

Substituent effects on intermolecular hydrogen bonding from a lattice gas theory for lower critical solution points: Comparison with experiments on aqueous solutions of alkylpyridines

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The lattice-gas models of reentrant phase transitions in binary mixtures with hydrogen bonding, introduced and studied by Walker, Vause, and Goldstein, are shown to be sensitive to subtle changes in the molecular properties of the mixture components. Specifically, the phase equilibria in aqueous mixtures of alkylpyridines (methyl, dimethyl, and ethyl) are matched with the theoretical parameters describing the strength and orientational specificity of the intermolecular hydrogen bonding. The parametric trends are found to agree with those expected from consideration of the electronic and steric effects of *ortho*-, *meta*-, and *para*-alkyl substitution in aromatic compounds. These trends also correlate well with other thermodynamic and kinetic data on these alkylpyridines. Critical exponent renormalization in these systems is also discussed.

INTRODUCTION

Binary liquid mixtures which possess an upper critical solution temperature (UCST) are quite common^{1,2}: Many aromatic molecules in solution with moderately polar solvents show this behavior. The existence of an UCST highlights the competition of favorable intermolecular energetics for like molecules (leading to phase separation at low temperatures) and mixing entropy (the dominant force at high temperatures). Lower critical solution temperatures (LCSTs), on the other hand, can usually be understood in terms of the *orientational* degrees of freedom of the component molecules, in addition to the positional freedom. Many years ago,³ it was suggested that directionally specific interactions, such as hydrogen bonds and dipolar forces, can lead to a macroscopically disordered (compositionally homogeneous) yet microscopically correlated (intermolecularly bonded) system at low temperatures. Such interactions lead to the "freezing out" of orientational entropy, which compensates for the increased mixing entropy below the LCST. Thus, the total entropy of the system, substitutonal + orientational, does decrease monotonically with temperature, satisfying the requirements of thermal stability (specific heat ≥ 0) and the third law of thermodynamics.

Lattice-gas^{4,4} theories of highly directional interactions in binary mixtures have centered around the concept of discretizing the orientational phase space of molecules, and singling out a small subset of the possible configurations of nearest neighbors as energetically more favorable than the rest—the intermolecular hydrogen bond. Such interactions were studied by Barker⁵ and others in the quasicheical approximation, and those theories are capable of producing good agreement with experimentally determined thermodynamic excess functions in polar mixtures, such as acetone + chloro-

form. More recently, the decorated-lattice theories of Wheeler and co-workers⁶ have been shown to be quite successful in describing phase separation in systems with closed-loop phase diagrams (i.e., having both an UCST and LCST, at the extremes of a miscibility gap).

The lattice-gas theories introduced by Walker and Vause,⁷⁻⁹ and further studied by Goldstein and Walker,¹⁰ have been shown to be descriptive of a wide variety of phase transition phenomena. In particular, methods have been developed for mapping experimental data on phase separation, as a function of various perturbations, onto the global phase diagrams of the Hamiltonians studied. Detailed comparisons of the theory to experiments on the effect of electrolytes, dilute third components, pressure, and isotopic substitution have shown that the models are sensitive to small variations in the intrinsic molecular properties which govern the existence of the miscibility gap(s). The parametric trends in these studies are generally in accord with a specific, microscopic description of the important physics in the systems.

In this paper, we extend the comparison of the WV theories to more experimental studies on binary solution phase equilibria. It is shown that the trends in upper and lower critical solution temperatures in a series of aqueous solutions of closely related derivatives of pyridine can be described quite simply by the theories. In particular, the parameters describing the relative strength of the intermolecular hydrophilic and hydrophobic interactions, and the directional specificity of the hydrogen bonding, correlate well with the expected dependence due to substituent effects on the steric and electronic properties of the organic species.

Outline of paper

In Sec. I we briefly review the WV theories and the straightforward statistical mechanical analysis used to approximate the thermodynamic properties. The relevance of the theoretical parameters to actual physical

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systems is discussed. Section II describes the methods of comparison between experimental phase diagrams and the theories, and summarizes the results of comparisons with the experiments on aqueous alkylpyridine solutions. In Sec. III, we describe plausible *molecular* interpretations of the parametric trends, and show that they are in qualitative agreement with experimentally determined thermodynamic and kinetic properties for these systems. Finally, a discussion of critical exponent renormalization in these systems, along with possible experiments, appears in Sec. IV. Section V is a summary of the work.

I. THEORY

The WV theory⁷⁻¹⁰ accounts for the orientational and substitutional degrees of freedom of the molecules in solution by assigning to each site on a d -dimensional hypercubic lattice two spin variables: Spin-1/2 Ising variables $s_i = \pm 1$ (A, B) represent the identity of the molecule in an $A + B$ mixture, while q -state Potts¹¹ model spins $\sigma_i = 1, 2, 3, \dots, q$ represent the discretization of single particle orientational phase space. We consider only pairwise interactions among nearest neighbors, and study the temperature-reduced Hamiltonian

$$-\beta\mathcal{H} = \sum_{\langle ij \rangle} [K_1(1 - \delta_{s_i s_j})\delta_{\sigma_i \sigma_j} + K_2(1 - \delta_{s_i s_j})(1 - \delta_{\sigma_i \sigma_j})], \quad (1)$$

