

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, UNIVERSITY OF MALAYA]

The Osmotic Properties of Aqueous Sodium Chloride-Cesium Chloride Mixtures at 25°

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Isopiestic vapor pressure measurements have been made of mixtures of sodium and cesium chloride in aqueous solution and from the results the variation of the activity coefficient of each salt with change in its molality at constant total molality of the solution has been studied.

Owen and Cooke¹ applied the isopiestic vapor pressure method to determine the thermodynamic properties of potassium and lithium chloride when mixed in aqueous solution at constant total molality. Similar measurements have been reported recently² on potassium chloride-sodium chloride mixtures. Nearly all other mixtures which have been studied have included hydrochloric acid as one component and the present study is intended to extend our knowledge of two salt mixtures.

TABLE I

ISOPIESTIC SOLUTIONS OF CESIUM CHLORIDE AND SODIUM CHLORIDE OR CALCIUM CHLORIDE

m_{CsCl}	m_{NaCl}	m_{CaCl_2}	m_{NaCl}	m_{CaCl_2}	m_{NaCl}	m_{CaCl_2}	m_{NaCl}	m_{CaCl_2}
1.996	1.773	3.671	3.117	5.248	4.291	6.081	4.871	
2.439	2.139	4.215	3.526	5.358	4.363	6.436	5.120	
3.158	2.718	4.999	4.108	5.509	4.476	7.475	5.803	
3.319	2.840							
m_{CsCl}	m_{CaCl_2}	m_{CsCl}	m_{CaCl_2}	m_{CsCl}	m_{CaCl_2}	m_{CsCl}	m_{CaCl_2}	
7.856	2.947	9.261	3.279	9.620	3.361	10.985	3.652	
7.879	2.949	9.354	3.302	10.364	3.525	11.630	3.779	
8.455	3.089							

TABLE II

OSMOTIC AND ACTIVITY COEFFICIENTS OF CESIUM CHLORIDE AT 25°

m	ϕ	γ	m	ϕ	γ
2.0	0.864	0.496	6.0	0.945	0.480
2.5	.871	.485	7.0	.966	.486
3.0	.880	.479	8.0	.989	.496
3.5	.891	.475	9.0	1.004	.503
4.0	.901	.474	10.0	1.013	.508
4.5	.913	.474	11.0	1.018	.512
5.0	.923	.475			

activity coefficient of this salt has already been measured up to 3 m by the e.m.f. method³ and up to 5 m by the isopiestic method⁴; the latter measurements not being carried to higher concentrations although cesium chloride is a very soluble salt because a 5 m solution is in equilibrium with saturated potassium chloride and, at that time, no other reference salts were available. Measurements have now been made up to 11.63 m (Table I) and the osmotic and activity coefficients calculated (Table II) to supplement those given earlier.⁵

For work on the mixtures six stock solutions containing sodium and cesium chloride in different ratios were prepared and with these isopiestic measurements were made over the range 0.5 to 6 m , using sodium chloride as reference salt. Isopiestic measurements were made as close as possible to round values of m and interpolated within a very small concentration range. Table III records these isopiestic ratios $R = m_{\text{R}}/m$ where m is the total molality of the mixed salt solution and m_{R} that of the sodium chloride solution of the same vapor pressure. The molality of cesium chloride in the mixture will be denoted by m_1 , that of sodium chloride by m_2 , where $m_1 = xm$ and $m_2 = (1-x)m$.

Discussion

If Harned's rule holds for this pair of salts

$$\log \gamma_1 = \log \gamma_{1(0)} - \alpha_{12}m_2 \quad (1)$$

$$\log \gamma_2 = \log \gamma_{2(0)} - \alpha_{21}m_1 \quad (2)$$

and

$$55.51/xm^2 \times \log a_{\text{w}(0)}/a_{\text{w}(x)} = (\alpha_{12} + \alpha_{21})x - 2\alpha_{21} \quad (3)$$

where $a_{\text{w}(x)}$ is the water activity of a mixed salt solution of total molality m , and $a_{\text{w}(0)}$ that of a sodium chloride solution of the same molality. The latter is represented very faithfully over the range $2 \leq m \leq 6$ by the empirical equation

$$-\log a_{\text{w}(0)} = 0.00215 + 0.01172m + 0.0013m^2 \quad (4)$$

Thus for any value of m , the right-hand side of

TABLE III

ISOPIESTIC RATIOS OF CESIUM CHLORIDE-SODIUM CHLORIDE MIXTURES WITH RESPECT TO SODIUM CHLORIDE AS REFERENCE SALT

m	$x = 0.1335$	0.2698	0.3689	0.4989	0.6354	0.7978	1.0
$m = 0.5$	$R = .9908$.9823	.9785	.9685	.9608	.9521	0.9435
$m = 1.0$	$R = .9858$.9723	.9629	.9511	.9405	.9291	.9193
$m = 1.5$	$R = .9807$.9628	.9505	.9361	.9256	.9139	.9024
$m = 2.0$	$R = .9766$.9568	.9406	.9258	.9118	.9014	.8893
$m = 2.5$	$R = .9727$.9499	.9324	.9150	.9002	.8882	.8763
$m = 3.0$	$R = .9695$.9436	.9249	.9051	.8892	.8759	.8641
$m = 3.5$	$R = .9665$.9378	.9179	.8960	.8788	.8643	.8529
$m = 4.0$	$R = .9635$.9327	.9114	.8876	.8691	.8535	.8421
$m = 5.0$	$R = .9596$.9234	.9000	.8729	.8518	.8340	.8216
$m = 6.0$	$R = .9570$.9157	.8902	.8606	.8375	.8168	.8026

Experimental

Before proceeding to work with the mixed salts some measurements were made on cesium chloride alone. The

(1) B. B. Owen and T. F. Cooke, Jr., *THIS JOURNAL*, **59**, 2273 (1937).

