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Reverse Osmosis Separation of Some Monoamino Monocarboxylic Acids in Aqueous Solutions Using Cellulose Acetate Membrane

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The ***reverse*** osmosis separation of some monoamino monocarboxylic acids (1.0×10^{-3} mol/*l*) in single aqueous solutions was carried out by batch cell under an operating pressure of 20 Kg/cm²•G at a temperature of 30°C. using DDS-cellulose acetate membrane. Taft's polar parameter ($\Sigma\sigma^*$), Taft's steric parameter (ΣE_s) and nonpolar parameter (ΣS^*) governing reverse osmosis separations of nonionized polar aliphatic and alicyclic organic compounds could be applied to amino acids whose substituents are composed of hydrocarbon, such as aliphatic amino acids and part of aromatic amino acids. These three parameters ($\Sigma\sigma^*$, ΣE_s, ΣS^*) were correlated with polarity of covalent bond, molecular weight of substituent, and interaction energy of London-van der Waals dispersion force, respectively. As a result, these characteristic parameters were also applied to sulfur-containing amino acids, aromatic amino acids, and hydroxy amino acids. The calculated values of rejection of amino acids based on these parameters agreed with observed values approximately. Also, the separation of monoamino monocarboxylic acids in binary aqueous solution system containing L-alanine (1.0×10^{-3} mol/*l*) was carried out by reverse osmosis under the same operating conditions. As a result, preferential permeability of L-alanine was governed with Taft's polar parameter of added amino acids in the concentration range of added amino acids ($<1.0\times10^{-3}$ mol/*l*), in which the formation of adsorbed layer of added amino acids on the surface of membrane might be taken place.

INTRODUCTION

The asymmetric cellulose acetate membranes which were developed by Loeb and Sourirajan for the purpose of desalination about two decades ago are still industrially important ones and have been a model of synthetic polymer membranes up to date. The studies of mechanism for reverse osmosis have been done extensively regarding the separation of inorganic salts. As a result, various kinds of theory are proposed as follows; solution-diffusion mechanism (Lonsdale ***et al.,*** 1965, 1971), concept of pore (Glueckauf, 1967; Bean, 1969) and phenomenological treatment (Kedem and Katchalsky, 1958) etc. Also, regarding the separation mechanism of organic compounds, Matsuura ***et al.*** (1976, 1977) have analyzed the permeation of nonionized polar aliphatic and alicyclic organic compounds in single solution system, and proposed the equation of permeation which was based ***on*** a porosity of membrane and molecular

parameters, such as hydrogen bonding action, hydrophobic action and steric effect. But there is little systematic researches concerning the separation of ionic organic compounds by reverse osmosis. On the other hand, amino acids are amphoteric electrolytes existing as zwitter ions in aqueous solutions. Amino acids are present in many biochemical systems. It is very interesting that they are found in the primeval sea as a first formed life relative organic substance, therefore, an investigation on reverse osmosis separation of amino acids using cellulose acetate membranes might make a contribution to not only a clarification of permeation of ionic organic compounds and an application of the membrane process to biochemical and chemical industry, life science, etc. but also a future development of polymer membranes.

The purpose of this work was to study the criterion for the separation of monoamino monocarboxylic acids in single and binary aqueous solution systems with cellulose acetate membranes by reverse osmosis as a fundamental.

MATERIALS AND METHODS

Monoamino monocarboxylic acids of aliphatic, hydroxy-substituted, sulfur-containing, and aromatic types were reagent chemicals and cellulose acetate membranes used were DDS-600, 800, 870 and 880. They were supplied by De Danske Sukkerfabrikker.

The concentration of amino acid in single aqueous solution was measured by a spectrophotometer, Hitachi Model 100-30. Amino acids in binary aqueous solution were analyzed with paper chromatography or thin-layer chromatography, and determined by the use of a densitometer, DMU-33C (Toyo-Kagaku Sangyo, Inc.). The concentration of sodium chloride was measured by a conductivity bridge, CD-35M II (MS, Inc.).

A batch of stirred cell (Bio Engineering RO-3) was used in all the experiments. The feed volume was 200 ml, the effective area of membrane was 32.2 cm^2, and the rotational speed of an internal magnetic stirrer was 300 rpm. The cell was immersed in a water bath kept at 30°C. The operating pressure was 20 $Kg/cm^2 \cdot G$. The feed concentration of amino acid in single aqueous solution was 1.0 x 10^{-3} mol/*l*. The mixed amino acids in binary aqueous solution were prepared by dissolving L-alanine (1.0×10^{-3} mol/*l*) and added amino acids (2.5 x 10^{-4}, 6.7 x 10^{-4}, 1.5 x 10^{-3} and 4. Ox 10^{-3} mol/*l*) in deionized water. The sampling method was as follows: When the solution was in a single system, 6. Oml of permeate was collected as permeate sample after discarding initial 2. Oml of permeate. When the solution was in a binary system, 8.0 ml of permeate was collected as permeate sample after discarding initial 8.0 ml of permeate. Before the experiments on reverse osmosis separation of amino acid solutions, membranes were always tested with distilled water and 5000 ppm of sodium chloride aqueous solution, and the relation between pure water permeability A and rejection η of sodium chloride was checked.

