Upper Consolute Temperature of Water-Phenol Systems with Some Additives

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Using upper consolute temperatures (UCT) and corresponding consolute compositions (CC) of water-phenol systems with each of 0.1 mol kg^{-1} salts and acids, 1.0% polyethylene glycol 200, 0.01 mol kg^{-1} surfactant and aromatic compounds, we obtained 0.01 mol kg^{-1} CaF$_2$ and CrCl$_3$ compositions. Focusing on UCT and CC, the role of valence electrons and shell number, basicity, hydrophilic, hydrophobic and π conjugated electrons of corresponding additives are reported. The surfactants and π conjugation electrons are noted to decrease the UCT in a constant ratio that depicts the state and inherent strength of ionic and molecular-water interactions. The data are useful in the investigation of cloud points of immiscible solutions based on the Hofmeister series.

INTRODUCTION

The use of critical solvents is a very useful approach for applications of mixed solvents in several techniques hence their physicochemical characterization is in high demand. Therefore upper consolute temperature (UCT) and consolute composition (CC) data of immiscible solvents with various additives are of industrial interest [1] for the investigation of cloud points [2], however limited studies are available in the literature. Such solvents are soluble at higher temperatures and become insoluble at NTP with separate phases; the additives solubilize and maintain the solubility in each other even at NTP. The additives effectively establish the interactions with both the solvent phases destabilizing their structure with a decrease in their chemical potential, which permits the solubilization of the solvents in each other at the chemical level.

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The UCT data depend on the size and shell numbers of the ions when used as additives, although Singh [3] performed critical studies on the Hofmeister series to investigate such effects of a few alkali salts on proteins. Hence, we chose to investigate the UCT and CC properties of immiscible solvents with various additives due to a paucity of reliable data [4]. We studied several categories of salts, including (a) monovalent (NaF, NaCl, NaBr, KCl, KBr, NH$_4$Br, NH$_4$SCN), di- (MgCl$_2$, CaF$_2$, CaCl$_2$, SrCl$_2$) and trivalent (AlCl$_3$, CrCl$_3$, FeCl$_3$) salts, (b) mono- (formic), di- (oxalic, malonic, succinic) and tribasic (citric) acids; glycerol and urea, (c) CTAB (cetyltrimethyl ammonium bromide), TEAB (tetraethylammonium bromide), CPC and CPB (cetylpyridinium chloride and bromide) cationic; LDS and SDS anionic and CA (cetylalcohol), butanol, polyethyleneglycol 200 (PEG 200) and EGMDE (ethyleneglycol monododecylether) nonionic surfactant, (d) benzene, naphthalene, anthracene, as well as chrysene, toluene and xylene (derivatives). We measured the effects of ionic, hydrophilic and hydrophobic interactions on UCT values to

illustrate their thermodynamic treatment.

EXPERIMENTAL

Aqueous salts and acids (0.1 mol kg^{-1}), and 1.0% PEG 200, surfactant and aromatic compound solutions (0.01 mol kg^{-1}) in phenol were prepared (w/w). Due to their solubility, CaF$_2$ and CrCl$_3$ (0.01 mol kg^{-1}) aqueous solutions were used. Each of aqueous additive+phenol and water+phenolic solution in 2:8 ratio were taken separately in 150 mm × 15 mm borosil glass cells mounted on a stainless steel stand placed in a paraffin oil-filled thermostat. Gentle heating with smooth stirring was achieved using a 25 watt immersion rod connected to autocut the electric relay through the contact thermometer. The phase dissolution and formation on air-cooling was viewed using a cathetometer and temperatures were noted within ±0.1 °C uncertainty.

Materials

AR phenol, naphthalene, anthracene and additives were used as received; benzene was purified removing thiophene with concentrated H$_2$SO$_4$ followed by NaOH treatment and distillation over CaCl$_2$. Glycerol was treated with concentrated H$_2$SO$_4$ and demineralized, water was triple distilled with KOH and KMnO$_4$ (conductivity, 1×10^{-6} Ω^{-1} cm^{-1}).

RESULTS AND DISCUSSION

Phenol weights in percent (wt%) were calculated from the equation as follows: (Amount of phenol for each individual set)/(Total amount of phenol) × 100. The wt% was plotted against corresponding temperatures for the UCT and CC values. An apex point on the plot was chosen and its x and y coordinates gave the numerical values of UCT and CC (Table 1). The measurements were repeated several times with the water-phenol system, which were in close agreement with previously published reports [5]. Values were noted with ±0.12 °C and ±0.25% errors, respectively, in UCT and CC data.

