1)
b × 10^5 (m^3)	0.3007C + 8.4539 (0.9997)	0.3055C + 8.499 (0.9999)	0.3092C + 8.5433 (1)	0.3124C + 8.5881 (1)
π × 10^{-8} (Pa)	-0.0018C^4 + 0.0267C^3 - 0.1407C^2 + 0.1729C + 5.3065 (0.9918)	-0.0058C^4 + 0.0702C^3 - 0.2932C^2 + 0.3369C + 5.1322 (0.9992)	-0.0037C^4 + 0.0456C^3 - 0.1853C^2 + 0.1505C + 5.0346 (0.9996)	-0.1296C + 4.9875 (0.9906)
V_f × 10^7 (m^3)	0.0014C^4 - 0.0179C^3 + 0.0888C^2 - 0.1769C + 1.1036 (0.942)	0.004C^4 - 0.0479C^3 + 0.2017C^2 - 0.3154C +	0.0028C^4 - 0.0353C^3 + 0.1475C^2 - 0.2158C +	0.0014C^4 - 0.0151C^3 + 0.062C^2 - 0.0791C + 1.5191 (0.9277)

		1.2685 (0.9942)	1.3969 (0.9925)	
$\tau \times 10^{13}$ (s)	$-0.0086C^4 + 0.107C^3 - 0.5136C^2 + 1.3275C + 8.6245$ (0.9911)	$-0.0175C^4 + 0.2138C^3 - 0.9182C^2 + 1.7614C + 8.0322$ (0.9988)	$-0.0109C^4 + 0.136C^3 - 0.574C^2 + 1.1187C + 7.7093$ (0.9996)	$-0.0044C^4 + 0.0481C^3 - 0.1986C^2 + 0.512C + 7.4509$ (0.9736)
$(\alpha/f2)cl \times 10^{15}$ (s^2 m^{-1})	$-0.0013C^4 + 0.0161C^3 - 0.0767C^2 + 0.194C + 1.2641$ (0.9904)	$-0.0026C^4 + 0.0314\ C^3 - 0.1352C^2 + 0.2588C + 1.1966$ (0.9987)	$-0.0017C^4 + 0.0208\ C^3 - 0.0874C^2 + 0.1675C + 1.1682$ (0.9995)	$-0.0007C^4 + 0.007C^3 - 0.0291C^2 + 0.075C + 1.1471$ (0.9703)

Table 4. The least-squares equations and regression coefficients for THF-EMBHBC solutions at 298, 303, 308 and 313 K.

Parameter	Least squares equations (regression coefficients, R^2)			
	298 K	303 K	308 K	313 K
ρ (kg m^{-3})	4.8302C + 885.25 (0.9954)	3.8025C + 882.16 (0.9913)	3.6977C + 876.77 (0.9899)	3.644C + 870.98 (0.9923)
$\eta \times 10^{-3}$ (Pa s)	0.0256C + 0.5328 (0.9131)	0.0275C + 0.4714 (0.9423)	0.0204C + 0.4468 (0.9368)	0.0217C + 0.4187 (0.9529)
U (m s^{-1})	3.4821C + 1277.8 (0.9793)	3.2424C + 1255.2 (0.9902)	3.6111C + 1231.4 (0.9954)	3.7166C + 1208.1 (0.9945)
$Z \times 10^{-6}$ (kg m^{-2} s^{-1})	0.0093C + 1.1311 (0.9949)	0.0077C + 1.1072 (0.9927)	0.0078C + 1.0796 (0.993)	0.0077C + 1.0522 (0.9937)
$\kappa a \times 10^{10}$ (Pa^{-1})	-0.0729C + 6.9173 (0.9914)	-0.0662C + 7.1941 (0.9912)	-0.0735C + 7.5203 (0.9924)	-0.0788C + 7.8655 (0.9924)
$L_f \times 10^{11}$ (m)	-0.0288C + 5.4083 (0.9919)	-0.0259C + 5.5657 (0.9917)	-0.0284C + 5.7419 (0.9929)	-0.03C + 5.9248 (0.9929)
$R_m \times 10^4$ ($m^{10/3}$ $s^{-1/3}$ mol^{-1})	0.4367C + 8.8488 (0.9998)	0.4516C + 8.8247 (0.9999)	0.4571C + 8.8221 (0.9999)	0.4614C + 8.8242 (1)

