175. *Osmotic Behaviour of Aqueous Salt Solutions at Elevated Temperatures. Part II.*[1]

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Experimental osmotic coefficients for representative aqueous salt solutions at 121° are presented as a function of concentration. Results are also recorded for a single concentration at 142°. At fixed concentration, the pronounced variations in the osmotic coefficient ratios (normalized to sodium chloride) of the multivalent salt types follow a linear temperature dependency from 25° to 142°. The 1-1 salts, with the exception of lithium chloride, show variations of only a few per cent in the osmotic ratios over the same temperature range.

As a continuation[1,2] of a general investigation of the osmotic behaviour of aqueous electrolytes at elevated temperatures, representative salt solutions have been studied over the temperature range 100° to ~150° by the isopiestic technique.

Design details of the unit and its modification for the present work are recorded elsewhere.[1,3] In brief, a magnetic balance is operated in a vapour chamber 20 in. in diameter. This arrangement permits the weighing, *in situ*, of aqueous solutions contained in 16 titanium dishes. The total weight of each dish plus solution is ~11 g. The design allows all transfers of dishes, variations in vapour pressure, etc., to be performed without exposing the internal system to outside conditions. In principle, therefore, the accuracy in determining the osmotic coefficients is essentially controlled by one's ability to weigh at elevated pressures, temperatures, and variable humidities.

The experimental part of this investigation was concerned with the osmotic behaviour of a variety of aqueous salt solutions over a concentration range from ~0·5 molal to approximately the limit of solubility. Data for one concentration at 142° are also given. In addition, comparisons with previous work at 25° and 100° are made and the temperature dependence of osmotic ratios (to sodium chloride) for the various salt types in the temperature range from 25° to ~150° is considered.

EXPERIMENTAL

Fifteen runs were made at 121·1°. Duplicate solutions of seven salts were simultaneously equilibrated with a pair of sodium chloride solutions contained in titanium dishes and with a 200 ml. reservoir of sodium chloride solution.

As before,[1] the systems studied were lithium, potassium, cæsium, and barium chloride, and sodium, magnesium, and uranyl sulphate. All salts were weighed directly into the titanium dishes. The hygroscopic nature of lithium chloride and uranyl sulphate necessitated the use of weighing burettes and independent analysis of the respective stock solutions. In all other cases dry salts were weighed. Sample sizes were selected to ensure the presence of at least 1 g. of water at equilibrium in each solution.

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[1] Part I, Patterson, Gilpatrick, and Soldano, *J.*, 1960, 2730.

[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.

[3] Fox and Soldano, unpublished work.

Since the system was operated at vapour pressures greater than 1 atm., variations of chamber pressure required provision for both the removal and the injection of water into the central chamber. The weighing apparatus was considerably improved by elimination of the electronic null-point detecting mechanism. By means of an autocollimator, a sharply defined light-beam is transmitted through a quartz window into the pressure chamber and reflected back *via* an optically flat stellite mirror mounted on the end of the beam of the magnetic balance. Not only does this direct visual observation permit more reliable performance of all manipulations, but it also affords considerable information on the dynamics of the equilibrating system at elevated temperatures. For example, the slightest thermal instability caused condensation on the quartz window or on the stellite mirror. Of course, the rapid mass transfer which occurs at the higher temperatures, because of the high concentration of water in the vapour phase, greatly decreased the time required for attainment of equilibrium. For the most part, equilibrium was obtained within a day without any stirring. No results were accepted that could not be reproduced at least twice in as many days.

The weights of the solution dishes were compared with four titanium–platinum standards varying from 7 to 13·5 g.

RESULTS

Because of the lack of reliable reference data at temperatures above 100°, the experimental data are presented, in a form free from interpretative bias (Table 1), as isopiestic ratios relative to sodium chloride.

