

Thermodynamic Interactions between PVA-Solvent Mixtures, by Means of Inverse Gas Chromatography Measurements

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Due to the fact that polyvinyl alcohol (PVA) is one of the most employed polymeric materials, it is important to analyze its interactions with solvents. In order to reach this achievement, the infinite dilution solvent activity coefficients and the Flory – Huggins interaction parameters of several PVA – alcohol mixtures have been determined by means of Inverse Gas Chromatography (IGC) measurements. The obtained values decrease with temperature, which is in agreement with the original Flory – Huggins theory. From the previous values, the solubility parameter of the PVA material was also determined. The reliability of the data was analyzed by comparing the heats of the vaporization of the alcohols, calculated from the activity coefficient values, with the ones estimated with the Watson method.

1. Introduction

Nowadays, the polymeric materials are widely employed in the chemical industry; therefore it is fundamental to study the thermodynamic properties of their mixtures with several solvents. Among them, polyvinyl alcohol (PVA) is especially relevant due to its applications in paper coatings, and in membrane separations (Yeom, 1996).

Polymer-solvent mixtures are quite different from conventional mixtures because there is a great difference between the sizes of the molecules of each compound. For this reason, in order to characterize thermodynamically these mixtures, non-conventional techniques, such as swelling (Victorino et al. 2009) or inverse gas chromatography (Conder and Young, 1979), are needed.

By means of the above mentioned techniques, the Flory Huggins theory can be employed to model the phase equilibrium of these PVA-solvent mixtures. This theory allows the calculation of the polymer-solvent interaction parameter (χ) and also the solubility parameter of the polymer (δ_2). The importance of these two values is because they are considered as a criterion to select a suitable solvent for an industrial process and also to predict solubility, degree of swelling, or polymer –solvent compatibility.

So, the aim of this work is to determine the polymer –solvent interaction parameters of different PVA – solvent mixtures, as well as to calculate the solubility parameter of the employed PVA.

2. Experimental section

2.1 Materials

PVA material (99% hydrolyzed) with a weight-average molecular weight of 130000, was purchased from Aldrich. All the employed solvents were also purchased from Aldrich and they were employed without any purification step. The Chromosorb W/AW DMCS 80-100 mesh employed as a support was also purchased from Aldrich.

2.2 Experimental procedure

The stationary phase used in this work for the IGC technique was obtained by initially preparing 300 g of a 1% (w/w) solution of PVA in water, and depositing it onto a weighted amount of support (17 g). Afterwards, the mixture was dried under vacuum, by slow evaporation in a rotavapor, while being continuously stirred to ensure homogeneous mixture (evaporation time was 8h). The final amount of PVA which coated the support was 10.6 % w/w, determined by thermal gravimetric analysis, in a Seiko EXSTAR 6000 TG/DTA 6200 equipment.

Afterwards, the coated support was packed into a ¼ in. nominal diameter column, which was installed in a VARIAN 3800 gas chromatography, equipped with a thermal conductivity detector and an electronic flow controller.

All the measurements were carried out with a helium flow of 10 mL/min, as a carrier gas, and in a temperature range between 100°C and 120°C. The amount of solvent injected was 0.2 µL along with 0.8 µL of air, as an inert component.

2.3 Calculations

According to IGC technique (Conder and Young, 1979), in a solvent (1) – polymer (2) mixture, the relation between the infinite dilution mass-based activity coefficient of the solvent, (Ω_1^∞) and the retention volume of the solvent (V_g), is given by eq. (1), where T is the temperature in K, R is the ideal gas constant, M_1 is the solvent molecular weight and f_1^0 is the standard fugacity of the solvent. Usually this last value is calculated by using Virial EOS truncated after the second term, as shown in eq. (2).

$$\ln(\Omega_1^\infty) = \ln\left(\frac{R \cdot T}{V_g M_1 f_1^0}\right) \quad (1)$$

$$\ln(\Omega_1^\infty) = \ln\left(\frac{RT}{V_g M_1 p_1^0}\right) - \frac{(B_{11} - V_1) p_1^0}{RT} \quad (2)$$

In this last equation, B_{11} is the solvent second term of the Virial EOS, p_1^0 is the solvent vapor pressure and V_1 is the solvent molar volume.

