

Астрахань - 2018

ФГБОУ ВО «Астраханский государственный медицинский университет» Минздрава России

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РАСТВОРЫ

(учебно-методическое пособие)

Астрахань 2018 УДК: 541.8 ББК 24.5 Л69

Логинов П.В., Николаев А.А. Растворы: Учебно-методическое пособие для иностранных студентов (на англ. языке). – Астрахань: Изд-во Астраханского ГМУ, 2018. – 32 с.

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SOLUTIONS

(text-book for foreign students)

Astrakhan-2018

The general information about solutions is given in this textbook. The following topics are included in the book: concentration units and colligative properties, solutions of electrolytes, buffer solutions, Colloidal solutions, and solutions of macromolecular compounds. The material is accompanied by numerous problems which will help students in mastering the topics. The text-book may be useful for medical and biological students.

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The textbook is printed in accordance with the decision of the editorial publishing council of Astrakhan State Medical University

ISBN 978-5-4424-0362-6	© Loginov P.V., Nikolaev A.A.
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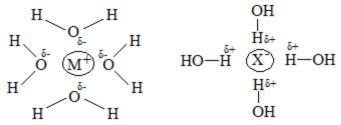
Topic 1. Concentration units and colligative properties Solution is a mixture of two or more components.

1. Dissolution.

At room temperature ionic compounds can dissolve well only in polar liquids. In order to dissolve an ionic compound the lattice must be broken up. This requires the lattice energy to be put in. The separate ions are then solvated by solvent molecules. These cluster (get together) around the ions:

(i) positive ions are surrounded by the negative ends of the dipoles of the solvent molecules;

(ii) negative ions are surrounded by the positive ends of the dipoles of the solvent molecules, i.e.



When the solvent is water we speak about *hydration*; in case of any other solvent we just speak about *solvation*. Solvation (or hydration) gives out energy as opposite charges come together. This energy change is called the enthalpy change of hydration (or solvation) and given the symbol $\Delta H^{\circ}_{hydr./solv}$.

2. Concentration units. They are:

- 1) mass fraction percentage, ω %;
- 2) molar concentration (molarity), C;
- 3) normality, C_N;

4) titre (or titer), T^1 .

$$C = \frac{n}{v} = \frac{m}{MV} \implies \underline{m} = \underline{CMV}, V - \text{volume, L or dm}^3$$

 $n = \frac{m}{M}$ n – number of moles; M – molecular weight

¹ This concentration unit is widely used in the Russian Federation and some other countries (*red*.)

Normality $C_N = \frac{C}{f_{eq}} = \frac{m}{f_{eq}MV} = \frac{m}{M_e V}$,

where $M_{\text{e}}-\text{equivalent}$ weight, $f_{\text{eq}}-\text{equivalence}$ factor.

Equivalence factors for certain classes of compounds:

$$f_{eq}(acids) = \frac{1}{basicity}; \text{ eg. } f_{eq}(H_2SO_4) = \frac{1}{2}$$

$$f_{eq}(bases) = \frac{1}{n(OH)}; \text{ eg. } f_{eq}[Fe(OH)_3] = \frac{1}{3}$$

$$f_{eq}(salts) = \frac{1}{n_{Me}Val_{Me}}; \text{ eg. } f_{eq}[Al_2(SO_4)_3] = \frac{1}{2 \cdot 3} = \frac{1}{6}$$
where n_{Me} – number of metal atoms; Val_{Me} - valency of Me.

Equivalent weight in acid-base and redox reactions:

 $H_2SO_4 + 2NaOH = Na_2SO_4 + 2H_2O$

In this reaction it is *two* hydrogens that are substituted by sodium atoms in the sulfuric acid molecule, therefore $f_{eq}(H_2SO_4) = \frac{1}{2}$; $f_{eq}(NaOH) = 1$ (There is just one hydroxyl group in sodium hydroxide which participates in the interaction). Thus, $M_e(H_2SO_4) = M \cdot f_{eq} = 98 \times \frac{1}{2} = 49 \text{ g mol}^{-1}$.

$$\begin{split} H_2SO_4 + NaOH &= NaHSO_4 + H_2O\\ f_{eq}(H_2SO_4) &= 1; \ f_{eq}(NaOH) &= 1 \end{split}$$

In redox reactions, the equivalence factor describes the number of electrons that an oxidizing or reducing agent can accept or donate respectively:

 $\frac{2KMnO_4}{oxidant} + \frac{10FeSO_4}{reductant} + \frac{8H_2SO_4}{medium} = 2MnSO_4 + 5Fe_2(SO_4)_3 + K_2SO_4 + 8H_2O_4 +$

$$\begin{array}{c|c} 2 & Mn^{+7} + 5e^{-} \rightarrow Mn^{+2} & f_{eq} = 1/5 \\ 5 & 2Fe^{+2} - 2e^{-} \rightarrow 2Fe^{+3} & f_{eq} = 1 \end{array}$$

$$\frac{\text{Titre of a solution}}{T = \frac{m}{v}} \begin{bmatrix} g \\ ml \end{bmatrix} \longrightarrow m = TV \quad (1)$$

$$C_N = \frac{m}{M_{\theta}V} = \frac{m}{M_{\theta}V(ml) \times 10^{-3}} \longrightarrow m = C_N M_e V \cdot 10^{-3} \quad (2)$$

(1) = (2)
$$\Longrightarrow$$
 T Ψ = C_NM_e $\Psi \cdot 10^{-3}$; $T = \frac{C_N M_e}{1000}$
 $C_N M_e = \frac{C \cdot f_{eq}M}{f_{eq}}$ = CM; $T = \frac{CM}{1000}$

 $\begin{array}{c} \hline C \text{ connection between molarity and percentage} \\ \hline C = \frac{\omega\% \cdot 10\rho}{T} \\ \hline T = \frac{CM}{1000} \\ \hline \rho - \text{density; for diluted solutions } (\rho \approx 1) \\ \hline T = \omega \end{array}$

Problems

1) How many grams of lithium chloride are required to make 1L of a 3M solution? $m = CMV = 3M \times 42.5 \text{ g mol}^{-1} \times 1L = \underline{127.5 \text{ g}}$ M (LiCl) = 7 + 35.5 = 42.5 g mol^{-1}

2) What is the mass fraction percentage, normality and titre of the 0.8 M solution of $Fe_2(SO_4)_3$ if the density of the solution is considered to be 1 g ml⁻¹?

$$C[Fe_{2}(SO_{4})_{3}] = 0.8 \text{ M} \qquad C = \frac{\omega\% 10 \rho}{M} = \frac{\omega\% 10}{M} \implies \omega\% = \frac{CM}{10}$$

$$\rho = 1 \text{ g ml}^{-1} \qquad \omega\% = \frac{0.8 \times 400}{10} \implies \omega\% = \frac{32 \%}{10}$$

$$C_{N} - ? \ \omega\% - ? \text{ T} - ? \qquad \omega\% = \frac{0.8 \times 400}{10} = 32 \%$$

$$M [Fe_{2}(SO_{4})_{3}] = 56 \times 2 + 96 \times 3 = 112 + 288 = 400 \text{ g mol}^{-1}$$

$$2) C_{N} = C / f_{eq} = 0.8 \times 6 = 4.8 \text{ N}$$

$$f_{eq} = \frac{1}{2 \cdot 3} = \frac{1}{6}$$

$$3) \text{ Titre of the solution T } (\rho = 1)$$

$$T = \omega = 0.32 \text{ g/ml}$$
Answer: 4.8 N; 0.32 g/ml; 32 %.

