Osmotic Properties of Some Aqueous Solutions at 45° C.

K. LAMAR HELLAMS, C. STUART PATTERSON, BRYANT H. PRENTICE, III, and MARY JANE TAYLOR
Department of Chemistry, Furman University, Greenville, S. C.

Isopiestic ratios to NaCl are reported for KBr, LiCl, KCl, CsCl, $BaCl_2$, and Na_2SO_4 in H_2O at 45° C. The ratios for KBr check quite closely those predicted by extrapolation of Smith's boiling point data. Ratios for the other salts show consistency with existing data. The apparatus used is found satisfactory at 45° C. but changes are necessary before extension to higher temperatures.

EXTENSIVE DATA on osmotic and activity coefficients of aqueous electrolytes are available at 25° C. from a variety of experimental methods (*6*). For years the only measurements at substantially higher temperatures were those by Smith, Johnson, and Hirtle (*3, 8, 9*) who studied NaCl and KBr in the range from 60° to 100° C. by the boiling point elevation method. Recently, extensive measurements have been made on a variety of electrolytes at high temperatures (*4, 10, 11*) by a modification of the isopiestic technique used widely at lower temperatures (*7*). Work is also underway on extension of the reference data by an absolute method (*1*). So far the work of these investigators has been confined to the important region above 100° C. so that there still exists a dearth of data in the temperature range between 25° C. and the lowest temperature studied by Smith. This gap is made the more serious since the extrapolation of Smith's high temperature data does not give satisfactory consistency with measurements at lower temperatures (*2*).

As a first step in a study of this intermediate temperature range, a series of isopiestic experiments at 45° C. was conducted, designed to test the feasibility of removing equilibrated solutions at this temperature, protected only by a common glass cover plate, followed by rapid cooling and replacement of this cover with individual lids. The principal objective has been to explore this possible adaptation of the usual method with minimum elaboration of apparatus and techniques.

Special attention has been given to the isopiestic ratio of KBr to NaCl because these are the two salts studied in separate determinations by Smith. Neither set of data fits too well with measurements at lower temperatures, and a part of the present work was designed to test the consistency of the two sets of high temperature values. Isopiestic ratios to NaCl are also reported for LiCl, KCl, CsCl, $BaCl_2$, and Na_2SO_4 at 45° C. for the concentration range 0.6 to 3.0 molal (reference salt concentrations) and are compared with the recent isopiestic measurements on these salts at higher temperatures.

EXPERIMENTAL

Materials. Reagent grade chemicals were dried and used without further purification. Analysis showed that purity of each material was better than the experimental uncertainty of the measurements on the salt. Lithium and cesium chlorides were weighed from weight burets as (volumetrically standardized) stock solutions, whereas the other salts were weighed directly into the equilibration cups as solid reagents.

Apparatus and Procedure. Equilibrations were carried out in shallow 1-inch diameter silver dishes held in contact with a heavy gold-plated copper block contained in a 250-mm. glass vacuum desiccator. The desiccator, immersed in a 45° C. water bath, sat on a turntable tilted at 10° from the horizontal and rotated at 18 r.p.m. to provide stirring of the solutions. A heavy disk of safety plate glass was suspended above the cups from a hook connected through a stainless steel bellows in the desiccator's top to a handle outside. The bellows allowed sufficient vertical and angular movement to permit lowering of the glass plate onto the cups when the run was completed, usually after about three days. The cups were then removed as quickly as possible from the desiccator and set on a cold brass plate. After a 3- to 4-minute period, the solutions had cooled very nearly to room temperature while the cover plate was still noticeably warm, thus preventing condensation under the plate. At this point the large plate was removed and individual preweighed glass covers were quickly placed on the cups before determination of the equilibrium weights.

RESULTS

Nineteen runs were made in which solutions of three to six different salts were simultaneously equilibrated with NaCl solutions. From two to five samples of each salt were used. An average of four NaCl samples was used per run. Of the 79 sets of replicates, 61 showed a precision of better than 0.5% average deviation from the mean; 14 fell between 0.5 and 1.0% and 4 exceeded 1%. Three of the latter were Na_2SO_4 and the other was $BaCl_2$. Significantly, the larger deviations (>0.5%) reflect uncertainty in isolated samples and not general failure of a run. This statement is supported by the fact that the weighted average of the deviations for all samples in any given run falls below 0.5% with one exception. Such a random occurrence of the larger deviations, which resulted from the tedious technique employed, probably represents failure to detect some elusive errors (spillage, spattering, leaks, etc.). These errors were usually quite obvious and resulted in a significant sample casualty rate. In the few cases when only two samples survived, percentage difference between the two values is reported. Results are given in Table I as smoothed isopiestic ratios (to NaCl) at round molalities of each salt read from a large scale plot of R *vs.* m.

