

Infinite Dilution Activity Coefficients of *n*-Alcohols as a Function of Dextrin Concentration in Water-Dextrin Systems

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The effect of dextrin concentration on the ability of water-dextrin systems to retain alcohols has been studied by measuring alcohol infinite dilution activity coefficients with a specially designed apparatus. Measurements of activity coefficients have been performed at 298.1 K for methanol to 1-hexanol in water and in water-maltodextrin and water- β -cyclodextrin systems.

Organoleptic qualities of food are considerably modified during food processing. The modifications occurring in real food are difficult to study because of its chemical complexity (numerous substrates, simultaneous presence of polar and nonpolar volatile components). As a simplification, models of solutions are selected that are composed of one substrate and one volatile component. The final objective of working on such selected solutions is to obtain enough information to be able to predict some characteristic properties of food such as its retention of volatile components.

Recently, group contribution concepts have been developed (Derr and Deal, 1969; Fredenslund et al., 1975, 1977; Kojima and Tochigi, 1979). They are very attractive because they allow mixture properties to be calculated provided the interaction parameters between the different groups constituting the molecules of the mixtures are known. As the number of all different possible groups is much lower than that of all existing molecules, there is a great advantage in using group contribution methods. The actual methods are not adapted to very complex molecules (Le Maguer, 1981); thus, in order to work on food molecules, it will be necessary to develop a specially suited group contribution concept with defining representative groups and combination laws for group properties (the positions of the groups in the three-dimensional molecules have to be taken into account). To begin with, some model mixtures must be selected to perform experimental measurements involving all the various groups. For this reason, *n*-alcohol and *n*-alkane infinite dilution activity coefficients have been measured (Lebert and Richon, 1984) in pure olive oil with the stripping technique from Richon and Renon (1980). This technique is a modification of those described in other papers (Leroi et al., 1977; Richon et al., 1980). In this paper, results are presented for *n*-alcohol infinite dilution activity coefficients in water and in water-maltodextrin and water- β -cyclodextrin systems.

MATERIALS AND METHODS

The origin and purity of the alcohols are given in Table I. Water is purified by distillation in a quartz apparatus; the β -cyclodextrin is provided by Roquette Freres with a certified minimum purity of no less than 99 wt% and mean molecular mass of 1176. The main impurity is the α -cyclodextrin. The maltodextrin (MD 03) from Roquette

Table I. Origin and Purity of the *n*-Alcohols

name	origin	minimum certified purity, %
methanol	Carlo Erba	99.9 (v/v)
ethanol	Carlo Erba	99.9 (v/v)
1-propanol	Carlo Erba	99.9 (v/v)
1-butanol	Prolabo	99.5 (GLC)
1-pentanol	Prolabo	99.0 (GLC)
1-hexanol	Prolabo	98.0 (GLC)

Table II. Infinite Dilution Activity Coefficient at 298.1 K of Methanol in Maltodextrin (1)-Water (2) Systems as a Function of Maltodextrin Weight Fraction

W_1	$\gamma_{me,wm}^\infty$	$\gamma_{me,wm}^\infty/\gamma_{me,w}^\infty$
0	1.65 ± 0.01	1
0.0356	1.58 ± 0.02	0.958
0.0383	1.60 ± 0.01	0.970
0.0418	1.55 ± 0.01	0.939
0.0785	1.50 ± 0.01	0.909
0.0818	1.48 ± 0.02	0.897
0.0824	1.47 ± 0.01	0.891
0.1333	1.38 ± 0.02	0.836
0.1356	1.35 ± 0.02	0.818
0.1391	1.35 ± 0.02	0.818
0.1911	1.23 ± 0.01	0.745
0.1963	1.21 ± 0.01	0.733
0.2003	1.20 ± 0.02	0.727
0.2438	1.06 ± 0.01	0.642
0.2475	1.07 ± 0.01	0.648
0.2518	1.05 ± 0.01	0.636

Freres has a broad molecular mass dispersion (see Figure 1).

The technique used in this work has been fully described in previous papers (Leroi et al., 1977; Richon et al., 1980). The special equilibrium cell for high activity coefficients is that described by Richon and Renon (1980).

For high activity coefficients, the expression that relates the activity coefficients to the measured experimental data is

$$\gamma_i^\infty = -\frac{1}{t} \ln \frac{S_i(t)}{S_i(0)} \frac{RTN}{D + \frac{V_G}{t} \ln \frac{S_i(t)}{S_i(0)}} \frac{1}{P_1^s} \quad (1)$$

This equation is a simplification of Duhem and Vidal's equation (1978) when the corrective term accounting for the variation of the total gas flow rate due to the vaporization of solute is neglected.

