

Generalizing Binary Solubility Data for Low-Volatile Liquids in Supercritical Fluids

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Abstract—Experimental data on the binary solubilities of a large number of low-volatile liquids in supercritical solvents (carbon dioxide and propane) are generalized by the entropy method of the similarity theory over wide temperature and pressure ranges. Two groups of similar systems are revealed which correspond to different entropy ranges of the pure solvent. The mechanism of the dissolution of liquids in supercritical fluids was found to be mainly physical.

EXISTING GENERALIZATION METHODS

The key parameters that govern the feasibility of the separation of a mixture by supercritical fluid extraction are the binary solubilities of the components of the mixture in the extractant over a wide range of state variables.

Several approaches to predicting the binary solubilities of liquids in compressed gases are known [1–4]. An expression has been derived [1] for calculating the fugacity coefficients f_i of the components of a mixture with regard for the nonideality of the gas phase:

$$\ln f_i = 2(y_i B_{ii} + y_j B_{ij})/v_m - \ln z_m, \quad (1)$$

where y_i and y_j are the concentrations (mole fractions) of the components; B_{ii} is the second virial coefficient, which accounts for the interaction between identical molecules; B_{ij} is the second virial cross coefficient, which accounts for the interaction between different molecules; and v_m and z_m are the molar volume and the compressibility of the gas phase, respectively. Within the framework of the thermodynamic similarity method, B_{ij} is computed by various relations of the form

$$B_{ij} = \varphi(P_i^{\text{cr}}, P_j^{\text{cr}}, v_i^{\text{cr}}, v_j^{\text{cr}}, \tau_{ij}, \omega_{ij}), \quad (2)$$

where P^{cr} and v^{cr} are, respectively, the critical pressure and the critical molar volume of the component; $\tau_{ij} = T/T_{ij}^{\text{cr}}$ is the characteristic temperature; and ω_{ij} is the characteristic acentricity factor. There is a comprehensive review [2] of methods for calculating the characteristic cross parameters of mixtures, including higher order virial coefficients. ω_{ij} is usually defined as the arithmetic mean of the acentricity factors of the mixture components. It was suggested [1] to calculate the characteristic temperature T_{ij}^{cr} with the use of the empirical binary intermolecular interaction parameter k_{ij} :

$$T_{ij}^{\text{cr}} = (T_i^{\text{cr}} T_j^{\text{cr}})^{1/2} (1 - k_{ij}). \quad (3)$$

A generalized formula for k_{ij} has been derived [1] for the interaction of organic liquids with a compressed gaseous solvent. The formula gives k_{ij} as a function of the number of carbon atoms in the molecule of the dissolved liquid:

$$k_{ij} = 0.0279 \ln n, \quad (4)$$

where n is the number of carbon atoms in the molecules of dissolved n -paraffins, ketones, alcohols, and aromatic hydrocarbons. The interactions of nonpolar molecules with one another and of nonpolar molecules with polar molecules have been considered. The generalized formula is empirical, and the discrepancy between the parameters k_{ij} obtained by experimental data processing and the generalized curve considerably exceeds the experimental error.

The binary solubilities of low-volatile substances, including solids, have been represented [3] as a function of the solvent density:

$$\ln(yP/P^0) = A + B(\rho - \rho^0), \quad (5)$$

where y is the binary solubility (mole fraction), P is the pressure in the system, P^0 is the standard pressure, ρ is the solvent density, and ρ^0 is the standard solvent density. The parameters A and B are interrelated by

$$A = C + \ln(P_v/P^0) + B\rho^0, \quad (6)$$

where P_v is the saturated vapor pressure of the solute at the temperature of the mixture. The temperature and pressure dependences of the parameters A , B , and C near the critical point of the pure solvent are neglected. It is not surprising that the discrepancy between the calculated and experimental values of the binary solubility sharply increases with increasing distance from the critical point of the pure solvent. It would therefore be unreasonable to extrapolate the parameters A , B , and C determined in the immediate vicinity of the critical

point of the pure solvent to a wider range of state variables.

Among the theoretically substantiated methods of predicting the binary solubilities of low-volatile substances in supercritical fluids are the molecular statistical methods [4]. However, the empirical potential functions used in calculations describe the intermolecular force fields only approximately. It is known [5] that, in the neighborhood of the critical point of a pure substance, there is a fluctuation region in which the distribution of fluctuations is non-Gaussian. Between the fluctuation and the regular regions, there is a so-called crossover region, where the substance shows a transitional behavior. The crossover region is also very difficult to describe by molecular statistical methods. Thus, the fluctuation, crossover, and regular regions of states of the fluid phase of a solution are extremely difficult to characterize by a single intermolecular interaction potential function, while deriving an individual function for each of the three regions will mean an empirical approach. Moreover, this approach will lead to the problem of function joining at the region boundaries and, therefore, to a greater error.

