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FACTOR OF THERMODIFFUSION OF BINARY MIXTURES CONTAINING ALCOHOL VAPOR

A. G. Shashkov,[a] **A. F. Zolotukhina,**[a]
V. B. Vasilenko,[b] **and O. A. Kolenchits**[a]

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Thermodiffusion separation of the binary mixtures of argon with an ethanol, n-propanol, and iso-propanol vapor and the binary mixtures of ethanol with an n-propanol and iso-propanol vapor has been measured in the temperature range 331–347 K by the two-flask method and the thermodiffusion factor has been determined. The experimental values of the thermodiffusion factor have been compared to the results of calculation according to the Chapman–Enskog theory.

Investigation of the temperature dependence of the factor of thermodiffusion of mixtures containing alcohol vapor is of interest from the viewpoint of both obtaining information on intermolecular interactions of substances and using experimental data directly for practical purposes (calculations of technological processes) and scientific developments. In particular, the values of α_T of vapor mixtures are required for determination of the critical supersaturation in investigating the process of volume condensation of the vapor [1].

The results of measurements of the factor of thermodiffusion of the binary mixtures of argon with the vapor of ethyl (CH_3CH_2OH), *n*-propyl ($CH_3CH_2CH_2OH$), and *iso*-propyl ($(CH_3)_2CHOH$) alcohols that were carried out by us in the temperature range 279.5–325.0 K by the two-flask method have been given in [2]. The mixtures with a low concentration of the alcohol vapor (x_2 = 0.01, 0.03, and 0.05) were investigated with the aim of studying nucleation in the supersaturated vapor by the diffusion-chamber method [1].

The present work is a continuation of investigations of the thermodiffusion factor of mixtures containing alcohol vapor. By using the two-flask method [3], here we have extended the temperature range of determination of α_T of the Ar–CH_3CH_2OH, Ar–$CH_3CH_2CH_2OH$, and Ar–$(CH_3)_2CHOH$ mixtures with the aim of approaching diffusion-chamber conditions as close as possible. Measurements of the thermodiffusion separation of mixtures of the same composition as those in [2] were carried out at a constant temperature of the cold volume of a thermodiffuser T_c = 295 K and with variation of the hot-volume temperature T_h from 373 to 413 K. Furthermore, in this work, we have obtained, by the same method, data on the factor of thermodiffusion of the binary mixtures of the vapor of ethyl alcohol with the vapor of *n*-propyl and *iso*-propyl alcohols at the same temperatures T_c and T_h. The molar concentration of the heavy-component vapor in the mixture was equal to x_2 = 0.3, 0.5, and 0.7 at a total pressure of the mixture in the thermodiffuser of $\sim 0.01 \cdot 10^5$ Pa.

The binary mixtures were composed at room temperature according to the partial-pressure method. Chemically pure alcohols and pure (A grade) argon (argon content no less than 0.9999) were used as the components. The concentration of the mixture after its separation was analyzed by the katharometric method.

The value of the factor of thermodiffusion α_T of the binary systems was determined from the relation [4]

$$\alpha_T = \frac{S}{x_1 x_2 \ln (T_h / T_c)}, \quad (1)$$

where $x_2 = 1 - x_1$ and S is the measured value of the thermodiffusion separation of the mixture.

[a]A. V. Luikov Heat and Mass Transfer Institute, National Academy of Sciences of Belarus, 15 P. Brovka Str., Minsk, 220072, Belarus; [b]New Lisbon University, Lisbon, Portugal. Translated from Inzhenerno-Fizicheskii Zhurnal, Vol. 78, No. 3, pp. 82–85, May–June, 2005. Original article submitted July 5, 2004.

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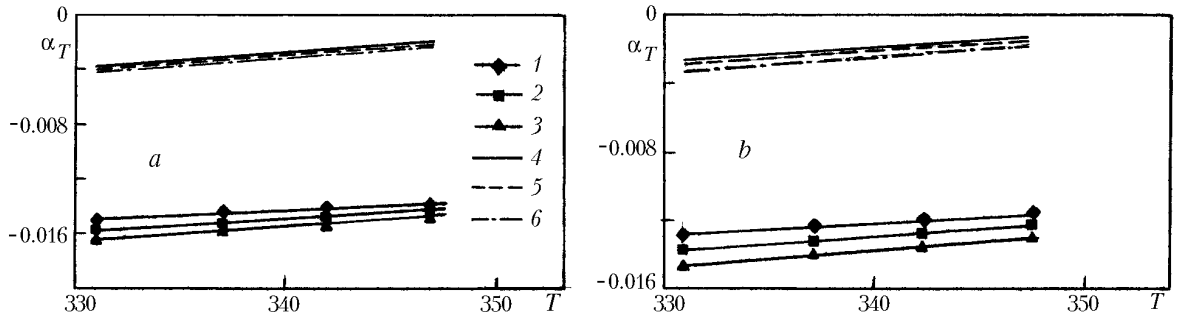

Fig. 1. Factor of thermodiffusion of the alcohol-vapor mixtures ethanol–*n*-propanol (a) and ethanol–*iso*-propanol (b) vs. temperature. The experimental data (curves 1–3) and the results of calculation by the Kihara method (curves 4–6) have been obtained for the following concentrations of the alcohol vapor: 1 and 4) x_2 = 0.7; 2 and 5) 0.5; 3 and 6) 0.3. *T*, K.

