CROATICA CHEMICA ACTA CCACAA **69** (3) 1149–1158 (1996)

ISSN-0011-1643
CCA–2365

Original Scientific Paper

On the Counterion Adsorption Equilibrium

Mihovil Hus

Faculty of Forestry, University of Zagreb, Svetošimunska 25,
10000 Zagreb, Croatia

Received July 6, 1995; revised October 13, 1995; accepted November 3, 1995

The adsorption equilibria of a radio-labelled europium ion and other counterions on previously prepared, dried Ag_2S, AgI, AgBr and AgCNS precipitates were investigated. The influence of temperature and surface ion concentration on adsorption equilibria of europium and barium ions was also investigated. Values $(z - z')a$ or a from the equation for the Schulze-Hardy rule in Mirnik's ion exchange theory have been calculated from the measured adsorbed quantities of europium ion. Calculated values for $(z - z')a$ or a for the europium – other counterion couple show the valence effect. Less pronounced differences in $(z - z')a$ or a values obtained for counterions with equal valence depend on the counterion nature, analogously to the lyothropic series at coagulation. The results obtained are discussed considering the previously known values of a constant from the Schulze-Hardy rule for particular counterion couples, and the chemical behaviour of particular counterions in the adsorption systems followed. The adsorption of europium ion was followed by the radioactive tracer technique.

INTRODUCTION

The solid phase surfaces of low soluble silver salts have a significant adsorption capacity for ions from solution. It is commonly assumed that crystal structure defects cause the adsorption of surface ions,[1] *i.e.*, constituent or other ions[2] on the solid phase surface. By interaction of thus charged surface and counterions from the solution the electrical double layer is formed. The adsorbed quantity of counterions could be measured on the solid phase separated from the solution. It was shown previously that the adsorbed quantity of counterions follows the Langmuir type of isotherm,[1] which for the corresponding concentration of counterions achieves the maximal quantity. Maximal adsorption quantity for counterions depends on the solid phase characteristics and on the presence of surface ions.[2] Two or more counterions in solution would be adsorbed together onto the solid phase surface. The quantity of each counterion adsorbed depends on its concentration, as well as on the concentration of other counterion. This pointed to the counterion exchange on the solid phase surface. The equilibrium between the two adsorbed counterions is expressed by the equation[3,4]

$$\log (c'/c) = \text{const.} + \log [x/(1-x)] \qquad (1)$$

where c and c' are concentrations of two counterions, while x is the fraction of the adsorbed counterion quantity with concentration c'. For the case when $x = 0.5$, the characteristic counterion concentrations $c_{x=0.5}$ are defined. It is a well-known fact that numerous salts with significant ion surface adsorption, like silver salts for instance, form stable colloid solutions. Surface ions act as stabilization ions, while counterions play the role of coagulation ions.

The critical coagulation concentration (c.c.c.) is the characteristic value for colloid solutions. At this characteristic concentration, the aggregation of particles occurs. The ratio of critical coagulation concentrations (c.c.c.) for two counterions is formulated as the Schulze-Hardy rule. This empirical rule was theoretically interpreted with the D.L.V.O. theory,[5,6] which, however, did not completely explain the experimental results. Težak's[7] interpretation was based on the ratio of Bjerrums distances. Mirnik deducted the equation of the linear Schulze-Hardy rule for various characteristic magnitudes related to counterion adsorption in his ion-exchange theory[8–10] and later works.[11–13] The ratio of Bjerrums distances in Težak's interpretation and the characteristic constant in Mirnik's interpretation have the same meaning.[9]

According to the ion-exchange theory,[9] the Schulze-Hardy rule for different surface phenomena can be formulated as:

$$\log (c'/c) = (z - z')a \qquad (2)$$

where c and c' are characteristic concentrations of counterions, expressed[8] in mol dm^{-3} z^{-1}, and z and z' are the corresponding charges. The constant a has the following meaning:

$$a = \mu_{\mathrm{A}^-_{\mathrm{ads}}} / R\ T \qquad (3)$$

where $\mu_{\mathrm{A}^-_{\mathrm{ads}}}$ is the chemical potential of the adsorbed surface ion, while R and T have their usual meaning.

