846. *Isopiestic Vapour-pressure Measurements of Aqueous Salt Solutions at Elevated Temperatures. Part III.*[1]

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Experimental osmotic coefficients for representative aqueous salt solutions at 140° are presented as a function of concentration. Osmotic coefficients are briefly compared as functions of temperature (25°, 100°, 121°, and 140°) and of concentration.

As a continuation of a general programme of investigating the osmotic behaviour of aqueous electrolytes at elevated temperatures,[1-3] representative salt solutions were studied at 140·3° as a function of concentration. Design details of the equipment and its subsequent modifications are presented elsewhere.[1,3] The emphasis of the present study was essentially that of characterizing experimentally the osmotic behaviour of representative charge types at a variety of aqueous solution concentrations ranging from 0·3m to approximately the limit of salt solubility. In addition, a brief comparison has been made with those results previously obtained at 25°, 100°, and 121°.[2-4]

Isopiestic r ratios at 140·3° with NaCl as standard

Molality of each salt (m.)	ϕ NaCl (est.)	LiCl	KCl	CsCl	$BaCl_2$	Na_2SO_4	$MgSO_4$	UO_2SO_4
0·25	0·902				0·887			
0·30	0·903		1·005		0·882	0·764		
0·35	0·904	1·035	1·000		0·874	0·763		
0·40	0·905	1·036	0·998		0·866	0·757		
0·45	0·906	1·038	0·994		0·850	0·748		
0·50	0·907	1·038	0·994		0·835	0·740		
0·55	0·908	1·039	0·990		0·813	0·732		
0·60	0·910	1·040	0·975		0·785	0·715		
0·65	0·9120		0·973		0·718	—		
0·70	0·9135	1·040	0·971		0·657			
0·75	0·9150	1·041	0·971		0·602		0·427	0·414
0·80	0·917	1·043	0·970		0·578		0·428	0·410
0·85	0·919	1·044	0·969		0·548		0·426	0·405
0·90	0·920	1·044	0·968		0·543		0·405	0·400
0·95	0·922		0·970					
1·00	0·925	1·046	0·972	0·929	0·529		0·416	0·400
1·20	0·932	1·049	0·961	0·912	0·513		0·418	0·393
1·40	0·941	1·051	0·957	0·903	0·483		0·415	0·393
1·60	0·949	1·054	0·954	0·898	0·464		0·421	0·390
1·80	0·958	1·055	0·944	0·897	—		0·438	0·396
2·00	0·967	1·064	0·941	0·892			0·445	0·398
2·50	0·998	1·095	0·945	0·925			0·462	0·412
3·00	1·026	1·115	0·941	0·910			0·480	0·427
3·50	1·051	1·140	0·939	0·913			0·490	0·440
4·00	1·075	1·166	0·937				0·502	0·450
4·50							0·513	0·460
5·00		1·240	0·934				0·524	0·468
5·50		1·282	0·933				0·533	0·476
6·00		1·310	0·932				0·542	0·483
6·50			0·931				0·551	0·490
7·00			0·931				0·560	0·497
7·50							0·568	0·504
8·00			0·935					0·510
9·00								0·523
10·00								0·536

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[1] Part II, Soldano and Patterson, *J.*, 1962, 937.

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

[3] Patterson, Gilpatrick, and Soldano, *J.*, 1960, 2730.

[4] Robinson and Stokes, " Electrolyte Solutions," Butterworths Scientific Publns., London, 1955.

