Osmometry in Vapour Phase. I.
Osmotic Coefficients of Some Electrolytes at 40°C

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The scope of the applicability of osmometry in vapour phase to the study of aqueous solutions was tested by determining the osmotic coefficients of six electrolytes of different type at 40°C.

It is the comparative isopiestic method [1, 2] which was mostly used for the determination of the osmotic coefficients of electrolytes and non-electrolytes hitherto listed at the temperatures differing from the freezing point or boiling point of aqueous solutions. The solutions of NaCl and KCl are usually used as reference standards. The osmotic and activity coefficients of these standards have been established by a direct but difficult determination of water activity or calculated from electromotive forces. The accurate isopiestic method is generally applicable over the whole temperature range between the freezing and the boiling points of solution. Nevertheless, at lower concentrations some difficulties appear and the molality $m = 0.1$ is considered to be the lower limit of applicability for binary electrolytes [1]. The common concentrations of physiological solutions, however, vary just at the proximity of that limit.

In the cases of the solutions of similar or greater dilution only osmotic data determined from freezing point depression or boiling point elevation at normal pressure are often available and practically used. Data obtained at other temperatures are rather scarce. The osmotic coefficients of a limited number of electrolytes calculated from the activity coefficients on the basis of the Gibbs—Duhem equation make exception [1] (p. 53). The activity coefficients are obtained by measuring the electromotive force of corresponding galvanic cells the realization of which is not practically feasible with a number of other electrolytes. Conversely, it would be useful to obtain the activity coefficients by calculation from the osmotic coefficients in this case [2] (p. 263).

The aim of this study was to test the possibility of using osmometry in vapour phase for the determination of osmotic coefficients of substances in dilute aqueous solutions at 40°C. Since the method is of comparative character, the substances selected for the first experimental study involved some electrolytes of different types; among them a suitable standard substance could be found. Osmometry in vapour phase was described mainly as a rapid and simple method for the determination of molecular weights of the substances dissolved in non-aqueous solvents, *e.g.* benzene [3, 4]. It has not often been used for aqueous solutions [9, 5] because of the necessity of more complicated instrumental equipment.

Experimental

Chemicals

The anal. grade salts without further purification were used except ephedrine chloride (EPHCl) which was recrystallized from aqueous ethanol and dried carefully at about

110°C. In a similar way, sodium and potassium salts were dried. The concentration of $MgSO_4$ and $ZnSO_4$ solutions was determined chelatometrically (eriochrome black T while the weighted amount was used for the calculation of the concentration of other salts.

Equipment and measurements

The measurements were made with a Dampfdruckosmometer Knauer Model 1970 instrument using a two-thermistor probe suited for all kinds of solutions. At the terminal points of the probe the thermistors were isolated by sealing them into the glass capillaries round which a miniature corrosion resistant metal spiral was coiled. Consequently, a sample of solution put on the first thermistor by means of a syringe as well as pure water put on the second one does not form a rounded drop but spreads along the spiral on the whole surface of capillaries. The vapour cell where the probe was placed was electronically thermostated.

Table 1

Dependence of the change in thermistor resistances (ΔR) on the molatily (m) of NaCl solutions

	ΔR	Ω
	I	II
0.04	41.0	41.0
0.07	73.0	72.0
0.10	101.5	104.5
0.14	144.0	145.5 '
0.17	173.5	175.0
0.20	205.0	205.0
k_1	1024.3 ± 6.7	1031.0 ± 8.1

k_1 — coefficient in equation (1).

The thermometric device of the osmometer (Temperatur-Meßgerät Knauer) was connected with an electronic line recorder eK BT1 (VEB). The recorded deflection corresponded to the arisen difference between the thermistor resistances ΔR. In the circuit between the probe and the thermometric device a decade resistance was placed by means of which the deflection was calibrated and the range of the recorder changed.

Provided aqueous solutions were used at the temperature of the vapour cell (40°C) a bithermal distillation equilibrium was established between the sample of solution on the first thermistor and water on the second one in $2-3$ minutes. For the highest concentrations used, the arisen difference between the resistances of thermistors ΔR was as much as 250 Ω and it did not usually vary by more than ± 1 Ω. The zero position of blank test (water on both thermistors) did not change in repeated measurements with steady-state instrument by more than 3 Ω in one hour.