RESULTS AND DISCUSSION

1. Equation of transport

Rejection η(—) is defined as follows;

$$\eta \equiv \frac{C_2 - C_3}{C_2} \tag{1}$$

where C_2 is concentration of solute at the membrane surface (g-mol/cm³) and C_3 is concentration of solute in permeate (g-mol/cm³). Generally, C_2 differs from concentration of solute in feed solution C_1(g-mol/cm³). C_2 is obtained from the following equation.

$$C_2 = C_3 + (C_1 - C_3)\exp\left[\frac{N_w + N_s}{c_1 \cdot k}\right] \tag{2}$$

where N_w is molar flux of water (g-mol/cm²•sec), N_s is molar flux of solute (g-mol/cm²•sec), c_1 is molar density of feed solution (g-mol/cm³), and k is mass transfer coefficient (cm/sec). Mass transfer coefficient k depends on the shape of cell and streaming state of solution in the cell. On the cell used in this study, k can be represented as follows;

$$k = 7.586\left(\frac{D}{l}\right)Re^{0.420}\,Sc^{1/3} \tag{3}$$

where D is diffusivity (cm²/sec), l is inside diameter of cell (cm). Re is Reynolds number (—), and Sc is Schmidt number (—). Solute transport parameter $D/K\delta$ is defined as follows;

$$D/K\delta \equiv \frac{N_s}{C_2 - C_3} = \frac{JC_3}{C_2 - C_3} = J\left(\frac{1}{\eta} - 1\right) \tag{4}$$

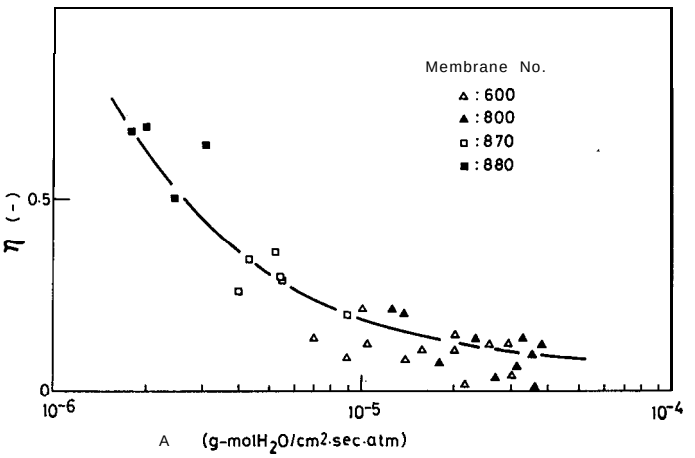

Fig. 1. Relation between η and A for 5000ppm of NaCl aqueous solution.

where J is volume flux of permeate ($cm^3/cm^2 \cdot sec$).

k for sodium chloride was 9.73×10^{-3}cm/sec. Fig. 1 shows the relation between rejection η of sodium chloride and pure water permeability A, which was obtained by using various DDS-cellulose acetate membranes.

2. Prediction of permeation of amino acid **in single aqueous solution systems**

Following equation is proposed for solute transport parameter $D/K\delta$ of nonionized polar aliphatic and alicyclic compounds (Matsuura *et* al., 1976, 1977).

$$\ln(D/K\delta) = \ln C^* + \rho^* \Sigma\sigma^* + \delta^* \Sigma E_s + \omega^* \Sigma S^* \quad (5)$$

where $\ln C^*$ is a constant depending on the porous structure of membrane surface, the chemical nature of membrane material, and the nature of functional group in solute molecule. $\rho^* \Sigma\sigma^*$, $\delta^* \Sigma E_s$ and $\omega^* \Sigma S^*$ are polar effect, steric effect, and nonpolar effect, respectively. $\Sigma\sigma^*$ and ΣE_s are Taft's polar and steric parameters, respectively, and ΣS^* is nonpolar parameter (modified Small's number). ρ^*, δ^* and ω^* are the characteristic proportionality constants associated with $\Sigma\sigma^*$, ΣE_s and ΣS^*, respectively. Though ρ^* and ω^* don't depend on the porous structure of membrane surface, δ^* does. Physicochemical properties of some amino acids of aliphatic and aromatic types are shown in Table 1. The nonpolar effect $\omega^* \Sigma S^*$ may be considered negligible if the molecular structure of solute contains a straight chain involving no more than three carbon atoms not associated with a polar functional group. Therefore, following equation is applied to glycine and L-alanine.

$$\ln(D/K\delta) = \ln C^* + \rho^* \Sigma\sigma^* + \delta^* \Sigma E_s . \quad (6)$$

Both $\Sigma\sigma^*$ and ΣE_s in L-alanine is zero. Therefore, $\ln C^*$ is **as follows;**

$$\ln C^* = \ln(D/K\delta)_{\text{L-alanine}} . \quad (7)$$

From Eq. (6), δ^* is as follows ;

$$\delta^* = \frac{\ln(D/K\delta) - \ln C^* - \rho^* \Sigma\sigma^*}{\Sigma E_s} \quad (8)$$

Table 1. Summary of physicochemical properties of some amino acids.

Solute number	Amino acid	R in R—CH(NH_2)COOH	ΣE_s (—)	$\Sigma\sigma^*$ (—)	ΣS^* $\left(\frac{\sqrt{cal \cdot ml}}{g\text{-}mol}\right)$	$k \times 10^4$ (cm/sec)
1	Glycine L-alanine	H CH	0.00 *1.24*	*0.490* 0.000	*214 90*	78
2		CH_3				70
3	L-valine	$(CH_3)_2CH$	-0.47	***-0.190***	***456***	61
4						57
5	L-isoleucine L-leucine	$(CH_3)(C_2H_5)CH$	-0.93 *-1.13*	-0.125 *-0.210*	*589 589*	57
6	DL-norvaline	$CH_3(CH_2)_2$	-0.36	-0.115	***480***	61
7	DL-norleucine	$CH_3(CH_2)_3$	-0.39 -2.55	-0.130 0.600	*335 613*	57
8	D-phenylglycine	C_6H_5				57
9	L-phenylalanine	$C_6H_5CH_2$	-0.38	0.215	468	55

