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An experimental investigation and modelling of the solubility, density and surface tension of 1,1,1,3,3-pentafluoropropane (R-245fa)/synthetic polyolester compressor oil solutions

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Abstract

This paper reports experimental data for the solubility, density and capillary constant for solutions of refrigerant 1,1,1,3,3-pentafluoropropane (R-245fa) with polyolester compressor oil Planetelf ACD 100FY over a wide range of temperatures and concentrations. The experimental data were obtained in the temperature range from 333 to 425 K and at pressures up to 33 bar using static methods. Based on information for the capillary constant, the surface tension of the solutions R-245fa/Planetelf ACD 100FY is determined. The enthalpy of liquid phase of the R-245fa/Planetelf ACD 100FY solutions is calculated. The analysis of the behaviour of the excess thermodynamic functions is carried out. Information about the changing concentration of refrigerant in the liquid phase of the refrigerant/oil solutions (ROS) and in the surface layer of the liquid phase of the ROS at increasing temperature is presented.

Keywords: Adsorption; Capillary constant; Density; Enthalpy; Refrigerant; R-245fa; Oil; Surface tension; Solubility

1. Introduction

Advances in science and technology contribute to the material and technical potential of industrial countries in view of the progressive tendency of environment global degradation. The current international agreements addressing global environmental issues such as Montreal and Kyoto Protocols provide the guidelines needed to ensure that all refrigerant are environmentally safe. The Montreal Protocol has provided a reasonable, orderly and cost-effective replacement of all ozone depleting substances. The new ozone-safe refrigerant R-245fa (1,1,1,3,3-pentafluoropropane, $CHF_2CH_2CF_3$) has been offered recently as a substitute for R-11 (trichloromonofluoromethane, CCl_3F), R-114 (dichloro-1,2-tetrafluoro-1,1,2,2-ethane, $CClF_2CClF_2$) and R-141b (dichlorofluoroethane, CH_3CCl_2F) in the field of air conditioning, especially in low-pressure water chillers, as well as high temperature heat pumps. At the same time the optimal choice of new working fluids for the refrigeration industry is a complex scientific and technological problem. It is necessary to account for the number of contradictory factors, relevant to the ecological, toxicological, technological, thermodynamic and economic aspects. The energetic efficiency of refrigeration systems depends both on the choice of refrigerant and on the optimal choice of compressor oil. The presence of oil admixtures in the refrigerant has a great influence on the thermodynamic properties of the working fluid and thus on the performance of the refrigeration cycle [1–5].

Experimental data and different models for predicting the thermodynamic properties of the refrigerant/oil solution (ROS) are reported in [6–24]. It may be concluded that experimental data for the solubility and viscosity of the ROS can easily be found. At the same time, information on the capillary constant, pseudocritical parameters, density and surface tension for the ROS are practically absent from the existing literature. Different modern models reported in [6–8,13–15,17,18,20,21] have been used for predicting the thermodynamic properties of the ROS. However, the problems in calculating the caloric properties of the ROS remain indeterminate within the frameworks of such

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Nomenclature

a^2	capillary constant (m^2)
$\bar{a}^2$	weighted average value of the capillary constant (m^2)
b	radius of curvature of liquid's meniscus in capillaries (m)
b_R	coefficient in Eq. (1)
B	liquid density amplitude
C_P	heat capacity ($J\,kg^{-1}\,K^{-1}$)
F	crossover function
g	acceleration due to gravity ($m\,s^{-2}$)
h	height of rising (m)
H, ΔH	enthalpy, enthalpy of mixing ($J\,kg^{-1}$)
m	mass (kg)
M	molecular weight ($kg\,mol^{-1}$)
n	refractive index
P	pressure (bar)
R	universal gas constant ($J\,mol^{-1}\,K^{-1}$)
t	reduced temperature
T	temperature (K)
V	volume (m^3)
w	weight concentration
Y	properties

Greek symbols

α_R	Riedel's criterion
β	critical index
μ	dynamic viscosity (Pa s)
ν	kinematic viscosity ($m^2\,s^{-1}$)
ρ	density ($kg\,m^{-3}$)
σ	surface tension ($N\,m^{-1}$)
τ	logarithmic reduced temperature

Subscripts and superscripts

ad	additive property
C	property under critical conditions
i, k	order numbers of capillaries
l	liquid phase
OIL	property of oil
R	property of the pure refrigerant
RSV	reference state value
S	property of the ROS under saturation conditions
v	vapor phase
‾	property '‾' is the pseudoproperty

models. It should be emphasized that information about caloric properties of the ROS is important for the proper calculation of the refrigeration cycles when compressor oil admixtures are taken into account.

Analysis of papers, where experimental data for the ROS was presented [9–12,16,17,19,20] indicates that the "stable" time-invariable values of the investigated parameters can be determined for thermodynamic functions measured by dynamic methods (for example, the circulation method used in [17]). The same "stable" time-invariable values can be obtained in conditions of constant stirring of the sample investigated in the experimental cell. However, these "stable" values of the thermodynamic properties may significantly differ from the proper values. The deviation of the values of thermodynamic functions in "stable" equilibrium from the proper values also depends on the temperature, the viscosity of the liquid solution, the concentration of the ROS and the intensity of stirring. As mentioned in previous papers [22–24], the uncertainties of the experimental data for thermodynamic properties of the ROS depend on the correct estimation of thermodynamic equilibrium in the experimental cell at the different parameters. The resulting problem is the change of the concentration of the liquid phase of the ROS at isochoric increase of temperature of a two-phase sample in the experimental cell. The change of the concentration of the ROS will be larger at the increasing of the vapor phase of the sample investigated [22,24]. This fact should be considered when analyzing the experimental data. It is well-known that for an experimental cell which contains ROS, the time taken to establish thermodynamic equilibrium at constant temperature can be defined by the rate of the diffusion processes between the vapor phase (which consists virtually of pure refrigerant) and the liquid solution (which consists of refrigerant and compressor oils) [25]. Despite multiple investigations of the thermodynamic properties of the ROS [6–23], the question of the difference between the concentration of the surface layer of the liquid phase and the concentration of the liquid phase of the ROS still remains poorly investigated. It should be pointed out here that many questions related to experimental investigation of the systems refrigerant—compressor oil were discussed in detail by the authors in [24].

2. Results and discussion

In this paper we measure the solubility, density and capillary constant of the solutions of R-245fa with polyolester compressor oil Planetelf ACD 100FY in a glass experimental cell using static methods without stirring of the refrigerant/oil solution (ROS) at the moment of measurement. A schematic outline of the experimental setup is given in Fig. 1.

