PHYSICAL EXTRACTION OF PROPIONIC ACID

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ABSTRACT

Extraction of propionic acid was studied using different diluents (aliphatic hydrocarbons, aromatic hydrocarbons, esters, alcohols and ketone). The data were presented in terms of distribution coefficient, partition coefficient (P) and dimerization constants (D). The differences in degree of extraction of propionic acid by these diluents were explained in terms of relative permittivity, dipole moment and E_T values. The value of P and D shows that there is a close relation between these values and the chemical nature of solvent. Attempts have been made to correlate $K_D^{diluent}$ with the physico-chemical parameters of the diluents chosen. However, no general correlation could be found. So it is necessary to have an empirical parameter that should give assessment of solvation energy of the solute and show the effect of intramolecular forces better. The parameters used in the study E_T parameter. It is found that higher the E_T value of the solvent higher is the $K_D^{diluent}$.Effect of temperature on P and D was also studied. Diluents oleyl alcohol, ethyl acetate, MIBK, 1-decanol and 1-octanol were used for the study. In alcohols P was found to increase with increase in temperature, however, for ethyl acetate and MIBK it decreases. ΔH and ΔS values were also calculated for the physical extraction of carboxylic acids using 1-octanol. It can be seen that ΔH and ΔS values were positive, thus the partitioning process is endothermic and is entropy driven process and the order of system increases.

Keywords*: Propionic acid, Extraction, Temperature, Partition coefficient, Dimerization constant*

1. INTRODUCTION

Physical extraction involves the extraction of solute into inert non reacting hydrocarbons and substituted hydrocarbons and is relatively free of complexities. Two factors need to be accounted to show the influence of diluents on the extraction: (a) partial dissociation of the acids in aqueous phase and (b) dimerization in the hydrocarbon phase. Another important parameter particularly in carbon bonded oxygen donor solvents is the water of hydration (Kertes and King, 1986). High attraction of binding of the acid with the water molecules requires large amount of solvent molecules so that they can compete with the water molecules that hydrate the acid at the interface. There are number of ways by which solvents for physical extraction can be classified. On the basis of molecular structure, they are classified as polar protic, dipolar aprotic and non-polar solvents.
Polar protic solvents: A polar protic molecule consists of a polar group OH and a non-polar tail.
Dipolar aprotic solvents: Dipolar aprotic molecules possess a large bond dipole moment (a measure of polarity of a molecule chemical bond). They do not contain OH group.
Non-polar solvents: Electric charge in the molecules of non-polar solvents is evenly distributed; therefore the molecules have low dielectric constant. Non-polar solvents are hydrophobic (immiscible with water). Non-polar solvents are liphophilic as they dissolve non-polar substances such as oils, fats, greases.
On the basis of nature, solvents are classified as inorganic and organic solvents.
Inorganic solvents: The most popular inorganic (not containing carbon) solvents are water (H_2O) and aqueous solutions containing special additives (surfactants, detergents, pH buffers and inhibitors). Other inorganic solvents are liquid anhydrous ammonia (NH_3), concentrated sulfuric acid (H_2SO_4), sulfuryl chloride fluoride (SO_2ClF).
Organic solvents: These are further subdivided into two types:
Oxygenated solvents: Oxygenated solvents are organic solvent, molecules of which contain oxygen. Oxygenated solvents are widely used in paints, inks, pharmaceuticals, fragrance sectors, adhesives, cosmetics, detergents, food industries. Examples of oxygenated solvents*:* alcohols, glycol ethers, methyl acetate, ethyl acetate, ketones, esters, and glycol esters.
*Hydrocarbon solvents***:** Molecules of hydrocarbon solvents consist only of hydrogen and carbon atoms. They are classified as

Aliphatic solvents:
Aliphatic solvents are having straight chain structure. Examples include hexane, kerosene, heptane etc.
Aromatic solvents:
Molecules of pure aromatic solvents have benzene ring structure. Examples of pure aromatic solvents are benzene, toluene and xylene.
Halogenated solvents
Halogenated solvent is an organic solvent, molecules of which contain halogenic atoms: chlorine (Cl), fluorine (F), bromine (Br) or iodine.
Natural solvents
There are solvents which are obtained from natural products like sunflower seeds (sunflower oil), coconut (coconut oil) etc.

Table 1: Partition and dimerization constants for extraction of different carboxylic acid using different diluents.

Diluent	P	D (l/mol)	Diluent	P	D (l/mol)
nitrobenzene	0.524	--	chloroform	0.110	30
15 % chloroform + n-heptane	0.008	0.007	nitrobenzene	0.160	11
n-hexane	0.005	9000	diethyl ather	1.750	0.1
chlorohexane	0.006	6500	diisopropyl ether	0.800	0.5
benzene	0.043	190	MIBK	2.150	--
toluene	0.034	230	cyclohexanone	3.300	--
xylene	0.030	310	n-butanol	3.200	--
carbon tetrachloride	0.015	940	n-pentanol	2.950	--

Kertes and King, (1986) presented the extraction of propionic acid using different diluents and the results have been reported in Table 1. The values of partition, dimerization and overall distribution coefficients have been stated. Very limited studies on physical extraction of propionic acid (that too scattered), can be found in literature. In view of this, in this chapter, the extraction of propionic acid was studied using different diluents: (a) aliphatic hydrocarbons: heptane, hexane, paraffin liquid, petroleum ether and kerosene; (b) aromatic hydrocarbons: benzene, toluene; (c) esters: butyl acetate, ethyl acetate; (d) alcohols: 1-octanol, 2-octanol, 1-decanol, 1-dodecanol, oleyl alcohol; and (e) ketone: MIBK. The data were presented in terms of distribution coefficient, partition coefficient and dimerization constants.

