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Solute Effects on Electromigration

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The kinetics of the solute effect on solvent electromigration and the vacancy-flow effect on solute electromigration have been analyzed. The Howard and Manning type analysis has been applied to the diffusion data of a number of solutes in Al, Cu, Ag, and Au for determining the required jumping-frequency ratios. The cross-term contributions to the electromigration flux are found to be negative for all the solutes analyzed, so the vacancy-flow effect reduces solute and solvent migration. However, the enhanced diffusivity of the solvent and the large effective charge of the solute overcompensate the negative vacancy-flow corrections. As a result, most of the solutes analyzed are predicted to enhance solvent electromigration except for Fe in Cu and Ag. The result is attributed to the particular behavior of the vacancy jumping around the impurity. Of particular interest also is that the predicted effect of Cu on Al in bulk crystal is inconsistent with the existing thin-film observations.

I. INTRODUCTION

Since the addition of copper was found to be effective in reducing electromigration damage in aluminum films,[1] the study of effects of solute addition on electromigration has drawn considerable interest. The problem of practical interest is a well-defined one: Which solute element can be added to reduce the damage produced by the vacancy flux in electromigration? In a dilute alloy, the total atomic flux, which causes the counter flow of the vacancies, comes mainly from the transport of the solvent atoms. It is therefore essential to study the solute effect on solvent electromigration. This effect is more important to electromigration damage than the electromigration of solute itself but has seldom been studied. Only recently, Doan[2] analyzed this problem in some detail. His interest was primarily in using the solute effect on electromigration as one of the input data for analyzing the impurity-diffusion kinetics. He proposed that the dependence of the inert-marker velocity on solute concentration can substitute for the solute-isotope effect, and when it is combined with the solute diffusivity and the solvent-enhanced diffusion, the various ratios of atom jumping frequencies can be determined. This is particularly useful when there are no suitable solute isotopes for isotope-effect measurements.

It is the objective of this paper to use the kinetic model to evaluate the solute effect on solvent electromigration for dilute alloys. It is hoped that by analyzing a number of solutes in the common fcc metals of Al, Cu, Ag, and Au, the results can lead to some general predictions about the solute effect, at least for bulk electromigration. In addition, the vacancy flow effect on solute electromigration will be calculated. It will be seen that such correction factor on the measured effective charge is usually not negligible and should be taken into account in data analysis.

In this paper, the expression for the atomic flux in electromigration will be derived first according to irreversible thermodynamics. Since a major part of the formulation can be found in recent literature,[3,4] only a brief derivation will be given here. The origin of the "vacancy-flow" effect for mass transport in electromigration will be indicated. In Sec. III, the Howard and Manning type kinetic analysis[5] will be used to determine the frequency ratios for a number of dilute fcc alloys. Based on these frequency ratios and the solute electromigration data, the vacancy-flow factor and the dependence of solvent electromigration on solute concentration can be calculated. Finally, some comments on the validity of extending the results to thin films will be made and the recent thin-film result of Cu in Al observed by Howard and Ross[6] will be discussed.

II. THERMODYNAMIC EXPRESSIONS FOR ATOMIC FLUX

Consider an homogeneous binary alloy of solvent a and solute b. At thermal equilibrium, the atomic flux under an applied electric field E can be related to the driving forces through the phenomenological coefficients L_{ij} as

$$\begin{aligned} J_a &= -L_{aa}\nabla\mu_a - L_{ab}\nabla\mu_b + L_{aa}Z_a^*eE + L_{ab}Z_b^*eE\,, \\ J_b &= -L_{ba}\nabla\mu_a - L_{bb}\nabla\mu_b + L_{ba}Z_a^*eE + L_{bb}Z_b^*eE\,, \end{aligned} \tag{1}$$

and the vacancy flux is

$$J_v = -(J_a + J_b)\,. \tag{2}$$

In Eq. (1), the flux is written explicitly into two parts: The first two terms on the right-hand side are the diffusion contributions due to the concentration gradients, and the others are the electromigration contributions induced by the field E.

Written in this way, μ_a and μ_b are only those parts of the chemical potential associated with the composition of the alloy, and the effective charge Z_i^* is related to the forces from the electric field and electron-wind effect.

