Polymer Bulletin 1, 459–464 (1979)

Polymer Bulletin

Evaporation of Polymer-Solvent Mixtures

Determination of Vapor Pressures from Gaseous Diffusion Coefficients

José Coca, Julio L. Bueno and Ricardo Alvarez

Department of Chemical Engineering, University of Oviedo, Oviedo, Spain

Summary

The *Stefan-Winkelmann* diffusion technique has been used to determine vapor pressures of high boiling point compound-solvents mixtures. Data are reported at a temperature of 67°C for the mixtures polyphenyl ether (6 rings) - benzene and carbowax 1500 - benzene and at a temperature of 100°C for the mixtures polyphenyl ether (6 rings) - toluene and tricresylphosphate-toluene. The range of concentration is only limited by the appearance of a solid phase, and results are in good agreement with those determined by vapor pressure osmometry.

Introduction

Methods for measurement of vapor pressures involve, in general, special techniques or commercial apparatuses often not available in the laboratory (*AMBROSE* 1975). Data on the vapor pressure of polymer-solvent mixtures are very important for technical purposes, particularly when dealing with drying operations.

The *Stefan-Winkelmann* method has been broadly used for measuring gas diffusion coefficients and a large number of data have been reported in the literature (*MARRERO* and *MASON* 1972). The determination of the diffusion coefficient requires a previous knowledge of the vapor pressure of the solvent and, therefore, the *Stefan-Winkelmann* method might be used to obtain vapor pressure data if the diffusion coefficient is known.

This additional use of the *capillary tube* difussion technique has been described in the literature for determining vapor pressures of aqueous solutions of sucrose and sodium chloride (*CRIDER* 1956), although the apparatus and experimental procedure differ from those used in this work.

0170-0839/79/0001/0459/$01.20

Some of the disadvantages of the conventional methods like vacuum problems, temperature reproductibility and operation difficulties may be avoided by the application of the *Stefan-Winkelmann* technique to determine vapor pressures in polymer solutions of industrial interest.

Theory

When a mixture of a non volatile component (*e.g.* a polymer) and a solvent A is heated and A vaporizes, being entrained by a gas B, the flux of component A through the gas-liquid interface, Figure 1, is given by:

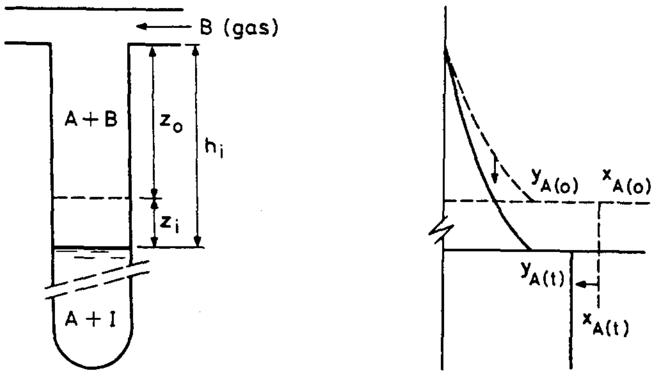

Figure 1. Evaporation capillary tube

$$N_{Az} = - c \, \mathcal{D}_{AB} \frac{dy_A}{dz} + y_A N_{Az} \qquad (1)$$

being,

$$N_{Az} = \frac{\rho_A}{M_A} \left| \frac{dh}{dt} \right| \qquad (2)$$

It can be shown (*COCA et al.* 1979) that the gaseous diffusion coefficient $\mathcal{D}_{AB}$ is independent of the composition of the liquid phase acting as evaporation medium, and therefore equation (1) can be written as:

$$(dh)(dz) = - \frac{\mathcal{D}_{AB} P\, M_A}{R\, T\, \rho_A} \left(\frac{d\, p_A}{P - p_A} \right) dt \qquad (3)$$

with the boundary conditions,

B.C. 1 $\quad y_A \big|_{h_i = o} = 0 \qquad p_A \big|_{h_i = o} = 0$

B.C. 2 $\quad y_A \big|_{h_i = h_i} = y_{Ai} \qquad p_A \big|_{h_i = h_i} = p_{Ai}$

integration of equation (3) yields,

$$h_i dz = - \frac{\mathcal{D}_{AB} P\, M_A}{R\, T\, \rho_A} \ln \left(\frac{P - p_{Ai}}{P} \right) dt \qquad (4)$$

For small intervals of z and t, equation (4) can be written

$$h_i \Delta z = K \ln \left(\frac{P - p_{Ai}}{P} \right) \Delta t \qquad (5)$$

being

$$K = - \frac{\mathcal{D}_{AB} P\, M_A}{R\, T\, \rho_A} \qquad (6)$$

If the diffusion coefficient $\mathcal{D}_{AB}$ is known, the vapor pressure can be obtained from a transposed form of equation (5). For the pure solvent, $\mathcal{D}_{AB}$ can be measured at the temperature of the experiment (if data are not available in the literature) and, with this value, the vapor pressure as a function of the liquid phase composition can be obtained.

Experimental

The apparatus used in this work has been described elsewhere (*MATO* and *BUENO* 1977) and only small modifications have been introduced. The capillary tube where the diffusion mixture is located and the diffusion chamber are placed inside a still, of the *Othmer's* type used to study vapor-liquid equilibrium. The boiling liquid inside the still ensures good thermostatic conditions and is continuously recirculated by condensing the vapors in a coiled tube condenser.