where, as usual, $\beta = 1/k_B T$ (k_B is the Boltzmann constant), $\sum_{\langle ij \rangle}$ is a sum over nearest neighbors, and $\delta_{s_i s_j}$ is the Kronecker delta. (A schematic illustration of the energy levels and their associated degeneracies is shown in Fig. 1 of Ref. 10.) In this simplest version of the WV theory, only hydrogen bonding between unlike components is considered, in the following way: Adjacent, unlike molecules in the same Potts state ($1 - \delta_{s_i s_j} = 1$, $\delta_{\sigma_i \sigma_j} = 1$) are considered to be bonded, and have a favorable energy of interaction K_1 , while nonbonded unlike molecules ($1 - \delta_{s_i s_j} = 1$, $\delta_{\sigma_i \sigma_j} = 0$) have a relatively unfavorable energy K_2 . The zero of energy is taken to be the like-like interactions. While, clearly, there are asymmetries in the actual AA and BB interactions, the simple Hamiltonian in Eq. (1) has been shown⁷⁻¹⁰ to be an accurate description of much of the phenomena in binary mixtures.

The primary feature of this Hamiltonian is that the bonding state K_1 , while most favorable energetically, is entropically disfavored: In order to describe the approximate angle of acceptance of a hydrogen bond,^{12,13} values of q on the order of several hundred are required, and thus the degeneracy of the bonding state, down by roughly a factor of q , is significantly lower than those of the 0 and K_2 levels. Thus, at high temperatures, the only important states are 0 and K_2 , which differ in symmetry essentially only in the ordering of the Ising variables. Hence, at some intermediate temperature, the system changes from paramagnetic (disordered with respect to the Ising variables) to ferromagnetic, meaning phase separated. Only at temperatures down by roughly a factor of $\ln q$ from that of the Ising transition will the K_1 level become important, and then the system mixes to take advantage of the favorable bonding energy.

Thus, two critical solution points appear and therefore a closed-loop phase diagram is generated.

The Hamiltonian in Eq. (1) has been studied by two methods; Migdal-Kadanoff^{14,15} position-space renormalization group theory,^{7,8,16} and a truncated high-temperature series expansion^{9,10} which, to leading order, maps the model onto the spin-1/2 Ising model. As in our previous work,¹⁰ the series expansion approximation is used in comparisons with experiments, since it yields closed-form expressions for the thermodynamic properties of interest and is more amenable to analyzing data. Extensive calculations¹⁶ have shown the two methods to agree with respect to the characteristics of the critical solution points, thermodynamic properties, and parametric trends predicted.

The series expansion analysis of Eq. (1) has been described in detail elsewhere.^{9,10} Therefore, only a brief discussion is given here. Consider the partition function Z for the system

$$Z = \sum_{\{s_i\}} \sum_{\{\sigma_i\}} e^{-\beta\mathcal{H}} = \sum_{\{s_i\}} \sum_{\{\sigma_i\}} \exp \left\{ \sum_{\langle ij \rangle} [K_1(1 - \delta_{s_i s_j})\delta_{\sigma_i \sigma_j} + K_2(1 - \delta_{s_i s_j})(1 - \delta_{\sigma_i \sigma_j})] \right\}. \quad (2)$$

Through a trivial rearrangement, this can be written as

$$Z = \sum_{\{s_i\}} \exp \left[K_2 \sum_{\langle ij \rangle} (1 - s_i s_j) \right] \times \left\{ \sum_{\{\sigma_i\}} \exp \left[-K_2(R+1) \sum_{\langle ij \rangle} 1/2(1 - s_i s_j)\delta_{\sigma_i \sigma_j} \right] \right\} \quad (3)$$

by the use of the identity $1 - \delta_{s_i s_j} = (1 - s_i s_j)/2$, for $s_i = \pm 1$, and using $R = -K_1/K_2$. Performing the sum over $\{\sigma_i\}$ in Eq. (3) and working to leading order in the variable v , where

$$v = e^{-K_2(R+1)} - 1, \quad (4)$$

one finds that the original system is described approximately by an Ising model with a temperature-dependent coupling K_{eff} given by

$$K_{\text{eff}} = \frac{-1}{T} + \ln \left[1 + \frac{1}{q} (e^{(R+1)/T} - 1) \right], \quad (5)$$

using the measure of temperature $T = -1/K_2$. This is an expansion in the variable v/q , which is a small parameter for large T and q , since $v/q \approx (R+1)/qT + \dots$. Because of the original Kronecker delta notation, $K_{\text{eff}} < 0$ for ferromagnetic ordering, and thus for $K_{\text{eff}} < -|K_c|$, the system is phase separated, while for $|K_{\text{eff}}| < |K_c|$, the system is homogeneous (paramagnetic). Here, K_c is the Ising critical coupling in the Kronecker delta notation ($K_c = -0.4434\dots$). As the energy ratio R is increased, for fixed directional specificity to the bonding q , the miscibility gap (difference in critical solution temperatures found from the equation $K_{\text{eff}} = -|K_c|$) shrinks, vanishing for R greater than some critical R . This is reasonable, since in that limit the strong, unlike-molecule attractive bonds always keep the system mixed.