3. Colligative properties of solutions.

Raoult's law: the relative lowering of vapour pressure for a solution is equal to the mole fraction of the solute when solvent alone is volatile.

$$\frac{\Delta p_A}{p_A} = x_B \qquad \qquad \text{A-solvent, B-solute}$$

$$p = p_A + p_B; p_B = 0$$

$$p = \underline{p_A} = \underline{p}_A^* \underline{x}_A$$

$$x_A + x_B = 1; x_A = 1 - x_B$$

$$p_A = \underline{p}_A^* (1 - x_B)$$

$$\frac{p_A}{p_A^*} = 1 - x_B$$
By rearrangement, $1 - \frac{p_A}{p_A^*} = x_B$

$$\frac{\underline{p}_A - p_A}{p_A^*} = \frac{\Delta p_A}{p_A^*} = x_B \text{ and } x_B = \frac{n_B}{n_A + n_B} = \frac{n_B}{\Sigma n}$$

$$\frac{\Delta p_A}{p_A^*} = \frac{n_B}{\Sigma n} \longrightarrow \Delta p_A = \frac{\underline{p}_A^* n_B}{\Sigma n}$$
 the lowering of vapour pressure.

The consequences from Raoult's law:

1) elevation of boiling point: the boiling point of the solution is higher than that of the solvent;

2) depression of freezing point: the freezing point of the solution is lower than that of the solvent;

3) osmotic pressure: $\pi = CRT$.

Questions to review.

1. What are colligative properties?

Colligative properties are those properties which depend on the number of solute and solvent particles but not on the nature of the solute. These properties are: 1) the lowering of vapour pressure; 2) the elevation of boiling point; 3) the depression of freezing point; 4) the osmotic pressure.

2. What are the ideal solutions?

The solutions that follow the Raoult's law are said to follow the ideal solution theory. Diluted solutions follow this theory. Even moderate-

ly concentrated solutions can follow this theory if solute-solute interactions are small. Certain non-electrolytes, such as toluene in benzene, follow the ideal solution theory over all concentrations.

3. What is osmosis?

If a solution is separated from the solvent by a semipermiable membrane which blocks the solute molecules but allows the passage of solvent molecules, then more solvent molecules will pass from the solvent side to the solution side than from the solution side to the solvent side. This phenomenon is called *osmosis*.

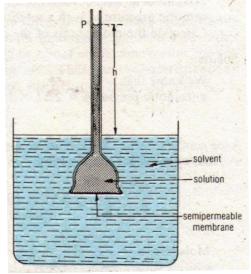


Figure 1. Osmosis and osmotic pressure: Osmotic pressure developed will be equal to hydrostatic pressure of the liquid column of height h

4. What is the osmotic pressure?

The passage of solvent through the membrane can be stopped if adequate pressure is applied on the solution side. This pressure is known as *osmotic pressure*. It is the osmotic pressure which is responsible for some of the effects (like climbing of water up a tall tree, and the bursting of red blood cells when placed in water).

bursting of red blood cells when placed in water). $pV = \frac{m}{M}RT = nRT; \ p = \frac{n}{V}RT = CRT \text{ or } \pi = CRT \text{ (osmotic pressure)}$

Topic 2. Solutions of electrolytes

There exist strong and weak electrolytes. Strong electrolytes dissociate completely into ions. They are strong acids, bases and soluble salts. Strong acids are HCl, HClO₄, H₂SO₄, HNO₃. Strong bases are alkalies.

Ostwald's dilution law states: the more the dilution, the more the degree of dissociation.

2) Isotonic coefficient (van't Hoff factor) $i = \frac{p}{N}$ P – number of particles as a result of dissociation; N – number of dissolved molecules. N α – number of dissociated molecules; N – N α = $\frac{N(1 - \alpha)}{n}$ non-dissociated molecules; <u>nN α </u> – number of ions formed as a result of dissociation. P = N(1 - α) + nN α = N[(1 - α) + n α]

$$i = \frac{\mathbb{N}[(1 - \alpha) + n\alpha]}{N} = 1 - \alpha + n\alpha = 1 - \alpha(1 - n)$$

$$i - 1 = -\alpha(1 - n)$$

$$i - 1 = \alpha(n - 1); \alpha = \frac{i - 1}{n - 1}$$

$$n = 2; \frac{\alpha = i - 1}{\alpha = \sqrt{KV}} (1)$$

$$(1) = (2) i - 1 = \sqrt{KV}$$

$$(i - 1)^2 = KV; K = \frac{(i - 1)^2}{V}$$

The van't Hoff factor is to be taken into account if it is necessary to calculate the osmotic pressure of a solution containing electrolytes, i.e. $\pi = iCRT$

Problem

What is the osmotic pressure of blood?

Solution

1) The isotonic solutions for blood are 0.9 % NaCl and 5 % $C_6H_{12}O_6$ solutions because they have the osmotic pressure equal to that of blood. Let's calculate the osmotic pressure of these solutions.

 $\frac{\omega\% (\text{NaCl}) = 0.85 \cdot 0.9 \%}{C = \frac{\omega\% \cdot 10 \cdot d}{M} \approx \frac{\omega\% \cdot 10}{M} = \frac{0.9 \times 10}{\frac{58.5}{58.5}} = 0.15 \frac{mol}{L} = 150 \text{ mol } m^{-3}$ M(NaCl) = 23 + 35.5 = 58.5 g mol⁻¹

 $\begin{array}{l} NaCl \rightarrow Na^{+} + Cl^{-} \ (100 \ \%, \ \alpha = 1) \\ T = 36.6 + 273.15 = 309.75 \approx 310 \ K \end{array} \qquad \alpha = i-1; \ i = \alpha + 1 = 1+1 = 2 \\ \end{array}$

 $\pi = 2 \times 150 \times 8.31 \times 310 = 772,830$ Pa ≈ 772.8 kPa 772.8 $\div 101.3 = 7.6$ atm

2) 5 % C₆H₁₂O₆ solution is not suitable for patients suffering from diabetes. Glucose is a non-electrolyte. Therefore, $\pi = CRT$.

 $C = \frac{5 \times 10}{180} = \frac{50}{180} = 0.28 \frac{mol}{L} = 280 \text{ mol } m^{-3}$ M(C₆H₁₂O₆) = 72 + 12 + 96 = 180 g mol⁻¹ $\pi = 280 \times 8.31 \times 310 = 721,308 \text{ Pa} \approx 721.3 \text{ kPa} (7.1 \text{ atm}).$ Therefore, on average the osmotic pressure of blood is about 7.4 atm (7.1 and 7.6 atm in our calculations) Answer: 7.4 atm. **Task**. Calculate the sum of coefficients in the left part of the short form of the ionic equation for the reaction between solutions of $Fe(OH)_3$ and H_2SO_4 . 1) 8; 2) 16; 3) 4; 4) 22.