Obviously, the Schulze-Hardy rule indicates a marked counterion valence effect. In addition, it was shown that at a given counterion valence, the c.c.c. value depends too, but less significantly, on the counterion nature, giving the lyothropic series.[1,14,15] This suggests that the counterion adsorption equilibrium might be dependent not only on the counterion charge, but on their chemical characteristics as well. Since it has been shown[2] that a greater counterion adsorption is obtained when surface ions form a salt of lower solubility with other solid phase constituent ion, it can be assumed that counterions that form a salt of lower solubility with the surface ion would be adsorbed more strongly.

The aim of this work is to reveal the effect of the counterion chemical nature on the counterions adsorption equilibrium by determination of $(z - z')a$ values. These values were determined from the experimental data on the relationship between the adsorbed quantity of the radio-labelled europium ion and the concentration of the other counterion present in the solution. The constant a in freshly prepared silver-iodide and silver-bromide precipitate[3,4,16,17] adsorption system has been determined in such a way. Since, in the fresh precipitate, dispersity has pointed to the effect on the adsorption capacity,[17] in this work, the counterion adsorption equilibria are investigated on the previously prepared, dried, Ag_2S, AgI, AgBr and AgCNS precipitate, as previously described.[2]

EXPERIMENTAL

Desorption of the europium ion with other counterions has been followed by the radioactive tracer technique.[2]

0.0001 or 0.0002 mol of dried Ag_2S, AgI, AgBr or AgCNS precipitates was added into 0.1 dm^3 of water solution, which contained all the components in their respective concentrations, including the radioactive marker ^{152}Eu. The suspension was mixed for an hour at 23 °C, and the solid phase was separated by filtration. The precipitate on the filter paper was rinsed three times with 0.01 dm^3 water and dried at 60 °C. Radioactivity of the weighted solid quantity was measured. The adsorbed europium ion quantity was calculated from the solid phase weight, from ^{152}Eu radioactivity and from the total radioactivity of the system.

Preparation of dried Ag_2S, AgI, AgBr and AgCNS precipitates was as follows: 0.5 mol dm^{-3} NaI, NaBr or NaCNS, respectively, was added under stirring into 2 dm^3 of 0.5 mol dm^{-3} $AgNO_3$ solution, or gaseous hydrogensulphide was introduced until the first signs of flocculation. The solution with the precipitate was stirred for several hours. The clear supernatant was decanted afterwards and the precipitate was rinsed repeatedly under stirring in doubly distilled water. Washing of the precipitates was repeated until a constant conductivity of the washing solution was reached. The washed precipitates were separated by filtration, dried at 60 °C, ground and sieved in order to get the 0.15–0.25 mm particle size fraction.

Standard 0.1 mol dm^{-3} salt solutions used were obtained by dissolving solid salts (Merck *p.a.*) in doubly distilled water. Standardization of salt solutions was achieved by standard analytical methods.

RESULTS AND DISCUSSION

The total amount of two counterions adsorbed from the solution on the solid phase surface in adsorption equilibrium equals the maximum possible quantity adsorbed. The adsorbed quantity of each individual counterion is proportional to its concentration according to the linear Schulze-Hardy rule equation for the equilibrium of two adsorbed counterions.[9]

$$\log (c'/c) = (z - z')a + \log [x/(1 - x)] \tag{4}$$

In this work, the $(z - z')a$ value is determined from equation (4) as an intercept on the log (c'/c) axis in the graphic presentation of the linear equation log (c'/c) *vs.* log $[x/(1 - x)]$. Values of log (c'/c) have been calculated from experimental conditions, while the log $[x/(1 - x)]$ values have been calculated from the measured adsorbed amount of europium ion, expressed in mmol Eu^{3+}/mol of the solid phase, for the respective europium ion concentration c' and the second counterion concentration c.

Europium ion concentrations c' giving the maximum possible amount adsorbed[2] were chosen for experiments, as well as the second counterion concentrations c where the fraction of the adsorbed europium ion x was between 0.150 and 0.850. The maximal estimated error of $(z - z')a$ values determination is ±0.1 under the experimental conditions used. Correlation coefficient values obtained for the $(z - z')a$ calculation suggest a good linear relationship of log c'/c and log $[x/(1 - x)]$ values calculated from experimental data.

The results for particular adsorption systems, together with the corresponding experimental data, are presented in Tables I–IV.