A more convenient way to understand the relevance of the parameters q and R is to discuss the global phase diagram, i. e., the parameter space of Eq. (1). In the

series expansion approximation, two such diagrams, for $q = 500$ and $q = 50$, are shown in Fig. 1. We consider each molecular system to be described by some value of q , and interactions $J_1 = -K_1/\beta$ (< 0) and $J_2 = -K_2/\beta$ (> 0). We choose the temperature scale $T = -1/K_2$, and thus the locus of experimental points for variable temperature is a ray from the origin with slope $-R = K_1/K_2$. High temperatures correspond to points near the origin, and ground states are at infinity. As Fig. 1 shows, for appropriate values of R , the experiment will cross the two-phase coexistence boundary twice (at L and U), and since this boundary is a line of Ising critical points, the crossing points are Ising critical solution temperatures, which is in agreement with theory and experiments on binary mixtures. At still lower temperatures, below the LCST, a transition to an antiferromagnetic (with respect to the Ising variables), ...*ABABABAB*..., ground state occurs. The system can be considered a crystal there, and so the transition is like freezing. In the series expansion approximation,^{9,10} this transition appears as an Ising antiferromagnetic critical point, whereas in the renormalization-group studies,^{7,8,16} it is a $2q$ -state Potts¹¹ transition, which for large q is first order in three dimensions.¹⁷ The first-order nature is in agreement with symmetry considerations regarding freezing.¹⁸

In this paper, we are only concerned with the critical solution points, so this qualitative error in the series expansion is not important.

In the global phase diagrams [Figs. 1(a) and 1(b)], we see that as q increases, the upper boundary of the ferromagnetic region rises, and it is easy to show that its height scales as $\ln q$. Thus, by variation of q and R the critical solution temperatures can be moved over a wide range.

II. COMPARISONS WITH EXPERIMENTS

Andon and Cox¹⁹⁻²¹ have studied the phase equilibria in aqueous solutions of alkyl-substituted pyridines.

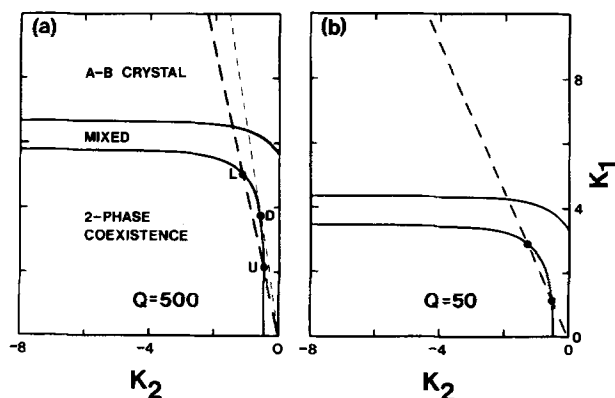


FIG. 1. Global phase diagram obtained in the series expansion approximation, for $q = 500$ (a) and $q = 50$ (b). The height of the two-phase coexistence-mixed (ferromagnetic-paramagnetic) boundary scales as $\ln q$. The rays in (a) and (b) produce critical solution points with a common ratio of LCST/UCST. The light dashed line in (a) indicates the experimental trajectory for a system with a critical double point (D).

TABLE I. Critical solution points in aqueous binary mixtures of alkylpyridines. Data are from Refs. 19 and 21.

Pyridine derivative	LCST(°C)	UCST(°C)
Unsubstituted		Miscible
2-methyl		Miscible
3-methyl		Miscible
4-methyl		Miscible
2,3-dimethyl	16.5	192.6
2,4-dimethyl	23.4	188.7
2,5-dimethyl	13.1	206.9
2,6-dimethyl	34.0	230.7
3,4-dimethyl	-3.6	162.5
3,5-dimethyl	-12.5	192.0
2-ethyl	-5.0	231.4
3-ethyl	-35 (est.)	195.6
4-ethyl	-19.0	181.8

Table I shows the critical solution points for the various methyl and ethyl derivatives. There is clearly a wide variation in the sizes of the miscibility gaps, as the number, position, and size of the alkyl groups are varied.

There are three fundamental parameters in the WV theory; the nonbonded and bonded AB interaction energies J_2 and J_1 , respectively, and the Potts variable parameter q . In principle, the three parameters could be uniquely determined from an experimental closed-loop temperature-composition phase diagram: There is a line in q - R space on which the critical solution temperatures have a given ratio, and further specification of the width of the miscibility gap (the length of tie lines) determines a unique set of parameters. In reality, there are two factors which complicate such a method. First, and most importantly, as with many binary mixtures of water and a larger organic species, the temperature-composition phase diagrams for all of the systems considered here are not symmetric about mole fraction $x = 1/2$, as are the lattice-gas theory predictions in this and previous papers.⁷⁻¹⁰ For the purpose of comparison, we use a symmetrization procedure²² as follows. In analogy to the functional form relating weight fraction w to mole fraction x ,

$$w = \frac{x}{x + p(1-x)}, \quad (6)$$

where p is a ratio of molecular weights, we define a symmetric variable ϕ ,

$$\phi = \frac{w}{w + p'(1-w)}, \quad (7)$$

and choose p' so that ϕ is symmetric. Symmetry means that $\phi = 1/2$ for the average of the weight fractions of A , say, in the coexisting phases. If that average is \bar{w} , then

$$p' = \frac{\bar{w}}{1 - \bar{w}}, \quad (8)$$

and, in general, p' is a function of temperature. While this procedure is useful for comparative purposes, it complicates a determination of trends in q from the various coexistence curves, since each phase diagram must be distorted a different amount to achieve symmetry.

