

The use of a thermoelectric osmometer to measure the osmotic coefficients of aqueous solutions of sodium salicylate at 25°

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The use of a thermoelectric osmometer to measure osmotic coefficients for the binary system water-sodium salicylate at low concentrations (0.0 to 0.3 molal) is described. The accuracy and reproducibility of the instrument have been enhanced by employing a microscope to measure sample and reference drop sizes. Activity coefficients, calculated from the osmotic coefficients obtained in these experiments, have been combined with density and diffusional measurements to calculate frictional coefficients for the system.

Diffusional measurements made on the system water-sodium salicylate have been combined with data received from measurements using a vapour pressure osmometer, to evaluate frictional coefficients. Unlike diffusional coefficients these last are independent of the reference frame used for measurement. The technique required to obtain meaningful and reproducible values for osmotic coefficients is discussed in detail.

THEORY

Expression for frictional coefficients

In a system of $q + 1$ components in which the solvent is designated by 0, and the solutes by $(1, 2 \dots q)$, the isothermal diffusional flow $(J_i)_S$ of component i produced by the chemical potential gradients X_k can be represented by equation (1) (Kirkwood, Baldwin & others, 1960)—

$$(J_i)_S = \sum_{k=0}^q (L_{ik})_S X_k \quad (i = 0, 1, 2 \dots q) \dots \dots \dots (1)$$

in which the flux J_i and the phenomenological constants L_{ik} are measured with respect to reference frame S.

For one dimensional flow at constant temperature and pressure,

$$X_k = - \left(\frac{\partial \mu_k}{\partial X} \right)_{T,P} \dots \dots \dots (2)$$

where

$$\mu_k = \mu_k^0 + RT \ln C_k y_k \dots \dots \dots (3)$$

in which μ_k and μ_k^0 are the chemical and standard chemical potentials of component k , R is the gas constant, T the absolute temperature, C_k the concentration in mol dm⁻³ and y_k is the corresponding activity coefficient.

By considering the relative velocities $(V_i)_S$ and $(V_k)_S$ of components i and k according to reference frame S, it is possible to write a restricted phenomenological equation (4), which in the form due to Dunlop (1964) is,

$$X_1 = \sum_{k=0}^q R_{1k} C_k [(V_1)_s - (V_k)_s] \quad \dots \quad \dots \quad (4)$$

and by using activity coefficient, density and diffusion data to calculate a frictional coefficient R_{1k} . For a two-component system—

$$R_{10} = \frac{\bar{V}_0 RT}{D_A} \left[1 + \frac{C_1}{\partial C_1} \frac{\partial \ln y_1}{\partial C_1} \right] \quad \dots \quad \dots \quad (5)$$

where \bar{V}_0 is the partial molar volume of the solvent, D_A the mutual diffusion coefficient, C_1 and y_1 are the concentration (mol dm⁻³) and activity coefficient of the solute.

EXPERIMENTAL

Materials

Sodium salicylate and Analar sodium chloride were purchased from British Drug Houses Ltd. The molecular weights were taken as 160.11 and 58.454 respectively.

Solutions

All solutions were prepared by weighing in air and were subsequently corrected for weight *in vacuo*. Before each diffusion measurement the densities of the initial solutions were determined in triplicate at $25 \pm 0.01^\circ$ using matched single-stem pycnometers each having a volume of about 30 cc. These were weighed against a calibrated sealed tare filled with air-free double distilled water, whose density was taken as 0.997048 g cc⁻¹.

By a least squares analysis it was found that the density in g cc⁻¹ of the sodium salicylate solution could be represented by the equation

$$d_4^{25} = 0.997048 + 0.41378\rho - 0.0506\rho^2 \quad 0 \leq \rho \leq 0.16 \quad \dots \quad (6)$$

with an average deviation of $\pm 0.0004\%$, where ρ is the concentration expressed in g cc⁻¹.

The osmotic coefficients of the solutions were measured on a Mechrolab Vapour Pressure Osmometer Model 302, an instrument which measures the depression in vapour pressure of a solvent when small quantities of solute are added to it.

The two principal units of the osmometer connected electronically by shielded cables are a thermally insulated "detector" module and a control module which also contains an amplifier and a D.C. Wheatstone Bridge.