In eq 1, N is the total number of moles of solvent. For a multicomponent mixture it is obtained from

$$N = \sum_i m_i / M_i \quad (2)$$

The number of moles of solvents is determined by accurate weighings within ± 0.1 mg. The solutes (about 10

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Table III. Infinite Dilution Activity Coefficient at 298.1 K of Ethanol in Maltodextrin (1)-Water (2) Systems as a Function of Maltodextrin Weight Fraction

W_1	$\gamma_{e,wm}^{\infty}$	$\gamma_{e,wm}^{\infty}/\gamma_{e,w}^{\infty}$
0	3.27 ± 0.05	1
0.0198	3.20 ± 0.07	0.979
0.0211	3.23 ± 0.06	0.988
0.0213	3.23 ± 0.05	0.988
0.0497	3.10 ± 0.06	0.948
0.0512	3.17 ± 0.06	0.969
0.0521	3.10 ± 0.07	0.948
0.0967	2.90 ± 0.07	0.887
0.0987	2.86 ± 0.06	0.875
0.1012	2.96 ± 0.08	0.905
0.1309	2.69 ± 0.07	0.823
0.1325	2.75 ± 0.05	0.841
0.1327	2.65 ± 0.04	0.810
0.1804	2.42 ± 0.04	0.740
0.1824	2.52 ± 0.07	0.770
0.1831	2.51 ± 0.08	0.768
0.2118	2.30 ± 0.06	0.703
0.2151	2.23 ± 0.05	0.682
0.2175	2.29 ± 0.08	0.700

Table IV. Infinite Dilution Activity Coefficient at 298.1 K of 1-Propanol in Maltodextrin (1)-Water (2) Systems as a Function of Maltodextrin Weight Fraction

W_1	$\gamma_{p,wm}^{\infty}$	$\gamma_{p,wm}^{\infty}/\gamma_{p,w}^{\infty}$
0	10.9 ± 0.2	1
0.0298	10.4 ± 0.1	0.954
0.0311	10.7 ± 0.1	0.982
0.0318	10.5 ± 0.2	0.963
0.0692	10.4 ± 0.1	0.954
0.0711	10.1 ± 0.1	0.927
0.0718	10.1 ± 0.2	0.927
0.1088	9.21 ± 0.3	0.844
0.1151	9.30 ± 0.2	0.853
0.1126	9.51 ± 0.2	0.872
0.1856	8.20 ± 0.1	0.752
0.1875	8.07 ± 0.1	0.741
0.1926	8.01 ± 0.2	0.734
0.2318	7.34 ± 0.2	0.673
0.2354	7.20 ± 0.1	0.661
0.2405	7.18 ± 0.3	0.658

Table V. Infinite Dilution Activity Coefficient at 298.1 K of 1-Butanol in Maltodextrin (1)-Water (2) Systems as a Function of Maltodextrin Weight Fraction

W_1	$\gamma_{b,wm}^{\infty}$	$\gamma_{b,wm}^{\infty}/\gamma_{b,w}^{\infty}$
0	45.1 ± 1.4	1
0.0098	44.4 ± 1.0	0.984
0.0105	46.0 ± 1.5	1.020
0.0126	44.9 ± 1.3	0.996
0.0818	40.4 ± 1.3	0.896
0.0829	39.9 ± 1.4	0.885
0.0863	40.6 ± 1.5	0.900
0.1654	35.2 ± 1.2	0.780
0.1691	35.6 ± 1.5	0.789
0.1703	35.4 ± 0.9	0.785
0.2036	32.4 ± 1.3	0.718
0.2051	31.9 ± 1.3	0.707
0.2095	32.9 ± 1.5	0.729
0.2438	29.5 ± 1.6	0.654
0.2454	29.4 ± 1.3	0.652
0.2467	29.2 ± 1.2	0.647

μL) are directly introduced inside the solvent (about 30 mL) by means of a GLC syringe. For details about the reliability of the stripping method, see the papers from Leroi et al. (1977) and Richon et al. (1980).