2. THEORY

Carboxylic acids mainly exist as dimmers in the organic phase owing to strong intermolecular hydrogen bonding, especially in non polar or slightly polar diluents. On the contrary, in the aqueous phase, they existed as monomers because of the intermolecular hydrogen bonding between the acids is destroyed owing to their preferential hydrogen bonding with the water molecules. At the pH less than the pKa values of acid, the acid can be assumed to be transferred into organic solvent by the following mechanism:
i) Ionization of the acid in the aqueous phase:

$$[HA]_{aq} \leftrightarrow H^+ + A^- \tag{1}$$
$$K_{HA} = [H^+][A^-] / [HA] \tag{2}$$

ii) Partition of the undissociated molecular acid between the two phases, aqueous (aq) and organic (org):

$$[HA]_{aq} \leftrightarrow [HA]_{org} \tag{3}$$
$$P = [HA]_{org} / [HA]_{aq} \tag{4}$$

iii) Dimerization of the acid in the organic phase:

$$2[HA]_{org} \leftrightarrow [HA]^2_{org} \tag{5}$$
$$D = [HA]_{2,org} / [HA]^2_{org} \tag{6}$$

Overall distribution coefficient is defined as the ratio of total (analytical) concentration of acid in all its forms (by partition, dimmers and as complexes) in organic phase and total (analytical) concentration of all its existing forms (dissociated and undissociated) in aqueous raffinate (Keshav et al., 2009f). It includes the effects like ionic strength, nature of ion concentration of H$^+$ etc. of solution constituents. For physical extraction, distribution coefficient can be defined as:

$$K_D^{diluent} = \frac{P + 2P^2 D[HA]_{aq}}{1 + K_{HA}/[H^+]_{aq}} \tag{7}$$

Under the experimental condition that pH of the aqueous solution was smaller than pKa of the acid (4.88) (Playne, 1985) and since, dilute solutions of acids were taken ($0.05 - 0.4$ kmol/m^3), effect of the acid dissociation was negligibly small. Thus the denominator term can be safely neglected and equation (7) can be modified to get

$$K_D^{diluent} = P + 2P^2 D[HA]_{aq} \qquad\qquad (8)$$

King and King (1986) stated that the values of P and D obtained by above equation may be misleading on account of two reasons: first, the degree of hydration of acid in organic phase is unknown and varies with concentration and second; the partition process defined by equation (7) requires quantities that measure the activity of the distribuend; the activity coefficient of the species in both phases and partition coefficient values in mol fraction scale.

3. EXPERIMENTAL

3.1. Chemicals

Propionic acid and the diluents: heptane, hexane, petroleum ether, paraffin liquid, kerosene, benzene, toluene, hexanol, 1-decanol, 1-octanol, 2-octanol, 1-dodecanol, oleyl alcohol, MIBK, butyl acetate, ethyl acetate are of technical grade and were used as supplied by suppliers. The various specifications of the diluents are given in Table 2. Distilled water was used to prepare the solutions of various concentrations of propionic acid solutions. NaOH used for titration is of analytical grade and was supplied by Ranbaxy, India. For the standardization of the NaOH, oxalic acid (99.8%) was obtained from s. d. Fine-Chem. Ltd., India. Phenolphthalein solution (pH range 8.2 to 10.0) was used as indicator for titration and was obtained from Ranbaxy, India. The initial aqueous acid concentrations range ($[HA]_o$) of (0.05 to 0.4) kmol/m^3 were used. Low concentration was used because propionic acid concentration in the fermentation broth is not greater than 0.5 kmol/m^3 (Lewis and Yang, 1992).

Table 2: List and specification of various diluents used for the extraction of propionic acid.

Solvents	MW	Molecular formula	Make	Purity (%)
Hexane	86.18	C_6H_{14}	Ranbaxy Ltd., India	99.5
n-Heptane	100.2	C_7H_{16}	Ranbaxy Ltd., India	99.0
Petroleum ether	87-114	-	s. d. Fine Chem. Ltd., India	99.0
Kerosene	170	-	-	-
Benzene	78.11	C_6H_6	Ranbaxy Ltd., India	99.0
Toluene	92.17	$C_6H_5CH_3$	Nice Ltd., India	99.0
Paraffin liquid (L)	-	-	RFCL Ltd., India	99.0
Paraffin liquid (H)	-	-	RFCL Ltd., India	99.0
Butyl acetate	116.16	$C_6H_{12}O_7$	SRL Ltd., India	98.0
Ethyl acetate	88.106	$C_4H_8O_2$	RFCL Ltd., India	99.0
MIBK	100.16	$CH_3COC_4H_9$	Ranbaxy Ltd., India	99.0
1-hexanol	102.2	$C_6H_{14}O$	Himedia India ltd.	99.0
1-Octanol	130.28	$CH_3(CH_2)_7\,OH$	Himedia India ltd.	98.0
2-octanol	130.3	$C_8H_{18}0$	Himedia India ltd.	99.0
1-Decanol	158.29	$CH_3(CH_2)_9OH$	Himedia India ltd.	98.0
Dodecanol	186.34	$CH_3(CH_2)_{11}\,OH$	Acros, USA	99.0
Oleyl alcohol	268.49	$C_{18}H_{36}O$	s. d. Fine Chem. Ltd., India	98.0

3.2. Procedure

Extraction experiments involve shaking of equal volumes of aqueous and organic phases for 12 h at constant temperature (305 K) in orbital shaking incubator (Metrex Scientific Instruments (P). Ltd. India) at 190 rpm, followed by settling of the mixture for at least 2 h at the same temperature in separating funnels maintained at that temperature in an incubator. Aqueous phase pH was measured by an Orion 3 star pH meter (Thermo Electro Corporation). Aqueous phase acid concentration was determined by titration with sodium hydroxide solution (0.02 N). The acid content in the organic phase was determined by a mass balance.