One can see from Eq. (1) that, in general, there are additional contributions to the flux of a particular component in the alloy due to the mass flow of the other component. Such contribution is linked to the driving force of the second component through the coefficient L_{ab}; so, in thermodynamics, the origin of such contribution is similar for diffusion and electromigration. This cross-term effect on electromigration is called the "vacancy-flow" effect.[7] This particular term is used because it indicates an extra mass flow of the b atoms, for example, caused by vacancies pushed to them in an opposite direction as a result of the flow of the a atoms. Such an effect influences the flux for both the solute and the solvent atoms, so there are vacancy flow factors for solute and solvent electromigration. From Eq. (1), one can see that the vacancy-flow terms are identical except for the different effective charges, so the absolute magnitude should be comparable for solute and solvent atoms in most cases. On the other hand, since the diagonal term in the solvent flux is much larger than that in the solute flux, the net effect is more significant for solute electromigration.

It is customary to write the electromigration flux in terms of some apparent diffusivity and effective charge, so a modified Nernst-Einstein relation can be used. A natural way would be to express the diffusion part of the flux (J_i^D) in terms of the intrinsic diffusion coefficient and write the electromigration flux (J_i^E) to be consistent with such diffusivity. Unfortunately, such notations are not adopted in the literature.[2] Instead, for dilute alloys, since the diffusivities are usually measured by tracer techniques, the diffusion coefficients used are related to those of the tracers. For dilute alloys, one can show that[8]

$$L_{aa} \simeq \frac{Nc_a}{kT} D_a \quad \text{and} \quad L_{bb} \simeq \frac{Nc_b}{kT} D_b f_b \,, \tag{3}$$

where D_a and D_b are the uncorrelated diffusion coefficients of the solvent and solute atoms, respectively, and f_b, is the solute correlation factor (so $D_b f_b$ equals D_b^*, the tracer diffusivity of the solute). Adopting the diffusivity expressions in Eq. (3), one can write the electromigration flux as

$$J_a^E = \frac{Nc_a D_a}{kT} Z_a^{**} eE \quad \text{and} \quad J_b^E = \frac{Nc_b D_b f_b}{kT} Z_b^{**} eE \,. \tag{4}$$

Here Z_a^{**} and Z_b^{**}, being called as the apparent effective charges, are experimentally measured parameters relating to the actual effective charge as

$$Z_a^{**} = Z_a^* \left(1 + \frac{L_{ab}}{L_{aa}} \frac{Z_b^*}{Z_a^*}\right) \quad \text{and} \quad Z_b^{**} = Z_b^* \left(1 + \frac{L_{ba}}{L_{bb}} \frac{Z_a^*}{Z_b^*}\right) . \tag{5}$$

In Eq. (5), the second term in the large parentheses comes from the vacancy flow effects and Manning[9] designated the ratio L_{ba}/L_{bb} as $2\langle n_p \rangle$ and called it the "vacancy-flow factor" for the solute. Clearly, a similar correction factor exists for solvent atoms. Using Eq. (3), one can show that

$$\frac{L_{ab}}{L_{aa}} = \frac{D_b^*}{D_a} \frac{L_{ab}}{L_{bb}} c_b \,. \tag{6}$$

So, instead of a constant correction as for Z_b^{**}, for Z_a^{**}, the vacancy-flow correction is linearly proportional to the solute concentration. For most substitutional alloys the sign of Z_b^* is expected to be the same as Z_a^*; so whether the vacancy-flow effect would increase or decrease the effective charge depends on the sign of L_{ab}/L_{bb}. This ratio can be positive or negative, depending on the details of the jumping process of the vacancy near the impurity as we will show later.

A good example to apply the above formulation is for electromigration of the tracer matrix atom. In this case, we have $Z_a^* = Z_b^*$ and $1 + L_{ba}/L_{bb} = 1/f_a$; so $Z_b^{**} = Z_a^*/f_a$. This indicates that the apparent effective charge of the tracer is larger than the actual effective charge by a factor equal to the inverse of the correlation factor. However, since there is also a correlation factor in the diffusivity [see Eq. (4)], the migration of the tracer can be considered effectively uncorrelated and with an effective charge equal to that of the host atom. In this sense, the effective charges measured by the tracer and marker motion methods (the latter measures the vacancy flux) should be identical and should both refer to the uncorrelated diffusivity.