Initially, we performed an experiment for determination of the critical solubility (liquid–liquid equilibrium) for the ROS R-245fa/Planetelf ACD 100FY. The critical solubility has a greater importance at the designing of the refrigeration system. As can be seen from Fig. 2 R-245fa dissolves well in the compressor oil Planetelf ACD 100FY at the temperature and concentration range which is typical for operation of the heat pump.

As was discussed above, the main problems in experiment are related to complex physical–chemical phenomena in relation to the establishment of thermodynamic equilibrium in the experimental cell. We found that the time taken to establish thermodynamic equilibrium depends on the concentration of ROS and the temperature level and may exceed 4–6 h. The question of the establishment of thermodynamic equilibrium in the experimental cell was discussed in detail in [24].

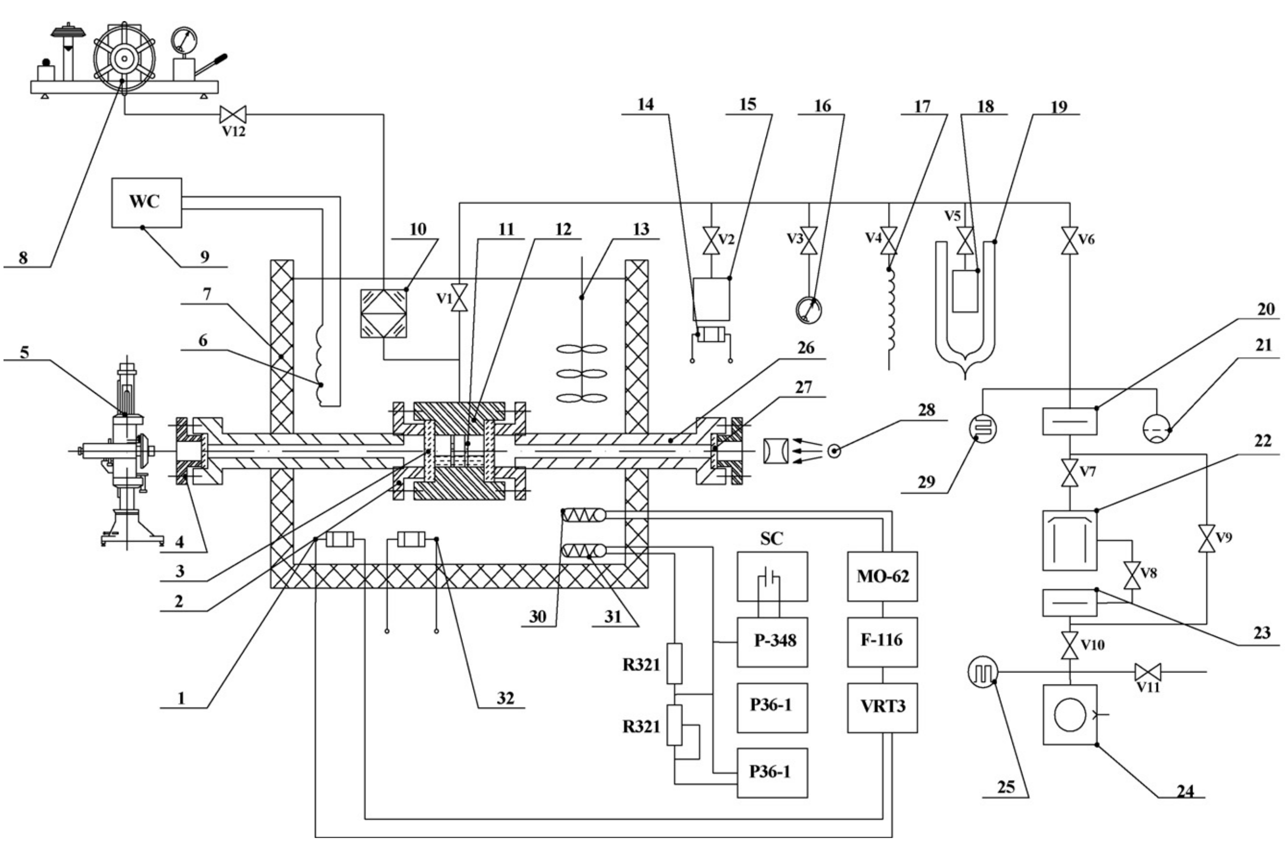

Fig. 1. Schematic of experimental set-up for investigation of the solubility, density and capillary constant of the ROS. (1) Sub-heater; (2 and 4) flanges; (3 and 27) quartz windows; (5) cathetometer; (6) heat exchanger; (7) thermostat; (8) deadweight pressure gage MP-60; (9) water cooler; (10) membrane null-indicator; (11) cassette with capillaries; (12) experimental cell; (13) stirrer; (14) electric heater; (15 and 18) balloon with refrigerant; (16) standard manometer; (19) Dewar vessel; (20 and 23) vacuum trap; (21) ionization gage; (22) diffusion pump; (24) fore pump; (25 and 29) thermocouple vacuum gauge; (26) watch tubes; (28) lamp; (30) thermometer of the temperature control system; (31) platinum resistance thermometer; (32) main heater.

Adsorption between liquid and gas on the phase boundary in the capillaries filled by the ROS has significant influence on the diffusion processes. Therefore, the capillary constant will depend not only on the composition of the liquid phase of the ROS but also on the composition of the surface layer that will be enriched with R-245fa. It may be assumed that an excess of R-245fa in the surface layer leads to decreases of the capillary constant and surface tension of the ROS (Figs. 3 and 4). As follows from (Fig. 3) small admixtures of R-245fa lead to significant decreases of the capillary constant of the ROS.

It might be explained by fact that the adsorption of the low-boiling component will be so intensive that the surface layer of the ROS will consist almost entirely of molecules of R-245fa. As a result, the concentration dependence of the capillary

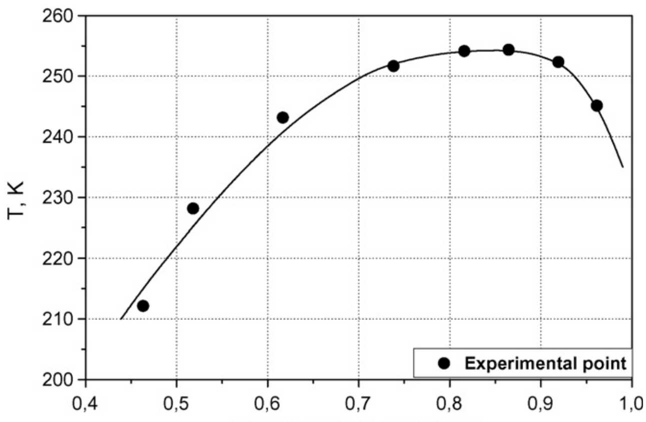

Fig. 2. Liquid–liquid equilibrium of the R-245fa with polyolester compressor oil Planetelf ACD 100FY.

