545. *The Osmotic Behaviour of Representative Aqueous Salt Solutions at* 100°.*

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Experimental osmotic coefficients for representative aqueous salt solutions at 99·6° are presented as a function of concentration. The results are shown to be consistent with established concepts of electrolyte solutions.

The recent emergence of aqueous-solution homogeneous-type reactors has focused attention on the limited amount of information available on the thermodynamic behaviour of aqueous electrolytic solutions at elevated temperatures. In the light of this need, a high-temperature isopiestic unit has been built in order to extend to higher temperatures this highly successful vapour-pressure technique pioneered by Stokes and Robinson.[1]

Details of construction and design of the present unit have been recorded.[2] In essence the apparatus consists of a magnetic balance operating in a water-vapour chamber. This arrangement permits weighing, *in situ*, of the equilibrium solutions contained in 20 titanium dishes, each of approximately 10 g. total weight. All transfers to and from the balance can be made without disturbing the internal system.

This investigation is primarily concerned with an examination of the osmotic behaviour of a variety of salt solutions over a limited concentration range above 1 m at 99·65°. The systems studied were selected so that the representative behaviour of typical 1-1, 1-2, 2-1, and 2-2 electrolytes at elevated temperatures and 25° might be compared. In the present work special emphasis is placed on the performance of the physical equipment and its reliability. A discussion of typical experimental conditions which would be encountered in any application of the isopiestic technique to elevated temperatures is also presented.

Experimental

Ten runs were made in which duplicate solutions of 7 salts were allowed to equilibrate with duplicate sodium chloride solutions and with a 100 ml. reservoir of sodium chloride solution at 99·65° ± 0·04°.

The systems studied were lithium, potassium, cæsium, and barium chlorides and sodium, magnesium, and uranyl sulphates. Where practicable, the solutes were weighed directly into titanium equilibration dishes. Owing to their hygroscopic nature, lithium chloride and uranyl sulphate were sampled by pipetting from stock ~1m- and ~2·5m-solutions, respectively. Sample sizes were selected to give at least 1 g. of water at equilibrium and yet maintain the total balance load within acceptable limits. This allowed the range from about 1m to 4·2m (reference-salt concentrations) to be covered by a series of equilibrations using the same salt samples.

Solution concentrations were changed by opening the unit and replacing the reservoir solution with a more concentrated one or by simply adding an estimated volume of water. This allowed the unit to be closed again after a minimum exposure and consequent loss of water which would result in salt deposition on the sides of the cups and would thus promote creeping. This problem is, of course, more severe here than in the usual room-temperature procedure. To offset this tendency for excessive loss of water from the cups during the initial phases of an equilibration, it was found desirable to place small dishes of pure water in the potassium chloride reservoir so that, during the initial period, water would tend to distil back into the sample

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* This paper is based upon work performed at Oak Ridge National Laboratory, which is operated for the Atomic Energy Commission by Union Carbide Corporation. A portion of this work was performed while the senior author was a member of the Chemistry Division of the Oak Ridge National Laboratory. Dr. R. E. Stoughton, who was in general charge of the effort during that interval, presented some of the data in preliminary form at a meeting of the American Chemical Society, Cleveland, Ohio, September, 1958.

[1] Stokes and Robinson, *Trans. Faraday Soc.*, 1941, **37**, 419.

[2] B. A. Soldano, R. W. Fox, R. Stoughton, and G. Scatchard, "The Structure of Electrolytic Solutions," John Wiley and Sons, Inc., New York, 1958, pp. 224—235.

dishes to replace the losses. This step was found to be profitable regardless of the net direction in which the water was expected to move in progressing toward eventual equilibrium. In particular, it was found superior to adding estimated portions to the individual dishes when moving to a more dilute point since the latter procedure prolongs the exposure time and causes water losses which may exceed the amount added and furthermore are variable from one solution to another. As an added check on the technique, the concentrations were initially selected in a few cases so that about half the cups approached equilibrium from the lower side and half from the upper side with respect to concentration. This should expose any inconsistencies caused by differences in rate of evaporation or condensation among the various solutions or by failure to allow enough time to overcome these differences.

Although the instrumentation and procedure for determining the equilibrium weights were as described elsewhere,[2] it proved necessary to adopt slightly more involved techniques in order to minimize errors caused by drifts in the electronic null detection system. Preliminary tests indicated that weighings on a given standard weight (dish) could be reproduced within acceptable limits for several hours at a time but that occasionally a rapid drift in reading set in and extended well beyond the desired limits of precision. It is believed that this arose, in part, because the present electronic null detection system has been pushed to the limit of its sensitivity. Further, the mechanical null properties cannot be reasonably expected to adjust to thermal changes in a manner identical with that of the electrical system. Because of the uncertainties introduced by this unpredictable behaviour, extensive tests were conducted to determine what procedures would give the most reliable results. Several points in this connection are pertinent:

(1) Since the characteristics of the system drifted sufficiently from day to day, best results were obtained if the current readings were compared directly with those for standard weights determined during the same time interval, rather than with a long-term average of the standard results (our previous policy).