4. RESULTS AND DISCUSSION

Figures 1(a – d) show the physical equilibria for extraction of propionic acid using aliphatic and aromatic hydrocarbons (hexane (Keshav et al., 2008b,c), , heptane (Keshav et al., 2008b,c,d; 2009a,c),, benzene (Keshav et

al., 2008b), toluene (Keshav et al., 2008b; 2009a), long chain aliphatic hydrocarbons mixture (paraffin liquid light (Keshav et al., 2008b,c), paraffin liquid heavy (Keshav et al., 2008b), petroleum ether (Keshav et al., 2008b,d,f; 2009a,c), kerosene), oxygenated diluents (ethyl acetate (Keshav et al., 2008d, 2009d), butyl acetate (Keshav et al., 2008b), methyl iso butyl ketone (Keshav et al., 2009h,e,f) and alcohols (hexanol (Keshav et al., 2009h), 1-octanol (Keshav et al., 2008a), 2-octanol (Keshav et al., 2009d), 1-decanol (Keshav et al., 2009c,d,f,h), do decanol (Keshav et al., 2008b), oleyl alcohol (Keshav et al., 2008d; 2009b)) respectively. Extraction was found to follow the trend alcohols > oxygenated diluents > aromatic hydrocarbons > aliphatic hydrocarbons > long chain aliphatic hydrocarbons mixture. This suggests that alcohols and oxygenated diluents are most effective in physical extraction of propionic from dilute solutions. With increase in acid concentration, $K_D^{diluent}$ was found to be nearly constant for alcohols and ketone, however, for aliphatic and aromatic hydrocarbons there is abrupt increase in $K_D^{diluent}$ values at high acid concentration (Table 3).

The reason of the behavior can be explained as follows. The extent of hydration of the acid and energy of the bond to water molecules are the two factors that affect extractability. Aliphatic hydrocarbons (hexane, heptane, kerosene, petroleum ether etc.) have very low solubility in water, so they behave close to ideality in term of volume changes when propionic acid at low concentration partitions between them. To obtain complete miscibility in the phases, very high concentration of propionic acid is required. At high acid content i.e. in water deficient situation, the solvation sheath around propionic acid is composed of both water and solvent molecules, thus making the solute species more like organic solvent. Thus appearance of abrupt value of $K_D^{diluent}$ at higher acid concentration was observed.

Aliphatic and aromatic hydrocarbons (hexane, heptane, benzene, toluene, paraffin liquid light, paraffin liquid heavy, petroleum ether and kerosene) are apolar aprotic solvents and are characterized by low relative permittivity(ε), low dipole moment, low E_T value and are unable to act as an hydrogen bond donor. So these solvents interact only slightly with the acid since only the non specific directional, induction and dispersion forces are operating giving very low $K_D^{diluent}$ values. Esters: butyl acetate, ethyl acetate, and ketone: MIBK on the other hand are dipolar aprotic solvents and have large relative permittivity (ε), dipole moment, and E_T values. Though these solvents do not act as hydrogen bond donors since C-H bonds are not sufficiently polarized, still they provide high $K_D^{diluent}$ values due to presence of ion electron pairs. Anion solvation occurs mainly by ion-dipole and ion-induced dipole forces. The latter are important for large, polarizable, soft anions, with low charge density. Therefore although these solvents tend to be poor anion solvators, they are usually better, the larger and softer the anion. Alcohols, considered as protic solvents, contain hydrogen atoms bound to electronegative element O (-O-H), are hydrogen bond donors. Their relative permittivity (ε) and E_T value are large, indicating them to be strongly polar. Thus they provide high $K_D^{diluent}$ values since they are good anion solvators due to their hydrogen bonding ability. The tendency becomes more pronounced as the charge density (ratio of charge to volume) of the anion to be solvated increases. Further alcohols are capable of being both acceptors and donors, as are the acids; give the highest $K_D^{diluent}$ followed by purely basic solvents such as ethers and ketones.

Table 3 shows the physical equilibria for extraction of propionic acid using different solvents. Partition (*P*) and dimerization (*D*) coefficients were also evaluated. Mutual solubility between an aqueous solution and a given solvent at fixed temperature is affected by the nature of distribuend and its total concentration in the system. Propionic acid is a weak carboxylic acid and mutual solubility's can cause dramatic volume changes particularly at higher acid concentrations. Mutual solubility increases the volume of organic layer at the expense of that of aqueous phase in equilibrium and it increases with increase in acid concentration. Another important thing to be mentioned here is that the values of *P* and *D* are not the values obtained by pure water and solvent phases. These are obtained by mutual saturation of the two phases, obtained by equilibrium between two mutually saturated phases rather that between pure water and solvent. However since only dilute concentrations of acid were taken in study (0.05 – 0.4 kmol/m³), there is low solubility of the phase and thus there is not much variance between these values and values from pure media.
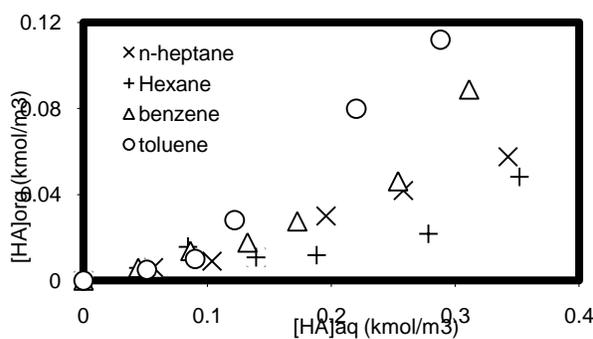
Figure 1 (a): Physical extraction equilibrium curves for extraction of propionic acid using different diluents (heptane, hexane, benzene and toluene)

