Activity Coefficient Studies in Ternary Aqueous Solutions at 298.15 K: H_2O + α-Cyclodextrin + Potassium Acetate and H_2O + 18-Crown-6 + Hydroquinone Systems[†]

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Activity coefficients of the components in aqueous ternary solutions containing a fixed concentration of α-cyclodextrin and 18-crown-6 at various concentrations of the third solutes potassium acetate and hydroquinone, respectively (concentration range (0.0 to 0.20) $\text{mol}\cdot\text{kg}^{-1}$), at 298.15 K were derived from vapor pressure osmometry. Also, data for the osmotic coefficients and activity coefficients for aqueous binary solutions of potassium acetate are obtained and used along with the data for aqueous binary hydroquinone solutions reported earlier to analyze the data of the ternary mixtures. It is observed that there is a lowering of activity coefficients of potassium acetate as well as of hydroquinone in the presence of α-cyclodextrin and 18-crown-6, respectively, which is being attributed to incorporation of the acetate ion and hydroquinone into the α-cyclodextrin and 18-crown-6 cavities, respectively, to form 1:1 inclusion complexes in the solution phase. The salting-in and thermodynamic equilibrium constant values have been determined using calculated transfer free energies and the method based on application of the McMillan−Mayer virial coefficient theory for solutions. It is noted that the complexation process is assisted by hydrophobic interaction between the complexed species. The apparent molar volume and calculation of virial coefficient for potassium acetate in binary aqueous solutions at 298.15 K are also reported and discussed.

Introduction

More than 50 years ago, aqueous solutions of inert gases and other solutes were studied to explain the formation of inclusion complexes or clathrate hydrates in solid form.[1] The loss of entropy or the negative excess entropies of the solutes in solution have been explained on the basis of structure making effect or formation of iceberg-like species around the solute molecules. The structure and geometries of such entities have been shown to resemble clathrate hydrates in the solid phase.[2–8] Upon the basis of such studies, many efforts were directed to understand the interactions and the nature of forces involved with the help of model compounds like alcohols and tetraalkyl ammonium salts in water.[4,5] The H-bonding, hydrophobic interaction concept, and finally the micellar interaction along with computer simulation studies have led to a better understanding of the nature of forces, bonding characteristics, and aggregation phenomena in aqueous and mixed aqueous solutions.[6−8]

In an important book titled "Non-stoichiometric compounds", Fetterly has discussed the formation of soluble complexes in the solution phase.[9] Upon the basis of the solubility data for aqueous urea solutions of fatty acids, he discussed the nature of interactions which ultimately lead to formation of channel compounds. The denaturing action of urea in aqueous protein solutions is well-known, and the studies related to these helped to understand salting-in/out effects and hydrophobic interactions both theoretically as well as experimentally.[10−12]

The thrust areas for the 21st century include the subject of supramolecules and self-assemblies.[13,14] By knowing the uses of these, especially in the fields of reaction kinetics, drug carriers, and medicinal chemistry, many efforts have been directed to study the chemistry of crown and cyclodextrin complexes.[15−18] Crown compounds form complexes with ions or neutral molecules if the size of the solute molecules matches with the host, i.e., crown cavity. Cyclodextrin forms both channel as well as cage compounds with a variety of solutes. The studies related to properties of aqueous solutions of these compounds are expected to increase our understanding about the molecular recognition and molecular transport phenomena.[19−23]

During the last about five years, we reported the measurements of osmotic coefficients, activity, and activity coefficient properties of electrolytes and nonelectrolytes as well as of surfactants in aqueous solutions of 18-crown-6 and also of aqueous cyclodextrin solutions.[24−30] It has been shown that the conformations of these host molecules, their H-bonding with water molecules in the cavities, as well as hydrophobic interaction along with the water structure making effect govern equilibrium properties in the solution phase. The observed enthalpy−entropy compensation effect[30,31] and application of McMillan−Mayer[32] and Kirkwood−Buff theories[33,34] for solutions to obtain second virial coefficient values for the solute molecules have helped us to understand solute−solvent and solute−solute association in such solutions.

We report in this article two case studies for aqueous solutions involving α-cyclodextrin and 18-crown-6 as host compounds. The osmotic and activity coefficient properties of binary solutions of these in water have already been reported by us.[24,28] The data of water activities of ternary aqueous solutions, water + α-cyclodextrin + potassium acetate and water + 18-crown-6

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+ hydroquinone, have been obtained and processed to obtain activity coefficients of the individual components in the solution phase.

To obtain information about salting constant and equilibrium constant values, a knowledge of activities in binary aqueous solutions is needed. We reported earlier the activity coefficient values for water + hydroquinone[35] which are used for the analysis of the data on ternary aqueous 18-crown-6 + hydroquinone solutions, while the osmotic and activity coefficient data for binary aqueous potassium acetate solutions are newly generated and used for the analysis of water activity data for ternary aqueous α-cyclodextrin + potassium acetate solutions at 298.15 K. These are further used to calculate the activity coefficients of the three components in the ternary aqueous mixture, which were utilized to calculate the Gibbs free energies of transfer of a solute in binary to ternary solutions. The estimated values of Gibbs free energies of transfer are used to evaluate pair and triplet interaction parameters by means of virial expansion of transfer Gibbs free energy as a function of both α-cyclodextrin or 18-crown-6 and guests (potassium acetate or hydroquinone) molality. The resulting salting-in parameter and equilibrium constant values for the complexation reaction are reported and discussed.