(2) Sufficient curvature in the current–weight relation was found (four standards varying from 7 to 13·5 g. were used) for unknown weights to be evaluated most accurately only if linearity were assumed over short intervals (about 1 g.) between standards. A given unknown weight was always evaluated (by using the analytical equation for a straight line in the two-point form) from a standard just above it and one just below it.

(3) Repeated weighings of a single standard showed that the occasional rapid drifts were completely unpredictable as to time of occurrence and magnitude of the change but generally were separated by periods of several hours during which reproducible readings could be made. It therefore became necessary to make a given weighing on the same plateau as its corresponding standard readings. This was best done by repeated weighings of the standards during the course of the various determinations. The sequence of unknowns was then usually begun again and each reweighed in the same order until the results for the several consecutive cups reproduced the previous readings satisfactorily. Any abrupt change in the balance response could easily be detected in this manner.

Discussion

The performance of the system can be evaluated by referring to Table 1, wherein the average values for measured pairs of isopiestic ratios are listed for each salt relative to sodium chloride. The isopiestic ratio, R, is defined as:

$$R = \phi/\phi_{\text{std}} = (\nu\text{m})_{\text{std}}/(\nu\text{m})$$

where ν is the idealized number of ions formed per mole of salt in the assumed standard state (*i.e.*, $\nu = 3$ for Na_2SO_4), m is the molality of the solute, and ϕ is the molal osmotic coefficient.[3] The last line of Table 1 records the mean standard deviation between pairs of measurements for each salt and demonstrates that the precision of the data is closely allied to the magnitude of the change in molality over the concentration range. For example, magnesium sulphate exhibits the best precision ($\sigma = 0{\cdot}0011$) and the smallest change in molality (97%). Uranium sulphate shows the next best precision ($\sigma = 0{\cdot}0022$) and the next smallest change in molality (142%) over the range of concentration measured.

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[3] Robinson and Stokes, "Electrolyte Solutions," Butterworths Scientific Publications, London, 1955, p. 28.

This linear correlation relating precision and percent molality change holds reasonably well for all cases except cæsium chloride and leads to the conclusion that the rate of attainment of equilibration must have affected the over-all precision, especially in those cases where large amounts of water had to be transported. It is to be expected, therefore, that longer equilibration periods and better temperature-control will contribute to an improvement in precision. Finally, standard deviations calculated for each experiment (*i.e.*, mean σ for the several salts at one equilibration) demonstrate that the over-all precision is reduced as smaller absolute amounts of water are determined at the higher molalities. This latter result is to be expected whenever progressively smaller quantities are weighed with a balance having a fixed minimum source of error.

TABLE 1. *Experimental isopiestic ratios measured at* 99·6°.[a]

Expt. No.	Average molality NaCl	Average isopiestic ratios relative to NaCl						
		LiCl	KCl	CsCl	Na_2SO_4	$BaCl_2$	$MgSO_4$	UO_2SO_4
1	0·958	1·008	0·965	0·941	0·717	0·895	0·504	0·460
2	1·096	1·012	0·961	0·930	0·697	0·897	0·521	0·465
3[b]	1·272	1·013	0·952	0·920	—	0·904	0·541	0·496
4[b]	1·850	1·035	0·938	0·905	—	0·930	0·624	0·549
5	1·955	1·040	0·938	0·904	0·635	0·933	0·636	0·553
6	2·360	1·049	0·928	0·897	0·626	0·942	0·693	0·587
7[b]	2·726	1·065	0·922	0·886	—	0·950	0·734	0·607
8	2·889	1·068	0·916	0·876	0·606	0·949	0·753	0·620
9	3·176	1·073	0·918	0·877	—	0·963	0·785	0·630
10	4·230	1·100	0·892	0·859	—	—	0·890	—
σ[c]		0·0032	0·0047	0·0080	0·0032	0·0039	0·0010	0·0022

[a] Data included in this Table represent values which had remained constant within experimental error for sets of weighings taken on at least two successive days after an initial equilibration period. Data for Na_2SO_4 are missing in Expts. 3, 4, and 7 because Na_2SO_4 was substituted for K_2SO_4, the original solute, which became saturated at an early stage. The values for the highest molalities of Na_2SO_4 and $BaCl_2$ are missing also because of saturation. [c] Standard deviation calculated for $\sigma = \sqrt{[\Sigma(\Delta x)^2/2n]}$, where Δx = difference between pairs and n = total experiments per salt.