The miscibility of water-phenol is temperature dependent due to weak chemical interactions, each of which is unable to destabilize the other's structure in order to solubilize it. Thus additives act as catalysts to destabilize the water, the phenol

structures, or both of them by establishing chemical bonds. Thus, salts are noted to destabilize the structure of water with stronger ion-water interactions integrating the water phase separating the phenol that requires higher thermal energy to mix. Thus the orders of UCT and CC are NH$_4$Br > NH$_4$SCN > NaBr > KI > RbCl > KCl> KBr > NaF > NaCl and NH$_4$SCN > NaI > NaBr >NH$_4$Br > NaCl > NaF > KBr > KI > KCl > RbCl, respectively, depicting a sequence of strength of ion-water interactions. The NaBr > NaF > NaCl trend of UCT and NaBr > NaCl > NaF of CC infer greater polarization [7-11] on Br$^-$ and effective nuclear charges on F$^-$ and Cl$^-$, influencing anionic hydration. The AlCl$_3$ > MgCl$_2$ > NaCl order of UCT, KCl > CaCl$_2$ and CrCl$_3$ > FeCl$_3$ trends of CC infer the directive of ionic size and valence electrons. It indicates higher temperature bearance for ionic hydration of smaller ions than those of the larger, probably due to effective nuclear charge.

The UCT and CC in the CaCl$_2$ > CaF$_2$ order infers that Cl$^-$ with the same cation strengthens the hydration and the CaCl$_2$ > MgCl$_2$ order for UCT and the CC of NaF > CaF$_2$ and NaBr > KBr, as well as the UCT and CC trend of CaCl$_2$ > SrCl$_2$ > MgCl$_2$ > CaF$_2$ confirm that greater cation size causes greater hydration. The CC for salts of Br$^-$ is found to be lower and the UCT greater than those of $^-$SCN of NH$_4$SCN, which may amount to $^-$S−C≡N ↔ S=C=N$^-$ resonating structures.

The maximum UCT and CC values of FeCl$_3$ and CaCl$_2$ were observed, with two values for each of the UCT and CC of FeCl$_3$. Note that FeCl$_3$ had the highest values for UCT, but its second CC value was the lowest of all salts tested. This could be attributed to a one-electron transfer from Fe^{3+} to phenol reducing Fe^{3+} to Fe^{2+}. Thus, the phenol concentration increases due to the weaker Fe^{2+}-water interactions than those of Fe^{3+}, illustrating that a higher temperature favors the breaking of weaker Fe^{2+}-water bonds, thereby releasing free Fe^{2+} to form a complex with phenol, which may be responsible for the second UCT. Furthermore, the half-filled 3d^5 orbital of Fe^{3+} and 3d^6 of Fe^{2+} may be accountable for the complex formation with water as the ligand.

The FeCl$_3$ > AlCl$_3$ > CrCl$_3$ order of UCT and AlCl$_3$ > FeCl$_3$ > CrCl$_3$ of CC trends direct that the fully filled 2s^{2}p^6 and the partially filled 3d^5 and 4s^{0}3d^3 orbitals alter salt-water interactions. The slightly lower UCT and CC of RbCl and the highest UCT of NH$_4$Br among monovalent salts along with the lower UCT and greater CC for NH$_4$SCN denote stronger

