

Thermodynamic Studies of Aqueous and CCl₄ Solutions of 15-Crown-5 at 298.15 K: An Application of McMillan–Mayer and Kirkwood–Buff Theories of Solutions

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The density and osmotic coefficient data for solutions of 15-crown-5 (15C5) in water and in CCl₄ solvent systems at 298.15 K have been reported using techniques of densitometry and vapor pressure osmometry in the concentration range of 0.01–2 mol kg⁻¹. The data are used to obtain apparent molar and partial molar volumes, activity coefficients of the components as a function of 15C5 concentration. Using the literature heat of dilution data for aqueous system, it has become possible to calculate entropy of mixing (ΔS_{mix}), excess entropy of solution (ΔS^E), and partial molar entropies of the components at different concentrations. The results of all these are compared to those obtained for aqueous 18-crown-6 solutions reported earlier. It has been observed that the partial molar volume of 15C5 goes through a minimum and that of water goes through a maximum at ~ 1.2 mol kg⁻¹ in aqueous solutions whereas the opposite is true in CCl₄ medium but at ~ 0.5 mol kg⁻¹. The osmotic and activity coefficients of 15C5 and excess free energy change for solution exhibit distinct differences in the two solvent systems studied. These results have been explained in terms of hydrophobic hydration and interactions in aqueous solution while weak solvophobic association of 15C5 molecules in CCl₄ solutions is proposed. The data are further subjected to analysis by applying McMillan–Mayer and Kirkwood–Buff theories of solutions. The analysis shows that osmotic second virial coefficient value for 15C5 is marginally less than that of 18C6 indicating that reduction in ring flexibility does not affect the energetics of the interactions much in aqueous solution while the same gets influenced much in nonpolar solvent CCl₄.

1. Introduction

Extensive research has been conducted on the ability of crown ethers (cyclic ethers) to form complexes with uni- and bivalent metal ions.^{1–6} The small values of entropy changes for complexation with the crown ethers have been attributed to relative contributions of cation and ligand dehydration and ligand conformation changes.^{2,3} However, it is not clear why such rings of the ligands are relatively rigid and do not lend themselves to significant conformational changes, and the significance of the role of solvent molecules is also not clear. Franks and Eagland⁷ have stressed that for many biochemical processes one of the initial steps is the binding of a small molecule or ion to a macromolecule. It is likely that native conformations can be described in terms of water binding and various other equilibria. Thus for aqueous solutions of polyethers, solute–solvent interactions are important.

The thermodynamic properties of aqueous solutions of small nonelectrolyte molecules are well documented.⁸ Attempts are being made to explain nonidealities produced in such mixtures of water structural changes and solute–solute interaction (hydrophobic effect); i.e., a transfer of a solute from an apolar to an aqueous environment, although energetically favored, $\Delta H < 0$, is nevertheless accompanied by an unfavorable entropy change increasing the solute–solute contact spontaneously.⁹ Using the Kirkwood–Buff theory of solutions, we have shown that increase of solute–solute interactions results in extrema in properties like excess free energy and excess entropy for aqueous solutions of alcohols.^{10,11} Our recent work¹² on variation of

activity coefficients in aqueous 18-crown-6 (18C6) solutions and CCl₄ solutions enabled us to draw the conclusion that in aqueous solutions the crown molecules dissolve with hydrophobic hydration as well as hydrophobic interaction. The presence of four water molecules was postulated to have 18C6 in *D*_{3d} cyclic form on the basis of hydration number obtained. The result of excess free energy change for CCl₄ solutions having differences to aqueous solutions have been explained in terms of conformational characteristics in the two solvent systems.

In a recent work we analyzed the excess thermodynamic properties of aqueous solutions of 18C6 with emphasis on the phenomenon of enthalpy–entropy compensation—a ubiquitous property of solvent.¹³ We observe a compensation temperature of 291 K (the data are at 298.15 K), and the ratio $\Delta H^E/\Delta S^E$ is not constant but decreases with an increase in 18C6 concentration if the experimental temperature is used. The result supports the hypothesis of the presence of clustered (H-bonded) and nonbonded (monomer) species in an aqueous–solvent system.¹⁴ Similar studies made for α -cyclodextrin (α -CD) in aqueous solutions revealed similar compensation effects and it is suggested that α -CD molecules may be present in a helix-type configuration and their hydration determined by thermal and structural changes occurring with respect to the solute as well as to the H-bonding interaction with solvent molecules.¹⁵

The molecular dynamics simulations as well as Monte Carlo simulation studies on aqueous solutions of alcohols and methane are fully consistent with all the experimental results on dilute solutions.^{16,17} They are particularly valuable because they provide an approximate shape of $W_{22}(r)$, solute potential energy

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function, which provides help to theoreticians engaged in calculations of macromolecule conformational stability. The molecular dynamic studies of Kowall and Geiger¹⁸ show that the hydrophobic hydration of 18C6 plays an important role in governing the conformational dynamics of 18C6 in aqueous solutions, while the ab initio studies¹⁹ indicate that the cooperative electrostatic interactions govern the hydration pattern of 18C6 in aqueous solutions. Similar studies made by Raghino et al.²⁰ and Straatsma and McCammon²¹ for 18C6 lead to the conclusion that dissolution of the crystal should lead to conformational changes. In a MC study of 18C6 in water as well as in CCl₄, the exploration of the conformation space was promoted by an umbrella sampling procedure.²² It has been shown that there are two CCl₄ molecules in the first solvation shell of CCl₄ molecules while the interaction between 18C6 and CCl₄ is weaker than that between 18C6 and water. Such simulation studies are limited for 15C5 molecules although its complexation with Li⁺, Mg²⁺ ions is known.²³ From IR studies²⁴ on aqueous solutions of 15C5 and 18C6, it has been postulated that the C–C bond of the chain assumes gauche conformation and the favorable dielectric constant around this stabilizes the particular conformation. However, the resulting hydration pattern in aqueous 15C5 is different from that of 18C6 indicating the importance of bridged (H-bonded) water molecules in the crown cavity. The hydration of 15C5 differs from that of 18C6 most probably as a result of the different conformational structure it assumes in aqueous solution. The studies made on solute proton and deuterium solvent relaxation rates²⁵ of 15C5 and 18C6 and D₂O also show important differences in hydration behavior which are also supported by neutron diffraction data.²⁶ It has been suggested that in aqueous 18C6 solutions large internal motion takes place in –CH₂ chains. The lengthening of reorientation times is considered to be a consequence of the increase of structure in aqueous medium. The hydration shell as well as the bridged water molecules is important in governing the structural entities in crown solutions. These effects appeared to be stronger in 18C6 than in 15C5. Therefore, considering the inadequate knowledge of the hydration shell of the 15C5 molecule, we undertook the measurements of osmotic coefficient and volume properties of aqueous solutions. The experimental results and the analysis are presented in the following pages.

