Carbohydrate Research, 132 (1984) 201–208
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

ENERGETICS OF THE INTERACTION OF D-FRUCTOSE AND D-GLUCOSE WITH SODIUM HYDROXIDE IN AQUEOUS ETHYL ALCOHOL, ACETONE, AND 1,4-DIOXANE MEDIA

SATYA P. MOULIK AND DIPTI BASU
Department of Chemistry, Jadavpur University, Calcutta 700032 (India)

(Received March 8th, 1984; accepted for publication, March 29th, 1984)

ABSTRACT

Both D-glucose and D-fructose bind NaOH at 303 K in aqueous medium, with association constants of 24 and 25 $L.mol^{-1}$, respectively. The polarity of the medium significantly affects the association process. Calculation has shown that, at 303 K, 1,4-dioxane, acetone, and ethyl alcohol can totally stop the association process between D-glucose and NaOH at dielectric constants of 52.2, 44.6, and 53.5, respectively, whereas the respective dielectric constants of the solvents required for completely stopping the association process between D-fructose and NaOH are 54.6, 47.0, and 55.0. At equidielectric levels, the changes in free energy for the binding process are more or less similar, whereas the enthalpy and entropy changes differ. In this regard, acetone is the most, and 1,4-dioxane the least, effective of the three solvents. In the mixed media, the binding process ends with an altered solvent structure. The ordering of the environment, that is, the ΔS°, exactly compensates the enthalpy, ΔH°, with a compensation temperature of 298 K. Except for acetone–water at ε 74.5, the energetics of the binding process for both of the carbohydrates are similar in all of the mixed media. The carbohydrate–base complexes are, therefore, physicochemically similar.

INTRODUCTION

Carbohydrates are known to interact with bases[1–6]. In this process, they undergo degradation, the mechanism and course of which have been studied in detail[7–9]. The interactions of salts with hexoses was studied by us[10], and the work was extended to use of certain bases[1,2,6]. It was observed that weak bases, and low concentrations of strong bases, do not readily degrade the sugars, but that they form fairly stable complexes with the hexoses[11–13]. This led us to conclude that a carbohydrate–base complex is formed prior to degradation. The stability constants and energetics of the interactions were evaluated. Such a study was also extended to the polymeric carbohydrate amylose[14]. Interaction of NaOH, KOH, $Ca(OH)_2$, and NH_4OH with this biopolymer was studied from physicochemical standpoints. In addition to lengthening the polymer coil, these bases showed a fair degree of bind-

0008-6215/84/$ 03.00

ing. In an attempt to determine the nature of the carbohydrate–base complex, the effect of the polarity of the medium was examined. It was observed that the stability of the complex was directly proportional to the dielectric constant of the medium, and an ion-dipolar type of association was anticipated, but a detailed investigation from the thermodynamic point of view was not conducted.

We now describe the dielectric constant-affected complexation of D-fructose and D-glucose with NaOH. The polarity of the aqueous medium was varied by adding ethyl alcohol, acetone, and 1,4-dioxane in various proportions. The energetics of the complexation process were evaluated under equidielectric conditions. It was expected that, under the conditions of equipolarity, specific effects of the added solvents would be displayed. Drastic degradations of D-fructose and D-glucose under the influence of NaOH had been studied by us[15], and specific roles of the nonaqueous solvents were anticipated from the results.

EXPERIMENTAL

Materials. — D-Fructose and D-glucose were A.R. (BDH) grade. The NaOH was G.R. (Merck). The nonaqueous solvent alcohol was supplied by EIPW, India. Acetone and 1,4-dioxane were obtained from SDS, India. The solvents were purified by distillation prior to use. Doubly distilled water of specific conductance 2.0–2.5 μmho.cm^{-1} at 298 K was used for preparing solutions.

Methods. — Resistance measurements were made with a Philips conductivity bridge operated in the range of minimum error. The dip type of conductivity cell used for measurements had a cell constant of 1.3 cm^{-1}.

All measurements were made for systems kept in a water bath held at a constant temperature of accuracy within ±0.02 K. Temperatures of experiments were 288, 298, and 303 K.