Experimental Work

α-Cyclodextrin procured from Lancaster, potassium acetate procured from BDH, and hydroquinone and 18-crown-6 procured from Merck were used without further purification. Initial handling of 18-crown-6, during stock solution preparation, was done in a drybox. The mass fraction of water of hydration in α-cyclodextrin (6.24 water molecules per α-cyclodextrin molecule) was estimated using the thermogravimetric analysis and microprocessor controlled automatic Karl Fischer Titrator. The details about water of hydration and preparation of solutions of α-cyclodextrin are given elsewhere.[28,29]

The solutions were prepared by mass using doubly quartz distilled water and reported on a molality basis (having an uncertainty of ± 0.0001 mol·kg^{-1}). The density measurements of aqueous solutions of potassium acetate were made using an Anton Paar digital densitometer (DMA 60/602) at 298.15 K. The uncertainty in the density data was found to be ± 0.005 kg·m^{-3}. The vapor pressures of binary and ternary aqueous solutions were measured using a KNAUER K-7000 vapor pressure osmometer having ± 0.001 K uncertainty in temperature. The uncertainty in the osmotic coefficient data was found to be ± 0.001. The details about the density and osmotic pressure measurements were reported earlier.[28]

Results

Binary Aqueous Potassium Acetate Solutions. Osmotic and Activity Coefficients. The osmotic coefficient (ϕ) values were determined for aqueous binary potassium acetate solutions at 298.15 K. Using the data of osmotic coefficients, the water activity (a_w) values have been calculated, which were further used to obtain the solvent activity coefficient (γ_1). The experimental osmotic coefficient data for aqueous potassium acetate solutions were expressed as a function of solute concentration (m_2/mol·kg^{-1}) using the polynomial equation

$$\phi = 1 + \sum_{i=1}^{n} A_i m_2^{i/2} \qquad (1)$$

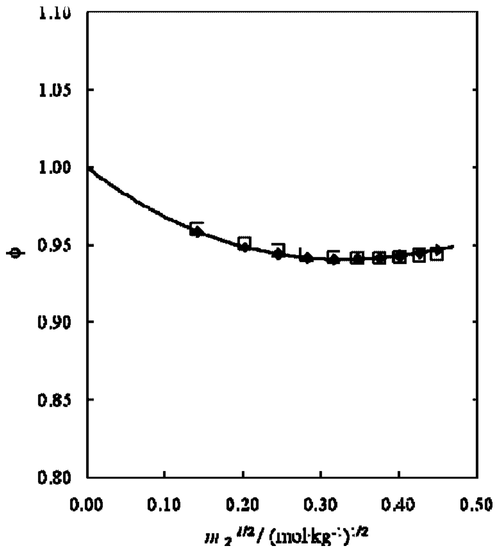

Figure 1. Variation of experimental osmotic coefficient (ϕ) of the water (1) + potassium acetate (2) system with the molality (m_2), at 298.15 K: ◆, experimental; □, literature, ref 37.

Table 1. Water Activity (a_w), Osmotic Coefficient (ϕ), and Activity Coefficient (γ) Data for Molality (m_2) in Water (1) + Potassium Acetate (2) Solutions at 298.15 K

m_2 / mol·kg^{-1}	x_2	ϕ	a_w	γ_1	$\gamma_\pm$	ΔG_m / J·mol^{-1}	ΔG^E / J·mol^{-1}
0.00000	0.00000	1.0000	1.00000	1.00000	1.00000	0.00	0.00
0.02009	0.00072	0.9586	0.99931	1.00003	0.87114	−14.93	−0.17
0.04064	0.00146	0.9487	0.99861	1.00007	0.83488	−27.75	−0.47
0.05975	0.00215	0.9442	0.99797	1.00012	0.81408	−38.82	−0.79
0.07966	0.00286	0.9418	0.99730	1.00016	0.79889	−49.80	−1.17
0.09983	0.00358	0.9408	0.99662	1.00021	0.78762	−60.48	−1.58
0.12021	0.00431	0.9409	0.99593	1.00025	0.77907	−70.90	−2.01
0.14036	0.00503	0.9417	0.99525	1.00028	0.77263	−80.90	−2.46
0.16072	0.00576	0.9431	0.99455	1.00031	0.76768	−90.75	−2.92
0.18090	0.00648	0.9449	0.99386	1.00034	0.76398	−100.28	−3.38
0.20147	0.00721	0.9471	0.99315	1.00036	0.76120	−109.78	−3.86

Table 2. Coefficients A_i for the Water + Potassium Acetate System, in Equation 1