2. Experimental Section

15-Crown-5 (98% pure) procured from Merck-Schuchardt, Germany, was used without further purification, and contact with atmospheric moisture was avoided by handling 15C5 in a drybox. The salt NaCl of AR grade (BDH) was dried under vacuum at 393 K for 24 h before use. All the solutions, either in water (quartz doubly distilled) or in CCl₄ (HPLC grade Merck), were prepared on a molality basis and converted to molarity scale using the density data at 298.15 K. A Mettler Toledo AB204-S balance, having a readability of 0.1 mg, was used to determine weight. The uncertainty in composition of solutions is of the order of $\pm 5 \times 10^{-5}$ mol kg⁻¹. The density measurements of aqueous and CCl₄ solutions of 15C5 were made using Anton Paar digital densitometer (model DMA 60/602) at 298.15 \pm 0.02 K. After the humidity and lab pressure corrections were applied, the uncertainty in the density measurements was found to be $\pm 5 \times 10^{-3}$ kg m⁻³. The osmotic coefficients (ϕ) of aqueous and CCl₄ solutions of 15C5 were determined using a KNAUER K-7000 vapor pressure osmometer at 298.15 \pm 0.001 K. The details about the calibration of

TABLE 1: Volumetric Data of Aqueous and CCl₄ Solutions of 15-crown-5 at 298.15 K

<i>m</i> /mol kg ⁻¹	<i>d</i> /kg m ⁻³	10 ⁻³ ϕ_v / mm ³ mol ⁻¹	10 ⁻³ \bar{V}_2 / mm ³ mol ⁻¹	10 ⁻³ \bar{V}_1 / mm ³ mol ⁻¹
15-crown-5 + H ₂ O				
0.00000	997.047	186.2 ^a	186.2 ^a	18.069 ^a
0.07737	999.695	186.0	185.9	18.069
0.32180	1007.658	185.8	185.2	18.072
0.49448	1013.035	185.4	184.7	18.076
0.66268	1018.034	185.2	184.3	18.080
0.87044	1023.973	184.8	183.8	18.084
1.05921	1028.784	184.9	183.9	18.088
1.32543	1035.477	184.6	183.8	18.090
1.52140	1039.972	184.6	183.9	18.088
1.72184	1044.527	184.4	184.0	18.082
2.03541	1050.950	184.3	184.5	18.063
15-crown-5 + CCl ₄				
0.00000	1584.382	195.5 ^a	195.7 ^a	97.085 ^a
0.03060	1580.081	195.5	196.0	97.083
0.06603	1574.972	197.0	197.8	97.077
0.15207	1563.091	197.5	199.1	97.047
0.33134	1539.709	198.3	200.7	96.967
0.44106	1525.318	199.8	201.9	96.944
0.65860	1500.236	200.6	200.6	97.078
0.66614	1500.126	200.1	200.0	97.088
0.80143	1487.494	199.4	197.1	97.372
0.91232	1475.642	200.3	195.5	97.756
1.05424	1466.720	198.2	189.5	98.492

^a Extrapolated values to infinite dilution (zero concentration).

vapor pressure osmometer for aqueous and CCl₄ media were described earlier.^{12,27} The accuracy in ϕ measurements was found to be better than $\pm 1 \times 10^{-3}$ at the lowest concentration studied.

3. Results

(i) Density and Osmotic Coefficient Data. The densities for aqueous and CCl₄ solutions of 15C5 were measured at 298.15 K from which the apparent molar volume (ϕ_v) of 15C5, the partial molar volumes of 15C5 (\bar{V}_2), and the partial molar volume of solvent (\bar{V}_1) in aqueous and CCl₄ solutions at 298.15 K were calculated using the usual equations.^{28,29} The density, ϕ_v , \bar{V}_2 , and \bar{V}_1 data are collected in Table 1 for aqueous and CCl₄ solutions of 15C5 at 298.15 K. The variation of partial molar volumes of solute and solvent as a function of solute concentration are shown in Figures 1 and 2 for 15C5–H₂O and 15C5–CCl₄ systems at 298.15 K, respectively.

Experimental osmotic coefficients (ϕ) of aqueous 15C5 solutions were determined over the concentration range 0.1–2.0 mol kg⁻¹. The data are well represented by the equation

$$\phi = 1 + 0.06310m + 0.00072m^2 \quad (1)$$

where m is molality of 15C5 in mol kg⁻¹. The osmotic coefficients of 15C5–CCl₄ solutions were determined over the concentration range 0.03–0.66 mol kg⁻¹ at 298.15 K, and the data are represented by the expression

$$\phi = 1 - 0.3164m + 0.0272m^2 \quad (2)$$

The osmotic and activity coefficient data of 15C5 in aqueous and CCl₄ solutions are collected in Table 2 at 298.15 K. The variation of osmotic coefficients of 15C5 in aqueous and CCl₄ solutions as a function of molality of 15C5 at 298.15 K is shown in Figure 3. It is observed that the osmotic coefficient of 15C5 increases in aqueous medium while that in CCl₄ medium decreases as the 15C5 concentration is increased. The solvent

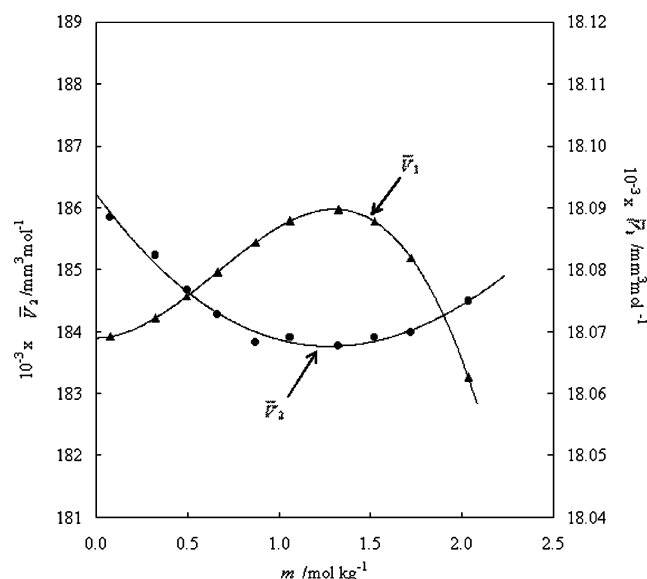


Figure 1. Variation of partial molar volume of water and 15C5 in aqueous solutions of 15C5 at 298.15 K.

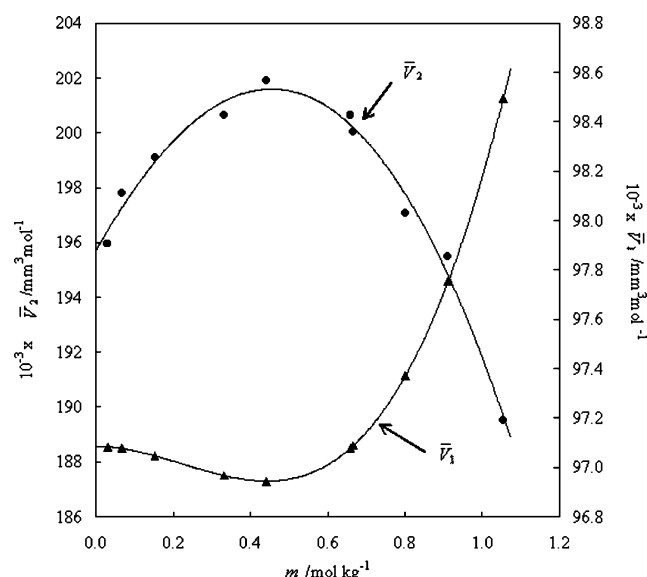


Figure 2. Variation of partial molar volume of CCl₄ and 15C5 in CCl₄ solutions of 15C5 at 298.15 K.

activity (a_1) and activity coefficients (γ_1) were calculated from experimental osmotic coefficient data using the expression

$$\phi = -\frac{\ln a_1}{(x_2/x_1)} \quad (3)$$

where x_1 and x_2 are the mole fractions of solvent and solute, respectively. The hydration numbers (h) of 15C5 in aqueous solutions were estimated using the water activity and following the Robinson and Stokes method as³⁰

$$a_w = \frac{1 - 0.018hm}{1 - 0.018(h-1)m} \quad (4)$$

where a_w is the water activity. The values of hydration number (h) of 15C5 in aqueous solutions were also included in the

TABLE 2: Osmotic and Activity Coefficient Data For Aqueous and CCl₄ Solutions of 15C5 at 298.15 K