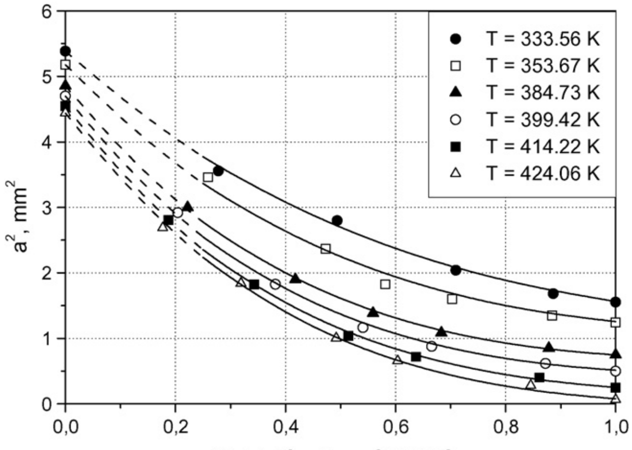

Fig. 3. Concentration dependencies on the capillary constant for the ROS R-245fa/Planetelf ACD 100FY.

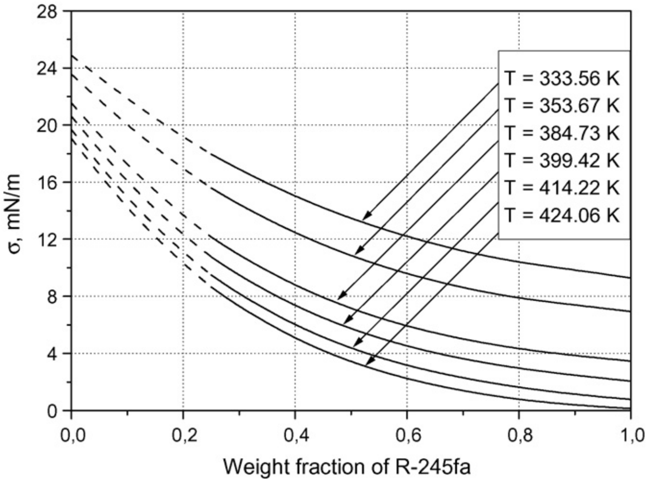

Fig. 4. Concentration dependencies the surface tension for the ROS R-245fa/Planetelf ACD 100FY.

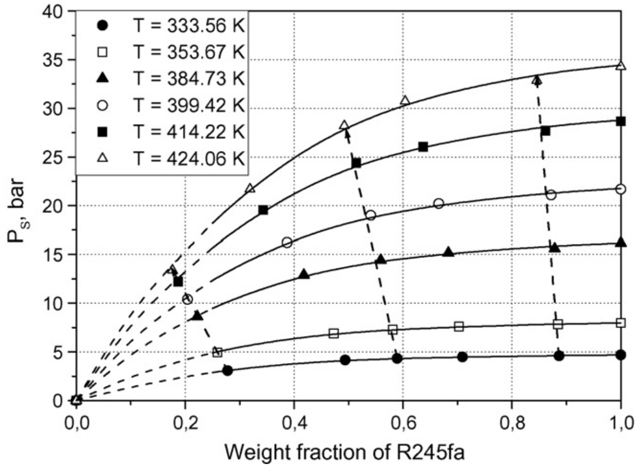

Fig. 5. Concentration dependencies the vapor pressure for the ROS R-245fa/Planetelf ACD 100FY.

constant of the ROS demonstrates flat behaviour. It can be seen in Fig. 3, especially in the concentration range $0.6 \leq w_R \leq 1.0$. Such behaviour is also typical for the surface tension of the ROS with a high concentration of refrigerant (see Fig. 4).

Concentration dependencies for the vapor pressure and density of R-245fa/Planetelf ACD 100FY are shown in Figs. 5 and 6. Analysis of experimental data obtained pointed to significant change of the concentration of the liquid phase of the ROS at increasing temperature of the sample in the experimental cell (Fig. 5). It is obvious that the change of the concentration will be more significant for ROS with a low concentration of refrigerant. The similar behaviour was observed for the system isobutane-mineral compressor oil [24].

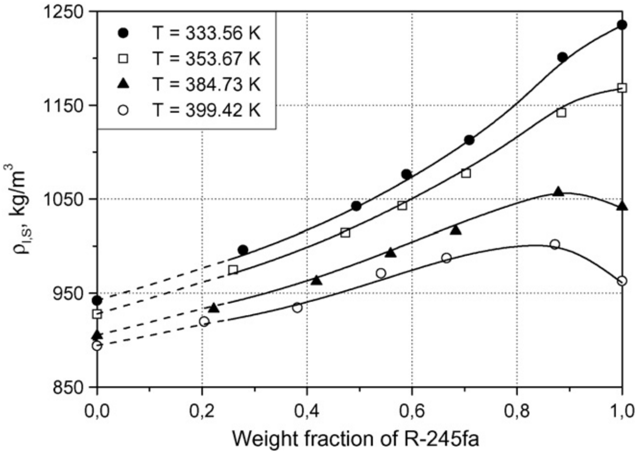

Fig. 6. Concentration dependencies the density for the ROS R-245fa/Planetelf ACD 100FY.

Table 1
Physical–chemical properties of the polyolester compressor oil Planetelf ACD 100FY

Properties	Values
Acid number, KOH for 1 g	<0.1
Flash point in open crucible (more than)	543.15 K
Solidification temperature	240.15 K
Pseudocritical temperature[a]	807 K
Pseudocritical pressure[a]	8.0 bar
Metal corrodibility in compressor oil	Negative
Water content	<50 ppm
Content of mechanical admixtures	Absent

[a] The pseudocritical temperature and pressure for polyolester compressor oil Planetelf ACD 100FY were experimentally determined by the method of pulse heating [30].

Thermodynamic and physical-chemical properties of the compressor polyolester oil Planetelf ACD 100FY are listed in Tables 1 and 2. Experimental data for the vapor pressure, density, capillary constant and surface tension of the ROS R-245fa/Planetelf ACD 100FY are summarized in Table 3.

