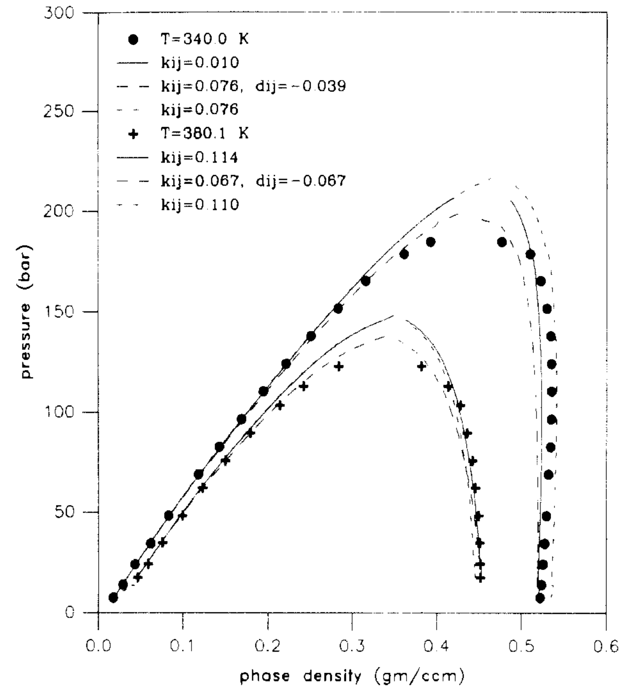

Figure 4. Pressure-density data for argon + *n*-butane at T = 340.0 and 380.1 K. The lines result from the PR-EOS with binary parameters fit to the composition data. Line legend as in Figure 1.

Table VI. Binary Interaction Parameters for the PR-EOS for the Argon + *n*-Butane System

	genlzd param	fluid-specific param		
	1 param	1 param	2 param	
T, K	k_{ij}	k_{ij}	k_{ij}	d_{ij}
340.0	0.076	0.010	0.076	-0.039
380.1	0.110	0.114	0.067	-0.067

were used to calculate the mixture parameters. The two adjustable binary interaction parameters, k_{ij} and d_{ij}, were obtained by fitting the data with the temperature and pressure as the independent variables and minimizing the errors in the vapor and liquid compositions simultaneously. The fitting procedure was done both for the case of $k_{ij} \neq 0$ and $d_{ij} = 0$, and for $k_{ij} \neq 0$ and $d_{ij} \neq 0$. Tables V and VI show the binary interaction parameters obtained in this way. It should be noted that the binary interaction parameters were fit just to the phase composition data, not to the phase densities.

Correlations for the systems we measured using the PR-EOS with generalized parameters (*3*) are not very good in the near-critical region and, in particular, results in an overprediction of the mixture critical pressure. Using the Xu-Sandler parameters (*4*) results in no significant difference in the average deviation between calculated and experimental compositions for both phases for each of the data points, but a mixture critical point that is in better agreement with experiment.

As suggested by Shibata and Sandler (*5*), using the Xu-Sandler parameters with two adjustable binary parameters gives a better correlation of the mixture behavior than when using just one parameter as seen in Figure 1, though the fits with one adjustable parameter give slightly better liquid volumes. This difference between the one- and two-parameter fits is evident for the system argon + *n*-butane in Figure 3. Figures 1 and 3 show the P-x-y data for both systems compared with the best calculated results obtained by using the Xu-Sandler equation of state parameters with two binary interaction parameters, and Figures 2 and 4 show the density data for these same systems.

The fits of the nitrogen + *n*-butane data are similar to those of Shibata et al. (*1*) for this mixture at 310 and 410 K, respectively. Also, the overprediction of the mixture critical pressure for the argon + *n*-butane system increases with increasing temperatures. Though the critical temperature of argon is approximately 25 K higher than the critical temperature of nitrogen, the critical molar volume of argon is much smaller than that of nitrogen. Since the PR-EOS fit of the argon + *n*-butane data is not as good as that for the nitrogen + *n*-butane system, it appears that in this case the effect of the size difference dominates over that of the energy difference for these mixtures of relatively simple molecules.

Glossary

a, b	equation of state parameters
k_{ij}, d_{ij}	binary interaction parameters
P	pressure
R	gas constant
T	temperature
v	molar volume
x	liquid-phase mole fraction
y	vapor-phase mole fraction
ρ	density

Registry No. Butane, 106-97-8; argon, 7440-37-1; nitrogen, 7727-37-9.