$m/\text{mol kg}^{-1}$	ϕ	a_w	γ_1	γ_2	$\Delta G^E/\text{J mol}^{-1}$	h
15-crown-5 + H ₂ O						
0.14289	1.0090	0.99741	0.99997	1.0182	0.07	4.3
0.30978	1.0196	0.99433	0.99988	1.0400	0.31	4.1
0.46334	1.0294	0.99144	0.99972	1.0605	0.69	4.0
0.66587	1.0423	0.98757	0.99942	1.0882	1.41	4.0
0.87878	1.0560	0.98342	0.99899	1.1182	2.46	3.9
1.05141	1.0671	0.97999	0.99855	1.1433	3.51	3.9
1.49706	1.0961	0.97087	0.99706	1.2109	7.07	3.8
1.58464	1.1018	0.96904	0.99670	1.2247	7.91	3.8
2.03374	1.1313	0.95940	0.99455	1.2984	12.96	3.7
15-crown-5 + CCl ₄						
0.03060	0.9875	0.99536	1.00005	0.9793	−0.07	
0.06603	0.9771	0.99013	1.00018	0.9564	−0.41	
0.15207	0.9518	0.97798	1.00086	0.9049	−2.27	
0.33134	0.8990	0.95521	1.00390	0.8117	−9.93	
0.44106	0.8668	0.94289	1.00686	0.7611	−16.78	
0.65860	0.8028	0.92189	1.01529	0.6685	−35.68	

Table 2, and its variation as a function of solute concentration is shown in Figure 4. The use of the Robinson and Stokes equation for obtaining hydration number was justified earlier by comparing the use of activity and NIR spectral data in its determination¹² which is in also agreement with FTIR²⁴ and simulation results.^{18–22} The activity coefficients of 15C5 (γ_2) in aqueous and CCl₄ solutions were calculated using the equation

$$\ln \gamma_2 = (\phi - 1) + \int_0^m (\phi - 1) d \ln m \quad (5)$$

The data of solute activity coefficient γ_2 for aqueous and CCl₄ solutions at 298.15 K are collected in Table 2, while their variation as a function of solute concentration is shown in Figure 5. The activity data which have been converted into the mole fraction scale were used to calculate Gibbs free energy change on mixing 15C5 with water and with CCl₄, i.e., ΔG_{mix} . Further, the activity coefficient data on a mole fraction scale were used to calculate the excess Gibbs free energy change (ΔG^E). It is found that ΔG_{mix} is negative in both the solvents and becomes more negative as a function of 15C5 concentration. The values of ΔG^E are positive in aqueous medium, and they increase as the concentration of 15C5 is increased while reverse is true in CCl₄ medium as shown in Figure 6. The solute activity coefficient γ_2 as well as excess free energy change for the solutions (Figures 5 and 6) vary with 15C5 concentration in different directions in the two studied solvent systems. In water, γ_2 and ΔG^E increase, while they decrease in CCl₄ solutions.

By use of our free energy data, and the excess enthalpy data reported in the literature³¹ in the form of enthalpy virial, the entropy of mixing (ΔS_{mix}), excess entropy of solution (ΔS^E), and the partial molar entropies of each constituent in binary aqueous 15C5 solutions at 298.15 K (0.01–0.1 mol kg^{−1}) were calculated. No such calculations were made in CCl₄ solutions since the heat data are not available in CCl₄ medium for 15C5 as a solute. The virial expansion of excess enthalpy (H^E) of 15C5 in aqueous solutions is given by the equation³¹

$$H^E = \phi_L = h_2m + h_3m^2 + h_4m^3 + \dots \quad (6)$$

where ϕ_L is apparent molar relative enthalpy of solution. Using the values of coefficients h_2 , h_3 , h_4 , etc., the ϕ_L values were

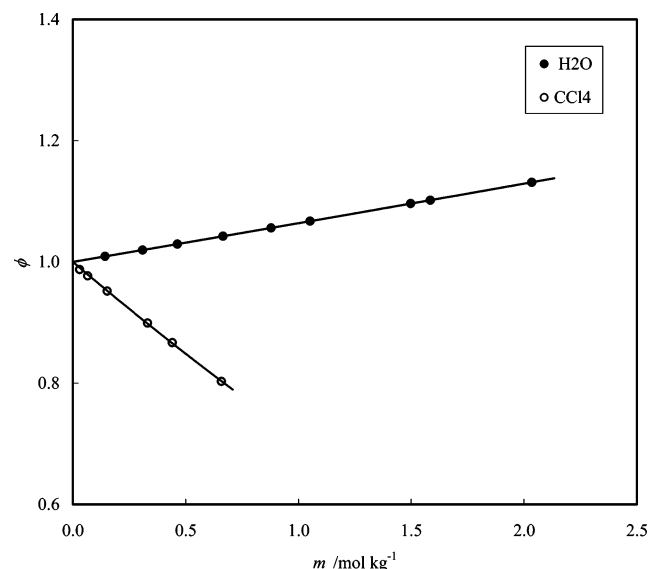


Figure 3. Osmotic coefficients of 15C5 in aqueous and CCl₄ solutions plotted as a function of 15C5 concentration at 298.15 K.

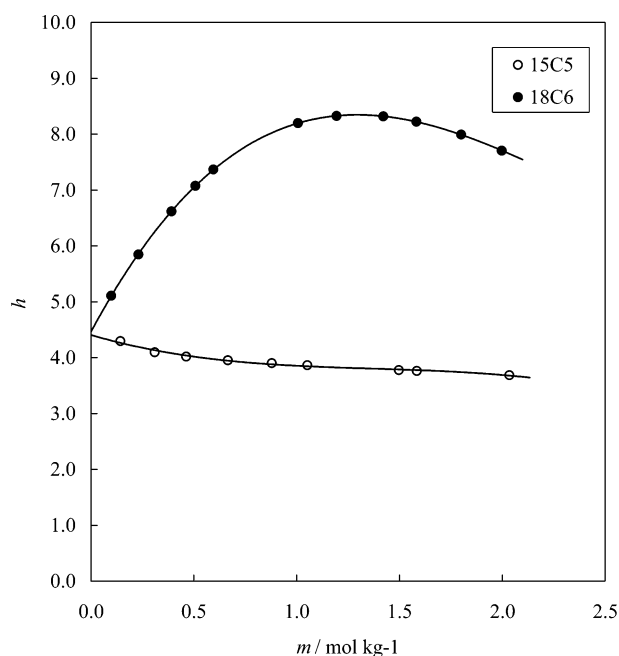


Figure 4. Variation of hydration number of 15C5 and 18C6 as a function of solute concentration in aqueous solutions at 298.15 K. The data for 18C6 are taken from ref 12.

calculated. The partial molar heat content of solvent (\bar{L}_1) and solute (\bar{L}_2) were determined using the equations³²

$$\bar{L}_1 = -\frac{n_2^2}{n_1} \left(\frac{\partial \phi_L}{\partial n_2} \right)_{T,P,n_1} \quad (7)$$

$$\bar{L}_2 = \phi_L + n_2 \left(\frac{\partial \phi_L}{\partial n_2} \right)_{T,P,n_1} \quad (8)$$

where n_1 and n_2 are the number of moles of solvent and solute, respectively. The data of \bar{L}_2 were plotted against n_1/n_2 which on extrapolation to zero value yields the relative partial molar heat content of pure solute (L_2), which is equal to 39.71 kJ mol⁻¹

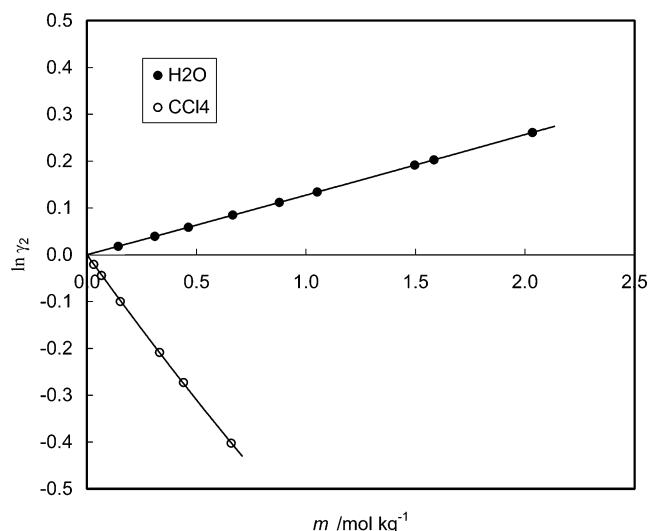


Figure 5. Variation of activity coefficient of 15C5 in aqueous and CCl₄ solutions as a function of molality of 15C5 at 298.15 K.