A thermostat and heater are inserted into the body of the thermal block and maintain the centrally situated vapour chamber at a constant temperature of $25 \pm 0.001^\circ$. Further holes machined into the block and opening into the vapour chamber accommodate the thermistor probe and six microsyringes and provide a horizontal viewing tube at the end of which an angled plane mirror is attached. By looking into the mirror, an image of the two carefully matched thermistor beads may be seen within the vapour-chamber.

To set up an experiment, a short glass cylinder was fitted with an absorbent wick and approximately half-filled with a sample of the same water used in preparing the solutions. This reservoir was placed at the base of the vapour chamber by raising and replacing the upper portion of the detector block; and the chamber was left overnight to attain temperature equilibrium.

Four syringes were filled in pairs with freshly prepared solutions of sodium chloride and sodium salicylate, the molalities of reference and unknown solutions being

approximately equal. The remaining syringes were filled with water; all were inserted in the block and allowed to equilibrate for 20 min before any measurement was attempted.

Using the microsyringe, one droplet of water was placed on the tip of each of the thermistor beads, and a stop-watch was started. Exactly 50 s later the bridge was brought to zero, this process taking exactly 8 s. After 2 min the galvanometer was brought to a point of balance. Further drops of water were added to the "sample" thermistor bead and the above process was repeated until no further adjustment of the bridge was necessary to maintain a state of balance. The drop of solvent on the "reference" bead remained unchanged throughout the course of any one experiment.

The sample drop was washed off with 5 drops of a salicylate solution, readings were taken using the same time schedule as above, until the resistance increment to balance the bridge remained constant to within ± 0.01 ohm for five successive drops of sample.

After washing the salicylate off with three drops of solvent when the bridge should show a dekastat reading of zero ohms, sodium chloride solution of the same molality as the salicylate most recently measured was placed on to the sample thermistor bead and the sample measurement was repeated. Finally, the sample bead was washed off with three drops of water and the zero was rechecked with solvent on both beads.

Using literature values (Robinson & Stokes, 1959) for the osmotic coefficient of the NaCl solution and knowing the molalities of solutes measured and their respective ohmic increments, a value for the osmotic coefficient of the salicylate solution could be calculated from the expression

$$\phi_x = \frac{\Delta R_x m_r \phi_r}{\Delta R_r m_x} \quad \dots \quad \dots \quad \dots \quad \dots \quad (7)$$

where ΔR is the resistance increment; m is the molality of the solute; and ϕ is the osmotic coefficient, the subscripts $_r$ and $_x$, referring to reference (NaCl) and unknown (Na salicylate) solutions respectively.

To obtain meaningful results, the drops on the reference and sample beads must be equal in size and the finite size of the reference bead is critical, moreover, estimates of drop size made with the unaided eye proved inadequate.

The viewing mirror was therefore soldered in a retaining clip at a suitable angle and the thermistor bead image was brought to a focus on the eyepiece of a compound microscope fitted with a ruled graticule. The substage lens of the microscope, the mirror and the sighting tube were enclosed in a light-tight cylinder made of black card to improve the definition of the image.

Diffusion measurements were made using a Gouy diffusimeter. The apparatus and the method of obtaining the diffusion measurements have been described previously (Deshmukh & Fleming, 1968) and only a brief description will be given here.

The light source is a water-cooled vapour pressure lamp used in conjunction with a Wratten 77A filter to isolate the mercury green line ($\lambda = 5460.7\text{\AA}$) and a Hilger and Watts source slit. Light from the illuminated slit is focussed by an achromatic doublet lens through the water-bath containing the Tiselius cell on to a Kodak Ortho 800 photographic plate.

Measurements of the fringe minima were measured to an accuracy of 0.001 mm using a Gaertner M2001P toolmakers' microscope. Details of calculating the mutual diffusion coefficient D_A , the refractive index increments $\Delta n/\Delta\rho$ and Q , the area of the fringe deviation graphs, have already been published by Woolf, Miller & Gosting (1962) and Deshmukh & Fleming (1968).