Figure 1 (b): Physical extraction equilibrium curves for extraction of propionic acid using different diluents (paraffin liquid light, petroleum ether, paraffin liquid heavy and kerosene)
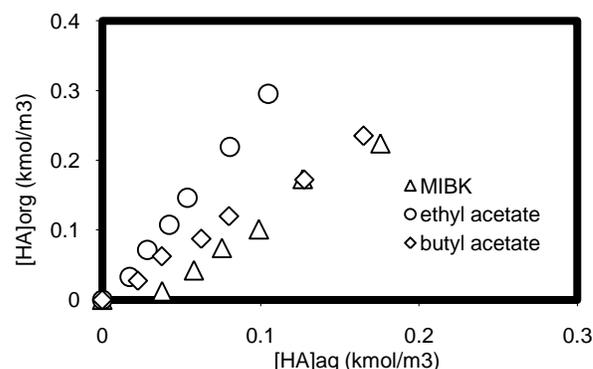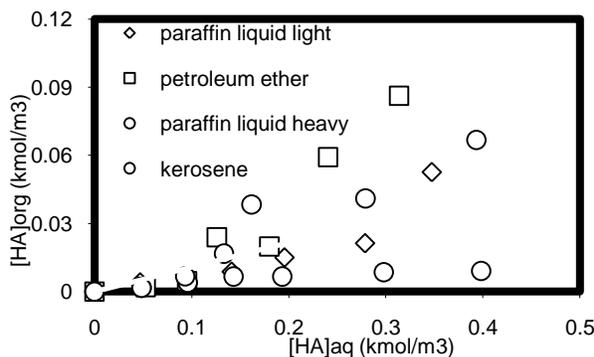

Figure 1 (c): Physical extraction equilibrium curves for extraction of propionic acid using different diluents (methyl isobutyl ketone (MIBK), ethyl acetate and butyl acetate)
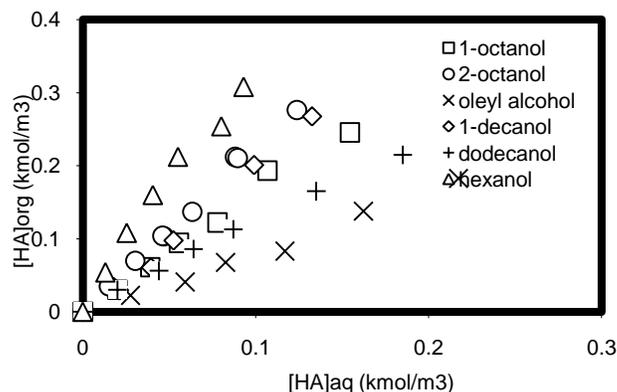

Figure 1 (d): Physical extraction equilibrium curves for extraction of propionic acid using different diluents (1-octanol, 2-octanol, oleyl alcohol, 1-decanol, 1-dodecanol and hexanol)

The values of P and D listed in Table 3 shows that there is a close relation between these values and the chemical nature of solvent. Alcohols as already discussed, are capable of being both acceptors and donors, thus expected to provide highest partitions coefficients (P). The D values on the other hand are very small or negligible due to stronger solute-solvent hydrogen bond in comparison to solute-solute bond, which would have lead to form dimmers. Thus, it can be ascertained that the values of P and D are inversely proportional to each other.

A number of studies have been made to carry out the influence of diluents on extraction equilibrium. Some of them quote a relationship between the distribution coefficient and other physico-chemical diluent parameters such as dielectric constant, dipole moment etc (Diamond, 1936; Kozime, 1987). In presented studies, attempts have been made to correlate $K_D^{diluent}$ with the physical parameters of the diluents chosen. The various physical properties of diluents used for comparison are given in Table 4. It can be found that higher $K_D^{diluent}$ values are obtained with higher dipole moment, higher dielectric constant, and lower log P values of the diluent except for alcohols. Further among the diluents of similar type specific observation can be defined. Among aliphatic hydrocarbons (hexane and heptane), it can be found that lower the molecular weight, lower the density and higher the refractive index of the solvent, higher is the $K_D^{diluent}$ value. Among benzene and toluene, introduction of side chain in toluene caused increase in $K_D^{diluent}$ value. Alcohols show an arbitrary behavior. $K_D^{diluent}$ was found to increase with increase in chain length from 1-octanol and 1-decanol when the OH group is at first carbon atom, however when OH is at second carbon atom (2-octanol) the values were much higher than the above two diluents (1-octanol and 1-decanol).

Lower alcohol 1-hexanol was found to give extremely high value of K_D^{diluent} in comparison to all other alcohols. The probable reason for that may be the high solubility is water of the former (0.59 g/100 ml at 20°C). Another alcohol, oleyl alcohol, because of its high viscosity failed to extract the acid physically thus yielding very low K_D^{diluent} values, much lower than even the active diluents.

Table 3: Physical equilibria of extraction of propionic acid using different diluents