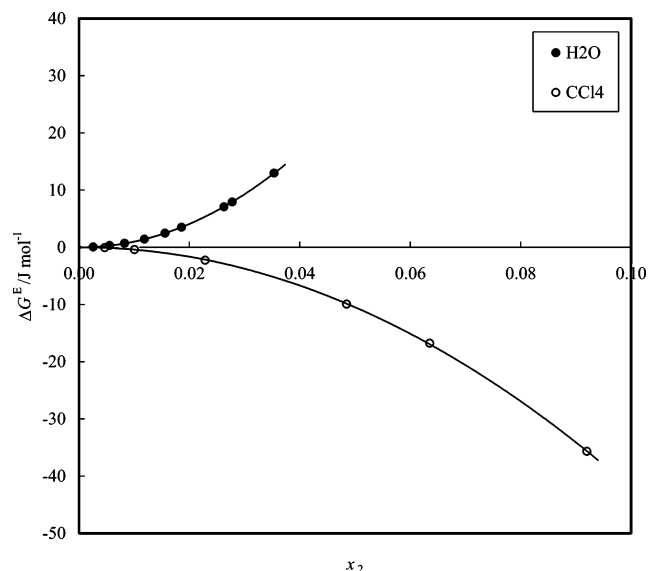


Figure 6. Plot of excess free energy of solution for aqueous and CCl₄ solutions of 15C5 at 298.15 K.

as reported earlier by Briggner and Wadsö.³³ The heat change due to mixing (ΔH_{mix}) is calculated for various 15C5 concentrations using the equation

$$\Delta H_{\text{mix}} = L - n_2 L_2 \quad (9)$$

where $L = n_1 \bar{L}_1 + n_2 \bar{L}_2$. By use of the data of ΔH_{mix} and ΔG_{mix} , the data for entropy of mixing (ΔS_{mix}) have been estimated. Similarly, the excess entropies of solutions (ΔS^E) were calculated from ΔG^E values. All these data are collected in Table 3. The variations of ΔH_{mix} , ΔG_{mix} , and $T\Delta S_{\text{mix}}$ values with mole fractions of 15C5 are shown in Figure 7.

Since the partial molar enthalpies of solvent water and 15C5 now become available, the calculations of partial molar entropies of solvent ($\bar{S}_1 - S_1^0$) and solute ($\bar{S}_2 - S_2^0$) have been made using the relations

$$(\bar{S}_1 - S_1^0) = \frac{\bar{L}_1}{T} - R \ln a_1 \quad (10)$$

$$(\bar{S}_2 - S_2^0) = \frac{(\bar{L}_2 - L_2)}{T} - R \ln a_2 \quad (11)$$

TABLE 3: Thermodynamic Data for Aqueous 15C5 Solutions at 298.15 K

$m/\text{mol kg}^{-1}$	$\phi_L/\text{J mol}^{-1}$	$\bar{L}_1/\text{J mol}^{-1}$	$\bar{L}_2/\text{J mol}^{-1}$	$L/\text{J mol}^{-1}$	$\Delta H_{\text{mix}}/\text{J mol}^{-1}$	$\Delta G^E/\text{J mol}^{-1}$	$\Delta G_{\text{mix}}/\text{J mol}^{-1}$	$T\Delta S_{\text{mix}}/\text{J mol}^{-1}$	$T\Delta S^E/\text{J mol}^{-1}$	$(S_1 - S_1^0)^E/\text{J mol}^{-1} \text{K}^{-1}$	$(S_2 - S_2^0)^E/\text{J mol}^{-1} \text{K}^{-1}$
0.14289	571	-1.4	1129	82	-100.5	0.066	-44.3	-56.2	-100.55	-0.005	-129.6
0.30978	1207	-6.4	2359	374	-213.7	0.308	-84.9	-128.8	-213.99	-0.021	-125.6
0.46334	1768	-13.9	3433	819	-314.1	0.687	-118.1	-196.0	-314.77	-0.044	-122.2
0.66587	2484	-27.8	4805	1654	-441.3	1.415	-158.1	-283.1	-442.67	-0.089	-117.9
0.87878	3220	-47.9	6247	2830	-568.7	2.457	-196.6	-372.0	-571.13	-0.152	-113.3

TABLE 4: Osmotic Virial Coefficients and the Limiting Kirkwood–Buff Integrals for 15C5 in Aqueous and CCl₄ Solutions at 298.15 K

	$10^{-3}NB_2^*/\text{mm}^3 \text{mol}^{-1}$	$10^{-6}NB_3^*/\text{mm}^6 \text{mol}^{-2}$	$-10^{-3}A_{2\text{min}}/\text{mm}^3 \text{mol}^{-1}$	$10^{-3}R_{2\text{min}}/\text{mm}^3 \text{mol}^{-1}$	$-10^{-6}A_{3\text{min}}/\text{mm}^6 \text{mol}^{-2}$	$10^{-6}R_{3\text{min}}/\text{mm}^6 \text{mol}^{-2}$	$10^{-3}G_{AA}^0/\text{mm}^3 \text{mol}^{-1}$	$10^{-3}G_{AB}^0/\text{mm}^3 \text{mol}^{-1}$	$10^{-3}G_{BB}^0/\text{mm}^3 \text{mol}^{-1}$	$10^{-3}NB_2^{*b}/\text{mm}^3 \text{mol}^{-1}$
15C5 + H ₂ O	249	59199	495	745	287506	346704	-17.3	-185.53	-498.18	249.1
15C5 + CCl ₄	-25	36125	808	783	346860	382985	-97.14	-194.21	50.25	-25.12
18C6 + H ₂ O ^a	278	226998	615	893	271051	498048	-16.96	-222.1	-576	288
18C6 + CCl ₄ ^a	-201	16700	1611	1410	535644	552344	-94.43	-232.4	364	-182

^a Data are taken from ref 12 and 43. ^b Values obtained using Kirkwood–Buff theory.

where S_1^0 is molar entropy of pure liquid water and S_2^0 is molar entropy of solute in a hypothetical ideal solution of unit mole fraction. The excess partial molar entropies of solvent ($\bar{S}_1 - S_1^0$)^E and solute ($\bar{S}_2 - S_2^0$)^E were further evaluated using equations^{34–38}

$$(\bar{S}_1 - S_1^0)^E = \frac{\bar{L}_1}{T} - R \ln \gamma_1 \quad (12)$$

$$(\bar{S}_2 - S_2^0)^E = \frac{(\bar{L}_2 - L_2)}{T} - R \ln \gamma_2 \quad (13)$$

The values of the parameters ($\bar{S}_1 - S_1^0$)^E and ($\bar{S}_2 - S_2^0$)^E are also collected in Table 4 for the studied concentrations of 15C5 in water at 298.15 K.

(ii) Application of McMillan–Mayer and Kirkwood–Buff theories. According to McMillan–Mayer theory³⁹ for a solution of a solute in solvent, the osmotic pressure, π , is given by

$$\frac{\pi}{kT} = \rho + B_2^* \rho^2 + B_3^* \rho^3 + \dots \quad (14)$$

In this expression ρ is the number density and B_2^* and B_3^* are the osmotic second and third virial coefficients, respectively.