RESULTS

The results of the diffusional measurements are shown in Table 1. Columns 1, 2 and 3 show the values of the mean concentration $\bar{\rho}$ of the solutions of sodium salicylate which are listed in g cc⁻¹, and in terms of the molar and molal scales respectively, where

$$\bar{\rho} = \frac{(\rho_A + \rho_B)}{2} \quad \dots \quad \dots \quad \dots \quad \dots \quad (8)$$

and ρ_A and ρ_B are the initial concentrations of the solutions above and below the boundary of the Tiselius cell.

Table 1. *Diffusional data for system water-sodium salicylate at 25°*

$\bar{\rho}$	$\bar{\rho}_r$	$\bar{\rho}_l$	$\Delta\rho$	$\Delta\rho_r$	$10^5 D_A$	$10^5 \frac{\Delta n}{\Delta\rho_r}$	J_m
0.005012	0.031304	0.031490	0.010025	0.062615	1.009 ₃	3291.8	94.27
0.024980	0.156022	0.158822	0.009988	0.062384	0.960 ₈	3270.9	93.35
0.049909	0.311725	0.322143	0.009939	0.062078	0.913 ₉	3256.5	92.54
0.099627	0.622258	0.663289	0.009920	0.061980	0.834 ₁	3219.7	91.23
0.149068	0.931060	1.024789	0.010055	0.062802	0.760 ₀	3200.5	91.94

Units: Concentrations: $\bar{\rho}$, g cc⁻¹; $\bar{\rho}_r$ mol litre⁻¹; $\bar{\rho}_l$ mol/1000 g.

Concentration difference: $\Delta\rho$, g cc⁻¹; $\Delta\rho_r$, mol litre⁻¹.

Diffusion coefficient: D_A , cm² s⁻¹.

Refractive index increment: $\frac{\Delta n}{\Delta\rho_r}$, litre mol⁻¹.

Columns 4 and 5 list the concentration differences in g cc⁻¹ and mol litre⁻¹ of solution, where

$$\Delta\rho = \rho_B - \rho_A \quad \dots \quad \dots \quad \dots \quad \dots \quad (9)$$

whilst the refractive index increments in litre mol⁻¹ appear in column 6 and were computed using the relation

$$\frac{\Delta n}{\Delta\rho_r} = \frac{J_M \lambda}{a \Delta\rho_r} \quad \dots \quad \dots \quad \dots \quad \dots \quad (10)$$

where J_M is the total number of fringes in the diffusion pattern.

Values of the area of the fringe deviation graph were computed and show that within the range of concentration the system is not concentration dependent.

The variation of the mutual diffusion coefficient D_A with $\bar{\rho}$ (g cc⁻¹) is summarized by the expression

$$D_A = 1.022_0 - 2.661_3 \bar{\rho} + 11.332_0 \bar{\rho}^2 - 35.34 \bar{\rho}^3 \quad 0 \leq \bar{\rho} \leq 0.15 \quad \dots \quad (11)$$

which was obtained by a least squares analysis of the data in columns 1 and 6.

Table 2. *Osmotic coefficient measurements for the system water-sodium salicylate at 25°*

m	ϕ	m	ϕ
0.02	0.944 ₄	0.10	0.918 ₂
0.03	0.940 ₂	0.15	0.909 ₈
0.04	0.932 ₉	0.20	0.901 ₆
0.05	0.929 ₁	0.30	0.895 ₆
0.08	0.922 ₀	—	—