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Solubilities of α-Anhydrous Glucose in Ethanol/Water Mixtures

G. L. Bockstanz, M. Buffa, and C. T. Lira*

Department of Chemical Engineering, Michigan State University, East Lansing, Michigan 48824-1226

Solubilities of α-anhydrous glucose in ethanol/water mixtures were determined at 35 °C. An isothermal method was used. The solubilities were modeled with a Redlich-Kister expansion.

Introduction

The solubility of D-glucose in solutions of ethanol and water has been studied and modeled in this work. Increased interest in biological molecules has revealed a need for thermodynamic properties of mixtures involving biological molecules. Despite the importance of sugars, relatively few thermodynamic data

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* Author to whom correspondence should be addressed.

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Table I. Solubility of D-Glucose in Water/Ethanol Mixtures at 35 °C

wt % ethanol	wt % water	wt % glucose	std dev[a]
99.58	0.00	0.42	0.01
88.03	9.78	2.19	0.07
74.11	18.53	7.36	0.14
69.52	21.62	8.85	0.41
58.62	26.50	14.88	0.35
46.57	31.05	22.38	1.31
35.73	35.73	28.55	1.09
34.59	36.56	28.85	2.26
26.31	36.00	37.70	0.27
19.87	36.90	43.23	0.55
15.63	36.47	47.90	0.73
13.04	37.20	49.76	1.27
11.32	39.48	49.20	0.60
9.86	38.11	52.02	0.56
6.72	38.14	55.14	0.44
6.58	37.22	56.20	2.10
0.00	41.82	58.18	0.15

[a] Standard deviation of experimentally measured glucose weight percentage.

are available for multicomponent mixtures involving sugars. Solubilities of D-glucose are presented for the system D-glucose–water–ethanol at 35 °C.

A thermodynamic model for this system is developed and compared to the experimental results of this investigation. An extensive analysis of D-glucose solubility in ethanol/water mixtures has not been published before this even though the importance of understanding this system is fundamental to many industrial and laboratory applications. Limited solubility data are presented by Saarnio and Kuusisto (*1*) where the solubilities of various sugars in different solvents were investigated. Only a few data points were reported on the solubility of D-glucose in ethanol/water mixtures.

Experimental Section

The solubility of D-glucose in ethanol/water mixtures was determined according to an isothermal method. Specially constructed glass test tubes were used as the equilibrium cells. A small glass port was attached near the bottom of a 25-mL test tube. A plunger was machined from aluminum and fitted with an O-ring to fit tightly against the inner wall of the test tube. Following loading of the cell, the port was used to expel the trapped air in the tube, leaving negligible vapor space above the liquid solution.

A predetermined ratio of water to ethanol was prepared and allowed to thoroughly mix in a stoppered 100-mL flask for at least 15 min. The solution was pipetted into the equilibrium vessel, and α-D-glucose was added in slight excess of its expected solubility limit. Stir bars were placed in the equilibrium vessels to ensure proper mixing. The tube was sealed with the plunger and the excess air was expelled. The tube was placed in the water bath and stirred for 48 h. Mixing for longer time periods did not alter the solubility measurements, so complete mixing and thermodynamic equilibrium were assumed.

The liquid portion of the solution was syringed off and placed into a small test tube. The liquid was centrifuged to remove any solid α-D-glucose particles suspended in the liquid. An aliquot of liquid was syringed into a preweighed evaporating dish. The weight of the liquid was measured, and the flask was dried in a vacuum oven at 55 °C until no further weight loss was detected. The remaining solid glucose was weighed.

The α-D-glucose (ACS reagent) was supplied by Aldrich Chemical Company. The ethanol was provided by Midwest Grain Products, 200 proof. The water was distilled grade. The temperature controller was a Cole-Parmer immersion circulator Model 1266-30. The temperature measurements were fixed at 35 ± 0.02 °C. A submersible magnetic stirrer was used to stir the solutions. An electronic balance was used to weigh the samples to an accuracy of ±0.3 mg.

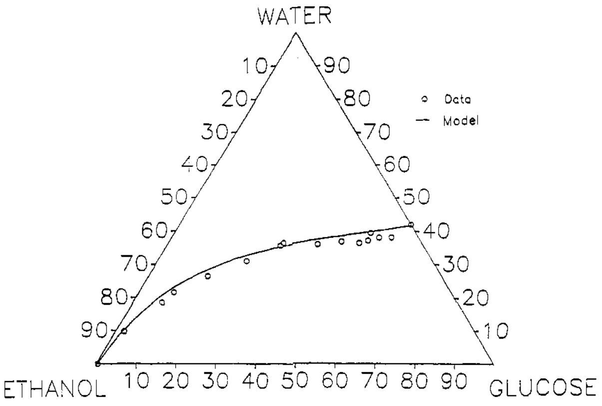

Figure 1. Experimental and calculated model of weight fractions for D-glucose solubility in water/ethanol mixtures at 35 °C.

