Calculating osmotic pressure of glucose solutions according to ASOG model and measuring it with air humidity osmometry

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Abstract: The osmotic pressure of glucose solution at a wide concentration range was calculated using ASOG model and experimentally determined by our newly reported air humidity osmometry. The measurements from air humidity osmometry were compared with the well-established freezing point osmometry and ASOG model calculations at low concentrations and with only ASOG model calculations at high concentrations where no standard experimental method could serve as a reference for comparison. Results indicate that air humidity osmometry measurements are comparable to ASOG model calculations at a wide concentration range, while at low concentrations freezing point osmometry measurements provide better comparability with ASOG model calculations.

Keywords: ASOG model; osmotic pressure; air humidity osmometry; freezing point osmometry.

INTRODUCTION

Osmotic pressure plays an important role in many fields, including medicine (Jacobi *et al*., 2011; Lütfioğlu *et al*., 2011), drug (Li *et al*., 2008), agriculture (Ayers *et al*., 1949), industry (Loeb *et al*., 2002), and others. In view of the fundamental scientific importance of osmotic pressure, it is not surprising that substantial effort have been dedicated to the development of analytical methods of measurement of the osmotic pressure. The most common methods of osmometry are membrane, freezing point and dew point, but no one has proved to be satisfying.

Membrane osmometry is a direct technique used for the measurement of solution's osmotic pressure. Although this method is based on a simple principle, it cannot measure the osmotic pressure of a solution of small molecules, largely because of the filtration ability of the membrane (Grattoni *et al*., 2008). Namely, the performance of membrane osmometry is limited by the properties of the membranes. Commercially available device made according to this method also called colloid osmometer. One important field of use for colloid osmometer is the measurement of the colloid osmotic pressure of blood, serum, plasma, or other body fluids in comparison to isotonic saline solution.

Commercially available freezing point and dew point osmometers are quick and easy to use and require sample volumes as small as a few micro liters. But they are also adequate for diluted solution. The limits of applicability of these two methods are strongly related to their measurement methods (Sweeney *et al*., 1993). Freezing point osmometer is limited by that the solutes may precipitate at decreasing temperatures during the measurement. Dew point osmometer is limited by that the concentrated solution has insufficient water condenses onto the thermocouple during the cooling period so that insufficient heat is generated to reach the lower detection limit.

Recently, we proposed an air humidity osmometry (Zhan *et al*., in press). In this method, the osmotic pressure is determined by measuring the relative air humidity in equilibrium with the solution. The most important advantage of this method is that it overcomes the defects of freezing point and dew point osmometries, which result from the heterothermal process in the measurement; therefore, this method is not limited to diluted solutions. The pocket humidity meter used in the new osmometry complements the commercial available osmometer in the high-osmotic-pressure range. Moreover, it is significantly simpler and cheaper.

According to the principles of physical chemistry, the osmotic pressure (π) and water activity (a_{H2O}) of a solution are related as $\pi = -\frac{RT}{V_{H2O}}\ln a_{H2o}$ (Adamson, 1986) and water activity is related to the concentration according to some physicochemical models. This implies that there is a certain relationship between the osmotic pressure and the concentration. If we can find out this relationship, the osmotic pressure could be calculated from the concentration. And then the π values calculated by physicochemical models and measured with air humidity osmometry would become controls for each other in concentrated solutions.

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There are many models can be appropriated for calculate activity coefficient of nonelectrolyte solutions. ASOG model is proposed according to combine the local-composition concept with group-contribution concept (Derr *et al*., 1969; Kojima *et al*., 1979). The equation of the model is simple and it has a good prediction performance, so its applications in the thermodynamic calculations of nonelectrolyte solution are very wide.

In the present article, we used a series of glucose solutions as a model to demonstrate our hypothesis. We calculated the water activity of these solutions using ASOG model. We compared the osmotic pressure calculated from the water activity with those determined by air humidity and freezing point osmometries and we showed that our method is much simpler and cheaper but with comparable accuracy.

Theoretic

A solution's osmotic pressure (π) and its solvent activity (a_{H_2O}) are related as

$$\pi = -\frac{RT}{V_{H_2O}} \ln a_{H_2O} \tag{1}$$

where V_{H_2O} is the partial molar volume of water, R is the universal gas constant, and T is the Kelvin temperature (Adamson, 1986). In practice, the molar volume of water is usually used as a replacement for V_{H_2O} in all osmometries (Zhan *et al*., in press).