Differences obtained in $(z - z')a$ determination for the same counterions in different adsorption systems, or counterions with equal valence in the same adsorption system, clearly show that the values of a for various europium – other counterion couples are not constant. Various values of a are reported in discussions of Mirnik's ion exchange theory, depending on the examined phenomenon, system and counterion couple. Values among 1.2–1.7 are reported for adsorption equilibria on fresh silver – iodide[3,4] precipitates, while a values of 1.0–1.9 are reported for various phenomena on silver halides and silver – rhodanide.[9,18] The theoretical value for silver – iodide[12] is reported to be 1.65. Values 1.3–2.0 for coagulation of silver – sulphide have been reported.[19] According to these data, the average value of a is ±1.5 in the adsorption equilibrium of two counterions whose charge differs by one unit.

As can be seen from Tables II and III, thorium ion shows lower values, like those that would respond to the counterion with charge number lower than 4+. Such thorium behaviour has been observed and explained by formation of a complex with anion and by hydrolysis.[20–22]

TABLE I

Adsorption system silver-sulphide

Second counterion	$c_{\mathrm{Ag_2S}}$	$c_{\mathrm{H_2S}}$	$c_{\mathrm{HNO_3}}$	$c'_{\mathrm{Eu(NO_3)_3}}$	$(z - z')a$
	mol dm^{-3}	mol dm^{-3}	mol dm^{-3}	mol dm^{-3} z^{-1}	
Al^{3+}	0.002	0.001	0.001	0.0003	–0.605
Cr^{3+}	0.002	0.001	0.001	0.0003	–0.270
La^{3+}	0.002	0.001	0.001	0.0003	–0.102
Ba^{2+}	0.002	0.001	0.001	0.0003	–1.360
Co^{2+}	0.002	0.001	0.001	0.0003	–1.500
Mn^{2+}	0.002	0.001	0.001	0.0003	–1.728
Ni^{2+}	0.002	0.001	0.001	0.0003	–1.618
Zn^{2+}	0.002	0.001	0.001	0.0003	–0.420

For the couple europium – other 3+ charged counterion, the (z – z')a value has to be zero. Significant differences from zero value for aluminium and chromium ions can be seen from Tables I to IV. The aluminium and chromium aberrations can be explained, like in coagulation processes, by hy-

TABLE II

Adsorption system silver-iodide

Second counterion	c_{AgI}	c_{NaI}	$c_{\mathrm{HNO_3}}$	$c'_{\mathrm{Eu(NO_3)_3}}$	$(z - z')a$
	mol dm^{-3}	mol dm^{-3}	mol dm^{-3}	mol dm^{-3} z^{-1}	
Th^{4+}	0.002	0.001	0.001	0.0003	1.395
Al^{3+}	0.002	0.001	0.001	0.0003	–0.376
Ce^{3+}	0.002	0.001	0.001	0.0003	0.022
Cr^{3+}	0.002	0.001	0.001	0.0003	–0.202
La^{3+}	0.002	0.001	0.001	0.0003	–0.096
Ba^{2+}	0.001	0.001	0.001	0.0001	–1.498
Ba^{2+}(70 °C)	0.001	0.001	0.001	0.0003	–1.470
Ba^{2+}	0.001	0.000005	0.001	0.0003	–1.369
Cd^{2+}	0.002	0.001	0.001	0.0003	–1.527
Hg^{2+}	0.002	0.001	0.001	0.0003	–0.288
Pb^{2+}	0.001	0.001	0.001	0.0001	–1.076
Cs^{+}	0.002	0.001	0.001	0.0003	–2.246
Na^{+}	0.002	0.001	0.001	0.0003	–2.668
H_2SO_4	0.002	0.001	0.001	0.0003	–2.596
HNO_3	0.002	0.001	0.001	0.0003	–2.501
$HClO_4$	0.002	0.001	0.001	0.0003	–2.826