Activity coefficients may be calculated from the data by graphical integration methods but very reliable results are contingent upon extension of these or complementary experiments to lower concentrations. Furthermore, osmotic coefficients, or even the isopiestic ratios themselves, serve just as well to reveal the effects of the various salts on the temperature dependence of the solvent's properties, which it is our primary aim to study.

A comparison of our results with data collected earlier by Soldano and Patterson (*9*) shows general agreement with

Table I. Isopiestic Ratios (to NaCl) at Round Molalities at 45° C.

m	LiCl R	KCl R	CsCl R	KBr R	Na_2SO_4 R	$BaCl_2$ R
0.5	...	0.970[a]	...	...	...	0.901
0.6	...	0.968	...	...	...	0.915
0.7	1.050[a]	0.965	...	...	0.728	0.926
0.8	1.055	0.962	...	...	0.717	0.935
0.9	1.061	0.960	...	...	0.708	0.946
1.0	1.065	0.957	0.928[a]	0.974[a]	0.700	0.957
1.1	1.070	0.955	0.925	0.972	0.693	0.967
1.2	1.075	0.953	0.922	0.970	0.688	0.977
1.3	1.080	0.951	0.919	0.968	0.682	0.986
1.4	1.085	0.948	0.916	0.966	0.676	0.993
1.5	1.090	0.946	0.913	0.964	0.672	0.997
1.6	...	...	...	...	...	1.000
2.0	1.108	0.934	0.900	0.954	0.653	...
2.5	1.128[a]	0.923	0.886	0.944	0.644	...
3.0	...	0.912	0.872	0.933	0.646	...
3.5	...	0.901	0.859	0.922	0.656	...

[a] Values obtained by a short extrapolation beyond the experimental range.

Table II. Consistency of Smith's NaCl and KBr Data

Comparison via Authors' Experimental R Values

(1) m_{KBr}	(2) R This Work	(3) m_{NaCl}	(4) ϕ_{NaCl} (Smith, Extrap.)	(5) ϕ_{KBr} (Calcd. from R and Col. 4)	(6) ϕ_{KBr} (Smith, Extrap.)	(7) $\Delta\phi$
1.0	0.974[a]	0.974	0.947	0.913	0.921	−0.008
1.5	0.964	1.446	0.963	0.928	0.932	−0.004
2.0	0.954	1.908	0.990	0.944	0.945	−0.001
2.5	0.944	2.380	1.021	0.964	0.963	+0.001
3.0	0.933	2.799	1.050	0.980	0.979	+0.001
3.5	0.922	3.227	1.081	0.997	0.997	0.000

[a] Obtained by a short extrapolation of R *vs.* m_{KBr}.

the interpolation to 45° implicit in their plot of R *vs.* T. The present measurements on LiCl are more consistent with the questionable 100° point than with those at the higher temperatures. Unfortunately, considerable difficulty was encountered with LiCl so that this is also one of the most uncertain points. The point for $BaCl_2$ shows a similar discrepancy. All the others seem to be consistent with existing data since the sparsity of current results and the large gap between 45° and 100° make a firm decision on the true course of the temperature dependence premature. The KCl ratios agree within 0.3% with those reported by Robinson (5).

Visible corrosion of the silver cups resulted with the KBr solutions, and although the errors seem to be within the experimental uncertainty (as determined by the weight loss of the cups) this point needs further study before extension to higher temperatures.

Consistency of the KBr data was tested by comparing with values obtained by extrapolation of Smith's ϕ's for NaCl and for KBr from the higher temperatures to 45° C. The extrapolated ϕ's for several molalities were read and plotted *vs.* m for each salt so that the ϕ at any m could be read. The consistency of the data was then determined as follows: From the experimental isopiestic ratios, R, the molalities of NaCl isopiestic with round molalities of KBr were calculated from the relationship,

$$m_{NaCl} = R \cdot m_{KBr} \qquad (1)$$

These values are listed in column 3 of Table II. Next the Smith ϕ's were read for these NaCl concentrations (column 4). The osmotic coefficients of KBr were then calculated from the relationship,

$$\phi_{KBr} = R \cdot \phi_{NaCl} \qquad (2)$$

Both Equations 1 and 2 follow directly from the definition of the isopiestic ratio and the thermodynamic condition for isopiestic equilibrium.

