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Experimental investigation of the density of hydrofluoroether HFE-73DE and its binary mixtures with ethyl acetate

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Abstract. This paper presents an experimental investigation of the density of hydrofluoroether HFE-73DE and its binary mixtures with ethyl acetate. Density measurements were carried out at atmospheric pressure in the temperature range 293–328 K using a Coriolis-type mass flow meter (Endress+Hauser Promass) operated in static mode. For both the pure fluid and the mixtures, density decreases approximately linearly with temperature, with the slope dependent on mixture composition. The resulting data set supports the development and validation of density correlations for HFE-73DE + ethyl acetate mixtures relevant to compact heat exchangers and electronics cooling applications.

1 Introduction

Compact heat exchangers and thermal control systems for modern electronics require working fluids combining low toxicity, high dielectric strength, and adjustable thermophysical properties. Fluorinated ethers (HFEs) from the 3M™ Novec™ series, such as HFE-7100, HFE-7200, HFE-73DE, and HFE-7300, have become attractive due to their chemical inertness, non-flammability, and moderate boiling points. Their main limitation is relatively low thermal conductivity and high cost, which motivates the exploration of mixtures enabling property tuning.

Binary mixtures of fluorinated fluids with organic esters, alcohols, or other HFEs can exhibit non-linear trends in density, viscosity, or heat capacity, providing flexibility unattainable with pure fluids. Understanding how composition and temperature affect density is particularly important because it determines buoyancy, pressure drop, and volumetric expansion during heating or boiling.

Previous studies [1, 2] analysed HFE mixtures under elevated pressures, but systematic experimental data at low pressures for HFE-73DE binary systems remain limited.

In another paper of Munoz-Rujaz et al. [3], the team examined the HFE-7500 + diisopropyl ether mixture up to 100 MPa and 353.15 K, validating high-pressure densities through simultaneous acoustic and densimetric measurements and providing empirical correlations for both datasets.

Dutkowski et al. [4] experimentally measured the density of water-based slurries with microencapsulated PCM (Micronal® DS 5039 X) near the melting range (10–30 °C, 2.15–8.60 wt%). Using a Coriolis flowmeter, they observed non-linear density variation with temperature and concentration, reflecting the solid, melting, and liquid phases. A theoretical model assuming independent expansion of water, paraffin, and PMMA matched the data well, confirming that the capsule shell does not restrict PCM expansion.

Zhu et al. [5] developed interpretable and high-accuracy heat transfer correlations for supercritical fluids using Genetic Programming-Symbolic Regression (GP-SR). Trained on ~2000 experimental data points, the optimal model (SR-4) achieved an MRE of 0.29% and MARE of 11.79%, improving accuracy by over 50% compared to traditional correlations. The model's structure revealed embedded physical mechanisms-including forced convection, buoyancy, and pseudo-boiling - thus combining predictive accuracy with clear physical interpretability.

In the study by Matsukawa et al. [6], the densities of homogeneous binary mixtures of CO_2/methanol and CO_2/ethanol were measured over the temperature range of 313–353 K, at pressures up to 20 MPa, and CO_2 mole fractions between 0 and 80%. The measurements were performed using a high-pressure vibrating-tube densimeter equipped with a circulation system and a variable-volume viewing cell. Both EoSs provided comparable accuracy in density prediction, and the inclusion of CO_2-alcohol association in the PC-SAFT model did not significantly improve the fit. The obtained parameter sets were further used to estimate vapor-liquid equilibria (VLE), yielding good agreement except near the critical region. The findings confirm that both SL and PC-SAFT EoSs can reliably describe the densities and VLE of CO_2-alcohol mixtures, provided that the parameters are derived from data covering a broad range of conditions that account for molecular association effects.

At Kielce University of Technology, the authors' team investigates flow boiling and convective heat transfer in minichannels using various dielectric refrigerants. The studies examine how thermophysical

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properties, channel geometry, and heating conditions affect heat transfer and flow patterns. The resulting experimental data provide a solid basis for CFD model validation and improving simulation accuracy.