The specific retention volume of the solvent (V_g) is given by eq. 3, where F is the volume flow rate of the carrier gas, corrected to the column temperature, t_r is the retention time of the solvent, t_m is the retention time of the inert, W_s is the amount of polymer packed in the column, and j is a correction factor. Due to the carrier gas is compressible, the difference between the column inlet pressure (P_i) and the column

outlet pressure (P_0) might cause an increasing of the volume flow rate along the column; therefore, a correction factor (j) is usually added (eq. 4).

$$V_g = \frac{j \cdot (t_r - t_m) \cdot F}{W_s} \quad (3)$$

$$j = \frac{3 \left(\frac{P_i}{P_0} \right)^2 - 1}{2 \left(\frac{P_i}{P_0} \right)^3 - 1} \quad (4)$$

In this work, molar volumes were calculated according to the Rackett model modified by Spencer and Danner (1972), the second terms of Virial EOS were evaluated with Tsonopoulos' correlation (1974), and the solvent vapor pressure values were taken from literature (Reid et al, 1987).

From the values of infinite dilution activity coefficient, the Flory Huggins interaction parameter (χ) can be determined by using eq. 5, where r is the ratio between molar volume of the polymer divided by the molar volume of the solvent, and ρ_1 and ρ_2 are the solvent and polymer densities respectively.

$$\chi = \ln(\Omega_1^\infty) - \left(1 - \frac{1}{r} \right) + \ln \frac{\rho_1}{\rho_2} \quad (5)$$

On the other hand, the Flory Huggins theory, modified by Blanks and Prausnitz (1964), allows establishing a relation between Flory Huggins parameter (χ) and the solubility parameters of polymer (δ_2) and solvents (δ_1), where χ_s is the entropic contribution to χ (eq. 6). This last value of χ_s is usually kept constant and equal to 0.34 (Blanks and Prausnitz, 1964).

$$\chi = \chi_s + \frac{V_1}{RT} (\delta_1 - \delta_2)^2 \quad (6)$$

Rearranging terms eq. 7 is obtained; so the polymer solubility parameters can be obtained from the slope of $(\delta_1^2/2 - \chi RT/2V_1)$ vs δ_1 , by simply knowing the solubility parameter of the solvent.

$$\left(\frac{\delta_1^2}{2} - \frac{\chi RT}{2V_1} \right) = \delta_2 \delta_1 - \left(\frac{\delta_2^2}{2} + \frac{\chi_s RT}{2V_1} \right) \quad (7)$$

3. Results and discussion

Table 1 shows the measured values of the retention volume (V_g), along with the calculated values of the infinite dilution activity coefficients (Ω_1^∞), and the Flory – Huggins interaction parameters (χ), for all the PVA – solvent binary mixtures, in the temperature range from 30 °C to 60 °C.

Table 1. Experimental results for the PVA alcohol-mixtures

Solvent	V_g (cm ³ /g)			Ω_i^∞			χ		
	100 °C	110 °C	120 °C	100 °C	110 °C	120 °C	100 °C	110 °C	120 °C
Water	129	129	82	13.44	9.82	11.46	1.28	0.97	1.13
Methanol	29	28	27	10.21	8.08	6.57	0.78	0.54	0.34
Ethanol	25	25	24	12.50	9.54	7.44	0.98	0.71	0.46
2-Propanol	24	24	23	11.48	8.74	6.83	0.89	0.61	0.37
1-Butanol	26	25	24	32.05	23.33	17.24	1.94	1.63	1.32
2-Butanol	25	24	23	17.35	13.01	10.09	1.33	1.04	0.79
t-Butanol	24	23	23	9.53	7.41	5.84	0.68	0.43	0.19
1-Pentanol	27	26	25	54.73	38.82	28.26	2.49	2.14	1.83
1-Hexanol	31	28	26	89.10	63.81	46.29	2.97	2.64	2.32
Cyclohexanol	31	28	27	95.50	67.57	48.12	3.21	2.86	2.53