Osmotic coefficients for KBr calculated in this way are given in column 5 of Table II. Column 6 gives the corresponding values obtained by extrapolation of Smith's KBr data. The former, then, depend upon Smith's NaCl data and the authors' experimental R's, whereas the latter depend solely upon Smith's KBr data. This procedure is entirely equivalent to a determination of R as a function of m from Smith's data on the two salts for comparison with the R's in Table I.

In the last column, the differences between the two sets of ϕ_{KBr} values are tabulated. Above 1.5 molal, the consistency between the two is remarkable. As indicated in Table I, it is just in the lower concentration range that the current data are weak so that the increased deviations there do not necessarily indicate an inconsistency in the extrapolated values. It is emphasized that even perfect agreement would still be only a test of the internal consistency of Smith's data since our method is a relative one. Any error characteristic of the boiling point method or auxiliary data, and consequently common to the data for both salts, might escape detection by isopiestic comparison. Furthermore, although the method used in the extrapolations was unbiased, it was nonetheless arbitrary. In particular it is virtually impossible, as indicated elsewhere (2), to extend the high temperature curve smoothly to include the 25° point. Consequently, extrapolations were made in each case giving practically no weight to that point.

These results, therefore, seem to indicate a high degree of consistency in the 60° to 100° C. data on NaCl and KBr, but they do not mitigate any of the discrepancy with the 25° point. Rather, the present work serves to accentuate the need for vapor pressure experiments of an absolute nature in the intermediate temperature range as the only way to resolve this problem. Such a program would provide reference standard data which would open up the field of isopiestic studies on a wide range of solutes and should, as a consequence, allow significant gains in our understanding of the interesting behavior of osmotic properties in this very important range. It is the absence of such reference standard data which prompts us to report in Table I only the isopiestic ratios and not values of properties such as f's or γ's derived on the basis of assumed reference standard data.

CONCLUSIONS

The results reported here indicate that the apparatus and techniques described are satisfactory for temperatures up to 45° C. Precision of the 45° C. data was acceptable and the data are consistent with published results within demonstrable experimental and extrapolation error. The present results have proved reproducible by each of four experimenters, three of whom were then undergraduate students, working independently.

In spite of the measure of success attained, it is doubtful that the present simple method can be usefully extended to temperatures much above 45° C. without modification of apparatus and/or procedure to counteract the attendant complications. Consequently, modifications before attempting measurements above 45° C. are planned.

ACKNOWLEDGMENT

We are grateful to G.E. Boyd and H.F. McDuffie for the loan of isopiestic equipment from the Reactor Chemistry Division of the Oak Ridge National Laboratory. Financial assistance from the Undergraduate Research Participation Program of the National Science Foundation is acknowledged. We thank B.A. Soldano for valuable help.

LITERATURE CITED

(1) Gardner, E.R., Jones, P.J., Nordwall, H.J. de, *Trans. Faraday Soc.* **59**, 1994 (1963).
(2) Harned, H.S., Owen, B.B., "The Physical Chemistry of Electrolytic Solutions," p. 363, Reinhold, New York, 1943.
(3) Johnson, G.C., Smith, R.P., *J. Am. Chem. Soc.* **63**, 1351 (1941).
(4) Patterson, C.S., Gilpatrick, L.O., Soldano, B.A., *J. Chem. Soc.* **1960**, p. 2730.
(5) Robinson, R.A., *Trans. Faraday Soc.* **35**, 1222 (1939).
(6) Robinson, R.A., Stokes, R.H., "Electrolyte Solutions," 2nd ed., Butterworths Scientific Publ., London, 1959.
(7) *Ibid.*, p. 117.
(8) Smith, R.P., *J. Am. Chem. Soc.* **61**, 500 (1939).
(9) Smith, R.P., Hirtle, D.S., *Ibid.*, **61**, 1123 (1939).
(10) Soldano, B.A., Patterson, C.S., *J. Chem. Soc.* **1962**, p. 937.
(11) Soldano, B.A., Meek, M., *Ibid.*, **1963**, p. 4424.