Diluent	$[HA]_o$ kmol/m³	$[HA]_{aq}$ kmol/m³	$[HA]_{org}$ kmol/m³	K_D^{diluent}	E%	pH$_{aq}$	P	D m³/kmol
hexane	0.05	0.044	0.006	0.134	11.80	3.17	0.045	53.802
	0.1	0.084	0.016	0.187	15.72	3.01		
	0.15	0.139	0.011	0.078	7.23	2.89		
	0.2	0.188	0.012	0.063	5.92	2.82		
	0.3	0.278	0.022	0.078	7.23	2.73		
	0.4	0.352	0.048	0.137	12.05	2.68		
n heptane	0.05	0.056	0.006	0.106	9.61	3.11	0.076	24.710
	0.1	0.104	0.009	0.087	7.99	2.96		
	0.15	0.139	0.011	0.077	7.16	2.89		
	0.2	0.196	0.031	0.160	13.77	2.81		
	0.3	0.258	0.042	0.162	13.96	2.75		
	0.4	0.342	0.058	0.168	14.38	2.69		
paraffin liquid(L)	0.05	0.047	0.004	0.085	7.86	3.15	0.051	18.454
	0.1	0.096	0.004	0.043	4.10	2.98		
	0.15	0.141	0.009	0.062	5.81	2.89		
	0.2	0.196	0.015	0.077	7.12	2.81		
	0.3	0.279	0.021	0.076	7.09	2.73		
	0.4	0.347	0.053	0.151	13.14	2.68		
paraffin liquid(H)	0.05	0.048	0.002	0.034	3.33	3.15	0.050	-
	0.1	0.096	0.004	0.042	4.00	2.98		
	0.15	0.143	0.007	0.047	4.44	2.88		
	0.2	0.193	0.007	0.034	3.33	2.81		
	0.3	0.298	0.002	0.007	0.67	2.72		
	0.4	0.398	0.002	0.004	0.42	2.65		
petroleum ether	0.05	0.053	0.002	0.038	3.65	3.12	0.009	5595.945
	0.1	0.095	0.005	0.049	4.64	2.98		
	0.15	0.126	0.024	0.190	15.96	2.91		
	0.2	0.180	0.020	0.110	9.92	2.83		
	0.3	0.241	0.059	0.246	19.74	2.76		
	0.4	0.314	0.086	0.275	21.56	2.71		
kerosene	0.05	0.048	0.002	0.034	3.33	3.15	0.170	-
	0.1	0.093	0.007	0.071	6.67	2.98		
	0.15	0.133	0.017	0.125	11.11	2.90		
	0.2	0.162	0.038	0.237	19.17	2.86		
	0.3	0.251	0.049	0.195	16.33	2.74		
	0.4	0.393	0.007	0.017	1.67	2.66		

	0.05	0.044	0.006	0.134	11.80	3.17		
	0.1	0.086	0.014	0.160	13.76	3.00		
benzene	0.15	0.132	0.018	0.134	11.80	2.90	0.031	400.110
	0.2	0.172	0.028	0.160	13.76	2.84		
	0.3	0.254	0.046	0.182	15.39	2.75		
	0.4	0.311	0.089	0.286	22.21	2.71		
	0.05	0.046	0.004	0.087	7.99	3.13		
	0.1	0.090	0.010	0.111	10.00	2.99		
toluene	0.15	0.122	0.028	0.230	18.73	2.92	0.084	77.844
	0.2	0.139	0.061	0.439	30.46	2.69		
	0.3	0.220	0.080	0.363	26.64	2.78		
	0.4	0.288	0.112	0.389	28.00	2.73		
	0.05	0.023	0.028	1.222	55.00	3.35		
	0.1	0.038	0.063	1.667	62.50	3.21		
butyl acetate	0.15	0.063	0.088	1.400	58.33	3.08	1.468	-
	0.2	0.080	0.120	1.500	60.00	3.02		
	0.3	0.128	0.173	1.353	57.50	2.91		
	0.4	0.165	0.235	1.424	58.75	2.85		
	0.05	0.017	0.033	1.914	65.68	3.42		
	0.1	0.028	0.072	2.529	71.66	0.00		
ethyl acetate	0.15	0.042	0.108	2.551	71.84	3.18	2.391	0.368
	0.2	0.054	0.146	2.726	73.16	3.12		
	0.3	0.081	0.219	2.724	73.15	0.00		
	0.4	0.105	0.295	2.820	73.82	2.96		
	0.05	0.037	0.013	0.347	25.75	3.22		
	0.1	0.054	0.046	0.865	46.38	3.12		
MIBK	0.15	0.069	0.081	1.182	54.17	3.06	0.670	4.283
	0.2	0.088	0.112	1.273	56.00	3.00		
	0.3	0.121	0.179	1.479	59.67	2.92		
	0.4	0.157	0.243	1.552	60.81	2.86		
	0.05	0.013	0.054	4.140	80.54	3.12		
	0.1	0.025	0.108	4.261	80.99	2.95		
hexanol	0.15	0.041	0.160	3.950	79.80	2.86	4.505	-
	0.2	0.055	0.212	3.860	79.42	2.84		
	0.3	0.080	0.254	3.176	76.05	2.75		
	0.4	0.093	0.308	3.311	76.80	2.71		
	0.05	0.020	0.030	1.500	60.00	3.38		
	0.1	0.039	0.061	1.572	61.12	3.20		
1- octanol	0.15	0.056	0.094	1.700	62.97	3.11	1.735	0.118
	0.2	0.078	0.122	1.572	61.12	3.03		
	0.3	0.107	0.193	1.813	64.45	2.95		
	0.4	0.154	0.246	1.590	61.39	2.87		

	0.05	0.015	0.035	2.306	69.75	3.46		
	0.1	0.030	0.070	2.306	69.75	3.27		
2-octanol	0.15	0.047	0.103	2.209	68.83	3.16	2.310	0.025
	0.2	0.063	0.137	2.162	68.38	3.08		
	0.3	0.088	0.212	2.409	70.67	3.00		
	0.4	0.124	0.276	2.232	69.06	2.92		
	0.05	0.021	0.029	1.397	58.27	3.37		
	0.1	0.039	0.061	1.546	60.73	3.20		
1 decanol	0.15	0.052	0.098	1.865	65.09	3.13	1.406	-
	0.2	0.147	0.053	0.358	26.37	2.88		
	0.3	0.099	0.201	2.030	67.00	2.97		
	0.4	0.133	0.267	2.018	66.86	2.90		
	0.05	0.020	0.030	1.500	60.00	3.38		
	0.1	0.044	0.056	1.273	56.00	3.17		
dodecanol	0.15	0.064	0.086	1.344	57.33	3.08	1.405	-
	0.2	0.087	0.113	1.299	56.50	3.00		
	0.3	0.135	0.165	1.222	55.00	2.90		
	0.4	0.185	0.215	1.162	53.75	2.82		
	0.05	0.028	0.023	0.818	45.00	3.29		
	0.1	0.059	0.041	0.691	40.88	3.10		
oleyl alcohol	0.15	0.083	0.068	0.818	45.00	3.01	0.702	0.682
	0.2	0.117	0.083	0.711	41.56	2.93		
	0.3	0.162	0.138	0.849	45.92	2.85		
	0.4	0.217	0.183	0.841	45.69	2.79		