A second complication is that in the theory we find that the maximum width of the coexistence curves is very insensitive to changes in q , for $q \gg 1$. Thus, any type of detailed numerical fitting procedure, even applied to symmetrized $T-x$ phase diagrams, is subject to considerable uncertainty.

The above factors are, in a sense, generic complications to the parameter determination. In the specific experiments considered here, there is the added complication that not all of the coexistence curves are available; instead, for some experiments described below, only the critical solution temperatures are reported.

The method we have chosen to fit the parameters is based on a simplifying assumption arising from microscopic considerations. In a homologous series of alkylated pyridines, we expect that the nonbonded interaction energy J_2 would be the least sensitive of the three parameters to molecular structure variations. Indeed, from thermodynamic data reported in the literature^{28,29} which we discuss later, it is seen that there can be dramatic effects on the steric and electronic properties of pyridine-solvent bonding interactions from varying substituents. Thus, our method of fitting the theoretical parameters is as follows: We choose a reference system for which there is a temperature-composition phase diagram, and transform the plot into a symmetrized graph. A value of q is chosen to give good agreement with the symmetrized curve, and an appropriate value of R for the proper LCST/UCST ratio. We are primarily interested in the trends in the parameters with molecular structure variation, and therefore consider the values of the parameters for the reference system to be suggestive of true interaction properties,

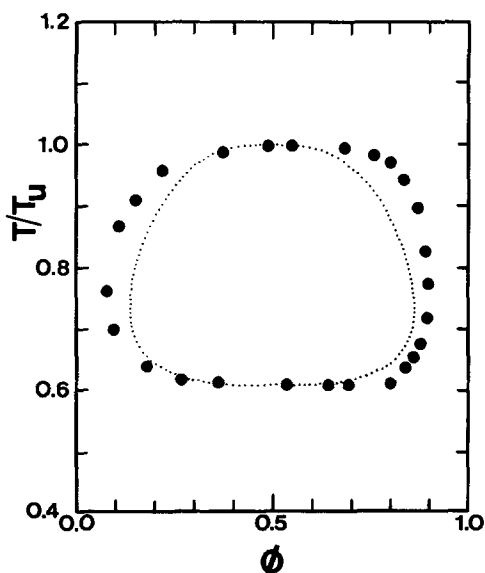


FIG. 2. Symmetrized temperature-composition curve for the system 2,6-dimethylpyridine + H₂O. The symmetrization procedure is described in the text. The dotted line is the lattice-gas calculation in the series expansion approximation, for $q = 500$ and $R = 5,670$. Although the agreement is good, the Migdal-Kadanoff approximation produces wider curves, in better agreement with the data.

TABLE II. Theoretical parameters for nine alkylpyridines which have a miscibility gap in aqueous solutions. The 2,6-dimethylpyridine + H₂O system (4) is the reference mixture. (see the text and Fig. 2). The nonbonding interaction is fixed for all these systems at 0.495 kcal/mol, and therefore the bonding interaction J_1 is just $-RJ_2$. Note how the 2,6-DMP shows both the largest directional specificity (q) and hydrogen bond strength ratio R . Compounds with a single *ortho*-methyl (1,2,3) show roughly the same directionality to the bonding, while those with no such substituent (5,6,8,9) show similar, but definitely lower directionality. These findings are in agreement with simple considerations of substituent steric effects. See the text for further discussion.

Pyridine derivative	q	$\ln(q-1)$	R	J_1 (kcal/mol)
1. 2,3-dimethyl	143	4.96	4.020	1.99
2. 2,4-dimethyl	144	4.96	4.078	2.02
3. 2,5-dimethyl	187	5.23	4.299	2.13
4. 2,6-dimethyl ^a	500	6.21	5.670	2.81
5. 3,4-dimethyl	67	4.19	3.055	1.51
6. 3,5-dimethyl	100	4.59	3.415	1.69
7. 2-ethyl	291	5.67	4.609	2.28
8. 3-ethyl	84	4.42	3.070	1.52
9. 4-ethyl	78	4.34	3.117	1.54

^aReference system.

but by no means definitive. We have chosen the measure of temperature $T = -1/K_2$, and therefore the value of the nonbonding interaction energy is $J_2 = -K_2/\beta = k_B T_u / T_u^*$, where T_u^* is the higher temperature solution to the equation $K_{eff} = -|K_c|$ [from Eq. (5)], and T_u is the actual upper critical solution temperature in K. We then fix the nonbonded interaction J_2 at the reference system value for all other systems, and vary q and R to satisfy two constraints; (i) the calculated ratio LCST/UCST for each system must agree with the experimental data, and (ii) the ratio of the UCST of any given system to that of the reference UCST_{ref} must also agree with the data. In this way, we are able to make a unique determination of q and R for each system, and use the second constraint to link the parameters from one system to the next.