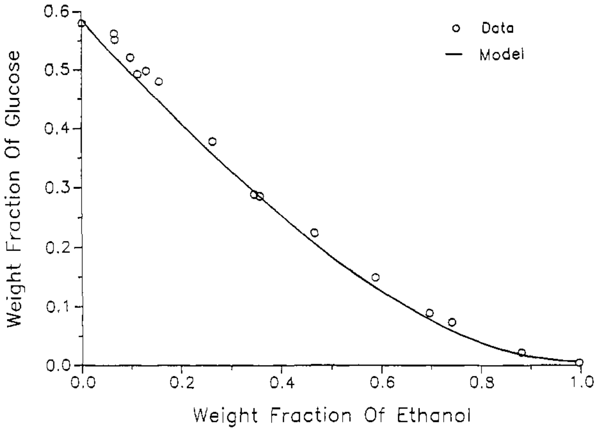

Figure 2. Experimental and calculated model of weight fractions for D-glucose solubility in water/ethanol mixtures at 35 °C.

Results and Discussion

The experimental results found in this investigation are shown in Table I. Each point is the average of four to six experimental runs at the same ethanol/water mixture. The data are presented in weight fractions with standard deviations of each individual run indicated. The data are shown in Figures 1 and 2. The solubility of D-glucose in solution decreases as the concentration of ethanol is increased. The experimentally determined solubility of D-glucose in pure water agreed very well with measurements of Young (*2*) and Shchukarev et al. (*3*).

As the water concentration was increased, the solubility increased rapidly. The solubility of D-glucose increased more slowly in the water-rich region. In this region the viscosity increased greatly, causing suspension of solid α-D-glucose. The amount of solid α-D-glucose in the solution phase was less than 0.01 g or an error of less than 1% in weight of α-D-glucose measured.

A thermodynamic model was developed to predict the solubility of D-glucose in ethanol/water mixtures. The model uses binary data from D-glucose/water, ethanol/water, and D-glucose/ethanol systems. The model is the Redlich–Kister expansion (*4*):

$$G^E_{tot} = Ax_{gl}x_{et} + Bx_{gl}x_{wat} + Cx_{et}x_{wat} + Dx_{et}x_{wat}(x_{et} - x_{wat})$$

x_{gl}, x_{et}, and x_{wat} are mole fractions of glucose, ethanol, and water, respectively. The constants A, B, C, and D are determined from binary experimental data. The ethanol/water system is the only binary system which justifies two parameters.

To determine the constant B, glucose–water binary data were used from Taylor and Rowlinson (*5*). These workers measured vapor pressures of aqueous glucose solutions at various temperatures. The model for the binary D-glucose/water system is

$$G^E_{gl/wat} = Bx_{gl}x_{wat}$$

This equation can be stated in terms of an activity coefficient:

$$RT\ln(\gamma_{wat}) = Bx_{gl}^2$$

The activity coefficient, γ_{wat}, can be calculated from the data from Taylor and Rowlinson (*5*). A plot of $\ln(\gamma_{wat})$ vs x_{gl}^2 yields a relatively straight line for the temperature range between 25 and 55 °C. By this method it was determined that $B = -4984.91$ J·mol^{-1}.

To determine the value for the constant A, a thermodynamic assumption was made. It was assumed that D-glucose in a saturated aqueous solution has the same activity as a D-glucose in a saturated ethanol solution. The model for this binary system is as follows:

$$G^E_{gl/et} = Ax_{gl}x_{et}$$

As before this equation can be expressed as

$$RT\ln(\gamma_{gl}) = Ax_{et}^2$$

Equating the activities at saturation gives the equation

$$(\gamma_{gl/et})_{sat} = \frac{(x_{gl/wat}\gamma_{gl/wat})_{sat}}{(x_{gl/et})_{sat}}$$

Saarnio and Kuusisto present D-glucose solubilities in pure ethanol and 96% ethanol/water solutions at 25, 50, and 78 °C (*1*). The solubility of D-glucose in pure ethanol was determined experimentally by using the same experimental technique described above. This value was determined to be 0.4185 wt % D-glucose. This value was used to determine the constant A = 9159.70 J·mol^{-1}. This solubility was slightly higher than that determined by Saarnio and Kuusisto. Based on our experience, their experiments may have been too short to obtain equilibrium.