To evaluate the solute effect, it is convenient to compare the atomic flux in the alloy to that in the pure solvent. To do so, we note that for dilute alloys

$$D_a = D_a(0)\,(1 + b' c_b) \,, \tag{7}$$

where $D_a(0)$ is the uncorrelated diffusivity of the pure solvent and b' is a constant. Combining Eqs. (4)–(7), one obtains

$$J_a^E = \frac{Nc_a D_a(0) Z_a^* eE}{kT} \left[1 + \left(b' + \frac{D_b^*}{D_a(0)} \frac{Z_b^*}{Z_a^*} \frac{L_{ab}}{L_{bb}}\right) c_b\right]$$

and (8)

$$J_b^E = \frac{Nc_b D_b^* Z_b^* eE}{kT} \left(1 + \frac{L_{ab}}{L_{bb}} \frac{Z_a^*}{Z_b^*}\right) .$$

In comparing the flux in the alloy and pure material, one should take into account the dependence of the alloy resistivity on the solute concentration which usually produces a larger E for the same current density j. In addition, the electron-wind parameter in the effective charge is inversely proportional to the resistivity. For nontransition metals, since electron wind is the dominant driving force, we have $Z_i^* \propto 1/\rho$. As a result, the product of $Z_i^* E$ is expected to be approximately the same for the alloy and the pure solvent at the same j. The following ratios for the atomic velocities and vacancy flux are all referred to the same current density:

$$\frac{v_a}{v_a(0)} \equiv 1 + \alpha_a c_b; \quad \alpha_a = b' + \frac{D_b^*}{D_a(0)} \frac{L_{ab}}{L_{bb}} \frac{Z_b^*}{Z_a^*} ,$$

$$\frac{v_b}{v_a(0)} \equiv \alpha_b = \frac{D_b^*}{D_a(0)} \left(\frac{Z_b^*}{Z_a^*} + \frac{L_{ab}}{L_{bb}} \right) , \tag{9}$$

$$\frac{j_v}{j_v(0)} \equiv 1 + \alpha_v c_b; \quad \alpha_v = \alpha_a + \alpha_b - 1 .$$

III. KINETIC ANALYSIS OF THE SOLUTE EFFECT

To evaluate the solute effect one requires data for Z_a^*, Z_b^*, $D_b^*/D_a^*(0)$, b', and L_{ab}/L_{bb}. While the values of Z_a^* and $D_b^*/D_a^*(0)$ can be measured directly, the other parameters have to be determined according to the frequency ratios of atomic jumps in the kinetic model of impurity diffusion. For fcc lattices, Manning[9] derived the following expression:

$$\frac{L_{ab}}{L_{bb}} = \frac{-2 + \phi\ \omega_3/\omega_1}{1 + \frac{7}{2} F\ \omega_3/\omega_1} , \tag{10}$$

where ϕ and F are both functions of ω_4/ω_0. The various atomic jumps are illustrated in Fig. 1. Doan[2] showed that b' is not exactly the enhancement factor for solvent diffusion as measured by tracer techniques; instead, it should be calculated according to

$$b' = -18 + 4 \frac{\omega_4}{\omega_0} \left(\frac{\omega_1}{\omega_3} + \frac{7}{2} \right) . \tag{11}$$

The frequency ratios required in Eqs. (10) and (11) can be determined by combining data of D_b^*, f_b, and the enhancement factor b measured by the tracer method.[5] There is no need to show in detail the procedures but to list the data required for such analysis in Table I and the frequency ratios so determined in Table II. In Table II, the results of several solutes were analyzed by other authors as indicated. For those solutes, in case that f_b is not available, the Lidiard "weak-binding" approximation[26] that

$$f_b = 1 - \frac{4 f_0}{b + 18} \frac{D_b^*}{D_a^*(0)} \tag{12}$$

is used; thus, a unique set of frequency ratios can be determined. For Fe in Ag, b has not been measured, so Eq. (12) is used to calculate b from the measured f_b.[23] For the solutes in Al, the values of L_{ab}/L_{bb} are obtained by Anthony[27] from the experiment which measures the solute redistribution induced by vacancy flux near sinks, and the b values are estimated from NMR[28] and dislocation-loop shrinkage rate[12] in dilute alloys at 300 °C. The procedure to determine frequency ratios for impurities in Al is different owing to the use of L_{ab}/L_{bb} instead of f_b. The values of ω_3/ω_1 for Zn and Mg in Al are somewhat different here from those given in Ref. 27, since Anthony used the "weak-binding" approximation in Eq. (10) which corresponds to setting $\phi = 3$ and $F = 1$. For Cu in Al, it is impossible to find a set of frequency ratios consistent with the available data, particularly to fit the large value of b; so b' is assumed equal to b in estimating α_a.