Table 1. The UCT and CC Data of Water-Phenol with Additives at 298.2 K

Table 1. Continued

Conc.	Additives	UCT (K)	CC (%kg l^{-1})	N[a]
		Monovalent salts		
	0[b]	338.8	36.30	21
0.1	NaF	304.2	33.41	15
0.1	NaCl	341.2	38.46	9
0.1	NaBr	348.8	44.35	17
0.1	NaI	349.6	45.48	17
0.1	KCl	345.6	22.92	9
0.1	KBr	345.2	32.95	17
0.1	KI	346.2	33.05	16
0.1	RbCl	345.1	26.60	16
0.1	NH$_4$Br	349.8	39.05	9
0.1	NH$_4$SCN	342.6	55.55	11
		Divalent salts		
0.1	MgCl$_2$	348.3	44.30	16
0.01	CaF$_2$	339.6	26.66	16
0.1	CaCl$_2$	362.7	66.66	13
0.1	SrCl$_2$	354.4	55.30	16
		Trivalent salts		
0.1	AlCl$_3$	357.7	56.90	31
0.01	CrCl$_3$	340.8	39.86	15
0.1	FeCl$_3$	371.9	43.50	21
0.1	FeCl$_3$	370.9	19.32	21
		Monobasic acids		
0.1	HCOOH	338.7	33.39	16
0.1	CH$_3$COOH	338.6	34.60	12
		Dibasic acids		
0.1	Oxalic acid	347.2	55.55	9
0.1	Malonic acid	344.6	56.88	12
0.1	Succinic acid	335.2	44.39	14
		Tribasic acid		
0.1	Citric acid	338.4	33.20	17
		Non-electrolytes		
0.1	Glycerol	343.6	30.70	16
0.4	Urea	343.3	38.49	9
0.6	Urea	335.8	47.26	9
0.4	Methylurea	343.6	47.81	9
0.4	Dimethylurea	341.8	48.22	9

Conc.	Additives	UCT	CC	N
		Aromatic compounds		
0.01	Benzene	367.7	57.15	11
0.01	Naphthalene	354.9	21.74	11
0.01	Anthracene	342.2	36.87	20
0.01	Chrysene	340.9	36.86	20
		Benzene derivatives		
0.01	Toluene	339.1	34.05	21
0.01	Xylene	339.2	31.46	21
		Cationic surfactants		
0.01	CTAB	335.2	47.29	10
0.01	TEAB	345.3	40.33	11
0.01	CPC	338.2	57.30	11
0.01	CPB	338.9	47.22	13
		Anionic surfactants		
0.01	SDS	333.7	54.54	8
0.01	LDS	328.3	54.54	10
		Nonionic surfactants		
0.01	Cetyl alcohol	341.8	28.87	16
0.1	Butanol	341.2	36.70	11
0.1	PEG200	349.9	19.27	14
0.1	EGMDE	348.1	25.27	16

[a]Number of data points. [b]0 indicates no additive to water+phenol. Abbreviations: CTAB (cetyltetraethyl-ammonium bromide), TEAB (tetraethylammonium bromide), CPC (cetylpyridinium chloride), CPB (cetyl-pyridinium bromide), LDS (lithium dodecylsulfate), SDS (sodium dodecylsulfate), PEG200 (polyoxyethylene-glycol), EGMDE (ethyleneglycol monododecylether).

anion-water interactions with NH$_4^+$. The smaller F$^-$ anion causes greater F$^-$-water interactions than those of Cl$^-$, and the slightly higher UCT with the larger Rb$^+$ than those of KCl and lowest CC among monovalent salts denote weaker interactions with larger cations. Perhaps their ionization potentials are responsible for such behavior. That divalent cations of chloride salts had higher UCT values than those of monovalent cations was reported (*e.g.* CaCl$_2$ and SrCl$_2$ show higher CC); however, CaF$_2$ produces lower CC values and stronger divalent cations-water interactions.

The higher UCT values of trivalent salts than those of

monovalent and divalent salts indicate stronger hydration of ions. However, the lower UCT values of Cr^{3+} may result from filling the d orbital of $Cr(OH)_3$. The higher UCT and CC of $AlCl_3$ confirms the stronger Al^{3+}-water interaction, indicating that here orbital also contributes in hydration.

The comparatively larger UCT and lower CC values of formic than acetic acid depict stronger hydrophobic interactions with phenol due to $-CH_3$. However, oxalic and malonic acids did have higher UCT and CC values than those of the monobasic acid where the $-CH_2-$ of malonic acid causes a hydrophobic effect even though its greater UCT indicates stronger hydrophilic interactions, with higher CC values also noted. The two $-CH_2-$ groups of succinic acid decrease the UCT and CC values by 9% thus the $-CH_2$-manifolds interactions.

The higher UCT and lower CC values for glycerol and citric acid than those of succinic acid confirms that the 3-COO^- and 1-OH groups of citric acid outweigh the hydrophobic interactions of 3-CH_2-. One effect the 3-OH groups of glycerol was higher UCT and lower CC values than those of citric acid, indicating the greater structure breaking effect of -OH than that of the 3-COO^- and 1-OH groups of citric acid.