A_1	−0.3908
A_2	0.7397
A_3	−0.3231
A_4	0.0660

where ϕ is the osmotic coefficients of solute molecules in aqueous binary solutions; A_1 is the Debye−Hückel constant equal to −0.3908 at 298.15 K;[36] and the other A_i coefficients have been obtained by the method of least-squares. The variation of osmotic coefficient as a function of solute concentration is given in Figure 1, and the data of osmotic coefficients and the A_i coefficients are collected in Tables 1 and 2, respectively. The mean molal activity coefficient of the solute molecule ($\gamma_\pm$) at molality (m_2) in binary aqueous solutions can be expressed in terms of A_i coefficients as

$$\ln \gamma_\pm = \sum_{i=1}^{n} \frac{2+i}{i} A_i m_2^{i/2} \qquad (2)$$

The solute activity coefficient values have been calculated using eq 2, and the data are collected in Table 1. The variation of ln $\gamma_\pm$ with the solute concentration and comparison with the literature values[37] is shown in Figure 2. The activity coefficient data, which have been converted to the mole fraction scale, were used to calculate the Gibbs free energy of mixing (ΔG_m) and excess Gibbs free energy (ΔG^E) of binary aqueous solutions,[38−41] and the values are included in Table 1. The corrections to the

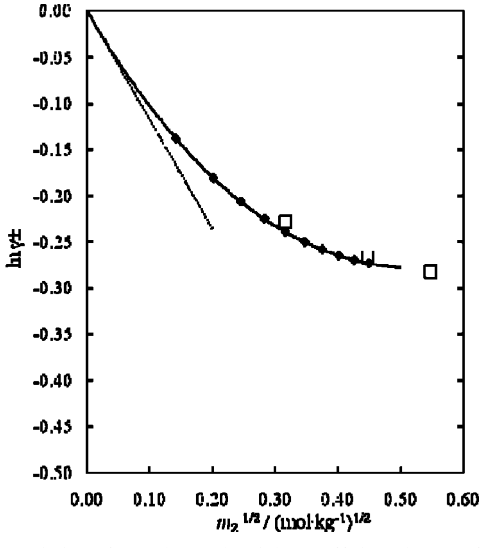

Figure 2. Variation of experimental activity coefficient (ln $\gamma_{\pm}$) of the water (1) + potassium acetate (2) system with molality (m_2), at 298.15 K: ♦, experimental; □, literature, ref 37; Debye−Hückel limiting law.

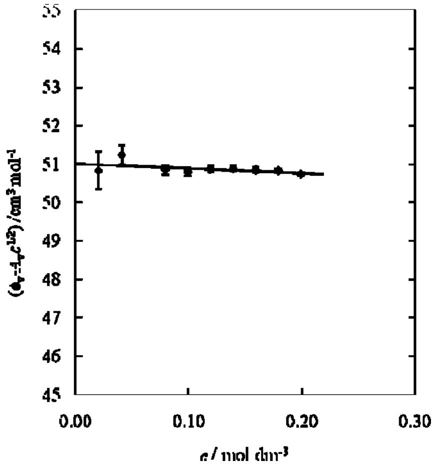

Figure 3. Variation of ($\phi_V - A_v \cdot c^{1/2}$) of the water (1) + potassium acetate (2) system as a function of concentration, at 298.15 K.

data in dilute concentration range due to hydrolysis of potassium acetate are being neglected.

Density and Apparent Molal Volume. The apparent molal volume data (ϕ_V) obtained from the density data at 298.15 K for aqueous potassium acetate solutions are expressed by the equation

$$\phi_v = \phi_v^0 + A_v c^{1/2} + B_v c \tag{3}$$

where ϕ_v^0 is the apparent molar volume at infinite dilution; A_v is the Debye−Hückel limiting law coefficient (equal to 1.868 at 298.15 K); and B_v is deviation constant.[42,43] The variation of $\phi_v - A_v \cdot c^{1/2}$ against c is shown in Figure 3.

Application of the McMillan−Mayer Theory. The solute−solute interactions are evaluated for aqueous solutions of potassium acetate in the dilute concentration region following the method reported by Harrington and Taylor.[44] This is done by determining the nonelectrolyte contribution to the solute activity coefficient by subtracting the Debye−Hückel electrostatic contribution from the solute activity coefficient (γ_2).

The activity coefficient of the solute (γ_2) in the dilute concentration range can be represented as

$$\ln \gamma_2 = -\alpha m_2^{1/2}(1 + b m_2^{1/2})^{-1} + \varpi m_2 \tag{4}$$

where α =1.173 $\text{kg}^{1/2}\cdot\text{mol}^{-1/2}$ at 25 °C and b = 1.0 $\text{kg}^{1/2}\cdot\text{mol}^{-1/2}$ and ω is the nonelectrolyte solute−solute interaction parameter. The subscript 1 is used for the properties of solvent and 2 is always for a solute for binary solutions. Hill[45] has shown that the Gibbs free energy for mole ratio of solute to solvent ($\bar{m}$)[44,46] can be expressed as