The long term stability of thermistors was examined by occasional measurements of the NaCl solutions which were used as standard for the determination of osmotic
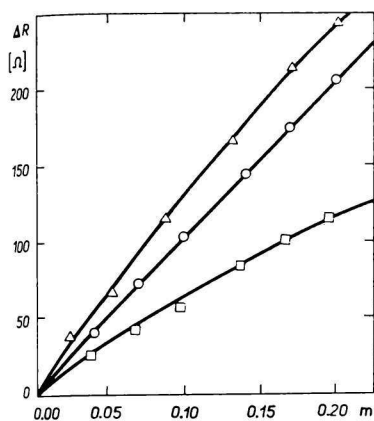
Fig. 1. Dependence of the change in thermistor resistances (ΔR) on the molality of solution (m). Solutions: ○ NaCl, △ Na$_2$SO$_4$, □ CuSO$_4$.

coefficients. Two series of measurements made one by one in a half-year period of time are given in Table 1. The observed difference between the series *I* and *II* is still within the limits of errors caused by other factors.

The solutions of other electrolytes were measured at equal or similar concentrations as the NaCl solutions. There are three typical dependences of ΔR on temperature which are presented in Fig. 1. Considering the pictured form, the relationship between ΔR and molality m was tested by the least-square method using both linear (*1*) and quadratic (*2*) functions:

$$\Delta R = k_1 m , \qquad\qquad (1)$$

$$\Delta R = k_1 m + k_2 m^2 . \qquad\qquad (2)$$

The suitability of these expressions was judged according to the magnitude of the calculated standard errors of coefficients k_1 and k_2. It was found that the linear function (*1*) was convenient for the studied electrolytes of uni-univalent type $I-I$ in the investigated concentration range while the quadratic function (*2*) had to be used for other electrolytes. The coefficients k_1 as well as the standard errors for NaCl are given in Table 1 while these values together with coefficients k_2 for other electrolytes are presented in Table 2.

Table 2

Coefficients of the relationship between ΔR and molality
Equations (*1*) and (*2*)

Electrolyte	k_1	$\pm s$	Electrolyte	k_1	$\pm s$	k_2	$\pm s$
KCl	1004	13	CuSO$_4$	679	14	−490	210
KClO$_4$	996	8	MgSO$_4$	685	20	−609	190
KNO$_3$	997	14	ZnSO$_4$	623	30	−160	200
EPHCl	972	14	Na$_2$SO$_4$	1402	25	−950	290

Calculation of activity coefficients

The molal activity coefficient φ of aqueous electrolyte is defined [1] (p. 48) by the expression

$$\varphi = -\frac{1000}{vmM_w} \ln a_w, \tag{3}$$

where a_w and M_w are the activity and molecular weight of water respectively, m denotes the molality of electrolyte and v is the number of ions into which a molecule of electrolyte is dissociated in solution.

The calculation of osmotic coefficients is based on the assumption that two solutions which show equal difference between the resistances of thermistors $\varDelta R$ have the equal activity of water at a given temperature. If one of them is considered to be a reference standard and denoted by index s, it holds according to equation (3)

$$v\varphi m = v_s\,\varphi_s\,m_s. \tag{4}$$

The solutions of NaCl were chosen as reference standard. However, the values of φ found in literature do not cover sufficiently the investigated concentration range from 0.04 to 0.02 m solutions at 40°C even if a temperature interpolation incorporated in Table 3 is used. For this reason the calculation of φ was carried out by means of the activity coefficients of NaCl published in a more recent paper [6] which covers a considerable range of temperature and concentration. The activity coefficients presented in that paper and related to 38°C were adapted by interpolation for 40°C. They are listed in Table 3. The osmotic coefficients have been calculated from these activity coefficients by an approximate numeric method [7] which is sufficiently accurate and does not require a complicated computational technique. All the osmotic coefficients obtained have been graphically smoothed by plotting them against $\sqrt{m}$ and the smoothed values some of which are

Table 3

Osmotic (φ) and activity (γ) coefficients of NaCl in aqueous solutions at 40°C

m	γ	φ	φ^d
0.01	0.900	0.967[a]	
0.02	0.870	0.959[a]	0.958
0.0256		0.9536[b]	
0.04			0.947
0.05	0.819	0.943[a]	0.943
0.0576		0.9400[b]	
0.10	0.774	0.931[a]; 0.931[c]	0.932
0.1024		0.9307[b]	
0.15			0.925
0.2	0.726	0.919[a]; 0.923[c]	0.921
0.3		0.916[c]	0.916

a) calculated from the presented activity coefficients.
b) interpolation 35—45°C; see [1] (p. 557).
c) interpolation 25—60°C; see [1] (p. 550 and 556).
d) smoothed values.

presented in Table 3 have been used for further calculations. In general, the values thus obtained are in good agreement with those calculated from the activity coefficients of NaCl published in anterior papers [8].