Urea with its ketone and amide groups does have a UCT almost equal to that of glycerol and higher CC values where an increase in the concentration of the former decreases UCT and increases CC values followed by N-substituted ureas [21]. These interactions match with those of the of surfactants, which display a decrease in interfacial potential with a decrease in UCT and an increase in CC values due to hydrophilic and hydrophobic interactions. Therefore, we conclude that glycerol and the ureas behave as surfactants, decreasing UCT and increasing CC values with anionic surfactants compared to those of cationic surfactants and inferring stronger interactions of SO_4^{2-} compared to those of Cl^- and Br^- of cationic surfactants.

The interaction of the -OH of citric acid and glycerol are compared with those of butanol, with 1-CH_3 and 3-CH_2-, and are found to decrease the UCT values by 2.5 °C and increase the CC by 6% more than those of glycerol, and increase UCT values by 2.7 °C and CC by 3% more than those of citric acid. These variations reveal the effect of -CH_3 and -CH_2- on hydrophobic interactions.

The UCT of cetyl alcohol is slightly higher than that of butanol (by 1.2%) and the CC is lower by 20% due to the hydrophobic interactions of the longer alkyl chain. Likewise the UCT values of EGMDE fall in the range of the values of the surfactants with lower CC by 30% compared to those of PEG200, indicating stronger hydrophilic interactions. The UCT values of PEG 200 are found to be near the values of the salts and with equal strength of interactions.

The UCT value of benzene is equal to those of the tri- and divalent salts, which infers that the strength of the hydrophobic interactions of benzene with phenol is equal to those of the hydrophilic salts. The rational decrease in UCT values from benzene to chrysene proves that the π conjugated electrons weaken the hydrophobic interactions and their perturbation may initiate hydrophilic interactions. The greater decrease in the UCT value for naphthalene compared to that of anthracene denotes greater activity of the two adjacent rings. A decrease of 27.60 °C and 23.09% in UCT and CC values of the aromatics toluene and xylene rebukes the contribution of -CH_3. The smallest change in UCT values and a 3% decrease in CC from toluene to xylene infer that the electron withdrawing -CH_3 group seriously disrupts the resonance system of the π conjugation.

Actually, the trends of oxalic > formic, citric > succinic of UCT and succinic > citric acid of CC, and UCT of oxalic > formic > citric > succinic and CC of oxalic > succinic > formic > citric indicate stronger hydrophilic interactions [7-13] of -COO^- and -OH compared to those of the weaker hydrophobic interactions [13-17] of -CH_2- of succinic and citric acids. Therefore, this basicity increases the UCT and CC values by 5.5%, but the equal number of -OH and 2-CH_2- and 1-CH- of glycerol find UCT trend to be glycerol > 0.4 m urea > 0.6 m urea with a reverse trend for CC values. This weakens the hydrophilic interactions [18,19] of the 3-OH of glycerol, which outweighs those of urea by 0.6% and citric acid by 23.3%.

The order of citric acid > glycerol for CC with reverse UCT values shows that -OH and -CH_2- increase mutual solubility. The order of TEAB > CPB > CPC > CTAB for UCT and the order of CPC > CTAB > CPB > TEAB for CC, and the order of LDS > SDS for UCT with equal CC values infer the polarizability [19-21] of the tetraethyl, cetyl and dodecyl alkyl chains. Four C_2H_5- groups cause stronger

hydrophobic interactions [20] and an ammonium ion causes hydrophilic interactions resulting in higher UCT and lower CC values where the cetyl and dodecyl alkyl chains of CPC, CPB, CTAB, LDS, and SDS show weaker interactions. The lower UCT and higher CC values of surfactants [20,22] compared to salts, acids and aromatics indicate stronger hydrophilic and hydrophobic interactions.

In general the UCT and CC values (Table 1) show an inverse relation with each other except in the salts, while the rest of the additives develop hydrogen bonds due to van der Waals forces. Halide salts of sodium increase in UCT values in the order of NaI > NaBr > NaF > NaCl, which reflects prominent anion-water interactions. The potassium halide salts show the order to be KI > KCl > KBr, with stronger I--water interactions. The differences between Na^+ and K^+ are due to the difference in size by one 3s to 4s orbital, respectively, which results in the weakening of Br--water interactions by 5.6%. Also, the NaI > NaBr > NaCl > NaF, KI > KBr > KCl order of CC supports this trend. Br--water interactions are stronger in the association of Na^+ than K^+. Thus, the larger the size of the anion, the stronger the interactions, and visa versa.

