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ENTHALPY OF PHASE TRANSITION AND PREDICTION OF PHASE EQUILIBRIA IN SYSTEMS OF GLYCOLS AND GLYCOL ETHERS

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Abstract: The PCEAS model was used to study the liquid–solid and liquid–vapor phase transitions at constant pressure in systems containing glycols and glycol ethers. This method is based on minimizing the excess Gibbs energy over the solvation parameter, which takes into account the processes of association of molecules in various phases. To compute the diagrams, the data on enthalpy and phase transition temperatures of pure components are required, while the information about the interactions in the binary system is not necessary. We present analytical expressions for the enthalpy of vaporization and enthalpy of melting of glycols and glycol ethers obtained with the theory of similarity using molecular weight, critical temperature, temperature of the triple point, and the number of carbon atoms in the molecule as the parameters. In the absence of information about the critical temperature, the enthalpy of vaporization may be calculated using the boiling point value. It is shown that the prediction of the enthalpy of melting and enthalpy of vaporization allows us to calculate of the phase diagram, as well as the azeotropic and eutectic parameters in water–glycol ether and glycol ether–alkane systems.

Keywords: modeling, glycol, glycol ether, PCEAS, enthalpy of vaporization, melting enthalpy, thermodynamic similarity, liquid–solid equilibrium, liquid–vapor equilibrium, eutectics, azeotrope

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INTRODUCTION

Glycols and glycol ethers are widely used as additives in food and cosmetics industries. Therefore, systems containing glycols and glycol ethers in mixtures with water, alkanes, and salts are actively studied [1–3]. These systems are the subjects of the current work because experimental and theoretical foundation for their application is lacking. There should be thermodynamic models that would be able to predict properties of pure components and phase equilibrium in systems containing glycols and glycol ethers with high accuracy.

For some of the members of the homology series, enthalpies of vaporization and melting are unknown or have not been measured with sufficient accuracy. In work [4] it has been noted that calculation of the parameters of eutectics and azeotrope mixtures used in technological processes of crystallization and rectification is complicated by the absence of accurate data on enthalpies of phase transitions of individual components.

Boiling temperature T_b and melting temperature T_m, pressure P, density ρ, enthalpy of vaporization ΔH_{vap}, and enthalpy of melting ΔH_m are determinative for computation of thermodynamic properties of pure substances and solutions. Prediction of the compound properties implies that the properties are determined basing on the compound structural formula. The theory connecting the structure of a molecule with its macroscopic parameters is not complete yet; therefore, it is necessary to summarize empirical data on the properties of various compounds. Method of thermodynamics similarity, which is a part of general similarity theory, forms theoretical basis for such a summary [5].

Enthalpy of vapor formation at normal temperature of boilingis called the enthalpy of vaporization. Solid–liquid and liquid–vapor phase transitions proceeding at normal temperature of melting are characterized by enthalpy of melting and enthalpy of vaporization. Methods of group contribution [6, 7] and quantum chemistry [8] are used for predictions.

Enthalpy of phase transition of a pure component may be found from pressure–temperature dependence curve of the two-phase equilibrium, which is expressed as the Clausius–Clapeyron equation:

$$\frac{dP}{dT} = \frac{\Delta H}{T\,\Delta V}, \qquad (1)$$

Provided that the evaporation heat does not depend on the temperature, vapor is considered an ideal gas, the volume of liquid is small compared to the gas volume, and the following equation may be written for the liquid–vapor coexistence curve:

$$\ln P = -\Delta H_{vap} / RT + const$$

If the data on vapor pressure are absent, enthalpy of vaporization may be calculated according to empirical equations, most of which are based on the data on critical parameters of the compounds [9, 10]. Critical properties of many gases and liquids are known or may be computed [11, 12]. In [13], an empirical formula is reported:

$$\Delta H_{\text{vap}} = \Delta H_{\text{tr}} \left[\frac{T_{\text{cr}} - T}{T_{\text{cr}} - T_{\text{tr}}} \right]^{z_{\text{cr}}^2 \left[(T - T_{\text{tr}}) / (T_{\text{cr}} - T_{\text{tr}}) \right]^{z_{\text{cr}}}},$$

where ΔH_{tr} is the enthalpy of vaporization in the triple point; T_{cr}, critical temperature; T_{tr}, temperature of the triple point; z_{cr} , specifies the number of similarity.

In work [13], authors arguethat a wide range of liquids, with the exception of quantum liquids, has a universal behavior on the evaporation curve. The group of substances with similar chemical structure is characterized by similarity parameters that vary upon transition to a different group. Similarity relations are associated with the concept of the critical state. According to the theory of similarity, a system of units is chosen in function of the nature of a subject under study and then the transition is made to non-dimensional, the so-called corrected, values. To perform such a change, that is, to transfer from one system to another, a linear transformation of values is to be done:

$$x_i^{'} = c_{x_i} x_i ,$$

where c_{x_i} is a constant value called the similarity parameter and x_i and x_i' are the respective values.