In Table III, the results of the solute effect on electromigration are summarized. The values of Z_b^* are calculated from the measured Z_b^{**} according to Eq. (5). The effect due to vacancy flow on solute electromigration can be seen by comparing Z_b^*/Z_a^* to L_{ab}/L_{bb} [see Eq. (9)]. The solute effect on solvent electromigration consists of two terms: b' coming from the enhanced diffusivity and a second term due to the vacancy-flow effect. These two contributions can be compared from values of α_a and b' in Table III. To complete the

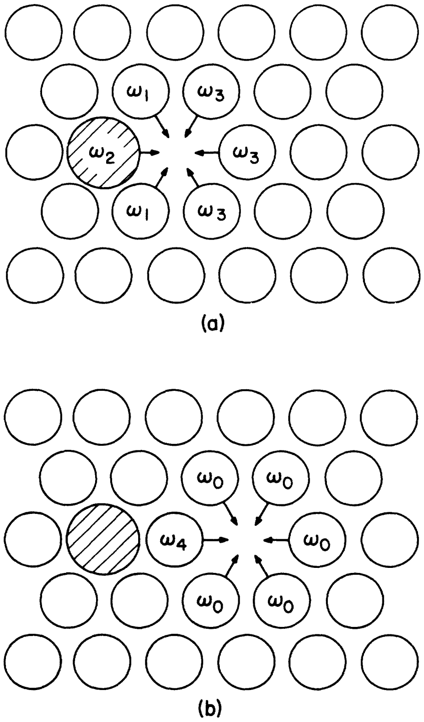

FIG. 1. Vacancy-jumping frequencies for jumps in (111) plane of fcc lattice: (a) vacancy next to solute atom; (b) vacancy dissociated from solute atom.

TABLE I. Data on solute electromigration and diffusion.

Solvent	Solute	z_b	T(°C)	Z_b^{**}	b	$D_b^*/D_a^*(0)$	Refs.
Al $Z_a^*=-17$ (Ref. 10)	Cu	1	585	~ 0	~ 100	0.86	11, 12, 13
	Zn	2	585	−20.5	16	2.56	14, 12, 13
	Mg	2	444	−39	20	4.60	14, 12
Cu $Z_a^*=-8$ (Ref. 15)	Zn	2	894.4	−21	7.2	3.56	16, 17
	Fe	?	1020	−51.8	−5	1.06	18, 19
Ag $Z_a^*=-12.5$ (Ref. 20)	Cu	1	727	−8	8.1	1.1	21, 5
	Zn	2	880	−21	12.7	3.70	18, 22
	Cd	2	727	−20	9.2	3.7	18, 5
	In	3	727	−40	18	5.3	18, 5
	Sb	5	727	−100	65.7	7.6	18, 5
	Fe	?	880	−52.4	−12.9	0.68	18, 23
Au $Z_a^*=-9.2$ (Ref. 26)	In	3	800	−9.3	63.5	8.99	24, 25
	Sn	4	800	−19.4	120	15.8	24, 25

table, α_v gives the change in vacancy flux per atomic percent of solute addition.

IV. DISCUSSIONS

One interesting general feature in the results of Table III is the negative sign of L_{ab}/L_{bb}. This indicates a retarding effect due to vacancy flow on both solute and solvent electromigration [see Eq. (9)]. This is a consequence of the fact that $\omega_3/\omega_1 < 2/3$ for all the solutes analyzed. [From Eq. (10), one sees that $L_{ab}/L_{bb} \leq 0$ if $\omega_3/\omega_1 \leq 2/\phi$; $\phi = 3$ for $\omega_4/\omega_0 = 1$ and $\phi < 3$ for $\omega_4/\omega_0 > 1$.] This result can be understood kinetically by referring to the atomic jumping processes illustrated in Fig. 1. A ω_3 jump dissociates the vacancy from the solute and a ω_1 jump maintains the vacancy-solute pair by having the vacancy jumping around the impurity. The solute would tend to hold up the directional flow of the vacancies if $\omega_3/\omega_1 < 1$, since it attracts the vacancy to stay a little longer around itself instead of kicking the vacancy out immediately along the driving force. The argument is, of course, not complete without considering the tendency for the vacancy to be attracted to the impurity from distant lattice positions which is precisely the reason for the ω_4/ω_0 dependence of the cross term effect.[29]