Procedure. — Stock solutions of D-fructose and D-glucose were prepared in distilled water, and stored in stoppered, Pyrex glass bottles, unnecessary exposure to air being avoided as far as practicable. The NaOH solution was standardized by titration against standardized HCl of G.R. (E. Merck) grade. Solutions of different concentrations of the carbohydrates were then prepared in aquo-organic media. In actual measurement, each solution contained 2mM NaOH which was in a wide test-tube into which the dip type of conductivity cell was placed. There were arrangements for addition of alkali and for bubbling nitrogen through the stopper of the wide test-tube. The tube was placed in the thermostated bath, and allowed to attain constant temperature, and nitrogen was continuously bubbled through the solution to keep air out. The resistance of the solution was measured. 2mM NaOH solution was then progressively added to the solution, and, after each addition, sufficient time was allowed for mixing and for attainment of the constant temperature, followed by measurement of the resistance. Sufficient data were collected for graphical evaluation of the stability constant[2]. The procedure was adopted for all three nonaqueous solvents studied. All runs were performed in duplicate to minimize experimental error.

RESULTS

The specific conductance of 2mM solutions was observed to decrease with increasing carbohydrate content, in water as well as in the mixed-solvent media. Evaluation of the carbohydrate–base association constant, K_A, was made from the following relationship, deduced earlier[2].

$$k'/k = 1 - (1000\, K_A/\mathrm{M})(k'c/k)$$

where k', k, M, and c are respectively the specific conductance of the solution in the presence of a carbohydrate, that in the absence of a carbohydrate, the molecular weight of the carbohydrate, and its concentration in g/mL.

The fit of this relation to the results was quite satisfactory, with a good degree of correlation (0.990). The association constants derived from the least-squares analysis at different dielectric constants of the media are given in Tables I and II.

Thermodynamic parameters were evaluated under equidielectric conditions. Differences among the solvents would then reflect their specific effects. Two dielectric constants, 76.5 and 74.5, were chosen. Lower polarity appreciably lessened the complexation, and was not used, in order to avoid the influence of experimental er-

TABLE I

ENERGETICS OF THE D-GLUCOSE–NaOH BINDING PROCESS IN DIFFERENT MIXED-SOLVENT MEDIA AT 303 K

Solvent	*Dielectric constant*	K_A *(L.mol^{-1})*	$-\Delta G^o$ *(kJ.mol^{-1})*	$-\Delta H^o$ *(kJ.mol^{-1})*	$-\Delta S^o$ *(J^o.K^{-1}.mol^{-1})*
Water	77.3	27.3	8.1	63.3	24.0
1,4-Dioxane–water	76.5	23.5	8.0	23.7	51.8
	74.5	22.6	7.9	22.3	47.5
Acetone–water	76.5	23.3	8.0	12.8	15.9
	74.5	23.1	8.0	5.9	7.4
Alcohol–water	76.5	24.0	8.0	14.2	20.2
	74.5	22.6	7.9	11.3	11.3

TABLE II

ENERGETICS OF THE D-FRUCTOSE–NaOH BINDING PROCESS IN DIFFERENT MIXED-SOLVENT MEDIA AT 303 K

Solvent	*Dielectric constant*	K_A *(L.mol^{-1})*	$-\Delta G^o$ *(kJ.mol^{-1})*	$-\Delta H^o$ *(kJ.mol^{-1})*	$-\Delta S^o$ *(J^o.K^{-1}.mol^{-1})*
Water	77.3	25.0	8.16	27.35	63.34
1,4-Dioxane–water	76.5	23.3	8.08	23.91	52.53
	74.5	22.6	7.90	21.83	46.0
Acetone–water	76.5	23.54	8.00	14.59	21.74
	74.5	23.30	7.98	10.51	8.46
Alcohol–water	76.5	24.02	8.05	16.43	27.62
	74.5	23.06	8.05	12.97	16.30

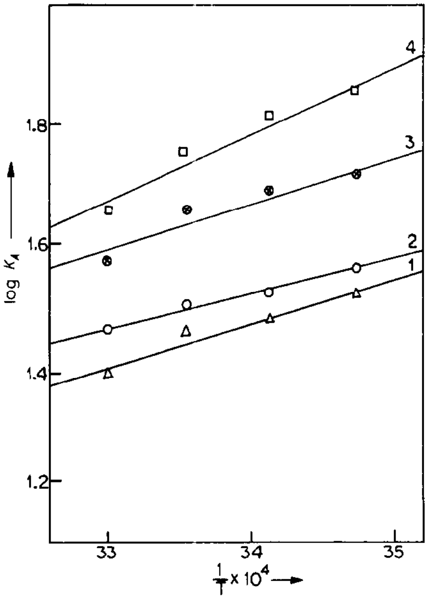

Fig. 1. Van't Hoff plot for the evaluation of ΔH° of the D-glucose–NaOH and D-fructose–NaOH interactions at different dielectric constants of the medium. [Curve 1, D-glucose–NaOH in alcohol–water medium at $\varepsilon = 76.5$; curve 2, D-glucose–NaOH in alcohol–water medium at $\varepsilon = 74.5$; curve 3, D-fructose–NaOH in acetone–water medium at $\varepsilon = 76.5$; curve 4, D-fructose–NaOH in 1,4-dioxane–water at $\varepsilon = 74.5$.]

rors on the results, particularly at higher temperatures (yielding lower association constants). The energetics were evaluated through determination of the association constants at temperatures of 288, 293, 298, and 303 K. Van 't Hoff plots yielded the enthalpy, ΔH°, from the slope (see Fig. 1). The entropy change, ΔS°, was calculated from the Gibbs equation. These values are also given in Tables I and II.

