

PRELIMINARY COMMUNICATION

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DISSOCIATION OF ORGANIC ACIDS AND INDICATOR DYES IN A MIXTURE OF BUTAN-1-OL (82 MASS.%) WITH WATER© 2001 N.O. Mchedlov-Petrosyan, O.N. Tychina,
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A tremendous number of data describing acid-base equilibria in alcohols and their mixtures with water are available in literature. However, the majority of them refer to methanol and ethanol. In this communication we report the results of a study of protolytic equilibria in the mixed solvent butan-1-ol – H₂O near the region of stratification, at 25 °C. The mass fraction of the alcohol was 82%. The above solvent possesses low relative permittivity ($\epsilon=20.8$) and relatively high molar fraction of water ($x_{\text{H}_2\text{O}}=0.47$). The goal in this work was to obtain the thermodynamic $\text{p}K_a$ values for a set of organic acids and common indicator dyes, and to compare them with the $\text{p}K_a$ values in water ($\text{p}K_a^w$) as well as in other solvents. The combination of potentiometrical (with glass electrode) and spectrophotometrical methods was used. Five buffer solutions are proposed as a set of standards for 82 mass.% butan-1-ol. Their pH values, standardized to infinite dilution in the given solvent, i.e. $\text{p}a_{\text{H}^+}^*$, were obtained within the range 2.5 to 12.2 by the US NBS method [1,2]. The results were confirmed in several cases through measurements with indicator dyes. These buffer solutions are used for calibration of cells with liquid junction, in order to determine the acidity of working solutions. The $\text{p}K_a$ values of dyes were obtained by using their absorption spectra in buffer solutions. The ionic strength was as a rule 0.01 M; Debye-Hückel equation was used for calculations of ionic activity coefficients. Some additional experiments showed that the association of ions can be neglected under chosen working conditions.

The thermodynamic $\text{p}K_a$ values of 37 substances (scale of molar concentrations) are plotted vs. the corresponding $\text{p}K_a^w$ values (Fig.1). The given mixed solvent (with $E_T^N = 0.657$) displays a certain differentiating action. The influence of 82 mass.% butan-1-ol is similar to that of 1,4-dioxane – water mixtures with $x_{\text{H}_2\text{O}}$ ca. 0.7 (ϵ 19 to 25); the $\text{p}K_a$ values of benzoic acid in 82 mass.% butan-1-ol and in 64 mass.% 1,4-dioxane are 7.42 and 7.40, respectively.

As it can be seen from Fig.1, the acid-base couples of various charge types and functional groups form several groups of points (carboxylic acids, phenols, sulfonephthaleins, cationic acids). Such a picture is typical for differentiating solvents, in accord with the classical studies of Izmailov [3,4] as well as of other authors [5-7], and can be explained in terms of Born-Brönsted approach [8] and of specific solvation of the species [3-6,9].

On the other hand, any classification of reactants with complicated structure into various groups is conventional. Within each group a further subdivision is possible. Moreover, in some cases a given substance can be simultaneously partially placed into two or more groups, with good reason. Such situation becomes understandable if we use the term 'fuzzy sets' [10,11].

The differentiating impact of 82% butan-1-ol is similar to that of methanol: practically all points in Fig.2 belong to a single strait line:

$$\text{p}K_a(\text{in } 82\% \text{ butan-1-ol}) = -1.84 + 0.997\text{p}K_a(\text{in } \text{CH}_3\text{OH}) \quad (1)$$

$$r = 0.988, n = 25, s = 0.53$$

Probably, the first term of the right part of equation (1) mainly reflects the difference between the proton medium effects, $\log \gamma_{H^+}$, in the two solvents.