Laws revealed for one system are correct for a group of similar systems, which allows obtaining information on the properties of unknown systems.

The method of thermodynamic similarity may be briefly characterized as a method of isolating a number of parameters that adequately define the thermal physical properties of a substance. In the cases when the data on critical parameters are absent, it is reasonable to use models allowing to present the enthalpy as a function of the boiling temperature T_{b} and other reliably defined parameters.

Kistyakovsky proposed a rule to define the entropy of vapor formation:

$$\Delta S_{\text{vap}} = \frac{\Delta H_{\text{vap}}}{T_{\text{b}}} = 8.75 + R \ln T_{\text{b}}, \quad (2)$$

which allows to calculate the entropy of vapor formation.

Equation (2) for various types of organic compounds rewritten by Vetere in the form of a function of T_{b} and molecular mass M, as well as other correlations, are reported in [7, 10].

MATERIALS AND METHODS

In the work, molar enthalpy of vaporization ΔH_{ev} at normal boiling point of a pure component for homology series of alkanes, alcohols, acids, glycols, and glycol ethers is expressed as a function of the number of carbon atoms N, relative molecular mass M, normal boiling temperature T_{b}, and the universal gas constant R:

$$\Delta H_{\text{ev}} = \frac{\alpha(N)}{R} \frac{MRT_{\text{b}}}{N} + B(N), \quad (3)$$

where $\alpha(N)/R$ is the determinative parameter of similarity, a non-dimensional coefficient; $B(N) = \beta(N)(-1)^N + \gamma(N)$ is the function introduced for a more accurate modeling of the enthalpy of vaporization for the members of a homology series with even and odd numbers of carbon atoms; and $\beta(N)$ and $\gamma(N)$ are expressed in J/mol.

Table 1 reports the $\alpha(N)$ coefficient of the equation (3) as a function of the number of carbon atoms in a molecule for glycols and glycol ethers, $\beta(N) = \gamma(N) = 0$.

Table 1. Parameters of the equation for calculation of the enthalpy of vaporization of the members of the homology series of glycols and glycol ethers

Homology series	$\alpha(N)$, J/(mol K)
Glycols	$\frac{N(N+1.1)}{1.7(N-1)}$
Glycol ethers	$\frac{N(N+1.1)}{1.15(N-1)}$

Figure 1 presents the experimental data and the results of prediction of the enthalpy of vaporization for a homology series of glycol ethyl ethers.

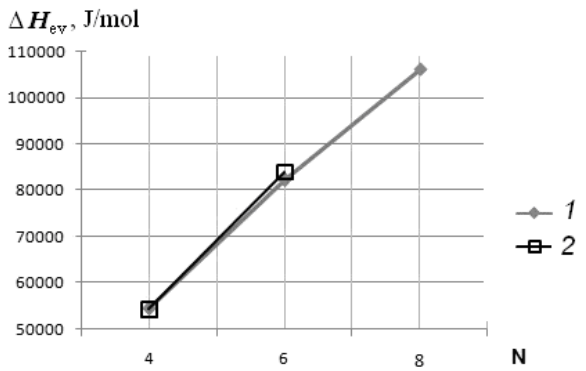

Fig. 1. Enthalpy of evaporation of the homology series of glycol ethyl ethers: *1* – ΔH_{ev}, according to formula (3), and *2* – ΔH_{ev} – the experimental data [14].

The following relation is proposed for these members of different homology series:

$$\frac{\Delta H_n^{\text{ev}} - B_n(N)}{\Delta H_m^{\text{ev}} - B_m(N)} = \frac{\alpha_n(N) M_n T_n^{\text{b}}}{\alpha_m(N) M_m T_m^{\text{b}}}, \quad (4)$$

where $B_i(N) = \beta_i(N)(-1)^N + \gamma_i(N),\ i = n, m.$

To relate the enthalpy of evaporation for different members of the same homology series with the number of carbon atoms N_1 and N_2, the following ratio may be used:

$$\frac{\Delta H_{N_2}^{\text{ev}} - B(N_2)}{\Delta H_{N_1}^{\text{ev}} - B(N_1)} = \frac{\alpha(N_2) M(N_2) T_{N_2}^{\text{b}}}{\alpha(N_1) M(N_1) T_{N_1}^{\text{b}}}, \quad (5)$$

where $\alpha(N_2)/\alpha(N_1)$ is the ratio of the determinative parameters of similarity.

Equation (1) may also be used to determine ΔH_b, but the data on the dependence of melting temperature on the pressure are available for a limited range of pure components.