Table 3. Molar Volume of Pure Solvent ($\bar{V}_1^0$), Molar Volume of Solute at Infinite Dilution ($\bar{V}_2^0$), Nonelectrolyte Solute−Solute Interaction Parameter (ω), and Solute−Solvent (NB_{11}^{*0}) and Solute−Solute (NB_2^{*0}) Virial Coefficients for the Water (1) + Potassium Acetate (2) System at 298.15 K

$\bar{V}_1^0$	$\bar{V}_2^0$	$RT\kappa_T$	ω	NB_{11}^{*0}	NB_2^{*0}
$\text{cm}^3\cdot\text{mol}^{-1}$	$\text{cm}^3\cdot\text{mol}^{-1}$	$\text{cm}^3\cdot\text{mol}^{-1}$	$\text{kg}\cdot\text{mol}^{-1}$	$\text{cm}^3\cdot\text{mol}^{-1}$	$\text{cm}^3\cdot\text{mol}^{-1}$
18.0682	50.87	1.12	0.3835	49.75	434.38

$$\frac{G}{N_1 kT} = \frac{\mu_1^0}{kT} + \frac{\bar{m}\mu_2^0}{kT} - \bar{m} + \bar{m}\ln\bar{m} + \frac{1}{2}A_{22}\bar{m}^2 + \frac{1}{3}B_{222}\bar{m}^3 + \ldots\ldots$$

where μ_1^0 and μ_2^0 are the chemical potentials for pure solvent and solute, respectively, whereas A_{22} and B_{222} are the pair and triplet interaction terms of solute particles. The A_{22} coefficient is related to the second osmotic virial coefficient B_2^{*0} by[45]

$$A_{22}V_1^0 = 2NB_2^{*0} - \bar{V}_2^{\infty} + Nb_{11}^0 \tag{5}$$

where V_1^0 and $\bar{V}_2^{\infty}$ are molar volume of pure solvent and partial molar volume of solute at infinite dilution, respectively; N is Avogadro's number; and Nb_{11}^0 is the solute−solvent cluster integral.

For a 1:1 electrolyte

$$2\ln\gamma_2^* = A_{22}\bar{m} + B_{222}\bar{m}^2 \tag{6}$$

where γ_2^* is nonelectrolyte contribution to the solute activity coefficient, $\omega = A_{22}M_1/2$ (M_1 is molar mass of solvent in $\text{kg}\cdot\text{mol}^{-1}$).

By using the relation between the solute−solvent cluster integral (Nb_{11}^0) and $\bar{V}_2^{\infty}$ as $Nb_{11}^0 = -\bar{V}_2^{\infty} + RT\kappa_T$ and eq 5, we can write

$$NB_2^{*0} = A_{22}V_1^0/2 + \bar{V}_2^{\infty} - RT\kappa_T/2 \tag{7}$$

where κ_T, the isothermal compressibility of solvent, is equal to $45.248\cdot 10^{-5}$ at 298.15 K. The value for the solute−solute virial coefficient (B_2^{*0}) has been calculated by obtaining the value of ω. The solute−solute interaction parameter, NB_2^{*0}, and solute−solvent interaction parameter, NB_{11}^{*0} (where $NB_{11}^{*0} = -Nb_{11}^0$), values at 298.15 K determined for potassium acetate are collected in Table 3.

Ternary Aqueous Mixtures. Activity Coefficients. The molal activity coefficient of nonelectrolyte host (γ_2) (α-cyclodextrin or 18-crown-6) in the ternary system (water (1) + host (2) + guest (3)) is expressed as a function of concentration of guest solute (m_3) (potassium acetate or hydroquinone) using the equation[35]

$$\ln\gamma_2 = \ln\gamma_2^0 + \sum_{i=0}^{\infty}\left(\frac{1}{i+1}\right)B_i m_3^{(i+1)} \tag{8}$$

where γ_2^0 is the activity coefficient of the nonelectrolyte host in binary aqueous solutions. A similar expression for the activity coefficient of guest solute (γ_3) may be obtained by applying the cross differentiation relation

$$\left(\frac{\partial \ln \gamma_2}{\partial m_3}\right)_{m_2} = \nu\left(\frac{\partial \ln \gamma_3}{\partial m_2}\right)_{m_3}$$

where ν is the number of ions formed by the dissociation of solute molecule.The result is

$$\ln \gamma_3 = \ln \gamma_3^0 + \sum_{i=0}^{\infty}\left[\frac{m_2}{\nu}\right]B_i m_3^i \tag{9}$$

where γ_3 is the activity coefficient of the solute in the ternary aqueous system and γ_3^0 is that in the binary aqueous system, whereas γ_3^0 values for hydroquinone are taken from the literature.[35] The coefficients B_i in eq 8 and 9 are related to an experimental quantity Δ defined as[40,41]

$$\Delta = -55.51 \ln a_w - m_2\phi_2^0 - \nu m_3\phi_3^0 \tag{10}$$

where ϕ_2^0 and ϕ_3^0 are the osmotic coefficients of the host and the guest solute, respectively, in binary aqueous systems, whereas Δ can be expressed in terms of concentration of guest (m_3/mol·kg^{-1}) as[35]

$$\Delta/m_2m_3 = \sum_{i=0} B_i m_3^i \tag{11}$$

The $\Delta/(m_2m_3)$ is obtained with the help of eq 10, and the coefficients B_i have been obtained using the method of least-squares (Table 4). The values of $\Delta/(m_2m_3)$ are recalculated using the least-squares fit coefficients B_i and were further used for the recalculation of water activity. The reliability of the data is expressed in terms of percentage relative difference given by[25]

$$\%\ \text{relative difference in } a_w = \frac{a_w(\text{cal}) - a(\text{obs})}{a_w(\text{obs})} \cdot 100 \tag{12}$$