Figure 2 shows the results for the reference system 2,6-dimethylpyridine, using $q = 500$ and $R = 5,670$. This value for q corresponds to an angle of acceptance of $\sim 10^\circ$, a reasonable size for a hydrogen bond.^{12,13} From the series expansion, the value of T_u^* is found to be 2.024, and thus $K_c^* = -1/2.024 = -0.494$, and the nonbonding energy is $k_B (503.9 \text{ K}) (0.494) = 0.495$ kcal/mol. For this system, the hydrogen bond strength is then $-R(0.495) = -2.81$ kcal/mol.

The parameters appropriate to the systems in Table I which show closed loops are collected in Table II. Discussion is reserved for Sec. III.

Andon and Cox¹⁹ have also studied the ternary systems water + base, where base is a mixture of 2,6-dimethylpyridine and either one of the monomethyl pyridines, or unsubstituted pyridine. In their studies, the weight fraction of water in all mixtures was kept constant at 70%, while the ratio of the components of the base was varied. This water fraction was chosen

to be close to both the LCST and UCST critical proportions in the system 2,6-dimethylpyridine + water. Therefore, while the reported solution temperatures are not truly *critical* solution temperatures, and are actually loci of first-order transitions, they are surely close to the CST's, and their trends can be taken to be those of the actual critical solution temperatures. Figure 3 shows the experimental solution temperatures as a function of the weight fraction of 2,6-DMP in the base component of the solution.

Now, the two derivatives of pyridine which comprise the basic component of these mixtures are sufficiently similar that the total solutions can be considered, for certain purposes, to be pseudobinary solutions. By this we mean that the mixture properties would be, in some sense, a compositionally weighted average of the pure component properties (i.e., in solution with water, alone). From a rigorously correct statistical thermodynamic point of view, the description of a three-component system requires a much more general Hamiltonian than Eq. (1). In particular, there must be a chemical potential controlling the density of the third component, along with appropriate component-component interaction terms.²³ Indeed, phenomena can occur in ternary mixtures which are not possible in simple binary mixtures. Many model calculations²⁴ with decorated-lattice theories of three-component systems have indicated several types of critical exponent renormalization which can arise in ternary systems, and there is experimental evidence for this.²⁵ Thus, the use of an effective two-component theory is based primarily on physically reasonable grounds, rather than rigorous proof. As such, caution in certain areas is

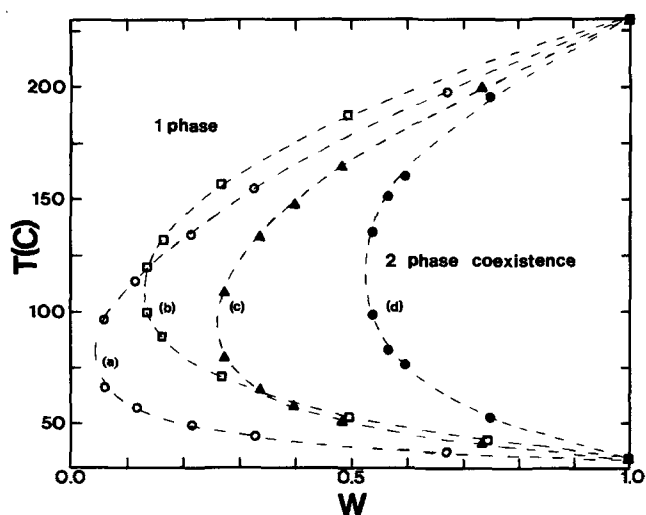


FIG. 3. Solution points as a function of the weight fraction W of 2,6-dimethylpyridine (2,6-DMP) in the basic component of the ternary systems 2,6-DMP + base + water. Here, base is (a) 3-methylpyridine, (b) 2-methylpyridine, (c) 4-methylpyridine, and (d) unsubstituted pyridine. The experimental points shown are not *critical* solution temperatures, since the experiments were done at a fixed composition of water (70% by weight) and the critical composition varies with the base composition. However, they differ little from the CST's. Note that all four of the bases are completely miscible with water. Data is from Ref. 19.

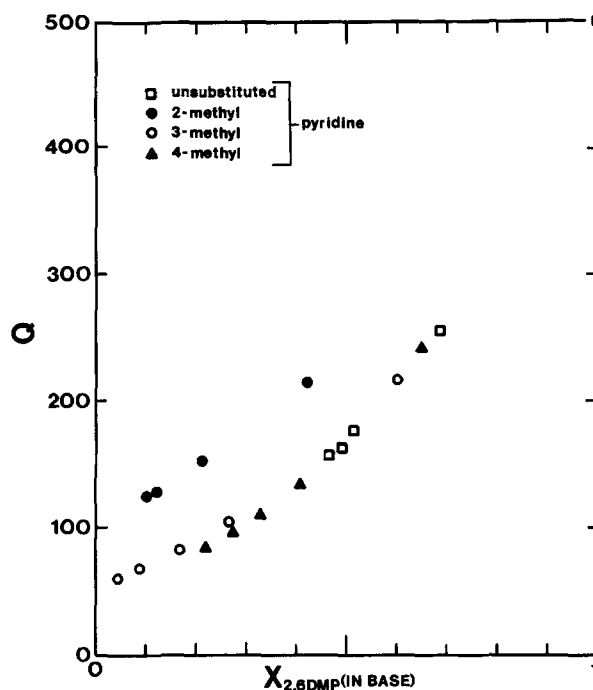


FIG. 4. Composition dependence (on a mole fraction basis) of the theoretical parameter q for the four systems whose solution points are shown in Fig. 3. Note how the 2-methylpyridine systems consistently have a larger q than the other three, which are roughly equivalent. This is consistent with the strong steric effects on intermolecular hydrogen bonding in *ortho*-substituted, rather than *meta*- or *para*-substituted systems.

warranted, but, as discussed below, some interesting questions do arise.