The experimental data for the density and vapor pressure of the ROS R-245fa/Planetelf ACD 100FY were described using

Table 2
Thermophysical properties of the polyolester compressor oil Planetelf ACD 100FY

T (K)	n	a^2 (mm^2)	ρ (kg m^{-3})	σ (mN m^{-1})	ν ($\times 10^{-7}$ m^2 s^{-1})	μ ($\times 10^{-5}$ Pa s)
270	1.4645	6.032	988.908	29.251	287.42	2842.31
280	1.4611	5.931	981.528	28.546	107.7	1057.08
290	1.4577	5.830	974.179	27.850	46.83	456.16
300	1.4543	5.728	966.855	27.157	22.99	222.31
310	1.4509	5.626	959.550	26.472	12.48	119.75
320	1.4475	5.524	952.258	25.795	7.36	70.06
330	1.4441	5.421	944.974	25.120	4.65	43.90
340	1.4407	5.318	937.692	24.453	3.11	29.12

Table 3
The experimental results for the vapor pressure, density, capillary constant and surface tension of the ROS R-245fa/Planetelf ACD 100FY

T (K)	w_R, R-245fa (initial[a])	w_R, R-245fa (corrected[b])	P_S (bar)	$\rho_{l,S}$ (kg m^{-3})	a^2 (mm^2)	σ (mN m^{-1})
333.56	1.0000	1.0000	4.689	1235.70	1.608	9.542
333.66	0.8898	0.8866	4.602	1205.20	1.684	9.744
333.56	0.7186	0.7094	4.490	1112.71	2.039	10.880
333.53	0.6010	0.5894	4.338	1076.42	-	-
333.53	0.5235	0.4939	4.172	1042.41	2.797	13.988
333.54	0.3093	0.2781	3.074	1002.61	3.554	17.193
333.56	0.0000	0.0000	0.000	942.54	5.385	24.888
353.67	1.0000	1.0000	7.991	1168.42	1.282	7.067
353.70	0.8898	0.8844	7.839	1141.94	1.345	7.250
353.68	0.7186	0.7027	7.599	1077.19	1.600	8.124
353.64	0.6010	0.5814	7.301	1042.87	1.824	8.976
353.65	0.5235	0.4730	6.888	1014.41	2.366	11.344
353.67	0.3093	0.2593	4.954	978.41	3.458	16.163
353.67	0.0000	0.0000	0.000	927.89	5.177	23.557
384.73	1.0000	1.0000	16.174	1041.24	0.758	3.515
384.64	0.8898	0.8783	15.575	1056.49	0.848	4.020
384.72	0.7186	0.6831	15.159	1015.85	1.085	4.943
384.77	0.6010	0.5589	14.402	992.00	1.382	6.181
384.75	0.5235	0.4177	12.894	962.50	1.897	8.317
384.75	0.3093	0.2222	8.617	932.99	2.999	13.108
384.73	0.0000	0.0000	0.000	905.18	4.854	21.547
399.42	1.0000	1.0000	21.731	962.48	0.502	2.031
399.33	0.8898	0.8723	21.084	1008.09	0.617	2.657
399.47	0.7186	0.6655	20.192	987.46	0.878	3.732
399.43	0.6010	0.5406	18.981	971.20	1.166	4.931
399.45	0.5235	0.3817	16.217	934.47	1.825	7.593
399.44	0.3093	0.2043	10.412	919.83	2.920	12.472
399.42	0.0000	0.0000	0.000	894.37	4.701	20.615
414.22	1.0000	1.0000	28.733	853.72	0.239	0.755
414.10	0.8898	0.8614	27.687	960.49	0.404	1.526
414.27	0.7186	0.6371	26.045	964.28	0.717	2.813
414.21	0.6010	0.5144	24.360	946.37	1.041	4.094
414.22	0.5235	0.3433	19.546	908.52	1.823	7.213
414.23	0.3093	0.1873	12.219	902.30	2.808	11.660
414.22	0.0000	0.0000	0.000	883.41	4.545	19.688
424.06	1.0000	1.0000	34.362	725.78	0.059	0.120
423.95	0.8898	0.8457	32.860	936.49	0.283	0.952
424.12	0.7186	0.6039	30.707	943.90	0.659	2.391
424.07	0.6010	0.4923	28.193	931.45	1.005	3.753
424.08	0.5235	0.3188	21.678	895.02	1.841	7.079
424.09	0.3093	0.1768	13.392	892.53	2.687	10.975
424.06	0.0000	0.0000	0.000	876.08	4.441	19.078

[a] Initial concentration of the ROS without taking into account the volume of the vapor phase.

[b] Corrected concentration of the ROS with taking into account the volume of the vapor phase.

the following equations [22–24]:

$$\ln P_S = \ln \bar{P}_C(w_R) - \alpha_R(w_R)\tau - b_R(w_R)\tau^{2.64} \quad (1)$$

$$\ln \rho_{l,S} = \ln \bar{\rho}_C(w_R) + B_l(w_R)\tau^{\beta F(\tau)} \quad (2)$$

$$F(\tau) = 1 - \frac{1.113\tau^{0.4}}{\ln \tau} \quad (3)$$

where P_S is the saturated pressure of the ROS, $\rho_{l,S}$ is the density of liquid ROS on the saturation line, $\bar{P}_C$, $\bar{T}_C$ and $\bar{\rho}_C$ are pseudocritical parameters of the ROS, α_R is a Riedel's criterion [26], B_l and b_R are the coefficients the of equations, w_R is the weight concentration of refrigerant, $\tau = \ln(\bar{T}_C(w_R)/T)$ is the logarithmic, reduced temperature, $F(\tau)$ is the universal cross-over function [23,27,28], the value of the critical index β is obtained from the theory of the critical phenomena and can be taken from theoretical estimation as 0.3245 [29]. The values of pseudocritical temperature of the ROS were determined by application of the method reported in [22,23]. The values of Riedel's criterion α_R, coefficient b_R and pseudocritical pressure $\bar{P}_C$ were obtained from fitting of the experimental data for vapor pressure of the ROS R-245fa/Planetelf ACD 100FY by Eq. (1). The concentration dependencies of the pseudocritical parameters were then described by the following correlations:

$$\bar{T}_C(w_R) = 427.20 + 6.4018(1 - w_R)^2 - 1.9595(1 - w_R)^4 + 67.1566 \cdot (1 - w_R)^6 \quad (4)$$

$$\bar{P}_C(w_R) = \frac{8.00 + 93.48245 w_R}{1 + 1.27687 w_R + 0.51732 w_R^2} \quad (5)$$

$$\bar{\rho}_C(w_R) = \frac{279.4874 + 40294.8979w_R - 67093.599w_R^2 + 29345.9038w_R^3}{1 + 52.4863w_R - 93.1758w_R^2 + 45.1571w_R^3} \tag{6}$$