The observed and calculated values of $\Delta/(m_1m_2)$ along with percentage relative difference in water activity are reported in Table 5. From the measured water activity, the activity coefficient of the solvent (γ_1) has been calculated. The activity coefficient for the host (γ_2) and activity coefficient for the guest solute (γ_3) are calculated using eqs 8 and 9, respectively, and are given in Table 6. The variation of γ_2 and γ_3 with solute concentration is shown in Figure 4.

Transfer Free Energies and Salting Constant. The McMillan–Mayer theory of solutions is used to evaluate the salting constant values. The method based on this theory expresses the Gibb's free energy of transfer of host (2) from water (1) to an aqueous solution containing solute (3) as[47,48]

$$\Delta G_{tr}^2(1 \rightarrow 1+3) = 2\nu m_3 g_{23} + 6\nu m_2 m_3 g_{223} + 3\nu^2 m_3^2 g_{233} + \text{........} \tag{13}$$

where m_2 and m_3 are the molalities of host (2) and solute (3), respectively, defined per kilogram of water and ν is the number of ions into which the electrolyte solute dissociates. The g_{23}, g_{223}, . . . are the pair and triplet interaction parameters, which take into account all sources of nonideality in the ternary system.

Table 4. Coefficients B_i for the Ternary System Water + 0.1 mol·kg^{-1} Host + Guest, in Equation 11

	water + potassium acetate + α- cyclodextrin	water + hydroquinone + 18-crown-6
B_0	−1.8922	−1.2266
B_1	15.5139	−14.7391
B_2	−76.0605	105.0931
B_3	138.6570	−227.1524

Table 5. Water Activity (a_w) for the Ternary System Water (1) + 0.1 mol·kg^{-1} Host (2) + Guest (3), at 298.15 K

m_3/mol·kg^{-1}	a_w	Δ/m_2m_3 (obs)	Δ/m_2m_3 (calc)	% error in a_w
Water (1) + 0.1 mol·kg^{-1} α-Cyclodextrin (2) + Potassium acetate (3)				
0.01094	0.99784	−1.7515	−1.7314	0.0000
0.02047	0.99754	−1.5950	−1.6053	0.0000
0.04673	0.99670	−1.2962	−1.3193	0.0002
0.06822	0.99601	−1.1381	−1.1438	0.0001
0.09256	0.99522	−1.0082	−0.9979	−0.0002
0.11732	0.99441	−0.9095	−0.8952	−0.0003
0.13850	0.99371	−0.8431	−0.8342	−0.0002
0.16330	0.99289	−0.7807	−0.7833	0.0001
0.18598	0.99212	−0.7345	−0.7458	0.0004
0.20829	0.99137	−0.6970	−0.7077	0.0004
0.23317	0.99052	−0.6625	−0.6524	−0.0004
Water (1) + 0.1 mol·kg^{-1} 18-Crown-6 (2) + Hydroquinone (3)				
0.01986	0.99764	−1.4561	−1.4797	−0.0001
0.03990	0.99737	−1.6987	−1.6619	0.0003
0.05993	0.99710	−1.7925	−1.7814	0.0001
0.07938	0.99685	−1.8370	−1.8481	−0.0002
0.10009	0.99659	−1.8577	−1.8768	−0.0004
0.12098	0.99633	−1.8610	−1.8738	−0.0003
0.14152	0.99607	−1.8524	−1.8516	0.0000
0.16202	0.99580	−1.8352	−1.8220	0.0004
0.16631	0.99575	−1.8307	−1.8160	0.0005
0.20357	0.99525	−1.7784	−1.7882	−0.0004

Table 6. Activity Coefficient (γ), Free Energies of Transfer (ΔG_{tr}), and Excess Free Energy (ΔG^E) for the Ternary System Water (1) + 0.1 *m* Host (2)+ Guest (3), at 298.15 K