TABLE III

Adsorption system silver-bromide

Second counterion	c_{AgBr}	c_{NaBr}	c_{HNO_3}	$c'_{Eu(NO_3)_3}$	$(z - z')a$
	mol dm^{-3}	mol dm^{-3}	mol dm^{-3}	mol dm^{-3} z^{-1}	
Th^{4+}	0.001	0.001	0.001	0.0002	0.679
Al^{3+}	0.002	0.001	0.001	0.0003	–1.004
Cr^{3+}	0.002	0.001	0.001	0.0003	–0.684
La^{3+}	0.001	0.001	0.001	0.0002	–0.152
Ba^{2+}	0.001	0.001	0.001	0.0002	–1.705
Pb^{2+}	0.002	0.001	0.001	0.0003	–1.044
Na^{+}	0.001	0.001	0.001	0.0002	–3.239
Tl^{+}	0.002	0.001	0.001	0.0003	–0.842

drolytic reactions[23,24] diminishing their charge number. The values for lanthanum ion in the AgBr system (Table III) are slightly higher than the experimental error.

As it can be seen from Tables I to IV, for the couple europium – other 2+ charged counterion, only cobalt in Ag_2S system; barium and cadmium in AgI system, and barium in AgCNS system satisfy the presumed $(z - z')a = -1.5$ value. Manganese and nickel in Ag_2S system, as well as barium in AgBr and Ag_2S systems have $(z - z')a$ value close to –1.5. Significant differences obtained for other counterions with 2+ charge would correspond to the behaviour of some counterion with charge number greater than 2+. This means

TABLE IV

Adsorption system silver-rhodanide

Second counterion	c_{AgCNS}	c_{NaCNS}	c_{HNO_3}	$c'_{Eu(NO_3)_3}$	$(z - z')a$
	mol dm^{-3}	mol dm^{-3}	mol dm^{-3}	mol dm^{-3} z^{-1}	
Al^{3+}	0.002	0.001	0.001	0.0003	–0.394
Bi^{3+}	0.002	0.001	0.001	0.0003	0.102
Cr^{3+}	0.002	0.001	0.001	0.0003	–0.298
La^{3+}	0.002	0.001	0.001	0.0003	–0.049
Ba^{2+}	0.002	0.001	0.001	0.0003	–1.446
Cu^{2+}	0.002	0.001	0.001	0.0003	–0.066
Hg^{2+}	0.002	0.001	0.001	0.0003	–0.585
Pb^{2+}	0.002	0.001	0.001	0.0003	–0.627
Na^{+}	0.002	0.001	0.001	0.0003	–2.748
Tl^{+}	0.002	0.001	0.001	0.0003	–1.556

that these counterions have a higher adsorbability than the europium ion with which they are in adsorption equilibrium.

High concentrations of the desorbing ion and respective anion could have influence on the maximal adsorbed quantity in the cases of europium ion desorption with 1+ valence counterions. Taking this into consideration, the $(z - z')a$ values obtained for sodium ion (Tables II, III, and IV) are close to the expected value of –3. The caesium ion behaviour in the AgCNS system, and particularly thallium ion in AgBr and AgCNS systems (Tables III and IV) differ a lot from the expected values.

Desorption of the europium ion with hydrogen ion from HNO_3, $HClO_4$ and H_2SO_4 acids in AgI system has been examined because of the possible influence of the corresponding anion. For all three cases, the $(z - z')a$ values for the hydronium ion were slightly lower than –3.

Previous research[25] shows that the europium ion behaves like a simple 3+ charged ion in adsorption systems. This means that the differences in $(z - z')a$ values, obtained for counterions of the same kind or of the same valence in the same or different adsorption systems, depend on their chemical properties, which are expressed in the particular adsorption system. These differences can be clearly seen from Tables I–IV.

Values of $(z - z')a$ must depend on the counterion valence solely if the linear Schulze-Hardy rule is valid. Differences between different adsorption systems could be expected due to different surface ions, whose chemical potential is contained in constant a. The differences in constant a values observed previously, as well as the existence of counterion lyothropic series, can be explained by the chemical effect (adsorbability, structure and hydration of ions).[14] Adsorbability is the characteristic of a particular counterion, while the structure and hydration of counterions depend on the adsorption system conditions as well. Significant aberrations of calculated the $(z - z')a$ values from the expected ones refer to counterions which are subject to hydrolysis and/or form salts of low solubility with the surface ion under the experimental conditions. These counterion chemical properties are not included into the Schulze-Hardy rule, so $(z - z')a$ or a values are different for counterions of the same valence.