Reaction constant (= 1.465) in hydrolysis reaction of ester (R'COOR, R and R' are aliphatic substituent) (Taft, 1956) was employed as numerical value of ρ^*. Relation between D/KS and pure water permeability A for L-alanine and glycine is shown in Fig. 2. The values $\ln C^*$ and δ^* are plotted in Fig. 3, which are calculated from Eqs.(7), (8) and plot points in Fig. 2. Using the results described above, ω^* for some aliphatic and aromatic amino acids was calculated. Fig. 4 shows the relation between ω^* and A. As mentioned above, ω^* doesn't depend on porous structure of membrane surface, i.e., pure water permeability A. The region of A about 6×10^{-6} to 1×10^{-5} g-mol $H_2O/cm^2 \cdot sec \cdot atm$ is satisfied. In this region of A, Eq.(5) which is proposed

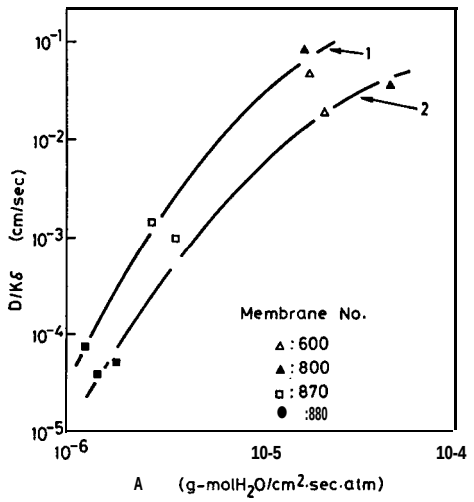

Fig. 2. Relation between $D/K\delta$ and A for glycine and L-alanine aqueous solution. Amino acid; 1: glycine, 2: L-alanine.

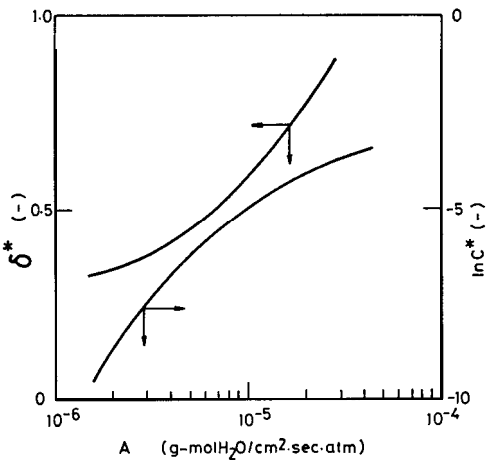

Fig. 3. Determination of ln C* and δ^*.

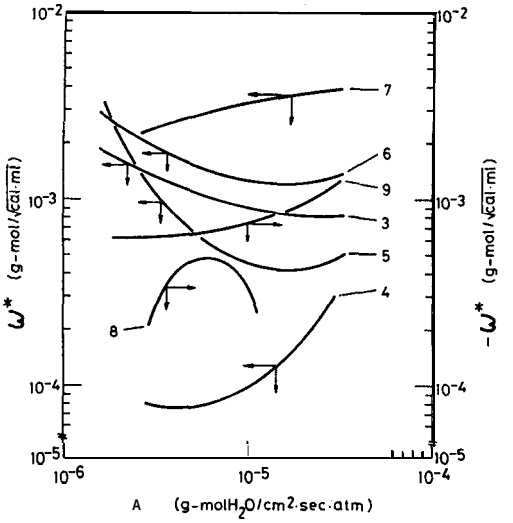

Fig. *4.* Relation between ω^* and A. Number is solute number of amino acid.

for nonionized polar aliphatic and alicyclic organic compounds can be applied to some amino acids of aliphatic and aromatic types which are ionic solutes. Therefore, preferential permeability of monoamino monocarboxylic acids is discussed at 8×10^{-6} g-molH_2O/cm²·sec·atm of A.

Though $\Sigma\sigma^*$ and ΣE_s for variety of substituents are tabulated in Taft's table (Taft, 1956), the number of substituent listed is not so many. On the other hand, ΣS^* is applied to substituents composed of hydrocarbon only (Matsuura and Sourirajan, 1973). Therefore, for the sake of application of Eq.(5) to sulfur containing, aromatic, and hydroxy amino acids, it is necessary to correlate characteristic parameters ($\Sigma\sigma^*, \Sigma E_s, \Sigma S^*$) with other physical quantities, and to obtain characteristic parameters which can be applied to these amino acids on using the correlation obtained. First, covalent bond between diverse atoms contains some polarity α (Nomura, 1971). As polarity α was measured (Azumi, 1969), it is possible to calculate the proportion of ionic bond in an optional substituent (R). On the representing proportion of ionic bond (polarity of covalent bond) by ***B, B*** was calculated in this study as follows ;

(ex. 1) L-serine ($R=CH_2OH$)

R-C: 2(C—H) + (C-O) + (O-H) + (C-C) .

Therefore,

B= (2x0.06+0.125+0.31+0.0)/5=0.111.

(ex. 2) L-tyrosine ($R=HOC_6H_4CH_2$)

R-C= (O-H) +7(C—H)+8(C—C).

Therefore,

$$B = (0.31 + 7 \times 0.06 + 8 \times 0.0)/16 = 0.046 .$$

Polar effect would be obtained in correlation with B. The relation between $\Sigma\sigma^*$ and B is illustrated in Fig. 5. Four kinds of plot were obtained as follows;

Plot (1): Substituents are constituted of aromatic ring and/or hydrocarbon.
Plot (2): Substituents are constituted of aromatic ring and/or hydrocarbon and/or hydroxyl group and/or oxygen atom.
Plot (3): Substituents are constituted of hydrocarbon.