Previous works by the group included experimental studies using test sections with rectangular minichannels [7], mini annular [8] and supported by complementary computational analyses. These employed several numerical approaches, such as CFD simulations, Trefftz function-based formulations, and finite element modelling with ADINA for comparative purposes [9]. At present, detailed thermal–flow simulations of minichannel systems are predominantly performed using the Simcenter STAR-CCM+ environment [10].

This paper extends earlier work by the authors on HFE-73DE + ethyl acetate mixtures to a broader range of compositions and temperature conditions, with emphasis on the density-temperature relationship and its engineering implications.

2 Binary Mixtures and Composition-Dependent Properties

Two completely miscible fluids with markedly different physicochemical characteristics were selected for analysis: the fluorinated ether HFE-73DE [11] and the organic ester ethyl acetate (EA) [12]. Their combination produces mixtures with intermediate thermophysical properties that can be tuned by adjusting the composition.

The present study investigated mixtures containing 10, 25, 50, and 75 mass% HFE-73DE, the remainder being ethyl acetate. The measured properties included density, kinematic viscosity, thermal conductivity, specific heat, and boiling temperature, all determined at atmospheric pressure and near room temperature (20 - 23 °C).

2.1 Base fluids

HFE-73DE (3M™ Novec™ 73DE) is a non-flammable, chemically stable fluorinated ether with high dielectric strength and low surface tension.

Table 1 shows the values of selected properties of the fluids HFE-73DE and ethyl acetate.

Table 1. The selected base fluids properties.

Mixture	HFE-73DE	Ethyl acetate
Density ρ [kg/m^3]	1520	894
Kinematic viscosity ν [mm^2/s]	0.403	0.463
Thermal conductivity [W/(m·K)]	0.075	0.149
Specific Heat [J/(kg·K)]	1020	2020
Saturation temperature T_{sat} [K]	314	350

The physical contrast between these fluids - density ratio ≈ 1.7 and boiling-point difference ≈ 36 K - and the fact that, with increasing HFE-73DE mass fraction, density increases while kinematic viscosity decreases, makes their mixtures useful for controlled adjustment of thermal and flow characteristics.

Binary mixtures were prepared with ethyl acetate covering mass fractions of 10 %, 25 %, 50 %, and 75 % HFE-73DE. All components were > 99 % purity and handled in sealed glass vessels to prevent evaporation. The 50/50 mass% mixture was prepared gravimetrically using an analytical balance (± 0.1 mg), sealed in glass vials, and conditioned for 24 h at 298 K before measurement.

2.2 Measured mixture properties

Selected thermophysical properties of the HFE-73DE + ethyl acetate mixtures (e.g., viscosity, thermal conductivity, and specific heat capacity) were determined experimentally; the measurement methods and uncertainty analysis are reported in [13]. The present paper focuses on density measurements.

The measured (in an external chemical laboratory; details in [13]; values at 20–23 °C, ~1 atm) parameters of the binary fluorinated mixtures are summarised in Table 2.

Table 2. The selected binary fluorinated mixtures properties.

Mixture (mass fraction)	10/90	25/75	50/50	75/25
Density [kg/m^3]	931	969	1035	1169
Kinematic viscosity [mm^2/s]	0.508	0.503	0.468	0.422
Thermal conductivity [W/(m·K)]	0.165	0.189	0.207	0.344
Specific Heat [J/(kg·K)]	504	313	445	972

2.3 Observed composition effects

The results show distinct non-linear dependencies of all measured properties on composition, confirming non-ideal mixture behaviour:

- Density rises almost monotonically with the HFE- 73DE fraction, from 931 kg m^{-3} at 10/90 to 1169 kg m^{-3} at 75/25.
- Viscosity decreases with increasing fluorinated component, facilitating higher Reynolds numbers and lower pressure drops in flow.
- Thermal conductivity increases non-linearly - more than doubling across the studied range - suggesting enhanced phonon coupling due to partial molecular ordering.
- Specific heat exhibits a non-monotonic trend, reaching a minimum at 25/75 and a maximum at 75/25, characteristic of weak molecular interactions and partial association effects.