Procedure.—Since the isopiestic technique at equilibrium ensures that the various salt systems (simultaneously in contact with each other *via* a common vapour phase) are at an identical thermodynamic water activity, the experimental results are presented in the Table as isopiestic ratios relative to an arbitrary standard (in this case sodium chloride). The isopiestic ratio at fixed water activity is defined as $R = \nu m_{\text{std}}/\nu m$, where ν is the idealized number of ions formed per mole of salt in the assumed standard state (*i.e.*, $\nu = 3$ for $BaCl_2$) and m is the molality of the solute. The experimental ratios for the 1-1 electrolytes at 140·3° are reported at rounded molalities obtained from an R—m plot. The overall precision was limited to $\pm 1\%$ because of fluctuations in the temperature of the air-thermostat. Figs. 1 and 2 present a comparison of these 140·3° data with those obtained at 25°, 100°, and 121·1°. The osmotic coefficients at 140°, 121°, and 100° were calculated on the basis of estimated ϕ_{NaCl} values obtained by extrapolating Smith's[5] boiling-point data for NaCl in conjunction with the

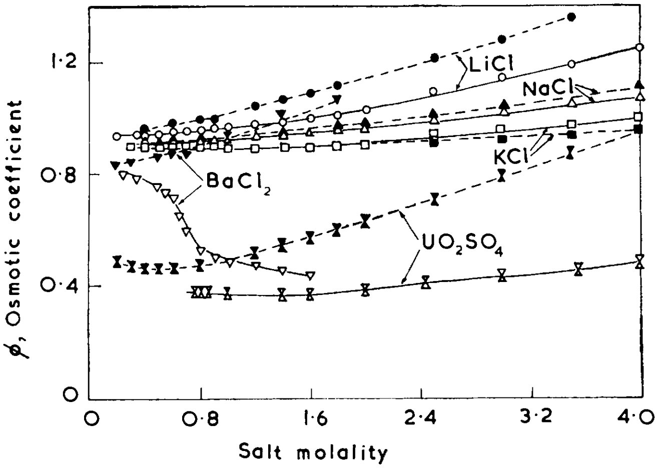

FIG. 1. Comparative osmotic coefficients at rounded molalities as a function of temperature (25° broken lines, 140° solid lines).

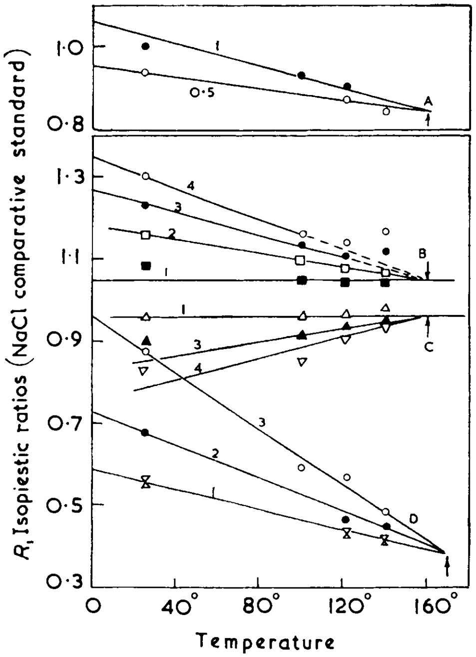

FIG. 2. Temperature-dependence of isopiestic ratios, normalized to NaCl, as a function of both salt concentration and salt type.

A, $BaCl_2$. B, LiCl. C, KCl. D, $MgSO_4$. At the molalities stated on the lines (*e.g.*, second line in A = 0·5m-$BaCl_2$).

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

equation $R\phi_{NaCl} = \phi_i$. These estimated coefficients are reasonably consistent with the comprehensive, primary standard sodium chloride data for temperatures of 100—260°, obtained by deNordwall and Gluckauf.[6]

Discussion.—Since the 140° data (Table) encompass an extended concentration range, a brief examination of the first-order effects accompanying variations of system temperature on the isopiestic ratios of aqueous salt solutions is possible. Comparison of these results with those previously reported for 100°, 121°, and 25° indicates (Fig. 2) that, at various fixed concentrations, the resultant ratios are, to a first approximation, linear with temperature. An examination of this correlation would entail the introduction of speculative elements beyond the purely experimental intent of this report and will not at this time be pursued.

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[6] H. J. deNordwall, personal communication.