 $\begin{array}{l} \downarrow 2Fe(OH)_{3} + 3H_{2}SO_{4} \rightarrow Fe_{2}(SO_{4})_{3} + 6H_{2}O \\ 2Fe(OH)_{3} + 6H^{+} + \frac{3SO_{4}^{2-}}{2} = 2Fe^{3+} + \frac{3SO_{4}^{2-}}{4} + 6H_{2}O \ (full \ form) \\ 2Fe(OH)_{3} + 6H^{+} = 2Fe^{3+} + 6H_{2}O \ (\div 2) \\ \hline Fe(OH)_{3} + 3H^{+} = Fe^{3+} + 3H_{2}O \ (short \ form); \ \sum = 1 + 3 = 4 \ (N_{2} \ 3). \end{array}$

Acids and bases

Acids were originally identified by their sour taste. Now they are recognized by the colour changes of dyes called indicators and by their reactions with metal oxides, hydroxides and carbonates, and also with metals themselves. All of these reactions produce ionic compounds called salts.

Bases were originally identified by their slimy feel. Now they are recognized by their effect on indicators, and by the fact that they react with acids. If a base dissolves in water it is called an alkali.

The reactions of acids

1) With bases (metal oxides or hydroxides), for example: $2HNO_3(aq) + CaO(s) \rightarrow Ca(NO_3)_2(aq) + H_2O(l)$ calcium nitrate $H_2SO_4 + 2NaOH \rightarrow Na_2SO_4 + 2H_2O$

2) With metal carbonates, for example:

 $2CH_{3}COOH + K_{2}CO_{3} = 2CH_{3}COOK + H_{2}CO_{3}$ potassium acetate

3) With reactive metals: $2HCl + Zn = ZnCl_2 + H_2\uparrow$

In each case the hydrogen of the acid is replaced by the metal to form a compound called a salt.

Theories of acidity

Many theories of acidity have been proposed, including the following. Arrhenius (1887) thought of acids as producing hydrogen ions (H^+) :

 $\mathrm{HCl} \rightarrow \mathrm{H^{+}} + \mathrm{Cl^{-}}$

 $H_2SO_4 \rightarrow 2H^{\scriptscriptstyle +} + SO_4{}^{2 \scriptscriptstyle -}$

Strong bases are completely dissociated into ions in aqueous solutions: NaOH \rightarrow Na⁺ + OH⁻.

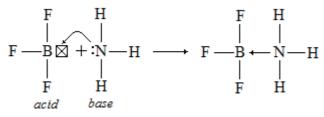
The Lowry-Brönsted description of acidity is the most generally useful current theory. This defines an acid as a substance which can donate a proton (an H^+ ion) and a base as a substance which can accept a proton:

$$\begin{array}{c} \text{HCOOH} \rightleftharpoons \text{HCOO}^{-} + \text{H}^{+} \\ acid & base & proton \\ \text{HCI} + \text{NH}_{3} \longrightarrow \text{NH}_{4}^{+} + \text{CI}^{-} \\ acid & base & conjugate & conj. base \\ acid & base & conjugate & conj. base \\ acid & base & conjugate & conj. base \\ acid & base & conjugate & conj. base \\ acid & base & conjugate & conj. base \\ acid & base & conjugate & conj. base \\ acid & base & conjugate & conj. base \\ acid & base & conjugate & conj. base \\ acid & base & conjugate & conj. base \\ acid & base & conjugate & conj. base \\ acid & base & conjugate & conj. base \\ acid & base & conjugate & conj. base \\ acid & base & conjugate & conj. base \\ acid & base & conjugate & conj. base \\ acid & base & conjugate & conj. base \\ acid & base & conjugate & conj. base \\ acid & base & conjugate & conj. base \\ acid & base & conjugate & conjug$$

In the second example the Cl⁻ ion has become a conjugate base, and NH_4^+ – a conjugate acid. HCl can also donate a proton to water. Therefore, water acts in this case as a base. On the other hand, water may act as an acid depending on the surroundings, for example:

$$\begin{array}{l} \text{HCl} + \text{H}_2 \bigcirc \rightleftharpoons \text{H}_3 \bigcirc^{+} + \text{Cl}^-\\ acid \ l \ base \ 2 \ cid \ 2 \ base \ l\\ \ddot{\text{NH}}_3 + \text{H}_2 \bigcirc \rightleftharpoons \text{NH}_4^+ + \text{OH}^-\\ base \ cid \end{array}$$

Another theory (the Lewis theory) is also used to describe acids. This theory regards acids as electron pair acceptors, and bases as electron pair donors in the formation of dative covalent bonds:



Hydrolysis of salts (additional material)

Some salts interact with water. They are said to undergo hydrolysis. The ions of weak electrolytes attract oppositely charged particles to produce new hydrolyzed ions, for example:

 $2NaOH + H_2C_2O_4 = Na_2C_2O_4 + 2H_2O$

sodium oxalate

Sodium oxalate is soluble in water and dissociates completely into ions. In fact sodium oxalate is hydrolyzed according to the equation:

$$Na_{2}C_{2}O_{4} \rightarrow 2Na^{+} + C_{2}O_{4}^{2-}$$

$$2Na^{+} + C_{2}O_{4}^{2-} + H_{2}O \rightleftharpoons 2Na^{+} + HC_{2}O_{4}^{-} + OH^{-}$$

$$H^{+} + OH^{-}$$

$$C_{2}O_{4}^{2-} + H_{2}O \rightleftharpoons HC_{2}O_{4}^{-} + OH^{-} \quad pH > 7$$

The pH range for phenolphthalein is 8-10. Therefore, sodium oxalate may be identified by the colour change of this indicator.

Task (choose the correct answer)

1. The formula to calculate the titre of a solution is:

- A. T = V/m;
- B. T = mV;
- C. T = cMV;
- D. T = ωd .

2. The titre of 554 ml solution containing 2.5 g of a solute is:

- A. 4.5 g/L;
- B. 221.6 ml/g;
- C. 0.00451 g/ml;
- D. 0.2216 L/g.

3. The strong electrolyte is:

- A. silicon dioxide;
- +B. sodium sulfate;
- C. the acetic acid;
- D. iron (III) hydroxide.

Topic 3. Buffer Solutions

Buffers are solutions which have the ability to resist changes of acidity or alkalinity, their pH remaining almost constant when small amounts of acid or alkali are added.

One example of a system involving a buffer is blood, whose pH is maintained at approximately 7.4. A change of as little as 0.5 of a pH unit is likely to be fatal.

Buffer solution is a mixture of a weak acid or base and a soluble salt of that acid or base. There are acidic and basic buffers.