m_3/mol·kg^{-1}	γ_1	γ_2	γ_3	ΔG^E/J·mol^{-1}	$\Delta G_{tr}{}^2$/J·mol^{-1}	$\Delta G_{tr}{}^3$/J·mol^{-1}
Water (1) + 0.1 mol·kg^{-1} α-Cyclodextrin (2) + Potassium acetate (3)						
0.00000	0.99996	1.0448	0.9110	0.09	0.0	−453.4
0.01094	1.00001	1.0243	0.8250	−0.06	−48.1	−414.8
0.02047	1.00005	1.0081	0.8041	−0.23	−86.6	−383.4
0.04673	1.00015	0.9703	0.7753	−0.79	−178.8	−311.0
0.06822	1.00023	0.9451	0.7628	−1.28	−242.2	−264.8
0.09256	1.00031	0.9209	0.7533	−1.86	−304.3	−223.7
0.11732	1.00038	0.8996	0.7465	−2.48	−359.9	−191.1
0.13850	1.00044	0.8833	0.7420	−3.02	−403.3	−168.3
0.16330	1.00049	0.8658	0.7381	−3.67	−450.6	−144.9
0.18598	1.00053	0.8509	0.7357	−4.27	−491.5	−124.2
0.20829	1.00057	0.8372	0.7344	−4.86	−529.6	−102.4
0.23317	1.00060	0.8231	0.7345	−5.49	−569.4	−73.5
Water (1) + 0.1 mol·kg^{-1} 18-Crown-6 (2) + Hydroquinone (3)						
0.00000	0.99996	1.0180	0.8650	0.01	0.0	−354.4
0.01986	1.00004	0.9909	0.8276	−0.10	−66.0	−429.7
0.03990	1.00013	0.9600	0.7981	−0.27	−143.4	−481.7
0.05993	1.00022	0.9274	0.7751	−0.49	−228.2	−514.1
0.07938	1.00032	0.8952	0.7578	−0.72	−314.9	−530.7
0.10009	1.00043	0.8614	0.7437	−0.98	−409.5	−536.6
0.12098	1.00054	0.8283	0.7329	−1.26	−505.5	−534.4
0.14152	1.00064	0.7974	0.7246	−1.53	−598.9	−528.1
0.16202	1.00075	0.7681	0.7178	−1.82	−690.7	−521.3
0.16631	1.00077	0.7622	0.7165	−1.88	−709.7	−520.1
0.20357	1.00094	0.7133	0.7052	−2.47	−872.2	−518.6

The Gibb's free energy for the transfer of solute from water to aqueous host solution is given by

$$\Delta G_{tr}^3(1 \rightarrow 1+2) = 2\nu m_2 g_{23} + 3\nu m_2^2 g_{223} + 6\nu^2 m_2 m_3 g_{233} + \text{........} \tag{14}$$

The variation of ΔG_{tr}^2 and ΔG_{tr}^3 with solute concentration is shown in Figure 5. At low host and guest concentrations, all triplet and higher-order terms can be neglected, and the pair interaction parameter g_{12} can be related to the familiar salting coefficient k_S by

$$RTk_S = 2\nu g_{23} \tag{15}$$

Transfer free energies for transfer of host from aqueous binary to ternary solutions containing other solutes have been used to

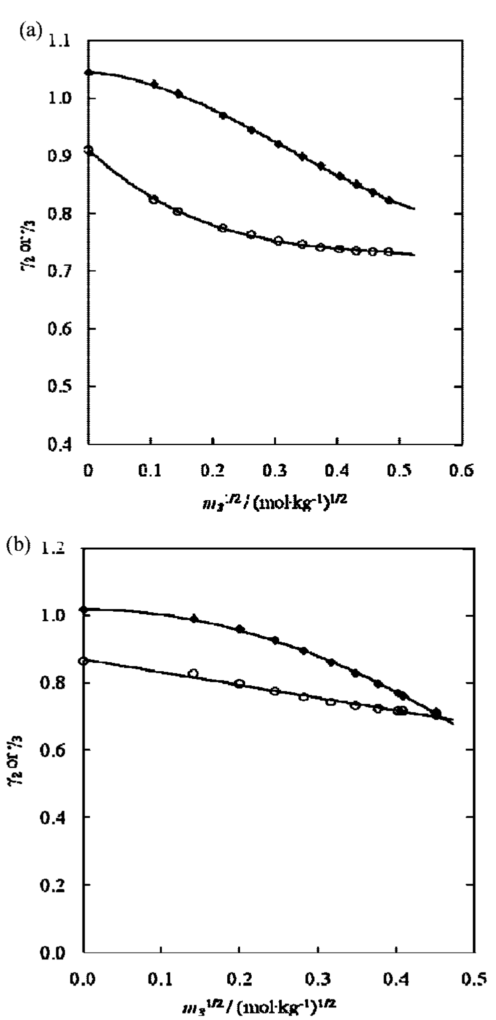

Figure 4. Variation of activity coefficient (γ) for (a) water (1) + 0.1 mol·kg^{-1} α-cyclodextrin (2) + potassium acetate (3), and (b) water (1) + 0.1 mol·kg^{-1} 18-crown-6 (2) + hydroquinone (3) as a function of molality (m_3) of guest solute (potassium acetate or hydroquinone) at 298.15 K: ◆, γ_2; ○, γ_3.

calculate pair and triplet interaction parameters using eq 13. The values of transfer Gibb's free energies are collected in Table 6 and the salting constant values are given in Table 7.