DISCUSSION

The results, presented in Figs. 2 and 3, indicated that, for both of the carbohydrates, the effectivity of the nonaqueous solvents in lowering the association constant (K_A) follows the order, 1,4-dioxane > acetone > alcohol. This is also the order of the solvents affecting the polarity of the medium. For D-glucose, the slopes of the lines produced by 1,4-dioxane, acetone, and alcohol are 3×10^4, 1.8×10^4, and 0.7×10^4, respectively. The respective slopes for D-fructose are 3.8×10^4, 2.5×10^4, and 1.6×10^4. Except for alcohol, the effectivities are comparable. When compared on the basis of the polarity of the medium, a linear trend is observed (see Figs. 4 and 5). The steep slopes of the lines mean strong dependence of K_A on ε. The extrapolated ε values that correspond to $K_A = 0$ are 52.2, 44.6, and 53.5, respectively, for 1,4-dioxane, acetone, and alcohol, for the D-glucose–NaOH system. The respective values are 54.6, 47.0, and 55.0 for the D-fructose–NaOH system. The minimum dielectric constant required for complex-formation is then 45.

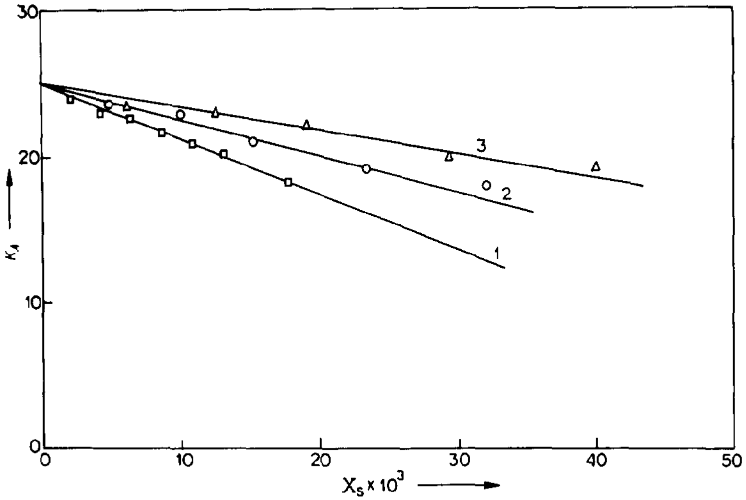

Fig. 2. Dependence of K_A on the mole fraction of the organic solvents for D-glucose–NaOH interaction at 303 K. [Curve 1, 1,4-dioxane–water; curve 2, acetone–water; and curve 3, alcohol–water.]

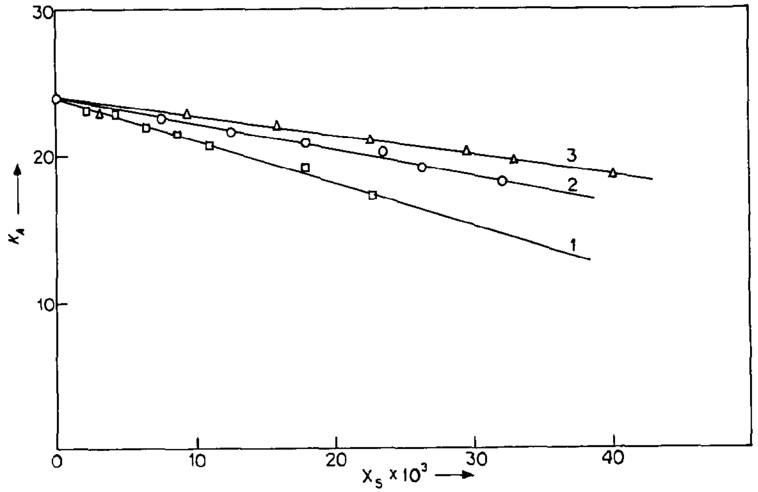

Fig..3. Dependence of K_A on the mole fraction of the organic solvents for D-fructose–NaOH interaction at 303 K. [Curve 1, 1,4-dioxane–water; curve 2, acetone–water; and curve 3, alcohol–water.]