Enthalpy of melting of a pure component may be presented for a molecule with the number of carbon atoms of N as a function of molar mass M, melting temperature T_m, and the universal gas constant R:

$$\Delta H_m = \frac{a(N)}{R}\frac{MRT_m}{N} + A(N), \quad (6)$$

where $A(N) = b(N)(-1)^N + c(N)$. Here $\alpha(N)/R$ is the determinative parameter of similarity, a non-dimensional coefficient; $b(N)$ and $c(N)$ are expressed in J/mol.

Table 2 provides the coefficients of the equation (3), $a(N)$, $b(N)$, and $c(N)$, as functions of the number of carbon atoms in the molecule. This presentation is not the only one possible and depends on the accuracy of experimental data used to approximate the enthalpy.

Table 2. Parameters of the equation used to calculate the enthalpy of melting of the members of homology series of glycols and glycol ethers

Homology series	$a(N)$, J/(mol K)	$b(N)$, J/mol	$c(N)$, J/mol
Glycols and glycol ethers ($1 \le N \le 10$)	$\frac{N^2+1}{26.5}$	0	–320 N+10755

Figure 2 presents the experimental data and predicted values of the enthalpy of melting for the homology series of glycols.

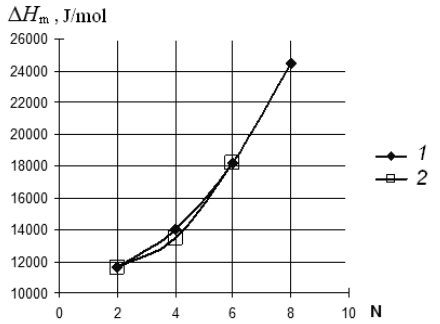

Fig. 2. Enthalpy of melting of glycols: *1* – ΔH_m according to the formula (3) and *2* – ΔH_m, the experimental data [14].

The similarity of the enthalpy of melting taken up to a constant $A(N)$ of the relevant members of homology series of glycols and glycol ethers is considered:

$$\frac{\Delta H_n^m - A_n(N)}{\Delta H_m^m - A_m(N)} = \frac{a_n(N)M_nT_n^m}{a_m(N)M_mT_m^m}, \quad (7)$$

where $A_i(N) = b_i(N)(-1)^N + c_i(N)$, i – series number.

The following ration is true for similarity of the enthalpy of melting between the different members of the same homology series with carbon atom numbers N_1 and N_2:

$$\frac{\Delta H_{N_2}^m - A(N_2)}{\Delta H_{N_1}^m - A(N_1)} = \frac{a(N_2)M(N_2)T_{N_2}^m}{a(N_1)M(N_1)T_{N_1}^m}. \quad (8)$$

Relation (9) allows to calculate of the enthalpy of melting using the known enthalpy of vaporization value:

$$\frac{\Delta H_m - b(N)(-1)^N - c(N)}{\Delta H_{ev} - \beta(N)(-1)^N - \gamma(N)} = \frac{a(N)T_m}{\alpha(N)T_b}. \quad (9)$$

Table 3 presents the relation between the parameters of similarity $a(N)/\alpha(N)$ for such a comparison.

Table 3. Relation between the parameters of similarity for the members of the homology series of glycols and glycol ethers

Homology series	$a(N)/\alpha(N)$
Glycols ($1 \le N \le 10$)	$\frac{(N^2+1)(N-1)}{15.59N(N+1.1)}$
Glycol ethers ($1 \le N \le 10$)	$\frac{(N^2+1)(N-1)}{23.04N(N+1.1)}$

The advantages of enthalpy of melting and enthalpy of evaporization calculations using the formula (4)–(5) and (7)–(8) is the decrease of the effect of systematic measurement errors in the course of molecular mass and melting temperature determination of the homology series members since they form a ratio in the formula (4)–(5) and (7)–(8). Relation (9) does not include molecular mass, which excludes the influence of molecular mass measurement error. Since ratio T_m/T_b is in the right side of the relation, the contribution of systematic error of temperature measurement to the error of enthalpy calculation decreases.

RESULTS AND DISCUSSION

Empirical models for calculation of enthalpy of evaporation and enthalpy of melting based on the data of phase transition temperatures, molecular mass, and the number of carbon atoms in the molecule were proposed. Upon serial application of the similarity theory, critical temperature and triple point temperature are introduced into the system as reducing parameters, allowing for a decrease of the error of determination of the phase transition enthalpy of a pure component to 1–2%.

The method of thermodynamic potentials was used as the mathematical method to study the phase equilibrium in real solutions [15, 16]. Phase chart eutectic and azeotropic systems (PCEAS) [17] is the model of state equation based on the minimization of excess Gibb's energy over the solvation parameter λ, characterizing the ratio of the number of A molecules to the number of B molecules in a compound.