Air humidity osmometry

According to Raoult's law, in ideal solution or diluted solution, the vapor pressure of water (p_{H_2O}) in equilibrium with the solution is proportional to the mole fraction of water (x_{H_2O}):

$$p_{H_2O} = p^*_{H_2O} x_{H_2O} \tag{2}$$

Where $p^*_{H_2O}$ is the equilibrium water vapor pressures of pure water.

In a real solution the activity of water (a_{H_2O}) should be used instead of the mole fraction of water, then Raoult's law can be written as

$$p_{H_2O} = p^*_{H_2O} a_{H_2O} \quad \text{or} \quad a_{H_2O} = \frac{p_{H2O}}{p^*_{H_2O}} \tag{3}$$

In fact, the relative air humidity (H_r) in equilibrium with the solution is just the water activity:

$$H_r = p_{H_2O} \big/ p^*_{H_2O} = a_{H_2O} \tag{4}$$

Thus the Eq. (1) can be expressed as

$$\pi = -\frac{RT}{V_{H_2O}} \ln H_r \tag{5}$$

Calculating osmotic pressure by ASOG model from concentration

The water activity can be express as: $a_{H_2O} = \gamma_{H_2O} x_{H_2O}$, here γ_{H_2O} is the activity coefficient of water. According to ASOG model, γ_{H_2O} can be written as:

$$\ln \gamma_{H_2O} = \ln \gamma^C_{H_2O} + \ln \gamma^R_{H_2O} \tag{6}$$

where γ^C_{H2O} is the combinatorial term and γ^R_{H2O} is the residual term.

For glucose solutions at 25°C, γ^C_{H2O} can be expressed as:

$$\ln \gamma^C_{H_2O} = \ln\left(\frac{1}{12-11x_{H_2O}}\right) + 1 - \left(\frac{1}{12-11x_{H_2O}}\right) \tag{7}$$

γ^R_{H2O} can be expressed as:

$$\ln \gamma_i^R = 1.6\times\left[-\ln\left(\frac{8.1178-6.5178x_{H_2O}}{12-10.4x_{H_2O}}\right)+1-\left(\frac{1.6x_{H_2O}}{8.1178-6.5178x_{H_2O}}+\frac{12.6768(1-x_{H_2O})}{38.5988-35.2183x_{H_2O}}\right.\right.$$
$$\left.\left.+\frac{14.2064(1-x_{H_2O})}{43.4992-37.8166x_{H_2O}}+\frac{0.3004(1-x_{H_2O})}{10.4478-9.9672x_{H_2O}}+\frac{0.5908(1-x_{H_2O})}{5.0307-4.0854x_{H_2O}}\right)\right] \tag{8}$$

After calculating the a_{H2O} according to Eq. (6), (7) and (8), the osmotic pressure was obtained by Eq. (1).

Experimental

Material

Glucose (AR≥99.5%) was purchased from Tianjin Kemiou Chemical Co., Ltd.

Instruments

A pocket humidity meter (Rotronic HydroPalm Hp22 with HygroClip HC2-S humidity sensor, Rotronic AG, Basserdorf, Switzerland), an environmental chamber (SDH401, Chongqing experiment equipment factory, Chongqing, China, the accuracy of temperature is ≤2°C, precision and reproducibility are ≤0.5°C), a freezing point osmometer (OSMOMAT 030, Gonotec GmbH, Germany, both of the accuracy and repeatability are 0.5%) and an electronic balance (FA2004, Liangping Co. Ltd. Shanghai, China.) were used. For the humidity meter, the H_r range is 0~1 with resolution 0.008, the temperature range is 40~100°C with the accuracy 0.1°C.

Methods and results

Measuring osmotic pressure by air humidity osmometry (Zhan et al., in press)

About 5 ml of sample solution was placed in a sealed conical flask. The humidity sensor was sealed at the headspace of the conical flask as shown in fig. 1. Then the

Table 1: Osmotic pressure of glucose solutions (298.15K)

m /mol·kg^{-1}	π / MPa			Equivalence margin for freezing point osmometry	Equivalence margin for air humidity osmometry
	Messured with freezing point osmometry	Messured with air humidity osmometry	Calculated by ASOG model		
0.3469	0.863±0.002	1.177±0.219	0.859	±0.08	±1.0
0.6942	1.790±0.002	2.040±0.300	1.733	±0.16	±1.20
1.0253	2.776±0.008	2.763±0.084	2.586	±0.23	±1.78
1.3844	3.931±0.013	3.929±0.676	3.534	±0.74	±2.44
1.7327	5.292±0.036	4.710±0.147	4.476	±0.94	±1.03
2.0776	--	5.991±0.227	5.429		±1.25
2.4287	--	6.884±0.311	6.419		±1.48
2.7146	--	7.483±0.313	7.238		±1.66
3.3187	--	9.043±0.152	9.002		±1.44
3.8582	--	11.338±0.267	10.610		±1.70
4.4343	--	13.047±0.414	12.356		±1.98
4.9867	--	14.618±0.274	14.051		±2.25

Mean±SD of three measurements

conical flask was put in the thermostatic oven that could maintain the temperature to 25°C. After 2h incubation (although the respond time of the humidity sensor is about 5s, about 1h are needed for the gas-liquid equilibrium), the relative air humidity in the conical flask, i.e. the H_r of the sample, was measured by the humidity meter. The osmotic pressure was calculated using the Eq. (5) and is listed in table 1 and shown in fig. 2.

