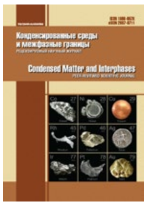

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Azeotropism of clathrate hydrates: a brief overview

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Abstract

Objectives: The objective of this work was to provide a review of the specific features of azeotropism manifestation in hydrate-forming mixtures. The physical basis of azeotropic behavior in clathrate hydrates and its relation to molecular structures and intermolecular forces are analyzed. The influence of hydrate system stability on azeotropic properties is considered, along with the effects of individual component characteristics such as molecular size and structure on azeotropy.

Experimental: Experimental methods for identifying azeotropy in clathrate hydrates are reviewed. Computational approaches to determining the azeotropic point are analyzed, and theoretical predictions are compared with experimental data for known azeotropic hydrates. A concise overview of hydrate-forming mixtures exhibiting azeotropic behavior is also presented.

Conclusions: Possible applications of azeotropic behavior in hydrate systems are discussed, highlighting its significant potential in practical and industrial contexts.

Keywords: Azeotropism, Azeotropic behavior, Azeotropic mixture, Clathrate hydrates, Hydrate-forming

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1. Introduction

The phenomenon of azeotropism, i.e., the ability of certain multicomponent systems to form inseparable boiling mixtures under specific conditions, is typically associated with the formation of associative intermolecular bonds [1]. It is widespread: approximately half of all studied liquid–vapor systems exhibit azeotropic behavior. Although this subject has been widely investigated in the literature [1–6], azeotropism in solid clathrate hydrate solutions remains relatively unexplored.

Azeotropes arise when a mixture deviates from Raoult's and Dalton's laws, which predict the equality of phase compositions and baric conditions, respectively. Such deviations result from physical and chemical effects including dipole–dipole interactions, molecular polarization, differences in van der Waals forces, and hydrogen bonding [6]. These factors can promote molecular association, dissociation, and solvation processes.

According to Konovalov's second law, azeotropic mixtures correspond to the extremal points of isobaric boiling point or isothermal vapor pressure versus composition curves. “Positive” azeotropes are associated with endothermic formation processes, while “negative” ones are exothermic. The decomposition of azeotropes is characterized by opposite enthalpy signs and energy magnitudes an order of magnitude smaller than the heat of vaporization, differing for each specific azeotrope.

Complex azeotropes can exhibit both minimum and maximum boiling points, and so-called “saddle-type” azeotropes do not fall strictly into positive or negative categories. As the boiling point or equilibrium pressure changes, the azeotropic composition shifts accordingly. Vrevsky demonstrated that in systems with vapor-pressure extrema, the azeotrope composition varies with temperature, reflecting a shift in vapor composition at equilibrium.

This implies that, at an azeotropic extremum, increasing the temperature raises the concentration of the component with the higher enthalpy of vaporization, and vice versa. Consequently, variations in thermobaric conditions alter the component concentrations and the azeotropic point itself; in some cases, the azeotropy may even disappear entirely.

Changes in mixture composition due to additional components also influence azeotropic behavior. When a small amount of a nonvolatile component is introduced, its effect depends on its impact on the mixture's vapor pressure. Similar equality effects in equilibrium phase compositions have been observed in crystalline phase–melt [12] and solid adsorbent–solution systems [13].

Clathrate hydrates, in this context, represent an especially intriguing research subject. They are crystalline compounds that form under specific thermobaric conditions from ice-like water molecule frameworks enclosing gaseous or liquid guest molecules in a quasi-liquid state. Owing to their structural and thermodynamic characteristics, clathrate hydrates hold great potential for gas storage, energy transport, and selective separation processes. The present work examines the features and possible applications of azeotropic phenomena in hydrate systems.

2. Azeotropism in clathrate hydrates

The phenomenon of azeotropism in hydrates was first observed experimentally in [15]. That study cast doubt on earlier interpretations by [7], who had considered double hydrogen sulfide hydrates as compounds of constant composition.

When analyzing the physical nature of azeotropy in clathrate hydrates, it is important to note that, in contrast to liquid solutions, intermolecular interactions between guest molecules confined within individual hydrate cavities are limited. If only one molecule is present per cavity, direct interaction between guest molecules is impossible. Instead, guest–host interactions occur between hydrate-forming molecules and the ice-like framework of water molecules through van der Waals forces. The strength of these interactions affects the Langmuir constants of the mixture components, which can be determined either directly using intermolecular interaction potential functions or by simplified empirical methods.