$b \times 10^5$ (m^3)	0.3889C + 8.0296 (0.9998)	0.4065C + 8.0489 (0.9998)	0.4129C + 8.0957 (0.9999)	0.4186C + 8.1485 (0.9999)
$\pi \times 10^{-8}$ (Pa)	-0.125C + 4.1241 (0.9628)	-0.11C + 3.9731 (0.9608)	-0.129C + 3.9508 (0.977)	-0.1223C + 3.9112 (0.9677)
$V_f \times 10^7$ (m^3)	$-0.004C^6 + 0.055C^5 - 0.235C^4 + 0.327C^3 + 0.172C^2 - 0.59C + 2.7709$ (0.9377)	$0.012C^4 - 0.134C^3 + 0.509C^2 - 0.713C + 3.221$ (0.8918)	$0.013C^4 - 0.146C^3 + 0.535C^2 - 0.638C + 3.356$ (0.9175)	$0.023C^4 - 0.232C^3 + 0.736C^2 - 0.685C + 3.516$ (0.9896)
$\tau \times 10^{13}$ (s)	$-0.010C^4 + 0.124C^3 - 0.511 C^2 + 0.941C + 4.69$ (0.9708)	$-0.012C^4 + 0.134C^3 - 0.506C^2 + 0.925C + 4.316$ (0.9887)	$-0.012C^4 + 0.133C^3 - 0.49C^2 + 0.797C + 4.312$ (0.9809)	$-0.02C^4 + 0.201C^3 - 0.637C^2 + 0.797C + 4.292$ (0.999)
$(\alpha/f2)cl \times 10^{15}$ (s^2 m^{-1})	$-0.015C^4 + 0.185C^3 - 0.764C^2 + 1.396C + 7.247$ (0.9651)	0.31C + 7.112 (0.9065)	$0.027C^3 - 0.231C^2 + 0.743C + 6.990$ (0.9458)	0.256C + 7.179 (0.9175)

Table 5. The least-squares equations and regression coefficients for CF-EMBHBC solutions at 298, 303, 308 and 313 K.

Parameter	Least squares equations (regression coefficients, R^2) [CF - EMBHBC]			
	298 K	303 K	308 K	313 K
ρ (kg m^{-3})	-1.8703C + 1477.5 (0.9954)	-1.6285C + 1467.5 (0.9911)	-2.138C + 1459.6 (0.991)	-1.5762C + 1447.1 (0.9912)
$\eta \times 10^{-3}$ (Pa s)	0.0293C + 0.6221 (0.986)	0.0283C + 0.5552 (0.9842)	0.0286C + 0.5194 (0.9949)	0.0288C + 0.4811 (0.9897)
U (m s^{-1})	2.9728C + 984.16 (0.9981)	2.931C + 968.21 (0.9937)	3.185C + 950.24 (0.996)	3.1543C + 932.99 (0.9988)
$Z \times 10^{-6}$ (kg m^{-2} s^{-1})	0.0028C + 1.4531 (0.9968)	0.0027C + 1.4208 (0.9899)	0.0026C + 1.3869 (0.9937)	0.0031C + 1.3502 (0.995)
$\kappa_a \times 10^{10}$ (Pa^{-1})	-0.0342C + 6.9922 (0.9975)	-0.0352C + 7.269 (0.9921)	-0.0388C + 7.5874 (0.9952)	-0.044C + 7.9378 (0.9982)