The result of the work is the computation of liquid–solid and liquid–vapor phase equilibrium in binary systems containing glycol ethers using the PCEAS software. Enthalpy of melting and vaporization for glycol ethers necessary for calculation were found using the models proposed in the work. Phase equilibria taking into account association and solvation of molecules were studied under normal atmospheric pressure.

Figures 3 and 4 present the liquidus and solidus in the systems of 2-methoxyethanol–water and 2-methoxy-ethanol–cyclohexane.

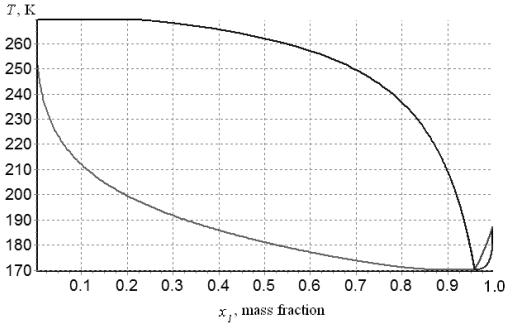

Fig. 3. Liquid–solid phase diagram of the 2-methoxyethanol–water system.

Table 4 provides for the results of calculations of eutectics and azeotrope parameters in systems based on glycol ethers.

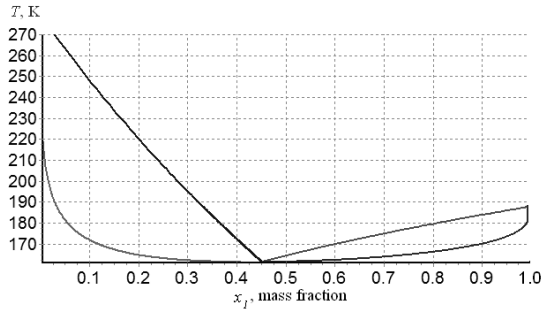

Fig. 4. Liquid–solid phase diagram of the 2-methoxyethanol–cyclohexane system.

Table 4. Computed and experimental eutectics and azeotrope parameters in systems containing glycol ethers

Solution	x_{eut}, mass., comp.	t_{eut}, °C, comp.	q_{az}, mass., comp.	t_{az}, °C, comp.	q_{az}, mass., exp. [18]	t_{az}, °C, exp. [18]
2-methoxyethanol−water	0.959	−102.87	0.21	99.77	0.212	99.75
2-methoxyethanol−cyclohexane	0.452	−111.66	0.09	77.56	0.080	79.80
2-methoxyethanol−heptane	0.404	−102.40	0.18	91.88	0.230	92.50
2-methoxyethanol–octane	0.809	−88.73	0.329	105.59	0.480	110.00
methyl carbitol–water	0.948	−91.09	non-azeotr.	non-azeotr.	non-azeotr.	non-azeotr.
methyl carbitol –undecane	0.959	−85.65	0.340	173.59	0.400 (v.)	178.70
2-ethoxyethanol−water	0.909	−80.57	0.297	99.74	0.300	99.30
2-ethoxyethanol−heptane	0.291	−97.74	0.147	93.69	0.140	94.50
2-ethoxyethanol–octane	0.801	−78.54	0.294	110.11	0.380	116.00
2-ethoxyethanol–nonane	0.606	−79.91	0.462	120.85	0.50	128.00

Figure 5 presents the dependence of boiling temperature on mass fraction of the first component in the 2-methoxyethanol–water system.

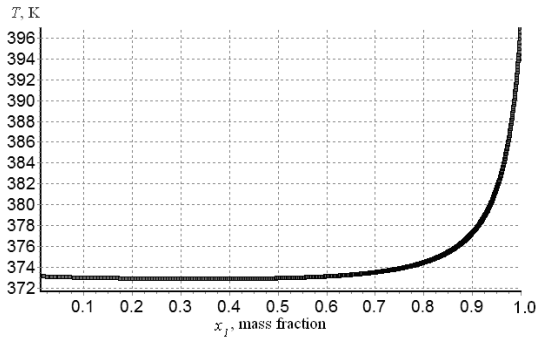

Fig. 5. Liquid–vapor phase diagram of the 2-methoxyethanol–water system.

Results of the calculations reported in Table 4 agree with the experimentally obtained parameters of eutectics and azeotropes [18].

CONCLUSIONS

Predicting thermodynamic parameters of glycols and glycol ethers based on the similarity theory allows to calculate phase diagrams of binary systems for which no experimental data on enthalpy of melting or enthalpy of evaporization of pure components is available. The method can be recommended when selecting components and composition in order to obtain the desired properties of the solution (temperature and enthalpy of melting and vaporization), which will greatly reduce the time and expenses spent on experiments.

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