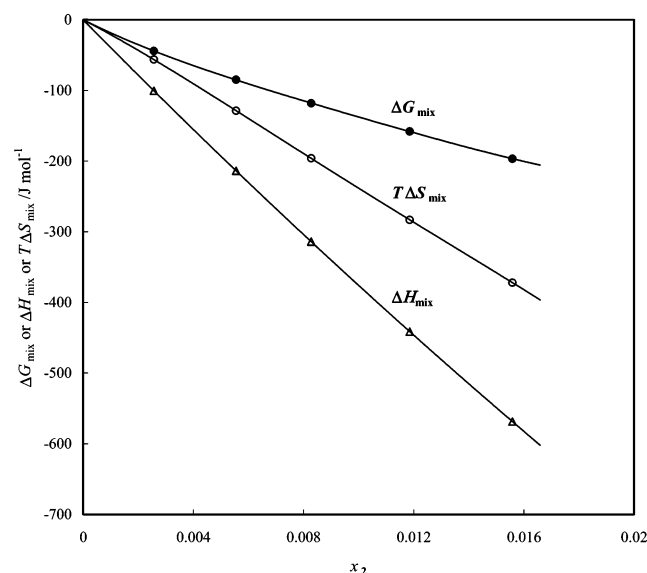


Figure 7. Plot of the thermodynamic parameters for mixing in aqueous 15C5 solutions as a function of mole fraction of 15C5 (x_2) at 298.15 K.

B_2^* and B_3^* can be calculated from experimental activity data and the partial molar volume of solute and solvent as⁴⁰

$$B_2^* = \frac{1}{N} \left[(\bar{V}_2^0 - V_1^0) + V_1^0 \left(\frac{1}{2} - B \right) \right] \quad (15)$$

$$B_3^* = \frac{1}{N^2} \left[(b/V_1^0) + g + (V_1^0 - \bar{V}_2^0) - V_1^0(1 - 2B)(V_1^0 - \bar{V}_2^0) + (V_1^0)^2 \left(\frac{1}{3} - C \right) \right] \quad (16)$$

where V_1^0 and \bar{V}_2^0 are the partial molar volumes of solvent and solute, respectively, at infinite dilution and are obtained by smooth extrapolation of partial molar volume data to infinite dilution (zero concentration of solute). B and C are the coefficients in the expression $\ln \gamma_1 = Bx_2^2 + Cx_2^3 + \dots$, while b and g in eq 16 are the coefficients in the following equations

$$\bar{V}_1 = V_1^0 + aC_2 + bC_2^2 \quad (17)$$

$$\bar{V}_2 = \bar{V}_2^0 + gC_2 + hC_2^2 \quad (18)$$

Here \bar{V}_1 and \bar{V}_2 are the partial molar volumes of solvent and solute, respectively, at concentration C_2 (molarity). The coefficients a , b , g , and h have been evaluated using the partial molar volume and molarity data of aqueous 15C5 solutions at 298.15 K.

Using the above eq 15 for B_2^* , the values of the pairwise interaction for many nonelectrolytes have been tabulated by Kozak et al.⁴⁰ They have also estimated the attractive and repulsive components for the osmotic second virial coefficients for many nonelectrolytes in water. For osmotic second virial coefficient, the minimum attractive ($A_{2\text{min}}$) and minimum repulsive contributions ($R_{2\text{min}}$) have been calculated using following equations

$$R_{2\text{min}} = f(4V_2^0) \quad (19)$$

$$A_{2\text{min}} = R_{2\text{min}} - NB_2^* \quad (20)$$

where f is the factor which is a measure of the ellipticity of the molecule and V_2^0 is the molar volume of pure solute. For 15C5, it is assumed that it exists as a spherical entity in aqueous medium, and hence f is unity.

The minimum attractive and minimum repulsive contributions to the osmotic third virial coefficient, i.e., $A_{3\text{min}}$ and $R_{3\text{min}}$,

respectively, have been calculated by using the following equations

$$R_{3\min} = 10(V_2^0)^2 \quad (21)$$

$$A_{3\min} = R_{3\min} - N^2 B_3^* \quad (22)$$

The data of osmotic second and third virial coefficients as well as their minimum attractive and repulsive contributions to solute–solute interactions in aqueous 15C5 solutions are collected in Table 4.

The precise and accurate activity coefficient data long with partial molar volume data of 15C5 in aqueous and CCl₄ solutions have been used to evaluate these Kirkwood–Buff (KB) integrals by means of using the following equations^{41–44}

$$G_{AB}(A \neq B) = G_{BA} = RT\kappa_T - \frac{\bar{V}_1 \bar{V}_2}{DV} \quad (23)$$

$$G_{ii} = G_{AB} + \frac{1}{x_i} \left(\frac{\bar{V}_j}{D} - V \right) \quad (24)$$

$i \neq j$

where

$$D = 1 + x_i \left(\frac{\partial \ln \gamma_i}{\partial x_i} \right)_{P,T} \quad (25)$$

In eqs 23–25, κ_T is the isothermal compressibility, \bar{V}_i is the partial molar volume of component i , x_i is the mole fraction of component i , V is the molar volume of the mixture, T is the absolute temperature, R is the gas constant, and γ_i is the activity coefficient of component i in the mole fraction scale. In eqs 23 and 24, subscript A is used for solvent (either water or CCl₄) and B for solute (15C5). The parameter D is estimated at each 15C5 concentration by plotting $\ln \gamma_i$ (activity coefficient of 15C5) as a function mole fraction of 15C5 and differentiating the resulting polynomial equation of third/fourth order with respect to mole fraction of 15C5 to get the required slopes. The same could have been accomplished by using the data of solvent activity coefficients and its mole fraction. It is known from the previous experience that the isothermal compressibility of solutions contribute negligibly to the G_{ij} values; hence in the application of eq 24 the κ_T values of solvents are being used.^{10,11} The KB integrals thus evaluated using eqs 23–25 are plotted in Figures 8 and 9 as a function of mole fraction (x_2) of 15C5 for aqueous and CCl₄ solutions, respectively, at 298.15 K. Checks of internal consistency and accuracy of calculations have been made by comparing the extrapolated values of G_{ij} functions in Figures 12 and 13 with the limiting values of the G_{ij} functions for $x_2 \rightarrow 0$ calculated using eqs 26–28

$$G_{AA}^0 = \lim_{x_2 \rightarrow 0} G_{AA} = RT\kappa_{T,A} - V_1^0 \quad (26)$$

$$G_{AB}^0 = \lim_{x_2 \rightarrow 0} G_{AB} = RT\kappa_{T,A} - \bar{V}_2^0 \quad (27)$$

$$G_{BB}^0 = \lim_{x_2 \rightarrow 0} G_{BB} = RT\kappa_{T,A} + V_1^0 - 2\bar{V}_2^0 - V_1^0 \left(\frac{\partial \ln \gamma_2}{\partial x_2} \right)_{T,P,x_2} \quad (28)$$

where V_1^0 is molar volume of pure solvent A (i.e., water or CCl₄), \bar{V}_2^0 is limiting partial molar volume of B, i.e., of 15C5,

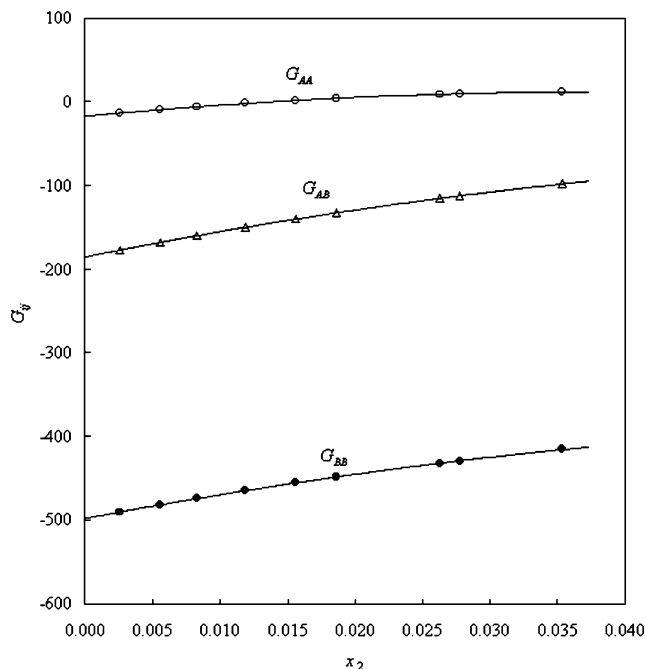


Figure 8. Plot of Kirkwood–Buff integrals as a function of mole fraction of 15C5 (x_2) for aqueous 18C6 solutions at 298.15 K.