The Schulze-Hardy rule is basically defined for critical coagulation concentrations, which is a criterion of the colloidal system stability. The electrostatic repulsion between of dispersed colloidal particles depends on the surface charge and/or the potential. Surface charge of the observed adsorption systems is defined as being due to the adsorption of the potential – determing ions.[26] Counterions adsorbed on such electrically charged surface diminish the surface charge and lead to coagulation. This is the reason why the lyothropic effect is explained by the differences in electrochemical double layer on the solid-liquid interface for different counterions.[14,15,27–29]

The electrical double-layer structure on the solid-liquid interface in Ag_2S and Ag-halide adsorption systems is equal to the electrical double layer of Ag_2S or Ag-halide electrode for the same conditions. Accordingly the characteristic magnitudes of the respective electrode and adsorption system can be qualitatively compared.

Differences in the AgI electrode capacity for caesium and barium ions relative to other ions of the same valence[30] are congruent with the differences in $(z - z')a$ for caesium and barium ions relative to other counterions of the same valence in the AgI adsorption system (Table II).

The congruence of the cobalt and zinc selectivity constant for Ag_2S electrode[31] with the differences in $(z - z')a$ values for the same ions in the Ag_2S adsorption system (Table I) can be also seen. All the aforementioned data suggest that the chemical nature of counterions, besides the charge, influences the effects which are a consequence of counterion adsorption in the same manner.

According to Eq. (3), constant a depends on the chemical potential of the adsorbed surface ion and on the temperature. The difference in $(z - z')a$ values amounts to 0.129 for barium in AgI adsorption systems, which significantly differs in iodide ion concentrations at 23.0 °C (Table II). This value is almost equal to the experimental error.

Differences in $(z - z')a$ values for barium in AgI adsorption systems at 23.0 °C and 70.0 °C are less than the experimental error, which can be seen from Table II. Significant changes were determined[27] for other electrokinetic magnitudes of the double layer on the AgI/electrolyte interface for the same difference in temperature.

It is obvious that, for constant a determination by the experimental method from two counterion adsorption equilibrium, the influence of the parameters contained in Eq. (3) cannot be resolved.

CONCLUSION

The influence of counterions on certain surface phenomena, coagulation in the first place, is defined as the Schulze-Hardy rule. Counterion adsorption, in fact the equilibrium of certain adsorbed species in the electrical double layer is the basis for all these surface phenomena. The solid phase in adsorption systems acts as a counterion ion exchanger, so the Schulze-Hardy rule is interpreted in terms of the ion exchange theory.[9] In this work, the $(z - z')a$ values and constant a have been determined from the two counterion adsorption equilibrium in four adsorption systems with several counterions. The results of constant a determination[3,4,9,12,18,19] and the knowledge of the impact of counterion chemical properties[14,15,21] have been respected. Evaluation of the calculated values for the europium – other counterion equilibrium revealed the fact that this value is not solely influenced by the counterion charge. The $(z - z')a$ values for counterions, which in the adsorption system are not in the simple ion form, should not be taken into account. Due to the experimental method used, determination of characteristic concentrations and constant a from the two adsorbed counterions equilibrium cannot give relations as precise as those obtained by the determination of critical coagulation concentrations. Nevertheless, differences in the calculated $(z - z')a$ values for equivalent counterions, whose solubilities of salts with surface ion differ significantly, are visible in this work. It should be mentioned that in later citing of the Schulze-Hardy rule with regand to the ion exchange theory,[11–13] or interpretations related to the D.L.V.O. theory,[32] the counterion chemical properties are not considered at all.

Acknowledgement. – The author is indebted to dr. K. Kvastek for data computation.