ENTROPY METHOD OF GENERALIZATION

Usmanov [6] has described the state of a system by dividing it into several elementary macroscopic subsystems. The state of each equilibrium subsystem can be characterized by some set of thermodynamic state variables and state functions. The state of one of the subsystems has been described [6] in terms of a phase space characterized by a certain probability density ρ , which is a function of the coordinates q_i and the molecular momenta p_i . Let us omit the intermediate computations and write Usmanov's additional similarity condition for molecular transfer processes:

$$\rho(\mathbf{q}, \mathbf{p}) = \text{idem.} \quad (7)$$

This condition means that the molecular processes in geometrically similar systems containing the same number of molecules are similar if and only if, at every moment of time, the probability density fields in the corresponding phase spaces are identical. Condition (7) is necessary but not sufficient. It imposes no requirements on the uniqueness condition, which apparently must take into account the properties of the molecules. The physical mechanism of the equilibrium dissolution of liquids in supercritical fluids ensures the virtually complete reversibility of the process [7]. Therefore, we can eliminate the time factor from our further considerations and obtain the final result with less difficulty. If the state of a subsystem changes, its representative point moves through the phase space along a certain trajectory. If the subsystem is a part of a system that is at thermodynamic equilibrium, the trajectory of the representative point lies within a thin layer near an equipotential surface. Obviously, the equation of motion of the representative point cannot be written in

an explicit form. Since the representative point moves in a varying probability density field and since condition (7) is valid, we can state that the relative velocity of the representative point is determined by the variation of ρ :

$$\bar{U} = \varphi(\text{grad}\rho). \quad (8)$$

As the probability density function, Usmanov [6] has used the canonical Gibbs distribution function

$$\rho = \exp[(F - E)/(kT)], \quad (9)$$

where F is the Gibbs free energy, E is the energy of the subsystem in a given microstate, k is the Boltzmann constant, and T is absolute temperature. The exponent in Eq. (9) can be expressed in terms of the entropy S :

$$(F - E)/(kT) = -S/k. \quad (10)$$

The following similarity equation has finally been obtained [6] for the relative molecular transfer rate:

$$\bar{U} = \varphi[(S_1 - S_2)/R], \quad (11)$$

where R is the universal gas constant.

More recently, Usmanov and his colleagues have successfully applied the entropy method of the similarity theory to generalizing experimental data on molecular heat conduction, viscosity, and diffusion of gases and liquids over wide temperature and pressure ranges.

For supercritical fluid extraction, very weak solutions are of practical interest. The state of such systems is characterized, with a high accuracy, by thermodynamic state variables and state functions of the pure solvent. The driving force of mass transfer of a component of a mixture from one phase into the other is the difference between the chemical potentials of this component in these phases. Under the additional condition of a constant temperature, the difference between the chemical potentials of the component in its two states, μ , is equal in magnitude, but opposite in sign, to the work done in the isothermal reversible transition of one mole of the component from one state into the other [7]. Here, scaling of the mass flux of the solute through the fluid (i.e., determination of \bar{U}) was performed in terms of the isothermal variation of the chemical potential of the pure solvent. The final similarity equation generalizing the solubilities of low-volatile liquids in supercritical fluids has the form [8]

$$\frac{y\Delta\mu}{y_{\Delta S}\Delta\mu_{\Delta S}} = \varphi\left(\frac{S_1 - S_2}{R}\right), \quad (12)$$

where $y\Delta\mu$ is the solute flux through a fluid layer of unit thickness when the entropy change across the layer is $(S_1 - S_2)$ and $y_{\Delta S}\Delta\mu_{\Delta S}$ is the scaled solute flux through a fluid layer of unit-thickness when the entropy change across the layer is ΔS . y and $y_{\Delta S}$ are the averages solubilities of the liquid in the supercritical fluid over the solvent entropy variation ranges $(S_1 - S_2)$ and ΔS , respectively. $\Delta\mu$ and $\Delta\mu_{\Delta S}$ are the changes in the chemical potential that correspond to $(S_1 - S_2)$ and ΔS , respectively.