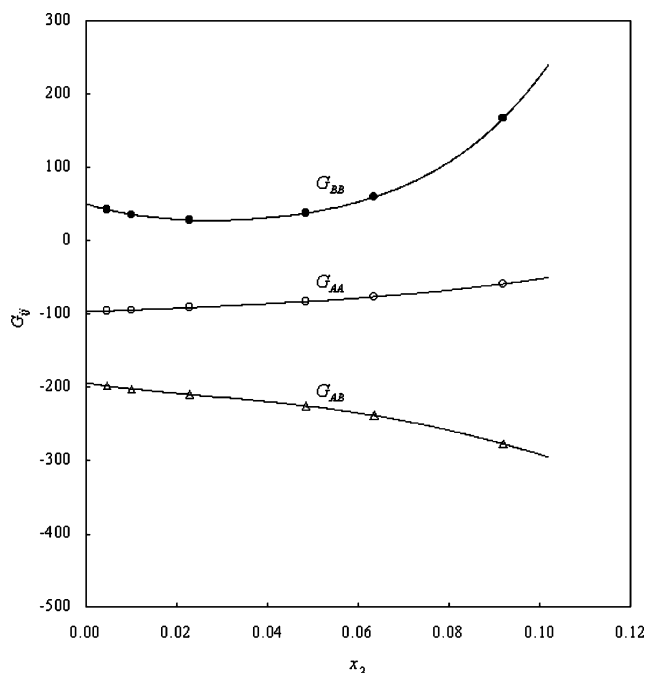


Figure 9. Plot of Kirkwood–Buff integrals as a function of mole fraction of 15C5 (x_2) for solutions of 15C5 in CCl₄ at 298.15 K.

and γ_2 is the activity coefficient of 15C5. G_{BB}^0 is related to the osmotic second virial coefficients B_2^* of 15C5 through eq 29

$$G_{BB}^0 = -2NB_2^* \quad (29)$$

where N is Avogadro's constant.^{41–43} The limiting values thus calculated are given in Table 4 along with the data obtained from the application of the McMillan–Mayer theory at 298.15 K.

4. Discussion

(i) Thermodynamic Analysis. The partial molar volume of 15C5 (\bar{V}_2) goes through a minimum in the range of 1–1.5 mol

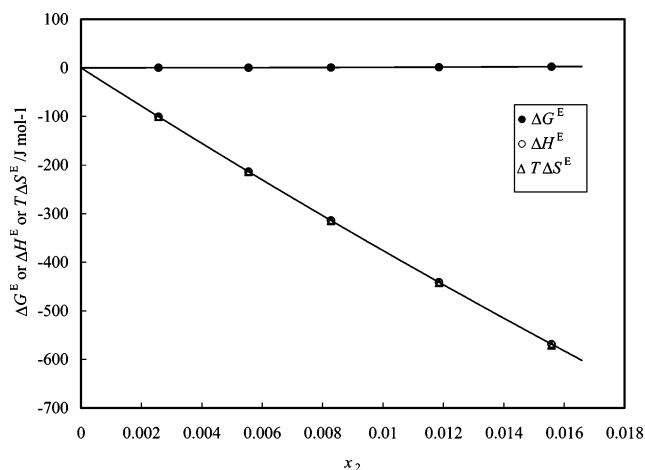


Figure 10. Plot of the excess thermodynamic properties in aqueous 15C5 solutions as a function of mole fraction of 15C5 (x_2) at 298.15 K.

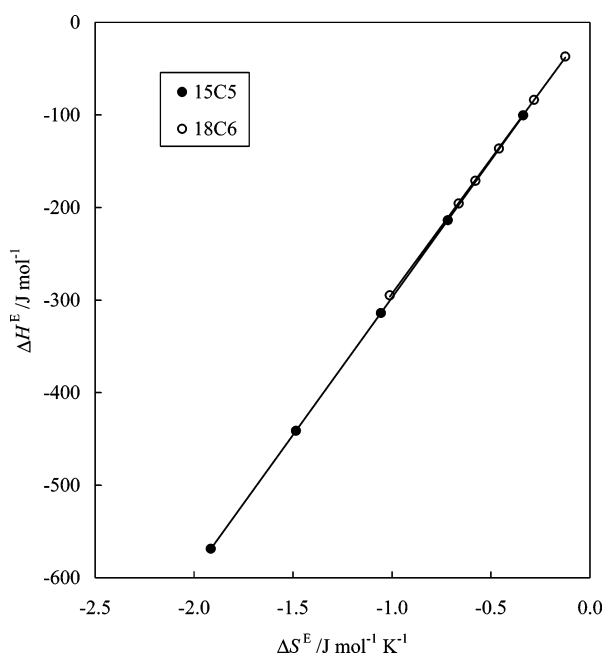


Figure 11. Correlation of excess enthalpy (ΔH^E) and excess entropy (ΔS^E) for aqueous solutions of 15C5 and 18C6 at 298.15 K. The data for 18C6 are taken from ref 13.

kg^{-1} in aqueous medium while it goes through a maximum at about 0.5 mol kg^{-1} in CCl_4 medium (Figures 1 and 2). The partial molar volume of water (\bar{V}_1) goes through a flat maximum in aqueous medium whereas in CCl_4 it goes through a weak minimum. Such a behavior in aqueous solutions is in conformity with literature findings on solutions of nonelectrolytes in water.⁴⁵ We attribute these observations in terms of increased solute–solute association because of overlap of cospheres of the solute meaning that 15C5 dissolves in water with hydrophobic hydration and interaction. However, \bar{V}_2 and \bar{V}_1 behavior in CCl_4 may be viewed as the manifestation of weak solute–solute association without solvent-induced cosphere overlap effect. The infinite dilution values (\bar{V}_2^0) have been estimated as 186.2×10^3 and $195.7 \times 10^3 \text{ mm}^3 \text{ mol}^{-1}$ in aqueous and CCl_4 medium, respectively. The agreement is satisfactory with the literature⁴⁶ value of $186.4 \times 10^3 \text{ mm}^3 \text{ mol}^{-1}$ in aqueous solutions, but in CCl_4 medium our value is smaller than the value of $202.3 \times 10^3 \text{ mm}^3 \text{ mol}^{-1}$ reported in the literature.⁴⁷ The excess partial molar volumes, $\bar{V}_2^E = \bar{V}_2^0 - V_2^0$ (where V_2^0 is molar volume of pure liquid 15C5), are found to be -17.2×10^3 and $-7.7 \times$

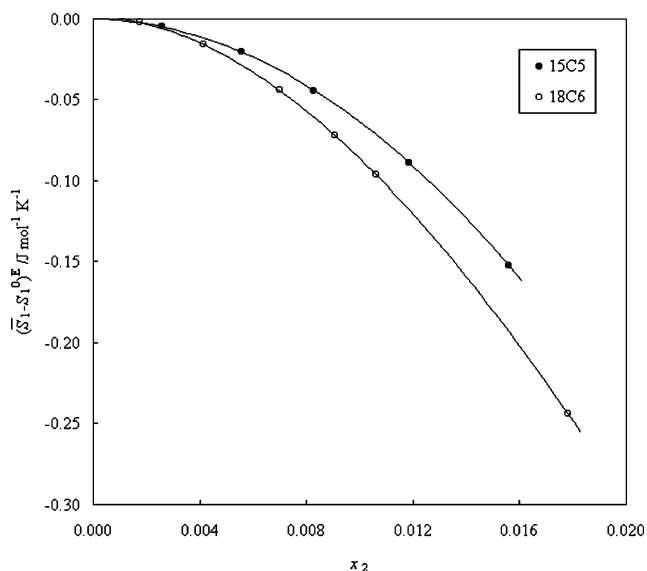


Figure 12. Variation of excess partial molar entropy of water as a function of mole fraction of solute (15C5/18C6) at 298.15 K. The data for 18C6 are taken from ref 13.