A negative L_{ab}/L_{bb} makes Z_b^{**} less than Z_b^*, and the difference equals the product of Z_a^* and L_{ab}/L_{bb}. For most of the solutes studied, Z_b^* is a factor of 2 or more larger than Z_a^*, so the vacancy-flow correction is usually about 25%. Cu in Al is an interesting exception since $Z_b^{**} \sim 0$.

Even though the vacancy flow retards the motion of the solute, migration of the solute is still expected to be significantly faster than a solvent atom in the pure material (check α_b in Table III). This is due to the large effective charge and diffusivity of the solute. The former is an indication that electrons scatter the impurity ion at the saddle-point configuration significantly more than the saddle-point solvent ion. It is interesting to examine, from a kinetic point of view, the factors involved in the diffusivity by recalling that[5]

$$\frac{D_b^*}{D_a^*(0)} = \frac{f_b}{f_a}\,\frac{\omega_4}{\omega_0}\,\frac{\omega_2/\omega_1}{\omega_3/\omega_1} . \tag{13}$$

Besides the correlation factors, a high solute diffusivity requires the vacancy not only to be around the impurity more often than away (so $\omega_3/\omega_1 < 1$), but also to have the tendency to jump toward the solute (so $\omega_4/\omega_0 > 1$) and then exchange with high probability (so $\omega_2/\omega_1 > 1$). As seen in Table II, the frequency ratios of all the solutes, except Fe in Cu and Ag, are so combined as to favor a high solute diffusivity. However, the same combination also yields a negative vacancy-flow correction

TABLE II. Jumping-frequency ratios for solute diffusion.

Solvent	Solute	ω_4/ω_0	ω_3/ω_1	ω_2/ω_1	f_b	Remarks and Refs.
Al	Cu	?	0.36	?	?	a
	Zn	1.3	0.27	0.58	0.73	b
	Mg	1.5	0.30	1.22	0.58	b
Cu	Zn	1.2	0.5	2.5	0.47	c, 17
	Fe	0.30	0.095	0.35	0.79	d, 19
Ag	Cu	1.0	0.29	0.29	0.86	d, 5
	Zn	1.3	0.39	1.5	0.57	c, 22
	Cd	1.0	0.26	1.3	0.57	d, 5
	In	1.3	0.30	1.8	0.54	d, 5
	Sb	3.1	0.26	0.70	0.72	d, 5
	Fe	0.17	0.23	1.2	0.59	e
Au	In	3.1	0.21	0.73	0.66	d
	Sn	6.7	0.31	0.90	0.63	d

[a] No consistent set of ratios can be obtained from data.

[b] Ratios determined from b, L_{ab}/L_{bb}, and $D_b^*/D_a^*(0)$.

[c] Analyzed by Manning as quoted in Refs. 17 and 22.

[d] f_b calculated from Eq. (12).

[e] b calculated from Eq. (12) for analysis.

TABLE III. Results on solute effects on electromigration.

Solvent	Solute	Z_b^*	Z_b^*/Z_a^*	L_{ab}/L_{bb}	α_b	b'	α_a	α_v
Al	Cu	−6.8	0.4	−0.4	~0	~100	~100	~100
	Zn	−33.9	2.0	−0.79	2.4	19.5	16.3	17.7
	Mg	−52.4	3.1	−0.79	8.3	23.0	14.2	21.5
Cu	Zn	−23.3	2.9	−0.29	7.3	8.4	6.1	12.4
	Fe	−61.3	7.7	−1.2	5.4	−1.2	−8.9	−4.5
Ag	Cu	−16.1	1.3	−0.65	0.56	9.8	9.1	8.7
	Zn	−27.6	2.2	−0.53	4.9	13.5	10.1	14.0
	Cd	−29.1	2.3	−0.73	4.5	11.4	6.5	10.0
	In	−48.9	3.9	−0.71	13.2	17.5	6.0	18.2
	Sb	−115.0	9.2	−1.2	47.5	73.1	7.5	54.0
	Fe	−58.0	4.6	−0.44	2.2	−12.6	−13.7	−12.5
Au	In	−22.2	2.4	−1.3	7.7	84.4	62.5	69.2
	Sn	−32.6	3.5	−1.4	25.9	162.3	101.8	126.7

to solute electromigration.