A. Acidic buffer

$$\begin{array}{c} \overbrace{CH_{3}COOH} \rightleftharpoons \overbrace{CH_{3}COO}^{+} + H^{+} \\ CH_{3}COONa \rightarrow \overbrace{CH_{3}COO}^{+} + Na^{+} \\ K_{a} = \underbrace{[CH_{3}COO'][H^{+}]}_{[CH_{3}COOH]} \Longrightarrow [H^{+}] = K_{a} \underbrace{[CH_{3}COO']}_{[CH_{3}COO']} \approx K_{a} \frac{C_{acid}}{C_{salt}} \\ \\ \underbrace{[H^{+}] = K_{a} \frac{C_{a}}{C_{s}}}_{-\log} & \left\{ \begin{array}{c} -\log \\ -\log \end{array} \right\} \\ pH = \underbrace{-\log K_{a} - \log \frac{C_{a}}{C_{s}}}_{pK} & or \end{array} pH = pK + \log \underbrace{[Salt]}_{[Acid]} pH \text{ of acidic buffer} \end{array}$$

If we need to prepare a buffer, Henderson-Hasselbalch equation looks like this:

$$pH = pK + \log \frac{C_s V_s}{C_a V_a}$$

B. Basic buffer

Basic buffer solution contains a weak base and its soluble salt. The example is ammonium buffer system NH₄OH/NH₄Cl.

$$NH_4OH \rightleftharpoons NH_4^+ + OH$$

 $NH_4CI \rightarrow NH_4^+ + CI^-$

Taking into account the same considerations and the equation pH = 14 - pOH, Henderson-Hasselbalch equation looks like that:

$$pH = 14 - pK_b^+ \log \frac{C_b V_b}{C_s V_s} pH \text{ of basic buffer (b - base)}$$

The ability of the buffer solution to resist the changes in pH value on addition of small amount of an acid or a base, is called *buffer action*.

Suppose a few drops of HCl are added to the acetic buffer: $CH_3COONa + HCl \rightarrow CH_3COOH + NaCl$ $CH_3COO^- + Na^+ + H^+ + Cl^- = CH_3COOH + Na^+ + Cl^ CH_3COO^- + H^+ = CH_3COOH$ If a few drops of NaOH are added, $CH_3COOH + OH^- = CH_3COO^- + H_2O$

Labwork

1) Calculate the ratio of 0.1 M CH₃COONa to 0.1M acetic acid to get 20 ml buffer solution with pH 4.523. The dissociation constant of the acid is 3×10^{-5} .

20 ml buffer; pH 4.523 $pH = pK + log \frac{C_g v_g}{C_g v_a}$ $C_s = C_a = C$ $pH = pK + log \frac{v_g}{v_a}$ $pK = -log_{10} K = -log (3 \times 10^{-5}) = -log 3 + log 10^{-5} = -log 3 + 5log_{10} 10$ = 5 - log 3 = 5 - 0.477 = 4.523 $4.523 = 4.523 + log V_s/V_a; log V_s/V_a = 0; V_s/V_a = 1 = 1 : 1$ Therefore, to obtain the 20 ml buffer we should mix equal amounts of CH₃COONa and CH₃COOH, i.e. 10 ml of each component.

2) How much of 0.3 M ammonium hydroxide should be mixed with 30 ml of 0.2 M solution of NH₄Cl to give a buffer solution of

pH 8.65? K_b (NH₄OH) = 1.8×10^{-5} . $pH = 14 - pK_b + log \frac{C_b C_b}{C_s V_s}$ pK_b = -log (1.8×10^{-5}) = $5 - \log 1.8 = 5 - 0.255 = 4.745$ 8.65 = $14 - 4.745 + log \frac{0.3 x}{0.2 \times 30} = 9.255 + \log \frac{x}{20}$ $-0.605 = \log \frac{x}{20}$; 0.605 = log (20/x); 4 = 20/x; x = 5 ml.

Answer: 5 ml.

Problems

1) Calculate pH of a buffer solution that is 0.04 M CH₃COONa and 0.08 M CH₃COOH at 25°C. $pK_a = 4.74$. Data: Solution C(CH₃COONa) = 0.04 M $pH = pK + log \frac{[Salt]}{[Acid]}$ $pH = 4.74 + \log(0.04/0.08) = 4.74 +$ $C(CH_3COOH) = 0.08 M$ $+\log 0.5 = 4.74 - 0.3 = 4.44$ $pK_a(CH_3COOH) = 4.74$ pH - ? Answer: pH 4.44. 2) Calculate the pH of 0.02 M HNO₂ that is dissociated by 50 %. $HNO_2 \leftrightarrow H^+ + NO_2^ C(HNO_2) = 0.02 M$ 1) $C_{H+} = C\alpha = 0.02 \times 0.5 = 0.01 = 10^{-2}$ $\alpha\% = 50\% (0.5)$ 2) pH = $-\log 10^{-2} = 2$ pH - ? Answer: pH 2

Additional problems

1) Calculate the pH of 0.01 M HCl.

2) Calculate the pH of 0.001 M KOH solution.

3) Calculate the pH of 0.002 M NaOH solution.

4) Calculate the pH of 0.1 M NH₄OH solution. K_b (NH₄OH) = 1.8 ×

10⁻⁵. (Answer: pH 11.11).

5) Calculate the pH of 0.1 M CH₃COOH solution. K_a (CH₃COOH) = 1.8×10^{-5} . (Answer: pH 2.9).

 $\begin{array}{l} \textit{Buffer capacity} \\ pH = pK \pm 1 \end{array}$

Problem

Calculate the pH range of high capacity buffer containing formic acid HCOOH. Ka(HCOOH) = 1.8×10^{-4} . Solution The buffer capacity is maximum near pK_a of the acid. 1) pK_a = -log (1.8×10^{-4}) = $4 - \log 1.8 = 4 - 0.255 = 3.745 \approx 3.75$ 2) pH = 3.75 ± 1 ; pH 2.75–4.75 Answer: 2.75–4.75.

Biological buffers

1) Hydrogen carbonate (hydrocarbonate) buffer system;

2) phosphate buffer system;

3) plasmatic protein buffer system;

4) hemoglobin-oxyhemoglobin buffer system.

Hydrocarbonate and plasmatic protein buffer systems act effectively in blood plasma. The two other systems act most effectively in erythrocytes.

1. **Hydrocarbonate** (hydrogen carbonate) buffer system consists of the carbonic acid H_2CO_3 and its soluble salt sodium hydrocarbonate NaHCO₃:

$$\begin{array}{ccc} (HA) & H_{2}CO_{3} \rightleftharpoons & HCO_{3} \\ (A^{-}) & NaHCO_{3} \rightarrow & HCO_{3} \\ \end{array} + H^{+} & salt \\ Action: NaHCO_{3} + HLac \leftrightarrow NaLac + H_{2}CO_{3} \leftrightarrow H_{2}O + CO_{2}{}_{(aq)} \\ & \uparrow \\ & CO_{2}\uparrow \end{array}$$

Carbon dioxide eliminates through the lungs.

2. **Phosphate buffer system** consists of two salts: NaH_2PO_4 and Na_2HPO_4 . The first one acts as an acid.

$$\begin{array}{l} \mathrm{NaH_2PO_4} \rightarrow \mathrm{Na^+} + \mathrm{H_2PO_4^-} \\ \int \mathrm{H_2PO_4^-} \rightleftharpoons \mathrm{HPO_4^{2^-}} + \mathrm{H^+} \\ \mathrm{Na_2HPO_4} \rightarrow \mathrm{HPO_4^{2^-}} + 2\mathrm{Na^+} \end{array}$$

The phosphate buffer system operates effectively in the internal fluid of all cells.