At the equidielectric value (ε = 76.5 and 74.5), the association constants, K_A, for both the D-fructose–NaOH and D-glucose–NaOH systems are ~23 L.mol^{-1}. The values in the aqueous medium are ~25 L.mol^{-1}. Although the changes in free energy are not appreciable, the changes in enthalpy and entropy are significant. Almost unaltered free-energy but altered enthalpy and entropy mean that the complexation process is not entropy-controlled. In the light of the energetics, 1,4-dioxane forms the solvent structure the most, and acetone the least, readily. On the whole, ordering of the environment is a general feature of the process.

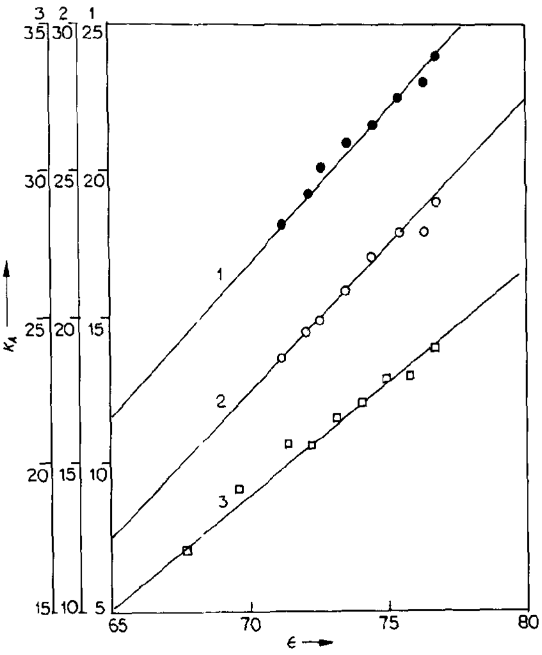

Fig. 4. Dependence of K_A on the dielectric constant of the medium for D-glucose–NaOH interaction at 303 K. [Curve 1, acetone–water; curve 2, alcohol–water; curve 3, 1,4-dioxane–water (ordinate scales correspond to curve numbers).]

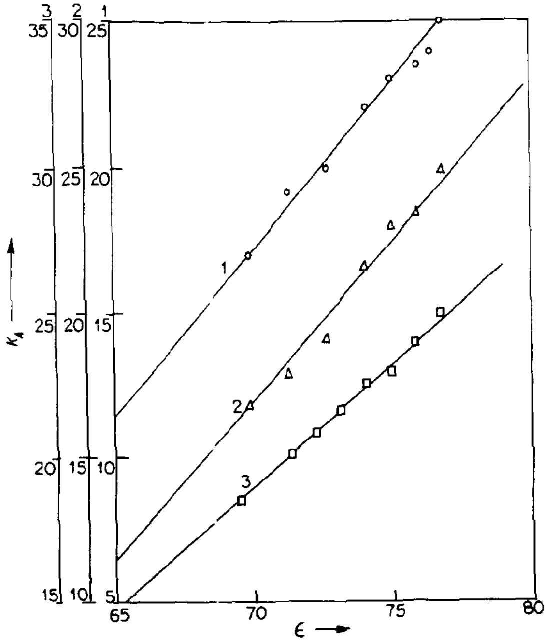

Fig. 5. Dependence of K_A on the dielectric constant of the medium for D-fructose–NaOH interaction at 303 K. [Curve 1, alcohol–water; curve 2, acetone–water; curve 3, 1,4-dioxane–water (ordinate scales correspond to curve numbers).]

