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Effect of an amphiphilic polymer on the evaporation behavior of its solutions in toluene and in water

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ABSTRACT

The evaporation behavior of solutions of an amphiphilic polymer, phosphonated polybutadiene in toluene and in water was studied by means of vapor pressure and evaporation rate measurements. The polymer reduces the vapor pressure and evaporation rate of toluene, while the opposite effect was observed in aqueous solutions. The effects were explained on the basis of the Flory-Huggins theory in the toluene solutions and the structure breaking effect in the aqueous solutions.

1. Introduction

Evaporation and condensation processes play an important role in various fields of science and technology. Although experimental and theoretical studies concerning the evaporation and condensation rates have a long history, it is still difficult to obtain the absolute rate. One of the main difficulties is due to the fact that there is not a clear view of the dynamic processes at liquid surfaces yet [1].

We have previously studied the capacity of an amphiphilic polymer, phosphonated polybutadiene (PPB) as collector of petroleum spills [2], which forms a direct emulsion of toluene in water, where the toluene droplets are interconnected by polymer chains so the emulsion cannot be diluted by water but floats on it. This emulsion was heated to break it and the volatile components were distilled to separate them. Although the boiling points of these components are 100 (water) and 110 °C (toluene), distillation begins at 180 °C when the liquid starts to boil. This phenomenon led us to investigate the effect of PPB on the liquid–vapor phase transition in both liquids, since the elucidation of this behavior may shed light on the mechanisms that govern the evaporation of solutions.

2. Experimental

Commercial polybutadiene (PASA S.A., Argentina; M_n: 102,500 g mol^{-1}; M_w/M_n: 2.02; 10% of 1,2-addition units) was used as received. The production and characterization of the phosphonated polybutadiene (PPB) was described elsewhere [2]. The equivalent weight of PPB is 899 ± 18, what means that there is one phosphonic group each 15.1 ± 0.3 butadiene monomers. The emulsion was broken by heating and the aqueous and toluene phases were separated by decantation. To determine the PPB content in each phase the polymer was weighed after the evaporation of the solvent of a known amount of solution in a previously weighed vessel.

The vapor pressure at different temperatures was measured by means of an isoteniscope following the procedure described in literature [3]. The evaporation velocity at different temperatures (22.0

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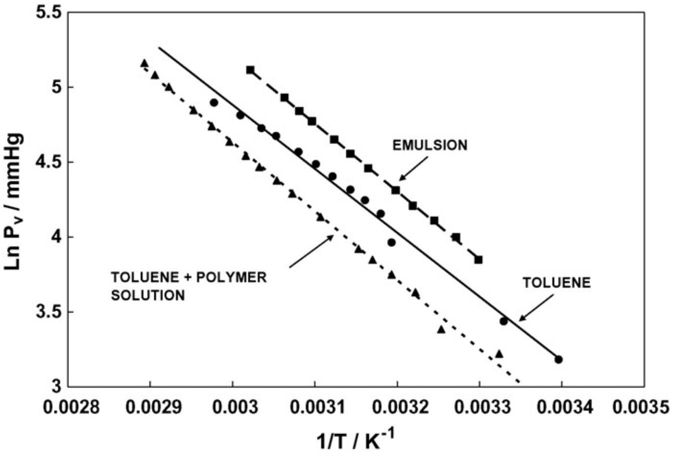

Fig. 1. Neperian logarithm of the vapor pressure (in mmHg) of pure toluene (●), of the toluene PPB solution obtained by rupture of the emulsion (▲) and the entire emulsion (■), as a function of the inverse of the absolute temperature.

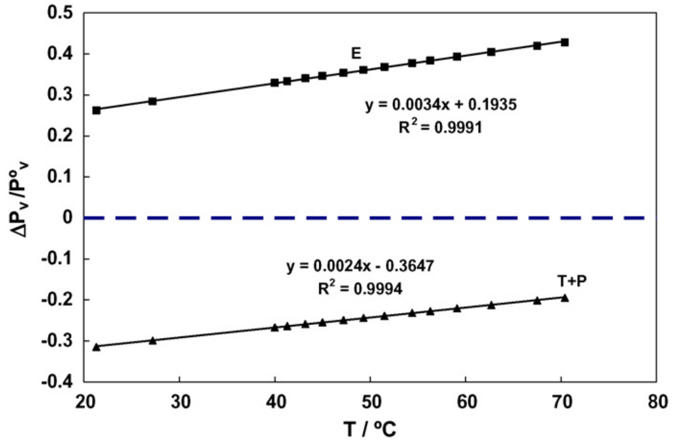

Fig. 2. $\Delta P_v/P_v{}^\circ$ as a function of absolute temperature for the complete emulsion (E, ■) and the P + T solution obtained by rupture of the emulsion (T + P, ▲).

and 34.0 ± 0.1 °C) was determined by measuring the loss of weight of a known volume of sample placed in a small pyrex cylinder having 2.9 cm internal diameter in a CAHN 1000 electrobalance, operating in a register range of 100 mg and an output of 10 mV. The pressure was 101.325 kPa. To avoid secondary Archimedes effects, a compensation container was hung in the other arm of the electrobalance. The thermocouple (Fe-constantan) was in contact with the solution through a thin glass sheath.