About the solute effect on solvent electromigration, it is convenient to separate it into terms due to the enhanced diffusivity (b') and the vacancy-flow correction [the second term of α_a in Eq. (9)]. For dilute alloys both factors are proportional to the solute concentration (the validity of this result is restricted to within the limit of solute solubility). By comparing the values of b' and α_a in Table III, the positive enhancement factor is generally expected to overwhelm the negative vacancy-flow correction, thus leading to an increase of the solvent electromigration. The exceptions are Fe in Cu and Ag, which have unique combinations of the atom jumping-frequency ratios. Comparing to the other solutes in Table II, Fe has a value of ω_4/ω_0 considerably less than unity. This factor when combined with a small ω_3/ω_1 yields a negative b' [see Eq. (11)] and α_a. In fact, α_a is sufficiently negative, so its sum with α_b gives a negative α_v which indicates a reduction in the vacancy flux due to the addition of iron impurities. Such combination of frequency ratios represents an interesting jumping process for the vacancies around the impurities. The value of $\omega_4/\omega_0 < 1$ implies that the vacancy does not prefer the associative jump with the solute; but the fact $\omega_3/\omega_1 < 1$ indicates that once the vacancy-solute pair is formed, the vacancy tends to stay bound. Energetically, this shows the existence of a higher potential barrier[30] for the dissociative jump ω_3 than for ω_1, and the same also for the associative jump ω_4 than for ω_0. The latter situation does not seem to exist for other solutes analyzed here. Judging from the temperature used and the values of the frequency ratios, the difference in the barrier heights is approximately 0.1 eV. This observation refers to the particular temperature used for analysis and may not be valid for other temperatures. Nevertheless, it appears that, kinetically, the reduction of the vacancy flux by solute addition requires some particular combination of frequency ratios for atom jumps which is more restrictive than the intuitive idea of having the vacancies strongly bound to the solutes thus being prevented from migration.

In this paper, we attempt to analyze as many solutes as possible. There are other interesting solutes with electromigration data but lacking diffusion data for analysis, in particular, the transition impurities in Ag.[18] If the behavior of the iron impurity is typical of the transition solutes, it would be very interesting to perform the necessary diffusion experiments so Doan's results can be analyzed. The predicted α_v and α_a have not been measured previously for all the alloys; therefore, it would be of interest to carry out some electromigration measurements of the solvent flux. Such results can also serve as a test for the kinetic model used to analyze the impurity diffusion. For this purpose, In and Sn in Au appear to be good candidates owing to the predicted large α_a and α_v; Sb and Au would also be suitable since there are careful measurements of electromigration.[31]

Finally, it is interesting to compare the results of Cu in bulk Al and in polycrystalline Al films. Our results for bulk electromigration give a large positive α_a and zero α_b, which indicates that Cu would considerably enhance the electromigration of Al but would migrate little itself. Both results disagree with the observation made by Howard and Ross in thin Al films.[6] By forming a Cu-Al region in an Al stripe and observing the formation of hillocks and voids on the alloy boundaries, they showed convincingly that Cu retarded the Al electromigration. Furthermore, a microprobe trace of Cu indicated that Cu migrated considerably along the electron-flow direction. Thin-film experiments are performed at relatively low temperatures, and the results are generally attributed to grain-boundary electromigration. At 300 °C, grain-boundary diffusion is certainly more important in Howard and Ross type experiments than for the bulk measurements at 585 °C. It is therefore significant that the solute effects for grain-boundary electromigration appear to be very different from that for volume electromigration, at least for Cu in Al. In fact, the kinetics must be such that Cu retards the vacancy electromigration at the grain boundaries but enhances it in bulk crystals. The intriguing nature of such solute effects leads to various interesting problems for future studies.

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