The isopiestic ratio at fixed water activity is defined as eqn. (1)

$$R = (\nu m)_{\text{std}}/(\nu m), \qquad (1)$$

where ν is the idealized number of ions formed per mole of salt in the assumed standard state (*e.g.*, $\nu = 3$ for Na_2SO_4), and m is the molality of the solute. The experimental ratios (Table 1) for the 1-1 electrolytes at 121·1° were smoothed by reading values at rounded concentrations from large-scale plots of isopiestic ratios R against molality. For comparison with 25° values, osmotic coefficients for 121·1° were calculated (eqn. 2) on the basis of estimated ϕ's obtained

TABLE 1.

Isopiestic R ratios at 121·1°.

Molality	ϕ_{NaCl} (est.)	Isopiestic ratio, R [eqn. (1)] with NaCl as standard						
		LiCl	KCl	CsCl	Na_2SO_4	$BaCl_2$	$MgSO_4$	UO_2SO_4
0·500	0·911							
0·5014[a]						0·8722		
0·594[a]					0·7363			
0·636[a]		1·031						
0·676[a]			0·7904					
0·6858[a]				0·9565				
1·00	0·930	1·045	0·9620	0·943	0·697	0·899		
1·25					0·678	0·912		
1·50		1·062	0·952	0·928	0·662	0·923		
1·56[a]							0·4205	
1·65[a]								0·397
1·75					0·649	0·929		
2·00	0·976	1·077	0·943	0·918	0·638	0·931	0·434	
2·25					0·627	0·932		
2·50		1·091	0·935	0·908	0·616	0·932	0·488	
2·70[a]					0·607			
2·75						0·931		
3·0	1·041	1·105	0·927	0·898		0·926	0·560	0·460
3·5		1·120	0·919	0·888			0·628	0·491
4·0	1·089	1·134	0·910	0·878			0·694	0·521
4·5		1·149	0·902	0·869			0·755	0·548
5·0			0·894	0·859			0·808	0·572
5·1[a]							0·817	
5·5								0·594
6·0								0·614
6·5								0·633

Experimental values. Others at rounded concentrations.

TABLE 2.

The temperature-dependence of ϕ_{salt}/ϕ_{NaCl} at fixed molality.

				Osmotic coefficient ratios			
Salt:	LiCl	$MgSO_4$	UO_2SO_4	KCl	$BaCl_2$	Na_2SO_4	CsCl
Molality:	(1·40)	3·04	3·42	1·55	1·12	1·54	1·59
Temp. (c)							
25·0°	1·120	0·881	0·804	0·9440	1·011	0·648	0·892
99·6	1·020	0·635	0·550	0·9445	0·915	0·6655	0·9385
121·1	1·059	0·542	0·487	0·9446	0·905	0·660	0·926
142·0	1·047	0·482	0·429	0·9446	0·873	0·634	0·920

by extrapolation of Smith's boiling-point data for sodium chloride.[4] ϕ is defined as $-(55{\cdot}5/\nu m)\ln a_w$, where a_w is the activity of the water (55·5 = number of moles of water per kilogram).

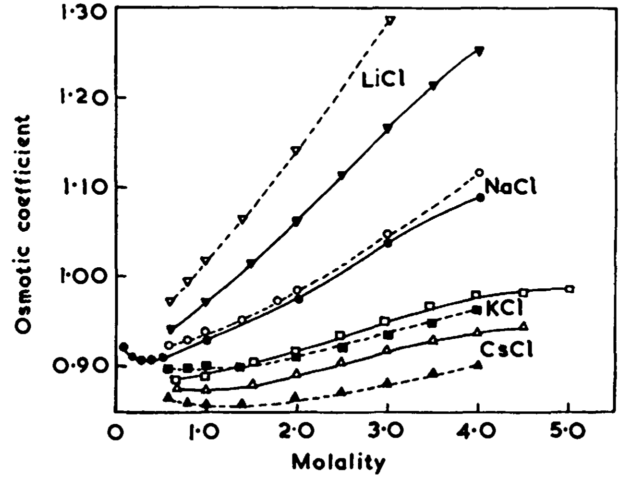

FIG. 1. Comparative osmotic coefficients for rounded molalities at 25° (broken lines) and 121·1° c (full lines).