The relationship between the product $\varphi_s\, m_s$ and ΔR of NaCl solution was expressed in a simple quadratic form

$$\Delta R = K_1\, \varphi_s\, m_s + K_2(\varphi_s\, m_s)^2. \tag{5}$$

The values of coefficients and their standard errors calculated by the least-square method are

$$K_1 = 1086.8 \pm 8.1; \; K_2 = 166 \pm 66.$$

By solving equation (5) with respect to $\varphi_s\, m_s$ and substituting into (4) we obtain the expression for the calculation of φ of an arbitrary electrolyte

$$\varphi = \frac{\nu_s}{\nu_m} \left(-\frac{K_1}{2K_2} \pm \sqrt{\frac{K_1^2}{4K_2} + \frac{\Delta R}{K_2}} \right). \tag{6}$$

ΔR of an examined electrolyte can be calculated for corresponding m from equation (1) or (2). The osmotic coefficients obtained are listed in Table 4.

Table 4

Osmotic coefficients of electrolytes determined by osmometry in vapour phase at 40°C

	φ							
	KCl	$KClO_4$	KNO_3	EPHCl	$CuSO_4$	$MgSO_4$	$ZnSO_4$	Na_2SO_4
0.04	0.919	0.911	0.912	0.889	0.604	0.606	0.566	0.830
0.10	0.911	0.904	0.905	0.882	0.574	0.569	0.554	0.788
0.15	0.905	0.898	0.899	0.877	0.550	0.540	0.544	0.753
0.20	0.900	0.892	0.893	0.871	0.526	0.510	0.535	0.720

EPHCl — ephedrine chloride.

Discussion

From the point of view of the factors influencing the applicability of osmometry in vapour phase [3] water has several disadvantages when compared with organic solvents, e.g. benzene. In particular, it is electric conductance, approximately twofold specific heat, fivefold heat of evaporation, and lower pressure of saturated vapour.

The conductance of water and aqueous solutions necessitates the isolation of thermistors. The sensing element together with a drop of water or solution has then a higher heat capacity and also a greater loss of heat. This fact usually reduces the so-called efficiency of the apparatus [3] and extends together with the lower vapour pressure the time necessary to reach the bithermal distillation equilibrium, which is anyhow only temporary. Moreover, the established temperature difference between the drops of solution and solvent is much lower here because it is inversely proportional to the specific heat of evaporation. The shortcomings could not be overcome quite satisfactorily in most equipments of older design [9].

As to the described equipment, the time necessary for the establishment of equilibrium (2—3 minutes) as well as the stability of equilibrium is on the level of the best results obtained with organic solvents [3]. This fact is evidently due to a special design of thermistor sensing element and a perfect thermostating of vapour cell. Though the pressure of saturated vapour of water at 40°C is only about 55 Torr, the results obtained indicate the possibility of measuring even at lower temperatures.

Owing to the high heat of evaporation, the optimum concentrations of solutions are higher than those with organic solvents. The concentration range from 0.02 to 0.25 m may be recommended for an electrolyte of the type $I-I$ while the higher value quoted does not represent the upper limit of applicability. The above range covers the region of physiologically important concentrations and moreover it corresponds sufficiently to the region of applicability of the isopiestic method.

The standard errors of the osmotic coefficients determined (Table 4) follow from the standard errors of the cofficients k_1, k_2 or K_1, K_2 given in Table 3. Thus for the electrolytes of the type $I-I$ they amount to $\pm 1-2\%$, for multivalent electrolytes to $\pm 3-4\%$. In the case of potassium chloride, this fact may also be verified by comparing the results with the osmotic coefficients calculated from the activity coefficients [1] (p. 558). The relatively less favourable results obtained with multivalent electrolytes are likely due to lower values of the measured $\varDelta R$ (except Na_2SO_4, see Fig. 1) as well as to different properties of their solutions.

The technically simple and rapid osmometry in vapour phase with the use of a modern equipment is therefore without doubt a useful supplementary method of the determination of osmotic coefficients, especially for those kinds of electrolytes and concentration regions where neither the measurement of electromotive force nor isopiestic method may be used. At the same time, the results presented illustrate the possibility of further application of this method to the study of aqueous solutions at the temperature close to that of physiological medium.

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