The coefficients of Eqs. (1) and (2) can be calculated as

$$\alpha_R(w_R) = \frac{3.46584 + 32.07823w_R}{1 + 3.2547w_R + 0.38112w_R^2} \tag{7}$$

$$b_R(w_R) = 11.9278 - 10.30784w_R + 4.25808w_R^2 \tag{8}$$

$$B_l(w_R) = \frac{1.7856 + 34.0612w_R - 58.08841w_R^2 + 26.27126w_R^3}{1 + 80.6512w_R - 150.3293w_R^2 + 71.06784w_R^3} \tag{9}$$

Proposed Eqs. (1) and (2) were applied to the description of the experimental data of pure substances and ROS [22–24,27] in concentration range $0.25 < w_R < 1$. These equations are simple, with few constants, and have high extrapolation abilities. The coefficients of the equations are independent of the range of the initially fitted information and have a physical meaning [23]. The pseudocritical temperature and pseudocritical pressure of the pure polyolester compressor oil Planetelf ACD 100FY were measured using the method of pulse heating [30] and were equal to $\bar{T}_C = 807$ K and $\bar{P}_C = 8$ bar correspondingly. The experimental data for the capillary constant of the ROS R-245fa/Planetelf ACD 100FY can be correlated by the polynomial dependencies:

$$\bar{a}^2 = [A(T) + B(T)w_R + C(T)w_R^2]^2 \tag{10}$$

where $A(T)$, $B(T)$, $C(T)$ are coefficients of polynomial equation. These coefficients are obtained from the following expressions:

$$A(T) = 3.1742 - 3.56966 \times 10^{-3}T + 5.04364 \times 10^{-6}T^2 - 6.0404 \times 10^{-9}T^3 \tag{11}$$

$$B(T) = -218.5875 + 2.2511T - 8.5702 \times 10^{-3}T^2 + 1.4191 \times 10^{-5}T^3 - 8.650 \times 10^{-9}T^4 \tag{12}$$

$$C(T) = -221.6562 + 2.5434T - 11.0202 \times 10^{-3}T^2 + 2.1348 \times 10^{-5}T^3 - 1.5532 \times 10^{-8}T^4 \tag{13}$$

The values of $A(T)$, $B(T)$, $C(T)$ were determined by fitting of the experimental data obtained. Expanded uncertainty, including standard uncertainty and components of uncertainty arising from random and systematic effects for thermodynamic properties of the ROS R-245fa/Planetelf ACD 100FY is estimated as $0.3 \leq \delta P_S \leq 2.7\%$, $0.8 \leq \delta\rho_{l,S} \leq 1.2\%$, $0.8 \leq \delta a^2 \leq 3.6\%$, $0.9 \leq \delta\sigma \leq 4.9\%$. The deviations of obtained experimental data for the vapor pressure, density and capillary constant from Eqs. (1), (2) and (10) are shown in Figs. 7–9. As is seen from Figs. 7–9, Eqs. (1), (2) and (10) sufficiently described experimental data obtained.

The concentration dependencies of the excess thermodynamic functions are shown in Figs. 10 and 11. The excess thermodynamic properties were calculated as a difference between the thermodynamic properties of the real solution and the properties of the solution calculated by an additive law

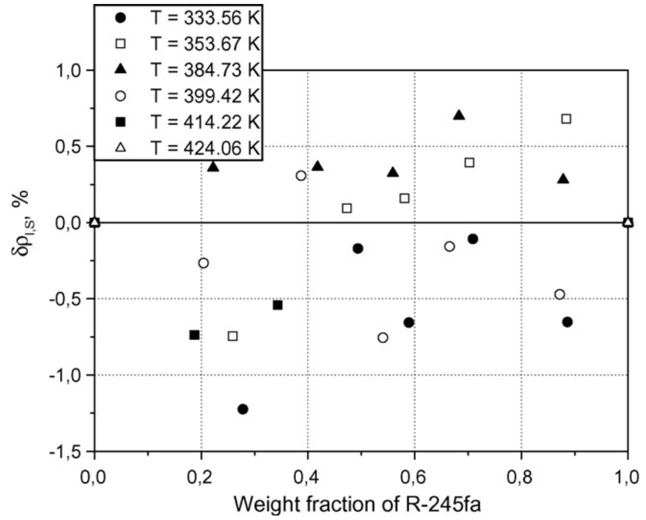

Fig. 7. Relative deviations of the experimental data for the liquid density of the ROS R-245fa/Planetelf ACD 100FY from calculated values by Eq. (2).

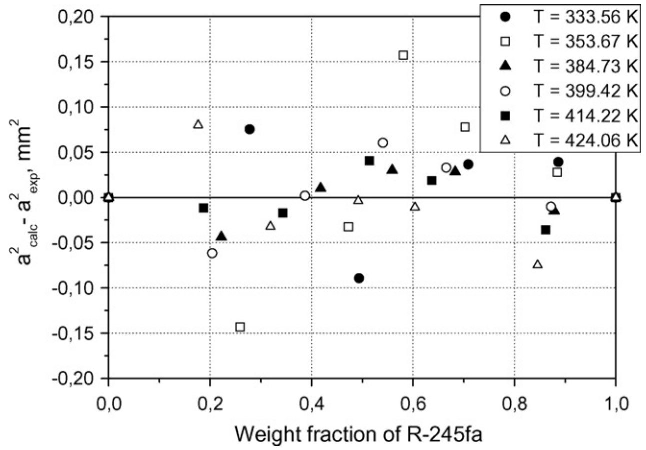

Fig. 8. Absolute deviations of the experimental data for the capillary constant of the ROS R-245fa/Planetelf ACD 100FY from calculated values by Eq. (10).

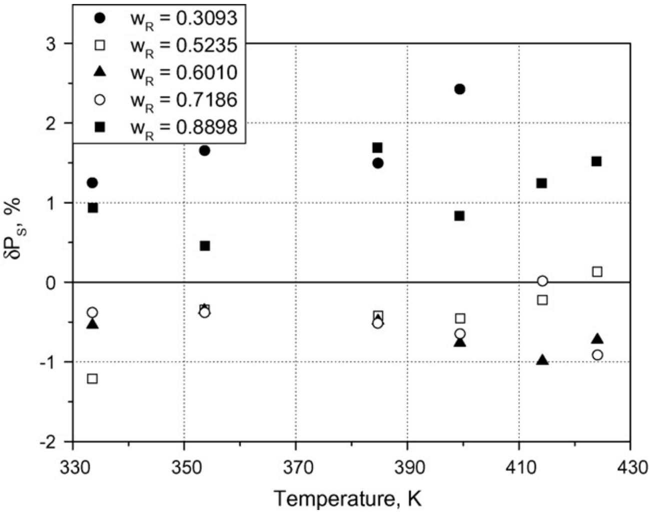

Fig. 9. Absolute deviations of the experimental data for the vapor pressure of the ROS R-245fa/Planetelf ACD 100FY from calculated values by Eq. (1).