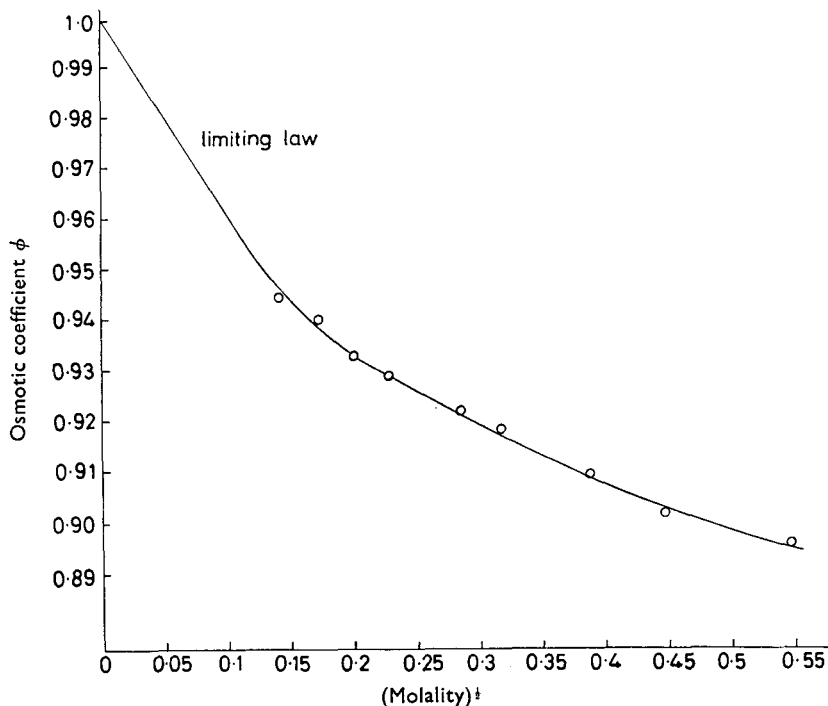


FIG. 1. Plot of osmotic coefficient against (molality)^{1/2} for water-sodium salicylate solution at 25°.

Table 2 summarizes the osmotic coefficient data, whilst Fig. 1 is a plot of osmotic coefficient ϕ against \sqrt{m} for sodium salicylate in water varying in molality m from 0 to 0.3. The values of the activity and frictional coefficients derived from these measurements are listed in Table 3.

Table 3. Activity coefficient data derived from vapour pressure measurements on system water-sodium salicylate at 25°

C	$\frac{\partial \ln \gamma_{\pm}}{\partial C}$	\bar{V}_0	$10^5 D_A$	$10^{-16} R_{10}$
0.05	-1.291	18.0679	1.001 ₄	4.183 ₉
0.10	-1.069	18.0678	0.982 ₂	4.072 ₉
0.15	-0.846	18.0675	0.964 ₁	4.055 ₇
0.20	-0.624	18.0671	0.947 ₂	4.138 ₁
0.25	-0.402	18.0665	0.931 ₄	4.325 ₉
0.30	-0.179	18.0659	0.916 ₄	4.624 ₇

Units: Concentration C, mol dm⁻³.
 Partial molar volume \bar{V}_0 , cm³ mol⁻¹.
 Diffusion coefficient D_A , cm² s⁻¹.
 Frictional coefficient R_{10} , erg cm s mol⁻¹.
 $R = 8.3144 \times 10^7$ erg deg⁻¹ mol⁻¹.
 $T = 298.15^\circ$ K.

The partial molar volume of the solvent \bar{V}_0 was calculated using the equation due to Geffcken (1931),

$$\bar{V}_0 = \frac{1000 \bar{V}_0^\circ}{1000 + C^2 \left(\frac{\partial \theta}{\partial C} \right)} \dots \dots \dots (12)$$

where \bar{V}_0° is the partial molar volume of pure solvent (18.0681 cc), θ is the apparent molar volume of the solute and C is the concentration of solute expressed in moles dm^{-3} .

To use this equation it was necessary to evaluate values of θ using the expression

$$\theta = \frac{1000}{C} \left(\frac{d_0 - d}{d_0} \right) + \frac{B}{d_0} \quad \dots \quad (13)$$

where d_0 is the density of water at 25° (0.997048 g cc^{-1}), d is the density of the solution at concentration C (mol dm^{-3}) and B is the molecular weight of the solute. Smoothed values of d were computed with the aid of equation (6).

Further regression analysis produced the relation

$$\theta = 94.14108 + 1.24667C + 0.23792C^2 - 0.30909C^3 \quad \dots \quad (14)$$

which after differentiation and evaluation for various rounded values of C was substituted into equation (10) to give a series of values for \bar{V}_0 which appear in column 3 of Table 3.