RESULTS

The infinite dilution activity coefficients of alcohols in water have been first measured and compared to literature data. Then, the influence on the alcohol infinite dilution activity coefficient of adding dextrans has been studied as

Table VI. Infinite Dilution Activity Coefficient at 298.1 K of 1-Pentanol in Maltodextrin (1)-Water (2) Systems as a Function of Maltodextrin Weight Fraction

W_1	$\gamma_{pe,wm}^{\infty}$	$\gamma_{pe,wm}^{\infty}/\gamma_{pe,w}^{\infty}$
0	192 ± 8	1
0.0582	179 ± 7	0.932
0.1564	155 ± 9	0.807
0.2123	133 ± 13	0.693

Table VII. Infinite Dilution Activity Coefficient at 298.1 K of 1-Hexanol in Maltodextrin (1)-Water (2) Systems as a Function of Maltodextrin Weight Fraction

W_1	$\gamma_{h,wm}^{\infty}$	$\gamma_{h,wm}^{\infty}/\gamma_{h,w}^{\infty}$
0	645 ± 32	1
0.02188	622 ± 29	0.964
0.0898	531 ± 30	0.823
0.2267	451 ± 30	0.699

Table VIII. Infinite Dilution Activity Coefficient at 298.1 K of Methanol in β -Cyclodextrin (1)-Water (2) Systems as a Function of β -Cyclodextrin Weight Fraction

W_1	$\gamma_{me,wc}^{\infty}$	$\gamma_{me,wc}^{\infty}/\gamma_{me,w}^{\infty}$
0	1.65 ± 0.01	1
0.00305	1.62 ± 0.01	0.982
0.00372	1.63 ± 0.02	0.988
0.00375	1.62 ± 0.01	0.982
0.00857	1.58 ± 0.02	0.958
0.00879	1.59 ± 0.02	0.964
0.00951	1.58 ± 0.01	0.958
0.01502	1.53 ± 0.02	0.927
0.01568	1.53 ± 0.02	0.927
0.01572	1.53 ± 0.02	0.927
0.02174	1.48 ± 0.01	0.897
0.02198	1.50 ± 0.02	0.909
0.02241	1.49 ± 0.01	0.903
0.02893	1.44 ± 0.01	0.873
0.02911	1.43 ± 0.01	0.866
0.02948	1.43 ± 0.02	0.866
0.03816	1.37 ± 0.01	0.830
0.03881	1.34 ± 0.01	0.812
0.03987	1.36 ± 0.02	0.824
0.04752	1.28 ± 0.02	0.776
0.04816	1.28 ± 0.01	0.776
0.04836	1.28 ± 0.01	0.776
0.05504	1.23 ± 0.01	0.745
0.05613	1.23 ± 0.01	0.745
0.05701	1.21 ± 0.01	0.733

Table IX. Infinite Dilution Activity Coefficient at 298.1 K of Ethanol in β -Cyclodextrin (1)-Water (2) Systems as a Function of β -Cyclodextrin Weight Fraction

W_1	$\gamma_{e,wc}^{\infty}$	$\gamma_{e,wc}^{\infty}/\gamma_{e,w}^{\infty}$
0	3.27 ± 0.05	1
0.00503	3.15 ± 0.06	0.963
0.02631	2.89 ± 0.06	0.884
0.04236	2.60 ± 0.06	0.795

Table X. Infinite Dilution Activity Coefficient at 298.1 K of 1-Propanol in β -Cyclodextrin (1)-Water (2) Systems as a Function of β -Cyclodextrin Weight Fraction

W_1	$\gamma_{p,wc}^{\infty}$	$\gamma_{p,wc}^{\infty}/\gamma_{p,w}^{\infty}$
0	10.9 ± 0.2	1
0.007523	10.6 ± 0.2	0.972
0.01844	9.88 ± 0.3	0.907
0.05204	8.96 ± 0.3	0.822

Table XI. Infinite Dilution Activity Coefficient at 298.1 K of 1-Butanol in β -Cyclodextrin (1)-Water (2) Systems as a Function of β -Cyclodextrin Weight Fraction

W_1	$\gamma_{b,wc}^{\infty}$	$\gamma_{b,wc}^{\infty}/\gamma_{b,w}^{\infty}$
0	45.1 ± 1.4	1
0.01516	43.3 ± 1.2	0.960
0.03283	37.9 ± 1.5	0.840
0.03915	38.2 ± 1.6	0.847

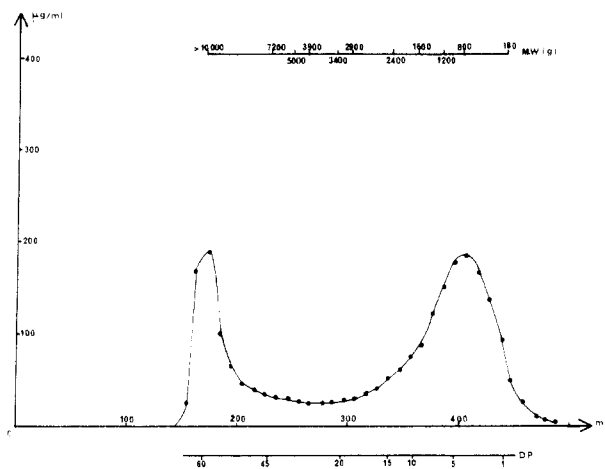


Figure 1. Gel filtration curve of maltodextrin MD03 on Sephadex G-50.