RESULTS

In the preceding section we considered in some detail the experimental precision obtained in applying the present isopiestic techniques to the elevated temperature range. Since the data collected (Table 2) constitute, in some degree, a representative cross-section of salt-type behaviour at 99·6°, one should briefly examine the comparative osmotic behaviour of these salts relative to that at 25°. Furthermore, it might prove profitable to determine what consistency these comparisons reveal between our results and those predicted by modern theories.

TABLE 2. *Osmotic coefficients for round molalities at* 99·6°.*

m	LiCl	NaCl[a]	KCl	CsCl	Na_2SO_4	$MgSO_4$	$BaCl_2$	UO_2SO_4
0·8	(0·967)	0·926					0·846	
0·9	(0·974)	0·930			0·667		0·858	
1·0	0·982	0·935	0·901	(0·880)	0·658		0·869	
1·2	0·999	0·945	0·902	0·872	0·648		0·893	
1·4	1·018	0·955	0·903	0·872	0·642		0·917	
1·6	1·039	0·965	0·907	0·875	0·638		0·942	
1·8	1·061	0·976	0·912	0·879	0·635	(0·463)	0·966	
2·0	1·084	0·986	0·918	0·884	0·633	0·477	0·991	(0·424)
2·5	1·141	1·016	0·935	0·898	0·631	0·534	1·053	0·463
3·0	1·194	1·048	0·953	0·912	0·630	0·616		0·505
3·5	1·243	1·077	0·969	0·926	(0·629)	0·712		0·548
4·0	(1·285)	1·105	0·983	0·941		0·822		0·591
4·5		(1·133)	0·995	0·956		0·936		0·630
5·0				0·972		(1·052)		0·666

* Values in parentheses were determined by a short extrapolation.

[a] Standard values with interpolations taken from ref. 4.

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[4] Smith, *J. Amer. Chem. Soc.*, 1939, **61**, 500; Smith and Hirtle, *ibid.*, 1939, **61**, 1123.

To facilitate such comparisons the data were smoothed by reading values at rounded concentrations from large-scale graphs of the isopiestic ratios *versus* molality. From these relative ratios osmotic coefficients at rounded concentrations were calculated by using Smith's b. p. data [4] for sodium chloride solutions at 99·6° as the reference standard. The resultant osmotic coefficients (Table 2) were then compared with those of the same molality at 25° (tabulated by Stokes and Robinson [3]). The results of these comparisons are shown in Figs. 1 and 2.

It is apparent that the alkali halides (Fig. 1) show only second- and third-place variations in their osmotic coefficients when compared with their equivalents at 25°. This does not imply that there is no significant change in these values with temperature, since the osmotic coefficient of the sodium chloride reference electrolyte (the only complete data [4] covering the range from 25° to 100°) shows a distinct maximum, when compared at a fixed concentration, in the general vicinity of 60°. What is implied, however, is that for this particular family of 1-1 electrolytes a standard of precision at elevated temperatures must be maintained which is comparable with that which is typical at 25°, if meaningful temperature-dependence information is to be obtained. One notes (Fig. 1) that the present development does reveal consistent third-place differences in the comparative osmotic coefficients of the alkali halides. It should be emphasized also that, for the most part, the data of this research at 100° maintain these small differences with very few experimental cross-overs when compared against the excellent data obtained by Stokes and Robinson [3] at 25°. No particular importance, however, can be attached to the

FIG. 1. *Comparative osmotic behaviour of univalent electrolytes at* 99·6° *and* 25·0°.