Using a form of the Gibbs–Duhem equation

$$-\ln \gamma_{\pm} = 1 - \phi + 2 \int_0^{\sqrt{m}} \frac{(1 - \phi)}{\sqrt{m}} \cdot d\sqrt{m} \quad \dots \quad (15)$$

mean molal activity coefficients γ_{\pm} were calculated from the osmotic coefficients ϕ , and the variation of γ_{\pm} with molality m is shown in Fig. 2. The integral in equation (15) was evaluated using Simpson's $\frac{1}{3}$ Rule, taking into account that

$$\lim_{m \rightarrow 0} (1 - \phi)/\sqrt{m} = 0.3903 \quad \dots \quad (16)$$

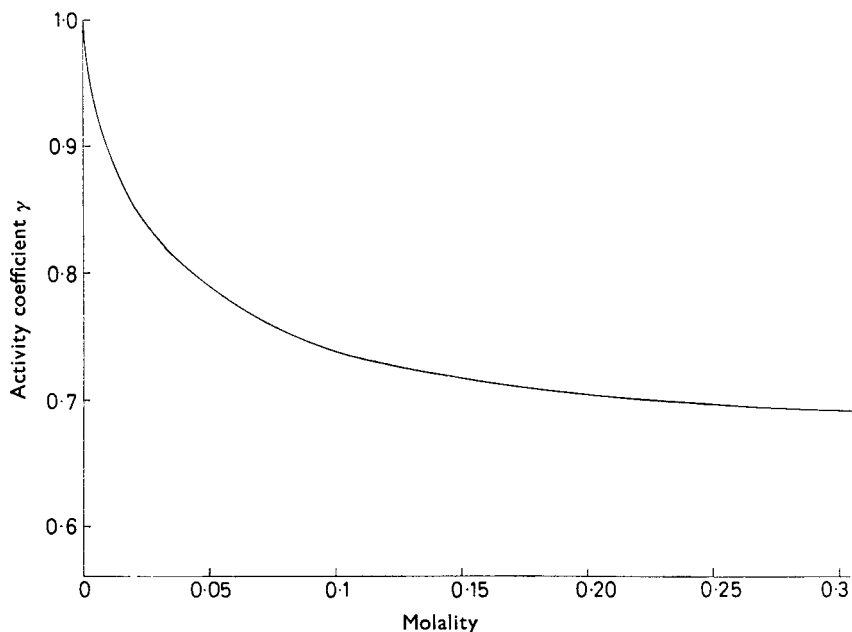


FIG. 2. Plot of activity coefficient against molality for water-sodium salicylate solutions at 25°.

The polynomial expression

$$\ln y_{\pm} = -0.15758 - 1.51386C + 2.22475C^2 \quad \dots \quad (17)$$

was obtained by least squaring and values of $\partial \ln y_{\pm} / \partial C$ were then obtained by differentiation and appear in column 2. The values of $\partial \ln y_{\pm} / \partial C$ were checked graphically by drawing tangents to a large scale graph of $\ln y_{\pm}$ against C .

The values of the mutual diffusion coefficient D_A of salicylate (column 4) at the relevant molarities were calculated using equation (11). The values for the frictional coefficient R_{10} could now be computed and are enumerated in column 5.

DISCUSSION

The calculations demonstrate how diffusion measurements allied to vapour pressure measurements may be used to evaluate thermodynamic parameters. The advantages of computing frictional coefficients in preference to other phenomenological coefficients are that they are independent of the measurement frames of reference. Thus the values of frictional coefficient may be compared directly with those measured on a diaphragm cell of the Stokes type.

With the advent of this type of thermoelectric osmometer sensitive to temperature changes of the order of 0.0001° , it is now possible to make direct measurements leading to a calculation of activity coefficients for a wide range of dilute solutions.

The technique of using the osmometer has been described in some detail, as considerable difficulty was experienced in obtaining reproducible results of satisfactory accuracy using water as a solvent.

In this series of experiments, it was found necessary to leave the osmometer for at least 12 h to equilibrate before attempting to take any readings.

Drop size and the timing sequence for each measurement are also critical. Furthermore, the readings for any one pair of solutions must be completed within 1 h since, the bridge fails to return to a balance point with solvent if left much longer than this.

However, by observing such precautions and by calculating the mean of several results for any one solution, the osmotic coefficient values are reproducible to within $\pm 0.5\%$ of a mean value.

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