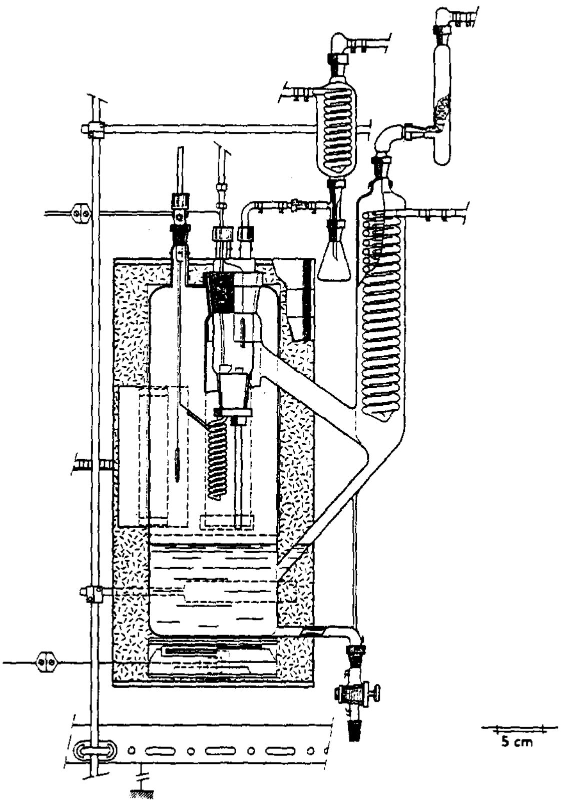

Figure 2. Adiabatic still and diffusion chamber

Dried and preheated air, at the temperature of the liquid in the still, flows over the top of the capillary tube sweeping the diffused vapors.

The descent of the diffusing liquid is measured by means of a cathetometer *Ealing*. By obtaining data of z *vs*. t, and using equation (5) values of $\mathcal{D}_{AB}$ (or p_{Ai} if $\mathcal{D}_{AB}$ is known) can be determined.

Benzene and toluene, *Fluka* analytical reagents, were distilled in a packed column and used as solvents. Two polymers (polyphenyl ether (6 rings), and carbowax 1500) and a high boiling point compound (tricresyl phosphate) were mixed with the forementioned solvents, the binary mixtures acting as the evaporation source. The non volatile compounds used in this work are common liquid phases in gas-liquid chromatography and its molecular weight was available.

Results

From experimental data of diffusion coefficients for benzene - air ($\mathcal{D}_{AB}$= 0.1139 cm^2/s at 67°C) and toluene-air ($\mathcal{D}_{AB}$= 0.1284 cm^2/s at 100°C) vapor pressure data of polyphenyl ether (6 rings), carbowax 1500 and tricresyl phosphate with the forementioned solvents are reported in table 1.

TABLE 1

Vapor pressure of polyphenyl ether (6 rings) (PPE), carbowax 1500 (CW 1500) and tricresyl phosphate (TCP) mixtures with benzene and toluene as solvents.

PPE-benzene 67°C		PPE-toluene 100°C		CW 1500-benzene 67°C		TCP-toluene 100°C	
% wt PPE	p_v mm Hg	% wt PPE	p_v mm Hg	% wt CW 1500	p_v mm Hg	% wt TCP	p_v mm Hg
5.94	498.8	2.49	557.0	3.03	500.0	2.19	560.0
7.31	492.8	2.74	556.1	3.59	498.0	2.80	554.7
8.01	492.3	3.14	554.6	4.62	495.3	3.37	554.4
12.18	491.5	4.62	552.8	6.08	494.0	4.81	553.4
20.06	487.1	9.25	549.4	7.35	493.3	5.97	552.8
23.02	484.8	13.58	548.3	9.67	492.1	10.69	550.6

The polymer concentration range at the temperature used in this work is only limited by the appearance of a solid phase and, therefore, vapor pressure data do not differ too much from the vapor pressure of the pure solvent, at the same temperature.

Experimental results reported in this work have been compared with data obtained by vapor pressure osmometry (*ALVAREZ* 1977), deviations are not higher than 1%.

In conclusion the *Stefan-Winkelmann* technique, as reported in this work, can be used to determine vapor pressures of polymer-solvent mixtures, provided that the diffusion coefficient of the system solvent-gas (*e.g.* air) is known at the temperature under study. This technique gives a good reproductibility and by changing the boiling liquid in the still data can be obtained at different temperatures.

Nomenclature

A : Vapour source
B : Flowing gas phase
c : Concentration, g-mol/cm^3
$\mathcal{D}_{AB}$: Molecular diffusion coefficient, cm^2/s
h_i : Total interface depth, cm
K : Parameter defined by equation (6), dimensionless
I : Polymer or high boiling point compound
M_A : Molecular weight
N_{Az} : Molar flux, g-mol/(cm^2)(s)
p_A : Partial pressure at the interface, atm
P : Total pressure, atm
R : Gas constant, (atm)(cm^3)/(°K)(g-mol)
T : Temperature, °K
t : Time, s
y_A : Molar fraction at the interface, dimensionless
z_o : Initial interface depth, cm
z_i : Drop of the interface depth, cm
z : Interface position

Greek letters
ρ_A : Density of the liquid phase, g/cm^3

References

1. ALVAREZ,R.: *Ph. D. Thesis, University of Oviedo* (1977)
2. AMBROSE,D.: *Exp. Thermodyn.* 2, 607 (1975)
3. COCA,J., *et al.*: *Unpublished work* (1979)
4. CRIDER,W.R.: *J.Am.Chem.Soc.* 78, 924 (1956)
5. MARRERO,T.R. and MASON,E.A.: *J.Phys.Chem.Ref.Data* 1, 1 (1972)
6. MATO,F. and BUENO,J.L.: *Anal.Quim.* 73, 108 (1977)

Received March 25, 1979