3. **Plasmatic protein buffer system** is represented by different protein molecules acting as polyelectrolytes. Just the only amino acid *histidine* possesses the remarkable buffer action at the pH values near the pH of blood plasma. The action of the proteinaceous buffer system can be described by the following scheme:

⁺NH₃—(R)—COO⁻ + H⁺ \rightarrow ⁺NH₃—(R)—COOH (acid neutralization) ⁺NH₃—(R)—COO⁻ + OH⁻ \rightarrow NH₂—(R)—COO⁻ + H₂O (alkali neutralization)

Hemoglobin-oxyhemoglobin buffer system

Inside erythrocytes pH is maintained at 7.25. The main buffer system in erythrocytes is hemoglobin buffer system which is a kind of protein buffer system. It consists of two forms: hemoglobin system HHb and oxyhemoglobin system $HHbO_2$.

A. Hemoglobin system

$$HHb \rightleftharpoons Hb^{-} + H^{+}$$

 $KtHb \rightarrow Hb^{-} + Kt^{+}$
B. Oxyhemoglobin system
 $HHbO_2 \rightleftharpoons HbO_2^{-} + H^{+}$
 $KtHbO_2 \rightarrow HbO_2^{-} + Kt^{+}$

Hemoglobin and oxyhemoglobin systems are connected to each other: $HHb + O_2 \leftrightarrow HHbO_2$.

Participation of hemoglobin in the pH regulation in blood is connected with its role in the oxygen and carbon dioxide transportation. Hemoglobin-oxyhemoglobin buffer system is closely connected with hydrogen carbonate system:

The proton formed as a result of dissociation interact with oxyhemoglobin ion:

$$H^+ + HbO_2 \rightleftharpoons HHbO_2 \rightarrow HHb + O_2$$

in tissues

The O_2 molecules interact with HHb in the lungs. Hydrogen carbonate ions take protons from oxyhemoglobin. The carbonic acid formed breaks down to give CO_2 which goes away through the air passages of the lungs:

pH of some biological fluids:

1) human blood = 7.38;

- 2) human saliva = 6.4;
- 3) human stomach fluid = 1.0;

4) human muscle fluid = 6.83.

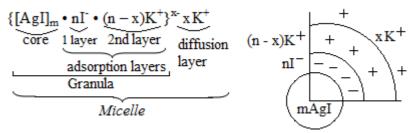
Topic 4. Colloidal solutions

Colloidal solutions are intermediate between true solutions and suspensions. The diameter of colloidal particles may range from 1 to 100 nm. A colloidal system is always heterogeneous and consists of at least two phases: the *disperse phase* and the *dispersion medium* (the medium in which these colloidal particles are dispersed).

The structure of colloidal particles

Let us mix two diluted solutions of AgNO₃ and KI, one of them being in the excessive amount (for example, potassium iodide KI). The structure of the colloidal particle (micelle) is as follows:

 $AgNO_3 + KI (excess) = AgI \downarrow + KNO_3$ $KI \rightarrow K^+ + I^-$

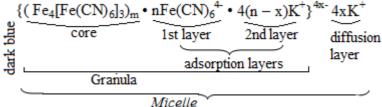


In this case, granule is charged negatively.

Labwork

1) Mix diluted solutions of $K_4[Fe(CN)_6]$ and $FeCl_3$. Write down the structures of two possible micelles.

 $3K_{4}[Fe(CN)_{6}] + 4FeCl_{3} = Fe_{4}[Fe(CN)_{6}]_{3}\downarrow + 12KCl$ a) $K_{4}[Fe(CN)_{6}]$ (excess) $\rightarrow 4K^{+} + Fe(CN)_{6}^{4}$



b) $FeCl_3 \rightarrow Fe^{3+} + 3Cl^{-}$

{($Fe_4[Fe(CN)_6]_3)_m \bullet nFe^{3+} \bullet 3(n-x)Cl^-$ }^{3x+} 3xCl⁻ greenish colour micelle (positively charged). 2) Mix diluted solutions of K₄[Fe(CN)₆] and CuSO₄. Write down the structure of the micelle in case of the excessive amount of potassium hexacyanoferrate (II) K₄[Fe(CN)₆]. K₄[Fe(CN)₆] + 2CuSO₄ = \downarrow Cu₂[Fe(CN)₆] + 2K₂SO₄ K₄[Fe(CN)₆] (excess) \rightarrow 4K⁺ + Fe(CN)₆⁴⁻ {(Cu₂[Fe(CN)₆])_m • nFe(CN)₆⁴⁻ • 4(n - x)K⁺}^{4x-} 4xK⁺ (red brick)

Properties of colloids

- 1) Mechanical properties
- 2) Optical properties of colloidal solutions
- 3) Electrical properties of colloidals

1. Mechanical properties of colloidals:

- a) Brownian motion;
- b) Diffusion;
- c) Coagulation and sedimentation.

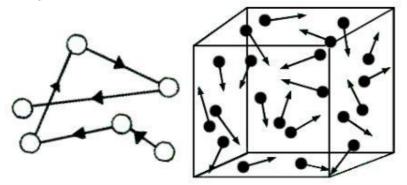


Figure 2. Brownian motion

The coagulation is a process of integration and aggregation of dispersed phase particles into larger aggregates which leads eventually to sedimentation. Coagulation processes take place in the blood.

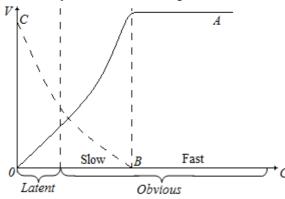
(i) Types of coagulation.

There are two types of coagulation: fast and slow.

$$\frac{\text{Slow:}}{\text{Fast:}} \circ + \circ \longrightarrow \infty \xrightarrow{+ \circ} & \overset{+ \circ}{\otimes} & \overset{+ \circ}{\otimes} & \overset{+ \circ}{\otimes} \\ \circ + \circ \longrightarrow \infty \xrightarrow{+ \infty} & \overset{+ \infty}{\otimes} & \overset{+ \otimes}{\otimes} & \overset{+ \otimes}{\otimes} \\ \circ + \circ \longrightarrow & \overset{+ \infty}{\longrightarrow} & \overset{+ \infty}{\otimes} & \overset{+ \otimes}{\otimes} & \overset{+ \otimes}{\otimes} \\ \end{array}$$

Coagulation can be caused by different external factors: raising or depressing the temperature, shaking, exposure to light, adding the chemical substances etc.

(ii) Coagulation kinetics. Adding the electrolyte solution to the colloidal system results in coagulation.



The more the concentration of electrolyte added, the more the coagulation rate.

Figure 3. Dependence of the coagulation rate (OA) and ζ -potential (CB) on the concentration of electrolyte add-

ed

Coagulation is then followed by sedimentation.

2. Optical properties: Tyndall effect.

When light passes through a sol, its path becomes visible because of scattering of light by colloidal particles. This is called Tyndall effect. Light beam is not visible in true solutions and water.