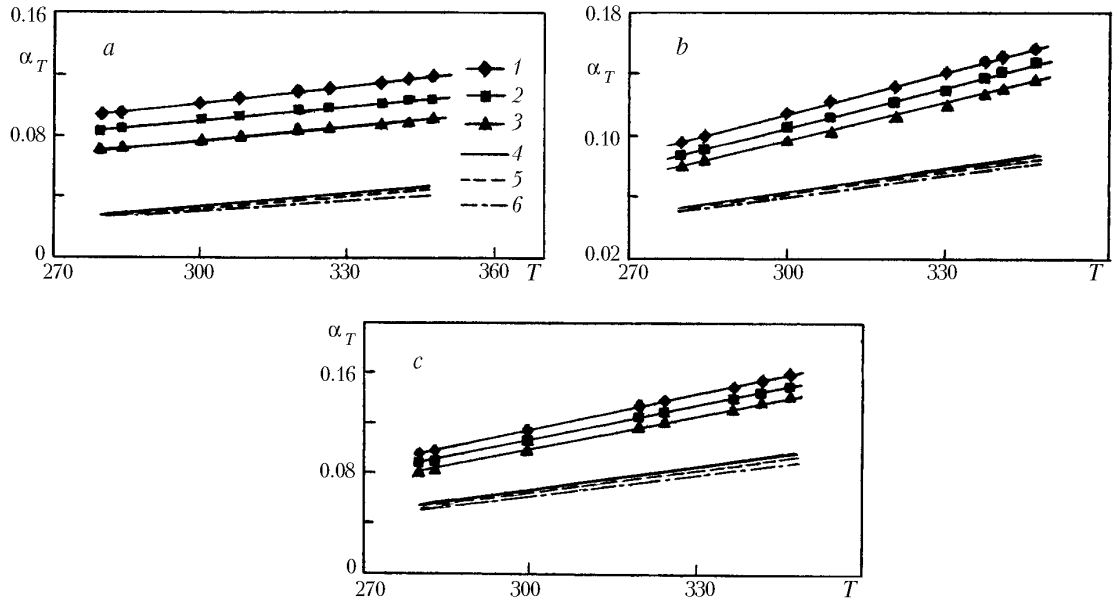

Fig. 2. Factor of thermodiffusion of the vapor-gas mixtures argon–ethanol (a), argon–*n*-propanol (b), and argon–*iso*-propanol (c) vs. temperature. The experimental data (curves 1 and 3) and the results of calculation by the Kihara method (curves 4–6) have been obtained for the following concentrations of the alcohol vapor: 1 and 4) x_2 = 0.01; 2 and 5) 0.03; 3 and 6) 0.05. *T*, K.

The averaged values of α_T were obtained from the results of no less than three experiments for each composition of the mixtures investigated. The error of the experimental data of α_T was estimated at 5–8% for a confidence level of 0.95.

The values of α_T were referred to the average temperature determined by the Braun formula [5]:

$$T = \frac{T_h T_c}{T_h - T_c} \ln \frac{T_h}{T_c} . \qquad (2)$$

Figure 1 shows the experimental dependence of α_T of the binary mixtures of the alcohol vapor on temperature for T = 330.9–347.4 K. Figure 2 gives the experimental values of the thermodiffusion factor of the mixtures of argon with the alcohol vapor, obtained by us in [2] and in the present work, at temperatures T = 279.5–347.4 K.

TABLE 1. Coefficients b_k of the Polynomial (3) Approximating the Dependence of the Experimental Values of α_T of the Mixtures on Temperature

Mixture	x_2	$b_1 \cdot 10$	$b_2 \cdot 10^3$	$b_3 \cdot 10^7$	T, K
CH_3CH_2OH—$CH_3CH_2CH_2OH$	0.7	0.1389	—0.2219	4.089	330—350
	0.5	0.3259	—0.3304	5.608	330—350
	0.3	—0.5181	0.1525	—1.350	330—350
CH_3CH_2OH—$(CH_3)_2CHOH$	0.7	—0.4427	0.1148	—0.624	330—350
	0.5	1.4050	—0.9641	15.055	330—350
	0.3	—0.2207	—0.0644	2.598	330—350
Ar—CH_3CH_2OH	0.01	—1.9551	1.5803	—19.634	280—350
	0.03	—0.9214	0.8753	—9.0026	280—350
	0.05	—0.3790	0.4676	—2.9434	280—350
Ar—$CH_3CH_2CH_2OH$	0.01	—0.8925	0.4382	7.9944	280—350
	0.03	—0.2879	0.04855	13.274	280—350
	0.05	0.7650	—0.6407	23.579	280—350
Ar—$(CH_3)_2CHOH$	0.01	—2.4212	1.4356	—8.0958	280—350
	0.03	—0.8925	0.4213	7.8813	280—350
	0.05	—1.7129	0.9500	—1.3471	280—350