The above results prove that the extractability of the acid may be correlated to some extent with the physico-chemical properties of the solvents, yet no general correlation could be found. The reason for that may be that the effect of diluent is determined by the ratio of the contribution of the solvation of acid to the free energy of extraction. Solvation is a complex mechanism and depends on different kinds of intermolecular forces which cannot be merely stated in terms of the above physicochemical parameters. However, K_D^{diluent} can be proposed to depend on the mechanism of extraction and nature of diluents used. Rozen (1962) correlated the influence of the diluent on the extraction with zero activity coefficients. However, the correct expression for effect of diluent on extraction equilibrium, requires paying attention on the method of expressing the distribution coefficient. In order to avoid the complications of effect of molecular and specific weights of the diluents, it is better to use mole fraction instead of activity to express the influence of diluent. Further it is necessary to extrapolate the distribution coefficient to extremely dilute solutions in order to eliminate the concentration activity coefficients.

Assuming the mutual solubility of water and diluent to be negligible, K_D^{diluent} can be expressed as

$$K_D^{\text{diluent}} = C / \gamma_o \quad or \quad \log K_D^{\text{diluent}} = \log C - \log \gamma_o \tag{9}$$

Where, γ_o is the zero activity coefficient of the acid in the solvent phase and C is a constant. The zero activity coefficients specifies the transfer energy of a substance passing from an infinitely dilute solution into the pure state and is determined by the energy of the crystal lattice of the distributed solute, less the energy of its solvation by the solvent. Since the energy of the crystal lattice for a given distributed solute is constant, $\log K_D^{\text{diluent}}$ should be a linear function of its solvation energy. So it is necessary to have an empirical parameter that should give assessment of solvation energy of the solute and show the effect of intramolecular forces better. The parameters most frequently used are Z parameter (Kosower , 1958) which account for the influence of the solvent on the position of the charge transfer band in the spectrum of alkylpyridine iodide, and the E_T parameter (Dimroth, 1963) which is based on the absorption spectrum of pyridinium-N-phenol-betaine. In these co-ordinates, which are in satisfactory agreement with each other, the position of the charge transfer band (kcal/mol) is used as the characteristic of the solvent. E_T was used

here to describe the effect of solvent polarity on $K_D^{diluent}$ since it has been determined for number of solvents. Table 5 shows the $K_D^{diluent}$ values against the E_T values of the corresponding solvents. It is found that higher the E_T value of the solvent higher is the $K_D^{diluent}$. Some discrepancy arises in the case of extraction using ethyl acetate and oleyl alcohol, where high water solubility and highly viscous nature of respective diluents can be the cause of their abruptly higher and abruptly lower $K_D^{diluent}$ values obtained, respectively.

Table 4: Various physicochemical properties of diluents chosen in extraction of propionic acid.

Solvents	MW	molecular structure	BP ºC	MP ºC	Solubility in water	ρ g/cm³	RI	μ cP	ε	Log (P)	DM	E_T
Hexane	86.18	C_6H_{14}	68.7	-95	immiscible	0.671	1.3723	0.294	2.0	3.70	0.08	31.0
n-Heptane	100.2	C_7H_{16}	98	-90.61	immiscible	0.6795	1.3851	0.386	1.9	4.66	0	31.1
Petroleum ether	87-11	--	20-75	-73	immiscible	--	--	--	--	--	--	--
Kerosene	170	--	147	-73	Insoluble	0.817	1.443	--	1.8	--	--	--
Benzene	78.11	C_6H_6	80.9	5.5	1.79 g/l	0.873	1.4979	0.652	2.3	2.13	0	34.3
Toluene	92.17	$C_6H_5CH_3$	110.6	-93	0.053g/100 ml	0.865	1.497	0.590	2.379	2.69	0.36	33.9
Paraffin liquid (L)	--	--	--	--	--	0.820-0.880	1.473-1.483	--	1.9-2.5	--	--	--
Paraffin liquid (H)	--	--	--	--	--	0.875-0.905	--	--	--	--	--	--
Butyl acetate	116.16	$C_6H_{12}O_7$	126	-78	0.7 g/100ml	0.879	1.394	0.832	5.1	1.82	1.84	38.5
Ethyl acetate	88.10	$C_4H_8O_2$	77.6	-84	very high	0.894	1.3704	0.426	6.0	0.73	1.88	38.1
MIBK	100.16	$CH_3COC_4H_9$	114-117	-84.7	1.91 g/100ml	0.829	1.395	0.58	12.4 (62 oF)	--	4.2	39.4
1-hexanol	102.2	$C_6H_{14}O$	151.8	-52	0.59g/100 ml	0.814	--	--	13.3	2.03	1.66	48.8
1-Octanol	130.28	$CH_3(CH_2)_7OH$	195	-15.5	0.30mg/l	0.827	1.4295	8.925	10.3	3.00	1.71	48.3
2-octanol	130.3	$C_8H_{18}O$	178.5	-38.6	0.096 ml /100 ml	0.820	1.424	--	--	2.72	--	48.2
1-Decanol	158.29	$CH_3(CH_2)_9OH$	230	7	0.37g/100 ml	0.827	1.4295	8.925	8.1	4.23	--	48.1
Dodecanol	186.34	$CH_3(CH_2)_{11}OH$	260-262	24	immiscible	0.831	1.4413	--	6.5	--	--	47.5
Oleyl alcohol	268.49	$C_{18}H_{36}O$	330-360	13-19	insoluble	0.845-0.855	1.461	--	--	--	--	49.0

BP: boiling point; MP: melting point; RI: refractive index; ρ: density of pure liquid; μ: viscosity; ε: dielectric constant; log(P): octanol water partition coefficient; DM: Dipole moment

Table 5 Effect of $K_D^{diluent}$ on E_T parameter.