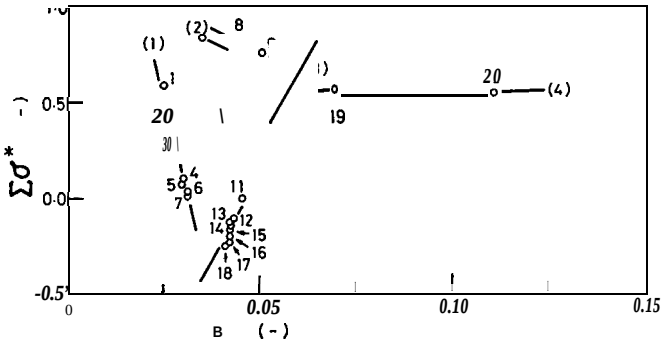

Fig. 5. Relation between Taft's polar parameter and polarity of covalent bond. R in R–Y(R: Substituent, Y: Functional group); 1: C_6H_5, 2: $(C_6H_5)_2CH$, 3: $C_6H_5CH_2$, 4: $C_6H_5(CH_3)CH$, 5: $C_6H_5(CH_2)_2$, 6: $C_6H_5(C_2H_5)CH$, 7: $C_6H_5(CH_2)_3$, 8: $C_6H_5OCH_2$, 9: $C_6H_5(OH)CH$, 10: H, 11: CH_3, 12: n-C_2H_5, 13: n-C_3H_7, 14: $(CH_3)_2CHCH_2$, 15: n-C_4H_9, 16: $(CH_3)_2CH$, 17: $(CH_3)(C_2H_5)CH$, 18: $(C_2H_5)_2CH$, 19: CH_3OCH_2, 20: $HOCH_2$.

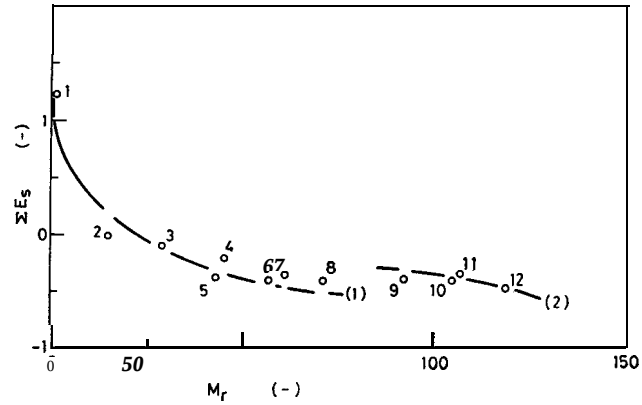

Fig. 6. Relation between Taft's steric parameter and molecular weight of substituent. Substituent; 1: H, 2: CH_3, 3: C_2H_5, 4: CH_3OCH_2, 5: n-C_3H_7, 6: n-C_4H_9, 7: CH_3SCH_2, 8: n-C_5H_{11}, 9: $C_6H_5CH_2$, 10: $C_6H_5(CH_2)_2$, 11: $C_6H_5OCH_2$, 12: $C_6H_5(CH_2)_3$.

Plot (4) : Substituents are constituted of hydrocarbon and/or hydroxyl group.

Next, as steric effect depends on the size and shape of solutes, it would be related to a molecular weight of substituent. Fig. 6 shows the relation between ΣE_s and molecular weight of substituent M_r. In this case, two kinds of plot were obtained as follows;

Plot (1) : Substituents are constituted of hydrocarbon and/or sulfur atom and/or oxygen atom.

Plot (2) : Substituents are constituted of aromatic ring and/or hydrocarbon and/or oxygen atom.

On the other hand, nonpolar effect would be depended on the hydrophobic interaction energy between membrane and solute, which is represented by interaction energy of London-van der Waals dispersion force E_l (erg) as follows (Chu, 1971) ;

$$E_l = -\int_{V_s} d\tau_s \int_{V_m} d\tau_m \frac{n_s n_m A}{l_o^6} \tag{9}$$

And, London-van der Waals constant A(erg•cm^6) is represented as follows;

$$A = \frac{3}{2} \cdot \frac{\alpha_s \alpha_m I_s I_m}{I_s + I_m} \tag{10}$$

where A is whole volume of substance considered (cm^3), $d\tau$ is volume fraction of substance considered (cm^3), n is number of molecule contained in 1 cm^3 of substance considered (number/cm^3), l_o is intermolecular distance (cm), α is polarizability (cm^3), and I is ionization potential (erg). Subscripts s and m refer to solute and membrane, respectively. The cylindrical pore model for skin layer of cellulose acetate membrane is shown in Fig. 7. Pore radius r_1 of membrane whose pure water permeability A and rejection of sodium chloride are 8×10^{-6} and 0.21, respectively was calculated by the use of C. P. Bean Equation (Bean, 1969) as follows;

$$r_1 = 1 \times 10^{-6} \text{ (cm)}. \tag{11}$$

Now, the hydrophobic interaction would be taken place between a single solute molecule existing at the center of cylindrical pore (inside diameter$=r_1$, outside diameter$=r_2$, length$=2Z_o$) and methyl groups in cellulose acetate is assumed. Change in hydrophobic interaction energy ***AE,*** which takes place when a single solute molecule moves from bulk phase to center of pore is as follows;

$$\Delta E_l = (E_l)_{\text{pore}} - (E_l)_{\text{bulk}} . \tag{12}$$

In bulk phase, the distance between a solute molecule and methyl group is long enough. Therefore, we obtain

$$(E_l)_{\text{bulk}} = 0. \tag{13}$$

From Eqs.(9),(12),(13), following equation is obtained.

