On the Anomalous Thermal Diffusion Observed in Mixed Electrolyte Solution

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The appearance of a kind of diffusion potential caused by thermal separation or thermal diffusion potential in solid systems(1) was pointed out by Wagner. The similar phenomenon in aqueous systems, though expected theoretically, seems not to have been observed.

The present writer made a series of experiments on a number of electrolytes in aqueous solutions with a thermal diffusion apparatus of Clusius and Dickel type, and observed, independently of Gillespie and Breck,(2) an anomalous phenomenon, i. e., so-called "negative effect" or enrichment of some ions at the hotter region of the apparatus in the mixed electrolyte solutions.(3) By his investigation continued thereafter,(4) it seemed probable that the effect was brought about by a kind of potential produced by the difference of thermal diffusion velocity of each ion. An experimental basis of this proposition was the absence of the mutual effect when a non-electrolyte, such as urea, was added to sodium chloride or when sulfuric acid, having the same degree of thermal diffusion velocity, was added to the solution of hydrogen chloride. Finally, though qualitatively, the mechanism was theoretically supported after the method of Abegg and Mose(5) who, introducing the idea of diffusion potential, could derive the change of diffusion velocity of an electrolyte by the uniform addition of another electrolyte, but the negative effect could not be derived.

Recently, Guthrie, Wilson and Schomaker(6) made a theoretical formulation of the separation of solution in general with the same idea of thermal diffusion potential even in the case when the Clusius-Dickel's separation column was used. Thus the treatment of G. W. and S. is much valuable to the discussion about the anomalous effect mentioned above.

According to Guthrie and others, separation ratio of AX-BX type, R_a, which is defined by the ratio of the concentration of A ion at the bottom of the separation apparatus to that at

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(1) C. Wagner, *Ann. der Phys.*, (5) **3**, (1929); **6**, 370 (1930).

(2) L. J. Gillespie and S. Breck, *J. Chem. Phys.*, **9**, 370 (1941).

(3) K. Hirota, this Bulletin, **16**, 232 (1941); *J. Chem. Soc. Japan* **63**, 105 (1942).

(4) K. Hirota, *J. Chem. Soc. Japan*, **64**, 112 (1943); *cf. Chem. Abst.*, **41**, 3346 (1947).

(5) Abegg and Mose, *Z. physik. Chem.*, **30**, 545 (1899); W. Nernst, *Z. phyik. Chem.*, **2**, 613 (1888).

(6) G. Guthrie, J. N. Wilson and V. Schomaker, *J. Chem. Phys.*, **17**, 310 (1949).

the top, is given by

$$R_a = \left\{(u_a+u_x)R_{ax}c_a + [(u_a+u_x)(u_b+u_x)R_{ax} - u_a(u_b+u_x)R_{ax}]\frac{c_b}{u_x}\right\} \times \frac{1}{(u_a+u_x)c_a+(u_b+u_x)c_b} \qquad (1)$$

where R_{ax} and R_{bx} are the separation ratios of AX and BA, respectively, while u_i is ionic mobility of i-ion and c_a and c_b, concentrations of AX and BX, respectively.

Applying the formula to HCl-NaCl and HCl-NH_4Cl systems, G. W. and S. could derive the negative effect with much success. However, as these systems are only a special part of writer's data, it will be interesting to extend the check of the formula over the other systems when the concerned electrolytes are different or when the concentrations of both electrolytes are not equal, as will be done in the present note.

Table 1

Summarised Results for the Check of Eq. (1)

Expt. No	Concentration c_a	c_b	Separation ratio**) A(obs.)	A(calc.)	B(obs.)	B(calc.)	Remark
I. HCl (A)-NaCl (B)							
1	0.50	0.50	1.34	1.39	0.97	0.96	——
2	0.050	0.530	1.47_7	1.78 (1.51)	1.02_9	1.02 (1.03)	R_{ax} 1.16 R_{bx} 1.046
3	0.35	2.54	1.47_6	1.07 (1.78)	1.03_3	1.01 (1.02)	R_{ax} 1.25 R_{bx} 1.06
4	0.130	2.79	1.54	1.81 (1.68)	1.05_4	1.03 (1.05)	R_{ax} 1.20 R_{bx} 1.06
5	0.0186	2.51	1.65	1.88 (1.59)	1.05_5	1.04 (1.06)	R_{ax} 1.17 R_{bx} 1.06
II. NH_4Cl (A)-NaCl (B)							
6	0.01	0.10	1.00_4	0.99 (1.02)	1.04_4	1.06 (1.05)	R_{ax} 1.026 R_{bx} 1.044
7	1.00	0.96	0.99*)	0.99	1.05_2	1.06	——
III. HCl (A)-NH_4Cl (B)							
8	0.50	0.50	1.42	1.46	0.89	0.86	——
IV. NaOH (A)-NaCl (B)							
9	0.044	0.089	1.42	1.75	1.13	0.88	——

Calculated values not in parentheses are determined by use of R_i's of one normal, i.e., 1.22 for HCl, 1.047 for NaCl, 1.010 for NH_4Cl and 1.30 for NaOH, while those in parentheses by use of R_i's in the last column of the table.

*) R_i at the third hour is used.

**) Slight difference of the calculated values from the values of Guthrie and others (Nos. 1 and 8) will be due to the difference of ionic mobilities used in the calculation.