Diluent	E_T	$K_D^{diluent}$	Diluent	E_T	$K_D^{diluent}$
hexane	31.0	0.063	dodecanol	47.5	1.299
n heptane	31.1	0.160	1 decanol	47.7	1.865
benzene	34.3	0.160	1- octanol	48.1	1.572
toluene	33.9	0.363	2-octanol	48.2	2.162
ethyl acetate	38.1	2.726	hexanol	48.8	3.780
MIBK	39.4	1.273	oleyl alcohol	49.0	0.711
butyl acetate	38.5	1.500			

Attempts were also made to correlate P and D values with the physico-chemical properties however no generalization could be made. It may be stated that alcohols (protic solvents) and esters and ketones (dipolar aprotic solvents) have higher P values and lower D values in comparison to aliphatic and aromatic hydrocarbons. The reason of this is the improved solvation of the acid by hydrogen bonding in case of alcohols and ion pair interactions in case

of esters and ketones. Kertes and King (1986) correlated partition coefficient with the interfacial tension of the solvent-water pair. The plot of log P versus interfacial tension was found to yield a straight line for solvents having interfacial tension value greater than 9 dynes/cm. The relation was valid in view of lipophilic-hydrophilic balance in the character of propionic acid.

Table 6: Effect of temperature on partition (P) and dimerization (D) coefficients for extraction of propionic acid using different diluents.

Diluent	Temp. K	$[HA]_o$ kmol/m^3	$[HA]_{aq}$ kmol/m^3	$[HA]_{org}$ kmol/m^3	$K_D^{diluent}$	$E\%$	pH_{aq}	P	D m^3/kmol
ethyl acetate	305	0.05	0.017	0.033	1.914	65.68	3.42	1.536	2.626
		0.1	0.042	0.058	1.367	57.76	3.18		
		0.2	0.054	0.146	2.726	73.16	3.12		
		0.4	0.105	0.295	2.820	73.82	2.96		
	313	0.05	0.021	0.029	1.431	58.86	3.37	1.358	1.752
		0.1	0.038	0.062	1.652	62.29	3.21		
		0.2	0.070	0.130	1.846	64.86	3.05		
		0.4	0.127	0.273	2.153	68.29	2.91		
	333	0.05	0.022	0.028	1.308	56.67	3.36	1.277	0.474
		0.1	0.040	0.060	1.500	60.00	3.20		
		0.2	0.095	0.105	1.105	52.50	2.98		
		0.4	0.150	0.250	1.667	62.50	2.87		
MIBK	305	0.05	0.029	0.022	0.754	43.00	3.28	0.707	10.550
		0.1	0.044	0.057	1.299	56.50	3.17		
		0.2	0.075	0.125	1.667	62.50	3.04		
		0.4	0.132	0.268	2.030	67.00	2.90		
	313	0.05	0.048	0.002	0.042	4.00	3.15	0.077	668.378
		0.1	0.072	0.028	0.389	28.00	3.05		
		0.2	0.105	0.095	0.913	47.71	2.96		
		0.4	0.166	0.234	1.406	58.43	2.85		
	333	0.05	0.048	0.002	0.034	3.33	3.15	0.011	37182.645
		0.1	0.065	0.035	0.538	35.00	3.07		
		0.2	0.100	0.100	1.000	50.00	2.97		
		0.4	0.163	0.237	1.449	59.17	2.85		
1-decanol	305	0.05	0.021	0.029	1.397	58.27	3.37	1.390	1.433
		0.1	0.039	0.061	1.546	60.73	3.20		
		0.2	0.147	0.053	0.358	26.37	2.88		
		0.4	0.133	0.267	2.018	66.86	2.90		
	313	0.05	0.021	0.029	1.431	58.86	3.37	1.404	0.400
		0.1	0.041	0.059	1.431	58.86	3.19		
		0.2	0.077	0.123	1.593	61.43	3.03		
		0.4	0.153	0.247	1.622	61.86	2.87		
	333	0.05	0.018	0.032	1.727	63.33	3.40	1.685	0.073
		0.1	0.037	0.063	1.727	63.33	3.22		
		0.2	0.077	0.123	1.609	61.67	3.03		
		0.4	0.143	0.257	1.791	64.17	2.88		
Oleyl alcohol	305	0.05	0.028	0.023	0.818	45.00	3.29	0.743	0.369
		0.1	0.059	0.041	0.691	40.88	3.10		
		0.2	0.117	0.083	0.711	41.56	2.93		
		0.4	0.217	0.183	0.841	45.69	2.79		
	313	0.05	0.024	0.026	1.083	52.00	3.33	0.751	0.354