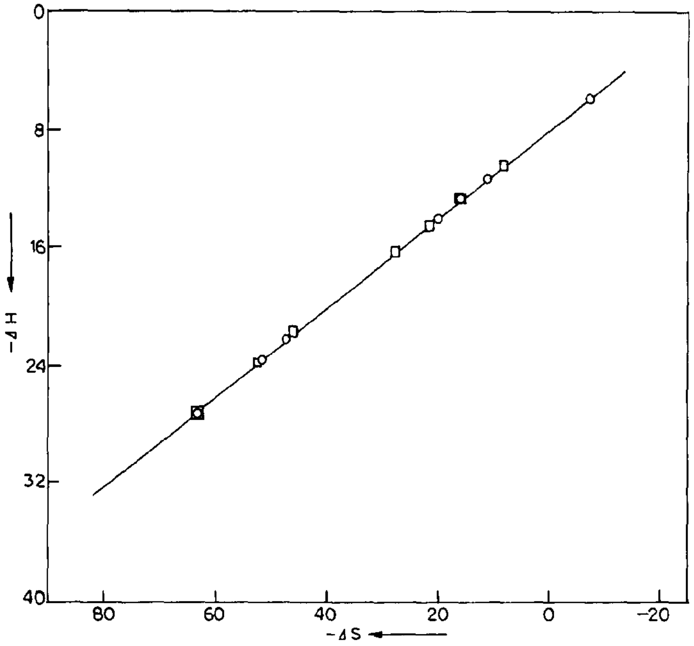

Fig. 6. Enthalpy–entropy compensation plot for D-glucose–NaOH and D-fructose–NaOH interaction. [Key: ○ = D-glucose–NaOH; □ = D-fructose–NaOH.]

Almost the same magnitudes of ΔH° and ΔS° had been observed for amylose–base interactions[14]; the ΔG° values, on the other hand, are low. The two sets of data for each solvent at two, not widely different, dielectric constants have a common feature, that is, ΔH° and ΔS° increase with decrease in ε. Increase in the proportion of a solvent causes evolution of less heat, and, consequently, an increase in the entropy change; this is particularly prominent in the case of acetone. Like many equilibrium processes[16,17], the enthalpy and entropy nicely compensate each other; this is shown in Fig. 6. The line has a correlation coefficient of $r = 0.99$. The compensation temperature, 302 K, agrees closely with the experimental temperature of 303 K. A single line closely describing the behavior of both of the carbohydrates means a similar physicochemical nature of the complexes[18]. Except for acetone–water at ε 74.5, the energetics for both D-glucose–NaOH and D-fructose–NaOH systems are close. The base NaOH binds similarly with both D-glucose and D-fructose (similar ΔG°), the structural arrangement of the solvent in all situations being affected by the nonfree part of the involved heat.

ACKNOWLEDGMENT

D.B. thanks the University authorities for the use of laboratory facilities.

REFERENCES

1 S. P. MOULIK AND A. K. MITRA, *Carbohydr. Res.*, 28 (1973) 371–377.
2 S. P. MOULIK AND D. P. KHAN, *Carbohydr. Res.*, 41 (1975) 93–104.
3 S. J. ANGYAL, *Tetrahedron*, 30 (1974) 1695–1702.
4 A. P. G. KIEBOOM, T. SPOORMAKER, A. SINNEMA, J. M. VAN DER TOORN, AND H. VAN BEKKUM, *Recl. Trav. Chim. Pays-Bas*, 94 (1975) 53–59.
5 A. P. G. KIEBOOM, H. M. A. BUURMANS, L. K. VAN LEEUWEN, AND J. VAN BENSCHOP, *Recl. Trav. Chim. Pays-Bas*, 98 (1979) 393–394.
6 S. P. MOULIK AND A. K. MITRA, *Carbohydr. Res.*, 29 (1973) 509–512.
7 C. A. LOBRY DE BRUYN AND W. ALBERDA VAN EKENSTEIN, *Recl. Trav. Chim. Pays-Bas*, 14 (1895) 203.
8 J. HONEYMAN, *Recent Advances in the Chemistry of Cellulose and Starch*, Interscience, New York, 1959.
9 M. S. FEATHER AND J. F. HARRIS, *Adv. Carbohydr. Chem. Biochem.*, 28 (1973) 161–224.
10 S. P. MOULIK AND D. P. KHAN, *Carbohydr. Res.*, 36 (1974) 147–157.
11 N. ROY AND A. K. MITRA, *Carbohydr. Res.*, 24 (1972) 175–179.
12 S. P. MOULIK AND A. K. MITRA, *Carbohydr. Res.*, 23 (1972) 65–74.
13 S. P. MOULIK, A. K. MITRA, AND K. K. SEN GUPTA, *Carbohydr. Res.*, 19 (1971) 416–418.
14 S. P. MOULIK AND S. GUPTA, *Carbohydr. Res.*, 112 (1983) 123–136.
15 S. P. MOULIK, D. BASU, AND P. K. BHATTACHARYA, *Carbohydr. Res.*, 63 (1978) 165–172.
16 R. LUMRY AND S. RAJENDER, *Biopolymers*, 9 (1970) 1125–1227.
17 S. P. MOULIK, S. RAY, AND A. R. DAS, *J. Phys. Chem.*, 81 (1977) 1766–1769; *Colloid Polym. Sci.*, 257 (1979) 182–191.
18 S. PAL AND S. P. MOULIK, *J. Lipid. Res.*, 24 (1983) 1281–1290.