As suggested in [16], a significant difference between the Langmuir constants of two components can lead to azeotropic behavior at corresponding partial pressures P_A and P_B. Qualitatively, at equilibrium the mole fraction of component A in the vapor phase equals that of component B in the hydrate phase:

$$\frac{C_A}{C_B} > 1, \tag{1}$$

$$\frac{P_A}{P_B} < 1. \tag{2}$$

Before proceeding to discuss the specific features and conditions under which azeotropism arises, it is useful to recall that hydrate cavities (Fig. 1) typically comprise 12–20 water molecule tetrahedra with oxygen atoms at the vertices and hydrogen bonds along the edges [17]. Molecules of small characteristic diameter (up to 5.5 Å) can occupy all cavity types, whereas larger molecules (5.5–7.5 Å) are confined to the larger *T*, *T'*, *P*, and *H* cavities.

Among known hydrate structures, the cubic CS-I and CS-II types are the most common, whereas the hexagonal (structure H) occurs less frequently (Table 1). CS-I has a body-centered cubic lattice containing 46 water molecules, comprising two small and six large cavities (Fig. 2). CS-II, with a face-centered cubic lattice of 136 water molecules, contains 16 small and eight large cavities. HS-III consists of 34 water molecules forming three small, two medium, and one large cavity.

The stability of a crystalline hydrate phase depends strongly on the fraction of occupied cavities. When the number of guest molecules is insufficient for a given pressure, temperature, and composition, the hydrate becomes unstable and dissociates. Thermodynamic studies show that hydrates formed from larger guest molecules (e.g., propane) exhibit lower equilibrium dissociation pressures than those formed from smaller ones (e.g., methane). Consequently, hydrates formed from mixed gases have equilibrium pressures closer to those of the component with the lower dissociation pressure.

For instance, a mixture containing 99 mol % methane and 1 mol% propane forms hydrates with a lower dissociation pressure than either pure methane or propane. Several studies have further shown that some ternary mixtures, such as methane–propane–water, exhibit equilibrium pressures even lower than those of the corresponding binary gas–water systems. At 278 K, a 25 mol % methane–propane mixture forms hydrates with a dissociation pressure below that of either pure gas. Propane in the gas phase forms hydrates at a pressure roughly 10% lower than that required for pure propane hydrate formation. In this particular ternary system, an azeotropic composition exists at which the dissociation pressure reaches a minimum compared with both individual hydrates.

The enhanced stability of hydrates formed from certain mixtures, reflected by their reduced

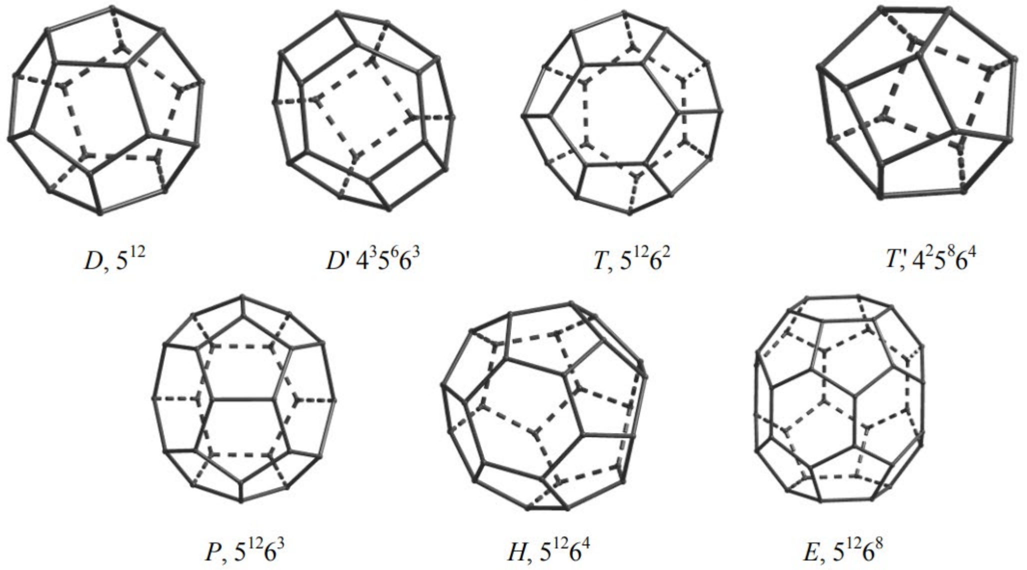

Fig. 1. Polyhedrons of hydrated frameworks – cavities (m^γ – γ faces with the number of edges m)