Since data for ethanol and water binary systems are very well documented, a two-parameter Redlich–Kister expansion is used. Activity coefficients were determined using ethanol/water vapor–liquid equilibrium data (*6*). The excess Gibbs energy is

$$G^E = Cx_{et}x_{wat} + Dx_{et}x_{wat}(x_{et} - x_{wat})$$

which can also be expressed in terms of activity coefficients which is shown as

$$RT\ln(\gamma_{et}) = (x_{et} - 1)^2C + (4x_{et}^3 - 9x_{et}^2 + 6x_{et} - 1)D$$

A plot of

$$\frac{\ln(\gamma_{et})}{(x_{et} - 1)^2} \text{ vs } \frac{(4x_{et}^3 - 9x_{et}^2 + 6x_{et} - 1)}{(x_{et} - 1)^2}$$

yields a straight line where the intercept is the constant C and the slope is the constant D. It was found that $C = 3213.86$ J·mol^{-1} and $D = -824.92$ J·mol^{-1}.

Table II. Predicted Solubility of D-Glucose in Ethanol/Water at 35 °C

wt % ethanol	wt % water	wt % D-glucose	wt % ethanol	wt % water	wt % D-glucose
99.22	0.00	0.78	75.53	19.07	5.41
98.30	0.91	0.79	72.12	20.90	6.98
96.10	3.08	0.82	68.18	23.20	8.63
94.03	4.72	1.25	63.12	26.00	10.88
92.78	6.04	1.27	55.73	29.08	15.20
91.61	7.10	1.29	51.24	30.85	17.91
90.15	8.11	1.74	45.81	32.59	21.60
89.38	8.85	1.76	39.69	34.52	25.79
88.47	9.75	1.78	32.45	36.28	31.26
86.95	10.80	2.25	24.22	37.91	37.87
85.92	11.79	2.28	15.12	39.45	45.42
84.29	12.94	2.77	10.31	40.36	49.33
82.66	14.06	3.27	5.24	41.00	53.76
80.79	15.42	3.79	0.00	41.85	58.15
78.57	17.08	4.34			

The completed form of the model is

$$G^E_{tot} = -4984.91x_{gl}x_{wat} + 9159.70x_{gl}x_{et} + 3213.86x_{et}x_{wa} - 824.92x_{et}x_{wat}(x_{et} - x_{wat}) \text{ J·mol}^{-1}$$

Figures 1 and 2 compare the predicted solubility with the experimental results. The agreement is generally very good. The model predicts slightly smaller solubility than the data indicate with the largest discrepancy in the water-rich region of the curve. The disagreement is most likely due to uncertainties in the glucose–ethanol binary constant in the model.

Experimental errors may be introduced if some D-glucose monohydrate forms in the solid in addition to D-glucose anhydrate (*2*, *7*). If the monohydrate forms, water molecules are incorporated in the crystals, thus making the solution more ethanol rich. The Hahn precipitation rule states that coprecipitation of microimpurities in crystals of the macrocomponant always occurs when the microcomponent is included isomorphously into the crystal lattice of the macrocomponent or when it contributes to normal lattice formation (*8*). The data was not corrected for this phenomena because there was no way of accurately quantifying the amount of D-glucose monohydrate present in the system. We do not believe this phenomenon to be a major contributor to experimental error. The isothermal experimental method used in this analysis did not provide the proper conditions for formation of metastable glucose monohydrate. The error due to this effect is estimated at less than 1% in weight of D-glucose measured.

The viscosity of the solutions increased greatly as the solubility of D-glucose increased in the water-rich region, thus making the solutions more difficult to handle and leading to an estimated error of less than 1% in weight of D-glucose measured. Drying of the D-glucose solutions also became more difficult. Evaporation of the ethanol during the preparation or mixing process would have resulted in a higher solubility value. Ethanol evaporation during sample preparation from the ethanol/water mixture was determined to be negligible after conducting a timed evaporation experiment using a gas chromatograph to determine ethanol and water concentrations.

Conclusions

The solubility of D-glucose in ethanol/water solutions was shown to follow a logical progression of high solubility in the water-rich region to very low solubility in the ethanol-rich region. The model developed here accurately predicts the solubility of D-glucose in ethanol/water mixtures. The model is based on binary solubility data of the three components and does not contain ternary perameters.

Further investigation into the role of the different crystal structures of D-glucose and its effect on solubility in ethanol/

water mixtures is needed to ensure more accurate data and modeling. This work did not attempt to compensate for the difference in D-glucose crystals because of the difficulty in quantifying the amount of each type of crystal present in solution.