Diluent	Temp								
		0.1	0.048	0.052	1.083	52.00	3.15		
		0.2	0.101	0.099	0.977	49.43	2.97		
		0.4	0.195	0.205	1.047	51.14	2.81		
	323	0.05	0.027	0.023	0.823	45.14	3.29		
		0.1	0.055	0.045	0.823	45.14	3.12	0.759	0.253
		0.2	0.117	0.083	0.716	41.71	2.93		
		0.4	0.216	0.184	0.852	46.00	2.79		
	333	0.05	0.027	0.023	0.882	46.86	3.30		
		0.1	0.046	0.054	1.161	53.71	3.16	0.972	0.218
		0.2	0.101	0.099	0.977	49.43	2.97		
		0.4	0.190	0.210	1.102	52.43	2.82		
2-octanol	305	0.05	0.015	0.035	2.306	69.75	3.46		
		0.1	0.030	0.070	2.306	69.75	3.27	2.289	-
		0.2	0.063	0.137	2.162	68.38	3.08		
		0.4	0.124	0.276	2.232	69.06	2.92		
	313	0.05	0.014	0.036	2.646	72.57	3.48		
		0.1	0.027	0.123	4.469	81.71	3.29	3.522	-
		0.2	0.062	0.138	2.241	69.14	3.09		
		0.4	0.117	0.283	2.431	70.86	2.93		
	333	0.05	0.013	0.037	2.750	73.33	3.49		
		0.1	0.025	0.125	5.000	83.33	3.32	3.835	-
		0.2	0.058	0.142	2.429	70.83	3.10		
		0.4	0.110	0.290	2.636	72.50	2.95		
1-octanol	298	0.05	0.014	0.036	2.472	71.20	3.47		
		0.1	0.056	0.144	2.571	72.00	3.11	2.391	0.391
		0.2	0.080	0.220	2.750	73.33	3.02		
		0.4	0.104	0.296	2.846	74.00	2.96		
	308	0.05	0.015	0.035	2.378	70.40	3.46		
		0.1	0.051	0.149	2.906	74.40	3.13	2.918	0.212
		0.2	0.076	0.224	2.927	74.53	3.03		
		0.4	0.104	0.296	2.846	74.00	2.96		
	318	0.05	0.012	0.038	3.054	75.33	3.51		
		0.1	0.050	0.150	3.004	75.03	3.14	3.022	0.075
		0.2	0.073	0.227	3.123	75.74	3.05		
		0.4	0.096	0.304	3.158	75.95	2.98		
	328	0.05	0.014	0.036	2.682	72.84	3.49		
		0.1	0.050	0.150	3.017	75.10	3.14	2.890	0.051
		0.2	0.077	0.223	2.898	74.35	3.03		
		0.4	0.100	0.300	2.991	74.94	2.97		

Effect of temperature on P and D was also studied (Keshav et al., 2009b,d). Diluents oleyl alcohol, ethyl acetate, MIBK, 1-decanol and 1-octanol were used for the study. 1-octanol has been used as diluent for particular applications in the field of environmental and medicinal industry. 1-octanol/water partition coefficient (P_{ow}), which is the quantitative parameter for accessing the interaction between aqueous phase and organic phase, is one of the most important parameters employed for estimating a chemical's environmental fate and toxicity. Table 6 shows the effect of temperature on physical extraction of propionic acid using ethyl acetate, MIBK, 1-octanol, 1-decanol and oleyl alcohol.

In alcohols P was found to increase with increase in temperature, however, for ethyl acetate and MIBK it decreases. None of diluents except MIBK have significant D values. Considering the particular significance of 1-octanol/water partition coefficient (P_{ow}), the thermodynamics of extraction was studied. For the physical extraction of carboxylic acids using 1-octanol, the changes in Gibbs free energy function (ΔG) of interaction between acid and biofilm indicating the various interactions in the partitioning process of acid transferring from water to lipid phase and thus judge the spontaneity of partition was calculated from the following equation

$$\Delta G = \Delta H - T\,\Delta S \qquad\qquad\qquad (10)$$

where ΔH and ΔS are enthalpy and entropy of partition process of acid transferring from water phase to lipid phase. ΔG is related to diluent/water partition coefficient as

$$\Delta G = -2.303\ RT \log P \tag{11}$$

where R is universal gas constant and T is temperature in K. Combining equations (10) and (11)

$$\log P = -\frac{\Delta H}{2.303RT} + \frac{\Delta S}{2.303R} \tag{12}$$

Thus, the plot of log P versus $1/T$ would give the values of ΔH and ΔS. ΔH and ΔS values were calculated as, 5.866 kJ/mol and 27.363 J/mol K. It can be seen that ΔH is positive, thus the partitioning process is endothermic. The reason of this being that the interaction between acid and diluents is less powerful than that between acid and water molecule owing to electrostatic force, hydrogen bond and hydrophobic interaction etc. So the energy was needed to break the old bonds and form new bonds. ΔS value for the extraction of propionic acid is also positive, thus the partitioning process is entropy driven process and the order of system increases.

CONCLUSIONS

Physical extraction of propionic acid using different diluents was studied. The following conclusion can be made:
1. Extraction was found to follow the trend alcohols > oxygenated diluents > aromatic hydrocarbons > aliphatic hydrocarbons > long chain aliphatic hydrocarbons mixture. This suggests that alcohols and oxygenated diluents are most effective in physical extraction of propionic from dilute solutions. Their hydrogen bond donor ability and high relative permittivity (ε) and E_T value could be suggested as the reason for higher extractions in these diluents.

2. With increase in acid concentration, K_D^{diluent} was found to be nearly constant for alcohols and ketone, however, for aliphatic and aromatic hydrocarbons there is abrupt increase in K_D^{diluent} values at high acid concentration.

3. Partition (P) and dimerization (D) coefficients were also evaluated. The values of P and D shows a close relation with the chemical nature of solvent.

4. Extractability of the acid was correlated with the physico-chemical properties of the solvents, yet no general correlation could be found. The reason for that may be that the effect of diluent is determined by the ratio of the contribution of the solvation of acid to the free energy of extraction. Z parameter and the E_T parameter, which give the assessment of solvation energy of the solute and show the effect of intramolecular forces better, were found to explain the trend of extraction. E_T parameter, whose values could be successfully obtained for different diluents, was finally employed for the comparison. It is found that higher the E_T value of the solvent higher is the K_D^{diluent}.

5. Effect of temperature on P and D was also studied using different diluents (oleyl alcohol, ethyl acetate, MIBK, 1-decanol and 1-octanol). For the physical extraction of carboxylic acids using 1-octanol ΔH and ΔS values were calculated as, 5.866 kJ/mol and 27.363 J/mol K. It can be seen that ΔH is positive, thus the partitioning process is endothermic. ΔS value for the extraction of propionic acid is also positive, thus the partitioning process is entropy driven process and the order of system increases.

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