RESEARCH NOTE

Determination and correlation of the water activity of propylene glycol solutions

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The water activity ($a_w$) of propylene glycol (PG) solutions in the range 2.03–8.65 g PG/100g water is derived from the measurement of their freezing points. Resulting data follow closely Norrish's equation, $a_w = (1 - x_P) \exp(-Kx_P^2)$, where $x_P$ is the molar fraction of PG and $K$ is a constant which may be related to the structure of the solute molecule. The dimensionless parameter $K$ has a value of 4.04 ± 0.22. Some physico-chemical aspects of water activity lowering in propylene glycol solutions are discussed.

Keywords: water activity, cryoscopic, Norrish equation, propylene glycol, polyols.

INTRODUCTION

Propylene glycol (PG) has been widely used to reduce the water activity ($a_w$) of intermediate moisture food formulations (Heidelbaugh & Karel, 1975; Sloan & Labuza, 1976). However, considerable disagreement exists between different authors about the $a_w$-lowering characteristics of propylene glycol, as shown by the data of Loncin (1975), Sloan and Labuza (1975, 1976), Verlinde et al. (1975) and Kamman et al. (1978). This may be attributed, at least in part, to the fact that PG is relatively volatile and may contaminate the sensors of electric hygrometers, frequently used for water activity determination (Pollio et al., 1986).

It has been suggested (Ferro Fontán & Chirife, 1981) that the determination of $a_w$ from measurement of the freezing points of aqueous solutions may be valuable in the case of relatively volatile solutes, such as propylene glycol. The present work reports on the determination (and correlation with concentration) of the water activity of propylene glycol solutions using cryoscopic measurements.

MATERIALS AND METHODS

The water content of propylene glycol (1,2-propanediol; analytical grade, BDH Chemicals Ltd, Poole, UK) as determined by the Karl-Fisher method (AOAC, 1983) was 1.1% (w/w) and allowed for making up solutions in distilled water.

Water activity was derived from freezing point data on four solutions between 2.03 and 8.65 g PG/100g water. Freezing points were determined with a Milk Cryoscope Advanced Instruments 4DII (Cambridge, MA, USA) which was calibrated using standard solutions of sodium chloride. The thermodynamic relationship between $a_w$ and freezing point depression ($\theta_F$) may be expressed by the following equation (Ferro Fontán & Chirife, 1981),

$$-\ln a_w = 9.693 \times 10^{-3} \theta_F + 4.761 \times 10^{-6} \theta_F^2$$ (1)

The only assumption introduced in this expression was that the difference between the molal heat capacities of liquid water and ice is independent of temperature in the range $T_F - T_F$ (the freezing point of pure water to the freezing point of the solution). As the present work deals with minimum freezing points of only about −3°C, this assumption introduces practically no error in the numerical...
expression (Equation (1)) (Ferro Fontán & Chirife, 1981). Four or more replicate measurements of freezing points were made at each concentration and, as shown previously (Miracco et al., 1981), the error in freezing point determination does not exceed the two standard deviation levels, or about 0.006°C. The corresponding error in water activity (estimated from Eqn (1)) is about 0.0001; consequently it is safe to express $a_w$ values derived from measured freezing points to four decimal places.

RESULTS AND DISCUSSION

Figure 1 shows the literature data on water activity of propylene glycol solutions (Plitman et al., 1973; Loncin, 1975; Sloan & Labuza, 1975; Verlinde et al., 1975; Kamman et al., 1978) together with the behaviour derived from Raoult's law as reference. The data of Kamman et al. (1978) on propylene glycol solutions in brain heart infusion (BHI) broth were recalculated as % w/w in water solution to account for the contribution of BHI solutes (Chirife et al., 1982). The $a_w$ data of Loncin (1975) and Sloan and Labuza (1975) are lower than those reported by the other researchers; in particular, Loncin's values show a pronounced negative deviation from Raoult's law.

The freezing-point-derived $a_w$ data obtained in the present study for PG solutions are shown in Fig. 2 and compared with $a_w$ data reported by Weast (1985), also calculated from freezing point data; good agreement is observed between both sets of data. It is noteworthy that the freezing-point-derived $a_w$ data were limited by the equipment (milk cryoscope) to a maximum depression of about -3°C, corresponding to approximately 10 g PG/100 g water. A computer program was used to calculate the best $K$ value for all data reported in Figure 2 (present and Weast's data) applying Norrish's equation, which is usually used for correlating water activity data in non-electrolyte solutions (Chirife et al., 1980).

$$a_w = X_1 \exp \left(-K X_2^2\right)$$

where $X_1$ and $X_2$ are molar fractions of water and solute respectively, and $K$ is a parameter to be determined. The value found for $K$ was 4.04 ± 0.22 and the modest error (0.22) evidenced the goodness-of-fit of data to Norrish's model.

According to Norrish (1966), the parameter $K$ might be correlated with the number of -OH groups in the molecules of sugars and polyols. Chirife et al. (1980) found a linear relationship between $K$ and the number of -OH groups for glycerol, erythritol and sorbitol, and following this dependence (without determining $a_w$ experimentally) they tentatively assigned a value of $K = 1$ to propylene glycol. However, this simplifying assumption ignored the influence of groups different from -OH and/or the spatial conformation of the polyol molecule on the $K$ value. This can be seen by comparing literature values of $K$ for different polyols (Chirife et al., 1980, 1984; Alzamora & Chirife, 1984). Values of the parameter $K$ for glycerol (1.16), erythritol (1.34), arabinol (1.41), ribitol (1.49) and sorbitol (1.65) increase with the number of -OH groups in the molecule, but the $K$ values for xylitol (1.66) and mannitol (0.906) are...
different from those of arabitol and sorbitol although they have, respectively, the same number of -OH groups. Differences in the spatial conformation of arabitol and mannitol as compared to sorbitol and xylitol (Di Paola & Belleau, 1972) might explain this behaviour. In addition to the number of -OH groups and spatial conformation, other functional groups may also play a role in the $a_w$-lowering characteristics of a solute molecule. In propylene glycol ($K=4.04$) and 1,3- and 2,3-butylen glycol ($K=3.47$ and 4.78, respectively), the -CH$_2$ group interacts with the -CHOH one and repulsive forces prevail between them. On the other hand, the interaction between the CHOH–CHOH groups is small, indicating that attractive and repulsive forces present nearly cancel (Okamoto & Wood, 1978). These effects may explain the behaviour of propylene glycol which differs somewhat from that of alditols but resembles that of the butylene glycols (Alzamora & Chirife, 1984).

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REFERENCES


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