The Flory – Huggins interaction parameter value can be used as a criterion to analyze the compatibility of a polymer – solvent pair so that, the lower the Flory-Huggins parameter, the higher the compatibility. According to this statement, the most compatible solvent for the PVA studied here should be *tert*-butanol.

In Table 1, it can also be observed that, except for the PVA-water mixture, both the infinite dilution activity coefficient and the Flory-Huggins parameters tend to decrease with temperature. This is in agreement with the assumptions of the original Flory Huggins theory, although in literature (Ovejero et al., 2009) there can be found some examples which show that the dependence is not clear.

The Flory – Huggins parameter involves two contributions, one entropic and one enthalpic. The entropic is related to the free volume of the solvent, and is expected to increase with temperature, because the free volume of the solvent value also increases with temperature. The enthalpic is related to the intermolecular forces between the polymer and the solvent, which tend to decrease with temperature. So, the overall dependence with temperature will depend on the prevailing effect.

The irregular behavior of the PVA-water mixture might be due to the fact that the hydrogen bonds of the water are so strong, that its enthalpy of vaporization is really high. This means that the theoretical retention time along the IGC column should be much bigger than for the other compounds. However, because of the low molar mass of the water, the retention time is not as big as it should be, and this results in certain irregularities.

Once the Flory – Huggins parameters were calculated, the solubility parameter of the PVA was determined from the slope of the plot ($\delta_1^2/2 - \chi RT/2V_1$) vs δ_1 (eq. 7). As an example, Figure 1 shows the plots at 100 °C. The obtained values at the three studied temperatures were 27.6 MPa^{1/2}, 28.4 MPa^{1/2} and 27.8 MPa^{1/2}, at 100°C, 110°C and 120°C respectively. The influence of the temperature over the solubility parameter is almost negligible, as it was expected.

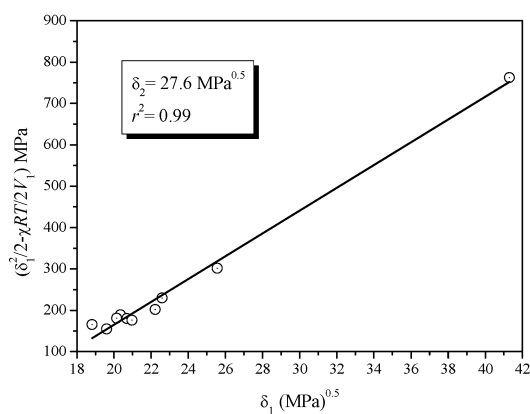


Figure 1. Plot for the calculation of the solubility parameter of the PVA

Finally, from the obtained activity coefficient values, the values of the heat of vaporization of the solvents ($\Delta_{\text{vap}}H_1$) could be determined (eq. 8) by calculating the partial molar heat of mixing, $\Delta_{\text{mix}}H_1$ (eq. 9), and the heat of solution $\Delta_s H_1$, (eq. 10), (Romdhane et al., 1992). These values, derived from the experimental data, were compared with the ones estimated by the Watson model (1943), in order to check the goodness of the experimental data, like a kind of consistency test. This comparison is summarized in Table 2. As it can be seen, the difference between both values is always less than 10%, what allows assuring the quality of the experimental data.