$L_f \times 10^{11}$ (m)	-0.0134C + 5.4373 (0.9977)	-0.0136C + 5.5945 (0.9923)	-0.0149C + 5.7673 (0.9954)	-0.0166C + 5.9518 (0.9981)
$R_m \times 10^4$ ($m^{10/3}\,s^{-1/3}\,mol^{-1}$)	0.1616C + 8.0395 (1)	0.1631C + 8.045 (1)	0.1681C + 8.0379 (0.9999)	0.1663C + 8.0577 (1)
$b \times 10^5$ (m^3)	0.152C + 7.9548 (1)	0.1542C + 8.0023 (1)	0.1591C + 8.0437 (1)	0.1582C + 8.1106 (1)
$\pi \times 10^{-8}$ (Pa)	$-0.002C^4 + 0.038C^3 - 0.212C^2 + 0.439C + 3.936$ (0.9445)	$-0.005C^4 + 0.059C^3 - 0.272C^2 + 0.475C + 3.803$ (0.9564)	$-0.002C^4 + 0.035C^3 - 0.189C^2 + 0.385C + 3.781$ (0.8767)	$-0.002C^4 + 0.03C^3 - 0.143C^2 + 0.299C + 3.71$ (0.9138)
$V_f \times 10^7$ (m^3)	$0.006C^4 - 0.09C^3 + 0.465C^2 - 1.001\,C + 3.036$ (0.9827)	$0.012C^4 - 0.150C^3 + 0.675C^2 - 1.26C + 3.494$ (0.9901)	$0.007C^4 - 0.099C^3 + 0.508C^2 - 1.120C + 3.696$ (0.9613)	$0.007C^4 - 0.091C^3 + 0.437C^2 - 1.021C + 4.042$ (0.9753)
$\tau \times 10^{13}$ (s)	$-0.006C^4 + 0.105C^3 - 0.611C^2 + 1.565C + 5.644$ (0.9881)	$-0.012C^4 + 0.165C^3 - 0.767C^2 + 1.609C + 5.254$ (0.9911)	$-0.006C^4 + 0.101C^3 - 0.543C^2 + 1.362C + 5.181$ (0.978)	$-0.007C^4 + 0.086C^3 - 0.401C^2 + 1.079C + 5.02$ (0.9862)
$(\alpha/f^2)cl \times 10^{15}$ ($s^2\,m^{-1}$)	$-0.001C^4 + 0.021\,C^3 - 0.122C^2 + 0.309C + 1.131$ (0.9867)	$-0.002C^4 + 0.033C^3 - 0.154C^2 + 0.321C + 1.071$ (0.9901)	$-0.001C^4 + 0.02C^3 - 0.113C^2 + 0.277C + 1.076$ (0.9755)	$-0.002C^4 + 0.018C^3 - 0.086C^2 + 0.225C + 1.061$ (0.9845)

Table 6. Thermodynamic activation parameters (ΔG^*, ΔH^*, and ΔS^*) for DO-EMBHBC, THF-EMBHBC and CF-EMBHBC solutions.

System	ΔG^*, J mol^{-1}					ΔH^* kJ mol^{-1}	ΔS^* J K^{-1} mol^{-1}
	Conc. (Wt %)	298 K	303 K	308 K	313 K		
DO - EMBHBC	0.25	4233.7	4210.8	4170.4	4138.0	6.19	-6.54
	0.50	4286.6	4288.0	4238.8	4165.5	6.74	-8.15
	0.75	4356.5	4349.1	4279.8	4211.1	7.36	-10.03
	1.00	4440.7	4407.6	4303.5	4269.1	8.14	-12.37
	2.00	4501.5	4457.2	4362.5	4285.3	8.93	-14.82

	3.00	4566.3	4491.3	4402.6	4343.3	9.09	-15.17
	4.00	4618.1	4535.5	4465.5	4384.7	9.21	-15.41
	5.00	4631.2	4558.4	4532.6	4387.2	9.13	-15.06
THF - EMBHBC	0.25	2719.3	2598.5	2662.1	2775.0	1.37	4.31
	0.50	2862.0	2706.0	2759.7	2825.2	3.22	-1.42
	0.75	2912.6	2785.5	2850.3	2868.9	3.32	-1.52
	1.00	2897.9	2852.4	2858.0	2884.3	3.12	-0.80
	2.00	2948.6	2906.8	2877.5	2870.6	4.52	-5.31
	3.00	3046.4	2970.3	2944.1	2976.3	4.47	-4.87
	4.00	3065.6	3100.1	3040.6	3155.7	1.29	5.95
	5.00	3143.9	3122.4	3084.6	3218.1	4.91	-5.91
CF - EMBHBC	0.25	3226.2	3161.5	3164.6	3174.9	4.13	-3.12
	0.50	3231.4	3169.4	3172.8	3140.7	4.83	-5.41
	0.75	3264.8	3143.7	3205.6	3260.8	2.98	0.77
	1.00	3282.6	3184.3	3216.8	3282.2	3.12	0.41
	2.00	3367.4	3273.7	3325.0	3373.6	2.97	1.21
	3.00	3424.2	3392.3	3455.2	3496.7	1.76	5.51
	4.00	3569.5	3513.2	3589.8	3607.4	2.44	3.71
	5.00	3645.4	3596.3	3672.9	3748.6	1.78	6.22