TABLE 2. Force Parameters of the Potential (12-6-3)

Component of the mixture	ε/k, K	σ, nm	δ
Ar	124.0	0.3418	—
CH_3CH_2OH	387.2	0.4821	0.24
$CH_3CH_2CH_2OH$	402.5	0.5241	0.18
$(CH_3)_2CHOH$	387.0	0.5290	0.18

The experimental values of the thermodiffusion factor were processed by the least-squares method. Table 1 gives the coefficients of the polynomial

$$\alpha_T = \sum_{k=1}^{n} b_k T^{k-1}, \tag{3}$$

approximating the experimental dependences of α_T of the investigated mixtures of the alcohol vapor and the vapor-gas mixtures on temperature.

Figures 1 and 2 also give results of the calculation of α_T by the Kihara method of a rigorous molecular-kinetic theory. For the mixtures consisting of polar components (Fig. 1) or containing a polar component (Fig. 2), the thermodiffusion factor was calculated using the potential (12-6-3). For argon we used the potential parameters [5] (Table 2) obtained from the data on viscosity, whereas for the alcohol vapor (Table 2) we used the parameters calculated from the relations [5, 6]:

$$\varepsilon/k = 0.75\, T_{cr}, \ \sigma = (0.013698\, T_{cr}/p_{cr})^{1/3}, \ \delta = \mu^2/(2\varepsilon\sigma^3), \tag{4}$$

where ε is expressed in J, T_{cr} is expressed in K, σ is expressed in atm, and μ is expressed in D (1 D = $3.1623 \cdot 10^{-25}$ $N^{1/2} \cdot m^2$). The data on the critical parameters and on the dipole moments of the alcohols were taken from [7, 8].

As is seen from the figures, the disagreement between the results of experiment and those of calculation is quite considerable for all the mixtures investigated, i.e., theoretical data are capable of describing the experimental dependence $\alpha_T(T)$ only qualitatively. It is noteworthy that the preliminary calculation of this dependence using the force

parameters of the potential (12-6-3) (these parameters were obtained in [9] for the alcohol vapor from the data on viscosity) has shown an even larger disagreement with experimental values. Therefore, we may state that only experiment can be used at present as quite a reliable source of obtaining data on the thermodiffusion factor of mixtures containing polar components: the vapor of ethanol, *n*-propanol, and *iso*-propanol.

NOTATION

b_k, polynomial coefficients; k, Boltzmann constant; p, pressure; S, separation of the starting mixture in the thermoduffuser; T, temperature; x, molar concentration of the components of the starting mixture; α_T, thermodiffusion factor; δ, ε/k, and σ, force parameters of the potential (12-6-3); μ, dipole moment. Subscripts: c and h, cold and hot volumes of the thermodiffuser; 1 and 2, first (light) and second (heavy) components of the binary mixtures investigated experimentally; cr, critical values of temperature and pressure.

REFERENCES

1. A. G. Sutugin, A. A. Lushnikov, and Z. I. Kottsev, Methods of calculation of spontaneous condensation, *Teor. Osnovy Khim. Tekhnol.*, **10**, No. 3, 400–413 (1976).
2. A. G. Shashkov, A. F. Zolotukhina, and V. A. Kurbanov, Experimental study of the thermodiffusion factor of some vapor–gas mixtures with a low concentration of vapor, *Inzh.-Fiz. Zh.*, **43**, No. 2, 320 (1982). (Deposited at VINITI on 30.03.82, rec. No. 1466-82.)
3. A. G. Shashkov, A. F. Zolotukhina, M. F. Laranzheira, V. B. Vasilenko, and M. A. Kuna, An automated setup for investigation of the thermal diffusion and mutual diffusion of gas mixtures, *Inzh.-Fiz. Zh.*, **71**, No. 1, 182–190 (1998).
4. K. E. Grew and T. L. Ibbs, *Thermal Diffusion in Gases* [Russian translation], GITTL, Moscow (1956).
5. J. O. Hirschfeld, C. F. Curtiss, and R. B. Bird, *Molecular Theory of Gases and Liquids* [Russian translation], IL, Moscow (1961).
6. V. E. Alemasov, A. F. Dregalin, A. P. Tishin, and V. A. Khudyakov (Eds.), *Thermodynamic and Thermophysical Properties of Combustion Products: Handbook*, Vol. 1. *Computational Methods* [in Russian], VINITI, Moscow (1971).
7. L. P. Filippov, *Similarity of Properties of Substances* [in Russian], Izd. Mosk. Univ., Moscow (1978).
8. R. C. Reid, J. Prausnitz, and T. Sherwood, *Properties of Gases and Liquids* [Russian translation], Khimiya, Leningrad (1982).
9. E. A. Mason and L. Monchick, Heat conductivity of polyatomic and polar gases, *J. Chem. Phys.*, **36**, No. 6, 1622–1639 (1962).