Discussion

Activity Coefficient and Volume Data for Aqueous Binary Potassium Acetate Solutions. An observation from Figure 1 reveals that the osmotic coefficient for aqueous potassium acetate solutions decreases as a function of the square root of concentration of the salt. The data are compared with the literature data,[37] and it is seen that at higher concentrations there are small differences. However, the literature data are based on isopiestic vapor pressure measurements and from about 0.1 mol·kg^{-1} of salt concentration. Similar behavior is noted for the variation of mean activity coefficient of the salt (Figure 2). It is noted that the curve of $\ln \gamma_\pm$ exhibits positive deviation from the limiting Debye–Hückel law. The apparent molar volume of the salt (Figure 3) shows negligible dependence on salt concentration in the studied region (b_V parameter of eq 3 is almost zero). The limiting apparent molar volume obtained after smooth extrapolation is 50.87 cm^3·mol^{-1} which is a little higher than that reported in the literature[49] based upon summation of individual partial molar volumes of ions [(49.5 ± 0.7) cm^3·mol^{-1}]. The values of free energy of mixing and excess free energy change for dissolution of potassium acetate in water are negative (Table 1). The application of the McMillan–Mayer theory of solution to the above data yielded the values for solute–solvent and solute–solute virial coefficients. It is seen from Table 3 that the solute–solvent virial coefficient is the same as that of the magnitude of partial molar volume, while the value of the solute–solute virial coefficient (NB_2^{*0}) is high, which is also higher than that of NaCl as quoted by Harrington and Taylor.[44]

Ternary Aqueous Solutions of Potassium Acetate-α-cyclodextrin. It is observed from Figure 4 that the mean activity coefficient of potassium acetate as well as that of α-cyclodextrin decrease with an increase in concentration of potassium acetate. This is being attributed to formation of the inclusion complex with α-cyclodextrin as a host. In a stoichiometric concentration (concentration required for complete complexation between host and guest, i.e., 0.1 mol·kg^{-1} in the present case) region, γ_3 is more or less constant, and the trace activity coefficient is less than one. The transfer free energy changes for transferring α-cyclodextrin to aqueous potassium acetate are negative (Figure 5a), while the same is initially negative and increases in magnitude as a function of salt concentration for transfer of potassium acetate from aqueous to aqueous α-cyclodextrin solutions. Thus, the inclusion of the acetate ion in the cavity and the formation of the anionic α-cyclodextrin charge skeleton along with K^+ ions at the rim may be forming a unique ion pair, of which energetics show a repulsive trend; i.e., the stability of the inclusion entity is greatest when the guest is at low concentration while it gets affected due to ion–ion interaction at higher guest concentrations. The application of the McMillan–Mayer theory of solutions reveals that the pair interaction parameter g_{12} as well as the triplet interaction parameter g_{112} are negative (Table 7) validating the proposal of complexation. The salting constant is negative, while the equilibrium constant is of the order of 4.2 ($\log K = 0.62$). It is also seen from the table that interactions between α-cyclodextrin–salt–salt (g_{233} parameter) are not favored at all (positive magnitude). All these point out that there is a formation of an inclusion complex of stoichiometry 1:1 for α-cyclodextrin and potassium acetate in aqueous solutions.

Ternary Aqueous Solution of Hydroquinone and 18-Crown-6. In the above discussion, we referred to a transfer of an electrolyte from an aqueous to an aqueous–α-cyclodextrin (host) system; however, the situation changes when we examine the results of transferring hydroquinone (nonelectrolyte guest) to aqueous-18-crown-6 (host) solutions. We observe from Figure 4 that the activity coefficients of both 18-crown-6 and hydroquinone decrease with an increase in concentration of hydroquinone (a flat region is noted in the stoichiometric concentration region). The trace activity coefficient for hydroquinone is less than unity, and hence again inclusion of hydroquinone in 18-crown-6 cavities can be proposed. This is supported by the observed fact that the transfer free energies are negative (Figure 5). The transfer free energy change for transferring hydroquinone from water to aqueous 18-crown-6 solutions shows a minimum at a 1:1 stoichiometric concentration of hydroquinone, while at higher hydroquinone concentration, the value changes marginally. The application of the MM theory to evaluate the pair and triplet interaction parameters to this system formulates the best part of this investigation. From Table 7, we note that the pair (host–guest) interaction parameter (g_{23}) is negative as well as the triplet interaction parameter (g_{223}); thus, the 1:1 complex is

Table 7. Pair (g_{23}) and Triplet Interaction (g_{223} and g_{233}) Parameters, Salting Coefficients (k_S), and Thermodynamic Equilibrium Constants (as log *K*) of the System Water (1) + 0.1 mol·kg^{-1} Host (2) + Guest (3), at 298.15 K