Registry No. D-Glucose, 50-99-7; EtOH, 64-17-5.

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Isobaric Vapor–Liquid Equilibrium for the Cumene–*m*-Cresol and Phenol–*m*-Cresol Systems at 13.33 kPa

Emilio Cepeda,* Cristina González, Jose M. Resa, and Cristina Ortiz de Salido
Ingeniería Química, Facultad de Farmacia, Apartado 450, Vitoria, Spain

Isobaric vapor–liquid equilibrium data are reported for the cumene–*m*-cresol and phenol–*m*-cresol systems at 13.33 kPa. The activity coefficient data were tested for thermodynamic consistency by the methods of Herington, Black, and van Ness and correlated by using the Norrish and Twigg and Wilson equations. The results suggest that *m*-cresol can be used as a solvent for extractive distillation of cumene–phenol mixture with cumene as an overhead product.

Introduction

Cumene can be converted to phenol and acetone via cumene hydroperoxide (*1*). In this process, cumene free of phenol is required for recycling to the cumene oxidation stage because the presence of phenol is detrimental for the oxidation. The separation of the cumene–phenol mixture is difficult because it presents an azeotropic point at atmospheric pressure (*2*) and low pressures would be necessary to make it disappear. Extractive distillation can be used to separate the mixture with an appropriate solvent. Scheibel (*3*) has suggested that the screening of the solvents might be found between the members of homologous series of the components, and he recommends as the lowest boiling point one that does not form an azeotrope. In this case, we have chosen 1-octanol and *m*-cresol as solvents. The UNIFAC method can be used (*4*) to calculate the selectivity at infinite dilution in the alcohols that we have chosen as solvents.

The selectivity at infinite dilution

$$S_1{}^{\infty}{}_2 = (\gamma_1{}^{\infty}/\gamma_2{}^{\infty})_{\text{solvent}} \qquad (1)$$

was calculated for cumene–phenol in 1-octanol and *m*-cresol by means of Fredenslund programs (*5*), and the results are listed in Table I.

Although 1-octanol seems to be the most adequate solvent for the extractive distillation, its recuperation would be difficult because 1-octanol forms an azeotrope with phenol. This azeotrope, with a mole fraction of 0.335 of phenol, has been predicted with the UNIFAC method at 463.15 K.

Vapor–liquid equilibrium data are necessary to be sure that an azeotrope with cumene does not form. In the present paper, the vapor–liquid equilibria of the cumene–*m*-cresol and phenol–*m*-cresol systems were measured at 13.33 kPa. Data on these systems are not found in the literature at temperatures and pressures comparable to those of the present work.

Table I. Selectivity at Infinite Dilution in Solvents for Cumene (1)–Phenol (2) at 443.15 K

solvent	$S_1{}^{\infty}{}_2$
m-cresol	1.9043
1-octanol	4.3953

Table II. Physical Properties of Pure Compounds: Density, Refractive Index, and Boiling Point

	ρ, g/cm^3		n_D		T_B, K	
	obsd	ref *13*	obsd	ref *13*	obsd	ref *13*
cumene (T = 298.15 K)	0.8574	0.8575	1.4889	1.4889	425.54	425.54
phenol (T = 318.15 K)	1.0542	1.0545	1.5400	1.5402	454.96	454.98
m-cresol (T = 298.15 K)	1.0306	1.0302	1.5399	1.5396	475.5	475.38

Table III. Vapor–Liquid Equilibrium Data for the Cumene–*m*-Cresol System at 13.33 kPa

x	y	T, K	γ_1	γ_2
0.0676	0.4850	398.41	1.9596	1.0000
0.1041	0.6045	392.41	1.9354	1.0000
0.2305	0.8048	377.89	1.9376	1.0171
0.3164	0.8423	373.93	1.6929	1.1004
0.4067	0.8832	370.13	1.6087	1.1387
0.4870	0.9010	368.85	1.4383	1.1848
0.6273	0.9265	366.68	1.2492	1.3416
0.7106	0.9401	365.36	1.1426	1.5357
0.8379	0.9568	363.20	1.1056	2.1685
0.9210	0.9805	362.53	1.0583	2.1290
0.9642	0.9922	362.15	1.0373	1.9137

Experimental Section

Measurements were made in a vapor recirculating type equilibrium still. The experimental apparatus and procedure have been described in a previous paper (*6*).

Cumene was supplied by Merck, phenol was supplied by PANREAC, and *m*-cresol was supplied by Scharlau. They are analytical-grade reagents and were purified by distillation under vacuum in a laboratory column. Physical properties of these components are listed in Table II along with their literature values.

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