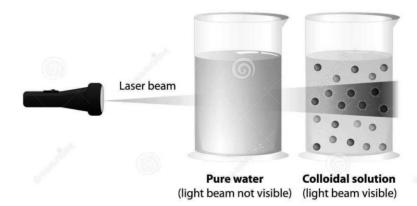


Figure 4. Tyndall effect

It is possible to measure the size of colloidal particles using ultramicroscope. Let's consider this method.

m - total mass of disperse phase;

 m_0 – the mass of a colloidal particle;

n – number of the particles in the visible area.

$$\begin{array}{l} m = m_0 n = V dn; V = \frac{m}{d n} \\ m_0 = V d, \qquad V = \frac{4}{3} \pi r^3 \end{array} \right\} \Longrightarrow \frac{m}{n d} = \frac{4}{3} \pi r^3; r = \sqrt[3]{\frac{3m}{4\pi n d}}$$

where V is volume of a particle, d is its density.

If it is necessary to calculate the diameter of colloidal particles,

$$D = 2r = 2\sqrt[s]{\frac{3m}{4\pi nd}} = \sqrt[s]{\frac{8 \times 3m}{4\pi nd}} = \sqrt[s]{\frac{6m}{\pi nd}} \approx \sqrt[s]{\frac{2m}{nd}}$$

3. Electrical properties of colloidals:

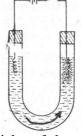
a) electrokinetic potential (ζ -potential);

b) electrokinetic phenomena.

Colloidal particles posess some type of electric charge. Depending on the charge, they move towards a positive or a negative electrode

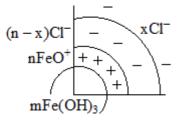
when an electric field is applied to a colloidal dispersion. Such movement is referred to as *electrophoresis*.

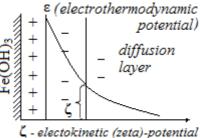
FeCl₃ + 3H₂O → Fe(OH)₃↓ + 3HCl nFe(OH)₃ + nHCl = nFeOCl + 2nH₂O nFeO⁺ nCl⁻



 $\{[Fe(OH)_3]_m \bullet nFeO^+ \bullet (n-x)Cl^-\}^{x+} xCl^-$

The granule is positively charged, therefore the particles of the sol will move to cathode K(-).





Electrokinetic phenomena

1) *Electrophoresis* is a motion of particles under the influence of electric field.

2) *Electro-osmosis* is a motion of liquid in porous body under the influence of electric field.

It is possible to calculate zeta-potential and electrophoretic mobility of particles on the base of the data obtained on studying electrophoresis and electro-osmosis.

 $\zeta = \frac{\eta \mu_{\varepsilon}}{D}$ (Electrokinetic potential of a particle in electrophoresis)

 $\mu_{\varepsilon} = \frac{\varepsilon_0 \varepsilon \zeta}{n}$ (Electrophoretic mobility of a particle), where

 $D = \varepsilon_0 \varepsilon$ (dielectric permittivity of dispersion medium);

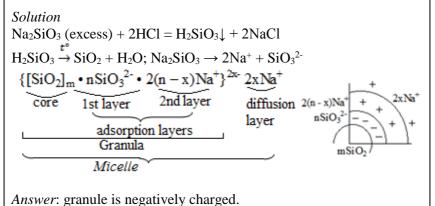
 ϵ_0 – permittivity of free space (vacuum), ϵ – dielectric constant of dispersion medium; η – dynamic viscosity.

 $\zeta = \frac{\eta \kappa}{i_{555}} V$ (Electrokinetic potential of a particle in electro-osmosis),

i – strength of current, \varkappa – specific electroconductivity, V – volume velocity.

Problem

Write down the structure of silicon dioxide micelle in case of excessive amount of sodium silicate solution mixed with HCl diluted solution.



	Finely dispersed systems	
Suspensions	Colloidal solutions (1-100 nm)	True solutions
and Emulsions	1. In solid dispersion medium	1. Molecular
>100 nm	(foam rubber)	solutions (sugar)
Tothpaste	2. In gaseous dispersion medium:	2. Solutions of
Tomato paste	a) solid dispersed phase (smoke);	electrolytes:
Milk	b) liquid phase (fog, clouds):	strong acids
mayonnaise	smoke + fog = smog (смог)	alkalis, bases
oil in water	3. In liquid dispersion medium	soluble salts

Topic 5. Solutions of macromolecular compounds

Liophobic (solvent-hating) sols:

Liophilic colloids:

a) solid phase (hydrosols);

b) gaseous phase (foams)

Solutions of macromolecular compounds (and gels)

In macromolecular colloids, the dispersed particles are themselves large molecules (usually polymers). A macromolecule is a large molecule commonly created by some form of polymerization. Biopolymers are nucleic acids, proteins and peptides, carbohydrates, and some lipids. In biochemistry, the term "macromolecule" is also applied to non-polymeric molecules with large molecular weight such as macrocycles. The constituent molecules from which macromolecules are assembled are called *monomers*.

1. Polyelectrolytes and proteins.

Polyelectrolytes are polymers whose repeating units carry an electrolyte group. These groups will dissociate in aqueous solutions (water), making the polymers charged. Polyelectrolyte properties are thus similar to both electrolytes (salts) and polymers, and are sometimes called polysalts. Like salts, their solutions are electrically conductive. Like polymers, their solutions are often viscous. We distinguish between plycations, polyanions, and polyampholytes. Many biological molecules are polyelectrolytes. Polyampholytes are polyelectrolytes which bear both cationic and anionic repeated groups. All proteins are polyampholytes, as some amino acids tend to be acidic while others are basic. Structure of proteins

Proteins are long polymers of amino acids linked by peptide bonds. There exist several levels of protein molecule organization:

1) *primary structure* is the sequence of amino acids linked by peptide bonds;

2) *secondary structure* formed with the help of hydrogen bonding (for example, alpha helix of protein molecule);

3) *tertiary structure* is the three-dimensional structure of globular proteins (formed by means of ester bonds, for example);

4) quaternary structure (hemoglobin molecule).

2. Properties of solutions of polymers and peptides.

1). Coacervation: the phenomenon of forming a liquid rich in polymer phase in equilibrium with another liquid phase.

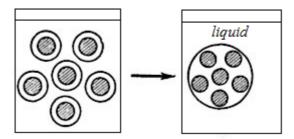


Figure 5. Coacervation: Hydrate shells join together

2). Denaturation of proteins involves the disruption and possible destruction of both the secondary and tertiary structures. Denaturation occurs because the bonding interactions responsible for the secondary and tertiary structures are disrupted. The most common observation in the denaturation process is the precipitation or coagulation of the protein molecule.

3). Osmotic and oncotic pressure: oncotic pressure is colloid osmotic pressure – the part of the osmotic pressure created by the larger colloidal solute components. Oncotic pressure is 0.5 % of the total osmotic pressure of blood plasma.

4). Viscosity of polymer solutions. The viscosity of even dilute polymer solutions is usually far larger than just the viscosity of the

background solvent, due to the large differences in size between the polymer and solvent molecules.

5). Electrophoretic mobility.

6). Gelation (transformation of a sol into a gel). Protein gels can be formed by the addition of salts, the action of enzymes, changes in pH or by the application of heat. At the isoelectric point (pI) proteins have no net charge, and therefore do not repel each other. When proteins are at their pI, this results in the formation of *strong gels*. pH ~ 5 is the pI of gelatin proteins. So,

The isoelectric point (pI), sometimes abbreviated to IEP, is the pH at which a particular molecule or surface carries no net electrical charge.