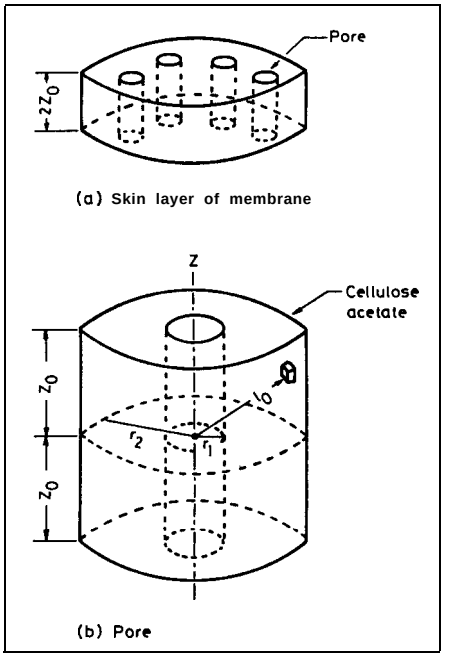

Fig. 7. Schematic representation of cellulose acetate membrane.

$$\Delta E_t = -\left(\int_{V_s} d\tau_s \int_{V_m} d\tau_m \frac{n_s n_m \Lambda}{l_o^6}\right)_{\text{pore}} . \tag{14}$$

Here, following assumption is set up.

$$Z_o, r_2 = \infty . \tag{15}$$

As solute considered is a single molecule, we obtain

$$\int_{V_s} d\tau_s\,(n_s) = 1 . \tag{16}$$

Also,

$$\Delta\tau_m = r\Delta\theta\Delta r\Delta Z \tag{17}$$

$$l_o = (r^2+Z^2)^{1/2} . \tag{18}$$

From Eqs. (14) ~(18), following equation is obtained.

$$\Delta E_t = \lim_{n\to\infty} \left[-\Lambda n_m \int_0^{2\pi} d\theta \int_{-Z_o}^{Z_o} \left[\int_{r_1}^{r_2} \frac{r\,dr}{(r^2+Z^2)^{1/2}}\right] dz\right] = -\frac{\pi^2 \Lambda n_m}{4 r_1^3} . \tag{19}$$

DDS-cellulose acetate membrane is taken as 2.5 cellulose acetate membrane. The molecular weight M of pentaacetyl-cellobiose which is a repeating unit of 2.5 cellulose acetate is 534. The density ρ of cellulose acetate is 1.30 (g/

cm^3). If a methylene is regarded as methyl group, the number of methyl group contained in a pentaacetyl-cellobiose is seven. Therefore, the number of methyl group contained in 1 cm^3 of 2.5 cellulose acetate n_m is calculated as follows ;

$$n, = (7)\left(\frac{\rho}{M}\right)N = 1.03 \times 10^{22} (\text{number}/cm^3) \tag{20}$$

where N is avogadro number.
Substituting Eqs.(10), (11) and (20) in Eq.(19) gives the following equation.

$$\Delta E_i = -(3.81 \times 10^{40}) \frac{\alpha_s \alpha_m I_s I_m}{I_s + I_m} (\text{erg}) \ . \tag{21}$$

a, is calculated by using following equation.

$$\alpha_s = \frac{3[R]}{4\pi N} \tag{22}$$

where *[R]* is molecular refraction. Ionization potential of an organic compound which is made by adding a single hydrogen atom to the substituent of amino acid was employed for that of amino acid. Polarizability α_s and ionization potential I_s of some amino acids of aliphatic and aromatic types are shown in Table 2. On the other hand, polarizability of methyl group α_m is 2.71 X 10^{-24} (cm"). Taking methyl group as methane, ionization potential of methyl group I_m is 2.09x 10^{-11} (erg). By inserting numerical values to Eq.(21), the relation between hydrophobic interaction energy ***AE,*** and nonpolar parameter ΣS^* is obtained, as shown in Fig. 8. Two kinds of plot were obtained as follows ;

Plot (1) : Substituents haven't aromatic ring.
Plot (2) : Substituents have aromatic ring.

Polarity of covalent bond ***B,*** molecular weight of substituent M_r and interaction energy of London-van der Waals dispersion force ***AE,*** of each amino acids, which were calculated by equations mentioned above were shown in Table 3. Taft's polar parameter $\Sigma\sigma^*$, Taft's steric parameter ΣE_s and nonpolar parameter ΣS^* which are applied to amino acids of hydroxy-substituted, aromatic, and sulfur-containing types were obtained by use of numerical

Table 2. Polarizability and ionization potential.

Solute number	Amino acid	$\alpha_s \times 10^{24}$ (cm^3)	$I_s \times 10^{11}$ (erg)
2	L-alanine	9.65	2.09
3	L-valine		
4	L-leucine	15.26	1.73
5		—	—
6	L-isoleucine DL-norvaline	13.39	1.80
7	DL-norleucine D-phenylglycine	17.46 15.26	1.51 1.73
8			
9	L-phenylalanine	19.33	1.48
10			
11	β-methyl-β-phenylalanine	11.52 21.13	1.88 1.46

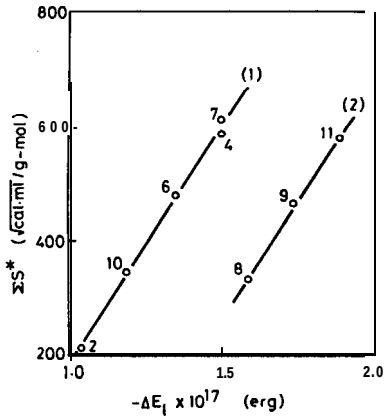

Fig. 8. Relation between nonpolar parameter and interaction energy of London-van der Waals dispersion force. Number is solute number of amino acid.

values in Table 3 and the correlations shown in Figs. 5, 6 and 8, and are shown in Table 4. The number in parenthesis shown in Table 4 is a plot number in Figs. 5, 6 and 8. In calculating of Taft's polar parameter, sulfur atom were taken as carbon atom, because electronegativity of sulfur atom is the same as that of carbon atom. Characteristic proportionality constant as-

Table 3. Summary of physicochemical properties.