Table 1. Filling of small and large cavities of hydrate structures KS-I and KS-II with molecules

		Structure of CS-I		Structure of CS-II	
Molecule		Small cavities	Large cavities	Small cavities	Large cavities
Hydrate former	Diameter, Å	Ratio of molecule/cavity sizes			
He	2.28	0.447	0.389	0.454	0.342
H_2	2.72	0.533	0.464	0.542	0.408
Ne	2.97	0.582	0.507	0.592	0.446
Ar	3.80	0.756	0.649	**0.756**	**0.579**
Kr	4.00	0.795	0.683	**0.795**	**0.609**
N_2	4.10	0.815	0.700	**0.815**	**0.624**
O_2	4.20	0.835	0.717	**0.835**	**0.640**
CH_4	4.36	**0.867**	**0.744**	0.867	0.664
Xe	4.58	**0.911**	**0.782**	0.911	0.698
H_2S	4.58	**0.911**	**0.782**	0.911	0.698
CO_2	5.12	1.018	**0.874**	1.018	0.780
N_2O	5.25	1.044	**0.897**	1.044	0.800
C_2H_4	5.50	1.094	**0.939**	1.094	0.838
C_2H_6	5.50	1.094	**0.939**	1.094	0.838
C_2H_2	5.73	1.139	**0.978**	1.139	0.873
c-C_3H_6	5.80	1.153	**0.990**	1.153	**0.883**
C_3H_8	6.28	1.249	1.072	1.249	**0.957**
i-C_4H_{10}	6.50	1.292	1.110	1.292	**0.990**
n-C_4H_{10}	7.10	1.412	1.212	1.412	1.081

* Filling means the impossibility of filling the cavities, no filling and bold numbers correspond to individual, other cases – to mixed hydrates.

equilibrium pressure, results from several competing effects. In propane hydrates, propane molecules occupy only the large cavities of CS-II; the stability of this structure thus depends critically on the filling of these cavities. Methane, having a smaller molecular size, can occupy the small cavities of CS-II and thereby contribute to its stabilization. Reducing the molar fraction of propane in a methane–propane mixture increases the stability of methane hydrates and decreases that of propane hydrates. Under certain conditions, specifically at an azeotropic point, the stabilizing effect of methane exceeds the destabilizing effect of propane, producing an overall pressure reduction required for hydrate formation.

According to [16], hydrogen sulfide can occupy small cavities within the hydrate lattice in double-phase systems. In the CS-I structure, the total contribution of hydrogen sulfide to cavity filling is negligible. In contrast, in CS-II hydrates, larger guest molecules populate the large cavities while hydrogen sulfide preferentially occupies the small ones, thereby enhancing stability through selective cavity occupation.

3. Experimental methods for determining azeotropism in hydrates

The authors of [24] investigated several hydrate-forming systems: methane–propane–water at 275.15 K and 278.15 K; krypton–propane–water at 276.15 K; methane–cyclopropane–water at 277.15 K and 281.15 K; and methane–isobutane–water at 274.35 K. The temperatures were selected to prevent the appearance of a liquid hydrate-forming phase. Azeotropic compositions were identified for methane (0.19 mol%) – propane (0.81 mol%) at 275.15 K and 0.245 MPa, and for