These deviations from ideal mixing indicate positive excess molar volumes and enthalpies, consistent with partial structural incompatibility between fluorinated and organic molecules. The overall trend reflects the competition between dispersion forces (dominant in HFE-73DE) and dipole-dipole interactions (in ethyl acetate). The observed density values for HFE-73DE agree within ± 0.3 % with those reported by 3M.

2.4 Engineering implications

The non-linear variation of properties with composition allows practical optimisation:

- Lower HFE-73DE fractions (10–25 %) yield lighter, less viscous fluids suited to low-pressure circulation.
- Intermediate compositions (50 %) offer balanced density and heat capacity, attractive for dielectric cooling loops.
- HFE-rich mixtures (≥ 75 %) provide higher thermal conductivity and lower expansion, improving stability under high heat flux.

Such tunability enables engineers to design custom working fluids with controlled thermal performance and compatible physical parameters for minichannel and microchannel heat exchangers.

2.5 Measurement Method

Density measurements were performed using a Coriolis-type mass flow meter (Endress+Hauser Promass series) operating in static mode. The instrument determines fluid density based on the resonance frequency shift of an oscillating measurement tube induced by the Coriolis effect. The measurement principle allows simultaneous determination of mass flow rate and density with high precision and repeatability.

Before testing, the flow meter was calibrated using distilled water and a reference HFE fluid to verify the factory calibration curve. Each measurement was carried out under atmospheric pressure and in isothermal conditions, maintained by a thermostatic bath with temperature stability better than ±0.02 K. The mixture was circulated in a closed loop to ensure homogeneity and to prevent gas bubble formation.

Density readings were recorded after full thermal equilibration, typically within 5-7 minutes at each temperature step. The instrumental uncertainty did not exceed ±0.2 kg m^{-3}, and the total expanded uncertainty (k = 2) was below ±0.4 kg m^{-3}. The recorded density-temperature data were subsequently fitted with a linear regression model:

$$\rho(T) = \rho_0 + a(T - T_0) \qquad (1)$$

where $\rho_0$is the density at $T_0 = 293.15$ K, and a is the temperature coefficient (kg m^{-3} K^{-1}).

3 Results

3.1 Temperature Dependence

Figure 1 shows the measured density of the 50/50 HFE-73DE + ethyl acetate mixture as a function of temperature. The density decreases linearly from 1189 kg m^{-3} at 293 K to 1151 kg m^{-3} at 328 K. The linear regression fit (solid line) matches the data points (symbols) with $R^2 = 0.9994$, confirming the validity of the correlation $\rho(T) = \rho_0 + a(T - T_0)$.

All examined fluids exhibited a monotonic, nearly linear decrease of density with temperature. The average slope for pure HFE-73DE was −1.25 kg m^{-3} K^{-1}, increasing in magnitude for mixtures containing ethyl acetate.

For example, the 25 % HFE-73DE mixture showed - 1.40 kg m^{-3} K^{-1}, and the 75 % mixture - 1.10 kg m^{-3} K^{-1}. This indicates stronger thermal expansion for co-solvent-rich compositions due to weaker intermolecular cohesion.