Again, using the reference system 2,6-dimethylpyridine + water, and its value of J_2 , q and R appropriate to each composition of base in the ternary mixtures are determined. The composition dependence of q is shown in Fig. 4, and is clearly smooth, but definitely not linear. However, as Fig. 5 shows, R varies almost perfectly linearly with mole fraction. Since R is related to the relative strengths of the hydrophilic and hydrophobic interactions, this smooth relationship is expected. Since we have held J_2 fixed, and therefore only truly varied J_1 as we change R , this linearity suggests that indeed J_2 is nearly constant. Also shown in the figure is the quantity $\ln(q-1)$ vs $x_{2,6-DMP}$ and it is a linear function of composition. This is easily understood if one considers that the entropy difference between bonded and nonbonded pair configurations is proportional to the difference in the logarithms of their statistical degeneracies.²⁶ Thus, that entropy difference ΔS_{bond} , defined by

$$\Delta S_{\text{bond}} = S_{\text{bond}} - S_{\text{nonbond}}, \quad (9)$$

is

$$\Delta S_{\text{bond}} \sim \ln(2q) - \ln[2q(p-1)] = -\ln(q-1). \quad (10)$$

Thus, the effective entropy of formation is a compositional average. The dashed lines in Figs. 5(a)–5(d) are linear least-squares fits to the calculated parameters. It is significant to note that the values of q vary

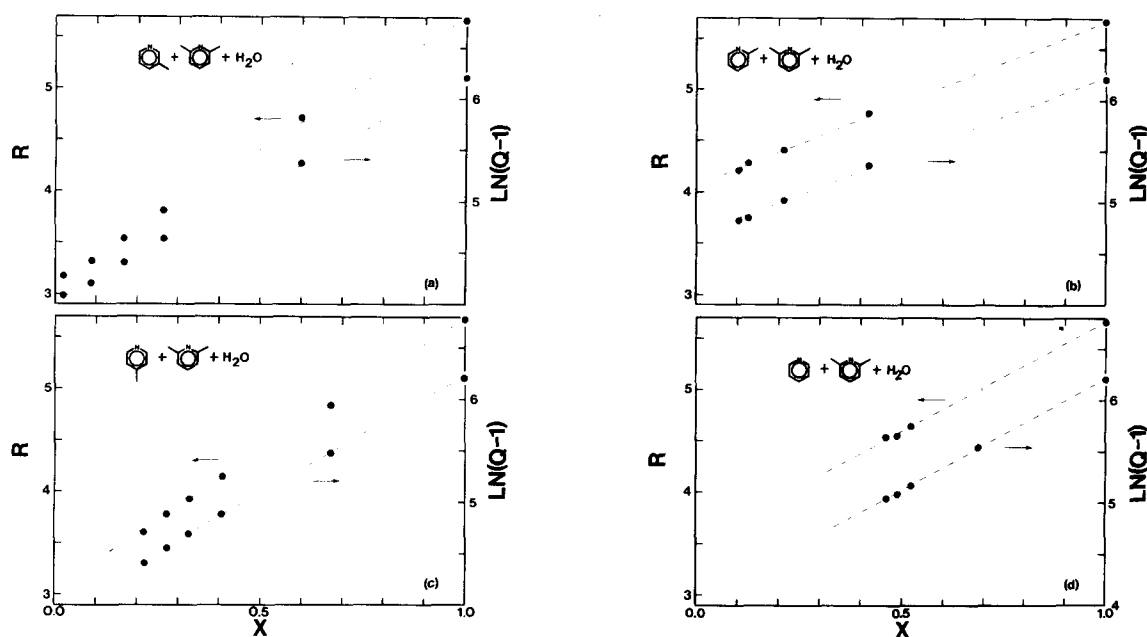


FIG. 5. Composition (x) dependence of R and $\ln(q-1)$ for the four systems 2,6-dimethylpyridine (x) + base ($1-x$) + H_2O (70% by weight in the total solution). Base is (a) 3-methylpyridine, (b) 2-methylpyridine, (c) 4-methylpyridine, and (d) pyridine. The linearity of R indicates that the hydrophilicity/hydrophobicity ratio of the pyridine fraction of the mixture is a composition average of the intrinsic properties of 2,6-DMP and the base. The quantity $-\ln(q-1)$ is essentially the entropy of formation of the intermolecular hydrogen bond, and is also essentially a pure composition average. The dashed lines in (a)–(d) are linear least-squares fits to the calculated parameters.

greatly with composition, over almost an entire order of magnitude, yet $\ln(q-1)$ is almost perfectly linear.

By extrapolating the lines in Figs. 5(a)–5(d) to zero mole fraction 2,6-DMP, the theoretical parameters appropriate to pyridine and the three monomethyl derivatives are determined. Recall that these four bases are miscible in all proportions with water, and yet by this dilution study their properties can be determined. These intrinsic parameters are collected in Table III.