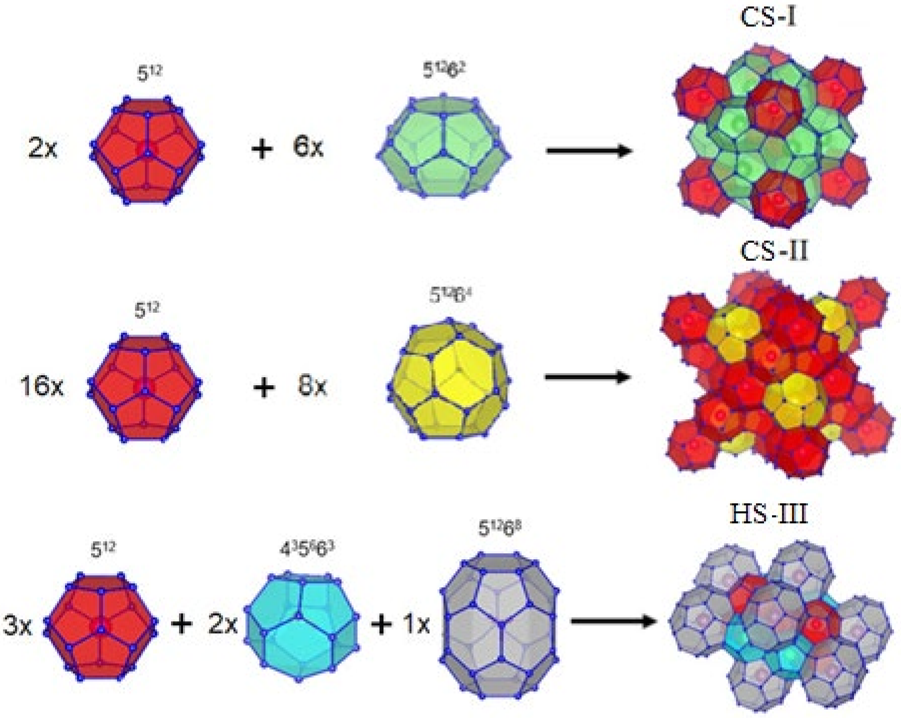

Fig. 2. Elementary cells of hydrate crystal lattices

methane (0.39 mol%) – propane (0.61 mol%) at 278.15 K and 0.458 MPa. Another azeotrope was observed for krypton (0.669 mol%) – propane (0.331 mol%) at 276.15 K and 0.231 MPa.

In [25], they presented the equilibrium conditions for hydrates of the binary mixtures Xe + C_3H_8, Kr + C3H8, and Kr + C_2H_6, for which they determined hydrate azeotrope formation temperatures of 273.5, 276.5, and 278.5 K, respectively.

A study [26] reported azeotropic mixtures of C_2F_6 and N_2 within the temperature range $T >$ 276.5 K. X-ray powder diffraction showed that ternary systems consisting of C_2F_6, N_2, and H2O form hydrates with CS-II for all concentrations of C_2F_6 studied in this experiment. The pressure-composition diagram obtained at two different temperatures (275.15 K and 279.15 K) shows that C_2F_6 is highly enriched in the hydrate phase at 275.15 K, while at 279.15 K, the $C_2F_6 + N_2 + H_2O$ system has an azeotrope with a hydrate composition that is the same as the vapor phase composition.

Experimental data from [24] also showed that methane–propane and propane–krypton systems form hydrate azeotropes in the temperature range 274.15–281.15 K, whereas methane–cyclopropane and methane–isobutane systems do not exhibit azeotropy under these conditions. These findings suggest that azeotropy originates from intrinsic features of hydrate crystal structures rather than from phase imperfections.

In [27], the azeotropic properties of clathrate hydrates formed by hydroquinone (HQ) with guest molecules of carbon dioxide (CO_2) and nitrous oxide (N_2O) were investigated. Structural features of β-HQ clathrates and cavity occupancy were characterized using scanning electron microscopy, X-ray diffraction, infrared and Raman spectroscopy, and solid-state nuclear magnetic resonance. Gas uptake and selectivity between CO_2 and N_2O were determined by gravimetric and concentration analyses of the clathrate phase.

4. Methods for calculating azeotropism in hydrates

The known conditions of the azeotropic state, such as temperature extrema or equality of the compositions of coexisting phases, serve as the basis for determining the composition of an azeotrope at a given pressure.

To evaluate the hydrate composition at the azeotropic point, derivatives of the mole numbers of each component are taken with respect to pressure, while setting the derivative of the chemical potential difference to zero. This ensures the condition of extremum, since the potential difference varies monotonically with pressure at constant temperature.

Following [23], for a system composed of two gases and water, the azeotropic composition can be described by:

$$y_1 = \frac{\gamma - 1 + (\gamma \cdot C_{22} - C_{11}) \cdot P}{\left[C_{11} - C_{12}(\gamma \cdot C_{22} - C_{21})\right] \cdot P}, \tag{3}$$

$$\gamma = \frac{\nu_1}{\nu_1} \cdot \frac{C_{12} - C_{11}}{C_{21} - C_{22}}, \tag{4}$$

where v_1 and v_2 represent the numbers of small and large cavities per water molecule in the hydrate, C_{ji} are the Langmuir constants for the *i-th* molecule and the *j-th* cavity.