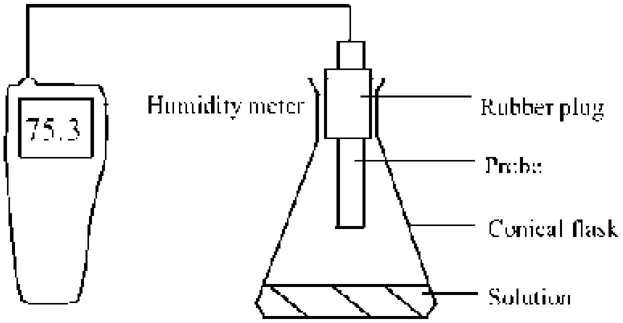

Fig. 1: Assembly used in the H_r determination by air humidity osmometry method.

Measuring osmotic pressure by freezing point omsmetry

The osmotic pressure of sample solution is measured using the freezing point osmometer. The results are also listed in table 1 and shown in fig. 2.

We used two one-sided test (TOST) procedure for testing equivalence (Schuirmann, 1981; Kirkwood and Westlake, 1981) and multiple testing corrections (Benjamini and Hochberg, 1995) were applied to control the false discovery rate. The statistical analysis was done using R (R Core Team, 2013) version 3.0.1. The result shows that the measurements from both freezing point osmometry and air humidity osmometry are comparable to those calculated by ASOG model. However, a more strict equivalence criterion can be established between the measurements from freezing point osmometry and ASOG model calculations, compared to the equivalence criteria between air humidity osmometry and ASOG model calculations, at low m's (mol/kg). table 1 gives the equivalence criterions, denoted as the percentage variation with respect to ASOG model calculations, which could be established between freezing point osmometry and air humidity osmometry, respectively, to control a false discovery rate of 5%.

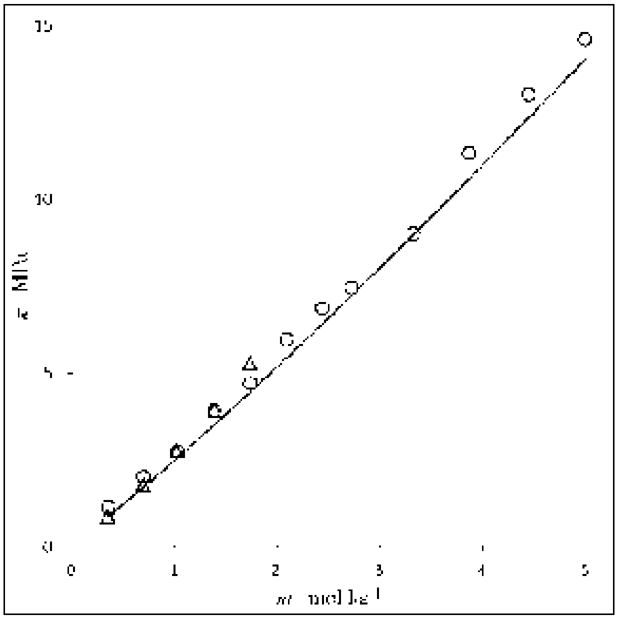

Fig. 2: The comparison of the osmotic pressure calculated by ASOG model and the measured one: ASOG model (-); air humidity osmometry (o); freezing point osmometry (Δ).

CONCLUSIONS

The osmotic pressure is a well-known colligative property of drug solutions there should be a relationship between the osmotic pressure and the concentration of drugs. This makes it possible to calculate the osmotic pressure, which is usually difficult to measure, from the concentration that is relatively easy to obtain.

We newly proposed an easy and cost efficient air humidity osmometry and applied this method in determining the osmotic pressure of a series of glucose solutions. Experiment showed that the air humidity osmometry is applicable to a wide range of concentrations and the measurements are comparable to ASOG model calculations. Although the air humidity osmometry is less comparable to ASOG model at low concentrations compared to the widely used freezing point osmometry, our method validates the theoretical ASOG model at high concentrations where no other experimental method has been proposed.

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