Table XII. Methanol Infinite Dilution Activity Coefficients in Water at 298.1 K Calculated by Using Literature Vapor-Liquid Equilibrium Data and Thermodynamic Models

lit.	thermodynamic models			
	Redlich-Kister	Van Laar	Wilson	N.R.T.L.
Mc Glashan and Williamson (1976)	1.76	1.80	1.71	1.73
Othmer and Benenati (1945)	1.75	1.69	1.71	1.70
Ramalho et al. (1961)	1.71	1.78	1.74	1.78
Verhoeve and De Schepper (1973)	1.81	1.79	1.83	1.73
Green and Vener (1955)	1.72	1.73	1.65	1.72
Butler et al. (1933)	1.58	1.57	1.61	1.59

Table XIII. Ethanol Infinite Dilution Activity Coefficients in Water at 25 °C Calculated by Using Literature Vapor-Liquid Equilibrium Data and Thermodynamic Models

lit.	thermodynamic models			
	Redlich-Kister	Van Laar	Wilson	N.R.T.L.
Carey and Bertelsen (1932)	3.61	3.57	3.76	3.56
Beebe et al. (1942)	3.34	3.42	3.39	3.26
Jones and Schoenberg (1943)	3.52	3.36	3.42	3.34

a function of the dextrans concentration in water. Our experimental results are reported in Tables II–XI along with each of the estimated experimental errors from the dispersion observed on at least five determinations. In Tables XII and XIII are given the values of the infinite dilution activity coefficients calculated from literature vapor-liquid equilibrium data by using some thermodynamic models. The values of the parameters adjusted for the different models in the case of methanol-water and ethanol-water are reported in Tables XIV and XV.

Alcohols in Water. The new experimental data are reported in Tables II–VII. Literature data (Tables XII–XIII) were obtained from a computer analysis performed on vapor-liquid equilibrium data using thermodynamic models. The simplex method (Fredenslund et al., 1977) was selected to adjust parameters of the four models involved in this work: Redlich-Kister, Van Laar, Wilson, and N.R.T.L. (see Appendix). Discrepancies between our results and those of the literature are consistently less than 15%. By examining these last tables, we may not that the

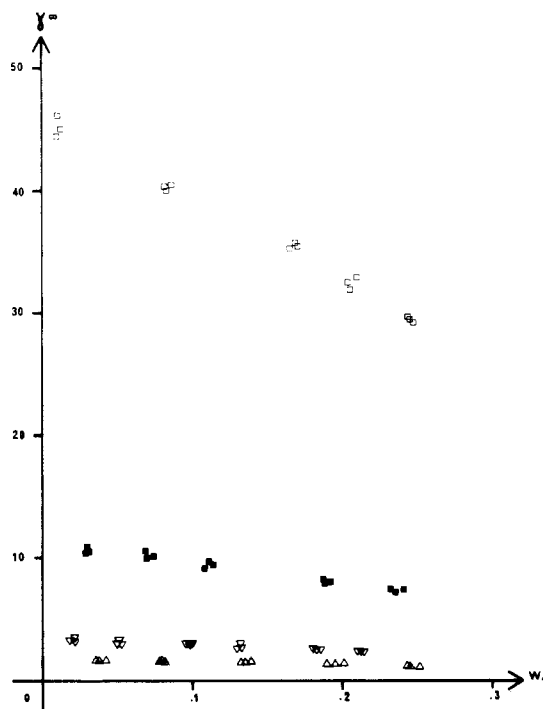


Figure 2. Infinite dilution activity coefficients of *n*-alcohol as a function of maltodextrin weight fraction in the maltodextrin (1)-water (2) system at 298.1 K: (□) 1-butanol; (●) 1-propanol; (▽) ethanol; (△) methanol.