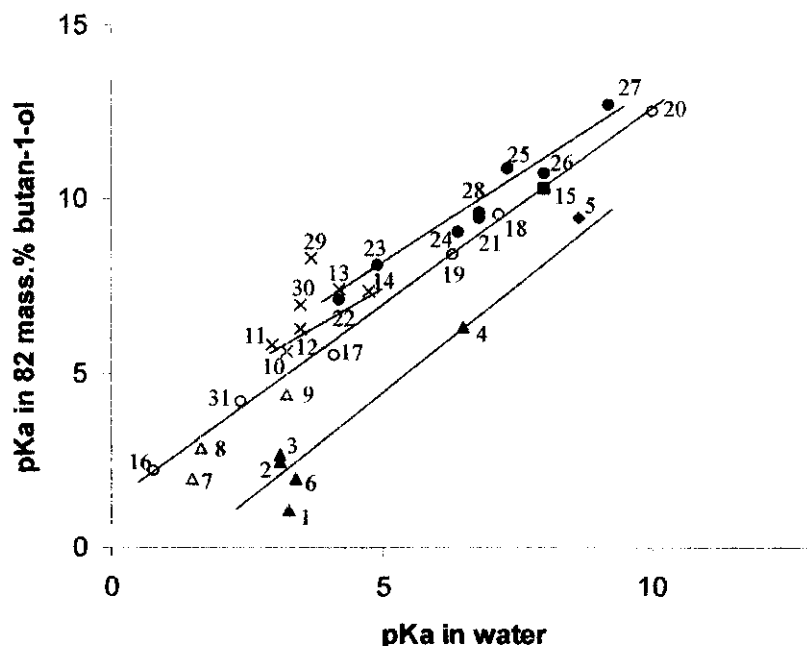


Fig. 1. The dependence of pK_a in 82 mass.% butan-1-ol vs. pK_a in water (the charge types are shown in parentheses): 1 - methyl yellow (+/0), 2 - hexamethoxy red (+/0), 3 - ethyl fluorescein (+/0) [1], 4 - neutral red (+/0), 5 - 4-(2,4,6-triphenylpyridinium-1-yl)-2,6-diphenylphenol (+/±), 6 - methyl orange (±/-), 7 - phenol red (±/-), 8 - thymol blue (±/-), 9 - sulfonefluorescein (±/-) [1], 10 - rhodamine B (+/±), 11 - salicylic acid (0/-), 12 - 3-nitrobenzoic acid (0/-), 13 - benzoic acid (0/-), 14 - acetic acid (0/-), 15 - diethylbarbituric acid (0/-), 16 - picric acid (0/-), 17 - 2,4-dinitrophenol (0/-), 18 - 4-nitrophenol (0/-), 19 - ethyl fluorescein (0/-) [1], 20 - phenol (0/-), 21 - sulfonefluorescein (-/=) [1], 22 - bromophenol blue (-/=), 23 - bromocresol green (-/=), 24 - bromocresol purple (-/=), 25 - bromothymol blue (-/=), 26 - phenol red (-/=), 27 - thymol blue (-/=), 28 - fluorescein (-/=, hydroxy group) [1], 29 - eosin (-/=, carboxylic group) [1], 30 - fluorescein (0/-, carboxylic group) [1], 31 - eosin (0/-, hydroxy group) [1].

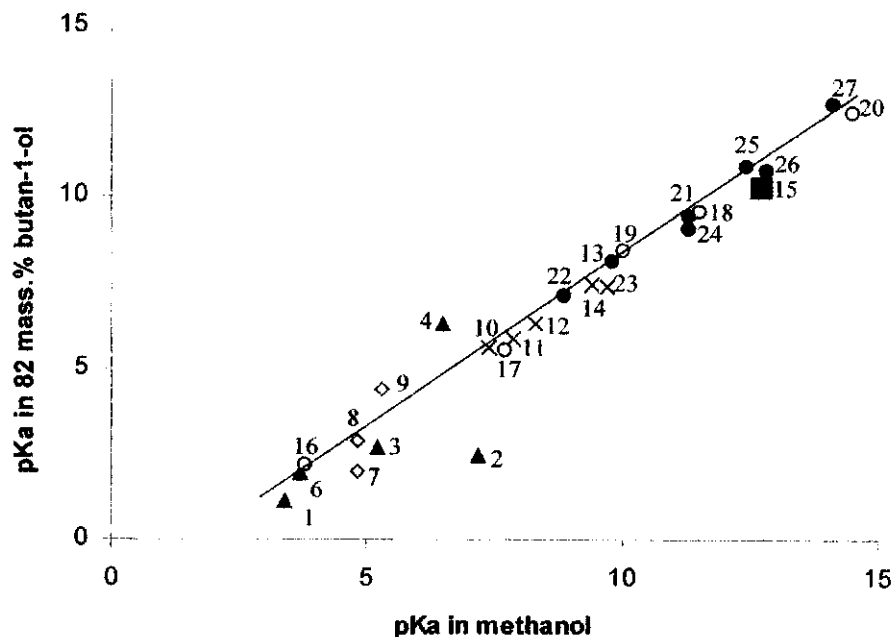


Fig. 2. The dependence of pK_a in 82 mass.% butan-1-ol vs. pK_a in methanol (the numbers of points - as in Fig. 1).

Preferential solvation, caused by the hydrophobicity of the species, is revealed to be one of the reasons for the dissimilarity between differentiating action of butan-1-ol – water mixtures and that of dipolar aprotic solvents and their mixtures with water. The significance of this effect is proved by additional studies within the range from 82 mass.% to 100% butan-1-ol [12].

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Kharkov University Bulletin. 2001. №532. Chemical Series. Issue 7(30). Н.О.Мчедлов-Петросян, О.Н.Тычина, Т.А.Бережная, О.В.Везденева. Диссоциация органических кислот и индикаторных красителей в смеси бутан-1-ола (82 масс.%) с водой.

При помощи потенциометрического и спектрофотометрического методов определены константы диссоциации серии органических кислот и индикаторных красителей в смеси бутан-1-ола (82 масс.%) с водой при 25 °С. Показано, что этот растворитель с достаточно высокой молярной долей воды ($x_{H_2O} = 0.47$) и относительно низкой диэлектрической проницаемостью ($\epsilon = 20.8$) дифференцирует кислотные свойства реагентов примерно так же, как и метиловый спирт. Анализ зависимостей значений pK_a в смешанном растворителе от значений pK_a в воде позволяет проследить роль типа заряда и природы функциональной группы. В то же время, классификация кислотно-основных пар носит до некоторой степени условный характер, в духе известных представлений о «нечетких множествах».