The full curve for sodium chloride is based on extrapolated values[5] as a standard.

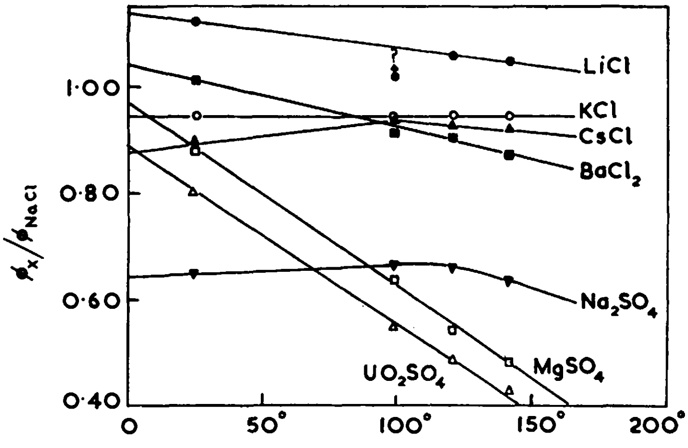

FIG. 2. Representative osmotic ratios relative to sodium chloride as a function of temperature at fixed salt molality.

It is apparent (Fig. 1) that the osmotic coefficients at 121·1° obey the same concentration-dependence as was observed by Robinson and Stokes[5] at 25° and that found in our previous work[1] at 100°. Further, our 121·1° data appeared to be free from experimental anomalies.

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

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

In many cases duplicates agreed within 0·1% in molality. Over 60% of all duplicate determinations agreed within 0·4% in the final equilibrium molalities. In no case was the final calculated molality of any pair at 121·1° in disagreement by an amount greater than 0·8%. It thus appears that, given a single primary standard, one can immediately employ both these 121·1° ratios and those previously measured at 100°,[4] to arrive at reliable information about the behaviour of these salts at elevated temperatures.

A primary standard is not needed to draw conclusions concerning the type of solution behaviour that one should expect with elevation of temperature. This information can be extracted from the experimental isopiestic ratios (Table 1) and the calculated osmotic coefficient ratios at fixed molality (Table 2). It becomes apparent, on inspection of Fig. 2, that the osmotic coefficient ratios relative to sodium chloride for the 1-1 electrolytes (at a fixed molality) show only minor variations over the temperature range from 25° to 142°. Potassium chloride maintains an almost exactly constant ratio to sodium chloride, and cæsium chloride varies only by ~3% over the 25°—142° temperature range. Lithium chloride continues to exhibit its anomalous behaviour (~12% variation in ϕ_{LiCl}/ϕ_{NaCl}). To be sure, the absolute values of the ϕ's do change but it appears that, given the ϕ_{25} value for a 1-1 salt, its behaviour up to 142° should be qualitatively predictable on the basis of the trends shown for the alkali halides.

In the case of the multivalent salts, our data [1] at 100°, 121°, and 142° (Fig. 2) clearly demonstrate the expected first-order variations in the osmotic coefficient ratios normally attributed to the ion-pair formation. Only in the case of sodium sulphate is this pronounced effect not evident (Table 2). In the last case, one is led to suspect that the sulphate ion in sodium sulphate has more in common with the bisulphate ion, since this multivalent salt appears to behave more like cæsium chloride than, *e.g.*, barium chloride.

For the 1-1 electrolytes the osmotic-coefficient ratios are relatively insensitive to temperature changes. This is in direct contrast to the pronounced linear temperature-dependence characteristic of the ratios for the multivalent-salt types. Equally significant, the temperature relationship (Fig. 2) points to a specific charge-type dependence, as shown by the relative slopes for the 2-2, 2-1, and 1-1 salt types.

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