REFERENCES

1. J. Lyklema, *Fundamentals of Interface and Colloid Science*, Vol. 1, Academic Press, London, 1991.
2. M. Hus and M. J. Herak, *J. Radioanal. Nucl. Chem.* **71** (1993) 407.
3. M. J. Herak and M. Mirnik, *Kolloid-Z.* **168** (1960) 139.
4. M. J. Herak and M. Mirnik, *Kolloid-Z.* **179** (1961) 130.
5. B. V. Derjaguin and L. Landau, *Acta Physicochim. URSS* **14** (1941) 633.
6. E. J. W. Verwey and J. Th. G. Overbeek, *Theory of the Stability of Lyophobic Colloids*, Elsevier, Amsterdam, 1948.
7. B. Težak, *Arhiv kem.* **22** (1950) 26.
8. M. Mirnik, *Croat. Chem. Acta* **42** (1970) 49.
9. M. Mirnik, *Croat. Chem. Acta* **42** (1970) 161.
10. M. Mirnik, *Croat. Chem. Acta* **42** (1970) 507.
11. M. Mirnik, *Croat. Chem. Acta* **61** (1988) 81.
12. M. Mirnik, *Croat. Chem. Acta* **64** (1991) 253.
13. M. Mirnik, *Croat. Chem. Acta* **67** (1994) 493.
14. J. Lyklema, *Croat. Chem. Acta* **42** (1970) 151.
15. J. Lyklema, *Croat. Chem. Acta* **48** (1976) 565.
16. M. J. Herak and M. Hus, *Compte-rendus du V émé Congrés International de la Détergence*, Editiones Unidas, Barcelona, 1969, Vol. II (part 1), p. 653.
17. M. Hus and M. J. Herak, *Colloid and Polymer Sci.* **254** (1976) 903.
18. M. Mirnik, *Nature* **199** (1963) 555.
19. M. Hus, M. Pavlović, and M. J. Herak, *Chem. Ind.* **40** (1991) 139.
20. K. F. Schulz and M. J. Herak, *Croat. Chem. Acta* **29** (1957) 49.
21. K. F. Schulz and M. J. Herak, *Croat. Chem. Acta* **30** (1958) 127.
22. E. Matijević, M. B. Abramson, R. H. Ottewill, K. F. Schulz, and M. Kerker, *J. Phys. Chem.* **65** (1961) 1724.
23. E. Matijević, K. G. Mathai, R. H. Ottewill, M. Kerker, *J. Phys. Chem.* **65** (1961) 826.
24. S. Kratohvil and E. Matijević, *J. Colloid Intrface Sci.* **24** (1967) 47.
25. M. J. Herak and M. Mirnik, *Kolloid Z-Z Polymere* **205** (1965) 129.

26. J. Lyklema, *Advan. Colloid Interface Sci.* **2** (1968) 65.
27. H. Bijsterbosch and J. Lyklema, *Advan. Colloid Interface Sci.* **9** (1978) 147.
28. M. A. Blesa and N. Kallay, *Advan. Colloid Interface Sci.* **28** (1988) 111.
29. N. Kallay, R. Sprycha, M. Tomić, S. Žalac, and Ž. Torbić, *Croat. Chem. Acta* **63** (1990) 467.
30. K. J. Pevereli and H. P. van Leeuwen, *J. Electroanal. Chem.* **110** (1980) 137.
31. Nj. Radić, and H. B. Mark, Jr., *Croat. Chem. Acta* **58** (1985) 179.
32. S. B. Hall, J. R. Duffield, and D. R. Wiliams, *J. Colloid Interface Sci.* **143** (1991) 411

SAŽETAK

O adsorpcijskoj ravnoteži protuiona

Mihovil Hus

Proučavane su adsorpcijske ravnoteže obilježenog europijeva iona i drugih protuiona na prethodno pripravljenim, suhim talozima Ag_2S, AgI, AgBr i AgCNS. Također je proučen utjecaj temperature i koncentracije površinskog iona na adsorpcijske ravnoteže europijevih i barijevih iona. Vrijednosti $(z - z')a$ ili a iz jednadžbe za Schulze-Hardy-jevo pravilo u Mirnikovoj teoriji ionske zamjene izračunane su iz izmjerenih količina adsorbiranog europij iona. Izračunate vrijednosti $(z - z')a$ ili a za par europij – drugi protuion pokazuju efekt valencije. Manje izražene razlike u vrijednostima $(z - z')a$ ili a za jednakovalentne protuione ovisne su o prirodi protuiona, analogno liotropnoj seriji kod koagulacije. Dobiveni rezultati diskutirani su uzimajući u obzir otprije poznate vrijednosti konstante a Schulze-Hardy-jeva pravila za pojedine parove protuiona kao i poznato kemijsko ponašanje pojedinih protuiona u ispitivanim sustavima. Adsorpcija europijevih iona određivana je tehnikom radioaktivnih obilježivača.