3. Donnan membrane equilibrium.

This equilibrium takes place due to a semipermiable membrane. Protein salt of sodium dissociates into protein polyanion and sodium cations as follows: $PtNa_z \rightleftharpoons Pt^{z-} + zNa^+$. Let's consider the case when the cells are put into the NaCl solution.

$$(C_{in} + x) \xrightarrow{Pt^{2}}_{Na^{+}} \xrightarrow{Na^{+}}_{Cl^{-}} \xrightarrow{Na^{+}}_{Cl^{-}} \xrightarrow{Na^{+}}_{Cl^{-}} \xrightarrow{(C_{out} - x)}_{(Cout - x)}$$
inside the cell

$$[Na^{+}]_{in}[Cl^{-}]_{in} = [Na^{+}]_{out}[Cl^{-}]_{out}$$

$$(C_{in} + x)x = (C_{out} - x)^{2}$$

$$C_{in}x + x^{2} = C_{out}^{2} - 2C_{out}x + x^{2}$$

$$C_{in}x + x^{2} = C_{out}^{2} - 2C_{out}x + x^{2}$$

$$C_{in}x + 2C_{out}x = C_{out}^{2}$$

$$x(C_{in} + 2C_{out}) = C_{out}^{2} \Rightarrow x = \frac{C_{out}^{2}}{C_{in} + 2C_{out}}$$
If $C_{out} \gg C_{in} \Rightarrow x = \frac{C_{out}^{2}}{C_{in} + 2C_{out}} = \frac{C_{out}}{2C_{out}} = \frac{C_{out}}{2}$

4. *Gels*.

A gel is a solid, jelly-like material that exhibits no flow when in the steady-state. It is necessary to distinguish between hydrogels, organogels and xerogels. *Hydrogel* is a network of polymer chains that can absorb water or aqueous solutions. Most authors agree on the fact that at least two components are needed for a gel: a network and a solvent. *Organogel* is a non-crystalline thermoplastic solid material composed of a liquid organic phase enclosed in a three-dimensional cross-linked network. *Xerogel* is a solid material formed from a gel by drying.

Whey protein gels are obtained by heating in two stages: (i) the first step involves changes in the conformation (usually induced by heat) or partial denaturation of the protein molecule; (ii) in the second step, a gradual association (or molecule aggregations of denaturated proteins) leads to increasing the viscosity.

Properties of gels

1). Swelling. The polymer network absorbs solvent without being dissolved. Such a process is referred to as 'swelling'. The swelling state is generally characterized by the degree of swelling:

$$\alpha = \frac{m - m_0}{m_0}$$
 $\alpha = \frac{v - v_0}{v_0}$, where

m, V – the final mass or volume, and

 m_0 , V_0 – the initial mass or volume of a polymer.

2). Physico-chemical properties of gels:

a) gels can absorb substances;

b) gels are characterized by diffusion of electrolytes and other substances;

c) gels containing electrolytes can conduct electricity;

d) chemical reactions in gels show the certain peculiarities:

- the reactions proceed slowly;
- the precipitates formed in the reactions are of periodic nature.



Figure 6. Liesegang rings

3). Gel aging. This is characterized by time-dependent changes in the chemical or physical structure, and the properties of a gel. It is the process by which liquid is separated from gel owing to further coagulation. Gel aging can involve polymerization, crystallization, aggregation, syneresis. These processes take place in our body and deal with the aging. Many gels display thixotropy – they become fluid when shaken, for example.

Problem

A polymer of 2 g was put into the tube containing petrol. The polymer was then taken out of the tube, its mass became equal to 2.4 g. Calculate the degree of swelling (in %) of the polymer. *Solution* The degree of swelling of a polymer is determined with the help of

The degree of swelling of a polymer is determined with the help of the following formula:

$$\alpha\% = \frac{m - m_0}{m_0} \times 100\%
\alpha\% = \frac{2.4 - 2.0}{2.0} \times 100\% = \frac{40}{2}\% = 20\%
Answer: 20\%.$$

Tasks (choose the correct answer)

1. Lyophilic colloid is:

- A. an emulsion;
- B. a suspension;
- C. a solution of protein;
- D. hydrosol of Fe(OH)₃.

2. Alpha-helix of the protein molecule is:

- A. the primary structure;
- B. the secondary structure;
- C. the tertiary structure;
- D. the quaternary structure.

3. The colloidal solution with the gaseous dispersion medium is:

- A. a suspension;
- B. a foam;
- C. the oxygenated mineral water; D. smog.

Additional material: Suspensions and Emulsions

Suspension is a heterogeneous mixture containing solid particles that are sufficiently large for sedimentation. Usually they must be larger than 1 micrometer. The internal phase (solid) is dispersed throughout the external phase (fluid) through mechanical agitation. Unlike colloids, suspensions will eventually settle. An example of a suspension is sand in water. The suspended particles are visible under microscope and will settle over time if left undisturbed. This distinguishes a suspension from a colloid, in which the suspended particles are smaller and do not settle. Colloids and suspensions are different from solutions, in which the dissolved substance (solute) does not exist as a solid, and solvent and solute are homogeneously mixed. The examples of suspensions are pastes (toothpaste, tomato paste).

Emulsion is a mixture of two or more liquids that are normally immiscible. Examples of emulsions include milk, mayonnaise, oil in water when shaken etc. Two liquids can form different types of emulsions. As an example, oil and water can form, firstly, an oil-inwater emulsion, where the oil is the dispersed phase, and water is the dispersion medium. Secondly, they can form a water-in-oil emulsion, where water is the dispersed phase and oil is the external phase, the dispersion medium. Multiple emulsions are also possible, including a 'water-in-oil-in-water' emulsion and an 'oil-in-water-in-oil' emulsion. Emulsions, being liquids, do not exhibit a static internal structure.

Problem for advanced level

Calculate the electrokinetic potential of the quartz surface on the data obtained in the study of electroosmotic fluid transport through a quartz membrane.

Given:	$\zeta = \frac{\eta \varkappa}{i\varepsilon_0 \varepsilon} V = \frac{\eta \varkappa}{i D} V$	
$i = 2 \times 10^{-3} A$	$0.02 \text{ ml s}^{-1} = 0.02 \text{ cm}^3/\text{s} = 2 \times 10^{-8} \text{ m}^3/\text{s},$	
$V = 0.02 \text{ ml s}^{-1}$	because $1 \text{ m} = 100 \text{ cm}$	
$\kappa = 1.2 \times 10^{-2} \text{ S m}^{-1}$	and 1 $m^3 = 10^6 cm^3$	
$\eta = 1 \times 10^{-3} \text{ Pa} \cdot \text{s}$	1) $D = \varepsilon_0 \varepsilon = 8.85 \times 10^{-12} \times 80.1 = 7.1 \times 10^{-10}$	
$\varepsilon = 80.1$	2) $\zeta = \frac{10^{-8} \times 1.2 \times 10^{-2} \times 2 \times 10^{-8}}{2 \times 10^{-8} \times 7.1 \times 10^{-10}} = \frac{1.2}{7.1} =$	
ζ-?		
	= 0.169 V = 169 mV	
$\varepsilon_0 = 8.85 \times 10^{-12} \mathrm{F m}^{-1}$		
Answer: 169 mV.		