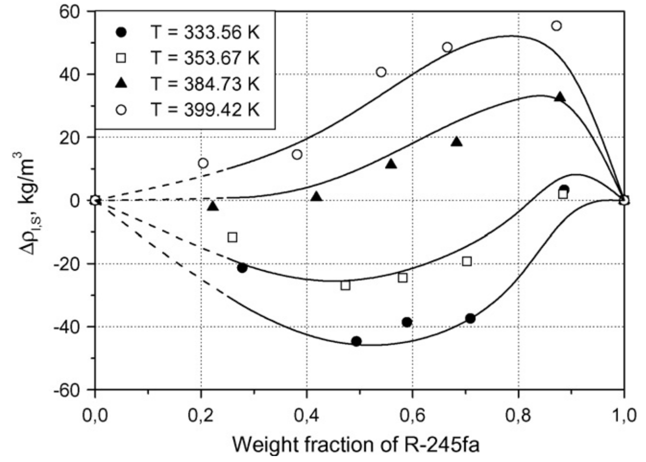

Fig. 10. Concentration dependencies on the excess functions for the density of the ROS R-245fa/Planetelf ACD 100FY.

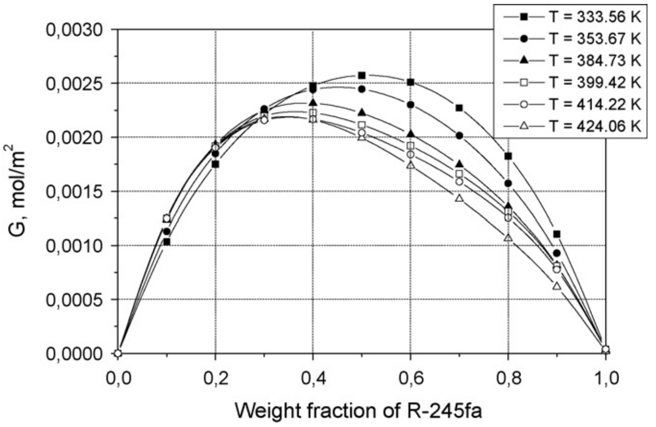

Fig. 12. Isotherms of the adsorption of R-245fa in liquid phase of the ROS R-245fa/Planetelf ACD 100FY.

using mass concentration of components ($Y - Y_{\mathrm{ad}}$). Moreover, the values of the excess functions for the density and surface tension of the ROS R-245fa/Planetelf ACD 100FY cannot be calculated by application of additive models. The excess functions for $\Delta\sigma$, Δa^2 have negative values and their absolute values increases as temperature increases. The concentration dependencies of the absolute values of $\Delta\rho_{\mathrm{l,S}}$ are shown in Figs. 10 and 11.

Information obtained for the surface tension on the interface between liquid and vapor makes it possible to perform a quantitative estimation of the adsorption of R-245fa in the surface layer of the ROS. The excess of R-245fa in the surface layer G can be calculated by the well-known Gibbs equation [31]:

$$G = -\frac{w_{\mathrm{R}}}{RT}\left(\frac{\partial\sigma}{\partial w_{\mathrm{R}}}\right)_T \tag{14}$$

The calculated isotherms for the ROS R-245fa/Planetelf ACD 100FY are shown in Fig. 12.

Since the surface tension of the solutions decreases as the concentration of R-245fa increases, then $(\partial\sigma/\partial w_{\mathrm{R}})_T \le 0$ and $G > 0$. Correspondingly, the concentration of R-245fa in the surface layer is larger than in the liquid phase of the solution (positive adsorption). The composition of the surface layer in the range $0.6 < w_{\mathrm{R}} < 1.0$ changes slightly (see Figs. 3 and 4). In that range of concentrations the surface layer is enriched by R-245fa. This fact can serve as an explanation of the small absolute values of the derivatives $(\partial\sigma/\partial w_{\mathrm{R}})_T \le 0$ at high concentration of R-245fa. The certain similarity in the behaviour of the concentration dependencies for the relative excess functions for the vapor pressure and surface tension of the ROS is also noteworthy (see Fig. 13).

It is reasonably safe to suggest that the effect of adsorption of the volatile component (refrigerant) in the surface layer of the ROS should be taken into account during modelling of phase equilibria of the ROS. Correspondingly, the vapor pressure of the ROS will be defined not only by the composition of the liquid phase but also by the concentration of the surface layer. The presence of an oil in the refrigerant leads to the creation of mixtures with strong zeotropic behaviour. For the calculation of the enthalpy of liquid phase of the ROS both the enthalpies of the liquid phases of the components and the enthalpy of mixing

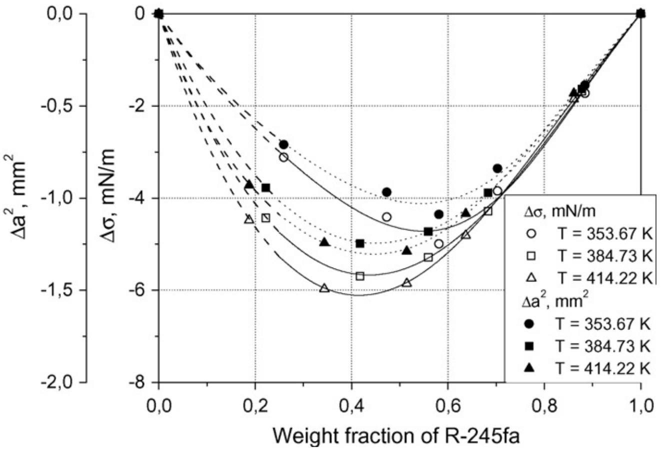

Fig. 11. Concentration dependencies on the excess functions for the surface tension and capillary constant of the ROS R-245fa/Planetelf ACD 100FY.

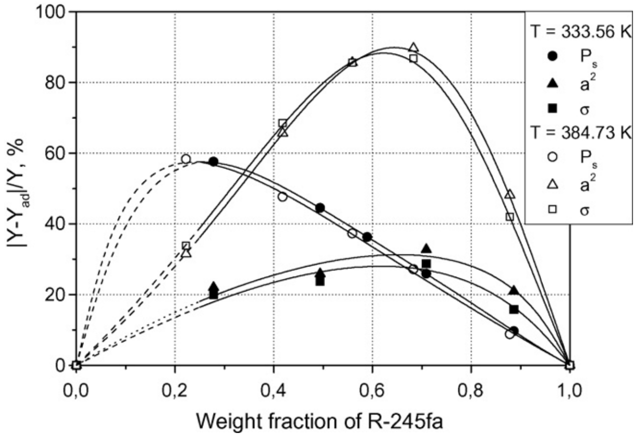

Fig. 13. Concentration dependence of relative changing of the excess functions for vapor pressure, surface tension and capillary constant of the ROS R-245fa/Planetelf ACD 100FY for isotherms: $T = 333.56$ K; $T = 384.73$ K.

are needed:

$$H_{l,S} = H_{l,R}w_R + H_{l,OIL}(1 - w_R) + \Delta H \tag{15}$$

where $H_{l,R}$, $H_{l,OIL}$ and ΔH are the specific enthalpy of the liquid phase of refrigerant and oil and the enthalpy of mixing and w_R is the weight concentration of the refrigerant.