	$\frac{g_{23}}{\mathrm{J\cdot kg\cdot mol^{-2}}}$	$\frac{g_{223}}{\mathrm{J\cdot kg^{2}\cdot mol^{-3}}}$	$\frac{g_{233}}{\mathrm{J\cdot kg^{2}\cdot mol^{-3}}}$	$\frac{k_S}{\mathrm{kg\cdot mol^{-1}}}$	log *K*
water + 0.1 mol·kg^{-1} α-cyclodextrin + potassium acetate	−878.4	−259.0	510.3	−1.4	0.62
water + 0.1 mol·kg^{-1} 18-crown-6 + hydroquinone	−1874.8	−71.6	−887.6	−1.5	0.65

stable and has an equilibrium constant value of the order of 4.5 (log $K = 0.65$). Thus, the incorporation of hydroquinone in 18-crown-6 cavities is attenuated by hydrophobic association or interaction. X-ray analysis of crystalline complexes of phenols with 18-crown-6 has been reported.[50] Especially 3-nitrophenol and 2-nitrophenol have been shown to form 1:1 solid complexes with 18-crown-6. Our results for 1,4-dihydroxy benzene, i.e., hydroquinone, thus also indicate 1:1 complexation in the solution phase of which X-ray data for solid are not yet reported.

Closer scrutiny of Table 7 reveals a more interesting fact; i.e., the g_{233} parameter which is a triplet virial coefficient is highly negative meaning that in these solutions the energy interaction between 18-crown-6−hydroquinone−hydroquinone molecules, i.e., the species in the form of 1:2 stoichiometry, is feasible and stable. The transfer free energy for hydroquinone from water to aqueous 18-crown-6 solutions (Figure 5b) thus substantiates the above explanation. It is suggested that the bridged water molecules in the crown cavity[21] may be getting replaced by −OH groups of the hydroquinone forming adduct of low stability ($k_S = -1.5$). The interaction parameter g_{122} (Table 7) is highly negative and indicates the possibility of the presence of dimeric hydroquinone cemented with the 18-crown-6 molecule. All these interactions thus result due to H-bonding and further stabilization by hydrophobic forces. Probably this is the best interpretation we can offer for the results obtained and the proposition of adduct formation in the solution phase. All these interactions thus lead to H-bonding and are stabilized by hydrophobic interaction in the solution phase.

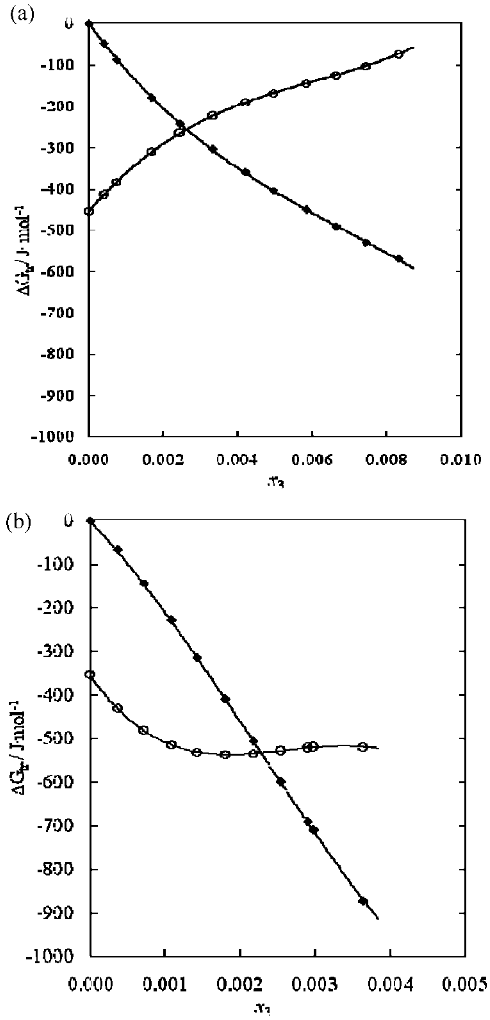

Figure 5. Variation of Gibb's free energy of transfer (ΔG_{tr}) for (a) water (1) + 0.1 mol·kg^{-1} α-cyclodextrin (2) + potassium acetate (3) and (b) water (1) + 0.1 mol·kg^{-1} 18-crown-6 (2) + hydroquinone (3) systems as a function of mole fraction of guest: ♦, host (α-cyclodextrin or 18-crown-6); ○, guest (potassium acetate or hydroquinone).

Conclusions

The measured osmotic and activity coefficient data at 298.15 K for aqueous solutions have been utilized to obtain transfer free energies of transfer of potassium acetate and hydroquinone from aqueous to aqueous solution containing host molecules α-cyclodextrin and 18-crown-6, respectively. The application of the McMillan−Mayer theory of solutions indicates the formation of the 1:1 complex in the case of potassium acetate with α-cyclodextrin, whereas hydroquinone forms 1:1 as well as 1:2 complexes with 18-crown-6 solutions. It has been shown that the potassium acetate anion occupies the cavity of α-cyclodextrin, while K$^+$ ions interact with the rim through −OH groups via ion−dipole interaction. The inclusion complexes of hydroquinone with 18-crown-6 seem to involve both H-bonding as well as hydrophobic interaction in aqueous media between guest molecules. The utility of pair and triplet interaction via application of the McMillan−Mayer theory of solution thus provides a better understanding of the complexed host−guest-type species in aqueous solutions.

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