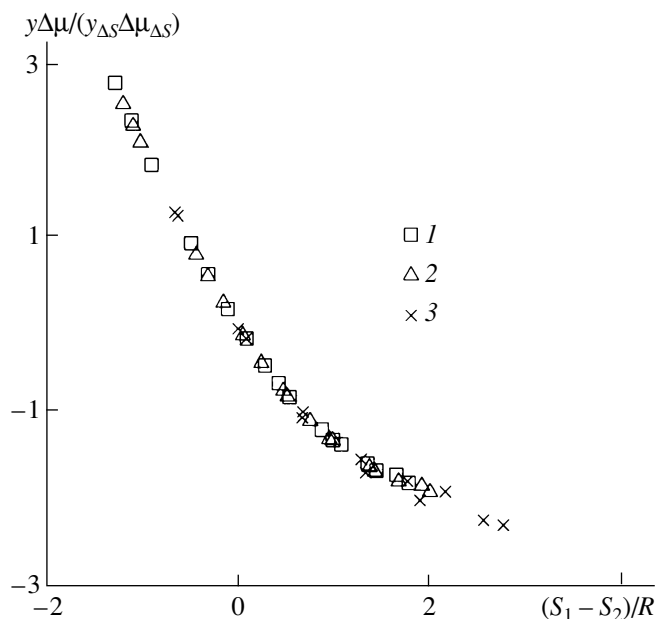


Fig. 1. Generalized binary solubility data for high entropies of a pure solvent (CO_2): (1) styrene, (2) ethylbenzene, and (3) acetophenone.

RESULTS OF THE GENERALIZATION

In this work, we generalize experimental binary solubility data for components of wastewater containing large amounts of hydrocarbons (phenol [9], ethylbenzene [10], styrene [10], acetophenone [11], and water [12]), components of crude glycerol (palmitic acid [13], stearic acid [14], oleic acid [14], and water [12]), and bottom components in triethylene glycol production (ethylene glycol [15], diethylene glycol [15], and triethylene glycol [15]) in supercritical carbon dioxide, and those for triethylene glycol and tetraethylene glycol in supercritical propane [16]. These systems were selected because they are of industrial importance and are very difficult to separate by conventional methods. The thermodynamic functions of carbon dioxide over a wide range of state variables, including the near-critical region, were calculated by Altunin's equation of state [17]. The thermodynamic functions of propane were calculated by the equation of state proposed by Thomas and Harrison [18]. Since the experimental data were obtained for different entropy ranges, we took $S_1 = 4.17 \text{ kJ}/(\text{kg K})$ for ethylbenzene, styrene, and acetophenone; and for the other substances dissolved in carbon dioxide, we accepted $S_1 = 3.3 \text{ kJ}/(\text{kg K})$. For the substances dissolved in propane, we took $S_1 = 5.0 \text{ kJ}/(\text{kg K})$. In all the cases, the solute mass fluxes were scaled over the entropy variation range $\Delta S = 0.1 \text{ kJ}/(\text{kg K})$. Figures 1 and 2 present the results of the generalization for two groups of similar systems. One can see that, in either case, the points representing binary solubilities lie along a single curve. Note that the substances are

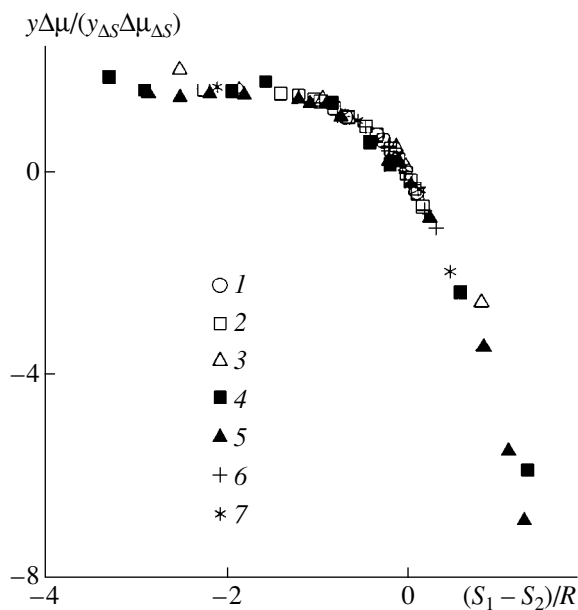


Fig. 2. Generalized binary solubility data for low entropies of pure solvents (CO_2 and C_3H_8): (1) water, (2) phenol, (3) ethylene glycol, (4) diethylene glycol, (5) triethylene glycol (in CO_2), (6) triethylene glycol (in C_3H_8), and (7) tetraethylene glycol.

grouped according to the range of the entropy of the pure solvent rather than their chemical nature. These data suggest that the mechanism of dissolution (including selective dissolution) in supercritical fluids is mainly physical. On the other hand, the evident distinction between the two generalizing curves indicates that, in the entropy ranges considered, dissolution in supercritical fluids proceeds by qualitatively different mechanisms. This inference is consistent with the fact that the thermodynamically rigorous Gibbs–Dalton equation exactly describes the binary solubilities of liquids in compressed gases at low pressures (when rising pressure causes a decrease in the solubility) but is qualitatively valid only for the solubilities at pressures above the critical pressure of the gaseous solvent [19].

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