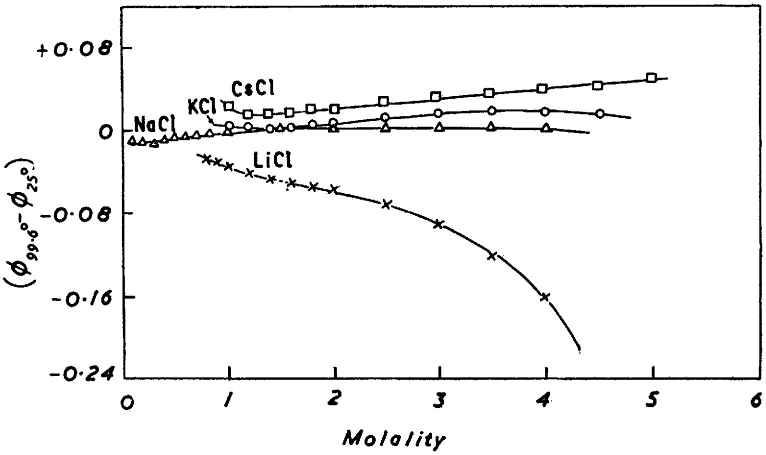
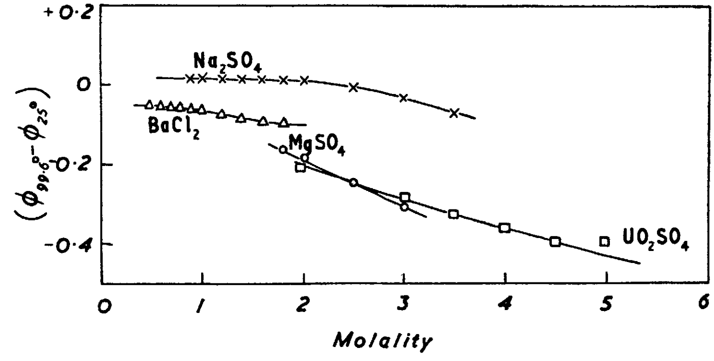


FIG. 2. *Comparative osmotic behaviour of multivalent electrolytes at* 99·6° *and* 25·0°.



curvature suggested by the potassium chloride results since these are subject to any change in the reference data. But the standard of performance justifies a certain confidence in the precision obtained by the present high-temperature apparatus.

In attempting to evaluate the accuracy of these 100° data, any evidence must remain inferential in light of the almost complete absence of high-temperature experimental data. One can, however, arrive at some assessment of the accuracy of the data, as contrasted with precision, by closely examining the magnitude of the $(\phi_{99\cdot6^\circ} - \phi_{25^\circ})$ values for the alkali halides. As expected, the special rôle that is characteristic of the Li^+ ion (and probably the H_3O^+ ion) in aqueous solutions is again confirmed by the negative sign of its comparative osmotic coefficient differences. At any fixed temperature the Li^+ ion invariably occupies a unique position whether one is considering the effective pressures of salt solutions, osmotic coefficients, or entropies, etc. This behaviour has often been attributed to the unique ability of the H_3O^+ and Li^+ ions, owing to their small size, actually to enter into the tetrahedral structure of water and *reinforce* its ice-like nature.

As the temperature is raised these two ions should become less effective as " ice-makers." Such a mechanism would account for the first-order *negative* differences in $(\phi_{99\cdot6^\circ} - \phi_{25^\circ})$ found for the lithium ion. Since the Li^+ and the H_3O^+ ion behave similarly, it appears that generalizations pertaining to the temperature-dependence of both the osmotic and activity coefficients of 1-1 electrolytes in water, based upon the unique H^+ ion as a reference, should be tempered.

On the other hand, the general position of the 1-1 electrolytes, when treated within the ice-making and -breaking concept of salts [5] in water, does provide some inferential evidence as to the accuracy of our 100° data. On the basis of many diverse " high-energy " approaches, such as the internal-pressure concept of Gibson and Loeffler [6] and the entropy studies of Latimer *et al.*,[7] the usual order of effectiveness as " ice-breakers " is $CsCl > KCl > NaCl > LiCl$. (These general approaches can be considered high-energy studies since they involve the concentration-dependence of ions wherein each charge can be considered a highly localized source of electrical energy. We are able to arrive at the identical salt order and sign, and thus similar conclusions, by comparing our osmotic coefficients at 100° with those found for the alkali halides at 25°. Differences of only a few units % in the experimental values are significant in these experiments. The consistency of order reflected in Fig. 1 suggests that the *accuracy* of the 99·6° data may be comparable with their *precision.*

As for the multivalent salts (Fig. 2), the temperature effect is quite pronounced, since a considerable drop in osmotic coefficients occurs with rising temperature. Because these salts have higher charges, the reduction in the dielectric constant of the solvent due to elevation of temperature should result in marked changes in their ability to affect the water. No attempt, however, will be made to treat our multivalent data within the ion-pair-formation concept.

Conclusions.—In view of the performance of the unit in its present stage of development, it seems reasonable to expect that a few minor modifications in technique and instrumentation should result in a consistent standard of performance equal to the best results cited in this paper.

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[5] Gurney, " Ionic Processes in Solution," McGraw-Hill Co., Inc., New York, 1953.
[6] Gibson and Loeffler, *Ann. N.Y. Acad. Sci.*, 1949, **51**, 727.
[7] Latimer, Pitzer, and Smith, *J. Amer. Chem. Soc.*, 1938, **60**, 1829.