Solute number	Amino acid	R in R—CH(NH$_2$)COOH	M_r (—)	B (-)	$\alpha_s \times 10^{24}$ (cm^3)	$I_s \times 10^{12}$ (erg)	$\Delta E_l \times 10^{17}$ (erg)	$k \times 10^4$ (cm/sec)
12								67
13	L-threonine L-serine	$CH_3CH(OH)$	45.08 31.35	0.084 0.111	12.17 10.37	1.70 1.75	-1.18 -1.02	62
14	L-homoserine	$HO(CH_2)_2$	45.08	0.084	12.24	1.70	-1.18	
15								62
16	Dopa·osine	$(OH)_2C_6H_3CH_2$	107.15 123.15	0.046 0.061	20.46 19.94	1.44 1.44	-1.75 -1.80	53 52
17								64
18	L-cysteine L-methionine	$CH_3S(CH_2)_2$	75.17 47.12	0.038 0.035	16.48 12.86	1.51 1.51	-1.16 -1.49	57
19								59
20	DL-ethionine DL-homocysteine	$C_2H_5S(CH_2)_2$	89.09 61.12	0.036 0.039	14.73 18.35	1.48 1.51	-1.32 -1.66	54

Table 4. Characteristic parameters.

Amino acid	$\Sigma\sigma^*$ (—)	ΣE_s (—)	ΣS^* $\left(\frac{\sqrt{\text{cal}\cdot\text{ml}}}{\text{g-mol}}\right)$
L-serine	0.555 (4)	−0.18(1)	203(1)
L-threonine	0.530(4)	−0.30(1)	340(1)
L-homoserine	0.530(4)	−0.30(1)	340(1)
L-tyrosine	0: 800 (2)	−0.38(2)	479(2)
Dopa	0.600(2)	−0.46(2)	521(2)
L-cysteine	−0.400(3)	−0.32(1)	323(1)
L-methionine	−0.290(3)	−0.46(1)	604(1)
DL-homocysteine	−0.360(3)	−0.40(1)	459(1)
DL-ethionine	−0.250(3)	−0.50(1)	748(1)

sociated with $\Sigma S^* \omega^*$ is represented from Eq.(5) as follows;

$$\omega^* = \frac{\ln(D/K\delta) - \ln C^* - \rho^* \Sigma \sigma^* - \delta^* \Sigma E_s}{\Sigma S^*} . \tag{23}$$

Fig. 9 shows the correlation between ω^* calculated by Eq. (23) and number of carbon atom in substituent (R). As a result, ω^* of aliphatic amino acids having straight substituent and hydroxy amino acids varies as the number of carbon atom, but ω^* of aliphatic amino acids having branched substituent, sulfur-containing amino acids, and aromatic amino acids varies inversely as the number of carbon atom. These relations were approximated by a first-order equation as follows:

For former,

$$\omega^* \times 10^5 = -544.7 + (214.6)(\text{number of carbon atom}). \tag{24}$$

For latter,

$$\omega^* \times 10^5 = 243.1 - (52.05)(\text{number of carbon atom}). \tag{25}$$

By using these approximate equations, calculated value of rejection of each amino acids were obtained, and compared with that observed, as shown in Fig. 10. Calculated value of rejection agrees with observed value approximately.

On the other hand, Matsuura and Sourirajan (1974) propose the next equation for the solute transport parameter $D/K\delta$ of α type of monoamino monocarboxylic acid.

$$\ln(D/K\delta) = \ln C^* + \rho^* pK_1 + \delta^* \Sigma E_s \tag{26}$$

where pK_1 is equilibrium constant. Amino acids for that Eq. (26) can be ap-

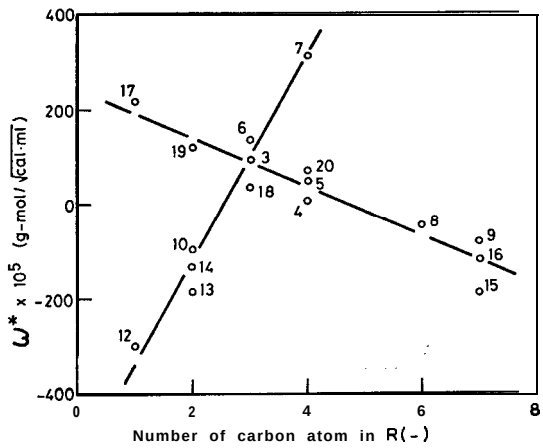

Fig. 9. Relation between ω^* and number of carbon atom in R. A: 8×10^{-6} g-molH_2O/cm²·sec·atm. Number is solute number of amino acid.

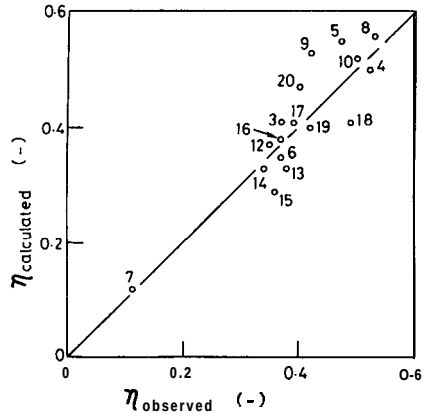

Fig. 10. Calculation of rejection of amino acid. A: 8×10^{-6} g-molH_2O/cm²•sec•atm. Number is solute number of amino acid.