Information on the enthalpy of the liquid phase of R-245fa is available and can be taken from [32]. The enthalpy of the compressor oil can be calculated from the experimental data for the heat capacity. The experimental data for polyolester compressor oil Planetelf ACD 100FY were obtained in the Department of Calorimetric Investigation, Institute of Physics, Saint-Petersburg State University using a differential scanning microcalorimeter DSC-11 manufactured by company SETARAM (France). The sensitivity of the calorimeter was 3×10^{-5} J s^{-1}. The uncertainties in determination of the temperature and heat capacity in the investigated range from 273 to 387 K did not exceed 0.2 K and 1.5% correspondingly for a heating rate of 5 K/min.

It should be pointed out that caloric properties of the ROS in the temperature range $273 < T < 387$ are critically important for the refrigeration industry. The temperature dependence of the heat capacity of compressor oils in the temperature range $273 < T < 387$ can be calculated using formulae:

$$C_{P_{OIL}} = 1.304 + 1.035 \times 10^{-3}T + 2.801 \times 10^{-6}T^2 \tag{16}$$

Correspondingly, the enthalpy of pure compressor oil can be defined as

$$H_{OIL} = \int_{273}^{T}(1.304 + 1.035 \times 10^{-3}T + 2.801 \times 10^{-6}T^2)\mathrm{d}T + H_{RSV} \tag{17}$$

where H_{RSV} = 200 kJ kg^{-1} is the reference state value for the refrigerants [32].

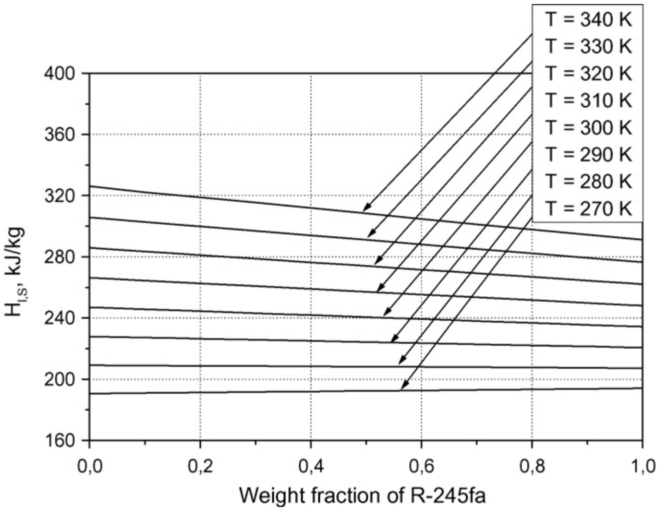

Fig. 14. Concentration dependencies on the enthalpy of liquid phase for the ROS R-245fa/Planetelf ACD 100FY.

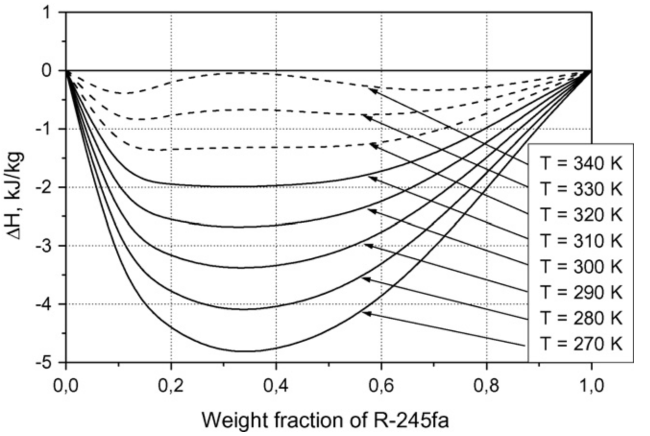

Fig. 15. Concentration dependencies on the excess enthalpy of liquid phase for the ROS R-245fa/Planetelf ACD 100FY.

For the calculation of the enthalpy of mixing experimental data for the saturation vapor pressure of the ROS R-245fa/Planetelf ACD 100FY were used. On the assumption that the vapor phase of the ROS contains only refrigerant, the heat of mixing can be defined as proposed in [33]:

$$\Delta H = -w_R \frac{RT^2}{2M_R}\left[\frac{\partial \ln P_S/P_R}{\partial T}\right]_{w_{OIL}} \tag{18}$$

The concentration dependencies of calculated values of the enthalpy of liquid and excess enthalpy of liquid phase of the ROS R-245fa/Planetelf ACD 100FY are shown in Figs. 14 and 15. As can be seen from Fig. 15 as the temperature increases the absolute value of the enthalpy of mixing decreases. At high temperature the uncertainty of determination of the enthalpy of mixing is comparable with the uncertainty of the initial information for the vapor pressure.

3. Conclusion

Experimental data for the solubility, density and capillary constant for the solution of the ozone-safe refrigerant R-245fa with polyolester oil Planetelf ACD 100FY are reported. The experimental data for the solubility, density, and capillary constant are sufficiently described by proposed equations in concentration range $0.25 < w_R < 1$. The vapor pressure and capillary constant of the refrigerant/oil solution (ROS) depend not only on the concentration of the liquid phase of the ROS but also on the composition of the surface layer. This important conclusion should be considered when developing models for the prediction of thermodynamic and caloric properties of the ROS. The information on solubility, density, surface tension of the ROS R-245fa/Planetelf ACD 100FY can be applied when designing evaporators, compressors, heat exchangers and other important parts of refrigeration systems. Finally, proposed results for caloric properties of the ROS R-245fa/Planetelf ACD 100FY can be successfully used for developing $\ln P - H$ diagrams for the correct calculation of refrigerating cycles with the presence of compressor oil admixtures in the working fluid.

4. Experimental section

In order to measure the thermophysical properties of the ROS R-245fa/Planetelf ACD 100FY, a complex experimental set-up has been designed. A schematic outline of the experimental setup is given in Fig. 1. The use of a glass experimental cell makes it possible to avoid most of the methodological uncertainties, which are typical for the experimental investigation of the thermodynamic properties of the ROS. Visual observations of the level of the liquid phase of the ROS in the glass cell make it possible to determine the volume of the liquid and vapor phases and the density (pycnometer method) and capillary constant (differential method of capillary rise) of the ROS.