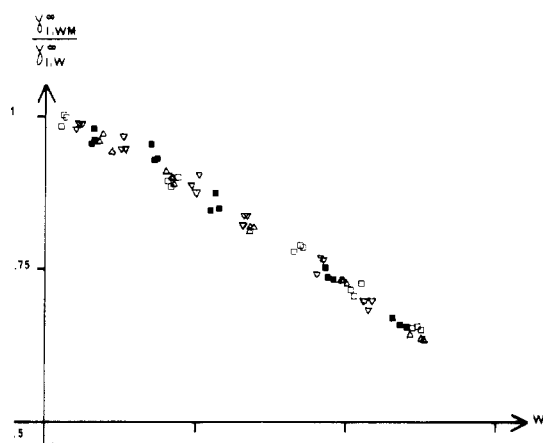


Figure 3. *n*-Alcohol reduced infinite dilution activity coefficients as a function of maltodextrin weight fraction in the maltodextrin (1)-water (2) system at 298.1 K: (□) 1-butanol; (●) 1-propanol; (▽) ethanol; (△) methanol.

choice of the model to treat vapor-liquid equilibrium data has a direct effect on the calculated data. Differences between data calculated through the different models can reach 6%.

The values of the infinite dilution activity coefficients are greater than 1 and an increasing function of alcohol chain length.

Alcohols in Water-Maltodextrin Systems. Aqueous solutions of maltodextrin ranging between 0 and 0.25 in maltodextrin weight fractions were prepared to measure the ability of maltodextrin to retain *n*-alcohols. Results are reported in Tables II–V and Figure 2. As a general conclusion, adding maltodextrin leads to a decreasing alcohol activity coefficient, which indicates that the maltodextrin has a positive effect in enhancing alcohol retention. The ratios of the infinite dilution activity coefficients of alcohols in water to those in water-maltodextrin systems are plotted in Figure 3 for methanol to 1-butanol, as a

Table XIV. Thermodynamic Model Parameters for Methanol-Water System

lit.	temp or pressure of lit. data	thermodynamic models				
		parameters	Redlich-Kister	Van Laar	Wilson	N.R.T.L.
Mac Glashan and Williamson (1976)	308.1, 323.1, 338.1 K	A1	0.553	0.637	0.554	0.751
		A2	-0.0822	0.492	0.949	-0.112
		A3	0.0056	-0.0014	-0.0025	-0.0024
		A4	0.0018	-0.0012	0.0089	-0.0010
Othmer and Benenati (1945)	200, 350, 500, 760 mmHg	A1	0.686	0.788	0.546	0.830
		A2	-0.0982	0.610	0.828	-0.0527
		A3	0.0014	-0.011	0.0019	-0.011
		A4	0.0025	-0.009	-0.0063	-0.0012
Ramalho et al. (1961)	760 mmHg	A1	0.641	0.811	0.426	1.183
		A2	-0.160	0.530	1.037	0.883
		A3	0.0201	-0.0094	-0.0021	-0.054
		A4	0.0307	-0.0104	-0.016	0.0029
Verhoeve and De Schepper (1973)	760 mmHg	A1	0.610	0.762	0.450	1.661
		A2	-0.133	0.512	1.031	0.258
		A3	0.0073	-0.0072	-0.0016	-0.0052
		A4	0.0026	-0.0081	-0.010	-0.0024
Green and Vener (1955)	760 mmHg	A1	0.680	0.812	0.464	1.535
		A2	-0.126	0.584	0.946	-0.355
		A3	0.0056	-0.0106	-0.0031	-0.022
		A4	0.0061	-0.0094	0.0202	0.0012
Butler et al. (1933)	298.1 K	A1	0.495	0.453	0.908	0.619
		A2	0.046	0.53	0.640	0.753
		A3	0	0	0	0
		A4	0	0	0	0

Table XV. Thermodynamic Model Parameters for Ethanol-Water System

lit.	pressure of lit. data, mmHg	thermodynamic models				
		parameters	Redlich-Kister	Van Laar	Wilson	N.R.T.L.
Carey and Bertelsen (1932)	380	A1	1.172	1.673	1.024	1.408
		A2	-0.436	0.903	1.349	-0.601
		A3	-0.0034	-0.016	-0.023	0.040
		A4	0.0021	-0.012	0.035	-0.011
Beebe et al. (1942)	760	A1	1.015	1.639	1.107	1.168
		A2	-0.572	0.766	1.411	1.216
		A3	-0.0029	0.016	0.0020	0.026
		A4	0.0135	-0.003	-0.019	-0.014
Jones and Schoenberg (1943)	95, 190, 380	A1	1.219	1.402	1.096	2.843
		A2	0.0183	1.233	1.426	-1.013
		A3	-0.0034	0.0076	-0.0011	0.036
		A4	-0.0057	-0.0043	-0.019	-0.023