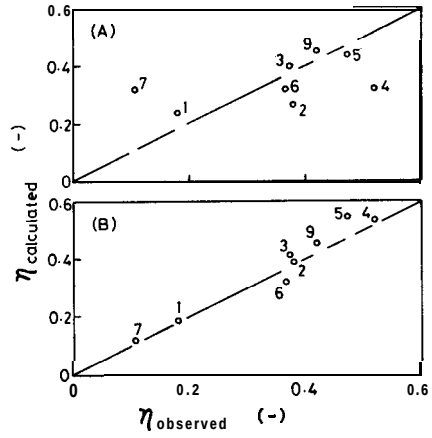

Fig. 11. Calculation of rejection of amino acid. $\eta_{observed}$ is author's data. (A): $\eta_{calculated}$ was calculated by Eq.(26). (B) : $\eta_{calculated}$ was calculated by Eq.(5). A: 8×10^{-6} g-molH_2O/cm²•sec•atm. Number is solute number of amino acid.

plied are aliphatic amino acids only because of the calculation method of ***BE,.*** Fig. 11 shows the comparison of the observed value of rejection obtained by authors with the calculated value of rejection obtained from Eq.(5) proposed by authors and with that obtained from Eq.(26), and indicates that Eq.(5) can predict rejection of amino acids more exactly than Eq. (26). Next, the observed values of rejection obtained by Matsuura and Sourirajan(1974) were analyzed by author's method mentioned above. As a result, the relation between ω^* and number of carbon atom in R was obtained, and shown in Fig. 12. This correlation obtained is consistent with that obtained by authors (ref. Fig. 9). Therefore, Eq.(5) is superior to Eq.(26) in the accuracy of a predic-

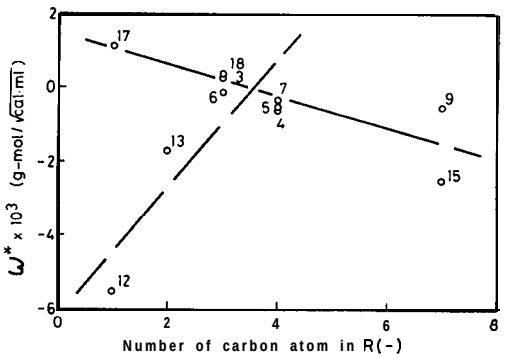

Fig. 12. Relation between ω^* and number of carbon atom in R. Data: Matsuura et al. (1974)'s data (Film No. 6). Number is solute number of amino acid.

tion of rejection and in the region of application for various series of amino acids.

3. Interaction between diverse amino acids on membrane-solution interface in binary aqueous solution systems

The reverse osmosis separation of fourteen kinds of solutions consisting of L-alanine (1.0 x 10^{-3} mol/*l*) and added amino acids (2.5 x 10^{-4}~4.0 x 10^{-3} mol/*l*) of aliphatic, hydroxy-substituted, sulfur-containing, and aromatic types was carried out. As a result, rejection of L-alanine was almost constant in the concentration range of the added amino acids (ca. 1. Ox 10^{-3}~4. 0 x 10^{-3} mol/*l*) in every respect of the system. But in certain system the rejection of L-alanine considerably increased at the concentration of the added amino acids (2.5 $\times 10^{-4}$ mol/*l*). On the other hand, the rejection of added amino acids was almost constant in the total concentration range of the added amino acids (2.5~ 10^{-4}~4.0$\times 10^{-3}$ mol/*l*) in most of the systems. Also, in single system the rejection of amino acids was almost constant in the concentration range 1.0$\times 10^{-3}$ to 4. Ox 10^{-3} mol/*l*, but decreased below at the conc. 1. Ox 10^{-3} mol/*l*, as shown in Fig. 13. Fig. 14 is a schematic diagram showing the amino acid separation as mentioned above. In order to investigate the interaction between L-alanine and added amino acid on the membrane-solution interface, four physical quantities were defined as follows;

$$\Delta\eta_1 \equiv \eta_a - \eta_b \tag{27}$$

$$\Delta\eta_2 \equiv \frac{\eta_c + \eta_d}{2} - \eta_e \tag{28}$$

$$\Delta\eta_3 \equiv \eta_f - \eta_g \tag{29}$$

$$\Delta\eta_4 \equiv \frac{\eta_h + \eta_i}{2} - \frac{\eta_j + \eta_k}{2} \tag{30}$$

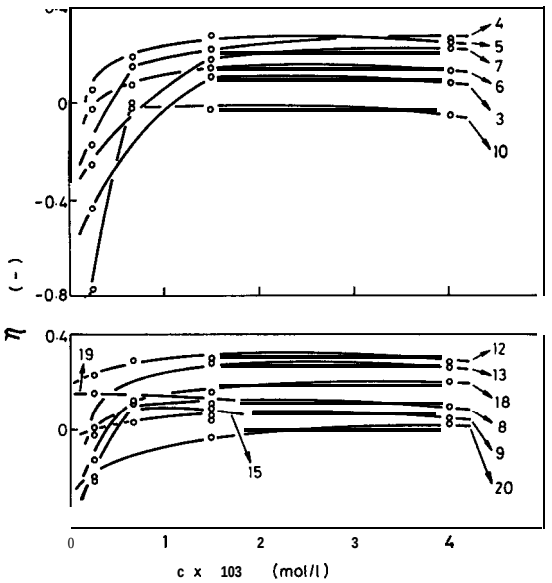

Fig. 13. Effect of concentration on rejection for single system. A: 8×10^{-6} g-molH_2O/cm²•sec•atm. Number is solute number of amino acid.