RECEIVED for review July 13, 1964. Accepted July 28, 1965.

Osmotic and Activity Coefficients of Some Nonelectrolytes

O. D. BONNER and WILLIAM H. BREAZEALE
Department of Chemistry, University of South Carolina, Columbia, S. C.

Osmotic and activity coefficients are reported for solutions of dextrose, *sym*-dimethylurea, and *meso*-erythrytol at 25° and 37° C. Osmotic coefficients are also reported at 60° C. for concentrated solutions of these compounds. The solvation of certain alcohols and sugars is indicated to be directly related to the number of polar groups per molecule.

OSMOTIC and activity coefficients have been previously reported for certain nonelectrolytes at 25° C.—e.g., sucrose (*6*), sorbitol (*2*), and urea (*3*). These data are of interest as these coefficients in aqueous solutions for sucrose and sorbitol are greater than unity while they are less than unity for urea. The original intention of the authors was to investigate solutions for sucrose and urea at temperatures above 25° C. so as to furnish additional information on the relative importance of solute-solute and solute-solvent interactions for these substances. However, considerable hydrolysis occurred when solutions of either of these nonelectrolytes were maintained at temperatures of 35° C. or higher, and this necessitated a search for compounds of the same types whose aqueous solutions were stable at temperatures above 60° C. Data are reported for these compounds.

EXPERIMENTAL

All determinations of osmotic and activity coefficients in concentrated solutions have been made by the isopiestic method. Platinum-clad silver dishes were used for the measurements at 25° C. The experimental procedures which were used at the other temperatures have been described earlier (*1*). Sodium chloride was used as the reference electrolyte for these isopiestic comparisons. The Mecrolab Model 301A Vapor Pressure Osmometer was used to supplement the isopiestic data in dilute solutions. Nonelectrolyte osmotic coefficients were calculated by comparison of dekastat readings for these solutions with those of sodium chloride solutions of similar water activity. The isopiestic data at 25°, 37°, and 60° C. may be reproduced with precisions of 0.1, 0.2, and 0.3%, respectively. The precision of the vapor pressure osmometer measurements at 25° and 37° C. is approximately the same as for the isopiestic comparisons. No measurements using the vapor pressure osmometer were attempted at 60° C.

DISCUSSION

Osmotic and activity coefficients of sodium chloride solutions at 25° C. are known with great accuracy (*5*). There appears to be a considerable discrepancy, however, among values obtained by various experimental methods at other temperatures. Values of ϕ at 40° and 60° C. calculated from electromotive force and boiling point measurements (with reasonable extrapolations) appear to differ by as much as 0.01 unit. The values of γ have an even greater uncertainty. Smoothed values of ϕ and γ at 37° C., corresponding to those presented by Harned and Owen (*5*), and at 60° C. corresponding to those in Robinson and Stokes (*6*) have been used in the calculation of the nonelectrolyte osmotic and activity coefficients (Table I). However, the uncertainty

Table I. Osmotic Coefficient Corrections for NaCl Solutions

m	$\phi_{37°} - \phi_{25°}$	$\phi_{60°} - \phi_{25°}$
0.5	0.001	...
1.0	0.005	...
1.5	0.007	0.014
2.0	0.007	0.016
2.5	0.008	0.018
3.0	0.006	0.016
3.5	0.006	0.012
4.0	0.006	0.010
4.5	0.005	0.010
5.0	0.005	0.010

Data have been smoothed and extrapolated. Data at 37° from Harned and Owen (*5*, p. 492). Data at 60° from Robinson and Stokes (*6*, p. 480).

Table II. Isopiestic Solutions at 25° C.

m(NaCl)	m(Dextrose)	m(NaCl)	m(Erythrytol)	m(NaCl)	m(Dimethylurea)
2.105	3.809	0.9145	1.678	1.252	2.875
2.293	4.146	1.006	1.847	1.642	3.977
3.162	5.838	1.144	2.103	1.920	4.770
3.216	5.922	1.415	2.617	2.309	5.945
3.732	6.995	1.642	3.058	2.853	7.620
4.139	7.868	2.309	4.390	2.871	7.704
4.707	9.130	2.779	5.378	4.023	11.764
5.641	11.542	2.853	5.549	...	...
...	...	2.861	5.555	...	...