III. INTERPRETATIONS

In this section, we give a molecular interpretation to the dominant parametric trends observed in the match to the experimental results of Andon and Cox. The primary trends observed are related to steric effects on the orientational dependence of the hydrogen bond interaction (the entropy of formation) and the strength of that interaction. Since we have chosen a fixed value for the nonbonding interaction energy, that appropriate to the reference system 2,6-dimethylpyridine, we must exercise caution in interpretations of those trends, since the parameter R is the ratio of bonded to nonbonded interaction energies, both of which, in principle, vary from system to system.

A. Orientational dependence of hydrogen bonds

The most obvious feature of the parameters in Tables II and III is the very high value of the entropy of formation of the hydrogen bonds $[-\ln(q-1)]$ for the 2,6-dimethylpyridine (2,6-DMP) system. This is in keeping with the steric hindrance caused by these bulky groups

directly adjacent to the ring nitrogen. The systems with one *ortho*-methyl group show bonding entropies intermediate between 2,6-DMP and those with no *ortho* substituents. 2-ethylpyridine is found between 2,6-DMP and 2-methylpyridine, and it is reasonable to ascribe this to the larger size of the ethyl group, which places more geometric constraints on the bonding interaction. Finally, all the compounds with no alkyl group adjacent to the nitrogen show approximately the same degree of orientational specificity ($q \sim 70$ –100), in keeping with the fact that the variations within this group are distant from the nitrogen.

It is interesting to point out that the values of q for these systems are such that the actual entropy of for-

TABLE III. Theoretical parameters for molecules which are miscible in all proportions with water, obtained from analysis of the dilution studies data in Figs. 3–5 (Ref. 19). Note that the directionality of hydrogen bonding, as reflected in the values of $\ln(q-1)$, is roughly the same for the three pyridine derivatives with no *ortho*-methyl group. As in Table II, the parameter J_2 is fixed at 0.495 kcal/mol, and $J_1 = -RJ_2$. The 2-methylpyridine shows much higher directionality and higher bond strength. These are explainable in terms of the methyl group's steric effects and electron-donating enhancement of the basicity of the nitrogen.

Pyridine derivative	q	$\ln(q-1)$	R	J_1 (kcal/mol)
1. Unsubstituted	57	4.03	3.520	1.74
2. 2-methyl	108	4.67	4.049	2.00
3. 3-methyl	56	4.02	3.083	1.53
4. 4-methyl	52	3.93	3.063	1.52

mation of hydrogen bonds, $-k_B \ln(q-1)$ is calculated to be in the range of -8 to -12 e.u., which is of the same scale as those determined in experiments on systems similar to those discussed here.^{21(b)}

B. Hydrogen bond strength

With the proviso given above for the interpretation of the trends in the parameter R , given our simplified fitting procedure, we can still make several fairly clear observations concerning the variation in hydrogen bond strength with alkyl substitution. The reference system, 2,6-DMP is distinct from all the others in its extremely large R value (Table II). It is well known²⁷ that substitution of electron donating groups in aromatic systems leads to enhanced electron density at the positions *ortho* to the substitution. A doubly *ortho*-substituted molecule should surely exhibit substantially increased basicity, as our calculations suggest. We find 2,3-DMP and 2,4-DMP to have comparable bond strengths, with the 2,4 isomer stronger. It is suggestive to interpret the slightly weaker 2,3 isomer bond as resulting from the less electron donation from the 3 position, relative to the 4 position. Given our simplifying assumption of constant J_2 , we must conclude that this is probably a fortuitous result. However, see the discussion in the next section for other thermodynamic data supporting this conclusion.

We find the system 2,5-dimethylpyridine to have a larger R and q than the closely related 2,3 compound, and no immediate explanation is clear. Indeed, this may be a system which points out a shortcoming of our parameter-fitting method. Given that this system has a very extended hydrocarbon structure, it may be that its hydrophobic interaction is substantially different from that of 2,6-DMP.

Within the group of the soluble alkylpyridines (Table III) studied by Andon and Cox, we see that 2-methylpyridine has the strongest bonding, as one might expect from electron-donation arguments. The other methyl-substituted systems show R values lower than pyridine itself, and, while it is attractive to consider that this is due to the greater hydrophobic interaction of these systems, a definitive statement is difficult, given our assumption of constant J_2 .

Thus, while one must exercise caution in interpreting the fine details of the parametric trends, it appears that the gross effects of alkyl substitution on the entropy and energy of hydrogen bonding have been described. Further, the linearity of the composition dependence of the parameters in the ternary systems lends support to our interpretation of those parameters, and our treatment of those systems as pseudobinary mixtures.

C. Correlations with other thermodynamic and kinetic data

Brown *et al.*²⁸ and others²⁹ have studied the basicities and rates of reaction of monoalkylpyridines and other derivatives with various molecules. The pKa's, shown in Table IV, show that substitution at the 2 and 4 positions results in enhanced basicity (enhanced electron density

TABLE IV. Basicity and kinetic data for various alkylpyridines, showing the correlation between the position of substitution and enhanced electron density at the nitrogen atom, and on the transition state properties in the reaction with methyl iodide. 2- and 4-methyl and ethyl substitution increases basicity relative to unsubstitution and 3-substitution. *Ortho*-alkyl groups increase the entropy of activation, by increasing the steric requirements of the transition state.