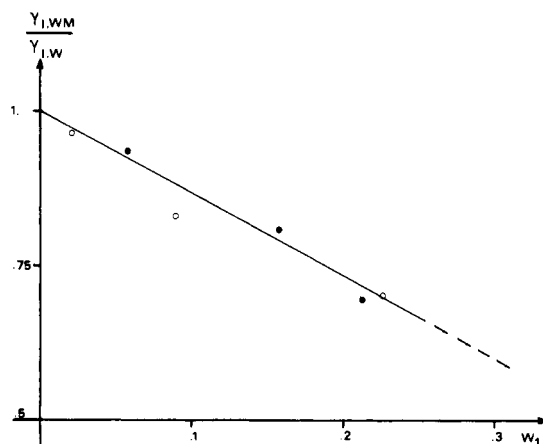


Figure 4. Comparisons between predicted and experimental *n*-alcohol reduced infinite dilution activity coefficients in the maltodextrin (1)-water (2) system at 298.1 K: (—) predicted curve; (●) 1-pentanol; (○) 1-hexanol.

function of maltodextrin weight fractions. The interesting remark is the 75 reduced activity coefficient values all lie on the same mean curve within the experimental error, indicating that this curve is not dependent on the nature of the alcohol chosen for its determination. Its equation is

$$\gamma_{i,wm}^{\infty} / \gamma_{i,w}^{\infty} = 1 - 1.329W_1 \quad (3)$$

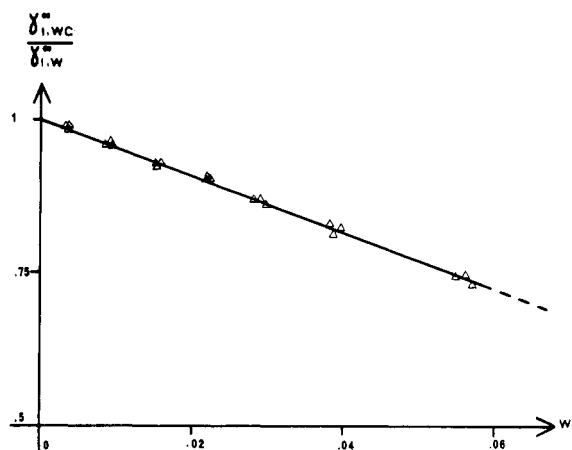


Figure 5. Methanol reduced infinite dilution activity coefficients as a function of β -cyclodextrin weight fraction in the β -cyclodextrin (1)-water (2) system at 298.1 K: (Δ) experimental data; (—) smoothed curve.

As a complementary test of the universality of the curve for alcohols in water-maltodextrin systems, measurements have been taken for 1-pentanol and 1-hexanol (Tables VI and VII). The new data are plotted in Figure 4 along with the adjusted curve (eq 3). The agreement between predicted and measured data is very good.

Alcohols in Water- β -Cyclodextrin Systems. Numerous measurements have been obtained for methanol in water- β -cyclodextrins (Table VIII). Reduced activity coefficients appear in Figure 5 along with the mean curve

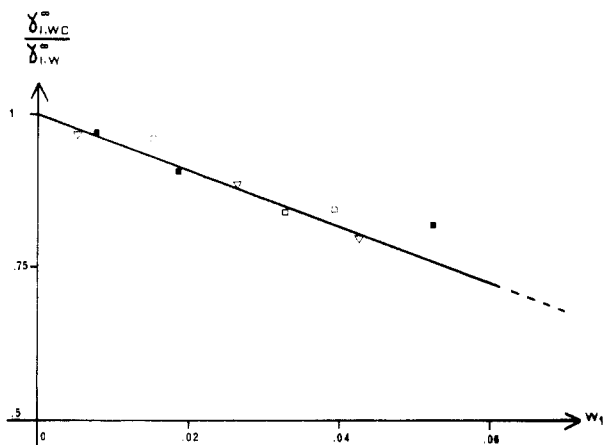


Figure 6. *n*-Alcohol reduced infinite dilution activity coefficients as a function of β -cyclodextrin weight fraction in the β -cyclodextrins (1)-water (2) system at 298.1 K: (\square) 1-butanol; (\blacksquare) 1-propanol; (∇) ethanol; (—) smoothed curve for methanol.