It is found by the writer that mixed solutions, having one ion in common, can generally be classified into following four categories, according to the change of separation ratio of each component as a result of mixing.

a) The separation of the components is independent of each other: HCl-H_2SO_4; Urea-NaCl.

b) The separation ratios of both components increase: NaOH-NaCl.

c) The separation ratios of both components decrease: H_2SO_4-Na_2SO_4.

d) The separation ratio of one component ion increases and that of the other and of the same electric sign decreases: NaOH-Na_2CO_3; HCl-NaCl; HCl-NH_4Cl; NaCl-NH_4Cl.

Among these systems, it is unnecessary to discuss on a), while the system having, at least, one bivalent ion is not suited for the check of Eq. (1), due to the marked change of activity by the existence of other ions. Therefore, the following systems, HCl-NaCl, HCl-NH_4Cl, NaCl-NH_4Cl and NaOH-NaCl will be discussed. The calculated result, as shown in Table 1, is obtained from the following constants.

The ionic mobility at 50° used in the calculation is: H^+ 450, Cl^- 116, NH_4^+ 115, Na^+ 82 and OH^- 280.(7) The separation ratios adopted in the table are those at the second hour, except the case of Expt. No. 7, though the values extrapolated to the infinite hour are more desirable from the theoretical reason. This is partly due to the convenience of comparing the results with those of G. W. and S.

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(7) Interpolated values taken from Landolt-Börnstein's Table.

Separation ratio of each component electrolyte of one normal is identified with R_t of mixed electrolyte solution: i. e., HCl 1.22, NaCl 1.047, NH_4Cl 1.010 and NaOH 1.30. It may be a matter of discussion that such a constant value of R_t is adopted throughout all the systems inspite of their conspicuous dependency on concentration.

In order to restrict the argument concerning the ambiguity in question, the concentration dependency upon R_t of hydrogen chloride, sodium chloride and ammonium chloride is determined with the same apparatus, the result being shown in Table 2.

Table 2

Separation Ratio at the Second Hour of Hydrogen Chloride, Sodium Chloride and Ammonium Chloride

Concn. HCl (Normal)	R_{HCl}	Concn. NaCl (Normal)	R_{NaCl}	Concn. NH_4Cl (Normal)	R_{NH_4Cl}
0.010	1.19	0.010	1.041		
0.029	1.16	0.025	1.042	0.020	1.018
0.037	1.15				
0.100	1.20	0.100	1.044	0.100	1.025
0.300	1.24				
0.500	1.26				
1.000	1.22	1.000	1.047	1.00	1.010
		2.91	1.065	3.06	1.007

It is noteworthy that in these concentration range there is no possibility of the negative effect regarding NaCl and NH_4Cl. Thus the argument against the proposition of thermal diffusion potential by ascribing the effect to the concentration dependency of the electrolyte concerned may be disappeared.

It can be said that the agreement is good when the concentration of both component is equal (Nos. 1, 6, 7 and 8 in Table 1), and that, besides the systems of HCl-NaCl and HCl-NH_4Cl, the negative effect is confirmed in NaCl-NH_4Cl system (No. 7) which is devoid of HCl. The situation is theoretically not wonderful, because with respect to thermal diffusion velocity which is nearly proportional to (Sep. ratio -1) owing to the narrow annular space of the apparatus used, sodium chloride is much larger than ammonium chloride, contrary to ordinary diffusion velocity.

On the other hand, the agreement becomes fairly worse when their concentrations are not equal (Nos. 2, 3, 4 and 5). Such deviation can be ascribed to the assumption of fixing R_t independently of concentration. Really it is found that by adopting such proper R_t's described in the last column of Table 1, the degree of coincidence is improved very much in every system except No. 3.

The unexpected positive effect of Cl^--ion, perfectly opposite to the theory, in NaOH-NaCl system cannot be explained by the above formula. It seems possible that this phenomenon is due to the concentration effect which, however, cannot be checked owing to the absence of data regarding sodium hydroxide. Nevertheless, it can generally be concluded that the system belonging to categories b) and c) cannot be derived from the theory, i. e., the theory can derive only the system belonging to the categories a) and d). Because, transforming Eq. (1), we obtain

$$R_a = R_{ax} + \frac{c_b(u_b + u_x)(R_{ax} - R_{bx})}{c_a(u_a + u_x) + c_b(u_b + u_x)} \cdot \frac{u_a}{u_x}, \tag{2}$$

it is clear that the ion of larger R_t increases and that of the smaller and of the same electric sign decreases by mixing two electrolytes which have the same ion in common. Thus the result might be ascribed to an effect of non-electrical interaction of ions, but it seems now that further experimental study is required before the attempt of detailed discussion on the systems of category b).(9)

However, it may be said that the occurrence of the thermal diffusion potential is reasonable by the description hitherto made and also that the negative effect is a particular case of such electric interaction between ions.

Summary

The application of the theoretical formula of Guthrie and others on the "negative effect" of thermal diffusion which was found by the writer is extended to the new data. The agreement of the theory with experiment is good in the systems of HCl-NaCl, HCl-NH_4Cl and NaCl-NH_4Cl, even when both components are of unequal concentration. However, in the system of NaCl-NaOH, the theory is perfectly failed, the reason being unknown.

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(8) The specification of the apparatus used: equidistance annular space, 1.5 mm.; its length, 94 cm.; volume of reservoirs, 23 cc.; higher temperature 76°,; lower temperature 25°. (*cf. this Bulletin*, **16**, 475 (1941).

(9) There is another possible point of discussion concerning the "forgotten effect" in the Clusius' apparatus, as shown by de Groot, Hoogenstraaten and Gorter [*Physica*, **9**, 923 (1942).] This effect seems not to be able to explain the anomaly of this system, as a result of simplified calculation attempted by the author.