The Cl^- also seems to enhance Cl--water associations, however, the Cl^- series is similar to that of Rb^+, with increasing cation size, UCT values increase by 7.5 and 0.7% for Na^+ and K^+, respectively. The I^- of NaI increases the UCT values by 5.3% compared to that of KI. Therefore, salts of halide anions in association with smaller cations develop stronger hydration than those of the larger cations; however, a larger anion like I^- in combination with a smaller cation possesses a greater UCT value. This infers that the size of either the cation or anion affects the interactions. But Br^- with a group cation like $NH4^+$ exceeds the UCT %shift of Na^+, K^+ and Rb^+, hence $NH4^+$-water interactions are stronger and withstand a greater temperature. Thus, with Br^- salts, all the hydrogens are strongly involved in hydrogen bonding with water. In contrast, with SCN^-, the UCT decreases by 10.8 and CC increases by 45.45%. Thus the SCN^- develops stronger hydrophobic interactions with phenol.

Notably, when we exchange divalent cations like Mg^{2+} for Ca^{2+} in the halide salts (Table 1), there is a sizeable increase in UCT and CC values with a lower percent shift for Sr^{2+}. The F^- with Ca^{2+} there are lower %shifts in UCT and CC values than those of the Cl^- salts, which is attributed to the low solubility

of CaF_2 in water. Thus, the dissociation of CaF_2 and NaCl remains unaffected in phenol.

The trivalent cations reported a higher %UCT shift except in $CrCl_3$. $FeCl_3$ has two points and $AlCl_3$ reports maximum% shift in CC that may be due to a vacant 3p orbital. Its cloudy solutions could provide a medium for breaking the hydrogen bonding of phenol and water. However, for the second UCT the shift in CC is very low. The stronger Al^{3+}-water interactions with maximum %CC shift results in the destabilization of phenol by Al^{3+}. $FeCl_3$ causes much stronger Fe^{3+}-water interactions than those of other salts.

The monobasic acids have lower %shifts in UCT and CC values, inferring stronger hydrophobic interactions of $-COO^-$ with an increase in UCT values by 0.5% from acetic acid where CH_3COO^- may interact both with phenol and water, and form a partial dimer of acetic acid that may contribute too. However, the decrease in UCT and CC values is seen more with oxalic acid, which decreases with the introduction of $-CH_2-$ from succinic acid to citric acid. Alcohols show a mixed trend of values.

Urea and $-CH_3$ substituted N-urea cause hydrophobic interactions (Table 1), the $-CH_3$ contribution from urea to methylurea is 1.1% (°C) but the shift in CC is 25.65%. From methylurea to dimethylurea this shift is 1.0% for the UCT and 1.0% for CC. This infers that dimethylurea changes hydrophilic interactions to hydrophobic.

Aromatic hydrocarbons report that π conjugation decreases the UCT in a ratio of 44:24.8:5.1:3.3 ratio for $3\pi:5\pi:7\pi:9\pi$ with a deeper decrease in CC for naphthalene. As with resonance energy, this ratio can be another critical thermodynamic criterion to define the role of the electron in the behavior of aromatics. The addition of $-CH_3$ to toluene resulting in xylene has no shift in UCT values, but CC decreases by 133.14% infers that the $-CH_3$ is an electron withdrawing group associated with urea and benzene that decreases the UCT and CC values, which verifies that electron withdrawing groups do strengthen hydrophobic interactions. Surfactants interact with both phases, but anionic surfactants interact more strongly than cationic and nonionic surfactants.

CONCLUSIONS

In general, the cations of the alkali metals of the IA group

in association with Cl⁻ increase the UCT and CC values as the cations increase in size, and those associated with I⁻ decrease both values. However, when Br⁻ is associated with the group cation NH_4^+ the figures are enhanced. But NH_4^+ in association with SCN^- has a lower UCT than NH_4Br, but a higher CC. Comparatively, the cation of chloride salts of the IIA group had UCT and CC values that became larger with the cation size, but these values for Ca^{2+} are higher even than Sr^{2+}, with the highest CC of all the additives. The nonionic additives have higher UCT and lower CC values than the mono and tribasic acids with values almost equal to the dibasic acids; these are also lower than those of the salts. Urea and the N-ureas average equal UCT and higher values of CC compared to the nonionic surfactants. The aromatic hydrocarbons have greater UCT and CC values; however, they decrease with the number of π conjugation bonds. Benzene derivatives report lower values for both characteristics compared to the rest of the additives, except the carboxylic acids.

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