The horizontal experimental cell (12) with quartz windows (3) had a volume of $191.335 \pm 0.022\ \mathrm{cm}^3$. The body of the experimental cell was made of stainless steel. Cassette with five calibrated capillaries (11) was placed inside the measuring cell. The radii of the capillaries were $r_1 = 0.1169$ mm, $r_2 = 0.0798$ mm, $r_3 = 0.0466$ mm, $r_4 = 0.0965$ mm, $r_5 = 0.03163$ mm correspondingly. The change in the level of liquid in the capillaries was estimated using cathetometer KM-8 (5) with an uncertainty of 0.015 mm. The air-tightness of the experimental cell was provided with the help of disconnecting ‘‘heat’’ valve V1. The temperature was kept constant in the thermostat (7). The thermostat temperature stability has been estimated to be within ±0.02 K. The sub-heater (1) and main heater (32) were connected to the temperature control system. The main part of the system used for temperature control was a thyristor regulator (model VRT 3), a thermometer bridge (model MO-62) and a platinum resistance thermometer (31). For measurements in the low-temperature range $T > 278$ K, the water was pumped out from water cooler. The experimental cell and components of the ROS were cleaned and evacuated with a vacuum system.

The pressure was measured by a deadweight pressure gage (8) with accuracy class 0.05. Membrane null-indicator (10) was used as a separator.

In order to clean the sample investigated from water admixtures and permanent gases the compressor oil was heated to $T = 388$ K and then evacuated for 60 s. The cleaning procedure was repeated several times. The purity of polyolester compressor oil Planetelf ACD 100FY was checked by a universal laboratory refractometer IRF-23.

A defined mass of the cleaned compressor oil was added to the experimental cell. After the experimental cell was closed and then evacuated. The necessary concentration of the ROS was achieved by the addition of R-245fa from the balloon (15). The mass of R-245fa was determined by the subsequent weighing of the balloon (15) with an analytical balance ADV-200M with an uncertainty 5×10^{-7} kg. The concentration of the liquid phase of the ROS can be determined by

$$w_\mathrm{R} = \frac{m_\mathrm{R} - m_\mathrm{v,R}}{m_\mathrm{R} + m_\mathrm{OIL} - m_\mathrm{v,R}} \tag{19}$$

where m_OIL is the mass of oil added to the experimental cell, m_R is the mass of refrigerant added to the experimental cell and $m_\mathrm{v,R}$ is the mass of vapor phase of refrigerant in the experimental cell. The mass of $m_\mathrm{v,R}$ was calculated from data obtained for the volume of vapor phase and from information about the density of superheated vapor for R-245fa at the parameters of the experiment [32]. The relative error in determination of mass concentration of the ROS can be estimated in the range from 0.01 to 0.15%.

The temperature was measured by a platinum resistance thermometer (model PTS-10) (31). The thermometer was placed in the vicinity of the experimental cell. The uncertainty in determining the temperature in the thermostat was estimated as ±0.02 K. Based on information about masses of R-245fa, oil and estimated volume of the liquid phase the density of the liquid phase of the ROS was calculated by the following formulae:

$$\rho_\mathrm{l,S} = \frac{m_\mathrm{l,S}}{V_\mathrm{l,S}} = \frac{m_\mathrm{R} + m_\mathrm{OIL} - m_\mathrm{v,R}}{V_\mathrm{l,S}} \tag{20}$$

where $m_\mathrm{l,S}$ is a mass of ROS in the experimental cell, $V_\mathrm{l,S}$ is a volume of liquid solution in the experimental cell obtained based on the results of preliminary calibration. The combined standard uncertainty in the determination of the density for the ROS R-245fa/Planetelf ACD 100FY can be estimated from 0.02 to 0.10%. The experimental cell was calibrated before experiment. Distilled water was applied as a reference fluid [32] for calibration of the volume of the experimental cell. The calibration was repeated many times in order to avoid random errors.

For investigation of the capillary constant of the ROS the modified differential method of capillary rise has been applied [34,35]. The essence of this method is measurements of the difference for height of rising of the liquid's meniscus in few capillary pair and following calculation of the weighted average value of Sugden parameter $\bar{a}^2_{ik}$. This makes it possible to significantly increase the accuracy of the experimental data. The capillary constant of the ROS can be calculated from the following expression:

$$a^2_{i,k} = \frac{\Delta h_{i,k}}{1/b_i - 1/b_k} \tag{21}$$

where $\Delta h_{i,k}$ is the difference for height of rising of the liquid's meniscus in capillaries, b_i and b_k are radii of the liquid's meniscus curvature. The weighted average value of the capillary constant can be determined in the following way:

$$\bar{a}^2 = \frac{\sum_{i \neq k, i=1}^{k} a^2_{ik} p_{ik1}}{\sum_{i \neq k, i=1}^{k} p_{ik}} \tag{22}$$

The statistical weight p_{ik} was calculated as an inverse value to maximal relative error of the measurement of the capillary constant a^2_{ik}. This allows a significant reduction in the influence of random errors in the measurements and a significant increase in the accuracy of the experiment. The maximum uncertainty in determining the capillary constant for the ROS R-245fa/Planetelf ACD 100FY was determined as $6.5 \times 10^{-3}\ \mathrm{mm}^2$.

The surface tension, capillary constant and densities of the liquid and vapor phases are related as

$$\sigma = \frac{(\rho_{\mathrm{l,S}} - \rho_{\mathrm{v,R}})}{2} \bar{a}^2 g \tag{23}$$

where $\rho_{\mathrm{l,S}}$ is the density of the liquid phase of the ROS, $\rho_{\mathrm{v,R}}$ is the density of the vapor phase of the ROS, g is the acceleration due to gravity ($g = 9.8073\ \mathrm{m\,s^{-2}}$). The combined standard uncertainty in the determination of the surface tension can be estimated from 0.8 to 2.2%. The refrigerant R-245fa has been acquired from Honeywell Fluorine Products Europe B.V. The purity of the R-245fa was 99.9 wt%. The thermodynamic properties of the R-245fa were taken from [32]. Commercial polyolester compressor oil Planetelf ACD 100FY was manufactured by Total for refrigerating compressors using HFC refrigerants. The purity of the polyolester compressor oil Planetelf ACD 100FY was 99.6 wt%. The good miscibility of the compressor oil with the refrigerant (see Fig. 2) should encourage good oil return characteristics especially in dry expansion evaporator, by maintaining low ROS viscosities in the compressor suction line.

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