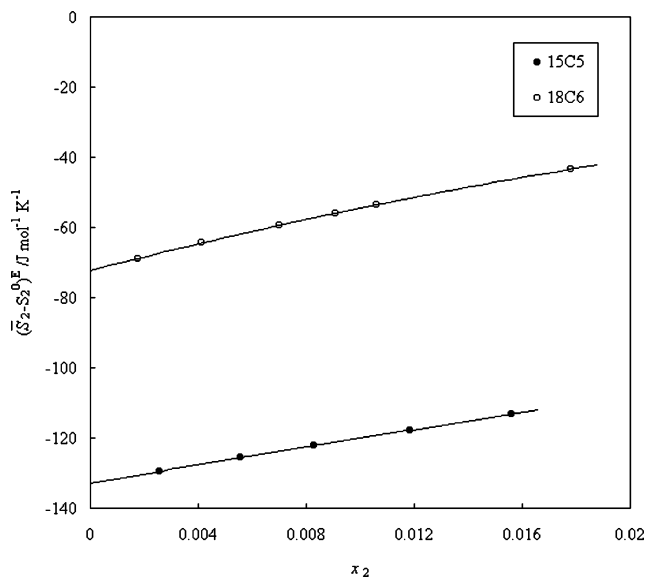


Figure 13. Variation of excess partial molar entropy of solute (15C5/18C6) as a function of mole fraction of solute (15C5/18C6) at 298.15 K. The data for 18C6 are taken from ref 13.

$10^3 \text{ mm}^3 \text{ mol}^{-1}$, respectively. Thus, 15C5 dissolves with a comparatively large volume loss in water than in CCl_4 indicating that the solute–solvent interactions are comparatively predominant in aqueous solutions because of the unique structural properties of water.

The variation of ϕ shows subtle differentiation between the modes of dissolution in two solvent media as ϕ increases and decreases respectively with increase in concentration of 15C5 in water and CCl_4 (Figure 3). Similar behavior was also observed for aqueous and CCl_4 solutions of 18C6 at 298.15 K.¹² These observations indicate further that there is positive deviation from Raoult's law in aqueous solutions, whereas the solutions in CCl_4 exhibit negative deviations from Raoult's law. With the solvent activity data obtained from ϕ data when utilized to obtain hydration number (eq 4), a value of 4.4 is obtained at infinite dilution which is the same as observed for 18C6 in aqueous solutions¹² meaning that at least four water molecules interact strongly with the crown ring. However, if the variations of hydration number (Figure 4) with concentrations of 15C5 and

18C6 are compared, important differences emerge. We observe that h increases initially in 18C6 solutions and goes through a flat maximum at higher concentrations, while for 15C5 it marginally decreases with increase in 15C5 concentration. The hydration for 18C6 is accounted in terms of two bridged water molecules for the oxygen in the ring while the other two interact by singly H-bonding with remaining two oxygens in the ring but in different planes. Similar interpretation cannot be advanced in the case of 15C5 because of its smaller ring size and comparatively more rigidity. The four water molecules can interact with four oxygens of the ring by single H-bond formation. Such an interpretation has also been advanced by Nickolov et al. to explain their infrared studies of 15C5–aqueous solutions.²⁴

We observed that all the thermodynamic mixing parameters are negative and the mixing process is enthalpy dominated. On comparison with aqueous 18C6 solutions,¹³ it is observed that the process of mixing is more entropy dominated in 15C5 solutions whereas the contribution of free energy is more in the case of 18C6 solutions although the overall mixing is enthalpy dominated in both cases. The enthalpy–entropy compensation phenomenon is also observed for 15C5 aqueous solutions (Figure 10). The excess free energy change is slightly positive while excess enthalpy and excess entropy nearly compensate yielding a compensation temperature (T_c) of 297 K as shown in Figure 11. This compensation temperature is much more than that for 18C6 ($T_c = 291$ K) but certainly less than the experimental temperature of 298.15 K. Thus the flexibility of the molecule certainly plays an important role in characterization of thermodynamic properties of the solvent system (Figure 12). This is best reflected in partial molar entropy values at infinite dilution obtained for 15C5 and 18C6 in water (Figure 13). We observed that the flexible 18C6 has a higher entropy value than 15C5. The partial molar entropy values increase with increase in solute concentration, as shown in Figure 13, indicating the presence of hydrophobic interactions in the studied concentration region. The decrease in $(\bar{S}_1 - S_1^0)^E$, i.e., excess partial molar entropy of solvent, as a function of 18C6 concentration has been attributed to complexing of water molecules in the 18C6 cavity. The large entropy loss for solute can arise from reduction of rotational and vibrational degrees of freedom of solute and/or an increased ordering of the solvent molecules. The negative value of $(\bar{S}_2 - S_2^0)^E$ at infinite dilution results from the 18C6–water interaction and facilitating the conversion of chaotic distribution of 18C6 conformers having C_i or C_s symmetry into a more orderly D_{3d} conformation having a cavity which also incorporates water molecules through H-bonds. However, the large negative value of $(\bar{S}_2 - S_2^0)^E$ at infinite dilution for 15C5 is in accordance with the more rigidity of the ring structure over the flexible 18C6 molecule.

(ii) McMillan–Mayer and Kirkwood–Buff Theories. We found from Table 4 that both theories yield the same values for B_2^* , however, the values are positive and negative in water and CCl_4 , respectively, providing the evidence of the structural characteristics of solvent systems. The attractive contribution ($-A_{2\min}$) is much more in CCl_4 solutions but at the same time is nearly compensated due to repulsive interactions, etc. We do not wish to discuss the higher order virial coefficients as they may be involving large errors.

The concentration dependence of G_{AA} , water–water affinity, exhibits positive slope in the studied concentration range indicating the enhancement of water structure as a function of 15C5 concentration. We note that G_{AB} and G_{BB} both increase with concentration in water meaning that both hydrophobic

interactions and hydrophobic hydration exist, giving credence to our earlier⁴³ explanations. However, in the case of aqueous solutions of 18C6 the minimum is observed for G_{BB} integral as a function of x_2 indicating that the solute–solute affinity decreases up to $\sim 0.01x_2$ where hydrophobic hydration is predominant while it increases after $\sim 0.01x_2$ showing the existence of hydrophobic interaction in the studied higher concentration region.⁴³ Such a minimum is not found in the case of aqueous solutions of 15C5 indicating that the hydrophobic interactions become slightly dominating over the hydration effects as the concentration is increased in the studied concentration range in accordance with the hydration number variation with concentration (Figure 4). In the case of CCl_4 solutions solute–solute interaction goes through a weak minimum indicating a very weak solute–solute association process or it may indicate weakening of strength of association process as the solute concentration increases.