(2) R. A. Robinson, Symposium on Electrochemical Constants, Washington, Sept., 1951; C. K. Lim, Thesis, University of Malaya, 1950.

equation (3) can be evaluated for each value of x and then least-squared to give α_{12} and α_{21} . The results of this calculation are given in Table IV.

(3) H. S. Harned and O. E. Schupp, Jr., *THIS JOURNAL*, **52**, 3886 (1930).

(4) R. A. Robinson and D. A. Sinclair, *ibid.*, **65**, 1830 (1943).

(5) R. A. Robinson and R. H. Stokes, *Trans. Faraday Soc.*, **46**, 612 (1949).

They represent the experimental values of R with an average error of 0.0005 which is less than the experimental error I would assign to R and it therefore follows that Harned's rule is applicable within the experimental error of these measurements.

TABLE IV
 α_{12} AND α_{21} FOR CESIUM CHLORIDE-SODIUM CHLORIDE MIXTURES

m	$-\alpha_{12}$	α_{21}	$(\alpha_{12} + \alpha_{21})$
0.5	0.035	0.056	0.021
1.0	.021	.047	.026
1.5	.0123	.0457	.0334
2.0	.0079	.0440	.0361
2.5	.0055	.0432	.0377
3.0	.0048	.0429	.0381
3.5	.0034	.0434	.0400
4.0	.0030	.0436	.0406
5.0	.0028	.0438	.0410
6.0	.0033	.0437	.0404

It has been claimed recently⁶ that if Harned's rule does hold, then $(\alpha_{12} + \alpha_{21})$ must be a constant independent of m . It can be seen from Table IV that although $(\alpha_{12} + \alpha_{21})$ does tend toward a constant value of about 0.04 in concentrated solution, there is a marked diminution in the more dilute solution. If $(\alpha_{12} + \alpha_{21})$ is put equal to 0.04 at $m = 0.5$, then the "best" values of α_{12} and α_{21} are -0.0223 and 0.0623 , respectively, and these represent the experimental values of R with a mean

(6) E. Glueckauf, H. A. C. McKay and A. R. Mathieson, *J. Chem. Soc.*, S 299 (1949).

deviation of 0.0016 compared with 0.0005 for the values given in Table IV. It must be admitted that measurements at this comparatively low concentration are difficult and it may be surprising to find an agreement with a mean deviation as low as 0.0005 in R . Nevertheless I do not think that the measurements could have been subject to a mean error of as much as 0.0016 in R and I believe, therefore, that these results are not consistent with a constant value of $(\alpha_{12} + \alpha_{21})$. It is also to be noted that this constancy of $(\alpha_{12} + \alpha_{21})$ results from the "cross-differentiation" relation

$$(\partial \ln a_1 / \partial m_2)_{m_1} = (\partial \ln a_2 / \partial m_1)_{m_2}$$

to which any *theoretical* relation in mixed salt solutions must conform. Harned, however, has never claimed that his rule is more than a useful but empirical equation representing certain observations within the limits of experimental error. One has only to add a very small quadratic term to either or both of equations (1) and (2) to destroy the necessity of a constant $(\alpha_{12} + \alpha_{21})$ and yet the contribution of the quadratic term may be well within the experimental error. For this reason I believe that Harned's rule can be used as an empirical equation when supported by experimental data even if $(\alpha_{12} + \alpha_{21})$ is not a constant. In the case of the cesium chloride-sodium chloride salt pair it appears to be valid.

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Irreversible Polarographic Reduction of Simple Metal Ions in the Presence of Acid Serum Albumin

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Shifts in the electrocapillary curve and other evidence suggest that proteins are readily adsorbed on the mercury drop during polarographic measurements. The effect of such adsorption on the reduction of simple metal ions has been studied, using serum albumin at low pH values, where no metal-protein complex formation occurs. It is found that a metal capable of forming a stable neutral or anionic complex with the inert electrolyte (Cd^{++} and Pb^{++} in KCl) gives a polarogram indistinguishable from that obtained in the absence of protein, whereas a metal present largely as uncomplexed cation (Cu^{++} , Cd^{++} and Pb^{++} in KNO_3) produces a highly irreversible wave. This phenomenon is ascribed to electrostatic repulsion between cations and the positively charged adsorbed layer. The irreversible waves were found to obey equations for activation-controlled reduction.

In the polarography of solutions containing serum albumin (in an H-type cell) the mercury drops falling to the bottom of the cathode compartment do not coalesce, presumably because a layer of serum albumin molecules is adsorbed on the drops as they fall through the solution. Since such a layer would be about 30 Å. thick, it prevents the customary formation of a mercury pool. This phenomenon appears to be independent of the pH, *i.e.*, of the charge on the protein molecules.

It can be concluded from this observation that serum albumin will also be adsorbed on the mercury drop during electrolysis, unless prevented by electrostatic repulsion. That this is indeed so is indicated by shifts in the electrocapillary curve caused by the presence of serum albumin.

The purpose of the present paper is to investigate whether this adsorbed layer interferes with the polarographic reduction of simple metal ions.

It has been shown in a previous paper that the combination of metals with serum albumin occurs at the same sites as are involved in combination with hydrogen ion.¹ In acid solutions, therefore, where an excess of hydrogen ions is present, no combination with metal ions was found to occur. It is in such solutions, therefore, that the effects of the adsorbed layer can be studied independently of complex formation.

In acid solutions the serum albumin molecule is positively charged. The full effects of adsorption should therefore be observed at applied potentials

(1) C. Tanford, *THIS JOURNAL*, **74**, 211 (1952).