3. Results and discussion

3.1. The PPB in toluene solution

3.1.1. Vapor pressure

Fig. 1 shows the results of vapor pressures, measured with the isoteniscope, of pure toluene, the unbroken emulsion (E) and the PPB solution in toluene (T + P, $C = 1.2679$ g%) obtained by emulsion breakage. The emulsion was broken at 110 °C (to ensure the complete process, it was heated under reflux at 120 °C for 15 min), but the P + T solution ebullition began at 170 °C.

By analysis of the data the enthalpy values of pure toluene ($\Delta H_{\text{vap,T}} = 35.5 \pm 0.8\,\text{kJ mol}^{-1}$), the T + P solution ($\Delta H_{\text{vap,T+P}} = 38.2 \pm 0.9\,\text{kJ mol}^{-1}$) and the complete emulsion ($\Delta H_{\text{vap,E}} = 37.6 \pm 0.4\,\text{kJ mol}^{-1}$) were obtained. The enthalpy of evaporation of the T + P solution was then 2.76 kJ mol^{-1} higher than that of the pure toluene used in the experiment.

On the other hand, the vapor pressure in the T + P solution is lower than that of pure toluene. Fig. 2 shows the relative change in vapor pressure $\Delta P_v/P_v{}^\circ$, where $\Delta P_v = P_v{}^\circ - P_{v,s}$, and $P_v{}^\circ$ is the vapor pressure of pure toluene and $P_{v,s}$ is that of the sample (P + T for the solution, E for the complete emulsion). For both samples $\Delta P_v/P_v{}^\circ$ is a linear function of temperature, showing high correlation coefficients.

The unbroken emulsion (E) shows a vapor pressure higher than toluene and T + P.

By using the Claussius–Clapeyron equation together with the values obtained for the P + T solution, the normal boiling point of the solution was computed, resulting $T_b = 116.8 \pm 2.8$ °C, which is considerably lower than the experimentally observed when the emulsion was broken in order to eliminate the toluene by distillation (~170 °C) to determine the polymer content in the hydrocarbon phase. As a consequence, the increase in the boiling point (from 110.6 in pure toluene to ~170 °C in the P + T solution) is in part caused by a combination of the vaporization enthalpy increase and vapor pressure decrease, but another mechanism must also be involved.

The ebulloscopic constant of toluene is $\Delta T/c_2 = k_{eb} = 3.33 \times 10^3\,^\circ\text{C mol}^{-1}$, where c_2 is the solute concentration in g L^{-1} [4] we computed the molar mass of the polymer was a very small value, confirming that colligative properties cannot be used in this kind of solutions.

The molar weight of the polybutadiene used in the synthesis was 102,500 Da, which, together with the molar weight of the monomer ($M_{\text{butadiene}} = 54.1\,\text{g mol}^{-1}$) gives an average of 1985 monomers per molecule. The proportion of phosphonic groups in PPB is 15.1 [2] thus living 897.8 phosphonic groups per PPB molecule, and then, the molecular weight of PPB results $M_{\text{PPB}} = 112{,}663$ Da. The polymer content in the solution was 1.2679 g%, that is to say $10.991\,\text{g L}^{-1} = 9.756 \times 10^{-5}\,\text{mol dm}^{-3}$. With these data we computed the value of the ebulloscopic increase that would be expected, $\Delta T = 3.25 \times 10^{-4}$ °C. As a consequence, the observed phenomenon cannot be caused by common colligative properties of solutions.

The system was then analyzed by means of the Flory-Huggins theory [5], which deals with a mixture of a solvent 1 and a polymeric solute 2, which behaves as a flexible chain formed by r flexible segments, each of them has the same size as the solvent molecules. In a system formed by N_1 solvent molecules and N_2 molecules of polymer, the total number of lattice sites is $(N_1 + rN_2)$. The fractions of sites occupied by solvent and polymer (Φ_1^* and Φ_2^*) are given by:

$$\Phi_1^* = \frac{N_1}{N_1 + rN_2} \text{ and } \Phi_2^* = \frac{rN_2}{N_1 + rN_2} \tag{1}$$

For real solutions of polymers, which are not athermal (i.e. those whose mixing enthalpy is zero, which approximately occurs when polymer and solvent have the same basic structure), the activity of solvent in the mixture is given by:

$$\ln a_1 = \ln(1 - \Phi_2^*) + \left(1 - \frac{1}{r}\right)\Phi_2^* + \chi\Phi_2^{*2} \tag{2}$$

and the related activity coefficient (on a mole fraction basis) is:

$$\ln\gamma_1 = \ln\left[1 - \left(1 - \frac{1}{r}\right)\Phi_2^*\right] + \left(1 - \frac{1}{r}\right)\Phi_2^* + \chi\Phi_2^{*2} \tag{3}$$

The value of γ_1 is strongly dependent on the value of r for low values of this parameter, however, for large ones ($r > 100$) γ_1 becomes independent on r. The semi-empirical Flory-Huggins interaction parameter χ represents the residual contribution caused by the mixing enthalpy, and is determined by intermolecular forces. It is supposed that χ is not dependent on the composition. However it was experimentally observed that this parameter is dependent on