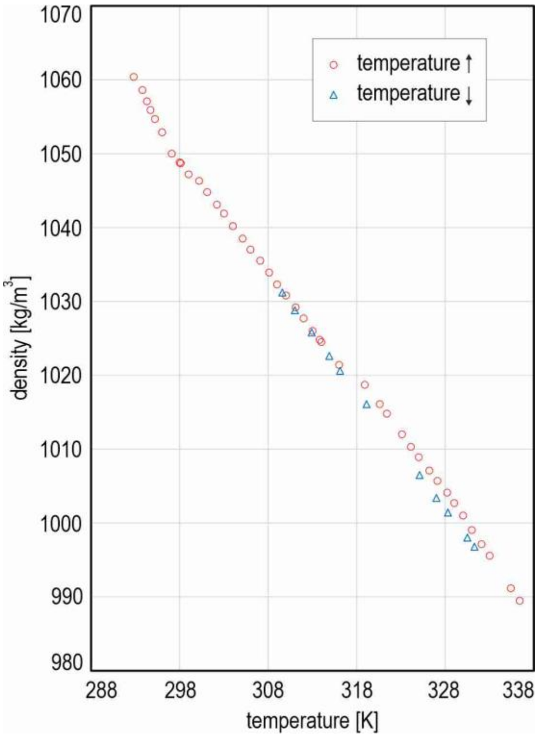

Fig. 1. Density of the 50/50 (mass%) HFE-73DE + ethyl acetate mixture as a function of temperature.

The results confirm the high thermal stability of HFE-73DE: no phase separation or visible degradation occurred over repeated heating-cooling cycles. Density-temperature curves are parallel and well described by the linear model ($R^2 > 0.999$).

3.2 Composition Dependence

At 25 °C, densities ranged from about 900 kg m^{-3} (for ester-rich mixtures) to 1520 kg m^{-3} (for pure HFE-73DE). The variation is nonlinear: the experimental values deviate from linear interpolation by up to ± 1.5 %, revealing mild excess-volume effects. The excess molar volume, estimated by:

$$V^E = \frac{1}{\rho_{\text{mix}}} - \left(\frac{x_1}{\rho_1} + \frac{x_2}{\rho_2}\right) \qquad (2)$$

is positive for all mixtures, increasing with temperature, which reflects expansion due to reduced packing efficiency of dissimilar molecules.

Such non-ideality, though moderate, influences the effective thermal expansion coefficient β:

$$\beta = -\frac{1}{\rho}\left(\frac{\partial \rho}{\partial T}\right)_p \quad (3)$$

which rose from 7.8×10^{-4} K^{-1} for pure HFE-73DE to 9.5×10^{-4} K^{-1} for the 25 % mixture.

4 Discussion

The combination of high base density and moderate thermal expansion makes HFE-73DE mixtures attractive for single-phase convective cooling in minichannel heat sinks. The linearity of ρ(T) simplifies implementation in CFD models, where temperature-dependent density directly affects buoyancy and flow acceleration.

Non-ideal mixing has practical implications: positive excess volumes lower density more than predicted by simple averaging, slightly increasing volumetric flow rate for a given pump speed. In low-pressure systems this can stabilise circulation and reduce the risk of vapour-lock during start-up.

The data also provide a basis for computing thermodynamic derivatives, such as the isobaric thermal expansion coefficient and massic heat capacity correlations, needed for two-phase design. Even without boiling data, the observed density trends allow estimation of saturation-temperature shifts due to entrainment or sequential evaporation effects, previously identified for HFE-73DE + ethyl acetate.

These relationships demonstrate that careful control of mixture composition enables engineers to balance three competing objectives: (i) low viscosity for minimal pressure loss, (ii) adequate density for pumping and heat removal, and (iii) predictable thermal expansion for mechanical stability.

5 Conclusions

Density–temperature relationship:

All examined fluids show a linear decrease of density with temperature in the range 293-328 K, with slopes between -1.1 and -1.4 kg m^{-3} K^{-1}.

Non-ideal mixing: Binary mixtures of HFE-73DE with ethyl acetate exhibit small but measurable positive excess volumes, reflecting weak molecular interactions and partial structural disorder. Thermal expansion: The volumetric expansion coefficient increases with the organic fraction, confirming enhanced compressibility and reduced molecular cohesion. Engineering relevance: The predictable behaviour of these mixtures supports their use as customisable, electrically inert working fluids for compact heat exchangers, especially in electronics and optical-device cooling. Future work: Further research will extend these measurements to high pressures and include viscosity and specific-heat determinations to develop full predictive correlations for CFD and system-level simulations.

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