Pyridine derivative	pKa ^a	log A	Reaction with CH ₃ I ^b	
			ΔH^\ddagger (kcal/mol)	ΔS^\ddagger (e. u.)
Unsubstituted	5.17	6.72	13.3	-29.8
2-methyl	5.97	6.46	13.4	-31.0
2-ethyl	5.97	6.31	13.7	-31.5
3-methyl	5.68	6.82	13.0	-29.4
3-ethyl	5.70
4-methyl	6.02	6.86	13.0	-29.2
4 ethyl	6.02
Derivative	pKa		Derivative	pKa
2,3-dimethyl	6.57 ^b		2,6-dimethyl	6.75 ^b
2,4-dimethyl	6.99 ^b		3,4-dimethyl	6.46 ^c
2,5-dimethyl	6.40 ^c		3,5-dimethyl	6.15 ^b

^aReference 28(a).

^b*Handbook of Chemistry and Physics*, 60th ed. (Chemical Rubber, Cleveland, 1979), p. D-162.

^cReference 28(b).

at the nitrogen), while 3-substituents have less of an effect. Further, 2,6-DMP is the strongest base by far, in agreement with its largest value of R .

The data on the thermodynamics of the reaction of the pyridines with methyl iodide is typical of that obtained for a variety of reactants, and brings out the role of steric effects in the series. 2-methyl and 2-ethylpyridine have the largest (in magnitude) entropy of activation, while the 3- and 4-methyl pyridines have comparable ΔS^\ddagger . These two also have the largest enthalpy of activation, indicating a stronger bond. Finally, of the systems with kinetic data shown in Table IV, and with the others reported by Brown *et al.*²⁸ *ortho* substituents have a large effect on the Arrhenius A factors, while *meta* and *para* substituents are very similar, with a lesser effect. This is further evidence for the larger geometric constraints of the *ortho*-substituted systems.

IV. EXPONENT RENORMALIZATION

It has been pointed out⁶⁻¹⁰ that the exponents which describe the power-law singularities of thermodynamic functions at critical solution points are expected to take on renormalized values under certain circumstances. For instance, at the merging of two critical solution points, to form a critical double point, the order parameter exponent β and correlation length exponent ν are predicted to double:

$$\beta_r = 2\beta, \quad (11)$$

$$\nu_r = 2\nu,$$

where the subscript r means "renormalized." This behavior can be understood heuristically by considering the global phase diagram in Fig. 1(a), and an experimental trajectory which is tangent to the "knee" of the

ferromagnetic-paramagnetic phase boundary. Such a path is shown by the light dashed line in the figure. For a small deviation t , along that ray, from the point of tangency (D), the critical surface falls away quadratically, proportional to t^2 , to leading order. Hence, a critical property such as the correlation length, which scales like $t^{-\nu} = [|T - T_c|/T_c]^{-\nu}$, now scales like $(t^2)^{-\nu} = t^{-2\nu}$. Such behavior has been seen in dense gases³⁰ (for the order parameter exponent). Experiments on a liquid crystal system,³¹ in which the addition of a second component causes the merging of two critical points, have detected a doubling of the correlation length exponents. It is also predicted^{10,32,33} that the specific heat at constant composition will be nondivergent at the double point. These conclusions satisfy the exponent hyperscaling relation.¹ The ability to locate the double points in the ternary systems discussed in this paper should allow for an easy verification of these phenomena, by light scattering, phase equilibrium, or calorimetric measurements.

Several others²⁴ have pointed out that in true three-component systems, the exponent characterizing the miscibility gap near the plait point should be renormalized from β to $\beta/(1 - \alpha)$, where α is the specific exponent of the binary system. This renormalization occurs in an isothermal experiment, where the relevant thermodynamic field is basically the chemical potential of the third component, whose presence increases the mutual solubility of the other two liquids.

Our use of a two-component theory to describe approximately these ternary systems will, of course, not predict this. However, it is emphasized that the renormalization discussed in this section occurs at fixed composition, and variable temperature. Still, it would be interesting to see what, if any, renormalization occurs in these pseudobinary mixtures, in both the thermal and composition "directions."

V. SUMMARY

We have shown that the lattice-gas theories of re-entrant phase transitions (i.e., closed-loop phase diagrams) are sensitive to the details of intermolecular interactions in binary and pseudobinary mixtures with homologous compounds. The properties are calculated from the relative values of upper and lower critical solution points, and dilution studies on miscibility. The gross effects of steric hindrance and substituent-enhanced basicity are seen, and are in qualitative agreement with thermodynamic and kinetic data on these systems.

A more probing evaluation of this sensitivity to molecular properties will be possible when the theory is developed to treat asymmetric phase diagrams accurately, as do the decorated-lattice theories of Wheeler *et al.*⁶ Then, it may be possible to make a consistent determination of the model parameters without the assumption of constant hydrophobic interaction energy, as in this work.

The ternary systems are ideally suited to testing the various predictions of critical exponent renormalization at critical double points. In particular, the predicted

nondivergent specific heat would be quite interesting to verify.

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