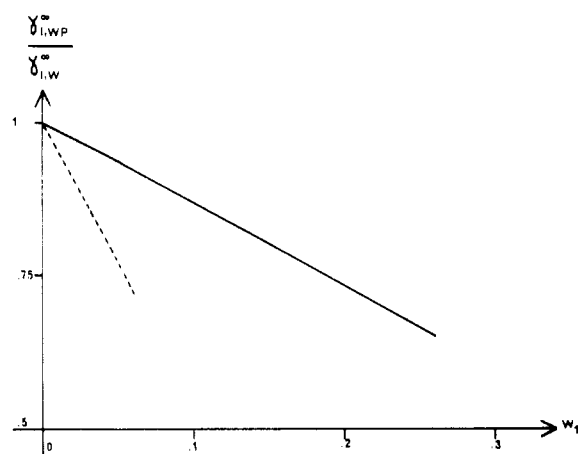


Figure 7. Influence of the dextrin nature on the alcohol reduced infinite dilution activity coefficients as a function of dextrin weight fraction in the dextrin (1)-water (2) system at 298.1 K: (—) maltodextrin; (---) β -cyclodextrin.

representing the data. The equation of this mean curve is

$$\gamma_{i,wc}^{\infty} / \gamma_{i,w}^{\infty} = 1 - 4.56W_1 \quad (4)$$

Reduced activity coefficients for ethanol, 1-propanol, and 1-butanol (Tables IX–XI) are plotted in Figure 6 along with the adjusted curve (eq 4). Similar to the water-maltodextrin systems, it seems that there is also a universal curve valid for all alcohols in water- β -cyclodextrin systems.

The curves obtained through eq 3 and 4 have been plotted in Figure 7. By its observation, several points can be made: (1) there are always positive deviations from the ideal case; (2) alcohol retention is a positive function of dextrin weight fractions; (3) at an equal weight fraction, alcohol retention by β -cyclodextrin is greater than that by maltodextrin.

CONCLUSION

The stripping method appeared to be very well suited to measure infinite dilution activity coefficients of alcohols in water-sugar systems. From the experimental results, it was shown that the maltodextrin and β -cyclodextrin increase the ability of water to retain alcohols in the liquid phase. In the present work, it has been noted that by using reduced activity coefficients (with respect to activity coefficient in pure water) and by only measuring the sugar concentration effect on one alcohol, it was possible to

predict the sugar concentration effect on the other alcohols.

Comparisons between infinite dilution experimental data from the stripping technique and the extrapolated data obtained from finite dilution vapor-liquid equilibria (VLE) determinations using a thermodynamic model give rise to the following remarks: (1) the models are not really accurate enough to be used for extrapolations at infinite dilution; (2) the calculated infinite dilution activity coefficients depend greatly on the data base, i.e., the accuracy and the number of VLE points, the distribution of VLE points along concentration range, etc. Therefore, the best way to get infinite dilution data is to measure them directly under the infinite dilution conditions.

Abbreviations Used: A_i , i th parameter of the thermodynamic models; D , carrier gas flow (pressure P , temperature T) (cm^3/min); N , number of moles of solvent; P , total pressure (atm); R , gas constant ($\text{cm}^3\text{-atm-g-mol}^{-1}\text{-K}^{-1}$); S , chromatographic peak area (arbitrary units); t , time (min); T , temperature (K); V_G , volume of vapor phase (cm^3); W , weight fraction; x , liquid mole fraction; y , vapor mole fraction; α , nonrandomness parameter in the expression of G for eq 4 of the Appendix; γ , activity coefficient; subscript i , component i ; b, 1-butanol; e, ethanol; h, 1-hexanol; m, maltodextrins; me, methanol; pe, 1-pentanol; w, water; wc, water- β -cyclodextrins; wm, water-maltodextrins; wp, water-dextrins; superscript S , saturated property; ∞ , infinite dilution property.

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APPENDIX

The analytical expressions for the activity coefficients (binary mixtures) from the different thermodynamic models (Prausnitz, 1969) used in this work are the following.

Redlich-Kister's equation

$$\ln \gamma_1 = (1 - x_1)^2 [Z_{12} + Z_{21}(4x_1 - 1)] \quad (1)$$

Van Laar's equation

$$\ln \gamma_1 = \frac{Z_{12}}{(1 + Z_{12}x_1/[Z_{21}(1 - x_1)])^2} \quad (2)$$

Wilson's equation

$$\ln \gamma_1 = -\ln [x_1 + Z_{12}(1 - x_1)] + (1 - x_1) \left(\frac{Z_{12}}{x_1 + Z_{12}(1 - x_1)} - \frac{Z_{21}}{(1 - x_1) + x_1 Z_{21}} \right) \quad (3)$$

N.R.T.L. equation

$$\ln \gamma_1 = (1 - x_1)^2 \left(\frac{Z_{21}G_{21}^2}{[x_1 + (1 - x_1)G_{21}]^2} + \frac{Z_{12}G_{12}}{[(1 - x_1) + x_1G_{12}]^2} \right) \quad (4)$$

with $G_{12} = \exp(-\alpha Z_{12})$ and $G_{21} = \exp(-\alpha Z_{21})$. In this work, α is equal to 0.3, a value recommended by Renon and Prausnitz (1968) for water-polar systems.