The equation shows that the hydrate composition in the azeotropic state strongly depends on the Langmuir constants, which in turn depend on the Kihara parameters of the hydrate formers and the cavity sizes.

To determine whether two hydrate formers are capable of forming an azeotrope, the ratio of their Kihara gas diameters to the cavity diameter is examined. This ratio by itself does not indicate the existence of an azeotropic state in the hydrate but only shows whether two types of gases can be geometrically combined to form an azeotropic mixture.

This ratio indicates geometric compatibility but does not necessarily guarantee azeotropy. Calculations [23] show that each cavity has an optimal ratio of Kihara diameter to cavity diameter of approximately 0.44. Based on this, the authors concluded that a ternary mixture will form azeotropic hydrates only if one of the hydrate-forming molecules has a ratio of large-to-small cavity diameters close to 0.44. Due to the presence of larger guest molecules, the cubic structure II hydrate is generally more stable than structure I; however, under certain conditions, structure I systems may also exhibit azeotropic behavior. Due to the presence of larger guest molecules, the hydrate of CS-II will generally be more stable than CS-I, however, under certain thermobaric conditions, systems with CS-I can also display azeotropic behavior.

Graphical interpolation techniques can be employed to estimate the hydrate composition at the azeotropic point for a fixed temperature. Grapho-analytical verification performed at 273.1 K confirmed azeotropy for several binary hydrate-forming mixtures: $H_2S–CH_4$, $H2S–C_2H_4$, $H_2S–C_2H_6$, $H_2S–CO_2$, and $H_2S–Br_2$. Additional verification for CS-II hydrates, including H_2S–i-C_4H_{10}, $H_2S–CHCl_3$, $H_2S–SF_6$, $C_3H_8–CH_4$, $C_3H_8–C_2H_6$, $C_3H_8–CO_2$, $C_3H_8–Br_2$, and i-$C_4H_{10}–CHCl_3$, showed that only CS-II hydrates containing hydrogen sulfide exhibit azeotropic behavior.

A practical approach for experimentally confirming hydrate azeotropes is the chromatographic method described in [28]. It involves the gradual evaporation of liquid mixtures with helium or hydrogen in a column packed with nonporous material lacking a stationary liquid phase. The presence of azeotropy in a given concentration range can be inferred by comparing the heights of final elution peaks; variations in peak height indicate azeotropic composition.

It is noteworthy that hydrogen sulfide strongly stabilizes hydrate structures due to its positive external electron field when rotating within the cavity [29]. In contrast, carbon dioxide experiences a negative external field, reducing its stabilizing effect.

Alternatively, azeotropic behavior can be predicted using iterative methods for component distribution within the hydrate phase, as proposed in [30]. These methods utilize equilibrium constants and incorporate kinetic factors associated with phase transformation rates.

4. Conclusion

Although the azeotropic behavior of clathrate hydrates presents remarkable scientific and technological potential, the number of published studies remains limited [31–35].

Reference [27] proposed the storage of greenhouse gases in hydroquinone clathrates, which demonstrate strong molecular selectivity over a broad temperature range (up to ~353 K) and at moderate pressures (<1 MPa). For hydroquinone clathrates with the composition 3HQβ·$0.42CO_2$·$0.43N_2O$, the total cavity occupancy was 0.82–0.84. The fraction of cavities filled with CO_2 increased linearly with its concentration in the feed mixture, while the N_2O occupancy decreased correspondingly.

From an industrial standpoint, the separation of azeotropic mixtures is one of the most challenging operations because the components undergo simultaneous vapor–liquid phase transitions. As suggested in [31], hydrate formation can be exploited as an alternative solid–liquid separation mechanism. The feasibility of such hydrate-based separation depends on the hydrate's crystal structure and bonding characteristics. For example, when separating cyclopentane and neohexane, both valuable hydrocarbon components and typical azeotrope formers, the use of hydrate formation enabled the purification of cyclopentane to 98.56 % yield, demonstrating the effectiveness of hydrate-based azeotrope separation technology.

Conflict of interests

The author declares that he has no known competing financial interests or personal relationships that could have influenced the work reported in this paper.

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