Table 2. Experimentally derived and estimated enthalpy values

Solvent	$\Delta_{\text{mix}}H_1^\infty$ (kJ/mol)	$\Delta_s H_1$ (kJ/mol)	$\Delta_{\text{vap}}H_1^{\text{exp}}$ (kJ/mol)	$\Delta_{\text{vap}}H_1^{\text{Watson}}$ (kJ/mol)	Dev (%)
Methanol	26.83	-7.80	34.63	31.75	9.1
Ethanol	31.64	-5.90	37.53	36.37	3.2
2-Propanol	31.63	-6.41	38.03	37.24	2.1
1-Butanol	37.80	-7.02	44.82	44.06	1.7
2-Butanol	33.01	-7.57	40.58	39.37	3.1
t-Butanol	29.86	-7.37	37.23	34.77	7.1
1-Pentanol	40.29	-8.37	48.66	47.27	2.9
1-Hexanol	39.91	-12.37	52.29	52.20	0.2
Cyclohexanol	41.77	-10.60	52.37	52.01	0.7

$$\Delta_{\text{vap}}H_1 = \Delta_{\text{mix}}\overline{H}_1^\infty - \Delta_s H_1 \quad (8)$$

$$\Delta_{\text{mix}}H_1^\infty = R \left[\frac{\partial(\ln(\Omega_1^\infty))}{\partial(1/T)} \right] \quad (9)$$

$$\Delta_s H_1 = -R \left[\frac{\partial (\ln(V_g^\circ))}{\partial (1/T)} \right] \quad V_g^\circ = V_g \left(\frac{273.15}{T} \right) \quad (10)$$

4. Conclusions

In this work, we have calculated the infinite dilution solvent activity coefficients and the Flory – Huggins parameters of several PVA – alcohol mixtures, in a temperature range from 100°C to 120°C. For all the mixtures, both parameters decreased with temperature. We have also calculated the solubility parameter of the employed PVA. As it was expected, the influence of the temperature over this parameter is almost negligible. Finally, the quality of the data was analyzed by comparing the values of the heat of vaporization of the solvents, obtained from the activity coefficient data, with the ones estimated with the Watson model. The differences between both values were always less than 10%.

References

- Blanks R.F. and Prausnitz J.M., 1964, Thermodynamics of polymer solubility in polar and nonpolar systems, *Industrial and Engineering Chemistry Fundamentals*, 3, 1-8.
- Conder J.R. and Young C.L., Eds., 1979, *Physicochemical measurement by gas chromatography*. John Wiley & Sons, New York.
- Ovejero G., Pérez P., Romero M.D., Díaz I. and Díez E., 2009, SEBS triblock copolymer-solvent interaction parameters from inverse gas chromatography measurements, *European Polymer Journal*, 45, 590-594.
- Reid R.C., Prausnitz J.M. and Poling B.E., 1987, *The properties of gases and liquids*. New York. McGraw-Hill.
- Romdhane I.H., Plana A., Hwang S. and Danner R.P., 1992, Thermodynamic interactions of solvents with styrene-butadiene-styrene triblock copolymers, *Journal of Applied Polymer Science*, 45, 2049-2056.
- Spencer C.F. and Danner R.P., 1972, Improved equation for prediction of saturated liquid density, *Journal of Chemical and Engineering Data*, 17, 236-241.
- Tsonopoulos C., 1974, An empirical correlation of second virial coefficients, *AiChE Journal*, 20, 263-272.
- Victorino I.R.S., Morais E.R., Agremis G.B., Maia, J.P. and Maciel R., 2009, Organic vapours sorption, diffusion and swelling in Poly (trimethyl silyl norbornene), *Chemical Engineering Transactions*, 17, 1485-1490.
- Watson K.M., 1943, Thermodynamics of the liquid state. Generalized prediction of properties, *Industrial and Engineering Chemistry*, 35, 398-401.
- Yeom C.K. and Lee K.H., 1996, Pervaporation separation of water-acetic acid mixtures through poly(vinyl alcohol) membranes crosslinked with glutaraldehyde, *Journal of Membrane Science*, 109, 257-265.