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Appendix

Formula to calculate ζ (zeta)-potential Micelle can be considered as spherical capacitor.

Micelle can be considered as spherical capacitor.

$$F = k \frac{q^2}{r^2}; E = \frac{F}{q} = k \frac{q^2}{qr^2} = k \frac{q}{r^2}$$

$$k = \frac{1}{4\pi \varepsilon_0}; E = k \frac{q}{r^2} = \frac{q}{4\pi \varepsilon_0 r^2} \text{ (intensity)}$$

$$E = \frac{q}{\varepsilon_0 4\pi r^2} = \frac{q}{\varepsilon_0 5} = \frac{\sigma}{\varepsilon_0}, \text{ where}$$
S - surface area, σ - surface density of charge, q - charge.

$$E = \frac{q}{\varepsilon_0 5}$$

$$E = \frac{u}{d}$$

$$\implies \frac{q}{\varepsilon_0 5} = \frac{u}{d} \implies C_0 = \frac{q}{u} = \frac{\varepsilon_0 5}{d},$$
where
U - voltage (potential), d - distance between plates in capacitor.

$$C = C_0 \varepsilon = \frac{\varepsilon_0 \varepsilon 5}{d} = \frac{D 5}{\Delta r}$$

$$\varepsilon_0 - \text{ permittivity of free space (vacuum), } \varepsilon - \text{ dielectric constant of dispersion medium.}$$

$$C = \frac{q}{\Delta \varphi}; \quad \frac{q}{\Delta \varphi} = \frac{D 5}{\Delta r}; \quad \frac{q}{d\varphi} = \frac{D 5}{dr}, \text{ where}$$

$$D = \varepsilon_0 \varepsilon \qquad S = 4\pi r^2$$

$$\frac{q}{d\varphi} = \frac{\varepsilon_0 \xi 4\pi r^2}{dr}$$

$$\int_{r} \frac{dr}{r^2} = \frac{4\pi \varepsilon_0 \varepsilon}{q} \int_{\varphi_1} \varphi d\varphi$$

$$\int_{r}^{r+\delta} \frac{dr}{r^2} = \int_{r}^{r+\delta} r^{-2} dr = -\frac{1}{r} | r + \delta = -\frac{1}{r+\delta} + \frac{1}{r} = \frac{1}{r} - \frac{1}{r+\delta} = \frac{r+\delta-r}{r(r+\delta)} = \frac{\delta}{r(r+\delta)}$$

1

$$\frac{\delta}{r(r+\delta)} = \frac{4\pi\varepsilon_0 s}{q} (\varphi_2 - \varphi_1), \text{ where } \varphi_2 = \zeta, \varphi_1 = 0. \text{ Thus,}$$

$$\frac{\delta}{r(r+\delta)} = \frac{4\pi\varepsilon_0 s}{q} \zeta$$

$$q = \frac{4\pi\varepsilon_0 s r(r+\delta)}{\delta} \zeta$$

The colloidal particle moves as a result of two forces: electrical force F_{el} and resistance force F_{res} , i.e.

$$\begin{aligned} F_{el} &= qE \quad \left| \begin{array}{c} F_{el} = \frac{4\pi\varepsilon_0\varepsilon r(r+\delta)}{\delta}E\zeta & (1) \\ F_{res} &= fv \quad F_{res} = fv = 6\pi\eta rv & (2), \text{ where} \\ f &= k\pi\eta r \ (k = 6 \text{ for spherical particles}); \ \eta &= dynamic viscosity, v = velocity; r + \delta = r + \Delta r. \\ (1) &= (2) \Rightarrow \frac{4\pi\varepsilon_0\varepsilon r(r+\delta)}{\delta}E\zeta &= 6\pi\eta rv \\ \frac{2\varepsilon_0\varepsilon(r+\delta)}{\delta}E\zeta &= 3\eta v \Rightarrow \zeta = \frac{3}{2} \frac{\eta v}{\varepsilon_0\varepsilon E} \cdot \frac{\delta}{r+\delta} = \frac{\eta v}{\varepsilon_0\varepsilon E} \left(\frac{3}{2} \cdot \frac{\delta}{r+\delta}\right) = \frac{\eta v}{\varepsilon_0\varepsilon E} \\ \frac{3}{2} \cdot \frac{\delta}{r+\delta} &= f \cdot \frac{\delta}{r+\delta} \approx 1 \\ \zeta &= \frac{\eta v}{\varepsilon_0\varepsilon E} = \frac{\eta v}{\eta E} = \frac{\eta \mu_e}{D} \ (\text{Electrokinetic potential of a particle}) \\ \mu_e &= \frac{D\zeta}{\eta} = \frac{\varepsilon_0\varepsilon\zeta}{\eta} \ (\text{Electrophoretic mobility of a particle}); \ \mu_e = v/E. \\ \text{It is possible to deduce the formula to calculate ζ -potential in electroosmosis. Let's introduce additional values. \\ V &= v \cdot S \ (volume velocity) \Rightarrow v = V/S \\ i &= \frac{U}{R} \\ R &= \rho \frac{l}{s} = \frac{1}{x} \frac{l}{s} \\ &= \frac{1}{s} \frac{l}{s} \\ \kappa - \text{specific electroconductivity;} \\ i &= \text{strength of current} \end{aligned}$$

$$\begin{cases} \zeta = \frac{\eta v}{DE} = \frac{\eta V}{DES} \\ E = \frac{i}{\kappa S} \end{cases} \xrightarrow{1 - \text{strength of current}} \zeta = \frac{\eta v}{DiS} = \frac{\eta \kappa}{iD} V = \frac{\eta \kappa}{i\varepsilon_0 \varepsilon} V \\ \zeta = \frac{\eta \kappa}{i\varepsilon_0 \varepsilon} V \\ \text{zeta-potential in electro-osmosis} \end{cases}$$

On the base of the data obtained on studying electrophoresis and electro-osmosis it is possible to calculate zeta-potential of particles.

 $\zeta = \frac{\eta \mu_{\varepsilon}}{D} \text{(Electrokinetic potential of a particle in electrophoresis)}$ $\mu_{\varepsilon} = \frac{\varepsilon_0 \varepsilon \zeta}{\eta} \text{(Electrophoretic mobility of a particle)}$ $\zeta = \frac{\eta \varkappa}{i \varepsilon_0 \varepsilon} V \text{ (Electrokinetic potential of a particle in electro-osmosis).}$

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РАСТВОРЫ

(учебно-методическое пособие для иностранных студентов)

Компьютерный набор – Логинов П.В. Форматирование и корректура – Николаев А.А. Технический редактор – Нигдыров В.Б.

ISBN 978-5-4424-0362-6

Подписано в печать 20.12.2017 г. Формат 60 × 90 1/16. Бумага офсетная. Гарнитура *Times New Roman* Усл. печ. лист. – 1,86; Уч.-изд. л. – 0,8 Тираж 300. Заказ № 4419 Издательство «ФГБОУ ВО Астраханский ГМУ» 414000 Астрахань, ул. Бакинская, 121