Measurement of Vapor Pressures of Electrolyte Solutions by Vapor Pressure Osmometry

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A method for vapor pressure measurement of salt solutions, in either water or nonaqueous solvents, is described. It makes use of vapor pressure osmometry technique in order to find the concentration of a salt solution of known vapor pressure which is isopiestic to the problem salt solution, both in the same solvent. Data for a wide range of concentrations (to near-saturation levels) of sodium iodide and copper(II) chloride solutions in ethanol at 25 °C are presented.

Introduction

Vapor pressure data for salt water solutions are available for a large number of compounds (see Robinson and Stokes (*1*) for a review), due to the frequent use of water in many industrial processes and its paramount importance in the biological systems. However, such data for nonaqueous solvents are rather scarce and generally less accurate.

In the present paper, a method for the measurement of vapor pressure of salt solutions is described. It makes use of the vapor pressure osmometry technique to find the concentration of a salt solution of known vapor pressure which is isopiestic to that under scrutiny. Data for a wide range of concentrations of sodium iodide and copper(II) chloride solutions in ethanol at 25 °C are presented.

Experimental Section

Measurements were carried out using a Knauer vapor pressure osmometer (Hebert Knauer & Co GmbH), which contains a Wheatstone bridge with a null detector and a measuring cell. Two branches of the bridge are glass-covered thermistors with equal ohmic value and temperature coefficients, which act as temperature sensors; a rheostat is connected in series with one of them. The sensitivity is 0.00001 °C for measurements of temperature differences. The thermistors are located in the vapor space of the measuring cell which is sealed in by a stainless steel cover and a Teflon gasket. A proportional controller keeps the temperature of the measuring cell to within ±0.001 °C. On top of the measuring cell, another thermostated metal block holds six syringes and it ensures that the syringes are maintained at the same temperature as the measuring cell.

The working temperature was 25 ± 0.02 °C according to the reading given by a thermistor calibrated by a quartz meter (Hewlet Packard, Model 2804A).

All the chemicals used, $CaCl_2 \cdot 2H_2O$ (Merck), $CuCl_2 \cdot 2H_2O$ (Panreac), LiCl (Merck), NaCl (Hopkin & Williams), LiBr (Aldrich), and NaI (Panreac), were analytical reagent grade. Anhydrous salt were desiccated in the oven at 120 °C until constant weight was obtained. Anhydrous calcium chloride and copper(II) chloride were obtained by desiccating the hydrated compounds in the oven at low pressure.

Commercial azeotropic ethanol was subjected to rectification at 1 atm pressure in a packed column with an efficiency equivalent to 25 theoretical plates. The intermediate fraction which distilled at constant temperature was collected. Absolute ethanol was obtained by a method previously used in this laboratory (*2*), exposing the azeotropic distilled fraction to a single process of adsorption in vapor phase through a 3 Å molecular sieve. The now purified ethanol was shown by gas chromatography to be free of contaminants.

To conduct an experiment, the salt solution of unknown vapor pressure (problem solution) was prepared together with several other salt solutions of known vapor pressure (reference solutions) in the same solvent. Reference solutions are selected so that their vapor pressures are close (one higher and one lower) to that estimated for the unknown vapor pressure solution. The problem solution (25-30 mL) was placed in the measuring cell and two of the syringes were refilled with the same solution. The four remaining syringes were each refilled with different reference solutions. Once the system reached constant temperature (1-2 h), the apparatus was zeroed by depositing a drop of problem solution of similar medium size to both thermistors. Replicates of the operation should provide a deviation in ΔR values less than 0.3%.

The measurement is then performed as follows. A fresh drop of problem solution is placed in one of the thermistors and one drop of reference solution on the other. Due to the difference of vapor pressure between the problem solution and the reference solution a variation in the solvent content of the drop of reference solution is produced which subsequently causes a difference in the temperature of both thermistors. This difference of temperature between thermistors varies with time and after several minutes reaches a plateau; a measured ΔR is then obtained from the apparatus.

It is advisable to repeat each measurement several times in order to ensure that the thermistor has been thoroughly washed with the reference solution being used. Measurements should be made without interruption between them, starting with the lowest concentration reference solution. The measurement is not significantly influenced by the addition of the reference solutions drops to the cell content because the resulting negligible alteration in the vapor pressure would produce a similar effect on the solutions of both thermistors so that the actual reading value would remain constant.