As all the equations were used to simultaneously represent data at different temperatures, the two parameters Z_{12} and Z_{21} have been taken as linearly temperature dependent with respect to eq 5 and 6:

$$Z_{12} = A_1 + A_2T \quad (5)$$

$$Z_{21} = A_3 + A_4 T \quad (6)$$

T is the temperature in kelvin.

The objective function relating experimental and calculated data is minimized by a sequential search procedure developed by Nelder and Mead (1965) from the simplex method introduced by Spendley et al. (1962).

Registry No. Methanol, 67-56-1; 1-hexanol, 111-27-3; maltodextrin, 9050-36-6; β -cyclodextrin, 7585-39-9; water, 7732-18-5; dextrin, 9004-53-9; 1-propanol, 71-23-8; 1-butanol, 71-36-3; ethanol, 64-17-5; 1-pentanol, 71-41-0.

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Relationship between Physical and Chemical Characters and Cooking Quality in Lentil

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The cooking quality (shear force) of 101 samples of three cultivars of lentil grown at several locations in 1980 and 1981 was related to their protein, hardness, phosphorus (P), Ca^{2+} , Mg^{2+} , Na^+ , K^+ , $(\text{Na}^+ + \text{K}^+)/\text{P}$, and $(\text{Ca}^{2+} + \text{Mg}^{2+})/\text{P}$ contents. The major significant correlation obtained was between cooking quality and $(\text{Ca}^{2+} + \text{Mg}^{2+})/\text{P}$ ratio, suggesting some role of these mineral elements in the cooking quality of the lentil. The cooking quality of 10 samples of lentil, having extreme values for shear force, was not related to seed size, hardness, or amylose content. The good-cooking lentil had significantly higher hydration coefficients (water uptake) than the poor-cooking lentil. However, the rate of water uptake was similar in both the good- and poor-cooking lentil samples. Scanning electron microscopy showed similar starch granules in both good- and poor-cooking lentil; nor were there any consistent differences in the differential scanning calorimetry properties of the starches. However, viscoamylograms of the lentil meals showed consistently higher peak and set-back viscosities for the good-cooking lentil samples.

The lentil is now a well-established crop in Western Canada. Saskatchewan is the major producer, the 1983 production area was 36 000 ha out of the total Canadian production of 46 000 ha. Lentil cultivars grown in Saskatchewan are Laird and Chilean (Chilean type), which are yellow cotyledon, large and medium seeded, respectively, and Eston (Persian type), which is a yellow cotyledon and small seeded lentil (Slinkard and Bhatta, 1979; Slinkard, 1981).

Cooking quality is the foremost quality criterion in lentil. In our previous studies (Bhatta et al., 1983, 1984), it was reported that location and season of growth (environments) had a major influence on the cooking quality of lentil. The intracultivar variability in cooking quality was 94-97% in Laird and Chilean grown in 1980 and 35-92% in Laird, Chilean, and Eston lentil grown in 1981. How environ-

ments exert such a large influence on the cooking quality of lentil is not known. A number of factors has been reported to affect cooking quality in legumes. An earlier study (Mattson et al., 1950) reported that cooking quality in pea was affected by the seed coat, the phytic acid and pectin contents of the seed, and the ratio between the monovalent (Na^+ , K^+) and divalent (Ca^{2+} , Mg^{2+}) ions. Later, Muller (1967) reported a relationship between cooking quality and phytic acid, Ca^{2+} , Mg^{2+} , and free pectin in a number of pulses. Other factors thought to influence cooking quality in pulses were thickness of the seed coat pallsade layer and the lignin and α -cellulose contents of the seed. Cell contents such as starch and protein had no detectable effect on the cooking quality of pulses. However, more recently Youssef et al. (1982) observed differences in amylograph peak viscosity and differential scanning calorimetry properties of starch isolated from hard and soft cooking faba bean. In another study (Wassimi et al., 1978), externally applied major and trace elements improved the cooking quality of lentil grown in a pot experiment, though no direct relationship was found

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