The mean square concentration fluctuations $N\langle(\Delta x)^2\rangle$ can be calculated knowing three KB integrals and using eq 30

$$N\langle(\Delta x)^2\rangle = x_1x_2[1 + \rho x_1x_2(G_{AA} + G_{BB} - 2G_{AB})] \quad (30)$$

where x_1 is the mole fraction of solvent, ρ is the average number density, and N is the total number of molecules within which the concentration fluctuations are considered. For an ideal solution ($G_{AA} = G_{BB} = G_{AB}$), $N\langle(\Delta x)^2\rangle$ is equal to x_1x_2 ($F = N\langle(\Delta x)^2\rangle/x_1x_2 = 1$). If the affinity between like species is stronger than that between unlike species, then the $N\langle(\Delta x)^2\rangle$ takes larger values than x_1x_2 ($F > 1$), and if the affinity between unlike species is stronger than that between like species, then the $N\langle(\Delta x)^2\rangle$ takes smaller values than x_1x_2 ($F < 1$). The quantity F can also be expressed in terms of thermodynamic properties as

$$\frac{1}{F} = \left(\frac{\partial \ln a_i}{\partial x_i}\right)_{T,P} = 1 + \left(\frac{\partial \ln \gamma_i}{\partial x_i}\right)_{T,P} = 1 + \frac{x_1x_2}{RT} \left(\frac{\partial^2 G^E}{\partial x_i^2}\right)_{T,P} \quad (31)$$

where a_i and γ_i are the activity and activity coefficients of species i and G^E is the excess free energy of solution.^{48,49} The concentration dependence of function F is shown in Figure 14 for aqueous and CCl_4 solutions of 15C5. All these are succinctly seen in the mean square concentration fluctuation parameter (Figure 15) as a function of mole fraction of 15C5. We observe much more microheterogeneity in CCl_4 solutions as compared to that of aqueous solutions. It is known that if the affinity between like species is stronger than that between unlike species, then $N\langle(\Delta x)^2\rangle$ takes a larger values than $x_1x_2(F)1$ (Figure 14). It is seen that for 15C5 molecules the affinity among themselves is stronger in CCl_4 than that observed in water. This can alternatively be said in terms of more affinity between 15C5 and water molecules in aqueous solutions. The analysis presented above distinctly show the influence of hydration and solute association via the F parameter obtained by application of KB theory to the activity and volume data for solutions of 15C5. Also the effect of ring flexibility has been clearly noted when the thermodynamic data are compared with similar data for aqueous 18C6 solutions at the same temperature.

4. Conclusions

The specific hydration pattern of aqueous solutions of 15C5 is studied with the help of volumetric, activity coefficient, and excess entropy properties at 298.15 K in aqueous solutions. The partial molar volumes of 15C5 in aqueous solutions and in CCl_4 solutions exhibit different behavior; in aqueous solutions it goes through a minimum indicating the presence of hydrophobic

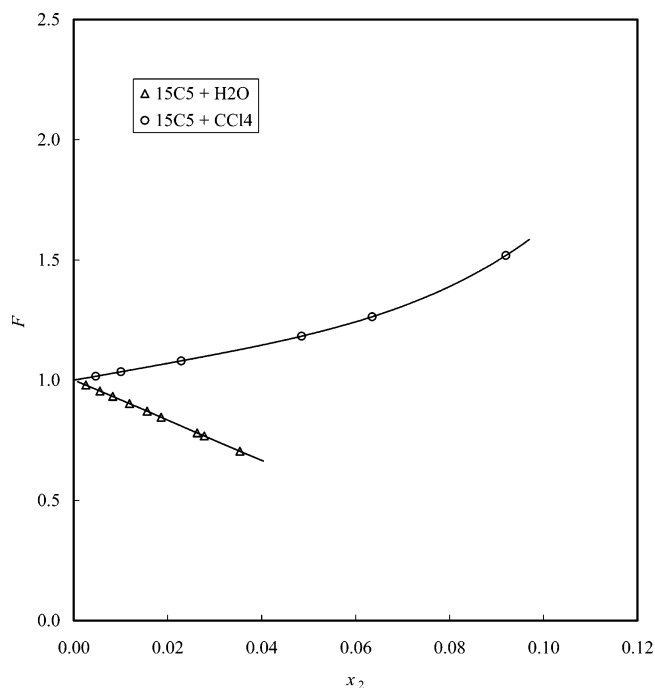


Figure 14. Plot of function F as a function mole fraction of 15C5 (x_2) for aqueous and CCl₄ solutions at 298.15 K.

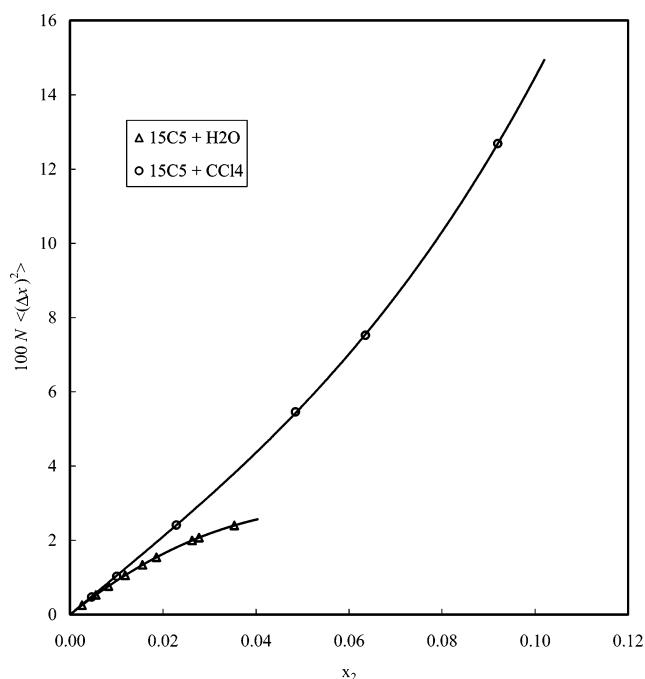


Figure 15. Plot of mean square concentration fluctuations as a function mole fraction of 15C5 (x_2) for aqueous and CCl₄ solutions at 298.15 K.

hydration. The hydration number at various concentrations remains constant, i.e., $h = 4$, in the studied concentration range whereas for 18C6 it increases from 4 to ~ 8 as concentration of 18C6 increases. Such a behavior is attributed to ring flexibility and conformational characteristics of 18C6. The variation of activity coefficient of 15C5 as well as excess free energy change for solutions in aqueous and CCl₄ media show distinct differences and emphasize the role of H-bonding in terms of solute–solvent interaction in aqueous solutions. The analysis of excess enthalpy and entropy changes reveals that dissolution of 15C5 is enthalpy dominated; however, the excess entropy change is more negative as compared to 18C6 in water. Although the

enthalpy changes are compensated by entropy changes in both the systems, 15C5 exhibits a hydrophobic interaction contribution much more when the water structure making effect is comparatively less as seen in the compensation temperature of 297 K as compared with 18C6, for which it is 291 K at the experimental temperature of 298.15 K. The structure making effect of 18C6 is thus attenuated due to the larger number of $-\text{CH}_2$ groups, proper symmetrical conformation, i.e., D_{3d} , and presence of bridging H-bonds as compared to that of 15C5. It is thus clear that although the odd number of oxygen atoms in the 15C5 ring show on an average four H-bonds, it does not lead to a cooperative binding mechanism. All the results are again examined by application of exact statistical theories of solutions, i.e., Kirkwood–Buff and McMillan–Mayer theories of solutions. The interactions in various pairs, i.e., solute–solvent, solute–solute, and solvent–solvent, again nicely show subtle differences in both the solvent media. The osmotic second virial coefficient for 15C5 obtained by both methods is in agreement. The attractive contribution is less than that of 18C6 in water indicating the importance of pair and triplet interactions in the presence of water as a solvent. The mean square concentration fluctuations as a function of concentration are greater in CCl₄ medium than that in aqueous solutions. These results establish that in aqueous solutions both hydrophobic hydration and hydrophobic interaction contribute in governing the solution properties whereas solute–solute interactions dominate over the solute–solvent interactions in CCl₄.

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