By operating in this way, four mean ΔR values are obtained, one for each reference solution being used. Due to the small range of ΔR values being used, ΔR values plotted versus the molality of reference solutions should provide a straight line. The point where the line intercepts the abscissa axis (i.e., $\Delta R = 0$) is the concentration corresponding to the molality of the reference solution, which is isopiestic to the problem solution.

Hypothetically, the evaporation of solvent from the problem solution placed in the measuring cell could lead to gradients of concentration inside it and modify the vapor pressure and the ΔR measured with time. However, by expanding the lag time before any measurement was made from 1 to 5 h, no variation from the previous ΔR value was observed with time.

Results and Discussion

The validity of the method described above was checked by measuring the vapor pressure of a water-NaCl solution at 25

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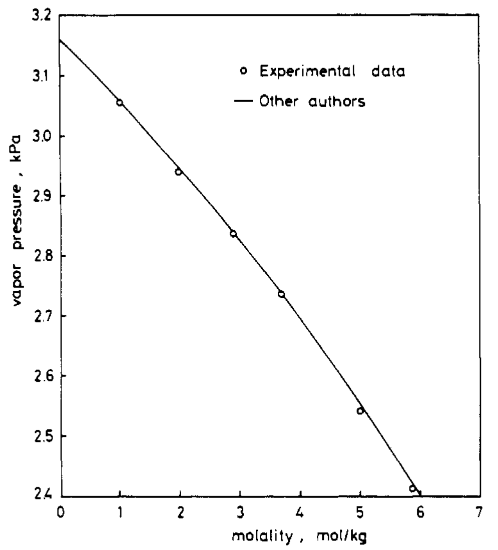

Figure 1. Vapor pressure for water-NaCl at 25 °C.

Table I. Vapor Pressures for Ethanol-Sodium Iodide at 25 °C

molality, mol/kg			vapor press., kPa	
NaI	LiCl	LiBr	ref LiCl	ref LiBr
0.51	0.53	0.53	7.59	7.59
0.59	1.01	1.01	7.26	7.26
1.47	1.43	1.44	6.88	6.87
1.89	1.79	1.77	6.55	6.53
2.48	2.27	2.25	5.93	5.95
2.61	2.34	2.33	5.83	5.83

°C, using several water-$CaCl_2$ solutions as a reference. Water-$CaCl_2$ solutions have been frequently used as reference solutions in the isopiestic method (*3*,*4*).

Figure 1 represents the variation of the water vapor pressure versus NaCl molality. The continuous line corresponds to the curve which best fits data reported by Pepela and Dunlop (*6*) and Gibbard et al. (*5*), while circles represent experimental data obtained in this paper. The low 0.005 kPa mean deviation and 0.009 kPa maximum deviation between both data sets indicates the close agreement between data reported here and that of the cited authors.

With the method shown to be trustworthy with aqueous systems, it was then used with nonaqueous solutions. The vapor pressures of ethanol-NaI and ethanol-$CuCl_2$ solutions were determined. They were measured against two different reference solutions, ethanol-LiBr and ethanol-LiCl, for which the only data available have been reported by Vlasov (*7*). Vlasov's data reliability is summarized by the following experimental conditions: static method, the difference between the levels in the mercury manometer being measured with a cathetometer to within 0.005 mm, ethanol-water content less than 0.03 wt %, temperature control to within 0.005 °C, and the vapor pressure determined from Student's distribution with a level of reliability of 0.98 and 17 degrees of freedom.

Table II. Vapor Pressures for Ethanol-Copper(II) Chloride at 25 °C

molality, mol/kg			vapor press., kPa	
Cu_2Cl	LiCl	LiBr	ref LiCl	ref LiBr
0.51	0.29	0.29	7.72	7.72
1.01	0.59	0.56	7.57	7.59
1.52	0.91	0.90	7.34	7.34
2.05	1.16	1.16	7.13	7.13
2.49	1.40	1.40	6.92	6.92
2.84	1.55	1.52	6.78	6.80

Table I shows the molality of ethanol-NaI solutions which are isopiestic to the ethanol-LiCl and ethanol-LiBr solutions chosen as reference solutions. Data of ethanol-NaI vapor pressure given in the table were obtained by interpolation from data of ethanol-LiCl and ethanol-LiBr vapor pressure reported by Vlasov (*7*).

Table II gives the equivalent results for ethanol-$CuCl_2$ solutions.

The intrinsic error of the method when used for nonaqueous systems should be similar to that observed for aqueous systems, although it is heavily dependent upon the accuracy of the vapor pressure of the chosen reference solution.

Registry No. NaI, 7681-82-5; $CuCl_2$, 7447-39-4; ethanol, 64-17-5.

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