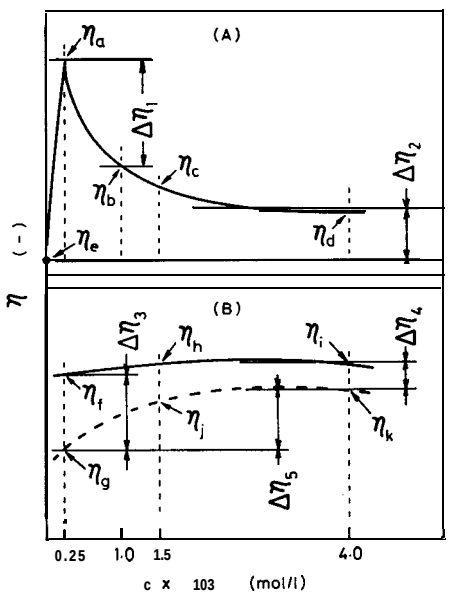

Fig. 14. Schematic representation of solute separation. (A) : L-alanine, (B): Added amino acid. Solid line: Binary system, broken line : Single system.

Table 5. Difference between amino acid rejection in binary and single systems.

Added amino acid	$\Delta\eta_1$ (—)	$\Delta\eta_2$ (—)	$\Delta\eta_3$ (—)	$\Delta\eta_4$ (—)
L-serine	0.02	0.10	0.15	0.15
L-threonine	0.08	0.11	0.09	—0.09
DL-2-aminobutyric acid	0.21	0.11	0.89	0.05
DL-norleucine	0.52	0.23	0.46	0.00
DL-norvaline	0.26	0.03	-0.17	0.15
L-leucine	0.30	0.23	0.44	0.03
L-valine	0.34	0.11	0.90	0.21
L-isoleucine	0.16	0.06	0.08	-0.11
L-methionine	0.03	0.21	0.35	0.02
DL-ethionine	0.06	0.27	0.48	0.28
DL-homocysteine	0.04	0.35		
L-phenylalanine	0.09	0.09	0.12	0.14
D-phenylglycine	0.02	0.10	0.14	-0.12
L-tyrosine	0.14	0.00	0.13	0.24

where η_a, η_b, ····· η_j and η_k are shown in Fig. 14. $\Delta\eta_1, \Delta\eta_2, \Delta\eta_3$ and $\Delta\eta_4$ in each system are tabulated in Table 5. $\Delta\eta_1, \Delta\eta_2, \Delta\eta_3$ and $\Delta\eta_4$ are positive in most of the system. Therefore, the rejection of both L-alanine and added amino acids is higher in a binary system than that in a single system. On the other hand, $\Delta\eta_1$ is greater in systems consisting of L-alanine and aliphatic amino acid than that in other systems. A cellulose acetate membrane is negatively charged slightly and basic. $\Delta\eta_1$ was correlated with Taft's polar parameter $\Sigma\sigma^*$ of each added amino acids, as shown in Fig. 15. As a result, when Taft's polar parameter of the added amino acid and that of L-alanine are close to each other, the rejection of L-alanine increases considerably, but when they are apart, the rejection of L-alanine is almost constant. On the other hand, the rejection of some amino acids especially such as aliphatic amino acids becomes positive to negative as the concentration of

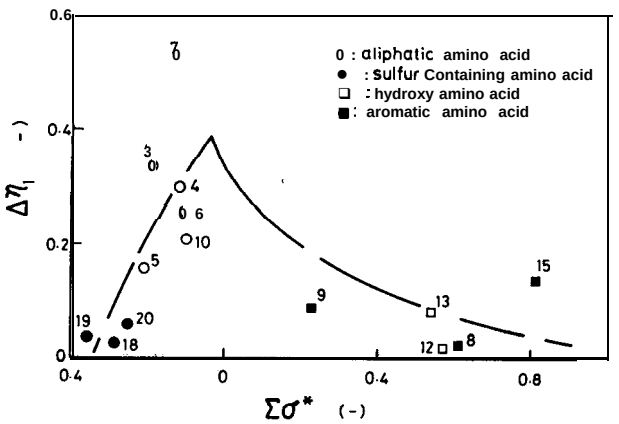

Fig. 15. Effect of Taft's polar parameter on $\Delta\eta_1$. A: 8 x 10^{-6} g-molH_2O/ cm^2•sec•atm. Number is solute number of amino acid.

feed solution decreases from 1.0 $\times 10^{-3}$ to 2.5 $\times 10^{-4}$ mol/l in single aqueous solutions, as shown in Fig. 13. This typical behavior was considered to be due to the surface flow of amino acids on the basis of the formation of adsorbed layer of amino acids on a surface of the membrane near the concentration of the feed solution (2.5 x 10^{-4} mol/l). Based on the assumption mentioned above, the relation between $\Delta\eta_1$ and $\Sigma\sigma^*$ of added amino acids shown in Fig. 15 is explained. In the first place, in systems consisting of L-alanine and aliphatic aminoacids, L-alanine interacts with an adsorbed layer of aliphatic amino acids near the concentration of added amino acid (2.5 $\times 10^{-4}$ mol/l). But L-alanine hasn't strong affinity for the adsorbed layer of aliphatic amino acids because Taft's polar parameter $\Sigma\sigma^*$ of aliphatic amino acid and that of L-alanine are close to each other, i.e., acidity of aliphatic amino acid is equal to that of L-alanine approximately. Therefore, the rejection of L-alanine increases at the concentration of the added amino acids (2.5~ 10^{-4} mol/l). Next, in systems consisting of L-alanine and added amino acids of hydroxy-substituted, sulfur-containing and aromatic types, the adsorption layer of added amino acids is formed near the concentration of added amino acid (2.5×10^{-4} mol/l), however, its thickness seems to be thinner compared to that of aliphatic amino acids according to Fig. 13. Furthermore, L-alanine has strong affinity for the adsorbed layer of added amino acids because Taft's polar parameter of added amino acid and that of L-alanine are apart. Therefore, the rejection of L-alanine doesn't increase so much at the concentration of the added amino acids (2.5~ 10^{-4} mol/l).

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